A STUDY OF THE PHOTOREARRANGEMENTS OF CRystalline
DIBENZOBARRELENE AND CYclohexenone DERIVATIVES

by

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Two series of compounds, 4,4-diarylcyclohexenones and 9-substituted dibenzobarrelenes, were synthesized and their photochemistry was investigated in the crystalline state and in solution medium. The differences in photoreactivity and product selectivity of these compounds between the solution and solid states have been determined, and possible structure-reactivity correlations are discussed based on X-ray crystallographic data for some of the substances.

The photorearrangement of 4,4-diarylcyclohexenones was found to be affected moderately by the crystal lattice. The migratory aptitude of the aryl groups for 4-phenyl-4-arylcyclohexenones was shown to be controlled to a lesser extent by the electronic effect in the solid state compared to solution. Irradiation of 4,4-diphenyl-6-methylcyclohexenone in the crystalline phase gave the same photoproducts and a similar product distribution as that in the solution phase. In this case, conformational analysis reveals that both pseudo-axial and pseudo-equatorial phenyl groups of the enone moiety are capable of migrating.

The di-π-methane rearrangement of a number of 9-substituted dibenzobarrelene derivatives gave two regioisomeric dibenzo-semibullvalene products upon photolysis in solution and in the solid state. In general, the effect of the crystalline environment on the reaction regioselectivity is found to be small. Resolved chiral substituents (handles) at the 9-position of the dibenzobarrelene moiety were used to force the compounds to crystallize in chiral space groups. Asymmetric inductions via photolysis of the chiral crystals varied from
small to moderate depending on the nature of the chiral substituent. It was found that, in some cases, asymmetric induction in the solid state is significantly higher than in solution, but is lower in one instance. In addition, the chiral crystalline environment has different effects on the asymmetric inductions in a dual pathway di-\(\pi\)-methane rearrangement.

The di-\(\pi\)-methane photorearrangement of 9,12-bridged dibenzobarrelene lactones was found to proceed very efficiently in solution and in the solid state. The unusual regioselectivity observed was rationalized in terms of an intramolecular steric effect rather than an electronic stabilizing effect. An absolute asymmetric synthesis with high optical yield was achieved by photolyses of chiral crystals of the achiral compound, methyl 3,5-dihydro-3-oxo-1H-5,9b[1',2']benzenonaphtho[1,2-c]furan-4-carboxylate. Photochemical [2+2] cycloaddition of this substrate to 1,3-dienes was found to be mechanistically interesting, involving an excited triplet state of 1,3-diene which is formed by energy transfer.

An unusual excited singlet state rearrangement of 9-chloromethyl substituted dibenzobarrelene diester was discovered. X-ray crystallographic analyses revealed that an intermolecular chlorine atom transfer is involved in the formation of unusual dibenzopentalene photoproducts. Finally, a novel solid state photochromism was found, and a radical species was proposed as the intermediate responsible for the observed photochromic phenomenon.
To my parents

and

To my wife and daughter
# TABLE OF CONTENTS

TITLE PAGE ................................................................. i

ABSTRACT ................................................................. ii

DEDICATION ................................................................. iv

TABLE OF CONTENTS ...................................................... v

LIST OF TABLES ............................................................ x

LIST OF FIGURES .......................................................... xi

LIST OF SCHEMES .......................................................... xiv

ACKNOWLEDGMENTS ....................................................... xviii

INTRODUCTION .............................................................. 1

I. Photochemistry in the Solid State ................................. 3

II. The Topochemical Principle ......................................... 7

III. Reactivity and Selectivity of Organic Reactions in the Crystalline State ........................................... 10

IV. Asymmetric Syntheses via Photoreaction of Chiral Crystals ......................................................... 16

V. Unimolecular Photorearrangements ................................. 22

A. Photorearrangement of Cyclohexenone Systems ................. 23

B. The Di-π-Methane Rearrangement .................................. 26

VI. Objectives of Present Research .................................. 32

RESULTS AND DISCUSSION ............................................... 37

I. Preparation of Starting Materials ................................. 38

A. Synthesis of Cyclohexenone Substrates .......................... 38
B. Synthesis of 9-Substituted 9,10-Ethenoanthracene Substrates ................................................... 40

C. Preparation of Crystalline Samples ......................... 47

II. Studies on 4,4-Diarylcy clohexenones ......................... 48

A. Photorearrangement of 4-Phenyl-4-
arylcy clohexenones ........................................... 48

1. Photochemistry of 4-Phenyl-4-p-cyanophenyl-
cyclohexenone (71b) and 4-Phenyl-4-p-
bromophenylcyclohexenone (71a) .......................... 50


3. Molecular Crystal Structure of 4-Phenyl-4-p-
bromophenylcyclohexenone (71a) and Its

Photochemical Implications ..................................... 59

B. Photorearrangement of 4,4-Diphenyl-6-
al kylcyclohexenones ......................................... 63

1. Photochemistry .............................................. 63

2. Product Ratio Studies on Enone 74a in

Solution and in the Solid State ............................... 67

III. Studies on the Di-α-Methane Photorearrangement of

9-Substituted Dibenzobarrelene Diesters ...................... 75

A. Photochemistry of 9-Formyl, 9-Hydroxymethyl and

9-Acetoxymethyl 9,10-Ethenoanthracene-11,12-
dicarboxylates (94, 95 and 93c) .......................... 77

B. Solid State Results ........................................... 81

1. Regioselectivity in the Solid State vs

Solution ...................................................... 81
2. Molecular Crystal Structure of 9-Formyl

9,10-Ethenoanthracene Diester 94 ............... 84

IV. Asymmetric Induction via Photoreactions of Chiral Crystals ........................................ 89

A. Studies on 9-Substituted Dibenzobarrelene Vinyl Monoesters ........................................ 89

1. Photochemistry of 9-Substituted Dibenzo-barrelene Vinyl Monoesters 99 and 100 .......... 92

2. Results on Diastereoselectivity in the Solid State vs Solution ......................................... 95

B. Studies on 9,10-Ethenoanthracene Diesters with Resolved Chiral Handles at the 9-Position .......... 97

1. Photochemistry .................................................. 97

2. Results on the Regio- and Diastereoselectivities .................................................. 98

3. Molecular Crystal Structure of Compound 93b and Its Photochemical Implications .............. 102

V. Studies on the Photoreactivity and Selectivity of Dibenzobarrelene Lactones ......................... 108

A. Photochemical Studies on Dibenzobarrelene Lactone-Ester 96 ........................................ 108

1. Photochemistry of Lactone-Ester 96 ....................... 108

2. Interpretation on the Reaction Regioselectivity of 96 in Solution .................................. 111

3. Absolute Asymmetric Synthesis via Photoreaction of Chiral Crystals of Lactone-Ester 96 ........ 116
4. Mechanistic Interpretation of the Solid State
   Asymmetric Induction from Lactone-Ester 96 .......... 125
B. Photochemistry of Methyl Lactone-Ester 97 .......... 127
   1. Photolysis of Methyl Lactone-Ester 97 in
      Solution ............................................. 128
   2. Solid State Results .................................. 132
C. Electronic versus Steric Effect in the
   Photorearrangement of Lactone 98 .................... 137
D. Studies on the Photoreactivity of 9,10-Etheno-
   anthracene Lactones 96, 97, 98 and 93c ............... 140
   1. Quantum Yield (\(\Phi\)) Measurements ............... 140
   2. Quenching Results on the Lactone-Ester 96 and
      Diester 93c ........................................... 144
E. Photocycloadditions of Lactone-ester 96 to
   1,3-Dienes ............................................. 148
   1. Cycloaddition of Lactone-ester 96 to
      2,5-Dimethyl-2,4-hexadiene ........................... 150
   2. Cycloaddition of Lactone-Ester 96 to
      1,3-Cyclohexadiene ................................... 155
   3. Mechanistic Studies on the Photocycloaddition
      of Lactone-Ester 96 to 1,3-Dienes .................. 167
VI. Studies on 9-Chloromethyl 9,10-Ethenoanthracene
   Diester 93d ........................................... 170
   A. Unusual Photorearrangement of 9-Chloromethyl
      Dibenzobarrelene Diester 93d ......................... 173
      1. Photolysis in Solution and in the Solid
         State ............................................... 173
2. Product Ratio Analysis ........................................... 175
3. A Possible Mechanism for the Formation
   of exo-Methylene Dibenzopentalenes
   196 and 197 ......................................................... 177
B. Solid State Photochromism of 9-Chloromethyl
   Dibenzoabarrelene 93d ........................................... 185
   1. General Observations on the Photochromism of
      Compound 93d. .................................................. 187
   2. Speculation on the Nature of the Colored
      Species .......................................................... 189

EXPERIMENTAL .......................................................... 194
   I. General .......................................................... 195
   II. Synthesis of Substrates ...................................... 199
      A. Cyclohexenone Derivatives ................................. 199
      B. Dibenzoabarrelene Derivatives ............................ 206
   III. Photochemical Studies ...................................... 228
      A. General Procedures ....................................... 228
      B. Photochemistry of Substrates ............................. 229
         1. Cyclohexenone Derivatives ............................... 229
         2. Dibenzoabarrelene Derivatives .......................... 240
      C. Quantum Yields and Quenching Studies .................. 268

REFERENCES ............................................................ 272
LIST OF TABLES

Table 1  Summary of Crystal Preparations ........................................ 47

Table 2  Photolysis of 4-Phenyl-4-p-cyanophenyl-cyclohexenone at Different Irradiation Wavelengths .................................................. 52

Table 3  Photolysis of 4-Phenyl-4-p-bromophenyl-cyclohexenone (71a) in Benzene under Varying Conversions ........................................ 54

Table 4  Migratory Selectivity of 4-p-Cyanophenyl- and 4-p-Bromophenyl-4-phenylcyclohexenones in Solution and in the Solid State .... 57

Table 5  Photoproduction Ratios of Endo:Exo (75a:76a) from Photorearrangement of 74a in Various Solvents ............................. 68

Table 6  Product Ratios from Photolysis of Enone 74a in the Solid State .......................................................... 70

Table 7  Product Ratios in Photorearrangement of 9-Substituted 9,10-Ethenoanthracenes ...................................................... 82

Table 8  Summary on the Reaction Diastereoselectivity of 99 .......................................................... 96

Table 9  Regio- and Diastereoselectivity in the Solid State and Solution ........................................................................ 99

Table 10  Asymmetric Inductions in the Solid State Photoreaction of Lactone-Ester 96 .................................................. 121

Table 11  Product Distributions in the Solution and the Solid State Irradiations of Lactones 96 and 97 ............................. 136

Table 12  Quantum Yields ($\Phi$) of Product Formation from Photolysis of Dibenzobarrelenes 96, 97, 98 and 93c ...................... 141

Table 13  Quantum Yields and Triplet Lifetimes of Some 9,10-Ethenoanthracenes ...................................................... 143

Table 14  Product Ratios from Photolysis of 9-Chloromethyl Dibenzobarrelene 93d in Different Media ............................. 176
LIST OF FIGURES

Figure 1  Composite Diagram Comparing the Packing of the Molecular Units within the Monomer and Dimer Crystal Structures of Benzylidene-cyclopentanone .................................................. 11

Figure 2  Pictorial Representation of "Reaction Cavity" Concept .................................................. 12

Figure 3  Partial $^1$H NMR Spectra of Dibenzobarrelenes 99 and 100 ............................................. 46

Figure 4  Stereodiagram of the Molecule of $trans$-5-Phenyl-6-p-bromophenylbicyclo[3.1.0]hexan-2-one (72a) .......................................................... 53

Figure 5  Stereodiagram of Cyclohexenone 71a with Disorder .................................................. 59

Figure 6  Crystal Packing Diagram of Cyclohexenone 71a .................................................. 60

Figure 7  Partial $^1$H NMR Spectra of $exo$-$trans$- and $endo$-$trans$-5,6-Diphenyl-3-methylbicyclo-[3.1.0]hexanones .................................................. 65

Figure 8  ORTEP Drawings of Molecular Mechanics Minimized Half-Migrated Triplet Biradicals ................. 68

Figure 9  Stereodiagram of the Molecule Dimethyl 9-Formyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (94) .................................................. 85

Figure 10 Crystal Packing Diagram of Dimethyl 9-Formyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (94) .................................................. 86

Figure 11 Partial $^1$H NMR Spectrum of Photoproduct 145 .................................................. 94

Figure 12 Partial $^1$H NMR Spectrum of Reaction Mixture from 93b .................................................. 100

Figure 13 Partial $^1$H NMR Spectrum of Reaction Mixture from 93a .................................................. 101

Figure 14 Molecular Crystal Structure and Packing Diagrams of Compound 93b .................................................. 103

Figure 15 Steric Effect in the Photorearrangement of 9-Substituted Dibenzobarrelene Diester 93b via Path B Mechanism .................................................. 107
Figure 16 Molecular Structure of Lactone-Ester 96 Showing H···H Contacts ........................................... 116
Figure 17 Partial $^1$H NMR Spectra of Lactone-Ester 96 ............................................................ 117
Figure 18 Stereodiagram of Compound 96 .......................................................................................... 118
Figure 19 Partial $^1$H NMR Spectra of the Photolysate of compound 96 in the Solid State .......... 122
Figure 20 Crystal Packing Diagram of Lactone-Ester 96 .................................................................. 127
Figure 21 Partial $^1$H NMR Spectra of Photoproduct 168 ............................................................... 130
Figure 22 Partial $^1$H NMR Spectra of Photoproduct 170 ............................................................... 131
Figure 23 Stereodiagram of Photoproduct 171 .................................................................................. 135
Figure 24 A Stern-Volmer Plot for the Formation of Dibenzosemibullvalene Lactone 153 from Lactone-Ester 96 in the Presence of 2,5-Dimethyl-2,4-hexadiene .................................................. 146
Figure 25 A Stern-Volmer Plot for Formation of Dibenzosemibullvalenes 120 and 124 from 93c in the Presence of 1,3-Cyclohexadiene ......................................................................................... 147
Figure 26 Partial $^1$H NMR Spectra of Photoadduct 185 ............................................................... 152
Figure 27 Structural Information of Photoadducts 185 and 186 ..................................................... 153
Figure 28 Partial $^1$H NMR Spectra of Photoadduct 186 ............................................................... 154
Figure 29 Structural Assignment of the [2+2] Adducts 187 and 188 ............................................. 157
Figure 30 Partial $^1$H NMR Spectra of Photoproduct 187 ............................................................. 158
Figure 31 Partial 2D COSY $^1$H NMR Spectrum of Photoproduct 187 ....................................... 159
Figure 32 Partial $^1$H NMR Spectra of Photoproduct 187 ............................................................. 160
Figure 33 Partial $^1$H NMR Spectra of Photoproduct 188 ............................................................. 162
Figure 34 Partial $^1$H NMR Spectra of Photoproduct 188 ............................................................. 163
Figure 35 Partial $^1$H NMR Spectra of Photoproduct 189 ............................................................. 165
Figure 36 Structures of Photoproduct 189 and Its Isomer 191 ......................................................... 166
Figure 37 Partial $^1$H NMR Spectra of Photoproduct 189 ............................................................. 166
Figure 38  FTIR Spectra of Crystalline 9-Chloromethyl Dibenzobarrelene 93d................................. 171
Figure 39  ORTEP Drawing of the Molecular Structure of Photopродuct 196................................. 174
Figure 40  ORTEP Drawing of the Molecular Structure of Photopродuct 197................................. 175
Figure 41  Crystal Packing Diagram of Compound 93d (β-form).................................................. 184
Figure 42  Intermolecular Contact in Crystal Structure of 220..................................................... 187
Figure 43  UV-VIS Absorption Spectrum of the Blue-Purple Species Formed in the Photochromic β-Type Crystals of 93d.................................................. 188
Figure 45  ESR Spectra of the Blue-Purple Species Formed in the Photochromic β-Type Crystals of Compound 93d.................................................. 191
Figure 46  Structures of Other Photochromic Dibenzobarrelene Compounds................................. 192
LIST OF SCHEMES

Scheme 1 Examples of Photoreactions in Solution versus the Solid State .................................................. 4
Scheme 2 Photochemical [2+2] Cycloadditions of trans-Cinnamic Acid in the Crystalline State ......................... 8
Scheme 3 Photodimerization of Benzylidene cyclopentanone ............................................................................. 10
Scheme 4 Reaction Controlled by "Steric Compression" .................................................................................. 13
Scheme 5 Absolute Asymmetric Synthesis by Solid State [2+2] Photocycloaddition ........................................... 19
Scheme 6 Absolute Asymmetric Syntheses via Norrish Type II and Di-π-Methane Reactions in the Solid State .......... 20
Scheme 7 Absolute Asymmetric Synthesis of β-Lactam .................................................................................. 21
Scheme 8 Photorearrangement of 4,4-Dimethyl-2-cyclohexen-1-one ................................................................. 24
Scheme 9 Phototransformations of 4-Phenyl-4-methyl-2-cyclohexen-1-one and 4,4-Diphenyl-2-cyclohexen-1-one .......... 25
Scheme 10 Representation of a Simple Di-π-Methane Rearrangement .............................................................. 27
Scheme 11 Examples of the Di-π-Methane Photorearrangement ....................................................................... 28
Scheme 12 Photorearrangement of the Barrelene Systems ................................................................................. 29
Scheme 13 Photochemical Transformation of Dibenzobarrelene Diester Derivative ........................................... 30
Scheme 14 The Di-π-Methane Photorearrangement of 9-Methyl Dibenzobarrelene Diester .................................... 31
Scheme 15 Photorearrangement of 4-Aryl-4-phenylcyclohexenones .................................................................. 33
Scheme 16 Photorearrangement of 4,4-Diphenyl-6-alkylcyclohexenones ........................................................... 34
Scheme 17 Photorearrangement of 9-Substituted Dibenzobarrelenes ................................................................. 35
Scheme 18 Syntheses of 4-p-Bromophenyl- and 4-p-Cyanophenyl-4-phenyl-cyclohexenones

Scheme 19 Synthesis of 4,4-Diphenyl-6-methylcyclohexenone (74a) and 4,4-Diphenyl-6-ethylcyclohexenone (74b)

Scheme 20 Preparation of 9-Substituted Anthracenes

Scheme 21 Preparation of Bridgehead Substituted Dibenzobarrelene Compounds via Diels-Alder Reaction

Scheme 22 Preparation of Lactone-Ester 96 and Methyl Lactone-Ester 97

Scheme 23 Esterifications between Alcohol 95 and the Corresponding Acid Chlorides

Scheme 24 Synthesis of 9-Substituted Dibenzobarrelene Monoesters

Scheme 25 Phototransformations of 4,4-Diaryl-cyclohexenones

Scheme 26 Photorearrangement of 4-Phenyl-4-arylcyclohexenones

Scheme 27 Conversion of Photoproducts 72a and 73a to the Known Cyano Derivatives 72b and 73b

Scheme 28 Mechanistic Presentation of the Photorearrangement of 4-Phenyl-4-arylcyclohexenones

Scheme 29 Orbital Overlap Arrangement in 1,2-Shift of Phenyl Group

Scheme 30 Steric Hindrance on the Rotation of the p-Bromophenyl Group in the Bulk Crystals

Scheme 31 Photochemistry of 4,4-Diphenyl-6-alkylcyclohexenones

Scheme 32 Syntheses of Photoproducts 76a and 76b and Epimerization of Photoproduct 75a

Scheme 33 Mechanism of Photorearrangement of 4,4-Diphenylcyclohexenones

Scheme 34 Conformational Equilibrium of 6-Methyl Cyclohexenone 74a
<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>Two Pathways of Photorearrangement of Cyclohexenone 74a</td>
<td>74</td>
</tr>
<tr>
<td>36</td>
<td>Phototransformation of Dibenzobarrelene Diesters to Dibenzosemibullvalenes</td>
<td>76</td>
</tr>
<tr>
<td>37</td>
<td>Phototransformation of 9-Substituted Dibenzobarrelenes</td>
<td>79</td>
</tr>
<tr>
<td>38</td>
<td>Synthesis of Photoproduct 119 by a Selective Reduction</td>
<td>81</td>
</tr>
<tr>
<td>39</td>
<td>Electronic Effect on Valence Tautomerization of Cycloheptatriene and Norcaradiene</td>
<td>84</td>
</tr>
<tr>
<td>40</td>
<td>Phototransformation of Unsymmetrical Dibenzobarrelene Diesters</td>
<td>88</td>
</tr>
<tr>
<td>41</td>
<td>Phototransformation of Dibenzobarrelene 11-Ester</td>
<td>90</td>
</tr>
<tr>
<td>42</td>
<td>Phototransformation of Methyl 9,10-Dihydro-9,10-Ethenoanthracene-9-carboxylate</td>
<td>91</td>
</tr>
<tr>
<td>43</td>
<td>Phototransformation of Dibenzobarrelene 9,11-Diesters</td>
<td>92</td>
</tr>
<tr>
<td>44</td>
<td>Photolysis of 9,11-Disubstituted Dibenzobarrelene 99</td>
<td>93</td>
</tr>
<tr>
<td>45</td>
<td>Phototransformation of 9,12-Disubstituted Dibenzobarrelene 100</td>
<td>95</td>
</tr>
<tr>
<td>46</td>
<td>Phototransformation of Dibenzobarrelene Diesters with 9-Resolved Chiral Handles</td>
<td>97</td>
</tr>
<tr>
<td>47</td>
<td>Di-π-Methane Photorearrangement of Acid-Ester 149</td>
<td>106</td>
</tr>
<tr>
<td>48</td>
<td>Photochemical Transformations of Lactone-Ester 96 and Its Analogue 93c</td>
<td>109</td>
</tr>
<tr>
<td>49</td>
<td>Independent Preparation of Photoproducts 152 and 153</td>
<td>111</td>
</tr>
<tr>
<td>50</td>
<td>Photorearrangements of Dibenzobarrelene Lactam 154</td>
<td>113</td>
</tr>
<tr>
<td>51</td>
<td>Di-π-methane Photorearrangement of Dibenzobarrelene Amine Derivative 160</td>
<td>114</td>
</tr>
<tr>
<td>52</td>
<td>Biradical Intermediates in Photorearrangement of Lactone-Ester 96</td>
<td>115</td>
</tr>
</tbody>
</table>
Scheme 53 Phototransformation of Methyl Lactone-Ester 97 in Solution ........................................ 128
Scheme 54 Photorearrangement of Methyl Lactone-Ester 97 in the Solid State ................................ 133
Scheme 55 Independent Syntheses of Photoproduct 171 and Its Isomer 172 ...................................... 135
Scheme 56 Di-π-Methane Photorearrangement of Lactone 98 ............................................................. 138
Scheme 57 Quantum Yield and Reaction Rate Relationships .............................................................. 143
Scheme 58 General Triplet Quenching Mechanism ............................................................................ 146
Scheme 59 Photocycloadditions of 1,3-Dienes ..................................................................................... 150
Scheme 60 [2+2] Photocycloaddition of Lactone-Ester 96 to 2,5-Dimethyl-2,4-hexadiene ..................... 151
Scheme 61 Photocycloaddition of Lactone-Ester 96 to 1,3-Cyclohexadiene ........................................... 155
Scheme 62 [4+2] Photocycloaddition of 9-Anthrylmethyl Methyl Fumarate ........................................ 167
Scheme 63 Photolysis of Lactone-Ester 96 in the Presence of 2,3-Dimethyl-2-butene ......................... 169
Scheme 64 Photorearrangements of 9-Chloromethyl Dibenzobarrelene 93d ........................................... 173
Scheme 65 Photorearrangement of Dibenzobarrelene via Its Singlet Excited State ............................... 178
Scheme 66 Photorearrangement of Labeled Benzobarrelene via S1 .................................................. 179
Scheme 67 Photorearrangements of 9,10-Dimethyl Dibenzobarrelene Diester 204 ......................... 180
Scheme 68 Photorearrangement of Dibenzoyl Dibenzobarrelene 211 ................................................. 181
Scheme 69 Proposed Mechanism for the Formation of Product 196 and 197 ............................... 182
Scheme 70 Phototransformation of Tetrachlorocyclohexadienone 218 ............................................. 184
Scheme 71 Photochromism of Tetrachlorodihydro-naphthalen-1-one (220) ................................. 186
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INTRODUCTION
During the past two decades, there has been a tremendous growth of research on organic chemical reactions in anisotropic or organized media such as crystalline solids, liquid crystals, micelles, monolayers, zeolites, host-guest complexes, polymer matrices and surfaces. The understanding of structure-reactivity relationships and the mechanisms of chemical processes has become wider as more chemical reactions were explored in these organized media.

It has been a prime goal of organic chemists to achieve reaction with high regio- and stereoselectivity by designing reaction systems that are similar to those of enzymatic processes. An outstanding feature of the enzymatic reactions is the high degree of order in the system and the strict control of molecular movement along the reaction coordinate (from reactant to product). By using a well organized system in which a chemical reaction proceeds, one might be able to mimic the enzyme process and control the direction of reaction in the sense of achieving high selectivity.

Crystalline phase is unique; it possesses the highest degree of order among the organized media. Therefore, it seems attractive to study chemical reactions in the crystalline solid. There are two important factors that govern a chemical reaction taking place in the crystalline phase: the conformation and the packing arrangement of the reacting molecules. Compared to isotropic (liquid) phases in which a flexible organic molecule may adopt many conformations owing to the fast equilibria between them, in the crystal the molecule will rarely adopt more than one conformation, and it is often found that organic molecules crystallize in or near their minimum energy conformations. Considering
that the outcome of the reaction is sensitive to the conformation, one may expect that the reaction in the crystalline phase would be more selective than that in solution. The packing pattern of the reacting molecules in the crystal is also crucial. That is, the neighboring molecules (the medium or the environment) around the reactant in the crystal may have such a profound effect on the reaction course that the chemical consequences would be controlled by the molecular packing arrangement.

I. Photochemistry in the Solid State

Although investigations of organic photoreactions in the solid state date back to the end of the last century, they have been studied widely only in recent years. Now, the involvement of X-ray crystallography and other solid state spectroscopic techniques such as magic angle spinning solid state $^{13}$C NMR have proved to be invaluable for structure-reactivity correlations. This is because they provide a detailed picture on the molecular structure and the packing arrangement of reactant (and product).

A number of review articles on solid state photochemistry has appeared in recent years, and many examples of solid state reactions have been reported. Scheme 1 shows some typical examples taken from the literature, which demonstrate completely different photochemical behavior of organic molecules in solution versus the solid state.
Scheme 1  Examples of Photoreactions in Solution versus the Solid State.
Quinkert and co-workers\textsuperscript{4} investigated the photoreaction of 1,1,3-triphenyl-2-propanone (1) in the solid state versus solution. They found that, in solution, photolysis of this compound led to the loss of carbon monoxide and the formation of three radical coupling products 2, 3 and 4 in a statistical ratio of 1:2:1. However, irradiation of crystals of 1 resulted in the exclusive product of 1,1,2-triphenylethane (3). In the same paper, they also reported stereospecific photoextrusion reactions of 1,3-diphenyl-2-indanones in the solid state compared to the same reactions in solution in which the stereochemistry of the product was governed by thermodynamic factors.

One of the earliest investigations of the effect of the crystalline environment on unimolecular photoreactivity was that of Matsuura et al.\textsuperscript{5} on santonin 5 shown in the middle of Scheme 1. Dienone 5 rearranges to lumisantonin 6 upon photolysis in benzene. On the other hand, products formed in the solid are mainly dimers which were assumed to be produced by the formation and subsequent dimerization of cyclopentadienone 7.

The third example is chosen from a series of investigations on the photochemistry of \( \alpha,\beta \)- and \( \beta,\gamma \)-unsaturated ketones by Scheffer, Trotter and co-workers.\textsuperscript{6} As shown in Scheme 1, compound 8 gives completely different results upon irradiation in the two media. In benzene, tetracyclic diketone 9 is formed, whereas tricyclic isomer 10 is observed in the crystalline phase. The authors established the structure-reactivity relationships in this phototransformation based on crystallographic studies.
The three examples above clearly demonstrate that molecular crystal lattice has a remarkable influence on the course and selectivity of organic reactions. In general, the crystalline environment controls the overall reaction pathways, and this environment provides organic chemists with an entirely new method to study chemical processes.

It is worth mentioning that it is easier to conduct organic photoreactions in the solid state than to perform thermal solid state reactions. The crystallinity of the sample is normally preserved during irradiation of the crystals, while thermal reactions often result in melting of the crystals. In the case that crystal melting accompanies the reaction process, the selectivity will normally be lower owing to the loss of topochemical control.

Although considerable progress has been made in the last two decades in the study of organic solid state chemistry, photochemistry in particular, much remains to be learned. In this field, many of the general rules of solution phase organic chemistry do not apply, and most of the investigations on this subject have been, and continue to be, at a descriptive stage. That is, the main task of a solid state chemist is to explain the results when an unexpected observation has been made in a solid reaction. Part of the reason lies in our present inability to predict the packing arrangements of organic molecules and our insufficient understanding of close molecular interactions in crystals.
II. The Topochemical Principle

Organic molecular reactions occurring in the solid state often differ from reaction in isotropic or fluid media. This is due to the fact that the reactants in the crystal sense the physical restraints given by the other closely packed molecules and this crystalline environment constrains the molecules or groups in their three-dimensional mobility along the reaction coordinate. In contrast, atomic and molecular motions in solution are free of such restraints, and it is well accepted that the reactivity of organic molecules in solution are controlled by such factors as electronic and steric effects.

The topochemical principle that underlies the entire field of organic solid state chemistry was originally postulated by Kohlshutter in 1918. According to Kohlshutter, a topochemically controlled reaction is one in which the nature of the products is governed by the influence of the three-dimensionally periodic arrangement of the molecules in the solid. This concept was termed the "topochemical postulate".

However, not much progress was made on the study of the solid chemistry until the early 1960s when Schmidt and co-workers started systematic investigations of solid state [2+2] photodimerizations by making use of the powerful technique of X-ray crystallographic analysis. As a result of their intensive studies on the factors that control the course of organic solid state photoreactions, Schmidt and co-workers provided strong experimental evidence for the topochemical postulate and stated that reactions in the solid state proceed with minimal atomic and molecular movement. Since then, the topochemical postulate has been
used as a fundamental principle in organic solid state photochemistry, and provides a basic understanding of a large number of solid state photoinduced reactions. An elegant example from the work of Schmidt and co-workers\textsuperscript{10} on the photocycloadditions of \textit{trans}-cinnamic acids in the solid state which best elucidates this basic principle is depicted in Scheme 2.

\begin{center}
\includegraphics[width=\textwidth]{Scheme2}
\end{center}

\textbf{Scheme 2} Photochemical [2+2] Cycloadditions of \textit{trans}-Cinnamic Acid in the Crystalline State.
trans-Cinnamic acid (11) crystallizes in three different morphologies known as the α-, β- and γ-forms. The α-form, which is characterized by an intermolecular center-to-center distance between double bonds of 3.6-4.1 Å, led to the formation of the centro-symmetric α-truxilic acid 12 upon UV irradiation. The β-type crystals, with a separation distance of 3.9-4.1 Å between the two double bonds and a plane of symmetry between two reacting molecules, formed mirror-symmetric β-truxilic acid 13. In contrast, no reaction was observed in the γ-modification of trans-cinnamic acid, which has a center-to-center distance of 4.7-5.1 Å and a non-parallel molecular arrangement in the crystal. In solution, trans-cinnamic acid (11) underwent only trans-cis photoisomerization, and no dimerization was observed.

Based on the photochemical and crystallographic studies of a large number of cinnamic acids, Schmidt and co-workers established structure-reactivity relationships for [2+2] photodimerizations in the crystalline phase. They suggested that the factors that control the course of solid state [2+2] cycloadditions lie in the separation distance and the intermolecular arrangement or mutual orientation of the reacting molecules in the crystals. Schmidt⁹,¹⁰ proposed a maximum intermolecular separation of 4.2 Å between the parallel aligned reactive double bonds as a general rule in the solid state [2+2] dimerizations. Despite some exceptions,³⁹ this well accepted criterion has been met among many subsequent solid state photodimerizations.
III. Reactivity and Selectivity of Organic Reactions in the Crystalline State

Representing a fully allowed topochemical reaction, a single-crystal to single-crystal or so-called topotactic transformation is one in which a solid sample preserves its crystallinity as reactants are completely converted into products. In such case not only the nature and stereochemistry of the product are nearly the same as those of the reacting molecule(s) packed within the perfect lattice, but also the molecular motions are kept to a minimum. Among the few known examples of single-crystal to single-crystal reactions, the photodimerization of benzylidenecyclopentanone 15 (Scheme 3), studied by Jones and Thomas, deserves to be mentioned.

\[
\begin{align*}
15 & \xrightarrow{h\nu} 16
\end{align*}
\]

Scheme 3  Photodimerization of Benzylidenecyclopentanone.

Crystallographic analysis demonstrated both the structural similarity and the similarity in cell dimensions between the reactive monomers and the dimers as shown in Figure 1. From the packing arrangement, it also revealed that the dimerization process requires
little motion of the atoms. It should be pointed out, however, that the vast majority of organic solid state photoreactions studied so far do not belong to this category. In most cases, the crystal lattice is destroyed due to the formation of products.

![Composite Diagram Comparing the Packing of the Molecular Units within the Monomer and Dimer Crystal Structures of Benzylidene cyclopentanone.](image)

Figure 1  Composite Diagram Comparing the Packing of the Molecular Units within the Monomer and Dimer Crystal Structures of Benzylidene cyclopentanone.

It is understood that the crystal lattice exerts specifically different effects in different directions, therefore the reaction taking place in the crystal is anisotropic. Under certain circumstances, extremely large strains from the crystalline environment may disfavor a certain reaction even though the reacting molecules pack within a bonding distance and with a favorable orientation. Cohen\textsuperscript{15} recognized such anisotropic effects and incorporated them under the intuitive concept of the "reaction cavity". Cohen reasoned that the reacting molecules in a crystal occupy a certain volume with a well defined
shape. This space occupied by the reacting molecule(s) is defined as the "reaction cavity" and it is surrounded by the other closely packed molecules. The atomic movement constituting the reaction will cause pressure on the cavity wall, which will tend to become distorted. However, any such distortion in shape will be resisted by the closely packed environment, and consequently only those reactions involving minimal change or distortion will be feasible (Figure 2). In other words, the topochemical postulate can be extended to "reactions that proceed under lattice control do so with minimal change or distortion of the surface of the reaction cavity".\(^\text{15}\) This concept has proved to be very useful in interpreting a variety of the organic solid state reactions, especially where more than one reaction pathway is allowed.

![Figure 2](image)

Figure 2  Pictorial Representation of "Reaction Cavity" Concept.

Scheffer, Trotter and co-workers\(^\text{16}\) have identified and systematically studied specific intermolecular effects that control the solid state photoreactivity of ene-dione, cyclohexenone, cyclohexa-
dienone and barrelene compounds. A certain expected reaction which does not occur in crystals owing to the severe steric interactions between the reactant and its surrounding molecules was described to be "steric compression" controlled. For example, cyclohexenone derivative 17 shown in Scheme 4 was found to be unreactive toward [2+2] photodimerization in the solid state in spite of the fact that the intermolecular distance and orientation between the enone double bonds are favorable for the dimerization. 16b

Scheme 4 Reaction Controlled by "Steric Compression".
This lack of reactivity was suggested to be due to the two specific short contacts between the methyl groups from the reacting molecules and those from the neighboring molecules in the lattice as seen in Scheme 4. Another example of such "steric compression" controlled solid state reaction has also been reported by Scheffer, Trotter and co-workers.  

More recently, other topochemical considerations that affect reactivity and selectivity in the photochemistry of organic solids have been introduced. These include "dynamic preformation" (introduced by Craig to emphasize the possible effect of electronic excitation in the molecular crystal), "local stress" and the role of defects on solid state reactions. These important concepts have been discussed in some of the review articles, and will not be included here.

Crystal Engineering

Although a number of remarkable, highly stereoselective reactions proceed smoothly in the crystalline phase, the specific packing arrangements inside the crystal which are required for achieving such high selectivity are given by nature rather than designed deliberately. Even though an understanding of the relationship between structure and reactivity enables one to explain product formation and reaction selectivity in many solid state reactions, these are still far from predicting the packing patterns of organic molecules in crystals. The reason is that the nature of intermolecular forces involved in determining the crystal structure is not yet sufficiently understood to allow selection between alternative possible arrangements. A theoretical
approach by application of molecular mechanics calculations to the solid state has proved to be successful in predicting some crystal packing.\textsuperscript{1b}

To achieve a desired product with specificity and to study solid state chemistry in a systematic way, one needs to know how to engineer a particular polymorphous form possessing the necessary topochemical attributes that would lead to the desired products. Schmidt with his colleagues delineated various ways of achieving this and coined the phrase "crystal engineering",\textsuperscript{9b} the idea being to steer molecules to pack in certain pre-determined arrangements during the growth of the crystals.

Today, such "crystal engineering" is possible, but only to a limited extent, on the basis of some empirical packing generalizations that have been uncovered over the past years.\textsuperscript{3aa} Several successful approaches have been reported in the literature, and some of the points are outlined as follows:

1). Complexation or co-crystallization with mercuric chloride to achieve a separation distance of 4 Å between double bonds for photodimerization.\textsuperscript{23}

2). Monochloro and dichloro substitution on aromatic rings to control the packing geometry with the shortest axis of the unit cell about 4 Å.\textsuperscript{24}

3). Formation of mixed crystals or solid solutions by using charge-transfer interactions or by incorporating a photostable compound into the lattice of a photoactive substrate to bring (different) potential reactants into face-to-face close packing arrangements.\textsuperscript{25}
Asymmetric synthesis has been an extensively studied area in organic chemistry, and many asymmetric synthetic methods have been developed for reactions in solution phase including asymmetric photoreactions. The basic principle involves the use of an external dissymmetric influence, such as a resolved chiral agent, chiral catalyst, chiral solvent or circularly polarized light in the case of some photoreactions. Therefore, optically active compounds can be generated by exerting such asymmetric influence on a prochiral or racemic reactant which leads to diastereomeric transition states of different energy. Although asymmetric syntheses by photochemical reactions in solution have been carried out in a number of cases, the method is limited owing to low optical yields.

It is also known that asymmetric synthesis can also be performed in the solid phase. This is reflected by the fact that crystal chirality can be transformed into permanent molecular chirality via a topochemically controlled solid state reaction. In recent years, such asymmetric transformations with high optical yields have been achieved by using the chiral influence from molecular crystals.

We know that molecular chirality results from the dissymmetric, three-dimensional arrangement of the constituent atoms or groups, whereas crystal chirality can be considered to be due to the similar spatial arrangement of the molecules in the crystal. It has been established that there is a total of 230 space groups in relation to the
symmetry of crystals. These represent the different symmetry arrangements in which molecules may pack. They can be classified as chiral or achiral depending on the presence or absence of certain symmetry elements. The chiral space groups, 65 out of the 230 possible ones, contain only symmetry elements of the first kind, i.e., translations, rotations and combinations of these. The most common chiral space groups for organic molecules are monoclinic $P2_1$ and orthorhombic $P2_12_12_1$. The 165 achiral space groups possess the symmetry elements of the first kind and of the second kind such as mirror or glide planes and/or centers of inversion.

It is well known that all optically active molecules must crystallize in chiral space groups, and it is also known that even highly symmetrical molecules (which are achiral) can form chiral crystals. For a racemic mixture, it may either aggregate to form a non-chiral racemic compound, or undergo a spontaneous resolution where the two enantiomers segregate into a conglomerate of chiral crystals. One such famous example is the separation of racemic sodium ammonium tartrate into pure enantiomorphous crystals by Pasteur.\textsuperscript{30} It is obvious that the effort of achieving high asymmetric induction via chemical reactions in the solid state will be focused on those organic molecules that crystallize in any of the 65 chiral space groups, although under certain circumstances some asymmetric syntheses have recently been achieved by using non-chiral or centro-symmetric crystals.\textsuperscript{32}
Absolute Asymmetric Synthesis

As it is mentioned above, achiral organic molecules may crystallize in either chiral or achiral space groups. In the former case, the molecules in the crystal experience a chiral crystalline environment. Provided that one or more chiral centers are generated in the solid state reaction, the crystal chirality may be converted into permanent molecular chirality in the product by a topochemically controlled process. Such a process that generates optically active products in the absence of any external chiral influence is referred to an "absolute asymmetric synthesis". This specific transformation cannot be performed in solution, where asymmetric induction must be transferred from one chiral system into another. Therefore, the absolute asymmetric synthesis may serve as a model process for the explanation of the origin of chirality in the molecules of nature. Several examples selected from the literature are shown in Schemes 5, 6 and 7.

Systematic studies of bimolecular [2+2] photocycloaddition reactions aimed at asymmetric synthesis in the solid state were carried out by Schmidt and co-workers. Irradiation of single crystals of pure 18 or 19 gave the optically inactive cyclobutane derivatives 20 and 21 respectively. However, when dilute (15%) solid solutions of 19 in 18, space group $P2_12_12_1$, were prepared and the longer wavelength absorbing thiophene compound 19 selectively photolyzed, a 70% enantiomeric excess of the chiral heterodimer 22 was achieved.
Scheme 5 Absolute Asymmetric Synthesis by Solid State [2+2]

Photocycloaddition.

Following the pioneering work of Schmidt et al., several other asymmetric transformations were reported. As shown in Scheme 6, Scheffer, Trotter and co-workers\textsuperscript{34} demonstrated that the adamantyl ketone derivative 23 crystallizes in the chiral space group $P2_12_12_1$. Irradiation of a single crystal of this ketone resulted in the formation of the cyclobutanol derivative 25 via the Norrish type II reaction with approximately 80% e.e. A second example was also offered by Scheffer, Trotter and co-workers.\textsuperscript{34} Upon irradiation of a chiral single crystal (space group $P2_12_12_1$), dibenzobarrelene diester 26 underwent a unimolecular rearrangement to afford dibenzosemibullvalene derivative 27 with quantitative enantiomeric excess. In contrast, photolysis of the same compound in an achiral crystal modification (space group Pbca) gave no optical activity. By determining the absolute configurations of both the reacting molecule in the chiral single crystal and its optically
active photoproduct, the authors demonstrated that this phototransformation proceeds stereospecifically through one of the four degenerate pathways in the solid state.

Scheme 6 Absolute Asymmetric Syntheses via Norrish Type II and Di-π-Methane Reactions in the Solid State.

As shown in Scheme 7, Toda and co-workers\textsuperscript{35} found that irradiation of N,N-diisopropylphenylglyoxylamide (28) in single chiral crystal form (space group $P2_12_12_1$) led to the formation of the optically active $\beta$-lactam 29 with 93% e.e.
Scheme 7 Absolute Asymmetric Synthesis of β-Lactam 29.

The examples above clearly indicate that stereospecific asymmetric transformations can be achieved by converting crystal chirality into permanent molecular chirality. Owing to the strict requirements for such processes, however, the development of new systems appropriate for such asymmetric syntheses has been slow. So far, only a few examples\textsuperscript{32,36} of absolute asymmetric synthesis have been described including the earlier report of an asymmetric gas-solid bromination reaction by Penzien and Schmidt.\textsuperscript{37} It is far from common that achiral organic molecules spontaneously crystallize in chiral space groups and undergo chemical reactions in such media to give optically active products. Even in some cases where these conditions have been met, one needs to use relatively large chiral single crystals to conduct such asymmetric transformations in a practical way. Another difficulty is that the field of crystal engineering is not so advanced that the desired chiral space group of organic crystals can be achieved.
The approach to overcome these problems is to use resolved chiral molecules, since all optically pure compounds must crystallize in chiral space groups. In the chiral crystals that consist of optically active molecules, the reacting molecule senses a chiral environment. Therefore, the asymmetric induction will be caused not only by the chiral center of the molecule but also by the chiral crystalline field. This is in contrast to the situation in solution, where the asymmetric induction is exerted solely by the chiral center of the molecule. For the purpose of studying asymmetric synthesis in the solid state, the chiral center used as a chiral handle can be designed in such a way that it is relatively far away from the site of reaction. Ideally, the chiral handle would be located at a site sufficiently remote so that no asymmetric induction is exerted when the reaction is carried out in solution. Thereby, the role of the chiral handle is simply to force the molecule into a chiral lattice. Under these conditions, the asymmetric induction in the solid state can be attributed exclusively to the chiral crystalline lattice. If the unreactive chiral handle is removable after the reaction, the optical activity of the product can then be determined. This may provide an alternative method of asymmetric synthesis in the solid state.

V. Unimolecular Photorearrangements

Most of the research papers published in the area of organic solid state chemistry during the past 25 years have been concerned with bimolecular reactions, especially intermolecular \([2+2]\) photocycloadditions, first studied by Schmidt with his collaborators at the
Weizmann Institute of Science. Approximately fifteen years ago, Scheffer, Trotter and co-workers initiated systematic investigations on unimolecular photorearrangement reactions in the crystalline state.

In contrast to bimolecular solid state processes, where the role of the crystal lattice is primarily one of locating a pair of reacting molecules within bonding distance of one another with an orientation favorable for reaction, unimolecular reactions occurring in organic crystals are controlled mainly by intramolecular geometric conformational factors. Although the crystal lattice still plays an important role, it has been considered that the packing arrangement exerts its influence mainly as a dynamic effect. This dynamic effect, first formulated qualitatively as the concept of the reaction cavity by Cohen, is reflected in the transition state where the non-bonded repulsive interactions resulting from the atomic and molecular interactions of the reactant with its surrounding molecules determine which pathways will be traversed. Very often they are those with the least motions.

A. Photorearrangement of Cyclohexenone Systems

One of the model reaction systems studied in this thesis is the photorearrangement of 4,4-diarylcyclohexenones. Unimolecular rearrangement of 4,4-disubstituted cyclohexenones in solution has been the subject of intensive study for nearly 30 years, not only from the viewpoint of mechanistic interests but also in its synthetic applications. Several reviews on this subject have appeared, which
best summarize the important features of these classic photorearrangements.

Normally upon photolysis in organic solvents, 4,4-dialkyl substituted cyclohexenones undergo unimolecular rearrangement leading to the formation of bicyclo[3.1.0]hexan-2-ones, so-called lumiketones, accompanied by ring contraction products. This kind of transformation is illustrated by the photorearrangement of 4,4-dimethyl-2-cyclohexen-1-one (30) to the lumiketone 31 and cyclopentenone 32,\(^\text{39}\) one of the earliest investigated systems (Scheme 8).

![Scheme 8 Photorearrangement of 4,4-Dimethyl-2-cyclohexen-1-one.](image)

It was pointed out that these reactions are competitive with photodimerization and photoreduction of the enones, and the yields of the lumiketone 31 are usually optimal in polar solvents such as t-butanol. Based on a survey of the photochemical behavior of a large number of cyclohexenones, Dauben and co-workers\(^\text{40}\) concluded that the presence of two substituents at the C-4 position (at least one of which
must be an alkyl group) is necessary for the formation of the lumiketone. If one of the substituents at C-4 is an aryl group, such as compound 33, the lumiketone rearrangement will compete with phenyl migration as shown in Scheme 9. Furthermore with two phenyl substituents at the C-4 position, such as found in enone 36a, the phenyl migration products 39a and 40a are exclusive.

Scheme 9  Phototransformations of 4-Phenyl-4-methyl-2-cyclohexen-1-one and 4,4-Diphenyl-2-cyclohexen-1-one.
Although it might be considered that the photorearrangement of 4,4-diaryl substituted cyclohexenones is an example of the di-\(\pi\)-methane rearrangement by a somewhat parallel mechanism, the reaction proceeds via the \(n-\pi^*\) excited state upon absorption of a photon and is followed by migration of the phenyl group and subsequent bond formation between C-2 and C-4 (Scheme 9).

B. The Di-\(\pi\)-Methane Rearrangement

The second reaction under investigation in the present thesis is the so-called di-\(\pi\)-methane rearrangement, one of the most thoroughly studied photochemical reactions.\(^4^3\) Its name is derived from the general observation that certain organic molecules in which two \(\pi\)-bonds are separated by an \(sp^3\)-hybridized or methane carbon atom undergo rearrangement upon absorption of a photon of light to give vinylcyclopropane derivatives. Scheme 10 illustrates the transformation of the simplest di-\(\pi\)-methane system, 1,4-pentadiene (41), along with the mechanism proposed by Zimmerman.\(^4^3\) Initial 2,4-bonding of the two \(\pi\)-bonds of 41 generates biradical 42, and this is followed by bond reorganization to biradical 43 and ring closure to vinylcyclopropane 44.
Scheme 10  Representation of a Simple Di-π-Methane Rearrangement.

This simple mechanism has wide application in predicting and describing a large number of examples of the di-π-methane rearrangement. However, it is necessary to point out that the biradical structures 42 and 43 in Scheme 10 are approximations of species along the reaction pathway and do not necessarily represent true intermediates.

Scheme 11 shows a variety of examples of photorearrangement of the di-π-methane systems. Here it can be noticed that both aliphatic and aromatic π-bonds are capable of participating in the process. It should be pointed out that the reaction multiplicity is dependent on the nature of the molecular structure. In general, acyclic di-π-methane reactants rearrange effectively from their singlet excited states, whereas cyclic ones prefer to undergo the rearrangement via their triplet excited states.
Scheme 11  Examples of the Di-π-Methane Photorearrangement.

One of the earliest examples of the di-π-methane rearrangement, reported by Zimmerman and co-workers, is the photochemical conversion of barrelene 54 to semibullvalene 55 using acetone sensitization. In contrast, cyclooctatetraene (56) is the major product upon direct
irradiation. Similar photochemical behavior was observed in the case of benzobarrelene 57, the triplet reaction giving benzosemibullvalene (58), while benzocyclooctatetraene (59) is formed by direct irradiation (Scheme 12).

There are many other examples belonging to this class of barrelene compounds. Among them, dibenzobarrelene diester derivatives, such as compound 60, are of special interest in this thesis. Ciganek was the first to demonstrate the di-\(\pi\)-methane photorearrangement of dibenzobarrelene 60 in solution. This reaction is consistent with the Zimmerman mechanism, in which the initial step involves bond formation between the vinyl carbon atom and the neighboring aromatic carbon atom (vinyl-benzo bridging). Subsequent reorganization and the ring closure produce dibenzosemibullvalene diester derivative 63. Scheffer, Trotter
and co-workers have recently studied the solid state photorearrangement of the substrate 60 together with some other similar derivatives. They demonstrated that the reactions proceed smoothly in the crystalline phase as well as in solution (Scheme 13).

Scheme 13  Photochemical Transformation of Dibenzobarrelene Diester Derivative.

When a substituent is introduced at the 9-position of the dibenzobarrelene system (e.g., compound 64 in Scheme 14), two different reaction pathways (path A and path B) leading to a pair of regioisomers 67 and 70 can be followed by applying the general mechanism. Based on a number of investigations on the regioselectivity of the photoreaction of 9-substituted dibenzobarrelenes in solution, it was suggested that the regioselectivity of such reactions is
generally determined by the electronic properties of the 9-substituents, which affect the relative stabilities on the initially formed intermediate species 65 and 68.

Scheme 14 The Di-$\pi$-Methane Photorearrangement of 9-Methyl Dibenzobarrelene Diester.
VI. Objectives of Present Research

It is apparent from the previous discussion that the establishment of basic theories and fundamental rules in solid state chemistry require that more solid state reactions be discovered and a better understanding of structure-reactivity relationships be gained. This leads to the objective of the present thesis, that is to explore more photochemical reactions in the crystalline phase and to understand crystalline effects on the photoreactivity of organic compounds. It is preferable that the photochemistry of the model systems chosen for study be well understood in an isotropic medium, i.e. solution, so that the primary research effort will be focused on the effect of the crystal lattice on reactivity and selectivity. The approach adopted in this thesis is primarily one of product analysis. In general, product(s) and product distribution of a photochemical transformation in solution and in the crystalline phase are studied. If a difference exists between the two, the main task will be to search those factors that cause the differences and to understand them from the viewpoint of the crystal lattice effect. From this, it is expected that certain structure-reactivity correlations can be established based on X-ray crystallography and other solid state structural and spectroscopic analyses.

The model system initially selected for study was the photoinduced rearrangement of 4,4-diaryl substituted cyclohexenones, in which the basic features of the photochemistry in solution have been established by Zimmerman and co-workers as discussed earlier. The first series of compounds chosen for investigation was 4-aryl-4-phenyl-2-cyclohexen-1-ones (71a and 71b) as shown in Scheme 15. Upon photolysis, the enone 71
may lead to the formation of rearranged products. Aryl group migration gives the compound 72. On the other hand, the product 73 is formed if phenyl group migrates. In their study of migratory aptitude of 4-aryl-4-phenylcyclohexenones (71b and 71c), Zimmerman and co-workers\textsuperscript{53} have demonstrated that an electronic stabilizing effect was responsible for the preference of aryl group migration over phenyl migration in solution.

![Scheme 15 Photorearrangement of 4-Aryl-4-phenylcyclohexenones.](image)

It is reasonable to assume that changing the substituent X will not affect the electronic structure of either the ground or the excited state of the enone moiety. Therefore, the main objective here is to determine the crystal lattice effect exerted on the migratory aptitude, as it is considered that the aryl groups which prefer to migrate in
solution may not migrate so well in solid state owing to their larger size.

As an extension of the above ideas, compounds 74 (R = methyl and ethyl) were designed. Application of the established mechanism predicts the formation of two structural isomers, 75 and 76. It can be also expected that in the solid state the molecules will take their lowest energy conformations, preferably the pseudo-chair conformation with the methyl group in pseudo-equatorial position. In such circumstances, the aim of the investigation is to find out how the crystal lattice will affect stereochemistry of the photoproducts (Scheme 16).

Scheme 16 Photorearrangement of 4,4-Diphenyl-6-alkylcyclohexenones.

The second proposed area of research was to investigate the solid state photochemistry of 9-substituted dibenzobarrelene diesters (general
structure 77), a di-π-methane system. Upon irradiation in solution, a unimolecular rearrangement of this type of compounds will lead to the formation of photoproducts 78 and 79 via reaction pathways A and B (refer to Scheme 14) respectively. The regioselectivity of this phototransformation is controlled by the electronic properties of the 9-substituent as discussed earlier. The first objective was to determine whether or not the electronic effect would still be a predominant factor in the solid state and to establish a general trend of crystal lattice effects on the reactivity and selectivity of 9-substituted dibenzobarrelene diesters. It was considered that a number of derivatives with different substituents at the 9-position, which do not disturb the electronic structure of the di-π-methane moiety, should be prepared in order to facilitate the investigation.

Scheme 17 Photorearrangement of 9-Substituted Dibenzobarrelenes.

\[ \text{E}=\text{CO}_2\text{CH}_3, \]
\[ \text{X}=\text{substituents} \]
The second major goal was derived from the fact that a resolved chiral substituent or handle at the 9-position of dibenzobarrelene would force the molecule to crystallize in a chiral space group. Photolysis of crystals of this type of compounds provides an opportunity to study the asymmetric inductions due to the influence of the chiral crystalline environment. It was thought that such influence might be different on the two pathways (path A and path B). If so, it would be interesting and worthwhile to find out the reasons that cause differences in asymmetric induction on the two pathways in the solid state.

Another important objective of the proposed research was to investigate the possibility that two or more crystal modifications might display different reactivity and/or selectivity in the solid state reaction. However, the existence of polymorphism is difficult to predict and to control. This has been a fascinating area, since more detailed structural information on the influence of reaction environment can be obtained wherever different photochemical behavior due to crystal morphology is observed.

The final objective of this thesis was developed, while the research was being carried out, from the realization that one of the target molecules under study crystallized in a chiral space group, but the molecule does not possess any chirality of its own. Therefore, the transformation of crystal chirality of the achiral starting material to the permanent molecular chirality of the products was studied. This provided another example of absolute asymmetric synthesis.
RESULTS AND DISCUSSION
I. Preparation of Starting Materials

A. Synthesis of Cyclohexenone Substrates

4-Phenyl-4-p-bromophenyl-2-cyclohexen-1-one (71a) and 4-phenyl-4-p-cyanophenyl-2-cyclohexen-1-one (71b) were prepared according to the procedures reported by Zimmerman et al.\(^5^3\) (Scheme 18). Addition of dimethyloxosulfonium methyldie (81) to p-bromobenzophenone (80) by the method of Corey and co-workers\(^5^4\) yields the corresponding epoxide 82, which is acid-catalyzed to rearrange to acetaldehyde 83. Condensation of 83 with methyl vinyl ketone leads to the formation of the desired compound, 4-phenyl-4-p-bromophenyl-2-cyclohexen-1-one (71a). The bromide 71a is then treated with cuprous cyanide by the method of Newman\(^5^5\) to give the corresponding cyano derivative 71b.

\[
\begin{array}{ccc}
\text{80} & + & \text{81} \\
\text{CHO} & \text{H} & \text{CHO} \\
\text{OH}^- & \text{OH}^- & \text{CuCN} \\
\text{83} & \text{82} & \text{71a} \\
\text{Ph} & \text{Ph} & \text{Ph} \\
\text{PhBr-p} & \text{PhBr-p} & \text{PhCN-p} \\
\end{array}
\]

Scheme 18  Syntheses of 4-p-Bromophenyl- and 4-p-Cyanophenyl-4-phenyl-cyclohexenones.
Synthesis of the C-6 alkyl substituted cyclohexenones began with the condensation between diphenylacetaldehyde (84) and methyl vinyl ketone to afford diphenyl cyclohexenone (36a), which was originally prepared by Zimmerman et al.\textsuperscript{42} A methyl or an ethyl group was then introduced at the C-6 position by the method of alkylation through an enolate intermediate.\textsuperscript{56} This resulted in the desired starting materials 74a,b as seen in Scheme 19. An alternative procedure to synthesize the methyl compound 74a and some other similar derivatives has recently been reported by Zimmerman and co-workers.\textsuperscript{57}

\textbf{Scheme 19} Synthesis of 4,4-Diphenyl-6-methylcyclohexenone (74a) and 4,4-Diphenyl-6-ethylcyclohexenone (74b).
B. Synthesis of 9-Substituted 9,10-Ethenoanthracene Substrates

A [4+2] cycloaddition reaction (Diels-Alder) between the appropriate 9-substituted anthracene and dimethyl acetylenedicarboxylate or methyl propynoate afforded each individual starting material.

Some of the 9-substituted anthracenes were prepared according to the known methods (Scheme 20); others are commercially available. 9-Anthracenemethanol acetate (87) was prepared by treatment of 9-anthracenemethanol (86) with acetyl chloride. Other 9-anthracenemethanol derivatives 89a-c were made from 9-chloromethylanthracene (88) by treatment with the corresponding acid according to the method of Stewart. The acetylene derivative 89c was also prepared by refluxing 9-anthracenemethanol (86) with propiolic acid in benzene, which gave a higher yield. α-Methyl 9-anthracenemethanol (91) was readily prepared by the reported procedure involving addition of methyl magnesium iodide to 9-anthraldehyde (90).

The bridgehead substituted dibenzobarrelene diesters 93a-d were synthesized by Diels-Alder reaction between the corresponding 9-substituted anthracenes 87-89a,b and dimethyl acetylenedicarboxylate (92) (Scheme 21). A mild reduction of compound 94, which is prepared by Diels-Alder reaction, with NaBH₄ at low temperature was used to prepare 9-hydroxymethyl 9,10-ethenoanthracene diester 95. Initial attempts to obtain this starting material by the direct [4+2] cycloaddition of 9-anthracenemethanol (86) to dimethyl acetylenedicarboxylate failed.
Scheme 20 Preparation of 9-Substituted Anthracenes.
Scheme 21  Preparation of Bridgehead Substituted Dibenzobarrelene Compounds via Diels-Alder Reaction.

The direct reaction between alcohol 86 and the acetylenic dienophile 92 afforded lactone-ester 96 instead. It is believed that the lactone-ester 96 was derived from the corresponding alcohol derivative.
95 by the elimination of methanol under the high temperature reaction conditions employed (Scheme 22). This was confirmed by a GC analysis (oven temperature = 220°C) of the authentic sample 95, which gave single peak with the same retention time as that of compound 96. Since the lactone-ester 96 showed interesting photochemical behavior both in solution and in the solid state, the methyl substituted analogue 97 was designed and synthesized by the similar procedure of heating a mixture of anthracene 91 and dimethyl acetylenedicarboxylate (Scheme 22).

Scheme 22  Preparation of Lactone-Ester 96 and Methyl Lactone-Ester 97.
Although the synthesis of the dibenzobarrelene diesters with chiral substituents at the 9-position, compounds 93a and 93b, was first attempted by esterification of the corresponding acid chlorides with the alcohol derivative 95 (Scheme 23), the approach was unsuccessful owing to poor yields.

![Scheme 23 Esterifications between Alcohol 95 and the Corresponding Acid Chlorides.](image)

Scheme 24 shows the preparation of the five-membered ring lactone 98 which was accomplished by an intramolecular Diels-Alder reaction of 9-anthrylmethyl propynoate (89c). 9-Substituted dibenzobarrelene vinyl monoesters 99 and 100 were made from the corresponding anthracene 89a and methyl propynoate (Scheme 24). Diels-Alder reaction between the two
compounds gave a 1:1 mixture of the head-to-head and the head-to-tail isomers. These two isomers were separated by column chromatography and were distinguishable from one another by the coupling constants between the bridgehead and vinyl protons. The assignment was based on the difference in the magnitude of this coupling, which is either vicinal coupling ($J = 6$ Hz) in compound 100 or four-bond coupling ($J = 1$ Hz) in compound 99 (Figure 3). The line broadening of the signals in the $^1$H NMR spectrum of compound 100 is probably due to the interactions between the two side chains, as the signals sharpened when the temperature was increased. In contrast, there is no such contact present in the isomer 99, and no line broadening was observed. This further supports the structural assignments.

Scheme 24 Synthesis of 9-Substituted Dibenzobarrelene Monoesters.

$$
R = (\pm)- \text{ or } (R)-(-)-\text{CH}_2\text{COCH(OMe)}\text{Ph}
$$
Figure 3 Partial $^1$H NMR Spectra of Dibenzobarrelenes 99 and 100.
All structures of the dibenzobarrelene compounds were established by analytical and spectroscopic methods and also by X-ray crystal structure analyses in some cases.

C. Preparation of Crystalline Samples

Except for the case of cyclohexenone 74b, which proved to be an oil at room temperature, all of the starting materials were obtained in crystalline form by recrystallization from suitable solvent(s). Most of the crystalline samples have relatively high melting points (Table 1), and this facilitates the photochemical studies of these compounds in the solid state.

Table 1  Summary of Crystal Preparations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystallization Solvent</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexenone 71a</td>
<td>ether/petroleum ether</td>
<td>123-124</td>
</tr>
<tr>
<td>Cyclohexenone 71b</td>
<td>diethyl ether</td>
<td>79-80</td>
</tr>
<tr>
<td>Cyclohexenone 74a</td>
<td>methylcyclohexane</td>
<td>99-100</td>
</tr>
<tr>
<td>Dibenzobarrelene 94</td>
<td>benzene</td>
<td>171-173</td>
</tr>
<tr>
<td>Dibenzobarrelene 95</td>
<td>methanol</td>
<td>174-176</td>
</tr>
<tr>
<td>Dibenzobarrelene 93c</td>
<td>acetone/hexane</td>
<td>162-163</td>
</tr>
<tr>
<td>Lactone-Ester 96</td>
<td>methanol/chloroform</td>
<td>171-172</td>
</tr>
</tbody>
</table>

(to be continued)
(continued from Page 47)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent Combination</th>
<th>Boiling Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Lactone-Ester 97</td>
<td>methanol/methylene chloride</td>
<td>191-192</td>
</tr>
<tr>
<td>Dibenzobarrelene 93d</td>
<td>methanol/chloroform</td>
<td>168-170</td>
</tr>
<tr>
<td>(±)-Dibenzobarrelene 93b</td>
<td>acetone/hexane</td>
<td>110-112</td>
</tr>
<tr>
<td>(S)-(+) Dibenzobarrelene 93b</td>
<td>acetone/hexane</td>
<td>178-180</td>
</tr>
<tr>
<td>(±)-Dibenzobarrelene 93a</td>
<td>acetone/hexane</td>
<td>141-142</td>
</tr>
<tr>
<td>(R)-(−)-Dibenzobarrelene 93a</td>
<td>acetone/hexane</td>
<td>141-143</td>
</tr>
<tr>
<td>(±)-Monoester 99</td>
<td>ethyl acetate/petroleum ether</td>
<td>194-195</td>
</tr>
<tr>
<td>(R)-(−)-Monoester 99</td>
<td>ether/petroleum ether</td>
<td>182-183</td>
</tr>
<tr>
<td>(±)-Monoester 100</td>
<td>ethyl acetate/petroleum ether</td>
<td>137-139</td>
</tr>
<tr>
<td>(R)-(−)-Monoester 100</td>
<td>ether/petroleum ether</td>
<td>156-158</td>
</tr>
</tbody>
</table>

In order to study the influence of crystal morphology on photoreactivity, each compound was recrystallized from different organic solvents or solvent mixtures. In some cases, recrystallization from melt was also carried out. In the case of compound 93d, crystal modification was successfully achieved. This will be discussed in detail in the latter part of the thesis.

II. Studies on 4,4-Diarylcylohexenones

A. Photorearrangement of 4-Phenyl-4-arylcylohexenones
The solution state photochemistry of 4,4-diphenylcyclohexenone (36a), 4,4-dibiphenylcyclohexenone (36b) and 4,4-di-α-naphthylcyclohexenone (36c) has previously been studied by Zimmerman and co-workers. Upon irradiation in solution, the diaryl substituted enones were shown to form the corresponding bicyclo[3.1.0]hexanones by migration of one of the aryl groups reacting via the triplet excited state. The major product in each case was found to have the trans geometry such as 39a-c (Scheme 25).

If the cyclohexenone is unsymmetrically substituted at the C-(4) position, i.e. the two aryl groups are non-identical, the migration of each aryl group will give a different product upon photolysis. Therefore, it would be of interest to investigate the migration aptitude in solution versus the solid state and to study how the crystal lattice affects the migratory ability of different aryl groups. The compounds chosen for these studies are found in the following sections.

Scheme 25 Phototransformations of 4,4-Diarylcylohexenones.
1. Photochemistry of 4-Phenyl-4-\(p\)-cyanophenylcyclohexenone (71b) and 4-Phenyl-4-\(p\)-bromophenylcyclohexenone (71a)

In an earlier study, Zimmerman, Rieke and Scheffer\textsuperscript{53} investigated the migratory aptitude of different aromatic groups that were attached at the C-(4) position of the cyclohexenone moiety in order to clarify the electronic properties of the excited state. They found that two substrates, 4-phenyl-4-\(p\)-cyanophenylcyclohexenone (71b) and 4-phenyl-4-\(p\)-methoxyphenylcyclohexenone (71c), had similar migration patterns. Upon photolysis, these two substrates led to the formation of compounds 72b and 72c as the predominant products by migration of the \(p\)-substituted phenyl groups (Scheme 26). As a result, it was concluded that irradiation gave an excited-state species (102) which was radical-like at the \(\beta\)-carbon atom of the enone moiety.

\begin{equation}
\text{Scheme 26 Photorearrangement of 4-Phenyl-4-arylcylohexenones.}
\end{equation}
Two compounds, 4-phenyl-4-p-bromophenylcyclohexenone (71a) and 4-phenyl-4-p-cyanophenylcyclohexenone (71b), were synthesized in this study. In order to make a comparison of the migratory aptitudes in solution and in the solid state, the solution phase photolysis of compound 71b was carried out under conditions similar to those reported by Zimmerman;\textsuperscript{53} the photochemistry of the p-bromophenyl analogue 71a in solution is original to this thesis.

Initially, irradiation of the p-cyanophenyl derivative 71b in benzene was performed by using wavelengths of $\lambda \geq 290$ nm (Pyrex filter). Results similar to those reported by Zimmerman et al.\textsuperscript{53} were obtained. It was found later that no cis photoproduct 103b could be detected if the sample was irradiated with wavelengths longer than 340 nm (using a uranium glass filter). The results of the wavelength dependency in the photolysis of 4-phenyl-4-p-cyanophenylcyclohexenone (71b) are summarized in Table 2. Our interpretation of the results is that the absorption of the primary photoproduct 72b at the longer wavelengths is minimal, so that the secondary photoreaction of 72b to give 103b is negligible under these conditions. However, such interconversion of the photoproducts is significant under the condition of $\lambda \geq 290$ nm irradiation.
Table 2  Photolysis of 4-Phenyl-4-p-cyanophenylcyclohexenone at Different Irradiation Wavelengths.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Condition</th>
<th>Conversion (%)</th>
<th>Percentage Yield 72b (%)</th>
<th>Percentage Yield 103b (%)</th>
<th>Percentage Yield 73b (%)</th>
<th>Ratio $(72b+103b)/73b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda \geq$ (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>290 nm</td>
<td>91</td>
<td>71</td>
<td>13</td>
<td>7</td>
<td>$12 \pm 1\textsuperscript{b}$</td>
</tr>
<tr>
<td>340 nm</td>
<td>99</td>
<td>91</td>
<td>0</td>
<td>8</td>
<td>$11 \pm 1$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Analysis by gas chromatography. \textsuperscript{b}The results obtained in this study are the same as those reported (ratio = $14 \pm 2.5$) by Zimmerman \textit{et al.}, see reference 53.

Photolysis of 4-phenyl-4-p-bromophenylcyclohexenone (71a) was conducted in solution (benzene or acetone) by using wavelengths longer than 340 nm. Two isomeric photoproducts were isolated in a preparative run and characterized as the bicyclic ketones 72a and 73a (Scheme 26). The structural assignments are based on spectroscopic information and on the conversion of each photoproduct to the known\textsuperscript{53} bicyclic cyano derivative 72b or 73b (Scheme 27). The trans geometry of the two aromatic groups on the three-membered ring is characterized by the coupling constant of 10 Hz, which is attributed to \textit{cis}-cyclopropyl CH-CH coupling.\textsuperscript{42,53,65} In the case of the bicyclic ketone 72a, the structure was also confirmed by an X-ray crystallographic analysis. This work was done by Ms. Christine Hwang, and the structural details have been documented in her thesis.\textsuperscript{66} The stereodiagram of the molecule,
trans-5-phenyl-6-p-bromophenylbicyclo[3.1.0]hexan-2-one (72a), is given in Figure 4.

Scheme 27 Conversion of Photoproducts 72a and 73a to the Known Cyano Derivatives 72b and 73b.

Figure 4 Stereodiagram of the Molecule of trans-5-Phenyl-6-p-bromophenylbicyclo[3.1.0]hexan-2-one (72a).
It was also found that the photoproduct 72a was the major one in the photolysis of 71a. The product ratio 72a/73a, which is summarized in Table 3, was found to be constant under different percentage conversions of the starting material. This ratio represents the relative migratory ability of the two aromatic groups in the solution phase.

Table 3  Photolysis of 4-Phenyl-4-p-bromophenylcyclohexenone (71a) in Benzene under Varying Conversions.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Conversion (%) of 71a</th>
<th>Yield 72a (%)</th>
<th>Yield 73a (%)</th>
<th>Ratio 72a:73a</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>11</td>
<td>5</td>
<td>69:31</td>
</tr>
<tr>
<td>25</td>
<td>17</td>
<td>7</td>
<td>71:29</td>
</tr>
<tr>
<td>41</td>
<td>28</td>
<td>13</td>
<td>68:32</td>
</tr>
<tr>
<td>54</td>
<td>39</td>
<td>17</td>
<td>72:28</td>
</tr>
<tr>
<td>84</td>
<td>57</td>
<td>27</td>
<td>68:32</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Analysis by gas chromatography.

The preference for the p-bromophenyl group migration leading to photoproduct 72a can be understood by applying the same mechanism which was proposed by Zimmerman and co-workers\textsuperscript{42,53} nearly two decades ago. Zimmerman \textit{et al.} suggested that the migration of the aromatic groups occurs through the half-migrated species 104 and 105 from the excited state intermediate 102 (Scheme 28). It is apparent that the biradical
species 104 would be more stabilized by the para-substituents (X = Br, CN and OMe) through resonance than the biradical 105. Therefore, the aryl group migrates preferentially. We note, however, that the migratory preference of the para-bromophenyl group is less than that of the para-cyano 71b (migration ratio of aryl:phenyl = 14 ± 2.5\(^{53}\)) or the para-methoxy derivatives 71c (migration ratio of aryl:phenyl = 12 ± 2.5\(^{53}\)).

![Scheme 28](image)

Scheme 28  Mechanistic Presentation of the Photorearrangement of 4-Phenyl-4-arylcyclohexenones.

2. Migratory Aptitude in the Solid State

In their very recent studies, Zimmerman and co-workers\(^{67}\) have reported the solid state photochemical behavior of compounds 36a-c (Scheme 25). They found that the photochemistry of these compounds in
solid state is quite similar to that in solution. In each case, the major solid state photoproduct was the trans-diaryl biscyclic ketone 39. However, it was found that the efficiency of the solid state reaction in terms of quantum yields was much lower than that in solution.

When crystals or powders of the p-cyanophenyl derivative 71b were irradiated at room temperature, the reaction was found to give the same photoproducts as in the solution phase reaction. But, the product distribution, i.e. the ratio (72b+103b)/73b, in the solid state was found to be quite different from that in solution. In the solid state, although p-cyanophenyl migration product 72b was still predominant, the formation of the phenyl group migration product 73b was increased compared to the value in benzene (Table 4). As the solid state photoreaction of 71b resulted in partial melting of the crystalline samples at high conversions of the starting material, the reaction was normally kept within 10-20% conversion in order to minimize the crystal melting.

Similarly, 4-phenyl-4-p-bromophenyl cyclohexenone (71a) gave the two corresponding bicyclic ketones 72a and 73a upon photolysis in the solid state. It was observed that the reaction of 71a in the solid state was inefficient. No more than 2% conversion of the starting material could be achieved even for a long period of irradiation (up to 48 hr) by using powdered samples of 71a. The product ratio 72a/73a was also found to be different from that in solution and it is included in Table 4. Single crystals of 71a were found to be photochemically unreactive (within detection limits).
Table 4  Migratory Selectivity of 4-p-Cyanophenyl- and 4-p-Bromophenyl-4-phenylcyclohexenones in Solution and in the Solid State.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>Conversion (%)</th>
<th>Migration Ratio $(72b+103b)/73b$</th>
<th>$72a/73a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyano 71b</td>
<td>Solution</td>
<td>99</td>
<td>11 ± 1</td>
<td></td>
</tr>
<tr>
<td>Cyano 71b</td>
<td>Crystal</td>
<td>20</td>
<td>2.2 ± 0.2\textsuperscript{b}</td>
<td></td>
</tr>
<tr>
<td>Cyano 71b</td>
<td>Crystal</td>
<td>40</td>
<td>3.1 ± 0.3\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>Bromo 71a</td>
<td>Solution</td>
<td>16</td>
<td>2.4 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Bromo 71a</td>
<td>Crystal</td>
<td>2</td>
<td>1.5 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Analysis by gas chromatography. \textsuperscript{b}Irradiation at 337 nm by using a nitrogen laser. \textsuperscript{c}Irradiation at 337 nm by using a nitrogen laser, partial crystal melting was observed.

A comparison of the product distributions in the crystalline and solution phases reveals that, for both substrates 71a and 71b, aryl group migration ($p$-cyanophenyl or $p$-bromophenyl) is predominant in both media. However, the photolysis in the solid state increases the amount of the phenyl group migration product. The medium effect on the migratory aptitude is significant in the photolysis of compound 71b, in which the migration ratio (Ar:Ph) changes from 11 ± 1 in benzene to 2.2 ± 0.2 in the solid state. The results for both compounds, 71a and 71b, seem to be in agreement with our initial ideas that aryl groups ($p$-
bromophenyl and p-cyanophenyl) might not migrate so well in the solid state owing to their larger sizes. Generally speaking, the p-cyanophenyl or p-bromophenyl group is larger in size than the phenyl group, although the difference between them is small. The migration of the para-substituted phenyl group leading to the major photoproducts 72a and 72b, which is favored in solution by the electronic effect, may involve more atomic and molecular motions overall in the solid state reaction. Therefore, more interference between the reacting molecule and the crystal lattice would be expected. Such a reaction pathway that results in more disturbance of the crystal lattice might be restrained by the lattice. On the other hand, formation of the bicyclic ketones 73a and 73b is more favorable due to reduced interference with the crystal lattice by the migration of the phenyl group.

Although such a speculation seems reasonable, further evidence to support this is needed from the point of view of a molecular crystal structure analysis. Owing to the poor quality of the crystals obtained for compound 71b, the molecular crystal structure of 71b has not been determined yet. In the case of compound 71a, however, the molecular crystal structure has been determined.\textsuperscript{66} The observed 1-2\% reaction by using powders of 71a could be ascribed to a surface photoreaction. It has been reported recently by Scheffer, Trotter and co-workers\textsuperscript{68} that reaction occurring on the surface of certain crystals gives lower selectivity compared to that in the bulk. In the following section, possible reasons for the lack of reactivity of enone 71a in the bulk are discussed.
3. Molecular Crystal Structure of 4-Phenyl-4-p-bromophenylcyclohexenone (71a) and Its Photochemical Implications

The stereodiagram of the molecule 71a is found in Figure 5, and the crystal packing diagram giving the relative positions of the molecules in a unit cell is presented in Figure 6.

From the crystal structure analysis, it was found that the p-bromophenyl group is situated in a pseudo-axial position on the cyclohexenone ring, whereas the phenyl group lies in a pseudo-equatorial position. Based on the established principles in solid state chemistry, we assume that the lack of photoreactivity for compound 71a in the solid state (bulk) might be due to a particular conformation that the cyclohexenone 71a adopts and/or the specific packing arrangement of the reacting molecules in the crystal, which perhaps prevents the aromatic groups from migrating.

Figure 5  Stereodiagram of Cyclohexenone 71a with Disorder.
From the packing diagram (Figure 6), it can be noted that the phenyl group of one enone molecule is closely packed with a neighboring molecule on the side that migration of the phenyl group from C-(4) to C-(3) is expected. Thus, if the phenyl group migrates (moving towards the other closely packed molecule), it would be likely to cause severe steric interactions between the phenyl group and the neighboring molecule. It is understood that such a reaction process will be topochemically unfavorable. Owing to this, we suggest that phenyl migration of 71a in the crystal might be impossible or at least inefficient.
On the other hand, the pseudo-axial para-bromophenyl group is free of any specific intermolecular contact so that para-bromophenyl migration leading to photoproduct 72a would be expected to proceed upon photolysis of 71a in the solid state. In fact, the formation of photoproduct 72a was insignificant when the bulk crystals of 71a were irradiated. One possibility that might be taken from the crystal structure analysis seems to suggest that the orientation of the p-bromophenyl group is unfavorable for the migration. It is well understood that, for a 1,2-shift or migration of a phenyl group, the plane of the aromatic ring should be perpendicular to the C(1)-C(2) bond (Scheme 29) in order to achieve a maximum orbital overlap. Such perpendicular orientation of the aromatic group is also retained in the half-migrated species (107). As depicted in Scheme 28, in order for the aryl group to migrate, the plane of the para-substituted aromatic ring should be orientated in a perpendicular position with respect to the C(3)-C(4) bond of the enone moiety. However, it can be visualized from the molecular stereodiagram (Figure 5) that the p-bromophenyl group is not orientated in the ideal position to allow maximum p-orbital overlap for the migration. In order to do so, the plane of the aromatic ring should be rotated by nearly 90°. But such rotation might be sterically hindered by the adjacent phenyl group in the solid state. Molecular models of the solid state enone conformation show that the rotation of the para-bromophenyl group could result in severe steric interactions between the ortho hydrogen atoms (H_a and H_b) from the two aromatic groups (Scheme 30). This intramolecular steric argument might explain why the crystal of 71a is photochemically inert.
Scheme 29  Orbital Overlap Arrangement in 1,2-Shift of Phenyl Group.

Scheme 30  Steric Hindrance on the Rotation of the p-Bromophenyl Group in the Bulk Crystals.
B. Photorearrangement of 4,4-Diphenyl-6-alkylcyclohexenones

1. Photochemistry

In further investigations of the crystalline lattice effect on the photochemistry of cyclohexenone compounds, the C-6 substituted diphenylcyclohexenones (74a,b) were synthesized (Scheme 19), and their photochemistry was studied.

Irradiation of 4,4-diphenyl-6-methylcyclohexenone (74a) was conducted in the crystalline phase and in solution as well. In both media, two isomeric phenyl migration products were detected by GC. The photoproducts were isolated in a large scale photolysis (in acetone) and characterized as the endo-trans- and exo-trans-5,6-diphenyl-3-methylbicyclo[3.1.0]hexanones (75a and 76a) by spectroscopic methods (Scheme 31). The endo-trans isomer 75a is the major photoproduct both in solution and in the solid state. However, the product ratio (75a:76a) varies with the solvent used in the solution photolysis, and the ratio also changes slightly in the solid state depending on the temperatures at which the crystals of 74a were irradiated (see following discussion on product ratio studies). The structural assignments of the endo- and the exo-trans isomers are based on a comparison of their \(^1\)H NMR spectra (Figure 7). First of all, the trans geometry of the two phenyl groups is again determined by the coupling constant of 10 Hz for the cis-cyclopropyl CH-CH coupling.\(^{42,65}\) The exo-trans isomer 76a gives a characteristic high-field (\(\delta = 1.15\) ppm) multiplet assigned to the hydrogen atom on the C-3 carbon atom. This high-field chemical shift is attributed to the shielding effect from the C-6 phenyl group. In
contrast, the endo-trans isomer 75a shows a doublet signal for the methyl group in the high-field region ($\delta = 0.20$ ppm) due to the same shielding effect of the aromatic ring.

Scheme 31  Photochemistry of 4,4-Diphenyl-6-alkylcyclohexenones.

The stereochemistry of the exo-isomer is also confirmed by an independent synthesis (Scheme 32). Methylation of the known compound, trans-5,6-diphenyl-bicyclo[3.1.0]hexanone (39a), gave only the exo-trans isomer 76a. It can be seen that addition of the methyl group should occur from the less hindered side which is the bottom side of the bicyclic ketone 39a. In addition, the epimerization of the endo isomer 75a to the exo isomer 76a (Scheme 32), in which the ratio of 75a:76a at equilibrium was determined to be 17:83 by GC, also supports the above structural assignments.
Figure 7  Partial $^1$H NMR Spectra of exo-trans- and endo-trans-5,6-
Diphenyl-3-methylbicyclo[3.1.0]hexanones.
In a similar fashion, photolysis of the ethyl derivative 74b in acetone gave the exo-trans and the endo-trans bicyclic ketones 75b and 76b in a ratio of 58:42 as shown in Scheme 30. The two photoproducts were isolated and characterized by spectroscopic methods and an independent synthesis of photoproduct 75b (Scheme 31). Since enone 74b proved to be an oil at room temperature, irradiation of this compound in the solid state was not carried out.

Here the author would like to mention that by the time this part of the work was completed, a report on the solution phase photochemistry
of compound 74a appeared. The results obtained in the present study proved to be the same as those reported.

2. Product Ratio Studies on Enone 74a in Solution and in the Solid State

Turning to the product ratio studies, it was interesting to find that, for both compounds 74a and 74b, the endo epimer 75 was formed in preference to the exo stereoisomer 76 in solution as well as in the solid state. Table 5 summarizes the endo:exo product ratios from the photolysis of the 6-methyl cyclohexenone 74a in solution. It has been suggested by Zimmerman\textsuperscript{57} that the photorearrangement of 4,4-diphenyl-6-methylcyclohexenone leading to the formation of the more sterically hindered endo product 75a (major photoproduct) is kinetically controlled. Further sensitization experiments carried out by Zimmerman and Weber\textsuperscript{57} showed that the reaction occurs from the triplet excited state of the enone moiety 74a. Based on kinetic studies and molecular mechanics calculations, these authors suggested that the half-migrated species 111 leading to the C-3 endo bicyclic photoproduct 75a is preferred energetically over the half-migrated species 112 or 113, which would afford the exo bicyclic photoproduct 76a (Figure 8). It was also concluded\textsuperscript{57} that the rate- and product-determining step of the rearrangement must come prior to or near the half-migration.
Table 5 Photoproduct Ratios of Endo:Exo (75a:76a) from Photorearrangement of 74a in Various Solvents.<sup>a</sup>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>n-hexane</th>
<th>benzene</th>
<th>acetone</th>
<th>acetonitrile</th>
<th>ethanol</th>
<th>methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ratio</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endo:Exo</td>
<td>78:22</td>
<td>74:26&lt;sup&gt;b&lt;/sup&gt;</td>
<td>70:30</td>
<td>66:34</td>
<td>57:43</td>
<td>55:45</td>
</tr>
</tbody>
</table>

<sup>a</sup>Analysis by gas chromatography. <sup>b</sup>Reported value was 79:21 by isolation, see reference 57.

Figure 8 ORTEP Drawings of Molecular Mechanics Minimized Half-Migrated Triplet Biradicals (From reference 57).
An interesting observation made in the present study is that the product ratio in the photolysis of 4,4-diphenyl-6-methylcyclohexenone (74a) is solvent-dependent as seen in Table 5. In general, non-polar solvents such as n-hexane and benzene give higher endo:exo ratios, while the ratios are lower in polar solvents (acetone, acetonitrile, methanol or ethanol). It is not yet clear why the solvent polarity has such an effect on the product selectivity in the photorearrangement of enone 74a. One possibility is that changing the solvent polarity may alter the nature of the excited state species of the enone moiety, such as reversing the (n-\pi*) to the (\pi-\pi*) energy levels or vice versa. These two different triplet excited state species may have the same or different photoreactivity and product selectivity.\textsuperscript{69} Another possible alternative, as suggested in some photoreactions of cyclohexenone compounds, is that the twisted excited species\textsuperscript{38a,38e} of the cyclohexenone moiety might be involved in the photorearrangement. Some evidence\textsuperscript{70} has been provided in recent years to support this alternative mechanism in the photochemistry of cyclohexenone derivatives. But it is not known how the solvent polarity would affect reaction selectivity through the mechanism of the twisted excited cyclohexenone species. Further studies need to be carried out in order to understand on the solvent effect on the photochemistry of enone 74a.

Product Ratios in the Solid State

Irradiation of crystals of 4,4-diphenyl-6-methylcyclohexenone (74a) at \( \lambda \geq 340 \text{ nm} \) was carried out at room and low temperatures, as the
photolysis at room temperature was found to result in partial melting of the crystals. The product distributions of the endo and the exo stereoisomers under various conditions were determined and are listed in Table 6.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>Crystal Melting</th>
<th>Endo 75a:Exo 76a</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>90</td>
<td>Yes</td>
<td>66 : 34</td>
</tr>
<tr>
<td>25</td>
<td>65</td>
<td>Yes</td>
<td>71 : 29</td>
</tr>
<tr>
<td>25</td>
<td>23</td>
<td>Partial</td>
<td>78 : 22</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>No</td>
<td>77 : 23</td>
</tr>
<tr>
<td>-25</td>
<td>6</td>
<td>No</td>
<td>80 : 20</td>
</tr>
<tr>
<td>-35</td>
<td>3</td>
<td>No</td>
<td>82 : 18</td>
</tr>
</tbody>
</table>

*Analysis by gas chromatography.

The results in Table 6 show that the solid state photolysis of compound 74a is very similar to its solution phase counterpart in terms of the photoproducts and product distribution. It can be also seen from Table 6 that the reaction selectivity is higher at low conversions and
at low temperatures. On the other hand, the selectivity decreases upon crystal melting, which is likely due to the partial loss of crystal lattice control over the reaction.

The overall mechanism for the photorearrangement of the C-6 substituted 4,4-diphenylcyclohexenones in solution was suggested by Zimmerman et al.\textsuperscript{57} to be similar to that for the 4,4-diarylcyclohexenones as shown in Scheme 33.

\begin{center}
\includegraphics[width=0.8\textwidth]{Scheme33.png}
\end{center}

\textbf{Scheme 33} Mechanism of Photorearrangement of 4,4-Diphenylcyclohexenones.
Although the proposed mechanism seems satisfactory in general, one thing is unclear. That is, the two phenyl groups are non-equivalent in terms of their stereochemistry relative to the C-6 methyl groups (R = methyl); one is cis to the 6-methyl and the other is trans. This difference can also be considered in another way. From molecular models and conformational analysis, it is apparent that 4,4-diphenyl-6-methylcyclohexenone (74a) may exist in two low-energy conformations in solution (Scheme 34). The two conformers are presumably in rapid equilibrium, but the conformation A will be predominant owing to less steric hindrance. It can be noted that, in either of the conformations, the two phenyl groups are non-equivalent. One phenyl group is pseudo-axial, the other is pseudo-equatorial. Bearing this in mind, it seems likely that the two phenyl groups could have different migratory aptitudes in the solid state.

Scheme 34 Conformational Equilibrium of 6-Methyl Cyclohexenone 74a.
In principle, both the pseudo-axial and the pseudo-equatorial phenyl groups are capable of migrating upon irradiation. In the proposed mechanism for photorearrangement of 4,4-diarylcylohexenones, Zimmerman suggested that the reaction proceeds by pseudo-axial phenyl group migration leading to the half-migrated species 116 (Scheme 33). In addition, it was suggested that aryl group migration from C-4 to C-3 and cyclopropane ring closure by bond formation between C-2 and C-4 may proceed in a concerted fashion (Scheme 33) to give the predominant trans diarylbicyclic ketone.

Based on the above, we propose that, in the case of 4,4-diphenyl-6-methylcylohexenone (74a), the two photoproducts 75a and 76a are derived from migration of different phenyl groups. As shown in Scheme 35, the migration of the phenyl group which is cis to the C-6 methyl group gives the endo-trans stereoisomer 75a, whereas the exo-trans isomer 76a is formed via the migration of the other phenyl group that is trans to the C-6 methyl. This assumption seems reasonable if one considers that phenyl migration and cyclopropyl ring closure are simultaneous as mentioned above. As a matter of fact, the concerted nature of phenyl migration and ring closure is supported by the evidence that the two phenyl groups for both photoproducts 75a and 76a are trans to one another.
Scheme 35  Two Pathways of Photorearrangement of Cyclohexenone 74a.

In the mechanism proposed above, we note that migration of the pseudo-equatorial phenyl group in conformation A (Scheme 34) will produce the endo-trans isomer 75a, and migration of the pseudo-axial phenyl will give the exo-trans isomer 76a. On the other hand, the situation is reversed in the case of conformation B (Scheme 34). As mentioned above, the pseudo-equatorial and the pseudo-axial phenyl groups in either of the conformations may show different migratory aptitudes upon irradiation. However, such differences in migration
tendency may not be easily distinguished in solution owing to the fast
equilibrium. In contrast, the solid state results may help to answer
this question because such conformational changes in crystals are
restricted. Without knowing the molecular and crystal structure at the
present time, we may assume that the conformation which enone 74a adopts
in the crystalline state would preferably be the conformation A. This is
based on the general observation that organic molecules are usually
found to crystallize in or near their minimum energy conformations.¹ If
this assumption stands, the pseudo-equatorial phenyl group would migrate
preferentially in the crystals of 74a, as the major solid state
photoproduct is the endo-trans stereoisomer 75a. Such a conclusion must
be regarded as tentative until further information on the crystal
structure of 74a becomes available. A final cautionary point is that the
solid state results might not be relevant to the same reaction in
solution, even though the products and the product ratios in the two
media are similar. In solution, alternative mechanisms leading to the
photoproducts 75a and 76a in the case of 4,4-diphenyl-6-
methylcyclohexenone might be possible, such as via the twisted
species.³⁸ᵃ,ᵉ Such a mechanism is probably unlikely in the solid state
because any drastic conformational or configurational changes will be
restrained by the crystal lattice.

III. Studies on the Di-π-Methane Photorearrangement of 9-Substituted
Dibenzoobarrelene Diesters
The photochemistry of dibenzobarrelene and several of its substituted derivatives in solution was first investigated by Ciganek in 1966. One typical example was that direct or sensitized irradiation of dimethyl dibenzobarrelene dicarboxylate 60 gave the corresponding dibenzosemibullvalene derivative 63 exclusively in solution (Scheme 36). Zimmerman and co-workers also studied the related photochemical transformations of barrelenes and benzobarrelenes in the mid-1960s. Based on their studies of a series of barrelene analogues, Zimmerman proposed the so-called di-π-methane rearrangement mechanism as discussed previously (Scheme 10 on page 27). Subsequent studies showed that the di-π-methane rearrangement of dibenzobarrelene compounds was a triplet-specific reaction, and that singlet state reaction by direct irradiation afforded dibenzocyclooctatetraene products.

Scheme 36 Phototransformation of Dibenzobarrelene Diesters to Dibenzosemibullvalenes.
In recent years, Scheffer, Trotter and co-workers$^{3t, 2}$ have studied the photochemical behavior of dibenzobarrelene compounds in the solid state. It has been demonstrated that these compounds, such as diesters 26 and 60, can also undergo smooth photorearrangement in the crystalline state giving the same products as found in solution. Garcia-Garibay et al.$^{61a}$ showed that the crystal lattice has significant effects on the reactivity and selectivity of such di-π-methane phototransformations of dibenzobarrelene diester derivatives.

The solution phase photochemistry of a number of 9-substituted 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate derivatives has been studied by Richard$^{51}$ and Iwamura$^{52}$. Initial investigations on the solid state photoreactions of 9-substituted ethenoanthracenes carried out by our group showed that the reactivity and regioselectivity of this phototransformation could be affected by the crystal lattice.$^{68, 71, 72}$

In order to test the generality of the crystal lattice effect on the regioselectivity of photochemical transformations of 9-substituted dibenzobarrelenes, several substrates were synthesized and photolyzed in the solid and solution phases.

A. Photochemistry of 9-Formyl, 9-Hydroxymethyl and 9-Acetoxyethyl 9,10-Ethenoanthracene-11,12-dicarboxylates (94, 95 and 93c)

Direct and acetone-sensitized irradiations of the title compounds were first carried out in solution (Scheme 37). Each photoproduct from the corresponding preparative photolysis was isolated and purified by
column chromatography, and the structures of the photoproducts were established by analytical and spectroscopic methods. Crystals of these compounds were irradiated at room temperature and the products were analyzed by comparison of their GC retention times and GC-MS data with the results from solution.

It was found that irradiation of the 9-formyl derivative 94 in both media led to the formation of a single product, 4b-formyl\textsuperscript{\dagger} dibenzosemibullvalene diester 118. In contrast, Iwamura et al.\textsuperscript{51} reported that the phototransformation of 94 in acetone gave both 4b- and 8b-formyl\textsuperscript{\dagger} isomers 118 and 122 in a ratio of 88:12. In the present study, therefore, this reaction was examined carefully in different solvents including acetone and deuterochloroform, and the photolysate was analyzed by GC and \textsuperscript{1}H NMR. It was shown that, in each case, the 4b-formyl isomer 118 is the only photoproduct.

\[†\text{ The systematic numbering for dibenzosemibullvalene structure is presented below:} \]
The solution phase photolysis of compounds 95 and 93c resulted in two regioisomeric dibenzosemibullvalene products in each instance. In the case of compound 95, the formation of product 123 was determined by a direct $^1$H NMR analysis of the reaction mixture in CDCl$_3$, as this compound decomposed to the corresponding lactone by an elimination of methanol during the purification procedure. This will be discussed in a subsequent part of the thesis. For both systems, it was determined that the 4b-substituted isomers 119 and 120 were the major photoproducts in solution. Solid state photolysis of 95 and 93c gave both regioisomeric dibenzosemibullvalenes with the 4b-substituted isomer as the predominant

Scheme 37 Phototransformation of 9-Substituted Dibenzobarrelenes.
photoproduct in each case; small amounts of other photoproducts were
detected by GC. These minor products were not characterized owing to the
inefficiency of the solid state reaction.

The structure of each photoproduct was derived by application of
the well established di-π-methane mechanism and supported by
spectroscopic studies. The regiochemistry of the photoproducts was based
primarily on the difference of chemical shifts for the cyclopropyl and
the benzylic methine protons of dibenzosemibullvalene diesters in the $^1$H
NMR spectra.\textsuperscript{50,51,52} Informatively, the methine proton at the 4b-
position appears at $\delta = 5.0$-$5.1$ ppm; in contrast, the 8b-proton on the
cyclopropane ring gives rise to a signal at $\delta = 4.2$-$4.5$ ppm. These
empirical values are considered to be general for compounds of this type
and are used to characterize and distinguish each dibenzosemibullvalene
product described in the present thesis. Furthermore, molecular crystal
structures of a few related dibenzosemibullvalene compounds have been
determined in our laboratory, and the structures obtained by X-ray
crystallographic studies are all in agreement with the assignment by the
spectroscopic methods.

In the case of photoproduct 119, the structure was also supported
by an independent synthesis (Scheme 38). A selective reduction of the
corresponding aldehyde 118, which was prepared from the photolysis of
compound 94\textsuperscript{52}, by sodium borohydride leads to 4b-hydroxymethyl
dibenzosemibullvalene diester 119.
B. Solid State Results

1. Regioselectivity in the Solid State vs Solution

The product distribution in solution and in the solid state, which represents the bridging regioselectivity for compounds 93c, 94 and 95, is summarized in Table 7. Firstly, it can be seen from the Table that the formation of the 4b-substituted dibenzosemibullvalene products is greatly favored for all three substrates, both in solution and in the solid state. Secondly, the data show that the difference in regioselectivity between solution and the solid state for the di-π-methane photoreaction of these compounds is small.
Table 7 Product Ratios in Photorearrangement of 9-
Substituted 9,10-Ethenoanthracenes.a

<table>
<thead>
<tr>
<th>9-Substituent</th>
<th>Medium</th>
<th>4b-isomer 118-120</th>
<th>8b-isomer 122-124</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO (94)</td>
<td>Acetone</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Crystal</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>CH₂OH (95)</td>
<td>Chloroformb</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Crystal</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>CH₂OAc (93c)</td>
<td>Acetone</td>
<td>89</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Crystal</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

aAnalysis by gas chromatography. bPhotolysis in CDCl₃; analysis by ¹H NMR.

The results obtained in the present study on the solution phase photochemistry of compounds 93c, 94 and 95 are in agreement with the general observations that were made in the photochemistry of the 9-substituted 9,10-ethenoanthracenes studied by Richard⁵¹ and by Iwamura.⁵² It was suggested⁵¹ that the key factor in understanding the substituent effects on the reaction regioselectivity lies in the initial stages of the rearrangement, in particular the relative stability of the first intermediates 117 and 121 (Scheme 37), since the initial step of the di-π-methane rearrangement has been suggested by Zimmerman⁴³ to be the rate-determining step. Iwamura⁵² argued that the 9-substituent affects the stability of the initially formed intermediates in the same
way as that observed in the substituent effects on the equilibrium between norcaradienes and the corresponding cycloheptatriene (Scheme 39). It is known experimentally\textsuperscript{73} as well as theoretically\textsuperscript{73} that electron-withdrawing groups, such as CN, CO\textsubscript{2}CH\textsubscript{3} and CHO, stabilize the cyclopropane ring and thus favor the norcaradiene tautomer 126 over the cycloheptatriene 125 (Scheme 39); in contrast, electron-donating groups, e.g. OCH\textsubscript{3}, may destabilize the cyclopropane ring and therefore shift the equilibrium toward the left. It should be mentioned that some converse experimental data exist\textsuperscript{74e} in regard to the destabilization of cyclopropyl ring by electron-donating groups. Such generalizations are useful in interpreting the regioselectivity in the photolysis of 9-substituted dibenzobarrelenes. Thus, if the substituent R is an alkyl or some other electron-donating group, the intermediate 121 would be less stable than 117. Therefore path A, with the initial benzo-vinyl bridging from the side without the 9-substituent, is the preferred pathway (Scheme 37) leading to the 4b-substituted dibenzosemibullvalene derivatives 118-120. Although pathway B leading to 121 would be expected to be favored by the electron-withdrawing group (CHO) in the case of 9-formyl derivative 94, the observed product 118 is formed exclusively through pathway A. This situation was suggested by Iwamura\textsuperscript{52} being due to that formation of the intermediate 121 is kinetically inhibited by the electron deficient group, although 121 might be thermodynamically more stable than cyclopropyldicarbinyl biradical 117.
Turning now to the bridging regioselectivity of the 9-substituted 9,10-ethenoanthracene derivatives 93c, 94 and 95 in the solid state, we note that the crystal lattice has only a slight effect on the reaction pathway; the observed regioselectivity in the crystalline phase is quite similar to that in solution, in which path A prevails. Such observations have also been made (see following sections) in the studies of other 9-substituted dibenzobarrelenes and it would seem to be a general trend for this class of compounds.

2. Molecular Crystal Structure of 9-Formyl-9,10-Ethenoanthracene Diester 94

In order to study structure-reactivity relationships in the solid state photochemistry of 9-substituted dibenzobarrelene diesters, crystal
and molecular structures of a number of these substrates have been determined in the present work. In general, specific molecular conformations and intermolecular arrangements of the reactants in the crystals are considered to be the key factors in understanding the solid state photochemical behavior.

The molecular crystal structure of 9-formyl dibenzobarrelene diester 94 is given in Figure 9. The crystal packing diagram is found in Figure 10.

![Figure 9](image)

Figure 9 Stereodiagram of the Molecule Dimethyl 9-Formyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (94).

---

† All crystal structures presented in this thesis were determined by Dr. P. R. Pokkuluri at Chemistry Department of UBC unless otherwise mentioned.
The crystal structure analysis revealed the interesting feature that the two ester groups of compound 94 are orientated differently in relation to the vinyl double bond in the solid state. The specific molecular conformation shows that the carbonyl group of one of the esters, which is on the C-(12) vinyl carbon atom of the molecule, is completely out of conjugation with the double bond; in contrast, the carbonyl group from the other ester is orientated in complete conjugation. If the electronic stabilizing effect of the ester substituents on the initial biradicals 117 and 121 determines the reaction regioselectivity, i.e. paths A and B (Scheme 37), one might expect that path B would be preferred in the solid state. This is because that the biradical intermediate 121 from the initial benzo-vinyl
bonding via pathway B would be more stabilized by the conjugated carbonyl group than the biradical intermediate 117 via pathway A, assuming that ester groups do not move or rotate in the solid state. But, the experimental result does not agree with such speculation. In the solid state photolysis, product 122 from path B was not observed.

In a comparison to the previous studies in our group,\textsuperscript{74,75} it seems to suggest that the steric effect from the crystal lattice may play a more important role in determining the regioselectivity of the di-$\pi$-methane photorearrangement in the case of compound 94 instead of the electronic stabilizing effect. In one instance of the previous work, Scheffer, Trotter and co-workers\textsuperscript{74} investigated the solution and solid state phototransformations of compounds 127a-d (Scheme 40), in which the methyl ester substituent remained unchanged while the second ester group was varied from ethyl to tert-butyl. In solution, there was a small preference in all four cases for formation of what was suggested to be the less hindered photoproduct 129, but in the solid state, the regioselectivity was irregular. The 129:131 ratio in the solid varied with the R group in the following way: 45:55 ($R$ = ethyl), 93:7 ($R$ = isopropyl), 99:1 ($R$ = (±)-sec-butyl) and 15:85 ($R$ = t-butyl). Two possible explanations were considered for the solid state results. The first one was that the preference for formation of either biradical 128 or 130 depends on which ester group is better oriented by the crystal lattice for radical stabilization through resonance. However, this was found subsequently to be incompatible with the crystal structure correlations. The second explanation involved the possibility of steric effects between the reacting molecule and its lattice neighbors, which was suggested to be the controlling factor. Scheffer\textsuperscript{75} reasoned that it
is the ester substituent attached to the bridging vinyl carbon atom that moves most during the initial stages of reaction, and that only the bridging which involves less intermolecular interactions in the ester movement might be favored in the solid state. Further calculations from a computer simulation of the ester motions in terms of the intermolecular non-bonded repulsion energies were in accord with the solid state results.

Scheme 40 Phototransformation of Unsymmetrical Dibenzoobarrelene Diesters.

(a) R = Et; (b) R = iPr; (c) R = (t)Bu; (d) R = tBu
IV. Asymmetric Induction via Photoreactions of Chiral Crystals

As was briefly discussed in the introduction section, organic molecules, either chiral or achiral, can crystallize in chiral space groups. Upon a chemical reaction of the chiral crystals, optically active products can be generated provided that the products are chiral. Such process involves a transformation of the crystal chirality into the molecular chirality of the products.

An interesting question one may ask is how great the asymmetric influence of the crystal lattice will be on the asymmetric induction of organic reactions. Several asymmetric syntheses with high optical yields by solid state photoreactions of organic chiral crystals have been achieved in recent years. In the present studies, the magnitude of this crystal asymmetric influence on the asymmetric induction is examined by performing solid state photochemical reactions of some dibenzobarrelene compounds with resolved chiral substituents at the 9-position of dibenzobarrelene diesters. By using optically pure starting materials, one is guaranteed that the substrates will crystallize in chiral space groups. The chiral substituents under investigation were designed in such a way that they are far enough away from the reaction center so that there should be little or no asymmetric induction in solution. Therefore, any asymmetric induction observed in the solid state can be attributed to the effect of the chiral crystal lattice.

A. Studies on 9-Substituted Dibenzobarrelene Vinyl Monoesters
In his early studies of the di-π-methane photorearrangement of dibenzobarrelene compounds, Ciganek\(^5\) showed that vinyl substituted dibenzobarrelene monoester 132 (R = CH\(_3\)) underwent triplet photorearrangement with complete regioselectivity to give dibenzosemibullvalene product 134 (R = CH\(_3\)) having the methyl ester group at the 8c-position (Scheme 41). Similar results were also found by Cristol\(^7\) in the case of compound 132 where R = CH\(_2\)CH\(_3\). This regiospecific reaction has been interpreted in terms of the favoured odd-electron center stabilization by the ester group on the proposed biradical intermediate 133. In contrast, irradiation of the 9-substituted ester 137 was found\(^5\) to give a 33:67 mixture of the two regioisomers, 139 and 141 (Scheme 42). This result was interpreted by Zimmerman\(^43b, 7\) in terms of destabilization of the cyclopropane ring in the biradical 138 leading to the isomer 139 by the electronegative ester group.

Scheme 41  Phototransformation of Dibenzobarrelene 11-Ester.
Recently, Scheffer and co-workers\textsuperscript{78} have demonstrated that dibenzobarrelene 9,11-diester 142 can undergo smooth di-\(\pi\)-methane rearrangements in the solid state as well as in solution. Direct irradiation of 142 in both media gave the corresponding dibenzosemibullvalenes 143 as the major products and also small amounts of dibenzocyclooctatetraene derivatives 144 (Scheme 43). In contrast, triplet-sensitized photolysis of 142 gave no 144, indicating that the formation of 144 was singlet-derived.

By attaching resolved chiral groups at the 9-position of the dibenzobarrelene skeleton, which directs the compounds to crystallize in chiral space groups, the authors\textsuperscript{78} observed a strongly reversed
diastereoselective phototransformation in the solid state compared to solution for compound 142a. In contrast, the photoreaction of 142b was found to be non-diastereoselective in both crystalline and solution phases.

\[
\begin{align*}
(a) & \quad E = \text{CO}_2\text{Me}; \quad E' = \text{CO}_2(-)-\text{menthyl} \\
(b) & \quad E = \text{CO}_2(-)-\text{menthyl}; \quad E' = \text{CO}_2\text{Me}
\end{align*}
\]

Scheme 43  Phototransformation of Dibenzobarrelene 9,11-Diesters.

As our efforts in studying the solid state asymmetric induction continue, some other dibenzobarrelene derivatives with resolved chiral handles at the bridgehead position were prepared, and the chiral crystal lattice effect on the diastereoselectivity of these compounds was examined in this thesis.

1. Photochemistry of 9-Substituted Dibenzobarrelene Vinyl Monoesters 99 and 100
9,11-Disubstituted dibenzobarrelene 99 and 9,12-disubstituted dibenzobarrelene 100 were prepared in both racemic and optically active forms. Direct and acetone-sensitized photolysis of compound 99, either (±)-99 or (R)-(−)-99, was first carried out in solution. As expected, a single regioisomer 145 was formed (Scheme 44). $^1$H NMR analysis indicated that two diastereomers were produced in nearly equal amounts (Figure 11). Structural assignment of the photoproduct was based primarily on the well known mechanism involved in such photochemical transformations and also on the spectroscopic data. The $^1$H NMR spectrum (Figure 11) was found to be in agreement with the assignment. The cyclopropyl methine proton resonates at $\delta = 3.75$ ppm for one diastereomer and at $\delta = 3.76$ ppm for the other. The benzylic protons from the two diastereomers were found at $\delta = 4.99$ and 5.01 ppm. Another observation in the direct irradiation of 99 was that the singlet-derived dibenzocyclooctatetraene derivative was not formed. Photolysis of the crystals of 99 gave the same products as those formed in solution.

![Scheme 44 Photolysis of 9,11-Disubstituted Dibenzobarrelene 99.](image)
In contrast, direct or acetone-sensitized irradiation of racemic 9,12-disubstituted 9,10-ethanoanthracene 100 afforded 146 as the only photoproduct in solution and in the solid state (Scheme 45). The assignment of the structure was also based on the well established mechanism and supported by the spectroscopic analyses. The structure of 146 is characterized in the $^1$H NMR spectrum by an AB quartet which is

![Figure 11 Partial $^1$H NMR Spectrum of Photoproduct 145.](image-url)
attributed to the non-equivalent cyclopropyl protons (CH-CH). It can be noted that no new chiral center is generated in the product 146, thus asymmetric induction was not examined in this case.

\[
\begin{align*}
\text{E} & \quad \text{hv} \quad \text{E} = \text{CO}_2\text{Me} \\
\text{CH}_2\text{R} & \\
\text{100} & \\
\text{R} & = (\pm)\text{-OCOCH(OMe)Ph}
\end{align*}
\]

Scheme 45  Phototransformation of 9,12-Disubstituted Dibenzobarrelene 100.

2. Results on Diastereoselectivity in the Solid State vs Solution

The results from the determination of the reaction diastereoselectivity of substrate 99 are presented in Table 8. The diastereomeric ratios were determined by integration of the corresponding benzylic proton signals for the two diastereomers (Figure 11). The measurement was also checked by integration of a second pair of the resonance for the methylene protons (CH\_2\_CO). First, an interesting observation drawn from the Table is that the solution phase photolysis of optically active 99 gave nearly no diastereoselectivity (diastereomer
ratio = 53:47, which is within the experimental error). In contrast, a higher diastereomeric ratio (38:62) was obtained in the solid state reaction. Apparently, the chiral center is situated far enough away from the reaction site so that it exerts little disymmetric influence on the initial benzo-vinyl bridging in solution. In the solid state, on the other hand, the higher diastereoselectivity can be attributed generally to the influence of the crystal lattice. However, it can be also seen from Table 8 that the racemic compound 99 gave the same diastereoselectivity in the solid state. Although the molecular crystal structures of both racemic and optically active 99 are not yet available, the results seem to imply that primarily an environmental rather than a molecular effect controls the diastereoselectivity of the phototransformation of 99.

Table 8 Summary on the Reaction Diastereoselectivity of 99.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>Conversion (%)</th>
<th>Diastereomer Ratio (145)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(±)-99</td>
<td>solution</td>
<td>99</td>
<td>52:48</td>
</tr>
<tr>
<td>(±)-99</td>
<td>crystal</td>
<td>10</td>
<td>39:61</td>
</tr>
<tr>
<td>(R)-(−)-99</td>
<td>solution</td>
<td>95</td>
<td>53:47</td>
</tr>
<tr>
<td>(R)-(−)-99</td>
<td>crystal</td>
<td>10</td>
<td>38:62</td>
</tr>
</tbody>
</table>

Analysis by $^1$H NMR.
B. Studies on 9,10-Ethenoanthracene Diesters with Resolved Chiral Handles at the 9-Position

1. Photochemistry

The photochemistry of the dibenzobarrelene diesters 93a and 93b is similar to the achiral compound 93c, which was discussed previously (Scheme 37 on page 79). Irradiation of both racemic and optically active 93a,b in solution as well as in the solid state led to the formation of two regioisomeric dibenzosemibullvalene derivatives 147 and 148 (Scheme 46). As expected, each regioisomer consists of two diastereomers. The reaction mixture from the photolyses of these compounds proved difficult to separate. Therefore, identification and quantification of the photoproducts (regioisomers and diastereomers) were based primarily on $^1$H NMR spectroscopy (Section IV.B.2.).

$$\begin{align*}
93 & \xrightarrow{\text{hu}} 147 + 148 \\
93a & : R = (\pm) \quad \text{or} \quad (R)-(-)-\text{OCOCH(OMe)Ph} \\
93b & : R = (\pm) \quad \text{or} \quad (S)-(-)-\text{OCOCH(Me)NHCOCMe} \\

d. & 
\end{align*}$$

Scheme 46 Phototransformation of Dibenzobarrelene Diesters with 9-Resolved Chiral Handles.
2. Results on the Regio- and Diastereoselectivities

For both compounds 93a and 93b, photoproduct 147 was the predominant regioisomer. This product could be differentiated from its regioisomer 148 on the basis of the chemical shifts of the non-aromatic methine protons in the \(^1\)H NMR spectra (Figures 12 and 13). Cyclopropyl methine protons such as those present in 147 are typically found at \(\delta = 4.4\) ppm, while the signals due to the benzylic methine protons of 148 resonate characteristically at \(\delta = 5.1\) ppm. Integration of these signals gave the ratios of the two regioisomers which are summarized in Table 9. Experimentally, the chemical shifts of these resonances were found to be slightly different for each diastereomer. Therefore, another integration of the signals corresponding to the diastereomers provided the diastereoselectivities reported in Table 9 as well. In each case, the diastereomer ratios were also checked by integration of a second pair of resonances (-OCH\(_3\) for 93a and -NHCOCH\(_3\) for 93b) and were found to be in agreement with the first integration. The results are reproducible to \(\pm 5\%\) from run to run.

Several interesting conclusions can be drawn from the results presented in Table 9. First of all it can be seen that, in general, regioselectivity is slightly lower in the solid state than in solution for both substrates. Secondly, it is interesting to find that diastereoselectivity varies with reaction medium as well as with the nature of the substrates. In the case of compound 93b, we see that irradiation of the chiral crystals gave higher diastereoselectivity in the formation of product 148b, but not in the regioisomer 147b. In
contrast, however, the diastereoselectivity observed for compound 93a is less in the solid state (50:50) compared to solution (68:32). An attractive explanation for the variability of the diastereoselectivity ratios is that the molecular and environmental effects of the chiral substituents may either reinforce or oppose one another in the solid state. Depending on their relative magnitude, opposing effects could lead to either reduced or reversed diastereoselectivity in the solid state compared to solution.

Table 9  Regio- and Diastereoselectivity in the Solid State and Solution.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Medium</th>
<th>Regioselectivity</th>
<th>Diastereomer Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>147:148</td>
<td>147</td>
<td>148</td>
</tr>
<tr>
<td>(S)-(+)-93b</td>
<td>Solution</td>
<td>85 : 15</td>
<td>55:45 52:48</td>
</tr>
<tr>
<td>(S)-(+)-93b</td>
<td>Crystal</td>
<td>68 : 32</td>
<td>47:53 75:25</td>
</tr>
<tr>
<td>(R)-(-)-93a</td>
<td>Solution</td>
<td>90 : 10</td>
<td>67:33 68:32</td>
</tr>
<tr>
<td>(R)-(-)-93a</td>
<td>Crystal</td>
<td>80 : 20</td>
<td>61:39 50:50</td>
</tr>
</tbody>
</table>

*Analysis by $^1$H NMR. Ratios were determined at complete conversion in solution and ≤ 50% in the solid state.
Figure 12  Partial $^1$H NMR Spectrum of Reaction Mixture from 93b.
Figure 13 Partial $^1$H NMR Spectrum of Reaction Mixture from 93a.
A conclusion that may be drawn from the above studies is that different chiral handles (substituents) may lead to different diastereoselectivity, both in the solid state and in solution. In particular, even minor changes on the substituents may result in completely different molecular crystal packing pattern in the solid, thus, leading to different diastereoselectivity. The magnitude of the asymmetric induction depends uniquely on the crystal lattice forces. It is also apparent that the nature and location of the chiral handle in relation to the site of reaction has a strong influence on the diastereoselectivity observed. The two chiral handles examined in this thesis, i.e. N-acetyl-L-alanine ester and (R)-(−)-methoxyphenylacetic acid ester, are quite different in nature. Although the separation distances between the chiral centers and the reaction site are nearly the same, the diastereoselectivities for the two systems are quite different in solution as well as in the solid state.

3. Molecular Crystal Structure of Compound 93b and Its Photochemical Implications

In general, the non-diastereoselectivity observed in the solution phase photolyses could be interpreted to be due to the remoteness and random orientation of the chiral handles in relation to the reaction centers, thus, the disymmetric influence of the chiral handles leading to diastereomeric transition states is small. One question, however, remains. That is, how the disymmetric influence from the crystal lattice has a different effect on the diastereoselectivity of the two pathways
(path A and path B). In other words, path B gives higher diastereoselectivity in the solid state reaction in the case of compound 93b, whereas path A is substantially non-diastereoselective. In order to understand such differences on the reaction diastereoselectivity in the dual pathways, the crystal structure of the molecule 93b was determined. Figure 14 shows both the molecular structure and crystal packing diagrams of compound 93b.
Compound 93b is found to crystallize in the space group $P2_12_12_1$, one of the most common chiral space groups for organic molecules. Two important features are noted in the crystal structure of 93b, one being intramolecular in nature and the other intermolecular. The specific molecular conformation of 93b is such that the 11-ester carbonyl group (crystal structure gives the number as 12-ester group) is nearly in complete conjugation. In contrast, the 12-ester carbonyl (crystal structure gives the number as 11-ester) is completely out of conjugation with the vinyl double bond. Intermolecularly, it can be noted that the hydrogen atom of the NH group in one molecule is hydrogen-bonded to the 12-ester carbonyl oxygen atom of the neighboring molecule (Figure 14). The hydrogen-bonding distance (N-H⋯O=C) is found to be 2.22 Å.

Turning to the interpretation of the solid state structure-reactivity relationships for compound 93b, as mentioned earlier, the regioselectivity (product ratio of 147:148) in the solid state reaction does not differ very much from the same reaction in the solution phase. A possible explanation drawn from the crystal structure analysis is as follows. It seems that the stabilization effect determined by the degree of conjugation of the carbonyl group on the initially formed radical intermediate species would favor the benzo-vinyl bridging on the side of the 9-substituent. Thus, more photoproduct 148b was formed in the solid state (147b:148b = 68:32) compared to solution (147b:148b = 85:15). The results are in agreement with such electronic stabilizing argument, but one thing should be pointed out. As discussed previously in the thesis, the steric effects from the crystal lattice could also be the key factors that control the regioselectivity in the di-$\pi$-methane
photorearrangement. In the case of compound 93b, the intermolecular hydrogen bonding effect (N-H···O=C) might be important. We considered that the benzo-vinyl bridging from the 12-vinyl carbon atom would result in motions of the ester group that is attached on the 12-vinyl carbon atom. However, the carbonyl oxygen atom of this ester group is hydrogen-bonded to the NH group of the neighboring molecule. Such hydrogen bonding might hinder the movement of the ester group in space, and consequently diminish the reaction. Based on such assumption, therefore, the electronic stabilizing effect and the crystal lattice steric effect exert their influences in opposite directions.

Hydrogen-bonding effects on di-π-methane regioselectivity have been studied in our laboratory.\(^7^9\) One interesting example is given below (Scheme 47). Photochemical transformation of acid-ester 149 in the solid state was found to be very different from its counterpart in solution. In dilute benzene, photoproduct 150 predominated (150:151 = 83:17), but in the crystalline state there was a nearly complete preference for the formation of regioisomer 151 (150:151 = 5:95). This was attributed to a difference in hydrogen bonding that exists in solution and in the crystal. Under the situation of intramolecular hydrogen bonding in dilute solution, formation of photoproduct 150 was favorable, which was interpreted as being due to development of partial positive charge on the carboxylic acid-bearing vinyl carbon atom as a result of internal proton transfer to the carbonyl oxygen atom of the ester group. In the crystal, it was demonstrated that there was strong intermolecular hydrogen bonding between carboxylic acid groups. For this reason, the authors suggested that hydrogen bonding "anchors" the carboxylic acid group and hinders the motions necessary for initial bonding at the vinyl
carbon atom to which the carboxylic acid group is attached. As a result, bonding at the other vinyl carbon atom and formation of the photoproduct 151 is the most favored in the crystal.

Scheme 47  Di-π-Methane Photorearrangement of Acid-Ester 149.

A speculation on the solid state diastereoselectivity of compound 93b may also be drawn from the crystal structure analysis. It can be noted that the two benzo-vinyl bridgings in path B mechanism (Figure 15) experience different spatial environment owing to the specific intermolecular contact in the crystal. On the side of the initial bridging B(II), the carbonyl oxygen atom of the 12-ester group is hydrogen-bonded by the NH group, and in addition, the space is relatively blocked by the methyl group from the neighboring molecule. In contrast, the space on the other side (initial bridging B(I)) is free of any intermolecular contact. Because of such differences in the reaction environment, it seems to be that the initial bonding on the less hindered side leading to one of the diastereomers (path B(I)) is preferred over the other. But, it is not absolutely known as to which
particular initial bridging gives the preferred diastereomer in the solid state photolysis. Furthermore, it is apparent by viewing the crystal packing diagram (Figure 14) that the initial benzo-vinyl bridging at the C-11 carbon atom (crystal structure gives the number as C-12), which is on the unsubstituted side of the dibenzobarrelene skeleton, is relatively free of any steric influence from the crystal lattice. In addition, the reaction site is separated from the chiral centers both intramolecularly and intermolecularly. This might account for the observation that the transformation via path A in the solid state is non-diastereoselective.

Figure 15  Steric Effect in the Photorearrangement of 9-Substituted Dibenzobarrelene Diester 93b via Path B Mechanism.
V. Studies on the Photoreactivity and Selectivity of Dibenzobarrelene Lactones

As discussed in the section dealing with the preparation of the starting materials, an earlier attempt to synthesize 9-hydroxymethyl-9,10-ethenoanthracene 95 by the Diels-Alder addition of dimethyl acetylenedicarboxylate to 9-anthracenemethanol resulted in the lactone-ester 96 (Scheme 22 on page 43). Photolysis of this compound in solution and in the solid state provided some interesting results in terms of photochemical reactivity and product regioselectivity. This led us logically to the preparation of some other similar lactone derivatives such as compounds 97 and 98. Photochemical studies on these substrates are included in this part.

A. Photochemical Studies on Dibenzobarrelene Lactone-Ester 96

1. Photochemistry of Lactone-Ester 96

As can be recognized, the ground state electronic structure of the lactone-ester 96 is much the same as that of its analogue compound 93c, which can be considered to be the ring-opened form of the lactone-ester 96. The photochemistry of dibenzobarrelene 93c has been discussed in a previous part of this thesis in which it was shown that photolysis of compound 93c gave predominantly 4b-acetoxymethyl dibenzosemibullvalene 120 both in solution and crystalline phase (Scheme 48). In a similar fashion, the lactone-ester 96 was expected to be capable of giving two regioisomeric di-π-methane photoproducts, 152 and 153 (Scheme 48) upon irradiation. It was also expected that the photoreaction of compound 96 would produce the rearranged polycyclic lactone 152 (4b-isomer) via path
A as the major photoproduct based on the general observations of a number of 9-substituted 9,10-ethenoanthracenes.\textsuperscript{51,52} Experimentally, however, direct or acetone-sensitized photolysis of the lactone-ester 96 in solution afforded compound 153 (8b-isomer) exclusively; no trace of 152 could be detected by GC or \textsuperscript{1}H NMR. In contrast, irradiation of crystals of 96 gave both photoproducts, 152 and 153, in a ratio of 13:87. Again, the solution photoproduct 153 is predominant. This unusual result in the di-π-methane reaction of 96 (compared to the phototransformation of compound 93c) led us to the question why the regioselectivity is completely reversed in this case.

\begin{center}
\textbf{Scheme 48} Photochemical Transformations of Lactone-Ester 96 and Its Analogue 93c.
\end{center}
The structures of photoproducts 152 and 153 were established by spectroscopic analyses. The regiochemistry is assigned by $^1$H NMR spectroscopy; particularly informative are the chemical shifts of the non-aromatic methine protons. The cyclopropyl hydrogen atom in the 4b-substituted isomer 152 is found at $\delta = 4.85$ ppm; on the other hand, the benzylic methine proton of product 153 appears at $\delta = 5.17$ ppm. This assignment is in agreement with the general trend$^{51,52}$ for compounds of this type and was confirmed by the following independent synthesis of photoproduct 152. Reduction of the aldehyde derivative 118, which is prepared by making use of the known 94-118 phototransformation,$^{52}$ gives the corresponding alcohol derivative 119. Acid-catalyzed cyclization of compound 119 yields the dibenzosemibullvalene lactone 152, which proved to be the same as the solid state photoproduct in the photolysis of compound 96 (Scheme 49).

The structure of 153 is also supported by lactonization of the 8b-hydroxymethyl dibenzosemibullvalene 123. In a workup procedure to separate the photoproduct 123 from the photolysate of 95, it was found that this material is unstable on silica gel column and underwent cyclization to produce the corresponding lactone derivative 153. This, in turn, confirms the structure of 123 as discussed in section III.B.1.
Scheme 49  Independent Preparation of Photoproducts 152 and 153.

2. Interpretation on the Reaction Regioselectivity of 96 in Solution

The regioselectivity observed in the di-π-methane photo-rearrangement of the lactone-ester 96 is unusual in that the photo-
transformation of 96 proceeds via path B exclusively compared to the analogue 93c, which affords the dibenzosemibullvalene 120 as the major photoproduct via path A.

One related example in the literature is the photorearrangement of dibenzobarrelene lactam derivative 154 (Scheme 50). Ciganek demonstrated that direct irradiation of the lactam 154 in THF yielded fused dibenzocyclooctatetraene 155, which was considered to be a singlet-derived product. In contrast, acetone-sensitized (triplet) reaction involved the di-π-methane reaction to give products 156 and 157. It was found that the rearrangement proceeds via the pathway B predominantly to give 157 as the major photoproduct. However, such regioselectivity in the di-π-methane rearrangement could not be explained by the electronic stabilizing effect, since of the two initially formed biradical species, the ditertiary biradical 158 should be favored over the tertiary/secondary biradical 159. In addition, the cyclopropane ring in the biradical 159 leading to the isomer 157 might be destabilized by the eletronegative amide group, which was proposed by Zimmerman as a possible reason for the regioselectivity in the case of methyl 9,10-ethenoanthracene-9-carboxylate (Scheme 42 on page 91). These arguments would favor formation of biradical 158, whereas in fact the rearrangement proceeds predominantly through biradical 159. However, no explanation was suggested.
In another example, Ciganek showed that acetone-sensitized irradiation of dibenzobarrelene amine derivative 160 formed regioisomers 162 and 164 (Scheme 51). In this case, the electronic stabilizing effect was followed, in which the major photoproduct 162 was formed via the more stable biradical intermediate 161.

Scheme 50  Photorearrangements of Dibenzobarrelene Lactam 154.
By comparison, the lactone-ester 96 studied in the present work shows different regioselectivity towards the di-π-methane reaction from the triester 93c. The proposed electronic stabilizing effect is also incompatible with the results. This is because the two biradical intermediates 165 and 166 from pathways A and B would be considered to be equally stabilized through conjugation by the carbonyl groups from the ester or the lactone (Scheme 52), but the cyclopropyl ring in the biradical 166 might be destabilized by the 9-alkyl group (electron-donating group), and this would disfavor the formation of biradical 166.
We have suggested\textsuperscript{81} that an intramolecular steric effect may be responsible for such reversed regioselectivity in the di-\pi-methane reaction of the lactone-ester 96. This comes from the realization that the conformationally rigid five-membered lactone is sterically hindered. Molecular models show that fairly severe steric interactions are present between the methylene hydrogen atoms of the lactone ring and the adjacent aromatic hydrogen atoms (Figure 16). A short contact between the two kinds of hydrogen atoms was first confirmed by an NOE experiment of $^1$H NMR spectroscopy (Figure 17), in which irradiation of the adjacent aromatic protons resulted in a signal enhancement of the methylene protons. In a later crystallographic study on the molecular crystal structure of lactone-ester 96, it is found that the concerned H···H distances are startlingly short, 2.06 Å on one side and a less severe
interaction of 2.43 Å on the other. The stereodiagram of molecule 96 is given in Figure 18. In solution, the H···H contacts will average to approximately \(2.06/2 + 2.43/2 = 2.25\) Å, which is well below 2.40 Å, the sum of the commonly accepted van der Waals radius of 1.20 Å for hydrogen. 82

To help to understand such steric effect, two initial benzo-vinyl bridgings for compound 96 are presented in Figure 16. a-x/a-x' bonding corresponds to the formation of 4b-isomer 152 and b-y/b-y' bridging leads to the 8b-isomer 153. Molecular model studies reveal that pathways b-y and b-y' leading to product 153 can relieve the H···H steric interactions to a much greater extent than pathways a-x and a-x'; the latter pathways (path A) afford 152 with the unfavorable H···H interactions basically intact. Therefore, path B (a-x and a-x' bonding) is suggested to be favored kinetically.

![Figure 16 Molecular Structure of Lactone-Ester 96 Showing H···H Contacts.](image)
Figure 17  Partial $^1$H NMR Spectra of Lactone-Ester 96. Top and middle:
NOE difference after irradiation. Bottom: without
irradiation.
3. Absolute Asymmetric Synthesis via Photoreaction of Chiral Crystals of Lactone-Ester 96

Absolute asymmetric synthesis refers to an asymmetric synthesis carried out in a closed system in the absence of any external chiral influence. It is a process unique to crystalline phase reactions. Such a process involves the first stage of spontaneous crystallization of an achiral molecule in a chiral space group, and then optically active product(s) is(are) generated during the second stage, which consists of a chemical reaction that transforms the crystal chirality into permanent
molecular chirality. The asymmetric induction comes directly from the asymmetric crystalline matrix.

Achiral organic molecules that crystallize in chiral space groups can be classified in two general categories according to their liquid phase conformational characteristics: \( ^8 \) (1) flexible molecules that adopt chiral conformations due to specific molecular arrangements in the solid state, while maintaining an average symmetry through fast conformational changes in solution; and (2) rigid molecules that cannot contribute to significant chiral conformations in solution or in the solid state except for minor deformations.

The lactone-ester 96, which is achiral, is found to crystallize in chiral space groups \( P2_12_12_1 \) from acetone/hexane or chloroform/methanol. It can noted that the lactone-ester is relatively rigid overall owing to the polycyclic fused ring system, except that a certain degree of motion of the vinyl ester group is possible. The molecular crystal structure of 96 (Figure 18) shows that the conformation of 96 in the solid state maintains roughly a plane of symmetry. Thus, the chirality of the crystals of 96 may be considered to come mainly from the disymmetric spatial arrangement of the molecules.

Asymmetric induction in the formation of photoproducts 152 and 153, in terms of enantiomeric excess, was examined both in solution and in the crystalline phase. The lactone-ester 96 in acetone was irradiated to completion on a preparative scale. The sole product 152 was purified by crystallization and shown to be optically inactive by using the chiral shift reagent, 3-(heptafluoropropyl hydroxymethylene, \( d- \)
camphorate)-europium (III) (abbreviated as Eu(hfc)₃). The regioisomer 153, which was not formed in the solution photolysis, was independently synthesized as shown in Scheme 49. This material was obtained as a racemic mixture.

Single crystals of 96 were selected randomly in the experiment and only one single crystal with or without slight crushing was used in each run. The samples were irradiated either with a mercury lamp (λ > 290 nm by using a Pyrex filter) or a nitrogen laser (λ = 337 nm) for 10-60 hr. The resulting crystalline solids were dissolved in CDCl₃ and then analyzed directly by polarimetry to determine the sign and magnitude of optical rotation of the reaction mixture. Following this, the same samples were analyzed by ¹H NMR with the chiral shift reagent, Eu(hfc)₃. The optical purities of photoproducts 152 and 153 from the solid state irradiation were determined by monitoring the methyl singlet from the ester group in each case. The results obtained are summarized in Table 10. A typical set of ¹H NMR spectra for the optical activity analysis of the photoproducts is given in Figure 19.
Table 10  Asymmetric Inductions in the Solid State Photoreaction of Lactone-Ester 96.

<table>
<thead>
<tr>
<th>Exper.</th>
<th>Temp. (°C)</th>
<th>Conversion (%)</th>
<th>Sign of Rotation</th>
<th>Enantiomeric Excess&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial 1</td>
<td>20</td>
<td>&gt;99</td>
<td>(-)</td>
<td>50 &lt;2</td>
</tr>
<tr>
<td>Trial 2</td>
<td>22</td>
<td>74</td>
<td>(-)</td>
<td>66 0</td>
</tr>
<tr>
<td>Trial 3</td>
<td>22</td>
<td>68</td>
<td>(-)</td>
<td>61 &lt;2</td>
</tr>
<tr>
<td>Trial 4</td>
<td>20</td>
<td>64</td>
<td>(+)</td>
<td>58 0</td>
</tr>
<tr>
<td>Trial 5</td>
<td>20</td>
<td>50</td>
<td>(-)</td>
<td>52 2</td>
</tr>
<tr>
<td>Trial 6</td>
<td>38</td>
<td>85</td>
<td>(-)</td>
<td>60 2</td>
</tr>
<tr>
<td>Trial 7</td>
<td>38</td>
<td>58</td>
<td>(-)</td>
<td>70 0</td>
</tr>
<tr>
<td>Trial 8</td>
<td>-5</td>
<td>92</td>
<td>(-)</td>
<td>64 _&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Trial 9</td>
<td>-5</td>
<td>34</td>
<td>(-)</td>
<td>63 _&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Trial 10</td>
<td>-20</td>
<td>52</td>
<td>(-)</td>
<td>100 0</td>
</tr>
<tr>
<td>Trial 11</td>
<td>-20</td>
<td>39</td>
<td>(+)</td>
<td>74 0</td>
</tr>
<tr>
<td>Trial 12</td>
<td>-20</td>
<td>34</td>
<td>(+)</td>
<td>70 0</td>
</tr>
<tr>
<td>Trial 13</td>
<td>-20</td>
<td>17</td>
<td>(-)</td>
<td>100&lt;sup&gt;c&lt;/sup&gt; 0</td>
</tr>
<tr>
<td>Solution</td>
<td>20</td>
<td>100</td>
<td></td>
<td>0 0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by integration of the corresponding split signals, using Eu(hfc)<sub>3</sub>, estimated 3% error according to reference 84.  
<sup>b</sup>Not measured.  
<sup>c</sup>Estimated 10% error due to the weak signals at low conversion.
Figure 19 Partial $^1$H NMR Spectra of the Photolysate of Compound 96 (Initially 10 mg, 0.03 mmoles) in the Solid State. Bottom: without Eu(hfc)$_3$. Middle: with $3 \times 10^{-6}$ mmoles addition of Eu(hfc)$_3$. Top: with $6 \times 10^{-6}$ mmoles addition of Eu(hfc)$_3$. 
The striking feature observed in the photolysis of the chiral crystals of 96 as seen in Table 10 is that photoproduct 152 is formed in high enantiomeric excess, whereas its regioisomer 153 is produced as a racemic mixture (within the limits of the method, approximately ±3% accuracy). To date, all reported absolute asymmetric syntheses (of which there are very few) have been concerned with a single pathway variety; that is, only one product is formed with high enantiomeric excess in most cases. The present study provides the first demonstration that photoreaction of a chiral crystal having dual pathways can lead to products of widely differing optical activity.

It can also be noted from Table 10 that higher optical yields for compound 152 are achieved by conducting the photolysis of the chiral crystals at lower temperatures, such as at -20°C. Raising the temperature causes a noticeable diminution of the enantioselectivity. In contrast, changing the reaction temperature has no effect on the enantioselectivity for the formation of product 153 in the solid state. It should be pointed out that the observed temperature effect on the enantioselectivity of the formation of 152 is not caused by the crystal melting of the sample, which may result in the loss of topochemical control over the phototransformation. Crystal melting was not observed under the microscope in any of the runs, even in the case of irradiation at the raised temperature (38°C). Under the conditions of room or higher temperatures, however, the starting single crystal was found to fall apart to powdery crystalline solid after the irradiation was completed. This is perhaps due to that accumulation of the photoproducts in the crystal may result in disruption of the bulk crystal lattice. If the
products are incapable of forming a solid solution with the reactant in the crystal lattice or vice versa, reorganization between products and the reacting molecules in the solid may be reflected by crystal breaking. Such crystal breaking during the photolysis of 96 was also evident at low temperatures, but was much less severe compared to the room temperature irradiation. It seems possible that, owing to the disruption of the crystal lattice, partial loss of topochemical control could result; this might explain the changes in enantioselectivity with temperature. Regarding the widely different enantioselectivities observed in the formation of the photoproducts 152 (ca. 60% e.e. at room temperature) and 153 (racemic), we suggest that the nature of the crystal structure determines overall regio- and enantioselectivity, and that the enantioselectivity need not be high in solid state asymmetric syntheses.

Another interesting point that deserves mention is the "spontaneous resolution" of achiral organic molecules into enantiomorphous antipodes. Under the present experimental conditions, both enantiomorphous forms of the chiral crystals of 96, i.e., the left- and the right-handed, are obtained from the crystallization. This is reflected by the sign of optical rotation of the optically active photoproduct 152 (Table 10). In some of the runs, the optically active product 152 shows a positive rotation, while others are negative. It is understood that the nucleation of achiral molecules to form an optically active chiral crystal is a process of symmetry breaking at a microscopic level, but the symmetry is restored in the crystallization in that statistically equal amounts of levo(l)- and dextro(d)-crystals will be obtained. Experiments on the crystallization of 1,1'-binaphthyl by
Pincock et al.\textsuperscript{85,86} clearly showed that the two enantiomorphs were found in equal proportions. However, enantioselective crystallization can be obtained by appropriate intervention such as seeding.\textsuperscript{87} That is, crystals with the same handness can be formed in excess over the other one by seeding the solution with one antipole. The seeding method was used in the crystallization of the lactone-ester \textit{96} in the present study for the purpose of obtaining large chiral single crystals. However, the optical purity of the resulting chiral crystals from the crystallization was not determined. Interestingly, Kondepudi and co-workers\textsuperscript{88} have demonstrated in a very recent report that, under well controlled crystallizing conditions, optically pure (99.7\%) crystals of an inorganic salt (NaClO\textsubscript{3}) could be formed by an asymmetric crystallization process from achiral species.

4. Mechanistic Interpretation of the Solid State Asymmetric Induction from Lactone-Ester 96

The question we asked ourselves is why the influence of the crystal lattice exerts different effects on the asymmetric induction in the dual pathways of compound \textit{96}. To help to understand the structure-reactivity relationships in such a phototransformation, the molecular crystal structure was examined again. We suggest that the difference may stem from an intermolecular steric effect in the crystal that favors path \textit{a-x} over path \textit{a-x}' (Figure 16). Such intermolecular steric effects in unimolecular processes are unique to solid state reactions. Molecular models show that as bonds \textit{a-x} and \textit{a-x}' begin to form, the COOCH\textsubscript{3} group at position \textit{a} swings through a wide arc either toward (a-x) or away (a-
x') from the viewer (Figure 16). However, the two pathways are differentiated by the specific spatial arrangement of the neighboring reactants. The crystal packing diagram (Figure 20) clearly shows that the latter pathway (but not the former) is hindered by a hydrogen atom from a neighboring molecule that lies 2.49 Å directly behind the ether oxygen atom of the ester group. This is substantially less than 2.72 Å, the sum of the van der Waals radii for oxygen and hydrogen. Therefore, a-x' bonding will be opposed by such steric hindrance. In contrast, it is apparent that both sides of the lactone ring are tightly packed, and this may account for the lack of enantioselectivity in the formation of the photoproduct 153 as well as the diminution in the relative amount of this product formed in the solid state (152:153 = 13:87) compared to solution (152:153 = 0:100). Similar steric effects have been suggested to be responsible for determining the regioselectivities of di-π-methane photoreactions in the solid state. Although such mechanistic speculations seem plausible, final confirmation of the structure-reactivity correlations must wait until the absolute configurations of both the starting material 96 and optically active product 153 are determined.
To extend the studies on the lactone-ester 96 which showed novel regioselectivity in the di-\pi-methane reaction and to further support the idea that intramolecular H⋯H steric interactions direct the regioselectivity, compound 97, which has a methyl group on the lactone ring, was synthesized. Since it is clear that the methyl group is bulkier than the hydrogen atom, one may expect that introduction the methyl group will create much more steric hindrance on one side of the lactone ring (CH₃⋯H interaction) than the other (H⋯H interaction). Based on our previous interpretation of the photochemistry of the lactone-ester 96, the initial benzo-vinyl bridging in the case of the methyl lactone-ester 97 should occur favorably through pathway B(I) by releasing the more severe CH₃⋯H steric hindrance upon irradiation.
In other words, we would expect that the di-π-methane photorearrangement of the methyl lactone-ester 97 occurs preferentially at the more sterically hindered side.

1. Photolysis of Methyl Lactone-Ester 97 in Solution

Direct or acetone-sensitized irradiation of the methyl lactone-ester 97 in solution phase was shown to give two photoproducts by GC and $^1$H NMR in a ratio of 77:23. Isolation of each photoproduct was accomplished by a preparative photolysis in acetone and subsequent purification through column chromatography. The two products were identified as the isomeric photoproducts 168 (77%) and 170 (23%) (Scheme 53).

Scheme 53  Phototransformation of Methyl Lactone-Ester 97 in Solution.
The structures of compounds 168 and 170 were established by spectroscopic analyses, particularly by comparison of their \(^1\)H NMR spectra with that of compound 153 from the solution photolysis of the lactone-ester 96, which proved to be quite similar. In regard to the stereochemistry of the two structures, NOE difference experiments were found to be very useful in differentiating the two epimers. Molecular models show that the lactone methyl group in the major photoproduct 168 is much closer to the adjacent aromatic hydrogen atom than is the lactone methine hydrogen atom. On the other hand, the situation is reversed for the isomer 170. An NOE difference measurement on compound 168 (Figure 21) shows that irradiation of the lactone methyl doublet leads to a signal enhancement of the adjacent aromatic hydrogen atom, but saturation of the lactone methine proton at \(\delta = 5.30\) ppm does not. These results support the structural assignment of compound 168. In a similar fashion, the structure of the epimer 170 is supported by NOE difference measurements (Figure 22). Irradiation of the lactone methine proton (CHCH\(_3\)) results in a signal enhancement of the adjacent aromatic proton, whereas no such enhancement is observed if the corresponding methyl hydrogen atoms (CHCH\(_3\)) are irradiated.

The assignment of the stereochemistry of the two epimers was also supported by the chemical shifts of the CHCH\(_3\) fragment in their \(^1\)H NMR spectra. As shown by the molecular model of compound 168, the concerned methyl group (CHCH\(_3\)) is found in the deshielding region of the aromatic ring. This is supported by the resonance of this methyl group at \(\delta = 2.05\) ppm compared to \(\delta = 1.55\) ppm for the corresponding methyl group in compound 170. In contrast, the methine proton (CHCH\(_3\)) in the case of
photoprodut 168 is situated in the deshielding region of the aromatic ring and therefore it resonates downfield (δ = 5.55 ppm) compared to that of the methine proton of isomer 170 (δ = 5.30 ppm).

Figure 21 Partial $^1$H NMR Spectra of Photoprodut 168. Bottom: routine spectrum. Top and middle: NOE difference after irradiation.
Figure 22  Partial $^1$H NMR Spectra of Photoprodct 170. Bottom: routine spectrum. Top and middle: NOE difference after irradiation.
Turning now to a discussion of the solution phase results, we note first of all that the regioselectivity is similar to that obtained in the case of lactone ester 96. That is, the rearrangement proceeds exclusively via the path B mechanism in solution. This observation is in agreement with the previous suggestion in the case of compound 96 that initial benzo-vinyl bridging is preferred via pathway B by releasing the intramolecular steric strain.

Secondly, strong support for the proposed steric effect on the regioselectivity of the photorearrangement of dibenzobarrelene lactones comes from the observation that the predominant photoproduct in the solution phase photolysis of the methyl lactone-ester 97 is the stereoisomer 168, which is derived from initial bonding at the more sterically hindered side (path B(I) in Scheme 53). It seems reasonable that release of the more severe steric interactions between the methyl group and the adjacent aromatic hydrogen atom by bond formation is preferred over release of the H⋯H steric interactions.

2. Solid State Results

In a fashion similar to the solid state photolysis of the lactone-ester 96, it was expected that, in principle, irradiation of the methyl lactone-ester 97 in the crystalline phase would proceed via both pathways A and B leading to two different regioisomers. It is apparent, however, that each pathway (path A or path B) is capable of producing a pair of diastereomers, since there are two different initial bridgings in each of the pathways. Therefore, four photoproducts could be possible upon photolysis of compound 97 in the solid state (Scheme 54). Products
168 and 170 are derived from pathway B as discussed in the previous section; regioisomers 171 and 172, which are not observed in the solution phase irradiation, are derived via pathway A (Scheme 54).

![Diagram of photorearrangement of Methyl Lactone-Ester 97 in the Solid State]

**Scheme 54** Photorearrangement of Methyl Lactone-Ester 97 in the Solid State.

In fact, irradiation of single crystals of 97 was found to produce only three photoproducts. Two of them were identified as compounds 168 and 170; the third product proved to be the isomer 171. The product ratio was determined to be 168:170:171 = 68:22:10 in the solid state, and the ratio was found to remain constant at various conversions of the starting material. However, the other isomer 172 could not be detected by GC and $^1$H NMR.
The structure of the solid state photoproduct 171 was established by FTIR, MS, $^{13}$C and $^1$H NMR spectroscopy, particularly based on the spectral similarity between the $^1$H NMR of compound 171 and its analogue 152. However, the product 171 could not be distinguished from its epimer 172 based on the spectroscopic analysis. The definitive evidence that confirms the structural assignment of 171 originates from the following independent synthesis of the two compounds, 171 and 172, and the subsequent determination of the crystal structure of 171.

Scheme 55 shows the preparation of compounds 171 and 172. It involves a Grignard reaction of dibenzosemibullvalene aldehyde 118 which was prepared according to the known procedure. In this step, two corresponding diastereomeric alcohol derivatives were formed by the addition of methyl magnesium bromide (CH$_3$MgBr) to the more reactive aldehyde carbonyl group. These two diastereomers, 173 and 174, were then separated at this stage. Acid-catalyzed lactonization of each of the alcohol derivatives 173 and 174 resulted in the formation of the corresponding dibenzosemibullvalene lactones 171 and 172 respectively. The structures of compounds 173 and 174 were assigned accordingly based on this transformation.

An X-ray crystallographic analysis of compound 171 proved the structural assignment. A stereodiagram of the molecule 171 is given in Figure 23. From this, the structure of the isomer 172 is reasonably assumed based on its spectroscopic data, which are similar to those of 171.
Scheme 55  Independent Syntheses of Photoproduct 171 and Its Isomer 172.

Figure 23  Stereodiagram of the Molecule 171.
Regarding the regioselectivity in the solid state reaction of the methyl lactone-ester 97, it is found that products 168 and 170, which originate from reaction pathway B, are predominant in the solid state. The photoproduct 171 via path A accounts for only 10% of the total yield. The product distributions in solution and in the solid state for both lactones, 96 and 97, are summarized in Table 11 for convenience of comparison between the two phototransformations.

Table 11 Product Distributions in the Solution and the Solid State Irradiations of Lactones 96 and 97.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>Product via Path A (%)</th>
<th>Product via Path B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactone 96</td>
<td>Solution</td>
<td>152 (0)</td>
<td>153 (100)</td>
</tr>
<tr>
<td>Lactone 96</td>
<td>Crystal</td>
<td>152 (13)</td>
<td>153 (87)</td>
</tr>
<tr>
<td>Lactone 97</td>
<td>Solution</td>
<td>171 (0) + 172 (0)</td>
<td>168 (77) + 170 (23)</td>
</tr>
<tr>
<td>Lactone 97</td>
<td>Crystal</td>
<td>171 (10) + 172 (0)</td>
<td>168 (68) + 170 (22)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Analysis by GC and $^1$H NMR.

By comparison, it can be seen from Table 11 that both compounds behave quite similarly in the di-$\pi$-methane photorearrangement. Upon irradiation in solution, they both proceed through pathway B exclusively to give corresponding dibenzoosemibullvalene products. On the other hand, both path A and path B photoproducts are formed in solid state irradiations, but pathway B is predominant in both cases.
We note that an interesting feature in the solid state reaction of the methyl lactone-ester 97 is the stereoselectivities in the pathways A and B. It can be seen from Table 11 that the product ratio of 168:170, which represents stereoselectivity in path B, is nearly unchanged by changing the reaction medium from solution phase (77:23) to the crystalline phase (68:22). In contrast, there is complete discrimination for the formation of photoproduct 171 via pathway A in the solid state photolysis. We suggest that such reaction stereoselectivity might stem from a specific crystal lattice effect. Although at the present time the molecular crystal structure of 97 is not available (X-ray crystallographic analysis were carried out, however, crystal structure has not been solved owing to disorder of the crystal), further structure-reactivity correlations can be possible from the crystallographic studies.

C. Electronic versus Steric Effect in the Photorearrangement of Lactone 98

In further efforts to study steric effects on the regioselectivity of the di-π-methane rearrangement of lactone-esters, the lactone 98 without the methyl ester group at the 11-vinyl carbon atom was synthesized by an intramolecular Diels-Alder cycloaddition of 9-anthrylmethyl propynoate (Scheme 24 on page 45). This is based on the following considerations. In principle, di-π-methane reaction of the lactone 98 may yield two regioisomeric photoproducts, 176 and 178 (Scheme 56). Ciganek has demonstrated that the di-π-methane rearrangement of compounds similar to 98, i.e. 9,12-bridged dibenzobarrelenes 154 and 160 (Schemes 50 and 51), give two
regioisomeric photoproducts upon irradiation in solution. In the case of the lactone 98, initial benzo-vinyl bridging at the bridgehead unsubstituted side \([C(11)-C(4a)]\) leading to the regioisomer 176 is expected to be predominant (Scheme 56), since the initially formed biradical intermediate species 175 will be more stabilized by the carbonyl group than 177. Such electronic stabilizing effects are supported by the work of others\(^{78}\) and also by the present studies discussed in a previous section of this thesis (Section IV.A.). By the steric argument discussed previously, however, the di-\(\pi\)-methane rearrangement of 98 would be expected to proceed via initial bonding at the bridgehead substituted side to give the regioisomer 178, as the steric interactions between the methylene hydrogen atoms and the adjacent aromatic hydrogen atoms are present in compound 98. Our ideas were (1) to find which effect, steric or electronic, would be the overriding factor that controls the reaction regioselectivity and (2) to study how the crystal lattice would affect the selectivity.

Scheme 56  Di-\(\pi\)-Methane Photorearrangement of Lactone 98.
Experimentally, the photorearrangement of lactone 98 proceeded to afford only product 176 upon irradiation in solution (both direct and acetone-sensitized) and in the solid state as well (Scheme 56). The $^1$H and $^{13}$C NMR, MS and FTIR spectra are in complete agreement with the assignment of structure 176. In particular, this photoproduct is characterized in its $^1$H NMR spectrum by a sharp singlet at $\delta = 3.97$ ppm which corresponds to the two cyclopropyl protons as expected for the mirror-symmetric dibenzosemibullvalene structure 176.

Thus, the above results demonstrate that the di-$\pi$-methane reaction of the lactone 98 is controlled by electronic stabilizing effects rather than steric effects. In addition, the reaction regioselectivity is not changed by the crystal lattice.

In comparison to the previous studies, it should be noted that the phototransformation of lactone 98 is quite similar to that of the 9,12-unbridged 9,10-ethenoanthracene 100 (Scheme 45). The common features in these phototransformations are (1) the photorearrangement proceeds in a regiospecific manner via initial bridging at the bridgehead unsubstituted side; the excited triplet state of 98 is perhaps involved, as acetone-sensitized photolysis gives the same product as direct irradiation and (2) the singlet-derived photoproduct, i.e., dibenzocyclooctatetraene derivative, is not formed with the direct irradiation of 98 and 100, whereas other similar compounds give the dibenzocyclooctatetraenes as the major photoproducts with the direct irradiation. The reason for this is yet unclear.
D. Studies on the Photoreactivity of 9,10-Ethenoanthracene Lactones 96, 97, 98 and 93c

In connection with the investigations of 9-substituted dibenzobarrelene compounds, we are interested in studying the photoreactivity possessed by this type of compound in terms of quantum yields ($\Phi$) and reaction rate constants ($k_r$) for the di-$\pi$-methane rearrangement. Originally, it was thought that the remarkable difference in regioselectivity between the lactone-ester 96 and the 9-substituted dibenzobarrelene diester 93c might be due to the relative reaction rates in pathways A and B. It was thought that the rate of initial bonding in path B for the lactone-ester 96 might be increased by the steric H···H interactions between the methylene and the adjacent aromatic hydrogen atoms compared to that in compound 93c without such steric interactions. Experimentally, it was noted that lactone-ester 96 and methyl lactone-ester 97 displayed qualitatively much higher reactivity than the dibenzobarrelene diester 93c under similar irradiation conditions, both in solution and crystalline states. Interestingly, even room light could cause significant photoreactions for the lactones 96 and 97 in the two media.

1. Quantum Yield ($\Phi$) Measurements

In the present studies, quantum yields ($\Phi$) were measured in benzene at $\lambda = 313$ nm by using standard procedures$^{89}$ (refer to Experimental section for details). Quantum yields ($\Phi$) for the formation of the photoproducts from each of the starting materials were averaged over several measurements and are summarized in Table 12.
Table 12 Quantum Yields (Φ) of Product Formation from Photolysis of Dibenzobarrelenes 96, 97, 98 and 93c.a

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Photoprodut</th>
<th>Quantum Yield (Φ)b</th>
<th>Total Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactone-Ester 96</td>
<td>153</td>
<td>0.48 ± 0.07</td>
<td>0.48 ± 0.07</td>
</tr>
<tr>
<td>Methyl Lactone-Ester 97</td>
<td>168</td>
<td>0.63 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>0.15 ± 0.03</td>
<td>0.78 ± 0.05</td>
</tr>
<tr>
<td>Lactone 98</td>
<td>176</td>
<td>0.020 ± 0.002</td>
<td>0.020 ± 0.002</td>
</tr>
<tr>
<td>Diester 93c</td>
<td>120</td>
<td>0.089 ± 0.009</td>
<td></td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>0.031 ± 0.004</td>
<td>0.12 ± 0.01</td>
</tr>
</tbody>
</table>

aIrradiation at 313 nm in benzene and analysis by GC. bQuantum yields were determined at the following concentrations: [96] = 0.01 M, [97] = 0.01 M, [93c] = 0.015 M and [98] = 0.01 M.

It can be seen from Table 12 that rearrangement of the lactone-ester 96 is much more efficient (Φ = 0.48) than that of the diester 93c (Φ = 0.12). It is clear that such a remarkable difference in reaction efficiency could only be ascribed to the structural difference between the two compounds. This seems to suggest that the high quantum yield observed for compound 96 may lie in the intramolecular steric interactions present in 96, if we assume that compounds 96 and 93c are
electronically equivalent. Further support for this speculation is found in the quantum yield measurement for the product formation from the methyl lactone-ester 97. Increasing the steric hindrance by substitution of a methyl group but without changing the electronic structure causes an increase in the quantum yield to $\Phi = 0.78$.

Quantum yields and triplet lifetimes for some other dibenzobarrelene compounds, which are taken from the literature, are listed in Table 13. It is interesting to compare these quantum yields with those determined in the present work (Table 12). First, we note that the quantum yields for the lactone-esters 96 and 97 are substantially higher than the rest of compounds (2.5-40 fold higher depending on the compound). Secondly, it can be seen that the quantum yields for the bridgehead-substituted diester 93c and the lactone 98 (Table 12) are approximately in the same range as those in Table 13.

It should be pointed out that the measured quantum yield $\Phi$ (overall reaction efficiency) is determined by the intersystem crossing quantum yield ($\Phi_{\text{isc}}$) and the reaction quantum yield $\Phi_T$ of the excited triplet state$^{90,91}$ as found in the equation (1) (Scheme 57). Speculation on the large difference between the triplet reaction efficiencies is not possible without knowing the intersystem crossing quantum yield ($\Phi_{\text{isc}}$) of each of the above compounds. It is clear, at least in the case of compound 97, that the intersystem crossing process must be very efficient, since the overall reaction quantum yield ($\Phi$) of 97 is close to unity. In fact, it has been suggested$^{92}$ that perhaps a very efficient intersystem crossing was involved in the di-π-methane rearrangement of some dibenzobarrelene compounds, as it was found that these compounds do
not react from their excited singlet states to give the corresponding
dibenzocyclooctatetraene products. In such cases, it can be assumed that
$\phi_{\text{ISC}} = 1.$

Table 13 Quantum Yields and Triplet Lifetimes of Some 9,10-
Ethenoanthracenes.

<table>
<thead>
<tr>
<th>Dibenzo-barrelene</th>
<th>Quantum Yield ($\Phi$)</th>
<th>Triplet Lifetime (ns)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Diagram 179]</td>
<td>0.12</td>
<td>0.2</td>
<td>76</td>
</tr>
<tr>
<td>![Diagram 180]</td>
<td>0.20</td>
<td>1.0</td>
<td>61a</td>
</tr>
<tr>
<td>![Diagram 181]</td>
<td>0.02</td>
<td>0.2</td>
<td>61a</td>
</tr>
</tbody>
</table>

$\Phi = \phi_{\text{ISC}} \times \Phi_T \quad (1)$

$\Phi_T = k_r / (\Sigma k_d + k_r) = k_r \times \tau \quad (2)$

Scheme 57 Quantum Yield and Reaction Rate Relationships.
Furthermore, it should be pointed out that the overall reaction efficiency in terms of quantum yields (\(\Phi\)) does not necessarily represent the relative reaction rates. In other words, quantum yields may not be used as relative measures of the reaction rate constants. This is because, in general, the quantum yield (\(\Phi\)) for product formation from a triplet reaction is governed by equation (2) in Scheme 57, where \(k_r\) is the reaction rate constant from the triplet, \(\Sigma k_d\) is the sum of non-reaction decay rate constants from the triplet and \(\tau\) is the lifetime of the excited triplet state. In order to speculate further on the higher reaction efficiencies observed for the lactone-esters 96 (\(\Phi = 0.48\)) and the methyl lactone-ester 97 (\(\Phi = 0.78\)) compared to the diester 93c (\(\Phi = 0.12\)), it is necessary to obtain the reaction rate constant (\(k_r\)) and the triplet lifetimes (\(\tau\)) for these compounds.

2. Quenching Results on the Lactone-Ester 96 and Diester 97.

Quenching experiments were carried out to determine the triplet lifetimes (\(\tau\)) for lactone-ester 96 and the diester 93c. In the present studies, 2,5-dimethyl-2,4-hexadiene and 1,3-cyclohexadiene with triplet energies of 59 kcal/mole and 53 kcal/mol\(^{89}\) respectively were used as the triplet quenchers. Although the triplet energies for compounds 96 and 93c are not known, it is estimated that both compounds have their triplet energies in the range 60-70 kcal/mol. This is based on the experimental results that the di-\(\pi\)-methane rearrangement (triplet reaction) of compounds 96 and 93c could be quenched by 2,5-dimethyl-2,4-hexadiene (\(E_T = 59\) kcal/mole) or 1,3-cyclohexadiene (\(E_T = 53\) kcal/mole), and could also photosensitized by benzophenone (\(E_T = 69\) kcal/mole).\(^{89}\) The relative quantum yields (\(\Phi_0/\Phi\)) were determined under various
concentrations of the quencher. According to the Stern-Volmer equation shown as follows, changes of $\Phi_o/\Phi$ as a function of the quencher concentrations obey a linear relationship.

$$\Phi_o/\Phi = 1 + k_q \tau [Q]$$

Where $\Phi$ and $\Phi_o$ are the quantum yields with and without the quencher, $k_q$ is the bimolecular quenching rate constant, $\tau$ is the lifetime of the excited state being quenched and $[Q]$ is the quencher concentration.

In the case of the lactone-ester 96, the experimental data were in good agreement with the Stern-Volmer equation. Plotting the quantum yields ($\Phi_o/\Phi$) against the concentration of the quencher (2,5-dimethyl-2,4-hexadiene) ranging from 0 - 0.04 M, gave a straight line shown in Figure 24. From the slope of the line, the $k_q \tau$ value is calculated to be $105 \pm 5 \text{ M}^{-1}$. By assuming diffusion controlled energy transfer from the excited triplet of compound 96 to the quencher, and by using the rate of diffusion in benzene as $k_q = 5.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, we arrive at a relatively long triplet lifetime of $21 \pm 2 \text{ ns}$ for the lactone-ester 96. The quenching process is considered to obey the following general mechanism (Scheme 58).
Scheme 58 General Triplet Quenching Mechanism.

Excitation of the reactant (A) by absorption a photon leads to the excited singlet state \(1_A^*\) which undergoes intersystem crossing to give the excited triplet state \(3_A^*\). Energy transfer from \(3_A^*\) to the ground state quencher (Q) results in the ground state of the reactant (A) and the excited triplet state of the quencher (Q).

\[
A \longrightarrow 1_A^* \longrightarrow 3_A^* \\
3_A^* + Q \longrightarrow 3_Q^* + A \\
3_Q^* \longrightarrow Q
\]

Figure 24 A Stern-Volmer Plot for Formation of Dibenzosemibullvalene Lactone 153 from Lactone-Ester 96 in the Presence of 2,5-Dimethyl-2,4-hexadiene.
However, it was found that 1:1 adducts between the lactone-ester 96 and the quencher 2,5-dimethyl-2,4-hexadiene or 1,3-cyclohexadiene were formed in significant amounts. Further experiments suggest that the cycloaddition reactions of the lactone-ester 96 to the quenchers might occur from the excited triplet state of the quenchers (see the discussion in the next section).

In contrast to the lactone-ester 96, it was found that the di-π-methane rearrangement of the diester 93c was inefficiently quenched by 1,3-cyclohexadiene in the concentration range 0 - 1.0 M. By the Stern-Volmer analysis (Figure 25), $k_{q\tau}$ is determined to be $0.59 \pm 0.02$ M$^{-1}$. Again, assuming diffusion controlled energy transfer and using the rate of diffusion in benzene as $k_q = 5.0 \times 10^9$ M$^{-1}$s$^{-1}$, the triplet lifetime $\tau$ is calculated to be $0.12 \pm 0.01$ ns.

![Figure 25 A Stern-Volmer Plot for Formation of Dibenzosemibullvalenes 120 and 124 from 93c in the Presence of 1,3-Cyclohexadiene.](image-url)
It is interesting to compare the triplet lifetimes of the lactone-ester 96 ($\tau = 21$ ns) and the diester 93c ($\tau = 0.12$ ns) with those determined by others as shown in Table 13. First, it can be noted that the dibenzobarrelene diester 93c has approximately the same short triplet lifetime as those compounds listed in Table 13. In contrast, however, the triplet lifetime of the lactone-ester 96 is remarkably longer (ca. 180-fold) than the diester 93c and other similar compounds in Table 13. The reason for such a remarkable difference in triplet lifetimes between compounds 96 and 93c is not immediately clear, as we know that triplet lifetime ($\tau$) is determined by the following equation:

$$\tau = \frac{1}{(k_d + k_p + k_r)}$$

where $k_d$ and $k_p$ are rate constants of radiationless decay and phosphorescence from the excited triplet state.

In principle, the reaction rate constants ($k_r$) could be calculated according to the above equation. However, we do not know the values of rate constants $k_d$ and $k_p$, and this prevents us from further speculation on the difference in photoreactivity between compounds 96 and 93c in the di-\(\pi\)-methane photorearrangement.

E. Photocycloadditions of Lactone-ester 96 to 1,3-Dienes

Photocycloadditions have long been the subject of research interest in the field of organic photochemistry with regard to their applications and mechanism. [2+2] Photocycloadditions of a wide variety
of organic compounds such as alkenes, saturated and unsaturated ketones have been studied extensively over the past several decades. 1,3-Dienes are commonly used as efficient triplet quenchers in the photoreactions of alkanones and \( \alpha,\beta \)-unsaturated ketones. On the other hand, 1,3-dienes can also participate in photocycloaddition reactions to give \([2+2]\) and \([4+2]\) adducts. Examples of this type of photoaddition are found in Scheme 59. The reaction is usually considered to occur from the molecules that are directly excited by absorption of a photon. However, it is possible that, if the excited molecules such as compounds 182 and 184 (\(E_T \geq 60\) kcal/mol) in Scheme 59 are capable of transferring their energy to the dienes (\(E_T = 53-60\) kcal/mol), the cycloaddition reaction could occur from the excited triplet state of the dienes. Such processes have been reported.\(^{95,96,97}\) In addition, the photocycloaddition of maleic anhydride 183 to triplet 1,3-dienes, which were indirectly excited by benzophenone-sensitization, has been reported\(^98\) (Scheme 59).

In our quenching studies on the lactone-ester 96, we found that 1,3-dienes not only quench the di-\(\pi\)-methane rearrangement of 96 but also form 1:1 adducts with it. Two 1,3-dienes, namely 2,5-dimethyl-2,4-hexadiene and 1,3-cyclohexadiene, were used in the studies of photocycloadditions of 96 to dienes.
Scheme 59  Photocycloadditions of 1,3-Dienes.

1. Cycloaddition of Lactone-ester 96 to 2,5-Dimethyl-2,4-hexadiene

A mixture of the lactone-ester 96 and 2,5-dimethyl-2,4-hexadiene (ratio = 1:4) in benzene was irradiated through a Pyrex filter (λ > 290 nm) until more than 95% of the starting material was converted. Column chromatography yielded the rearranged product 153, the [2+2] adduct 185
and the 1:1 mixture of adducts 185 and 186 (Scheme 60). GC analysis showed that the adduct 185 is the major [2+2] photocycloaddition product (GC ratio 153:185:186 = 1:1.6:1). The structures of the [2+2] photoadducts 185 and 186 were determined by MS or GCMS as well as by FTIR and $^1$H NMR spectra. The regio- and stereochemistry of the structures were assigned based primarily on routine $^1$H NMR, proton decoupling and NOE experiments.

Scheme 60  [2+2] Photocycloaddition of Lactone-Ester 96 to 2,5-Dimethyl-2,4-hexadiene.

The adduct 185 is characterized informatively by $^1$H NMR (Figure 26) as four high-field singlets, $\delta = 1.07, 1.16, 1.22$ and $1.64$ ppm, which correspond to the four non-ester methyl groups. Two of the methyl signals ($\delta = 1.22$ and $1.64$ ppm) are seen to be weakly coupled with the vinyl hydrogen atom ($J < 1$ Hz). The structural assignment of the
regiochemistry of 185 is supported by the NOE difference measurement (Figure 26). Irradiation of the methyl group ($^6$CH$_3$ of structure 185 in Figure 27) results in the signal enhancement of the bridgehead proton. Molecular model of compound 185 shows that the methyl group ($^6$CH$_3$) is close to the bridgehead hydrogen atom, and this is in agreement with the NOE results.

Figure 26 Partial $^1$H NMR Spectra of Photoadduct 185. Bottom: routine spectrum. Top and middle: NOE difference after irradiation.
The structure of the adduct 186 is also assigned based on an NOE experiment of the photoproduct mixture, 185 and 186. Partial $^1$H NMR data are presented in Figure 28. Again, saturation of the resonance ($\delta = 1.13$ ppm) of the high-field methyl group signal ($^a$CH$_3$ of the structure 186 in Figure 27) leads to a signal enhancement of the bridgehead hydrogen atom. This information supports the assignment of the regiochemistry of product 186.

Regarding the stereochemistry of the [2+2] adducts 185 and 186, the chemical shifts of the vinyl proton and the cyclobutyl proton were used to distinguish the two stereoisomers. In the case of isomer 185, the vinyl hydrogen atom is found to resonate at $\delta = 5.14$ ppm, and the chemical shift of the cyclobutyl hydrogen atom is at $\delta = 2.14$ ppm. In contrast, the stereoisomer 186 gives a relatively high-field doublet for the vinyl hydrogen atom at 3.40 ppm and the cyclobutyl proton resonates at $\delta = 3.05$ ppm. It can be seen clearly from molecular models that the cyclobutyl hydrogen atom from 185 lies in the shielding region of the...
aromatic ring, thus the resonance of this proton is found at relatively high-field ($\delta = 2.14$ ppm) compared to that in the isomer 186 ($\delta = 3.05$ ppm). A similar situation exists in the case of isomer 186 where the vinyl hydrogen resonates at $\delta = 3.40$ ppm owing to the shielding effect from the aromatics, compared to that of 185 ($\delta = 5.14$ ppm) which falls into the normal region for unshielded vinyl protons.

Figure 28 Partial $^1$H NMR Spectra of Photoadduct 186. Bottom: routine spectrum. Top: NOE difference after irradiation.
The stereochemical assignment of photoproduct 185 is also supported by the NOE observation (Figure 26). Irradiation of the methyl group (\(^{13}\text{C} \text{H}_3\) of 185 in Figure 27) leads to a signal enhancement of the cyclobutyl hydrogen atom, which is considered to be cis to this methyl group.

2. Cycloaddition of Lactone-Ester 96 to 1,3-Cyclohexadiene

In a similar fashion, photolysis of a mixture of the lactone-ester 96 and 1,3-cyclohexadiene (ratio 1:12) was performed and shown to give the compounds 187, 188, 189 and 190 (GC ratio = 11:3:1:2) (Scheme 61). Although traces of other photoproducts were detected by GC analysis of the reaction mixture, they could not be isolated owing to the small amounts present.

Scheme 61 Photocycloaddition of Lactone-Ester 96 to 1,3-Cyclohexadiene.
The major [2+2] photocycloaddition adduct 187 was isolated in pure crystalline form and fully characterized by $^1$H and $^{13}$C NMR, FTIR and MS spectroscopy. The FTIR spectrum of 187 shows two characteristic carbonyl absorptions, 1780 cm$^{-1}$ and 1723 cm$^{-1}$, which correspond to the functional groups of the saturated lactone and the ester. The assignment of the structure 187 was based primarily on $^1$H NMR spectroscopy. The proton decoupled, NOE difference and 2D COSY $^1$H NMR spectra of 187 are given in Figures 30 to 32. Compound 187 is characterized in its $^1$H NMR spectrum (Figure 30) by two vinyl protons at $\delta = 5.77$ and 5.90 ppm. A set of two doublets at $\delta = 4.87$ and 5.30 ppm was assigned to the lactone methylene hydrogen atoms. The bridgehead proton resonates at $\delta = 4.66$ ppm, and the ester methyl singlet was found at $\delta = 3.42$ ppm. In addition, multiplets at the region 1.4-2.4 ppm were ascribed to the protons that attached to the cyclohexene ring. One of the cyclobutyl hydrogen atoms, $H_a$ as shown in the structure 187 in Figure 29, is assigned to be adjacent to the vinyl group by the following evidence: as shown by the decoupled spectra in Figure 30, the multiplet from the vinyl proton ($H_d$) is changed to a doublet after the signal $H_a$ at $\delta = 2.31$ is decoupled; this doublet is due to the coupling of $H_d$ with the other vinyl proton ($H_c$). In turn, the multiplet due to $H_a$ becomes a doublet when $H_d$ is irradiated. Based on this assignment, the remaining hydrogen atoms in the region 1.4-2.4 ppm are assigned accordingly by the decoupled and 2D COSY $^1$H NMR spectra (Figures 30 and 31), which need not be discussed further. Final confirmation on the structure of 187 comes from the NOE difference observations (Figure 32), in which irradiation of the cyclobutyl hydrogen atom ($H_a$) leads to a signal enhancement of the bridgehead proton ($H_e$), whereas irradiation of the other cyclobutyl hydrogen atom
(H_b) results in the signal enhancement of one of the lactone methylene hydrogen atoms. The molecular model of 187 shows that the cyclobutyl hydrogen atom (H_a) is spatially closer to the bridgehead hydrogen atom (H_e), and H_b is closer to one of the lactone methylene protons.

Figure 29 Structural Assignment of the [2+2] Adducts 187 and 188.
Figure 30  Partial $^1$H NMR Spectra of Photoproduct 187. Bottom: routine spectrum. Middle: decoupled at 2.31 ppm. Top: decoupled at 5.76 ppm.
Figure 31  Partial 2D COSY $^1$H NMR Spectrum of Photoproduct 187.
Figure 32  Partial $^1$H NMR Spectra of Photoproduct 187. Bottom: routine spectrum.

Top four: NOE difference after irradiation.
Although the [2+2] adduct 188 (Scheme 61) was obtained as a mixture (ca. 65% pure), it could still be characterized readily by $^1$H NMR and GC-MS spectroscopy since the mixture contains the adducts 187 and 189 whose structures are known (see below for identification of photoproduct 189). The $^1$H NMR spectrum of 188 proved to be quite similar to that of its regioisomer 187, thus the structure of compound 188 is assigned in much the same way as that of 187. In particular, the multiplet at ca. 1.8 ppm in Figure 33 is ascribed to the cyclobutyl hydrogen atom $H_b$ of structure 188 (Figure 29), which is adjacent to the double bond. This is supported by decoupling experiments (Figure 33), which show that irradiation of $H_c$ at $\delta = 5.25$ ppm changes the $H_b$ multiplet to a doublet. Conversely, irradiation of $H_b$ converts the multiplet due to $H_c$ to a doublet. The cyclobutyl hydrogen atom $H_a$ is assigned to the resonance at 2.2 ppm (multiplet), as this multiplet ($H_a$) becomes a quartet (due to coupling by the adjacent $CH_2$) when $H_b$ is irradiated. The regio- and stereochemistry of adduct 188 is supported by the NOE experiments in a fashion similar to that described in the case of regioisomer 187. The NOE difference spectra of photoproduct 188 as found in Figure 34 show that irradiation of the cyclobutyl proton ($H_b$) leads to a signal enhancement of one of the lactone methylene hydrogen atoms. In contrast, an enhancement of the signal due to the bridgehead hydrogen atom ($H_e$) is observed when the second cyclobutyl hydrogen atom ($H_a$) is saturated. These observations are in agreement with the assignment of the structure 188.
Figure 33  Partial $^1$H NMR Spectra of Photoproduct 188. Bottom: routine spectrum. Middle: decoupled at $\delta = 5.25$ ppm. Top: decoupled at $\delta = 1.79$ ppm.
Figure 34 Partial $^1$H NMR Spectra of Photoproduct 188. Bottom: routine spectrum. Top and middle: NOE difference after irradiation.
The photo-adduct 189 (Scheme 61) is characterized in its FTIR spectrum by two strong carbonyl absorption bands at 1777 cm\(^{-1}\) and 1723 cm\(^{-1}\), which are ascribed to the saturated lactone and ester groups. The 1,4-cyclohexadiene moiety is identified by four sets of multiplets at \(\delta = 5.71, 5.99, 6.05\) and 6.14 ppm in the \(^1\)H NMR spectrum (Figure 35). The \(\text{CH}_2\) group of the 1,4-cyclohexadiene moiety is found at \(\delta = 2.58\) ppm as a multiplet, and the multiplet at \(\delta = 2.83\) ppm is assigned to the methine hydrogen atom of the cyclohexadiene. The possibility that this material has the 1,3-cyclohexadiene structure 191 (Figure 36) has been eliminated on the following basis: (1) the expected vicinal proton coupling between the methylene and the methine hydrogen atoms for the 1,3-cyclohexadienyl group is not observed in the \(^1\)H NMR spectrum; and (2) as shown in Figure 35, two of the multiplets corresponding to the vinyl protons (\(\delta = 5.71\) and 5.99 ppm) become doublets when the cyclohexadienyl methylene hydrogen atoms (\(\delta = 2.57\) ppm) are irradiated. Furthermore, the other two multiplets for vinyl protons become doublets upon decoupling of the cyclohexadienyl methine proton (\(\text{H}_D\)). These results suggest that the methylene and methine protons are both adjacent to two vinyl groups. The decoupling results are therefore inconsistent with the 1,3-cyclohexadienyl structure 191. The assignment of the regio- and stereochemistry to structure 189 is supported by the NOE difference experiments (Figure 37). Irradiation of the \(\alpha\)-hydrogen atom (\(\text{H}_a\)) which is adjacent to the lactone carbonyl leads to an enhancement of the signal of one of the lactone methylene protons. A molecular model of compound 189 shows that \(\text{H}_a\) is in close proximity to the lactone methylene hydrogen atom. A second irradiation at the cyclohexadienyl methine hydrogen atom (\(\text{H}_B\), \(\delta = 2.83\) ppm) results in an enhancement of
the signal due to $H_a$, which indicates that the 1,4-cyclohexadienyl group is cis to the methine hydrogen atom $H_a$.

![Partial NMR Spectra of Photoproduct 189](image)

Figure 35  Partial $^1$H NMR Spectra of Photoproduct 189. Bottom: routine spectrum. Middle: decoupled at $\delta = 2.57$ ppm. Top: decoupled at $\delta = 2.83$ ppm.
Figure 36  Structures of Photoproduct 189 and Its Isomer 191

\[ E = \text{CO}_2\text{CH}_3 \]

Figure 37  Partial $^1$H NMR Spectra of Photoproduct 189. Bottom: routine spectrum. Top and middle: NOE difference after irradiation.
The reduction product 190 (Scheme 61) was identified by GCMS and 
\(^1\)H NMR spectroscopy from a mixture of compounds 187, 189, 153, and 190 
(ca. 60% of 190). GCMS analysis of compound 190 gave m/e = 320 as the 
parent mass. It is apparent that reduction of the lactone-ester 96 by 
two hydrogen atoms had taken place, as its parent mass is m/e = 318. The 
trans stereochemistry of photoprodut 190 is confirmed by the \(^1\)H NMR 
spectrum, which proved to be identical to that reported by Okada et 
al.\(^{101}\) in their study of the [4+2] phototransformation of the anthracene 
derivative 192 to compound 190 (Scheme 62).

\[ \text{Scheme 62 [4+2] Photocycloaddition of 9-Anthrylmethyl Methyl Fumarate.} \]

3. Mechanistic Studies on the Photocycloaddition of Lactone-Ester 96 to 
1,3-Dienes

As discussed in the previous section of this thesis, the di-\(\pi\)-methane photorearrangement of the lactone-ester 96 is quenched 
efficiently by 1,3-cyclohexadiene or 2,5-dimethyl-2,4-hexadiene, and the
photocycloaddition adducts between 96 and the dienes were isolated. In view of the mechanism involved in the [2+2] photocycloaddition, we are interested in that whether the reactions occur from the excited triplet state of the lactone-ester 96 or from that of the 1,3-dienes.

First, the possibility that direct excitation of the 1,3-dienes is involved in the [2+2] cycloaddition reaction can be ruled out, since the irradiation was carried out under the condition of using a Pyrex filter ($\lambda > 290$ nm). Under such a reaction condition, 1,3-dienes will not absorb the light. It is apparent that the excited triplet state of compound 96 is formed initially through excitation of the lactone-ester 96 by absorption of a photon followed by a rapid intersystem crossing process.

From the above, three possible mechanisms can be considered for the formation of the photocycloadducts: (1) $\text{LE}^* + D \rightarrow \text{adducts}$, (2) $\text{LE}^* + D \rightarrow (\text{LE} \cdot \cdot \cdot \text{D})^* \rightarrow \text{adducts}$ and (3) $\text{LE}^* + D \rightarrow \text{LE} + \text{D}^* \rightarrow \text{adducts}$, where LE represents lactone-ester 96, D = 1,3-dienes and * stands for the excited state (triplet).

The following results seem to suggest that mechanisms (3) is perhaps involved. That is, quenching takes place first, and subsequent cycloaddition occurs from the 1,3-diene triplets. First of all, it was found that the lactone-ester 96 did not react with 2,3-dimethyl-2-butene to give the [2+2] adduct 193 (Scheme 63) when 96 and the alkene (ratio 1:10) were irradiated. The only photoproduct observed in this case was the rearranged dibenzosemibullvalene lactone 153. Based on the general premise that 2,3-dimethyl-2-butene is known as a fairly reactive substrate towards [2+2] photocycloaddition, one would expect that this
alkene would react with the excited triplet 96 to form [2+2] adducts if the [2+2] cycloaddition reaction is capable of competing with the di-p-methane rearrangement.

![Scheme 63 Photolysis of Lactone-Ester 96 in the Presence of 2,3-Dimethyl-2-butene.](image)

The quenching-cycloaddition mechanism (3) is also supported by the sensitization results. Photolysis of the lactone-ester 96 using triplet sensitizers such as benzophenone (\(E_T = 69 \text{ kcal/mol}\)) or benzil (\(E_T = 54 \text{ kcal/mol}\)) in the presence or absence of 1,3-cyclohexadiene (\(E_T = 53 \text{ kcal/mol}\)) was carried out at an irradiation wavelength of \(\lambda \geq 340 \text{ nm}\) (uranium glass filter). Under the present irradiation conditions, only the sensitizer (benzophenone or benzil) is excited. It was found that, in the absence of 1,3-cyclohexadiene, the di-\(\pi\)-methane rearrangement of the lactone-ester 96 can be sensitized by benzophenone but not by benzil. It was also found that, in the presence of the diene, the photolysis gives the expected cycloaddition products 187-190 with the
same product ratio by using either benzophenone or benzil as the
sensitizer. This provides evidence that excited 1,3-dienes may
participate in the photocycloaddition reaction with the lactone-ester
96. It should be pointed out, however, that the exciplex mechanism
(mechanism (2)) could not be ruled out in the present study.

VI. Studies on 9-Chloromethyl 9,10-Ethenoanthracene Diester 93d

The title compound, dimethyl 9-chloromethyl-9,10-dihydro-9,10-
ethanoanthracene-11,12-dicarboxylate (93d), was readily prepared by
Diels-Alder reaction of 9-chloromethylanthracene to dimethyl
acetylenedicarboxylate (Scheme 21 on page 42). It was interesting to
find that compound 93d crystallizes in three different crystalline
modifications. From diethyl ether/petroleum ether, needle and prism
crystals of 93d were formed. The two differently shaped crystals were
separated and shown to be dimorphic by their melting points and FTIR
spectra. The needle crystal, which is defined as the α-form of
crystalline compound 93d, has a melting point of 174-176°C whereas the
prism crystal (β-form) has a lower melting point of 168-170°C. It is
shown in Figure 38 that the FTIR spectra of the dimorphs are different
in the fingerprint region.
Figure 38 FTIR Spectra of Crystalline 9-Chloromethyldibenzobarrelene
d. (a) α-Form. (b) β-Form (c) γ-Form.
The above two polymorphic forms were also characterized by X-ray crystallographic analysis. The $\alpha$-form was determined to be in space group $P2_12_12_1$; in contrast, the $\beta$-form occupies space group $P2_1/c$. The $\beta$-crystal modification was also achieved by recrystallization of compound 93d from chloroform/methanol.

The third crystal modification ($\gamma$-form) was derived by recrystallization from acetone/hexane. Although the $\gamma$-type crystals (prisms) of 93d have the same melting point (168-170°C) as the $\beta$-type, their FTIR spectra (Figure 38) are slightly different from those of either the $\alpha$-form or the $\beta$-form crystals. The $\gamma$-type crystals also occupy the space group $P2_1/c$ (same as that of the $\beta$-form), but with different cell dimensions from the $\beta$-form (see Experimental for details). The uniqueness of $\gamma$-crystal modification was also supported by its different photochemical and photophysical behavior compared to the other two modifications.

It is well understood that crystalline polymorphs may differ from one another not only in their packing arrangements but also in subtle variations in the conformations of the constituent molecules. In such cases, one is provided with an opportunity to study the same reaction in more than one crystal modification. Thus, any differences in reactivity and selectivity that are observed between polymorphs may be ascribed to the structural (both molecular and crystallographic) differences, thereby providing more information on the structure-reactivity correlations.
A. Unusual Photorearrangement of 9-Chloromethyl Dibenzobarrelene Diester 93d

1. Photolysis in Solution and in the Solid State

The title compound 93d undergoes a di-π-methane rearrangement to give two regioisomeric dibenzosemibullvalene products 194 and 195 (Scheme 64) upon acetone-sensitized irradiation in solution. The two photoproducts, 194 and 195, are characterized by analytical and spectroscopic methods, particularly by the $^1$H NMR spectra in which the predominant photoproduct 194 shows a characteristic resonance at $\delta = 4.40$ ppm corresponding to the cyclopropyl proton. In contrast, the benzylic methine proton of the regioisomer 195 appears at $\delta = 5.13$ ppm. These assignments are in agreement with the typical chemical shifts for similar dibenzosemibullvalene compounds.\(^{51,52}\)

\[ E \xrightarrow{\text{hv}} E=\text{CO}_2\text{Me} \]

\[ 93d \quad 194 \quad 195 \]

\[ \begin{align*}
196 & \quad + \\
197 & \quad + 
\end{align*} \]

Scheme 64  Photorearrangements of 9-Chloromethyl Dibenzobarrelene 93d.
In contrast to the photolysis in acetone (triplet), irradiations in benzene, acetonitrile, carbon tetrachloride, chloroform and in the solid state afford two additional minor photoproducts which were characterized as the dibenzopentalene derivatives 196 and 197 (Scheme 64). Products 196 and 197 were isolated from a preparative photolysis in chloroform by column chromatography on silica gel and by fractional crystallization of each compound. As the spectroscopic data for these minor photoproducts were not sufficiently informative to allow for unambiguous structural assignments, their structures were established by X-ray crystallographic studies, which demonstrated that the two compounds have the novel, exo-methylene, pentalene-like structures 196 and 197. Their ORTEP drawings are presented in Figures 39 and 40, respectively.

Figure 39  ORTEP Drawing of the Molecular Structure of Photoproduct 196.
Figure 40  ORTEP Drawing of the Molecular Structure of Photoproduct 197.

2. Product Ratio Analysis

The product ratios from the photolysis of compound 93d in various solvents and in the crystalline state are summarized in Table 15.

The triplet state (acetone-sensitized) photochemistry of dibenzobarrelene 93d is unexceptional. Like many other similar compounds discussed in this thesis, the di-\(\pi\)-methane photorearrangement of compound 93d proceeds smoothly in acetone leading to the normal products 194 and 195. The regioselectivity in this case is also similar to that of the other compounds; dibenzosemibullvalene diester 194 is formed as the major photoproduct. Discussions on the solution phase
regioselectivity of similar compounds have been presented in the previous part of the thesis (section III.A.) and need not be repeated here.

Table 14 Product Ratios from Photolysis of 9-Chloromethyl Dibenzobarrelene 93d in Different Media.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Reaction Medium</th>
<th>Product Ratio\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>194</td>
</tr>
<tr>
<td>Acetone</td>
<td>4</td>
</tr>
<tr>
<td>Benzene</td>
<td>16</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>16</td>
</tr>
<tr>
<td>Chloroform</td>
<td>7</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>68</td>
</tr>
<tr>
<td>α-Crystal</td>
<td>3</td>
</tr>
<tr>
<td>β-Crystal</td>
<td>2</td>
</tr>
<tr>
<td>γ-Crystal</td>
<td>3</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Analysis by GC; the ratios determined by capillary GC peak areas (uncorrected for detector response). \textsuperscript{b}Estimated error ± 5%.
Since no trace of the two minor products 196 and 197 could be detected in acetone, it is considered that they are probably derived from singlet state reaction. This is supported by further photosensitization studies of 93d in chloroform using xanthone ($E_T = 74$ kcal/mol) as the triplet energy sensitizer, in which the formation of products 196 and 197 was not observed by GC (ratio 194:195 = 4:1).

Secondly, it can be noted from Table 15 that the product ratios change moderately upon varying the reaction medium from solution to the crystalline state. Although the di-π-methane rearrangement products 194 and 195 remain predominant in the solid state, the proportion of the singlet-derived photoproducts 196 and 197 increases noticeably. In addition, we also note that the regioselectivity in the di-π-methane rearrangement of 93d in solution (194:195 = 4:1) is different from that in the solid state (194:195 = 1:1). A final interesting point is that the three polymorphic crystals, i.e. α-, β- and γ-modifications, have quite similar photochemical behavior in that they are all photochemically reactive and the resulting photoproducts are the same with slightly different ratios.


As mentioned above, the formation of the unusual dibenzopentalene derivatives 196 and 197 was considered to be derived from an excited singlet state reaction. To help in understanding the speculation on the mechanism of their formation, a brief review of current literature on the singlet state reactivity of barrelene compounds is presented below.
In Scheme 12 (page 29), it was mentioned that direct irradiation of barrelene (56) and benzobarrelene (59) produces cyclooctatetraene (COT) derivatives via $S_1$. Similarly, singlet reaction of dibenzobarrelene (198) gives dibenzocyclooctatetraene (200) as the major photoproduct on direct irradiation (Scheme 65).\textsuperscript{104} It is generally agreed\textsuperscript{49,105} that the mechanism involves $[2\pi+2\pi]$ cycloaddition leading to the cage intermediate 199 (not isolated), and that this is followed by bond reorganization to form the COT derivative (Scheme 65).

\[
\begin{array}{c}
\text{198} \xrightarrow{\text{hv}} \text{199} \xrightarrow{\text{direct}} \text{200}
\end{array}
\]

Scheme 65  Photorearrangement of Dibenzobarrelene via Its Singlet Excited State.

The $[2+2]$ mechanism was supported by a deuterium labeling experiment in the case of benzobarrelene (201) (Scheme 66). Zimmerman et al.\textsuperscript{105} showed that the labeled compound 201 gives a COT derivatives with the labeling pattern shown in Scheme 66; the results are consistent with the $[2\pi+2\pi]$ cycloaddition mechanism.
However, it has been discovered recently that certain substituted dibenzobarrelene compounds form novel COT products through their singlet excited states via an alternative mechanism. Scheffer, Trotter and co-workers\textsuperscript{106} reported that direct irradiation of 9,10-dimethyl dibenzobarrelene diester 204 in solution yields the di-\(\pi\)-methane product 205 and the dibenzocyclooctatetraene derivative 207 (Scheme 67). The structure of photoproduct 207 was confirmed by an X-ray crystallographic analysis. The most interesting feature of the COT product 207 is that its formation could not be rationalized by the concerted \([2\pi+2\pi]\) mechanism, as by this mechanism one would predict that the COT derivative 210 with mirror (\(C_s\)) symmetry would be formed (Scheme 67). These authors also found that in the solid state phototransformation of compound 204, an unusual pentalene-like photoproduct 206 predominated. Based on the structure of this product, a non-concerted mechanism was proposed, which involves formation of the biradical intermediate 208 by
two 1,2-aryl shifts to the two vinyl carbon atoms of 204 as shown in Scheme 67. From the biradical species 208, it was suggested that the COT product 207 having C$_2$ symmetry could be formed by fragmentation, and that double 1,2-ester migrations to the radical sites would give the dibenzopentalene derivative 206 with the observed stereochemistry.

Scheme 67  Photorearrangements of 9,10-Dimethyl Dibenzobarrelene Diester 204.
Following the above publication, George and co-workers\textsuperscript{107} re-examined the structures of the photoproducts from the photolysis of dibenzobarrelene derivative 211, an analogue of compound 204. In an earlier report by these authors,\textsuperscript{108} a COT product with $C_s$ symmetry (compound 215) was assigned based on Zimmerman's $[2\pi + 2\pi]$ mechanism (Scheme 68). In their reinvestigation by X-ray diffraction method, George et al. found that in fact the COT formed has the structure with $C_2$ symmetry (compound 213). In addition, compound 211 was also found to rearrange to a dibenzopentalene derivative 214 (Scheme 68). These additional results are in agreement with the Scheffer's mechanism involving 1,4-biradical intermediate 212.

![Scheme 68 Photorearrangement of Dibenzoyl Dibenzobarrelene 211.](image-url)
In a fashion similar to the previously proposed mechanism, we suggested the following mechanism for the formation of photoproducts 196 and 197 (from direct irradiation in solution and in the solid state) in Scheme 69. It involves the key reaction intermediate, biradical 216, which is formed most likely through a non-concerted 1,2-aryl shift to opposite faces of the vinyl carbon atoms (C12 and C11) as shown by the arrows. Homolysis of the C-Cl bond of 216 would form monoradical 217 having an exo-cyclic methylene group plus a chlorine atom. The monoradical species 217 could recombine with the chloride atom to produce stereoisomers 196 and 197. The formation of elimination products by $\beta$-scission of a carbon-chlorine bond of a 1,4-biradical can be found in the work of Wagner et al.\textsuperscript{109} on the Norrish Type II reaction of $\delta$-chlorovalerophenone and related compounds. An alternative possibility is the direct transfer of a chlorine atom from the chloromethyl group of one biradical 216 to the secondary radical site of another.

Scheme 69  Proposed Mechanism for the Formation of Product 196 and 197.
Regarding whether the formation of epimers 196 and 197 from biradical 216 is intra- or intermolecular in nature, it seems likely that the intramolecular transfer of a chlorine atom is not possible on steric grounds. Molecular models indicate that the biradical intermediate 216 is rigid and nearly planar, and that chlorine atom of the chloromethyl group cannot approach to within bonding distance of the radical site. But direct recombination of an initially formed radical pair within a solvent cage is considered to be possible in the solution phase. Such a process was suggested by Wagner et al.\textsuperscript{109} in their Norrish type II work.

In contrast, an intermolecular chlorine atom transfer seems more likely in the solid state, as the intramolecular recombination of the radical pair would not appear to be feasible in the crystalline medium. Examination of the X-ray crystal structure of compound 93d (\(\beta\)-form) reveals that there exists a moderately short intermolecular contact of 4.28 Å (sum of the van der Waals radii for C and Cl is 3.55 Å\textsuperscript{82}) between the chlorine atom of one molecule and the bridgehead carbon atom C(10) of a neighboring molecule.

A crystal packing diagram is shown in Figure 41. It can be noted that in the proposed mechanism (Scheme 69), it is C(10) that becomes the chlorine-bearing carbon atom of photoproducts 196 and 197. Such a process of intermolecular solid state chlorine atom transfer was first suggested by Decoret et al.\textsuperscript{110} to account for the crystalline phase phototransformation of 2,4,6,6-tetrachlorocyclohexadiene derivative 218 to its cross-conjugated 2,4,4,6-tetrachloro isomer 219 (Scheme 70). In this case, it was shown by X-ray crystallographic analysis that the
intermolecular C(6)-Cl···C(4) contact is 4.6 Å. The existence of 4.28 Å intermolecular C···Cl contact in crystalline 93d (β-modification) is perhaps one reason for the formation of higher yields of stereoisomers 196 and 197 in the crystalline medium compared to that in solution.

Figure 41 Crystal Packing Diagram of Compound 93d (β-form).

Scheme 70 Phototransformation of Tetrachlorocyclohexadienone 218.
B. Solid State Photochromism of 9-Chloromethyl Dibenzobarrelene 93d

Photochromism is defined\textsuperscript{111} as the phenomenon whereby a substance undergoes a color change upon absorption of light. By definition, the process should be reversible, either thermally or photochemically.

Many photochromic systems are known and several have been thoroughly studied in solution and in the solid state as well.\textsuperscript{3s,t,z,112} One of the earliest examples of solid state photochromism is that of the tetrachlorodihydropnaphthalen-1-one derivative (220) (Scheme 71). It is of particular interest in relation to the present work on the photochromism of compound 93d.

The photochromism of compound 220 in the solid state was first investigated by Marckwald in 1899.\textsuperscript{113} Colorless crystals of this compound become deep blue upon UV-irradiation, and when placed in the dark or upon heating they revert to colorless. This photochromism also occurs in solution and has been studied for many years. It was originally thought by Scheible and Feichtmayr\textsuperscript{114} to be the result of carbon-chlorine bond homolysis to give a chlorine atom and the conjugated allyl radical 221a. In support of this idea, crystals of 220 are found to give rise to an ESR signal when photolyzed.\textsuperscript{115} However, later experiments by Zweegers \textit{et al.}\textsuperscript{116} showed that the decay rates of the colored species (absorption band at ca. 530 nm) and the species responsible for the ESR signal are different. These authors proposed that the carbenium ion 221b is the species responsible for the photochromism.
Noteworthy of the photochromic behavior of crystals of 220 is that this compound is trimorphic (space groups Pnma, P2_1/c, and Pn2_1a) and that only the one of these crystal modifications (Pnma) is photochromic in the solid.

By studying the crystal structure of each of the crystal modifications, Zweeger and co-workers\textsuperscript{116} suggested that the reverse process (decolorization) by recombination of the ion pair (Cl\textsuperscript{-} and the carbenium ion) in the photochromic crystals is retarded by a short (2.97 Å) intermolecular C=O···Cl contact (Figure 42). This contact, which is less than the sum (3.32 Å) of the Van der Waals radii for Cl and O,\textsuperscript{82} is absent in the non-photochromic modifications of 220. Therefore, the colored species might be formed, but be too short-lived to be detected in these cases.
Figure 42 Intermolecular Contact in Crystal Structure of 220.

1. General Observations on the Photochromism of Compound 93d.

Compound 93d was first irradiated in solution and found to be non-photochromic. As mentioned previously, compound 93d is obtained in three different crystalline modifications. Single crystals or powdered samples of each of the polymorphs were irradiated by either a UV lamp (Pyrex filter, $\lambda \geq 290$ nm) or a nitrogen laser ($\lambda = 337$ nm) for periods ranging from 30 s to 5 min. It was found that two of the crystal modifications, the $\beta$-form and the $\gamma$-form, are photochromic displaying different colors; however, the $\alpha$-type crystals are not photochromic.

When the $\beta$-type crystals of 93d are irradiated, the colorless crystals turn to a dark blue-purple color. The intensity of the color is proportional to the time of the irradiation (within 5 min). The photolyzed crystals lose their coloration in a few hours if the crystal
stands in the dark at room temperature. Heating the crystals can remove the color much faster. Also, the color disappears immediately after the photolyzed crystals are dissolved in a suitable solvent. Experiments showed that this is a reversible process which can be repeated many times without damaging the crystals. No photoproduct were detected by GC or FTIR. However, when the irradiation is prolonged for 2 h, the crystalline samples become permanently yellow in color accompanied by photoreactions.

The solid state UV-VIS absorption spectrum for the colored species (β-form) in KBr is shown in Figure 43. It displays a weak absorption band at \( \lambda = 577 \, \text{nm} \) which is absent before irradiation and could not be seen when the blue-purple color fades after heating of the KBr pellet.

![UV-VIS Absorption Spectrum](image)

**Figure 43** UV-VIS Absorption Spectrum of the Blue-Purple Species Formed in the Photochromic β-Type Crystals of 93d.
The photochromic behavior of the γ-type crystal modification is slightly different from that of the β-type. Upon irradiation for a few minutes, the colorless crystals (γ-type) become red-violet in color. Also, it is observed that the resulting color fades much faster to completely colorless (within ca. 5 min), compared to that of the β-type crystals (several hours). Another interesting feature of the photochromism of the γ-crystals is that they are thermally unstable at high temperature. When heated to 130-140°, the transparent crystals (m.p. 168-170°) turn opaque. These opaque crystals have exactly the same photochromic behavior (become dark blue-purple upon irradiation) as those of the β-type crystal modification. The FTIR spectrum of the opaque crystals indicates that the γ-type crystals have been converted to the β-form. This phenomenon is thought to be the result of a phase transition in the crystalline state. However, differential scanning calorimetry (DSC) measurements did not show a phase transition in the temperature range 35°-200°C. This result is puzzling because a phase transition without heat exchange would seem unlikely. The possibility that loss of solvent molecules trapped in the crystals causes the changes in crystal texture has been eliminated, since the mass of the sample after the DSC measurement remains unchanged.

2. Speculation on the Nature of the Colored Species.

The question is, what is responsible for the photochromic behavior of compound 93d? First, it is clear that this photochromism is caused by the formation of a certain species photoinduced in the crystalline
state, as 93d is not photochromic in solution. Secondly, the possibility that an impurity present in the crystals might be responsible for the photochromism is unlikely. This is because, as mentioned above, the α-type crystals are non-photochromic, while the β- and γ-type crystals are, and these polymorphic modifications can be interconverted by suitable recrystallization conditions. In addition, the β-type crystals (photochromic) were used to prepare thin polymer films; irradiation of the films did not cause photochromism.

The important observation that the trimorphs (α-, β- and γ-forms) exhibit different photochromic behavior strongly suggests that crystal packing is a key factor in determining this photochromism. In an attempt to identify the blue-purple species formed in the photochromic crystals (β-type), we were successful in detecting an ESR signal which may belong to the colored species. ESR spectra† of the irradiated crystalline compound 93d (β-type crystals) are shown in Figure 44. The g-value determined (g = 1.9915) indicates that the radical species is organic in nature. It is also observed that the intensity of this ESR signal decays with time and eventually is absent when the blue-purple color disappears.

† ESR measurements were kindly provided by Dr. F. G. Herring in the UBC Chemistry Department.
The information obtained here seems to suggest that a radical species is responsible for the photochromic behavior of crystalline compound 93d (β-form), assuming that the radical species is the same intermediate as that observed in the UV absorption spectrum at 577 nm.

Other dibenzobarrelene compounds investigated in our laboratory were shown to exhibit similar photochromic behavior. In one instance, crystals of compound 222 (Figure 45) turn purple upon UV-irradiation and the color fades with time in the dark. ESR spectrum of the irradiated
crystal shows a signal at a g-value of 2.0043. Similar to 93d, compound 222 is not photochromic in solution.

![Structures of Other Photochromic Dibenzobarrelene Compounds](image)

**Figure 46** Structures of Other Photochromic Dibenzobarrelene Compounds.

Regarding the nature of the radical species involved in the photochromism, one possibility is that formation of the biradical intermediate species from the triplet di-π-methane rearrangement or from the unusual singlet rearrangement (Scheme 69) of compound 93d might be responsible for the photochromism. But, we speculate that these biradical species would not absorb in the visible region (ca. 570 nm) to exhibit the dark blue-purple color. Secondly, in analogy to the photochromism of compound 220 (Scheme 71), it can be speculated that homolytic or heterolytic cleavage of the C-Cl bond of compound 93d would result in a radical or a positive charge present at the methylene carbon atom. Whether or not, however, the radical or ion species would absorb at ca. 570 nm is yet unknown. The fact is that the dibenzobarrelene derivative 223\textsuperscript{119} (Figure 45), which does not contain a chlorine substituent, is also photochromic in the solid state; the resulting
color and the ESR spectra of the irradiated crystals are very similar to those of compound 222. It seems that a mechanism involving the presence of a chlorine atom in the photochromism may not be necessary. On the other hand, it is also possible that different phenomena are responsible for the photochromism of these compounds.

Thus, the results from all of the above observations are not conclusive. The profile seems to be that a certain radical species, which is associated with the crystal lattice, is involved in this kind of solid state photochromism; whether the photochromism occurs through a unimolecular or bimolecular process is yet unclear. Examination of the crystal packing arrangement of compound 93d (β-type, Figure 42) provides no specific intra- or intermolecular contacts which could be related to the observed photochromism. Further X-ray crystallographic analysis of the α- and γ-modifications of compound 93d is required (crystal structures of the α-modification and the γ-modification have not been solved owing to disorder of the crystals). By comparison of their crystal structures, it might be possible to understand the different photochromic behavior of the polymorphs of compound 93d.
EXPERIMENTAL
I. General

Melting Points (m.p.)

All melting points were measured on a Fisher-Johns hot stage melting point apparatus and are uncorrected.

Infrared Spectra (IR)

Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform infrared spectrophotometer in either of the two ways: 1) as thin films between two sodium chloride plates for liquid or oily samples, 2) as KBr pellets prepared by grinding potassium bromide together with a sample (1-3 mg of the sample in 100-150 mg of KBr) and pressing the powdered mixture in a Perkin-Elmer 186-0002 evacuated die with Carver Model B laboratory press at 20,000 pounds per square inch (psi). Absorption maxima ($\nu_{\text{max}}$) are reported in reciprocal centimeter ($\text{cm}^{-1}$).

Nuclear Magnetic Resonance Spectra (NMR)

Proton nuclear magnetic resonance ($^1\text{H NMR}$) spectra were recorded in deuterochloroform on Bruker AC-200 (200 MHz), Varian XL-300 (300 MHz) and Bruker WP-400 (400 MHz) spectrometers at ambient temperature unless specified otherwise. Signal positions are reported as chemical shift ($\delta$) in parts per million (ppm) with tetramethyl silane (TMS) as an internal reference. Multiplicity of the signals, number of protons, coupling constant (J) in Hz and assignment are given in parentheses following the
chemical shifts. The multiplicities of the signals are abbreviated as follows: \( s \) = singlet, \( d \) = doublet, \( dd \) = doublet of doublets, \( t \) = triplet, \( q \) = quartet and \( m \) = multiplet.

Carbon nuclear magnetic resonance spectra (\(^{13}\)C NMR) were recorded either at 75.4 MHz on a Varian XL-300 spectrometer and/or at 50.3 MHz on a Bruker AC-200 spectrometer in deuterochloroform which was also used as the internal reference at ambient temperature. Chemical shifts (\( \delta \)) are reported under broad band proton decoupling \(^{13}\)C-(\(^1\)H) in ppm and are followed by their assignments which were determined by the attached proton test (APT) experiment.

Mass Spectra (MS)

Low and high resolution mass spectra were determined on a Kratos MS-50 mass spectrometer. Gas chromatography-mass spectral analyses (GC-MS) were performed on a Kratos MS-80PRF spectrometer coupled with a Carlo-Erba gas chromatograph.

Ultraviolet Spectra (UV)

Ultraviolet spectra were recorded on a Perkin-Elmer Lambda-4B UV/Vis spectrophotometer. Wavelength (\( \lambda \)) in nanometer (nm) and extinction coefficient (\( \epsilon \)) of each absorption maxima are given. Spectral grade solvents available from BDH were used without any further purification. Solid state UV spectra were measured by using the KBr pellet, which was prepared in the same way as that described in the FTIR
measurement. A blank KBr pellet was used as reference, and the sample KBr pellet contained 20-50 mg of the substrate in 100-150 mg of KBr.

Elemental Analyses (EA)

All elemental analyses were performed by the departmental microanalyst, Mr. P. Borda.

Optical Rotations (α)

Optical rotations (α) were measured on a Perkin-Elmer 141 polarimeter operated at the sodium D line (589 nm) in most cases unless otherwise specified. The instrument was calibrated both to [α]D20 = 0° with analytically pure chloroform and to [α]D20 = -50° (c = 5) with (1R,2S,5R)-(−)-menthol in ethanol. The temperature at which the optical rotation was measured was also recorded. Specific rotation, [α]D, was calculated by the following equation:

\[
[α]_D^\alpha = \frac{α}{1 \times c} \times 100
\]

Where \( t \) = the temperature at which the optical rotation was measured.

D = the sodium D line at 589 nm.

α = the recorded optical rotation in degrees.

l = the path length in decimeters.

c = the concentration of the sample solution in milligrams per 10 mL.
Chromatography

Gas liquid chromatography (GLC or GC) analyses were performed on a Hewlett Packard 5890A gas chromatograph fitted with a flame ionization detector, and the instrument was equipped with a Hewlett Packard 3392A integrator. All the chromatographic analyses were carried out on one of the following fused silica capillary columns: 1) a 15m x 0.25mm DB-1 column from J&W Scientific Inc., 2) a 15m x 0.25mm DB-17 column from J&W Scientific Inc., 3) a 20m x 0.21mm Carbowax 20M column supplied by Hewlett Packard.

Flash and conventional (gravity) column chromatographies were carried out by using 230-400 mesh silica gel (E. Merck) or neutral alumina (ICN Pharmaceuticals, Inc.) and with suitable solvent or solvent combinations.

Thin layer chromatographic analyses were performed on pre-coated silica gel plates (type 5554 from E. Merck).

Crystallographic Analyses

All crystal structures were determined on a Rigaku 4-circle diffractometer by the following people: Dr. Phani Raj Pokkuluri, Ms. Christine Hwang, Dr. Steven J. Rettig and Dr. James Trotter of the UBC Chemistry Department.

Solvents and Reagents
Unless otherwise specified, all the solvents and reagents were used directly without further purification. When further purification was needed, known methods and procedures were followed in each case.

II. Synthesis of Substrates

A. Cyclohexenone Derivatives

1-p-Bromophenyl-1-phenylethylene oxide (82)

The preparation was the same as that described by Zimmerman et al. p-Bromobenzophenone (20 g, 77 mmoles) from Aldrich dissolved in 40 mL of dimethyl sulfoxide was added into the dimethyloxosulfonium methylide solution which was obtained by dropping 90 mL of DMSO into a mixture of sodium hydride (4.8 g, ca. 60% pure) and trimethyloxosulfonium iodide (18 g, 82 mmoles) under nitrogen. The solution was stirred at room temperature for 1 hr and then heated to 50-55°C for 2 hr. The hot reaction mixture was poured into ice water and quickly extracted with diethyl ether. The ether extracts were washed, dried and concentrated in vacuum, leaving 22 g of a light yellow oil. The infrared spectrum showed no p-bromobenzophenone, but did exhibit a strong band at 908 cm⁻¹, characteristic of epoxides.¹²² ¹H NMR and IR spectra were in agreement with those reported. This crude oil was used directly without further purification in the next step.

IR (neat) ν_max: 1594, 1487, 1448, 1397, 1073, 1010, 908, 824, 760 700 cm⁻¹.
\(^1\)H NMR (60 MHz, CCl\(_4\)) \(\delta\): 7.2 (m, 9H, aromatic H), 3.1 (AB q, 2H, \(J = 6\) Hz, \(\text{CH}_2\)) ppm.

2-\(p\)-Bromophenyl-2-phenylacetalddehyde (83)

The same procedure described by Zimmerman et al.\(^53\) was used. \(p\)-Toluenesulfonic acid (1.0 g) was refluxed in 170 mL of benzene for 2 hr under nitrogen, and water was removed with a Dean-Stark tube. Freshly prepared epoxide 82 (22 g) dissolved in 20 mL of benzene was rapidly added into the above solution. The mixture was refluxed for 2 hr. The cooled benzene solution was washed with dilute aqueous sodium bicarbonate and water, dried and concentrated in vacuum, leaving 20 g of a brown oil. IR and \(^1\)H NMR spectra of this crude oil were in agreement with those reported\(^53\) and showed mainly the aldehyde. This crude material was also used without further purification in the following step.

IR (neat) \(\nu_{\text{max}}\): 2725, 1728 (C=O), 1488, 1074, 1011, 822, 701 cm\(^{-1}\).

\(^1\)H NMR (60 MHz, CCl\(_4\)) \(\delta\): 9.7 (d, 1H, \(J = 2\) Hz, CHO), 7.2 (m, 9H, aromatic H), 4.8 (d, 1H, \(J = 2\) Hz, CH-CHO) ppm.

4-Phenyl-4-\(p\)-bromophenyl-2-cyclohexen-1-one (71a)

The preparation was quite similar to that described by Zimmerman et al.\(^42,53\) The crude aldehyde 83 (10 g, 37 mmoles) and methyl vinyl ketone (2.9 g, 41 mmoles) were dissolved in 45 mL of diethyl ether under nitrogen in an ice-cooling bath. A solution of potassium hydroxide (1.6 g) in 10 mL of 90% ethanol was dropped slowly into the ether solution during 1 hr. The mixture was stirred under nitrogen at 0°C for 2 hr,
then poured into ice water and neutralized with diluted hydrochloric acid. The aqueous layer was extracted with diethyl ether. The combined ether extracts were washed, dried and concentrated in vacuum, affording 13 g of a dark brown oil. This oil was chromatographed on silica gel by using 10-30% diethyl ether in petroleum ether (30-60°) as the eluting solvent. It provided 2.6 g (yield 21% from p-bromobenzophenone) of the solid sample 71a), which was recrystallized from diethyl ether and petroleum ether (30-60°) giving light yellow prisms. m.p., 123-124°C (lit., 124-125°C).

IR (KBr) $\nu_{\text{max}}$: 1670 (C=O), 1600 (C=C), 1489, 1008, 894, 816, 782, 768, 705 cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.50-7.10 (m, 10H, aromatic H and COCH=CH), 6.23 (d, 1H, J = 10 Hz, COCH=CH), 2.68 (m, 2H, COCH$_2$CH$_2$), 2.42 (m, 2H, COCH$_2$CH$_2$) ppm.

$^{13}$C NMR (50 MHz) $\delta$: 198.44 (C=O), 155.34, 144.73, 144.66, 131.70, 129.43, 129.27, 128.75, 127.56, 127.15, 120.99 (vinylic C and aromatic C), 49.01 (quaternary C), 35.80, 34.80 (2 x CH$_2$) ppm.

UV (C$_6$H$_6$) $\lambda_{\text{max}}$: 341 nm (n-\pi$^*$, $\epsilon$ = 43).

MS m/e (relative intensity): 328 (M+2, 9), 326 (M$, 9), 284 (48), 205 (100), 189 (37). Exact mass calculated for C$_{18}$H$_{15}$BrO: 326.0306. Found: 326.0307.

Anal. calcd. for C$_{18}$H$_{15}$BrO: C, 66.07; H, 4.62; Br, 24.42. Found: C, 66.08; H, 4.68; Br, 24.40.

The structure of this compound was also supported by an X-ray diffraction analysis. The crystal data were as follows: C$_{18}$H$_{15}$BrO, monoclinic, space group P2$_1$/c, $a$ = 16.1567 (15)Å, $b$ = 9.1886 (28) Å, $c$ =
9.9959 (30)Å, $\beta = 95.80$ (2)$^\circ$, $V = 1476.4$ (7)Å$^3$, $Z = 4$, $D_x = 1.472$ g/mL, $R = 0.048$. The details were published elsewhere.\textsuperscript{66}

4-Phenyl-4-p-cyanophenyl-2-cyclohexen-1-one (71b)

The same method described by Zimmerman et al.\textsuperscript{53} was used. A mixture of the cyclohexenone 71a (3.0 g, 9.2 mmoles) and cuprous cyanide (1.6 g, 18 mmoles) was refluxed in 10 mL of N-methylpyrrolidone for 2 hr. The reaction mixture was cooled and poured into 5% aqueous NaCN solution (60 mL). The resulting mixture was shaken thoroughly, 280 mL of benzene was added and the mixture was shaken again. The benzene layer was separated and washed with 10% aqueous sodium cyanide, water, dried and concentrated in vacuum leaving 2.6 g of a dark brown oil. Chromatography on silica gel by using 10-20% diethyl ether and petroleum ether (30-60°) as the eluting solvent resulted in 1.6 g (yield 64%) of compound 71b. Recrystallization from diethyl ether afforded white crystals. m.p., 79-80°C (lit.,\textsuperscript{53} 81-81.5°C). The spectroscopic data were in agreement with those reported.\textsuperscript{53}

IR (KBr) $\nu_{\text{max}}$: 2229 (CN), 1682 (C=O), 1606, 1493, 1447, 891, 834, 698 cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.72-7.25 (m, 10H, aromatic H and COCH=CH), 6.23 (d, 1H, J = 10 Hz, COCH=CH), 2.68 (m, 2H, COCH$_2$CH$_2$), 2.42 (m, 2H, COCH$_2$CH$_2$) ppm.

$^{13}$C NMR (50 MHz) $\delta$: 197.93 (C=O), 154.28, 151.25, 143.80, 132.41, 129.79, 128.96, 128.47, 127.55, 127.45, 118.47, 110.96 (CH=CH, CN and aromatic C), 49.52 (quaternary C), 35.63, 34.67 (CH$_2$CH$_2$) ppm.
MS m/e (relative intensity): 273 (M⁺, 6), 245 (11), 231 (100), 216 (16), 115 (26). Exact mass calculated for C₁₉H₁₅NO: 273.1155. Found: 273.1157.

Anal. calcd. for C₁₉H₁₅NO: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.49; H, 5.53; N, 5.00.

Preparation of 4,4-diphenyl-2-cyclohexen-1-one (36a)

The same procedures described by Zimmerman et al. were performed. A mixture of 25.0 g (0.127 moles) of diphenylacetaldehyde from Aldrich and 9.0 g (0.13 moles) of methyl vinyl ketone in 200 mL of diethyl ether was stirred under nitrogen in an ice-cooling bath. A solution of 3.0 g (0.054 moles) of potassium hydroxide in 15 mL of 95% ethanol was added slowly during 20 min. After stirring for an additional 40 min at 0°C, the mixture was poured into ice water and the solution was neutralized with dilute HCl. The aqueous layer was extracted with ether and the extracts were washed, dried and concentrated in vacuum. The oily residue was dissolved in hot ethanol and crystallization resulted on cooling. Recrystallization of the crude solids from ethanol afforded 14.0 g (yield 42%) of colorless prisms. m.p., 90-93°C (lit., 91-94°C).

IR (KBr) νmax: 1673 (C=O), 1597, 765, 706 cm⁻¹.

¹H NMR (400 MHz) δ: 7.4-7.2 (m, 11H, aromatic H and COCH=CH), 6.22 (d, 1H, J = 10 Hz, COCH=CH), 2.71 (t, 2H, J = 7 Hz, COCH₂CH₂), 2.42 (t, 2H, J = 7 Hz, COCH₂CH₂) ppm.
$^{13}$C NMR (50 MHz) δ: 198.86 (C=O), 156.21, 145.43, 129.00, 128.21, 127.67, 126.88 (CH=CH and aromatic C), 49.31 (quaternary C), 35.92, 34.96 (CH$_2$CH$_2$) ppm.

MS m/e (relative intensity): 248 (M$^+$, 22), 219 (18), 206 (100), 191 (28), 91 (37). Exact mass calculated for C$_{18}$H$_{16}$O: 248.1202. Found: 248.1202.

Anal. calcd. for C$_{18}$H$_{16}$O: C, 87.06; H, 6.50. Found: C, 87.12; H, 6.45.

Preparation of 4,4-diphenyl-6-methyl-2-cyclohexen-1-one (74a)

Diisopropylamine (1.1 g, 11 mmoles) was dissolved in 10 mL of anhydrous THF and the solution was cooled to -10°C. To the solution, n-BuLi in hexane (ca. 0.97 M, 12 mL) was added and the mixture was stirred at -10°C for 30 min. 4,4-Diphenyl-2-cyclohexen-1-one (2.0 g, 8.1 mmoles) in 10 mL of anhydrous THF was added at -78°C and the mixture was kept stirring for an additional 30 min. Next, methyl iodide (6.0 mL, 96 mmoles) passed through basic alumina was dropped into the above solution and the resulting mixture was stirred at 0°C for 5 hr and then 10 hr at room temperature. The slightly yellow solution was poured into an aqueous NH$_4$Cl solution (conc. ca. 0.5 M). The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined ether extracts were washed, dried and concentrated in vacuum giving 2.2 g of a yellow oil. Chromatography of this oil on silica gel by using 10% diethyl ether in petroleum ether (30-60°) as the eluting solvent afforded 1.2 g (yield 57%) of a colorless oil which was crystallized from methylcyclohexane as colorless crystals. m.p., 99.5-
100.5°C (lit., 101-103°C). The spectroscopic data were in agreement with those reported.

IR (KBr) $\nu_{\text{max}}$: 1677 (C=O), 1492, 1447, 1380, 756, 703 cm\(^{-1}\).

\(^1\)H NMR (400 MHz) $\delta$: 7.45-7.15 (m, 11H, aromatic H and COCH=CH), 6.20 (d, 1H, J = 10 Hz, COCH=CH), 2.70-2.40 (m, 3H, CH\(_2\) and CH), 1.14 (d, 3H, J = 6.5 Hz, CH\(_3\)) ppm.

\(^13\)C NMR (75 MHz) $\delta$: 201.24 (C=O), 155.05, 147.73, 143.44, 128.61, 128.53*, 127.93, 127.12, 126.88, 126.66 (vinyllic CH and aromatic C), 49.96 (quaternary C), 44.45 (CH\(_2\)), 38.29 (CHCH\(_3\)), 14.76 (CHCH\(_3\)) ppm.

* Possibly two carbons here.

MS m/e (relative intensity): 262 ($M^+$, 20), 234 (20), 206 (100), 191 (40), 91 (65). Exact mass calculated for C\(_{19}\)H\(_{18}\)O: 262.1358; Found: 262.1355.


4,4-Diphenyl-6-ethyl-2-cyclohexen-1-one (74b)

The exact procedures were followed as in the preparation of compound 74a except that the methyl iodide was replaced by ethyl iodide (passed through basic alumina prior to use). Starting with 2.0 g of the cyclohexenone (36a), a crude brown oil 74b (2.2 g) was obtained. Purification of this oil by column chromatography on silica gel by using 5% diethyl ether in petroleum ether (30-60°) as the eluting solvent gave 710 mg (95% pure) of a colorless oil 74b. The spectroscopic data are as follows.
IR (neat) $\nu_{\text{max}}$: 1680 (C=O), 1598 (C=C), 1494, 1447, 1382, 1189, 755, 701 cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.4-7.1 (m, 11H, COCH=CH and aromatic H), 6.20 (d, $J = 10$ Hz, COCH=CH), 2.8-1.4 (m, 5H, CH$_2$CH$_3$ and COCH(Et)CH$_2$), 0.92 (t, 3H, $J = 7$ Hz, CH$_2$CH$_3$) ppm.

GC-MS m/e (relative intensity): 276 (M$^+$, 5), 248 (10), 219 (22), 206 (100), 191 (23), 165 (15), 115 (24), 91 (41). Exact mass calculated for C$_{20}$H$_{20}$O: 276.1511. Found from high resolution GC-MS: 276.1530.

B. Dibenzobarrelene Derivatives.

Methyl 3,5-Dihydro-3-oxo-$1\H=5_{5b}[1',2']$-benzenonaphtho[1,2-c]furan-4-carboxylate (96)

A mixture of 9-anthracenemethanol (4.0 g, 19 mmoles, Aldrich) and dimethyl acetylenedicarboxylate (3.5 g, 25 mmoles, Aldrich) was heated at 150-160°C for 3 hr. The cooled solid was recrystallized from CHCl$_3$ /CH$_3$OH, affording 1.8 g (yield 30%) of slightly brown crystals. Colorless prisms were obtained by refluxing compound 96 in CHCl$_3$ and CH$_3$OH with charcoal and then recrystallization from the same solvent mixture after the removal of the charcoal, m.p., 170-171.5°C.

IR (KBr) $\nu_{\text{max}}$: 1767 (lactone C=O), 1709 (C=O), 1647, 1456, 1437, 1310, 1248, 1230, 1177, 1114, 1039, 755, 734, 713 cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.55-7.05 (m, 8H, aromatic H), 5.82 (s, 1H, CH), 5.55 (s, 2H, CH$_2$), 3.89 (s, 3H, CH$_3$) ppm.
$^{13}$C NMR (75 MHz) $\delta$: 163.45, 163.38 (2 x C=O), 120.65, 124.69, 125.52, 126.09, 142.64, 142.98, 144.53, 147.53 (vinyllic C and aromatic C), 64.64 (CH$_2$), 58.67 (bridgehead C), 54.44 (CH$_3$), 52.69 (bridgehead CH) ppm.

MS m/e (relative intensity): 318 (M$^+$, 8), 290 (29), 262 (24), 230 (39), 215 (37), 202 (100), 101 (27). Exact mass calculated for C$_{20}$H$_{14}$O$_4$: 318.0892; Found: 318.0890.

Anal. calcd. for C$_{20}$H$_{14}$O$_4$: C, 75.46; H, 4.43. Found: 75.28; H, 4.50.

UV (MeOH) $\lambda_{\text{max}}$: 212 ($\epsilon$, 29200), 228 sh. ($\epsilon$, 2500) nm.

The structure of this compound was supported by the X-ray diffraction analysis. The crystal data were as follows: C$_{20}$H$_{14}$O$_4$, orthorhombic, space group P2$_1$2$_1$2$_1$, a = 10.3491 (8), b = 16.6204 (9), c = 8.9933 (6)Å, V = 1546.9 (2)Å$^3$, Z = 4, D$_x$ = 1.37 g/mL, R = 0.038. The details will be published elsewhere.

Preparation of $\alpha$-Methyl-9-anthracenemethanol (91)

9-Anthraldehyde (90) (1.5 g, 7.3 mmoles, Aldrich) in 20 mL of anhydrous benzene was dropped into the Grignard solution prepared from 0.30 g (12 mmoles) of magnesium and 1.40 g (9.9 mmoles) of methyl iodide in 20 mL of anhydrous diethyl ether. The mixture was refluxed for 30 min and then poured into 100 mL of ice water containing 2 mL of concentrated HCl. The organic layer was separated and the aqueous layer was extracted with ether (2 x 50 mL). The combined ether extracts were washed and dried. Removal of the solvents in vacuum left 1.6 g of a yellow solid
which was recrystallized from ether/hexane affording 1.1 g (yield 68\%) of yellow needle crystals. m.p., 124-126°C (lit., \textsuperscript{60} 125-126.5°C).

IR (KBr) \( \nu_{\text{max}} \): 3301 (OH), 1686, 1367, 1114, 1067, 1046, 890, 730 cm\(^{-1}\).

\(^1\)H NMR (400 MHz) \( \delta \): 8.75-7.40 (m, 9H, aromatic H), 6.48 (q, 1H, J = 7 Hz, CH), 2.23 (s, 1H, D\(_2\)O exchangeable, OH), 1.92 (d, 3H, J = 7 Hz, CH\(_3\)) ppm.

MS m/e (relative intensity): 222 (M\(^+\), 26), 207 (24), 179 (100). Exact mass calculated for C\(_{16}\)H\(_{14}\)O: 222.1045. Found: 222.1043.

Anal. calcd. for C\(_{16}\)H\(_{14}\)O: C, 86.45; H, 6.35. Found: C, 86.56; H, 6.29.

Preparation of Methyl 1-Methyl-3,5-dihydro-3-oxo-1H-5,9b[1',2']-benzenonaphtho[1,2-c]furan-4-carboxylate (97)

A mixture of 500 mg (2.3 mmoles) of \( \alpha \)-methyl-9-anthracenemethanol (91) prepared above and 500 mg (3.5 mmoles) of dimethyl acetylenedicarboxylate was heated at 140-150°C for 6 hr. The crude solid was chromatographed on silica gel by using 30% ethyl acetate in petroleum ether (30-60°) as the eluting solvent. This afforded 680 mg (yield 91\%) of a white solid, which was recrystallized from methanol and methylene chloride to give colorless prisms, m.p., 191-192°C.

IR (KBr) \( \nu_{\text{max}} \): 1767 (lactone C=O), 1736 (C=O), 1680 (C=C), 1456, 1433, 1285, 1230, 1145, 1078, 1011, 910, 763, 741, 719 cm\(^{-1}\).
$^1$H NMR (300 MHz) $\delta$: 7.82-7.00 (m, 8H, aromatic H), 5.96 (q, 1H, $J$ = 7 Hz, CH), 5.79 (s, 1H, bridgehead CH), 3.89 (s, 3H, COOCH$_3$), 2.30 (d, 3H, $J$ = 7 Hz, CHCH$_3$) ppm.

$^{13}$C NMR (75 MHz) $\delta$: 163.71, 163.09 (2 x C=O), 147.95, 145.74, 144.54, 144.06, 142.59, 126.00, 125.72, 125.49, 125.22, 124.78, 124.47, 123.24, 121.32 (vinylic C and aromatic C), 77.2 (CO$_2$CH$_3$), 61.01 (quaternary C), 554.73, 52.74 (2 x CH), 19.20 (CHCH$_3$) ppm.

MS m/e (relative intensity): 332 (M$^+$, 8), 304 (16), 272 (39), 262 (47), 244 (31), 229 (46), 202 (100), 189 (12), 100 (22). Exact mass calculated for C$_{21}$H$_{16}$O$_4$: 332.1049. Found: 332.1044.

Anal. calcd. for C$_{21}$H$_{16}$O$_4$: C, 75.89; H, 4.85. Found: C, 75.95; H, 4.85.

Preparation of 9-Anthrylmethyl Propynoate (89c)

Procedure (a) 9-Anthracenemethanol (2.0 g, 9.6 mmoles) and propiolic acid (1.0 g, 14 mmoles) in 50 mL of benzene were refluxed for 8 hr. The reaction mixture was cooled to room temperature and an additional 100 mL of benzene were added. The benzene layer was washed with dilute aqueous sodium bicarbonate, water and dried. Removal of the solvent left 2.5 g of a yellow solid. The crude solid was purified by chromatography on silica gel by using 10% ethyl acetate in petroleum ether (30-60°C) as the eluting solvent to afford 2.2 g (yield 88%) of a yellow solid. Recrystallization from acetone/cyclohexane gave yellow needle crystals, m.p., 98-100°C (lit.$^{123}$, 94-95°C).

IR (KBr) $\nu_{max}$: 3277 (C=CH$_2$), 2119 (C=O), 1718 (C=0), 1254, 927, 879, 749, 731 cm$^{-1}$.
\(^1\text{H NMR (300 MHz)} \delta: 8.58-7.45 (m, 9H, aromatic H), 6.28 (s, 2H, CH\(_2\)), 2.85 (s, 1H, CH) ppm.

\text{MS m/e (relative intensity):} 260 (M\(^+\), 27), 215(10), 191 (100), 178 (17), 165 (10). \text{Exact mass calculated for C}_{18}\text{H}_{12}O_2: 260.0838. \text{Found: 260.0837.}

\text{Procedure (b) A mixture of 9-chloromethylandanthracene} (908 mg, 4 mmoles), \text{propionic acid} (400 mg, 6 mmoles) and \text{triethylamine} (1.0 mL) in 10 mL of acetonitrile was refluxed for 4 hr. The solvent was removed by evaporation in vacuum, and the resulting mixture was chromatographed on silica gel by using 10-15\% ethyl acetate in petroleum ether (30-60°) as the eluting solvent to give 550 mg (yield 50 \%) of compound 89c.

\text{Preparation of 3,5-Dihydro-1H-5,9b[1',2']-benzenonaphtho[1,2-c]furan-3-one (98)}

9-Anthrylmethyl propynoate (89c) (800 mg) was heated at 130-140°C for 4 hr. The resulting crude solid was purified by chromatography on silica gel by using 15\% ethyl acetate in petroleum ether (30-60°C) as the eluting solvent to afford 470 mg (yield 59\%) of a yellow solid which was recrystallized from acetone/hexane to give colorless prisms, m.p., 247-248°C.

\text{IR (KBr) \nu_{max}: 1747 (C=O), 1654 (C=C), 1456, 1259, 1192, 1132, 1039, 1023, 1012, 764, 750, 720 cm}^{-1}.

\(^1\text{H NMR (300 MHz)} \delta: 7.82 (d, 1H, J = 7 Hz, vinylic CH), 7.45-6.95 (m, 8H, aromatic H), 5.53 (s, 2H, CH\(_2\)), 5.42 (d, 1H, J = 7 Hz, CH) ppm.
\[ ^{13} \text{C NMR (50 MHz)} \delta: 166.73 (C=O), 145.48 \text{ (vinylic CH), 144.13, 143.83, 142.86, 125.24, 120.39 (vinylic C and aromatic C), 65.51 (CH}_2, 57.41 \text{ (quaternary C), 53.20 (CH) ppm.} \]

\[ \text{MS m/e (relative intensity): 260 (M}^+, 43), 232 (26), 215 (100), 203 (56), 107 (6). \text{Exact mass calculated for C}_{18}\text{H}_{12}O_2: 260.0838. \text{Found: 260.0835.} \]

\[ \text{Anal. calcd. for C}_{18}\text{H}_{12}O_2: C, 83.06; H, 4.65. \text{Found: C, 82.80; H, 4.67.} \]

Preparation of 9-Anthrylmethyl Acetate (87)

9-Anthracenemethanol (1.0 g, 4.8 mmoles) and acetyl chloride (0.50 g, 6.4 mmoles) in 10 mL of anhydrous benzene containing a small amount of triethylamine were refluxed for 2.5 hr. Upon cooling, an additional 40 mL of benzene was added and the organic layer was washed with dilute aqueous sodium bicarbonate, water and dried. Concentration in vacuum afforded 1.0 g of a yellow solid. Recrystallization of the crude solid from ethanol gave 0.80 g (yield 67%) of yellow needle crystals. m.p., 110-111°C (lit.124, 111-112°C).

IR (KBr) \( \nu_{\text{max}} \): 1728 (C=O), 1246, 889, 734 cm\(^{-1}\).

\[ ^1\text{H NMR (400 MHz)} \delta: 8.55-7.48 \text{ (m, 9H, aromatic H), 6.18 (s, 2H, CH}_2, 2.10 \text{ (s, 3H, CH}_3 \text{) ppm.} \]

\[ \text{MS m/e (relative intensity): 250 (M}^+, 75), 191 (100), 179 (57), 165 (24), 151 (14). \text{Exact mass calculated for C}_{17}\text{H}_{14}O_2: 250.0994. \text{Found: 250.0992.} \]

\[ \text{Anal. calcd. for C}_{17}\text{H}_{14}O_2: C, 81.58; H, 5.64. \text{Found: C, 81.45; H, 5.80.} \]
Preparation of Dimethyl 9,10-Dihydro-9-acetoxymethyl-9,10-ethenoanthracene-11,12-dicarboxylate (93c)

A mixture of 500 mg (2.0 mmoles) of 9-anthrylmethyl acetate (87) and 300 mg (2.2 mmoles) of dimethyl acetylenedicarboxylate was heated at 150-160°C for 3 hr. The resulting solid was recrystallized from chloroform/ethanol to give 440 mg (yield 56%) of the title compound 93c as yellow crystals. Further purification by column chromatography and recrystallization from acetone/hexane afforded colorless prisms with m.p. 161.5-162.5°C.

IR (KBr) \( \nu_{\text{max}} \): 1737 (C=O), 1713 (C=O), 1628 (C=C), 1460, 1436, 1294, 1240, 1129, 1094, 1068, 749, 616 cm\(^{-1}\).

\(^1\)H NMR (400 MHz) \( \delta \): 7.47-7.01 (m, 8H, aromatic H), 5.63 (s, 1H, CH), 5.45 (s, 2H, CH\(_2\)), 4.77 (s, 3H, OCH\(_3\)), 4.76 (s, 3H, OCH\(_3\)), 2.14 (s, 3H, COCH\(_3\)) ppm.

\(^{13}\)C NMR (75 MHz) \( \delta \): 170.55, 166.84, 163.82 (3 x C=O), 150.87, 145.31, 143.69, 142.71, 125.52, 125.22, 123.83, 121.65 (vinylic C and aromatic C), 60.82 (CH\(_2\)), 54.73 (bridgehead C), 52.42, 52.19, 50.57 (bridgehead CH and 2 x OCH\(_3\)), 20.57 (COCH\(_3\)) ppm.

MS m/e (relative intensity): 392 (M\(^+\), 39), 350 (18), 332(17), 318 (21), 290 (100), 273 (24), 260 (62), 202 (47). Exact mass calculated for C\(_{23}\)H\(_{20}\)O\(_6\): 392.1260. Found: 392.1258.

UV (MeOH) \( \lambda_{\text{max}} \): 213 (\( \epsilon \), 54,000) nm.

Dimethyl 9,10-dihydro-9-formyl-9,10-ethenoanthracene-11,12-dicarboxylate (94)

A mixture of 9-anthraldehyde (5.0 g, 24 mmoles, Aldrich) and dimethyl acetylenedicarboxylate (5.5 g, 39 mmoles) was heated at 170-190°C for 2 hr. The crude product was dissolved in 10 mL of ethyl acetate under refluxing. Crystallization occurred upon cooling and standing overnight; yellow crystals (5.5 g) were collected by filtration and washing with cold benzene. Recrystallization from benzene gave 4.5 g of yellow crystals (yield 53%). Colorless prisms were obtained by chromatography on silica gel by using 20% ethyl acetate in petroleum ether (30-60°) as the eluting solvent and then recrystallization from benzene, m.p., 171-173°C.

\[ \text{IR (KBr) } \nu_{\text{max}}: 2760 \text{ (CHO)}, 1727 \text{ (C=O)}, 1631 \text{ (C=C)}, 1280, 1219, 760, 618 \text{ cm}^{-1}. \]

\[ ^1H \text{ NMR (400 MHz) } \delta: 10.83 \text{ (s, 1H, CHO)}, 7.55-7.05 \text{ (m, 8H, aromatic H)}, 5.64 \text{ (s, 1H, CH)}, 3.85 \text{ (s, 3H, OCH}_3) , 3.78 \text{ (s, 3H, OCH}_3) \text{ ppm.} \]

\[ ^{13}C \text{ NMR (50 MHz) } \delta: 197.39 \text{ (CHO)}, 166.46, 163.81 \text{ (2 x C=O)}, 148.72, 144.51, 144.27, 141.68, 128.34, 126.16, 125.42, 125.09, 124.47, 122.27 \text{ (vinylic C and aromatic C)}, 64.18 \text{ (bridgehead C)}, 52.59^*, 50.97 \text{ (2 x CO}_2\text{CH}_3 \text{ and bridgehead CH) ppm.} \]

* Possibly two carbons here.

\[ \text{MS m/e (relative intensity): 348 (M}^+\text{, 21), 316 (23), 290 (19), 260 (100), 229 (37), 202 (84). Exact mass calculated for C}_{21}H_{16}O_5: 348.0998; \]

\[ \text{Found: 348.1000.} \]

\[ \text{Anal. calcd. for C}_{21}H_{16}O_5: C, 72.40; H, 4.63. Found: C, 72.48; H, 4.80.} \]
The structure of this compound was also confirmed by an X-ray diffraction analysis. The crystal data were as follows: C_{21}H_{16}O_{5}, triclinic, space group PÌ, a = 10.176 (1), b = 12.075 (2), c = 8.077 (1)Å, α = 108.88 (1), β = 112.79 (1), γ = 83.86 (1)°, V = 865.6 (2) Å³, Z = 2, D_x = 1.34 g/mL, R = 0.040. The details will be published elsewhere.

**Dimethyl 9,10-dihydro-9-hydroxymethyl-9,10-enthenoanthracene-11,12-dicarboxylate (95)**

Powdered sample of dimethyl-9,10-dihydro-formyl-9,10-ethenoanthracene-11,12-dicarboxylate (94) (2.0 g, 5.7 mmoles) was suspended in 20 mL of methanol at 0°C and 130 mg (3.4 mmoles) of sodium borohydride added portion by portion with stirring until a clear solution was obtained. The mixture was stirred at 0°C for an additional 30 min, then poured into 100 mL of cold aqueous HCl solution (concentration 0.1 M). The white precipitate was filtrated, washed and dried in air, giving 2.0 g of crude 95. The solid was recrystallized from methanol affording 0.40 g of colorless prisms (yield 20%), m.p., 174-176°C.

**IR (KBr) ν_max:** 3499 (OH), 1712 (C=O), 1630 (C=C), 1476, 1459, 1438, 1296, 764, 616 cm⁻¹.

**¹H NMR (400 MHz) δ:** 7.50-7.00 (m, 8H, aromatic H), 5.58 (s, 1H, CH), 5.05 (d, 2H, J = 6 Hz, CH₂), 3.79 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 2.64 (t, 1H, J = 6 Hz, D₂O exchangeable, OH) ppm.

**¹³C NMR (50 MHz) δ:** 168.36, 164.34 (2 x C=O), 151.25, 145.74, 144.94, 143.58, 125.38, 125.27, 123.80, 122.30 (vinyllic C and aromatic
C), 59.79 (CH$_2$OH), 57.38 (bridgehead C), 52.59, 52.45, 50.96 (2 x CO$_2$CH$_3$ and bridgehead CH) ppm.

MS m/e (relative intensity): 350 (M$^+$, 3), 318 (36), 290 (60), 262 (43), 230 (54), 215 (52), 202 (100). Exact mass calculated for C$_{21}$H$_{18}$O$_5$: 350.1154. Found: 350.1147.

Anal. calcd. for C$_{21}$H$_{18}$O$_5$: C, 71.99; H, 5.17. Found: C, 71.82; H, 5.23.

Dimethyl 9,10-Dihydro-9-chloromethyl-9,10-ethenoanthracene-11,12-dicarboxylate (93d)

9-Chloromethylanthracene (2.27 g, 10 mmoles), available from Aldrich, and dimethyl acetylenedicarboxylate (1.60 g, 11 mmoles) were mixed and heated at 100-110°C for 3 hours. Column chromatography of the resulting reaction mixture on silica gel using 25% ethyl acetate in petroleum ether (30-60°C) as the eluting solvent gave 2.0 g (yield 54%) of yellow crystals. Colorless prisms were obtained by recrystalling twice from chloroform/methanol, m.p., 168-170°C (β-form crystal).

IR (KBr) $\nu_{\text{max}}$: 1729 (C=O), 1629 (C-C), 1433, 1313, 1284, 1269, 1237, 1214, 1122, 1062, 775, 759, 750, 706, 633 cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.6-7.0 (m, 8H, aromatic H), 5.59 (s, 1H, bridgehead H), 4.95 (broad s, 2H, CH$_2$Cl), 3.78 (s, 3H, CO$_2$CH$_3$), 3.80 (s, 3H, CO$_2$CH$_3$) ppm.

$^{13}$C NMR (50 MHz) $\delta$: 166.97, 164.01 (2 x C=O), 145.65*, 144.24, 143.01, 125.61, 125.18, 123.88, 122.11 (vinyllic C and aromatic C), 56.72 (bridgehead C), 52.49*, 50.85 (2 x CO$_2$CH$_3$ and bridgehead CH), 41.53 (CH$_2$Cl) ppm.
* possibly two carbons here.

MS m/e (relative intensity): 370 (M+2, 15), 368 (M+, 46), 308 (100), 215 (84), 191 (50). Exact mass calculated for C_{21}H_{17}ClO_{4}: 368.0816. Found: 368.0818.

Anal. calcd. for C_{21}H_{17}ClO_{4}: C, 68.39; H, 4.65; Cl, 9.61. Found: C, 68.37; H, 4.79; Cl, 9.44.

The structure of this compound was supported by an X-ray diffraction analysis. The crystal data were as follows: C_{21}H_{17}ClO_{4}, monoclinic, space group P2_1/c, a = 10.0865 (6), b = 16.207 (1), c = 11.2329 (9)Å, β = 107.636 (6)*, V = 1749.9 (2)Å^3, Z = 4, D_x = 1.400 g/mL, R = 0.042. The details were published elsewhere.\textsuperscript{118}

This crystalline material can also be obtained in other form of crystal modifications (polymorphs) by recrystallization from an appropriate solvent.

Needle crystals were obtained from diethyl ether/petroleum ether (30-60°), m.p., 174-176°C (α-form crystal). Space group P2_12_12_1.

IR (KBr) ν_{max}: 1718 (C=O), 1628 (C=C), 1457, 1434, 1312, 1271, 1211, 1119, 1056, 752, 631 cm\textsuperscript{-1}.

Rectangle crystals (γ-form) were obtained from acetone/hexane, m.p., 168-170°C (at 140°C, the clear crystals turn opaque). Monoclinic, Space group P2_1/c, a = 20.550, b = 10.513, c = 17.813 Å, β = 108.11°, D_x = 1.339 g/mL, R = 0.054.

IR (KBr) ν_{max}: 1718 (C=O), 1624 (C=C), 1459, 1265, 1236, 1213, 1078, 1059, 770, 755, 627 cm\textsuperscript{-1}.

Preparation of N-Acetylalanine 9-Anthrylmethyl Ester (89b)
(a) Racemic 89b

The reported procedures for preparation of other similar compounds were used here. A solution of (±)-N-acetylalanine (392 mg, 3 mmoles, Sigma), 9-chloromethyl anthracene (681 mg, 3 mmoles) and triethyl amine (0.42 mL) in 7 mL of acetonitrile was refluxed for 5 hr. Most of the solvent was removed and the resulting mixture was chromatographed on silica gel by using 50-100% ethyl acetate in petroleum ether (30-60°) as the eluting solvent; 890 mg (yield 92%) of yellow solid was collected after the chromatography. Recrystallization of the solid from acetone afforded yellow crystals, m.p., 170-172°C.

IR (KBr) $\nu_{max}$: 1729 (C=O), 1646, 1548, 1372, 1212, 1158, 886, 730 cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 8.55-7.45 (m, 9H, aromatic H), 6.27, 6.19 (two d, 2H, $J = 12$ Hz, CH$_2$OCO), 6.02 (d, 1H, $J = 7.5$ Hz, NHCOCH$_3$), 4.60 (quintet, 1H, OCOCH(CH$_3$)NH), 1.98 (s, 3H, NHCOCH$_3$), 1.31 (d, 3H, $J = 7.5$ Hz, CHCH$_3$) ppm.

$^{13}$C NMR (75 MHz) $\delta$: 173.28, 169.59 (2 x C=O), 131.23, 130.93, 129.39, 129.08, 126.71, 125.60, 125.08, 123.65 (aromatic C), 59.91 (CH$_2$OCO), 48.23 (COCH(CH$_3$)NH), 23.00, 18.34 (2 x CH$_3$) ppm.

MS m/e (relative intensity): 321 ($M^+$, 17), 191 (100). Exact mass calculated for C$_{20}$H$_{19}$NO$_3$: 321.1365. Found: 321.1365.

Anal. calcd. for C$_{20}$H$_{19}$NO$_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.77; H, 6.10; N, 4.20.

This racemic compound was analyzed by the chiral shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-(+)camphoratol] europium (III) derivative abbreviated as Eu(hfc)$_3$. 
(b) Optically Active 93b

A solution of (S)-(−)-N-acetylalanine (393 mg, 3 mmoles) from Sigma (99% pure), 9-chloromethylantracene (681 mg, 3 mmoles) and triethylamine (0.5 mL) in 7 mL of acetonitrile was refluxed for 6 hr. Upon dilution with 0.02% aqueous sodium bicarbonate (100 mL), the product was collected, washed and dried at room temperature; 880 mg (yield 91%) of the crude product was obtained, which was used in the next step without further purification. Pure (S)-(−)-N-acetylalanine 9-anthrylmethyl ester was obtained by recrystallization from ethanol as yellow crystals, m.p., 180-181°C.

IR (KBr) \( \nu_{\text{max}} \): 3294 (NH), 1732 (C=O), 1646, 1546, 1158, 731 cm\(^{-1}\).

\(^1\)H NMR (300 MHz) \( \delta \): 8.60-7.40 (m, 9H, aromatic H), 6.26, 6.18 (two d, 2H, \( J = 12 \) Hz, \( \text{CH}_2\text{CO} \)), 6.00 (d, 1H, \( J = 7.5 \) Hz, \( \text{NHCOCH}_3 \)), 4.61 (quintet, 1H, \( J = 7.5 \) Hz, \( \text{OCHOCH(CH}_3\text{)NH} \)), 1.99 (s, 3H, \( \text{NHCOCH}_3 \)), 1.31 (d, 3H, \( J = 7.5 \) Hz, \( \text{CHCH}_3 \)) ppm.

MS m/e (relative intensity): 321 (M\(^+\), 6), 208 (15), 191 (61) 179 (26), 44 (100). Exact mass calculated for C\(_{20}\)H\(_{19}\)NO\(_3\): 321.1365. Found: 321.1364.

Anal. calcd. C\(_{20}\)H\(_{19}\)NO\(_3\): C, 74.74; H, 5.96; N, 4.36. Found: C, 74.73; H, 6.02; N, 4.34.

\([\alpha]_D^{20} = -1.0^\circ \pm 0.1 \) (c = 3.0, CHCl\(_3\)). This compound was analyzed by the chiral shift reagent, Eu(hfc)\(_3\) and shown to be optically pure (e.e. > 99%).

Preparation of Dimethyl 9-(\( \alpha\)-N-Acetylamino-\( \alpha\)-methyl)acetoxymethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (93b)
(a) Racemic 93b

(±)-N-acetylalanine 9-anthrylmethyl ester (89b) (642 mg, 2.0 mmoles) and dimethyl acetylenedicarboxylate (284 mg, 2.0 mmoles) were heated at 130°C for 2 hr; 797 mg (yield 86%) of yellow solid was isolated upon purification by column chromatography. A white crystalline solid was obtained by recrystallization from acetone/hexane, m.p., 110-112°C.

IR (KBr) \( \nu_{\text{max}} \): 3257 (NH), 1752 (C=O), 1717 (C=C-C=O), 1638 (C=C), 1543, 1459, 1274, 1221, 1162, 762, 631 cm\(^{-1}\).

\( ^1H \) NMR (300 MHz) \( \delta \): 7.5-7.0 (m, 8H, aromatic H), 6.14 (d, 1H, \( J = 8 \) Hz, NH), 5.65 (s, 1H, bridgehead H), 5.58, 5.42 (two d, 2H, \( J = 12 \) Hz, \( \text{CH}_2\text{OCO} \)), 4.70 (quintet, 1H, \( J = 8 \) Hz, \( \text{CH(NH)}\text{CH}_3 \)), 2.80, 3.79 (two s, 6H, 2 x \( \text{CO}_2\text{CH}_3 \)), 1.98 (s, 3H, \( \text{NCOCH}_3 \)), 1.45 (d, 3H, \( J = 8 \) Hz, \( \text{OCOCH(CH}_3\text{)NH} \)) ppm.

MS m/e (relative intensity): 463 (M\(^+\), 10), 350 (5), 318 (18), 290 (38), 114 (57), 44 (100). Exact mass calculated for \( \text{C}_{26}\text{H}_{25}\text{N}_7 \): 463.1631. Found: 463.1626.

(b) Optically Active 93b

(S)-(−)-N-Acetylalanine 9-anthrylmethyl ester (89b) (1.8 g, 5.6 mmoles) and dimethyl acetylenedicarboxylate (0.80 g, 5.6 mmoles) were mixed together and heated at 120-130°C for 30 min. The cooled mixture was chromatographed on silica gel by using 40-60% acetone in petroleum ether (30-60°) as the eluting solvent. This afforded an oil which was crystallized from benzene. Yellow crystals (1.8 g, yield 69%), (S)-(+)
were obtained. Further recrystallization from acetone/hexane gave colorless crystals, m.p., 178-180°C.

IR (KBr) $\nu_{\text{max}}$: 3408 (NH), 1736 (C=O), 1713 (C=O), 1672 (NH=O), 1623 (C=C), 1527, 1436, 1252, 1217, 1134, 1069, 1051, 1003, 762 cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.45-7.00 (m, 8H, aromatic H), 6.07 (d, 1H, $J = 8$ Hz, NH), 5.64 (s, 1H, CH), 5.57, 5.43 (two d, 2H, $J = 12$ Hz, CH$_2$OCO), 4.70 (quintet, 1H, $J = 8$ Hz, COCH), 3.890 (s, 3H, OCH$_3$), 3.885 (s, 3H, OCH$_3$), 1.96 (s, 3H, COCH$_3$), 1.44 (d, 3H, $J = 8$ Hz, CH$_3$) ppm.

$^{13}$C NMR (50 MHz) $\delta$: 172.38, 169.91, 167.16, 163.80 (4 x C=O), 150.95, 145.33*, 144.12, 142.56, 142.51, 125.74, 125.70, 125.37, 125.32, 124.03, 123.98, 121.76, 121.49 (aromatic and vinylic C), 61.80 (CH$_2$OCO), 54.88 (bridgehead C), 52.59, 52.34, 50.67, 48.33 (2 x CO$_2$CH$_3$, bridgehead CH and NHCOCH$_3$), 22.98, 18.11 (COCH(NH)CH$_3$) ppm.

* possibly two carbons here.

MS m/e (relative intensity): 463 (M$^+$, 20), 350 (7), 318 (24), 290 (57), 262 (16), 230 (21), 215 (38), 202 (39), 114 (57), 86 (52), 44 (100). Exact mass calculated for C$_{26}$H$_{25}$NO$_7$: 463.1631. Found: 463.1629.

Anal. calcd. for C$_{26}$H$_{25}$NO$_7$: C, 67.38; H, 5.44; N, 3.02. Found: C, 67.67; H, 5.53; N, 3.04.

$[\alpha]_D^{20} = +0.4^\circ \pm 0.1$ (c = 3.0, CHCl$_3$). Also $[\alpha]^{20}_{365\text{nm}} = -33.3^\circ \pm 0.1$ (c = 3.0, CHCl$_3$). This compound was again analyzed by the chiral shift reagent, Eu(hfc)$_3$, and shown to be optically pure (e.e. > 99%).

The structure of this compound was also confirmed by an X-ray diffraction analysis. The crystal data were as follows: C$_{26}$H$_{25}$NO$_7$, orthorhombic, space group P2$_1$2$_1$2$_1$, a = 18.914 (4), b = 14.345 (1), c =
8.622 (1)Å, V = 2339.5 (5)Å³, Z = 4, Dₓ = 1.32 g/mL, R = 0.038. The
details will be published elsewhere.

9-Anthrylmethyl α-Methoxy Benzeneacetate (89a)

(a) (±)-89a

A solution of 680 mg (3.0 mmoles) of 9-chloromethylanthracene, 498
mg (3.0 mmoles) of (±)-α-methoxy benzeneacetic acid (Aldrich) and 0.5 mL
of triethylamine in 5 mL of acetonitrile was refluxed for 5 hours. The
solution was diluted with 50 mL of 0.04% aqueous sodium bicarbonate. The
resulting yellow solid was collected, washed with water and dried in
air, affording 1.0 g (yield 94%). Recrystallization from ethanol gave
orange flakes, m.p., 122-124°C.

IR (KBr) νmax: 1734 (C=O), 1455, 1275, 1198, 1176, 1157, 1121,
1059, 998, 926, 914, 880, 728, 695, 629 cm⁻¹.

1H NMR (300 MHz) δ: 8.6-7.2 (m, 14H, aromatic H), 6.30, 6.00 (two
d, 2H, J = 12 Hz, CH₂OCON), 4.76 (s, 1H, COCH(OCH₃)Ph), 3.38 (s, 3H,
OCH₃) ppm.

13C NMR (75 MHz) δ: 171.03 (C=O), 136.00, 131.23, 130.97, 129.30,
129.00, 128.65, 128.55, 127.12, 126.57, 125.71, 125.45, 125.03, 123.72
(aromatic C), 82.39 (ArCH₂OCON), 59.75 (OCH₃), 57.33 (CH(OCH₃)Ph) ppm.

MS m/e (relative intensity): 356 (M⁺, 12), 191 (84), 121 (100).
Exact mass calculated for C₂₄H₂₀O₃: 356.1413. Found: 356.1414.
Anal. calcd. for C₂₄H₂₀O₃: C, 80.88; H, 5.66. Found: C, 80.96; H,
5.62.
(b) (R)-(-)-89a

The same procedures as described in the above case were followed. A solution of 680 mg (3.0 mmoles) of 9-chloromethylantracene, 500 mg (3.0 mmoles) of (R)-(-)-α-methoxy benzeneacetic acid (Aldrich) and 0.5 mL of triethylamine was refluxed for 5 hours; 1.0 g (yield 94%) of the product was isolated as yellow solid after work-up. Recrystallization from ethanol afforded thin flakes, m.p. 145-147°C.

IR (KBr) v_{max}: 1734 (C=O), 1198, 1175, 1121, 997, 926, 880, 728, 628 cm^{-1}.

^1H NMR (300 MHz) δ: 8.55-7.25 (m, 14H, aromatic H), 6.99, 6.30 (two d, 2H, J = 12 Hz, CH_2CO), 4.78 (s, 1H, bridgehead H), 3.38 (s, 1H, OCH_3) ppm.

MS m/e (relative intensity): 356 (M^+, 12), 191 (83), 121 (100).

Exact mass calculated for C_{24}H_{20}O_3: 356.1413. Found: 356.1416.

Anal. calcd. for C_{24}H_{20}O_3: C, 80.88; H, 5.66. Found: C, 80.85; H, 5.65.

[a]_D^{20} = -69° ± 0.1 (c = 3.0, CHCl_3).

Dimethyl 9-(α-Methoxy-α-phenyl)acetoxyethyl-9,10-dihydro-9,10-etheno-anthracene-11,12-dicarboxylate (93a)

(a) (±)-93a

A mixture of 1.2 g (3.4 mmoles) of (±)-9-anthrylmethyl α-methoxy benzeneacetate, (±)-89a), and 0.50 g (3.5 mmoles) of dimethyl acetylenedicarboxylate was heated at 130°C for 2 hours. Chromatography of the reaction mixture on silica gel by using 30% ethyl acetate in
petroleum ether (30-60°) as the eluting solvent afforded 770 mg (yield 45%) of an oil which was crystallized from ethanol. Recrystallization from acetone/hexane twice gave colorless prisms, m.p., 141-142°C.

**IR (KBr) $\nu_{\text{max}}$:** 1753 (C=O), 1717 (C=C=O), 1630 (C=C), 1458, 1433, 1326, 1280, 1242, 1212, 1180, 1020, 744 cm$^{-1}$.

**$^1$H NMR (300 MHz) $\delta$:** 7.50-6.70 (m, 13H, aromatic H), 5.61 (s, 1H, bridgehead H), 5.63, 5.22 (two d, 2H, J = 12 Hz, CH$_2$OCO), 4.78 (s, 1H, CH(OCH$_3$)Ph), 3.79 (s, 3H, CO$_2$CH$_3$), 3.71 (s, 3H, CO$_2$CH$_3$), 3.45 (s, 3H, CH(OCH$_3$)Ph) ppm.

**$^{13}$C NMR (75 MHz) $\delta$:** 170.34, 166.67, 163.83 (3 x C=O), 150.81, 145.19, 145.08, 143.96, 142.42, 142.30, 135.50, 128.91, 128.72, 127.48, 125.53, 125.34, 125.20, 125.09, 123.87, 123.67, 121.96, 121.36 (aromatic and vinylic C), 82.19 (O$_2$CCH(OCH$_3$)Ph), 61.54 (CH$_2$OCO), 57.36, 52.46, 52.30, 50.58 (2 x CO$_2$CH$_3$, CH(OCH$_3$)Ph and bridgehead CH), 54.59 (bridgehead C) ppm.

**MS m/e (relative intensity):** 498 (M$^+$, 4), 121 (100). Exact mass calculated for C$_{30}$H$_{26}$O$_7$: 498.1679. Found: 498.1675.

**Anal. calcd. for C$_{30}$H$_{26}$O$_7$:** C, 72.27; H, 5.26. C, 72.34; H, 5.31.

**(b) (R)-(−)-93a**

A mixture of 820 mg (2.3 mmoles) of (R)-(−)-9-anthrylmethyl α-methoxy benzenecacetate (optically active 89a) and 400 mg (2.8 mmoles) of dimethyl acetylenedicarboxylate was heated at 130°C for 30 min. The resulting mixture was purified by column chromatography affording 245 mg (yield 21%) of optically pure sample, m.p. 141-143°C.
IR (KBr) \( \nu \text{max} \): 1753 (C=O), 1718 (C=C=C=O), 1630 (C=C), 1459, 1433, 1327, 1279, 1241, 1212, 1180, 1115, 1093, 1020, 769, 744, 696, 617 cm\(^{-1}\).

\( ^1H \) NMR (400 MHz) \( \delta \): 7.50-6.75 (m, 14H, aromatic H), 5.60 (s, 1H, bridgehead H), 5.62, 5.24 (two d, 2H, J = 12 Hz, CH\(_2\)CO), 4.78 (s, 1H, COCH(OCH\(_3\))Ph), 3.78 (s, 3H, CO\(_2\)CH\(_3\)), 3.72 (s, 3H, CO\(_2\)CH\(_3\)), 3.46 (s, 3H, CH(OCH\(_3\))Ph) ppm.

MS m/e (relative intensity): 498 (M\(^+\), 1), 215 (5), 121 (100).

Exact mass calculated for \( C\(_{30}\)H\(_{26}\)O\(_7\): 498.1678. Found: 498.1676.

Anal. calcd. for \( C\(_{30}\)H\(_{26}\)O\(_7\): C, 72.27; H, 5.26. Found: C, 72.22; H, 5.25.

\( [\alpha]_D \)\(^{20} \) = -4.0° ± 0.1 (c = 1.0, CHCl\(_3\)).

Methyl 9-(\( \alpha \)-Methoxy-\( \alpha \)-phenyl)acetoxyalkyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxylate (99) and Methyl 9-(\( \alpha \)-Methoxy-\( \alpha \)-phenyl)-acetoxyalkyl-9,10-dihydro-9,10-ethenoanthracene-12-carboxylate (100).

(Diels-Alder Reaction of 9-Anthrylmethyl \( \alpha \)-Methoxy Benzeneacetate and Methyl Propynoate)

(a) (\( \pm \))-99 and (\( \pm \))-100

A mixture of 1.7 g (4.8 mmoles) of (\( \pm \))-9-anthrylmethyl \( \alpha \)-methoxy benzeneacetate and 1.0 g (12 mmoles) of methyl propynoate in a sealed tube was kept at 150°C for 8 hours. The resulting brown gum was chromatographed on silica gel by using 20\% ethyl acetate in petroleum ether (30-60\°) as the eluting solvent. Two isomeric Diels-Alder adducts were crystallized out from the separated fractions; 330 mg (yield 13\%) of (\( \pm \))-99 were obtained and 210 mg (yield 8\%) of the other isomer, i.e.
(+)-100, were isolated. Characterization of the two isomers was as follows.

(i) Characterization of (+)-99

m.p. 193.5-195°C.

IR (KBr) \( \nu_{\text{max}} \): 1752 (C=O), 1715 (C=\text{C}-\text{C}=O), 1615 (C=C), 1459, 1435, 1328, 1315, 1296, 1260, 1215, 1176, 1126, 1114, 1045, 1016, 767, 757, 734, 586 cm\(^{-1}\).

\(^1\)H NMR (400 MHz) \( \delta \): 7.87 (d, 1H, J = 6 Hz, vinylic H), 7.45-6.80 (m, 13H, aromatic H), 5.87, 5.50 (two broad s, 2H, CH\(_2\)CO), 5.15 (d, 1H J = 6 Hz, bridgehead H), 4.77 (s, 1H, COCH\(_{\text{OCH}_3}\)Ph), 3.51 (broad s, 3H, CO\(_2\)CH\(_3\)), 3.45 (s, 3H, CH\(_{\text{OCH}_3}\)Ph) ppm.

\(^13\)C NMR (75 MHz) \( \delta \): 170.53, 165.50 (2 x C=O), 151.44, 145.13, 144.18, 144.10, 143.07, 135.83, 128.73, 128.60, 127.42, 124.97, 124.93, 124.89, 124.85, 123.49, 123.45, 121.94 (aromatic and vinylic C), 82.37 (O\(_2\)CC\(_{\text{OCH}_3}\)Ph), 62.40 (CH\(_2\)CO), 57.33, 51.52, 50.91 (CO\(_2\)CH\(_3\), CH\(_{\text{OCH}_3}\)Ph and bridgehead CH), 53.9 (quaternary C) ppm.

MS m/e (relative intensity): 440 (M\(^+\), 7), 215 (20), 121 (100).

Exact mass calculated for C\(_{28}\)H\(_{24}\)O\(_5\): 440.1624. Found: 440.1621.

Anal. calcd. for C\(_{28}\)H\(_{24}\)O\(_5\): C, 76.35; H, 5.49. Found: C, 76.48; H, 5.52.

(ii) Characterization of (+)-100

m.p. 137-139°C.

IR (KBr) \( \nu_{\text{max}} \): 1758 (C=O), 1708 (C=\text{C}-\text{C}=O), 1620 (C=C), 1455, 1437, 1331, 1302, 1229, 1205, 1178, 1152, 1112, 1074, 1058, 1014, 992, 766, 742, 697, 580 cm\(^{-1}\).
\( ^1 \text{H NMR} (300 \text{ MHz}) \delta: 7.52 (d, 1H, J = 1 \text{ Hz}, \text{ vinylic } H), 7.50-6.80 \) (m, 13H, aromatic H), 5.61 (d, 1H, J = 1 \text{ Hz}, bridgehead H), 5.43, 5.24 (two d, 2H, J = 12 \text{ Hz}, \text{CH}_2\text{OCO}), 4.90 (s, 1H, \text{COCH(OCH}_3\text{)}\text{Ph}), 3.75 (s, 3H, \text{ CO}_2\text{CH}_3), 3.48 (s, 3H, \text{CH(OCH}_3\text{)}\text{Ph}) \text{ ppm.}

\( ^{13} \text{C NMR} (75 \text{ MHz}) \delta: 170.96, 164.73 (2 \times \text{C=O}), 148.79, 146.15, 146.00, 145.40, 143.28, 143.22, 135.68, 128.87, 128.70, 127.29, 125.13, 125.01, 124.78, 124.73, 123.71, 123.63, 121.31, 121.12 (\text{aromatic and vinylic } C), 82.23 (\text{O}_2\text{CCH(OCH}_3\text{)}\text{Ph}), 63.02 (\text{CH}_2\text{OCO}), 57.31, 51.87, 50.27 (\text{CO}_2\text{CH}_3, \text{CH(OCH}_3\text{)}\text{Ph and bridgehead CH}), 53.77 (\text{bridgehead } C) \text{ ppm.}

\text{MS } m/e (\text{relative intensity}): 440 (M^+, 2), 215 (19), 121 (100). Explain mass calculated for C\text{28H24O5}: 440.1624. Found: 440.1625.

\text{Anal. calcd. for C\text{28H24O5}: C, 76.35; H, 5.49. Found: C, 76.48; H, 5.58.}

(b) (R)-(-)-99 and (R)-(-)-100

(R)-(-)-9-Anthrylmethyl \( \alpha \)-methoxyl benzeneacetate (880 mg, 2.5 mmoles) and methyl propynoate (1.0 g, 12 mmoles) in a sealed tube were heated at 150°C for 10 hours. The first column on silica gel, using 20% ethyl acetate in petroleum ether (30-60°) as the eluting solvent, separated the products from the reaction mixture. Further purification by a second column on silica gel by using 20% diethyl ether in petroleum ether (30-60°) as the eluting solvent resulted in 159 mg (yield 14%) of (R)-(-)-99 and 99 mg (yield 8%) of (R)-(-)-100. Spectroscopic data of the two isomers are listed below.

(i) Characterization of (R)-(-)-99

m.p. 182-183°C.
IR (KBr) $\nu_{\text{max}}$: 1752 (C=O), 1716 (C=C-C=O), 1615 (C=C), 1458, 1315, 1295, 1260, 1216, 1177, 766, 738 cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.88 (d, 1H, J = 6 Hz, vinylic H), 7.60-6.80 (m, 13H, aromatic H), 5.87, 5.50 (two broad s, 2H, CH$_2$OCO), 5.17 (d, 1H J = 6 Hz, bridgehead H), 4.78 (s, 1H, COCH(OCH$_3$)Ph), 3.52 (broad s, 3H, CO$_2$CH$_3$), 3.46 (s, 3H, CH(OCH$_3$)Ph) ppm.

MS m/e (relative intensity): 440 ($M^+$, 3), 215 (14), 121 (100).

Exact mass calculated for C$_{28}$H$_{24}$O$_5$: 440.1624. Found: 440.1633.

Anal. calcd. for C$_{28}$H$_{24}$O$_5$: C, 76.35; H, 5.49. Found: C, 76.31; H, 5.51.

$[\alpha]_D^{20} = -44^\circ \pm 0.1$ (c = 1, CHCl$_3$).

(i) Characterization of (R)-(−)-100

m.p. 156-158°C.

IR (KBr) $\nu_{\text{max}}$: 1759 (C=O), 1708 (C=C-C=O), 1628 (C=C), 1455, 1331, 1229, 1206, 1178, 1151, 1114, 1074, 767, 741 cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.52 (d, 1H, J = 1 Hz, vinylic H), 7.50-6.80 (m, 13H, aromatic H), 5.62 (d, 1H, J = 1 Hz, bridgehead H), 5.44, 5.25 (two d, 2H, J = 12 Hz, CH$_2$OCO), 4.90 (s, 1H, COCH(OCH$_3$)Ph), 3.75 (s, 3H, CO$_2$CH$_3$), 3.48 (s, 3H, CH(OCH$_3$)Ph) ppm.

MS m/e (relative intensity): 440 ($M^+$, 0.3), 215 (18), 121 (100).

Exact mass calculated for C$_{28}$H$_{24}$O$_5$: 440.1624. Found: 440.1626.

Anal. calcd. for C$_{28}$H$_{24}$O$_5$: C, 76.35; H, 5.49. Found: C, 76.19; H, 5.50.

$[\alpha]_D^{20} = -45^\circ \pm 0.1$ (c = 1, CHCl$_3$).
III. Photochemical Studies

A. General Procedures

All analytical photolyses, both in solution and in the solid state, were carried out by using a 450 W Hanovia medium pressure mercury lamp and/or a PRA UV-12 nitrogen laser from PRA Laser Inc. ($\lambda = 337.1$ nm) at room temperature unless otherwise stated. Spectral grade solvents (BDH) were used for solution phase photolyses and the concentration of the sample solution was kept at ca. 0.01 M. The samples were degassed by three freeze-pump-thaw cycles and sealed with paraffin film under a nitrogen atmosphere in each case prior to irradiation. Photolyses in the solid state were conducted either as single crystals in Pyrex or quartz tubes sealed under nitrogen or as powders sandwiched between two Pyrex microscope slide plates. The photolyzed samples were normally analyzed by GC, GC-MS, IR and $^1$H NMR.

For preparative scale photolyses in solution, 0.1 g to 2.0 g of the appropriate compound was dissolved in 250 mL of spectral grade solvent and put into a preparative photolysis apparatus. The solution was purged of oxygen by passing through a steady flow of nitrogen for 60 min before and during the whole irradiation period. The light source used was a 450 W Hanovia medium pressure mercury lamp and the desired output wavelength was achieved by using either a Pyrex glass filter ($\lambda > 290$ nm) or a uranium glass filter ($\lambda > 340$ nm). The photolyses were monitored and analyzed by GC and stopped when 90% or higher of the starting material was converted into photoproducts. The solvent was removed by evaporation in vacuum and the resulting photolysate was
subjected to column chromatography. Solid state photolyses on a preparative scale were performed by using powdered crystals (0.5 g to 2.0 g) between two Pyrex glass plates. The plates were placed near the light source (5-10 cm away) and irradiated at room temperature for a period of time until no further conversion of the starting material was observed by GC. After the photolysis, the solids were scraped off the glass plates and subjected to column chromatography. The photoproducts were separated (or partially separated) by column chromatography and further purified by recrystallization in the case of solid samples.

Low temperature photolyses were carried out by maintaining the sample in a cooling bath controlled by the Cryocool CC-100-II immersion cooling system from Neslab Instruments Inc. The temperature was kept within ± 1°C and the samples were irradiated with the Hanovia medium pressure mercury lamp or the nitrogen laser.

B. Photochemistry of Substrates

1. Cyclohexenone Derivatives

Photochemical Studies on 4-Phenyl-4-p-bromophenyl-2-cyclohexen-1-one (71a)

In Solution

Analytical photolyses were performed in acetone, acetonitrile and benzene. The reactions were analyzed by GC (DB-1, oven temp. = 190°C)
which showed two peaks corresponding to the photoproducts. The ratio of the two was constant in all three of the solvents.

In a preparative run, a solution of 500 mg of 4-phenyl-4-p-bromophenyl-2-cyclohexen-1-one (71a) in 250 mL of benzene was irradiated for 20 hours until more than 99% of the starting material was consumed. A uranium glass filter was used for \( \lambda \geq 340 \) nm. This limited the secondary photoreaction to a negligible amount. Removal of benzene in vacuum left a light oil. Part of this oil (250 mg) was chromatographed on silica gel by using 5-10\% diethyl ether/petroleum ether (30-60\°) as the eluting solvent. The first column afforded 55 mg of trans-5-phenyl-6-p-bromophenylbicyclo[3.1.0.]hexan-2-one (72a) and a 1:1 mixture of trans-5-phenyl-6-p-bromophenylbicyclo[3.1.0.]hexan-2-one (72a) and trans-5-p-bromophenyl-6-phenylbicyclo[3.1.0.]hexan-2-one (73a). Chromatographing a second time gave pure trans-5-p-bromophenyl-6-phenylbicyclo[3.1.0.]hexan-2-one (73a). Total yields were as follows: 135 mg (yield 54\%) of 72a; 40 mg (yield 14\%) of 73a and 70 mg of a mixture of the two.

Characterization of trans-5-Phenyl-6-p-bromophenylbicyclo[3.1.0.]hexan-2-one (72a)

This compound was recrystallized from ether/petroleum ether (30-60\°) after the chromatography to afford colorless prisms, m.p., 93-95\°C

IR (KBr) \( \nu_{\text{max}} \): 1724 (C=O), 1603, 1489, 919, 823, 763, 699 cm\(^{-1}\).

\(^1\)H NMR (400 MHz) \( \delta \): 7.5-7.2 (m, 9H, aromatic H), 3.03 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.69 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.38 (m, 2H, COCH\(_2\)CH\(_2\)), 2.05-2.20, 1.22-1.10 (m, 2H, COCH\(_2\)CH\(_2\)) ppm.
$^{13}$C NMR (50 MHz) $\delta$: 212.6 (C=O), 142.50, 133.92, 132.06, 130.97, 128.84, 127.23, 126.98, 121.48 (aromatic C), 43.21 (quaternary C), 40.95, 35.76 (cyclopropyl CHCH), 36.46, 27.05 (COCH$_2$CH$_2$) ppm.

MS m/e (relative intensity): 328 (M+2, 6), 326 (M+, 6), 286 (24), 284 (28), 205 (100), 91 (31). Exact mass calculated for C$_{18}$H$_{15}$BrO: 326.0306. Found: 326.0307.

Anal. calcd. for C$_{18}$H$_{15}$BrO: C, 66.07; H, 4.62; Br, 24.42. Found: C, 65.90; H, 4.66; Br, 24.35.

The structure of this compound was confirmed by an X-ray diffraction analysis. The crystal data were as follows: C$_{18}$H$_{15}$BrO, monoclinic, space group $I2/a$, a = 17.6073(39), b = 8.2133(20), c = 19.9763(50) Å, $\beta$ = 93.09(3)$^\circ$, $V$ = 2884.6(12) Å$^3$, Z = 8, $\rho$ = 1.508 g/mL, $R$ = 0.040. The details were published elsewhere. The structure was also supported by the following deuteration reaction and the transformation of this bromo derivative 72a to the corresponding cyano derivative 72b, which is a known compound.

(a) Deuteration of trans-5-Phenyl-6-p-bromophenylbicyclo[3.1.0]hexan-2-one.

A small piece of sodium was dissolved in 0.5 mL of CD$_3$OD. Two drops of this solution were added to a solution of trans-5-phenyl-6-p-bromophenylbicyclo[3.1.0]hexan-2-one (72a) in CDCl$_3$. The mixture was shaken for 5 min at room temperature and analyzed by $^1$H NMR, which showed that one of the methylene protons adjacent to the carbonyl group was selectively deuterated.
\[ ^1H \text{NMR (400 MHz)} \delta: 7.60-7.20 (m, 9H, aromatic H), 3.07 (d, 1H, J = 10 Hz, cyclopropyl H), 2.70 (d, 1H, J = 10 Hz, cyclopropyl H), 2.50-2.35 (m, 2H, COCHDCH\text{2}), 1.25 (t, 1H, J = 7 Hz, COCHDCH\text{2}) \text{ ppm.} \]

(b) Reaction of 72a with Cuprous Cyanide.

A mixture of \textit{trans}-5-phenyl-6-\textit{p}-bromophenylbicyclo[3,10]hexan-2-one (6 mg) and cuprous cyanide (10 mg) was refluxed in 1 mL of N-methylpyrrolidone for 2 hours. The mixture was poured into water. The aqueous layer was extracted with diethyl ether and the ether extracts were washed, dried and concentrated in vacuum. The resulting mixture was analyzed by GC and GC-MS, and the data were compared with those of \textit{trans}-5-phenyl-6-\textit{p}-cyanophenylbicyclo[3.1.0.]hexan-2-one (72b), one of the known photoproducts from the photolysis of 4-phenyl-4-\textit{p}-cyanophenyl-2-cyclohexen-1-one (71b).\textsuperscript{53} The product from this transformation proved to be the same as compound 72b by means of GC retention time and GC-MS data.

GC-MS m/e (relative intensity): 273 (M\textsuperscript{+}, 10), 244 (12), 231 (100), 153 (17), 115 (30), 91 (57).

Characterization of \textit{trans}-5-\textit{p}-Bromophenyl-6-phenylbicyclo[3.1.0.]hexan-2-one (73a)

This compound was recrystallized from diethyl ether/petroleum ether (30-60\textdegree) to give colorless prisms, m.p., 101-103.5\textdegree C.

IR (KBr) \( \nu_{\text{max}} \): 1718 (C=O), 1602, 1491, 1074, 860, 814, 703 cm\textsuperscript{-1}. 
\(^1\)H NMR (400 MHz) δ: 7.60-7.20 (m, 9H, aromatic H), 3.08 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.66 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.35-2.10, 1.25-1.10 (m, 4H, COCH\(_2\)CH\(_2\)) ppm.

MS m/e (relative intensity): 328 (M+2, 6), 326 (M\(^+\), 6), 286 (70), 284 (60), 219 (45), 205 (70), 189 (60), 128 (65), 115 (100). Exact mass calculated for C\(_{18}\)H\(_{15}\)BrO: 326.0306. Found: 326.0301.

Anal. calcd. for C\(_{18}\)H\(_{15}\)BrO: C, 66.07; H, 4.62; Br, 24.42. Found: C, 66.23; H, 4.65; Br, 24.30.

The structure of this compound was also confirmed by its conversion to the known cyano-substituted derivative 73b. The same procedure was used as in the previous case, and the product was also analyzed and characterized by GC and GC-MS in terms of the GC retention time and GC-MS data. The data were in good agreement with those of trans-5-p-cyanophenyl-6-phenylbicyclo-[3.1.0.]hexan-2-one (73b).

GC-MS m/e (relative intensity): 273 (M\(^+\), 5), 231 (100), 115 (62), 91 (25).

In the Solid State

Single crystals or crystalline powders of 4-p-bromophenyl-4-phenyl-2-cyclohexen-1-one were placed in Pyrex photolysis tubes. The samples were irradiated for 20-50 hours at room temperature using the Hanovia medium pressure mercury lamp with a uranium glass filter or the nitrogen laser. The resulting solids were analyzed by FTIR and GC.

Photolysis of 4-Phenyl-4-p-cyanophenyl-2-cyclohexen-1-one (71b)
The solution phase photolysis described by Zimmerman et al. was performed under the same conditions, and the results obtained were in agreement with those reported. However, a slight modification was carried out by changing the Pyrex filter to a uranium glass filter. This modification minimized the secondary photoreaction, i.e. the photoproduct of cis-5-phenyl-6-p-cyanophenylbicyclo[3.1.0.]hexan-2-one (103b) was not detected by GC under the experimental conditions. The products were analyzed and characterized by GC (Carbowax 20M column, oven temp. = 215°C) and GC-MS and $^1$H NMR.

Characterization of Photoproducts

(a) trans-5-Phenyl-6-p-cyanophenylbicyclo[3.1.0.]hexan-2-one (72b)
GC retention time (r.t.): 14.7 min.
$^{1}$H NMR (300 MHz) $\delta$: 7.70-7.00 (m, 9H, aromatic H), 3.12 and 2.76 (two d, 2H, J = 10 Hz, cyclopropyl CHCH), 2.60-1.00 (m, 4H, CH$_2$CH$_2$) ppm.
GC-MS m/e (relative intensity): 273 (M$^+$, 2), 231 (65), 153 (27), 115 (33), 91 (100).

(b) cis-5-Phenyl-6-p-cyanophenylbicyclo[3.1.0.]hexan-2-one (103b)
GC retention time: 15.4 min.
GC-MS m/e (relative intensity): 273 (M$^+$, 15), 231 (98), 153 (15), 128 (34), 115 (55), 91 (100).

(c) trans-5-p-Cyanophenyl-6-phenylbicyclo[3.1.0.]hexan-2-one (73b)
GC retention time: 16.9 min.
GC-MS m/e (relative intensity): 273 (M$^+$, 2), 231 (91), 154 (10), 129 (40), 115 (100), 91 (31).
The solid state photolysis of this compound was carried out using either crystals or powders at room temperature. The sample was photolyzed for 5 min to 4 hours using a uranium filter, partial melting was observed at high conversions of the starting material. The products and product ratios were analyzed by GC.

Photochemical Studies on 4,4-Diphenyl-6-methyl-2-cyclohexen-1-one (74a)

In Solution

Analytical photolyses in common organic solvents were carried out. In each case, the photolysate was analyzed by GC (Carbowax 20M column, oven temp = 215°C).

In a preparative run, 4,4-diphenyl-6-methyl-2-cyclohexen-1-one (600 mg) was photolyzed in 300 mL of benzene for 25 hours using the Hanovia lamp with a uranium glass filter under a nitrogen atmosphere. Benzene was removed in vacuum leaving 600 mg of an oil. The oil was chromatographed on silica gel by using diethyl ether and petroleum ether (30-60°) as the eluting solvent to give 320 mg (yield 53%) of an oil which was identified to be endo-3-methyl-trans-5,6-diphenylbicyclo[3.1.0.]hexan-2-one (75a), 40 mg (yield 7%) of exo-3-methyl-trans-5,6-diphenylbicyclo[3.1.0.]hexan-2-one (76a) and ca. 200 mg of a mixture of the two photoproducts.

Characterization of endo-3-Methyl-trans-5,6-diphenylbicyclo[3.1.0.]hexan-2-one (75a)
IR (neat) \( \nu_{\text{max}} \): 1719 (C=O), 1602, 1496, 1446, 1319, 764, 700 cm\(^{-1}\).

\(^1\)H NMR (300 MHz) \( \delta \): 7.45-7.23 (m, 10H, aromatic H), 3.04 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.80 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.74-2.44, 2.03-1.94 (m, 3H, COCH(CH\(_3\))CH\(_2\)), 0.17 (d, J = 7 Hz, CH\(_3\)) ppm.

MS m/e (relative intensity): 262 (M\(^+\), 15), 234 (15), 206 (100), 191 (25), 91 (30). Exact mass calculated for C\(_{19}\)H\(_{18}\)O: 262.1358. Found: 262.1350.

The structure of this compound was supported by the following epimerization reaction.

Epimerization of \textit{endo}-3-Methyl-\textit{trans}-5,6-diphenylbicyclo[3.1.0]-hexan-2-one (75a)

Compound 75a (2 mg) was dissolved in 1.0 mL of methanol. Two drops of CH\(_3\)ONa/CH\(_3\)OH (4.3 M) were added to the above solution. The resulting mixture was placed at room temperature and analyzed by GC until the ratio of 75a:76a (17:83) remained constant.

Characterization of \textit{exo}-3-Methyl-\textit{trans}-5,6-diphenylbicyclo[3.1.0.]hexan-2-one (76a)

IR (neat) \( \nu_{\text{max}} \): 1719 (C=O), 1603, 1496, 1447, 1320, 763, 700 cm\(^{-1}\).

\(^1\)H NMR (300 MHz) \( \delta \): 7.42-7.25 (m, 10H, aromatic H), 3.13 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.75-1.95 (m, 3H, cyclopropyl CH and CH\(_2\)), 1.12 (m, 1H COCH), 0.92 (d, 3H, J = 7 Hz, CH\(_3\)) ppm.

\(^{13}\)C NMR (50 MHz) \( \delta \): 215.0 (C=O), 143.09, 135.16, 129.92, 129.32, 128.90, 128.77, 127.35 and 127.04 (aromatic C), 41.01, 36.79 (quaternary C and CH\(_2\)), 40.82, 40.62, 37.26 (3 x CH), 15.10 (CH\(_3\)) ppm.
MS m/e (relative intensity): 262 (M⁺, 25), 234 (20), 206 (100), 191 (25), 91 (35). Exact mass calculated for C₁₉H₁₈O: 262.1358. Found: 262.1357.

The structure of this compound was also confirmed by the following independent synthesis.

**Methylation of trans-5,6-Diphenylbicyclo[3.1.0.]hexan-2-one.**

Diisopropyl amine (125 mg, 1.2 mmoles) was dissolved in 10 mL of anhydrous THF. n-BuLi in hexane (5 mL, ca. 0.26 M) was added at -10°C. The mixture was stirred at -10°C for 15 min, then cooled to -78°C. trans-5,6-Diphenylbicyclo[3.1.0.]hexan-2-one (39) (250 mg, 1.0 mmoles), which was prepared by Dr. Omkaram Nalamasu according to the literature, in 5 mL of anhydrous THF was dropped into the above solution and the resulting mixture was stirred at -78°C for 20 min. Next, 1.5 mL of CH₃I (passed through basic alumina) was added. The solution was kept stirring at room temperature for 16 hours, and poured into 1.5% aqueous NH₄Cl (20 mL). The aqueous layer was extracted with diethyl ether and the ether extracts were washed, dried and concentrated in vacuum leaving a yellow oil. A colorless oil (215 mg, yield 81%) was obtained by chromatography on silica gel by using diethyl ether/petroleum ether (30-60°) as the eluting solvent. This material was proved to be identical to exo-3-methyl-trans-5,6-diphenylbicyclo-[3.1.0.]hexan-2-one (76a) by the spectroscopic methods.

**Photolysis of 74a in the Solid State**

Photolyses in the solid state by using crystals or crystalline powders of 74a were carried out at either room or low temperatures under
the similar conditions to that described in the photolysis of 71a. In all cases, the photoproducts were routinely analyzed by GC.

Photochemical Studies on 4,4-Diphenyl-6-ethyl-2-cyclohexen-1-one (74b)

Analytical photolyses were performed in acetone, acetonitrile and benzene. The reaction mixture was analyzed by GC (Carbowax 20M column, oven temp = 215°C).

A preparative photolysis was carried out by using 700 mg of 4,4-diphenyl-6-ethyl-2-cyclohexen-1-one in 300 mL of acetone. The reaction was stopped after irradiation for 75 hours. GC analysis showed that over 90% of the starting material was consumed. Purification by column chromatography on silica gel by using diethyl ether/petroleum ether (30-60°C) as the eluting solvent gave two partially separated photoproducts which were characterized as follows.

endo-3-Ethyl-trans-5,6-diphenylbicyclo[3.1.0]hexan-2-one (75b)

This compound was obtained as an oil (85% pure).

IR (neat) \( \nu_{\text{max}} \): 1719 (C=O), 1603, 1496, 1447, 763, 700 cm\(^{-1}\).

\( ^1H \) NMR (400 MHz) \( \delta \): 7.45-7.20 (m, 10H, aromatic H), 3.03 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.79 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.70-2.00 (m, 3H, COCH(Et)CH\(_2\)), 0.58 (t, 3H, J = 7 Hz, CH\(_2\)CH\(_3\)), 1.05-1.20, -0.10 to -0.22 (m, 2H, CH\(_2\)CH\(_3\)) ppm.

GC-MS m/e (relative intensity): 276 (M\(^+\), 2), 248 (8), 219 (21), 206 (100), 191 (23), 91 (45). Exact mass calculated for C\(_{20}\)H\(_{20}\)O: 276.1514. Found: 276.1513.
exo-3-Ethyl-trans-5,6-diphenylbicyclo[3.1.0.]hexan-2-one (76b)

This material was also obtained as an oil (90% pure). The spectroscopic data were in good agreement with those obtained from the following independent synthesis.

Preparation of Compound 76b from Alkylation of trans-5,6-Diphenylbicyclo[3.1.0.]hexan-2-one.

n-BuLi in hexane (2.10 mL, ca. 1.1 M) was added into a solution of diisopropyl amine (260 mg, 2.57 mmoles) in 8 mL of anhydrous THF at -10°C. After 10 min stirring, trans-5,6-diphenylbicyclo[3.1.0.]hexan-2-one (500 mg, 2.01 mmoles) in 5 mL of anhydrous THF was dropped into the above solution and the resulting mixture was stirred at -78°C for 20 min. Ethyl iodide (2.0 mL, purified by passage through basic alumina in 5 mL of anhydrous THF) was then dropped into the above solution at -78°C. The mixture was stirred at room temperature overnight and workup the same as described previously; 400 mg (yield 73%) of exo-3-ethyl-trans-5,6-diphenylbicyclo[3.1.0.]hexan-2-one (76b) were obtained as a colorless oil which solidified on standing. Recrystallization from acetone/hexane afforded colorless prisms, m.p., 87-89°C.

IR (neat) $\nu_{\text{max}}$: 1719 (C=O), 1601, 1496, 1446, 1171, 763, 700 cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.45-7.25 (m, 10H, aromatic H), 3.13 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.70 (d, 1H, J = 10 Hz, cyclopropyl CH), 2.66-0.95 (m, 5H, COCH(CH$_2$CH$_3$)CH$_2$), 0.74 (t, 3H, J = 7 Hz, CH$_2$CH$_3$) ppm.

$^{13}$C NMR (50 MHz) $\delta$: 214.9 (C=O), 143.23, 135.12, 129.37, 128.85, 127.33, 127.16, 127.05 (aromatic C), 47.48, 41.28, 37.01 (3 x CH), 41.40, 34.36, 23.47 (CH$_3$CH$_2$, CH$_2$ and quaternary C), 11.29 (CH$_2$CH$_3$) ppm.
MS m/e (relative intensity): 276(M⁺, 12), 248 (30), 219 (60), 206 (100), 191 (65), 165 (30), 120 (64), 115 (58), 91 (96). Exact mass calculated for C₂₀H₂₀O: 276.1514. Found: 276.1513.

Anal. calcd. for C₂₀H₂₀O: C, 86.92; H, 7.29. Found: C, 87.11; H, 7.28.

2. Dibenzobarrelene Derivatives

Photochemical Studies on Methyl 3,5-Dihydro-3-oxo-1H-5,9b[1',2']-benzenonaphtho[1,2-c]furan-4-carboxylate (96)

In Solution

Photolyses in common organic solvents such as benzene, acetone (triplet sensitizer) or acetonitrile were carried out. In all cases, a single photoproduct was observed (GC condition: DB-1 column, oven temp. = 220°C). On a preparative scale, a solution of the title compound (50 mg) in 20 mL of benzene was degassed and irradiated for 10 hr to 100% conversion. Removal of the solvent gave 50 mg (yield 100%) of methyl 1,8-dihydro-1-oxo-1H-3a,8,12b-methanodibenzo[3,4:6,7]cyclohepta[1,2-c]furan-12c-carboxylate (153) as a white solid, which was recrystallized from diethyl ether and hexane to afford colorless prisms, m.p., 157-159°C.

IR (KBr) νmax: 1768 (lactone C=O), 1725 (C=O), 1240, 1107, 763, 741 cm⁻¹.

¹H NMR (400 MHz) δ: 7.55-7.15 (m, 8H, aromatic H), 5.17 (s, 1H, CH), 4.93, 5.15 (two d, 2H, J = 10 Hz, CH₂), 3.79 (s, 3H, OCH₃) ppm.
$^{13}$C NMR (75 MHz) δ: 170.00, 167.77 (2 x C=O), 146.48, 145.44, 132.15, 130.74, 128.96, 128.41, 127.48, 127.24, 125.24, 122.83, 122.56, 121.90 (aromatic C), 69.47, 62.82, 57.71 (cyclopropyl C), 64.41 (CO$_2$CH$_2$), 55.29 (CO$_2$CH$_3$), 52.60 (CH) ppm.

MS m/e (relative intensity): 318 (M$^+$, 43.1), 290 (40.2), 262 (36.5), 230 (51.6), 202 (100), 101 (18.5). Exact mass calculated for C$_{20}$H$_{14}$O$_4$: 318.0892. Found: 318.0892.

Anal. calcd. for C$_{20}$H$_{14}$O$_4$: C, 75.46; H, 4.43. Found: C, 75.19; H, 4.44.

This photoproduct from the solution phase photolysis was analyzed by $^1$H NMR with the chemical shift reagent, Eu(hfc)$_3$, which showed an equal amount of a pair of enantiomers.

In the Solid State

Irradiation of the sample crystals or powders was carried out for different periods of time so that the conversion of the starting material varied from 10% to 100%. It was found that two photoproducts were formed in the solid and that one of them, the major product 153, was the same as that from the photolysis in solution. It was also determined that the ratio between the two photoproducts in the solid state was conversion independent. Typically, 5-10 mg of the colorless crystals were placed in a Pyrex tube which was purged with nitrogen, and photolyzed for about 10-20 hr (the photolysis can be monitored by GC). After the irradiation, the yellow crystals were dissolved in CDCl$_3$. The photoproducts and product ratio were analyzed by both $^1$H NMR and GC-MS. On a preparative scale, the crystals (200 mg) were slightly powdered and placed between microscope slides. Then the sample was irradiated for 40
hr using the Hanovia medium pressure mercury lamp. The resulting yellow powder was subjected to column chromatography. However, attempts to separate the two photoproducts were not successful regardless of how the eluting solvent or the stationary phase (silica gel or alumina) were varied. Only a small amount of the major photoproduct was isolated. The minor solid state photoproduct was enriched up to 50% pure by repeated column chromatography. This mixture was analyzed by $^1$H NMR and GC-MS and proved to consist of the dibenzopentalene-lactone 152, a regioisomer of the major photoproduct. The structure of this was also confirmed by an independent synthesis.

Independent Preparation of Dibenzopentalene-lactone 152

$p$-Toluenesulfonic acid (hydrated, 57.5 mg) dissolved in 40 mL of benzene was refluxed for 1 hr, and water was removed by a Dean-Stark tube. Dimethyl 4b-hydroxymethyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]-cyclopropa[c,d]pentalene-8b,8c-dicarboxylate (119) (190 mg) dissolved in 4 mL of benzene was poured into the above cooled solution, and the mixture was refluxed for 3 hr. The benzene layer was washed with 3% aqueous sodium bicarbonate, water and dried. Removal of the solvent in vacuum left 190 mg of an oil which crystallized upon standing. Recrystallization from acetone afforded 130 mg (yield 75%) of colorless prisms, m.p., 248-250°C.

IR (KBr) $\nu_{max}$: 1775 (lactone C=O), 1727 (C=O), 1474, 1366, 1343, 1208, 1174, 1080, 1037, 915, 749 cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.62-7.13 (m, 8H, aromatic-H), 5.12-5.03 (two d, 2H, $J = 11$ Hz, CH$_2$), 4.85 (s, 1H, CH), 3.94 (s, 3H, COOCH$_3$) ppm.
$^{13}$C NMR (75 MHz) $\delta$: 172.00, 166.73 (2 x C=O), 151.00, 150.66, 135.22, 132.94, 131.75, 128.83, 128.71, 128.09, 128.02, 127.81, 126.26, 120.61, 120.56 (aromatic C), 75.52, 66.69, 57.34 (quaternary C), 72.41 (CO$_2$CH$_2$), 52.96 (CH), 50.96 (CO$_2$CH$_3$) ppm.

MS m/e (relative intensity): 318 (M$^+$, 5.9), 274 (5.1), 260 (35.0), 242 (10.5), 231 (10.3), 215 (90.8), 202 (35.5), 107 (10.5), 84 (83.1), 69 (52.5), 49 (100.0). Exact mass calculated for C$_{20}$H$_{14}$O$_4$: 318.0892. Found: 318.0898.

Anal. calcd. for C$_{20}$H$_{14}$O$_4$: C, 75.46; H, 4.43. Found: C, 75.60; H, 4.42.

Asymmetric Synthesis in the Solid State

Typically, a single crystal (weighing ca. 5-20 mg in each run) of the lactone-ester 96, space group $P2_12_12_1$, was irradiated with the Hanovia medium pressure mercury lamp or the nitrogen laser for 20-40 hours at various temperatures. The photolyzed crystals were dissolved in CDCl$_3$ and subjected to GC and $^1$H NMR analysis. In the latter case, a chiral shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphoratol] europium (III) (Eu(hfc)$_3$, Aldrich) was applied to determine the enantiomeric excess which was determined by the integration of the shifted peaks.

[2+2] Cycloaddition of the Lactone-Ester 96 to 1,3-Cyclohexadiene

Analytical photolyses of the [2+2] cycloaddition reaction were carried out in benzene or acetonitrile. Sensitization experiments were performed using pure acetone or benzil in benzene as sensitizers; a
uranium glass filter was applied in the latter case. In all runs, the reaction was monitored by GC (DB-1 or DB-17 column).

On a preparative scale, the lactone-ester 96 (300 mg, 0.94 mmole) and freshly distilled 1,3-cyclohexadiene (1.0 g, 12 mmole) in 10 mL of acetone were photolyzed for 5 hours. Removal of the solvent gave an oil which was chromatographed on silica gel by using 15% diethyl ether in hexanes as the eluting solvent; 97 mg (yield 26%) of white crystals were isolated by crystallization of the appropriate column fractions as the major [2+2] adduct 187. Three additional photoproducts, 188, 189 and 190 were also isolated in a small amounts.


m.p. 237-238°C.

IR (KBr) $\nu_{\text{max}}$: 1780 (lactone C=O), 1723 (C=O), 1458, 1432, 1279, 1235, 1045, 1010, 777, 639 cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.55-7.10 (m, 8H, aromatic H), 5.95-5.73 (m, 2H, CH=CH), 5.31, 4.88 (two d, 2H, J = 10 Hz, CH$_2$OCO), 4.67 (s, 1H, bridgehead CH), 3.44 (s, 3H, CO$_2$CH$_3$), 3.40-1.35 (m, 6H, -CH$_2$CH$_2$CH(R)CH$_2$) ppm.

$^{13}$C NMR (50 MHz) $\delta$: 170.87, 170.05 (2 x C=O), 141.84, 140.57, 140.32, 137.52, 129.64, 127.11, 126.93, 126.79, 126.759*, 124.70, 124.47, 122.49, 121.33 (aromatic C and vinylic C), 63.53, 21.48, 20.57 (3 x CH$_2$), 58.81, 58.23, 55.96 (3 x quaternary C), 54.26, 51.22, 33.92, 32.81 (CO$_2$CH$_3$, 3 x CH) ppm.

* possibly two carbons here.
MS m/e (relative intensity): 398 (M⁺, 2), 366 (8), 338 (5), 319 (100), 287 (19), 259 (43), 215 (37), 202 (30), 191 (63). Exact mass calculated for C₂₆H₂₂O₄: 398.1519. Found: 398.1523.

Anal. calcd. for C₂₆H₂₂O₄: C, 78.37; H, 5.57. Found: C, 78.54; H, 5.54.

The regio- and stereochemistry of photoproduct 187 were determined by proton decoupling, NOE difference and 2D COSY NMR experiments. See text for details.

(b) Characterization of the Minor [2+2] Adduct 188 (ca. 65% pure).

This product was obtained as an oil.

¹H NMR (400 MHz) δ: 7.60-7.00 (m, 8H, aromatic H), 5.97, 5.28 (m, 2H, CH=CH), 5.40, 4.88 (two d, 2H, J = 11 Hz, CH₂OCO), 4.57 (s, 1H, bridgehead CH), 3.32 (s, 3H, CO₂CH₃), 2.30-1.50 (m, 6H, CH₂CH₂CHRCHR) ppm.


The regio- and stereochemistry were determined based on proton decoupling and NOE difference experiments. See text for details.

(c) Characterization of Methyl 3,3a,5-Trihydro-3-oxo-cis-4-cyclohexadienyl-1H-5,9b[1',2']benzenonaphtho[1,2-c]furan-4-carboxylate (189).

2 mg, m.p. 145-150°C.

IR (KBr) ν_max: 1777 (lactone C=O), 1723 (C=O), 1458, 1301, 1220, 1138, 1021, 760, 683 cm⁻¹.
\(^1\)H NMR (400 MHz) \(\delta\): 7.60-7.00 (m, 8H, aromatic H), 6.19-5.68 (m, 4H, 2 x CH=CH), 5.38, 5.03 (two d, 2H, J = 11 Hz, CH\(_2\)OCO), 5.00 (s, 1H, bridgehead CH), 3.89 (s, 1H, CHCO\(_2\)), 3.55 (s, 3H, CO\(_2\)CH\(_3\)), 2.90-2.80 (m, 1H, CHR(CH=CH), 2.59 (m, 2H, CH\(_2\)(CH=CH)\(_2\)) ppm.

GC-MS m/e (relative intensity): 398 (M\(^+\), 6), 191 (60), 148 (15), 104 (100). Exact mass calculated for C\(_{26}\)H\(_{22}\)O\(_4\): 398.1519. Found: 398.1513.

The regio- and stereochemistry were determined based on proton decoupling and NOE difference experiments. See text for details.

(d) Characterization of Methyl cis-3,3a,4,5-Tetrahydro-3-oxo-1H-5,9b'[1',2']benzenonaphtho[1,2-c]furan-4-carboxylate (190) (ca. 60% pure).

\(^1\)H NMR (400 MHz) \(\delta\): 7.55-7.00 (m, 8H, aromatic H), 5.48, 5.11 (two d, 2H, J = 10 Hz, CH\(_2\)OCO), 4.77 (d, 1H, J = 1 Hz, bridgehead CH), 3.72 (s, 3H, CO\(_2\)CH\(_3\)), 3.29 (d, 1H, J = 7 Hz, CH), 3.04 (dd, 1H, J = 7 Hz and 1 Hz, CH) ppm.

GC-MS m/e (relative intensity): 320 (M\(^+\), 55), 191 (100). Exact mass calculated for C\(_{20}\)H\(_{16}\)O\(_4\): 320.1049. Found: 320.1049.

[2+2] Cycloaddition of the Lactone-Ester 96 with 2,5-Dimethyl-2,4-hexadiene

Analytical photolyses were performed in benzene or acetonitrile. Sensitization experiment was carried out using pure acetone as sensitizer. In all cases, the [2+2] reactions was analyzed by GC (DB-1 or DB-17 column).
On a preparative scale, a solution of the lactone-ester 96 (90 mg, 0.28 mmoles) and 2,5-dimethyl-2,4-hexadiene (100 mg, 1.1 mmoles) in 5 mL of benzene was irradiated for 1 hour. Removal of the solvent left an oil which was chromatographed on silica gel by using 20% ethyl acetate and petroleum ether (30-60°) as the eluting solvent. The separation was as follows: 49 mg (95% pure by GC, 40% yield) of an oily sample which was characterized as the [2+2] cycloaddition adduct 185, 25 mg of a 1:1 mixture of 185 and the stereoisomer 186 and 33 mg of the rearranged photoproduct 153.

(a) Characterization of the [2+2] Photoproduct 185.

This product was obtained as an oil.

\[ ^{1}H \text{NMR (400 MHz) } \delta: 7.65-7.00 \text{ (m, 8H, aromatic H), 5.28, 4.69 (two d, 2H, J = 10 Hz, CH}_2\text{OCO), 5.14 (m, 1H, CH=C(CH}_3\text{)_2), 4.70 (s, 1H, bridgehead CH), 3.30 (broad s, 3H, CO}_2\text{CH}_3\text{), 2.13 (d, 1H, J = 11 Hz, (CH}_3\text{)_2C=CH-CH), 1.66, 1.22 (two d, 6H, J = 1 Hz, (CH}_3\text{)_2C=CH), 1.19, 1.08 (two s, 6H, 2 x CH}_3\text{)} \text{ ppm.} \]

GC-MS m/e determined by chemical ionization (relative intensity): 429 (M+1, 100), 110 (65). Exact mass calculated for C\(_{28}\)H\(_{28}\)O\(_{4}\): 428.1988. Found: 428.1993.

The regio- and stereochemistry of photoproduct 185 were determined by NMR proton decoupling and NOE difference experiments. See text for details.

(b) Characterization of Photoproduct 186 (from a mixture of the isomers 185 and 186).

\[ ^{1}H \text{NMR (400 MHz) } \delta: 7.70-7.05 \text{ (m, 8H, aromatic H), 5.31, 4.77 (two d, 2H, J = 10 Hz, CH}_2\text{OCO), 4.74 (s, 1H, bridgehead CH), 3.38 (d, 1H, J =} \]
9 Hz, (CH₃)₂C=CH-CH), 3.33 (broad s, 3H, CO₂CH₃), 3.05 (d, 1H, J = 9 Hz, (CH₃)₂C=CH-CH), 1.60, 1.51, 1.31, 1.13 (four s, 12H, 4 x CH₃) ppm.


The regio- and stereochemistry of photoproduct 186 were determined based on NMR proton decoupling and NOE difference experiments. See text for details.

Photolysis of Dimethyl 9,10-Dihydro-9-formyl-9,10-ethenoanthracene-11,12-dicarboxylate (94)

In Solution

Analytical solution photolyses were carried out in acetone, acetonitrile and benzene; the photolysates were analyzed by GC (DB-1 column, oven temp. = 210°C). In addition, irradiation of 94 in CDCl₃ was performed and the reaction mixture was analyzed by NMR directly.

In a preparative run, the title compound 94 (2.0 g) was dissolved in 300 ml of acetone. The solution was deoxygenated with nitrogen for 1 hr before and during the photolysis and irradiated for 4 hr with the 450 W Hanovia medium pressure mercury lamp in an immersion well apparatus fitted with a Pyrex glass filter. The photolysis was monitored by GC until more than 99% of the starting material was consumed. Removal of the solvent left 2.0 g (yield 100%) of a yellow oil. Further purification by column chromatography by using 15% ethyl acetate in petroleum ether (30-60°C) as eluting solvent afforded a colorless oil
which was characterized as dimethyl 4b-formyl-4b,8b,8c,8d-tetrahydro-
dibenzo[a,f]cyclopropa[c,d]pentalene-8b,8c-dicarboxylate (118).

IR (neat) \( \nu_{\text{max}} \): 2740 (CHO), 1727(C=O), 1438, 1246, 1215, 760, 742 cm\(^{-1}\).

\(^1\)H NMR (400 MHz) \( \delta \): 10.19 (s, 1H, CHO), 7.45-7.10 (8H, m, aromatic H), 4.56 (s, 1H, CH), 3.90 (s, 3H, OCH\(_3\)), 3.73 (s, 3H, OCH\(_3\)) ppm.

\(^{13}\)C NMR (75 MHz) \( \delta \): 194.60 (CHO), 167.80, 167.77 (2 \times C=O), 147.40, 147.21, 134.40, 133.50, 128.12, 127.87, 127.83, 127.78, 125.95, 125.60, 121.81, 121.62 (aromatic C), 72.2, 68.8, 57.2 (quaternary C), 52.90, 52.59, 49.26 (2 \times CO\(_2\)CH\(_3\) and cyclopropyl CH) ppm.

MS m/e (relative intensity): 348 (M\(^+\), 22), 288 (10), 260 (100), 229 (19), 217 (24), 202 (58), 189 (15). Exact mass calculated for C\(_{21}\)H\(_{16}\)O\(_5\): 348.0998. Found: 348.0993.

Photolyses in the solid state were performed by using single crystals or powders, and the irradiated samples were dissolved in either CDCl\(_3\) directly for \(^1\)H NMR analysis or acetone for GC analysis. The photoproduct observed in the solid state was shown to be the same as that in solution.

**Photochemical Studies on Dimethyl 9,10-Dihydro-9-hydroxymethyl-9,10-
ethenoanthracene-11,12-dicarboxylate (95)**

**In Solution**

Irradiations of compound 95 in organic solvents such as acetone, acetonitrile, benzene, methanol and deuterochloroform were carried out.
Two photoproducts were observed by GC (DB-1 column, oven temp. = 230°C) and $^1$H NMR analyses.

In a preparative run, the title compound 95 (500 mg) in 200 mL of acetone was photolyzed for 2 hours. The solvent was removed in vacuum leaving an oil which was chromatographed on silica gel by using 20-40% diethyl ether in petroleum ether (30-60°) as the eluting solvent; 256 mg (yield 51%) of one of the photoproducts was obtained, which had identical $^1$H NMR and IR spectra to compound 119 prepared independently as described below. The other photoproduct was only observed by $^1$H NMR in the photolysis in CDCl$_3$ and was not isolated. Instead, 148 mg of a solid sample was obtained, which proved to be the same as the dibenzosemibullvalene lactone 153.

Preparation of Dimethyl 4b-Hydroxymethyl-4b,8b,8c,8d-tetrahydro-dibenzo[a,f]cyclopropa[c,d]pentalene-8b,8c-dicarboxylate (119)

Sodium borohydride (200 mg, 5.3 mmoles) was added slowly to a well stirred solution of 1.0 g (2.9 mmoles) of the dibenzosemibullvalene aldehyde 118 in 15 mL of methanol. The mixture was stirred at room temperature for 1 hr and poured into 100 mL of 0.2 M aqueous HCl solution. The solid was collected, washed and dried; 0.90 g of the crude product was obtained. Combined with another preparation, 1.6 g of the crude solid was chromatographed on silica gel and eluted with 40% ethyl acetate in petroleum ether (30-60°) affording 450 mg (yield 45%) of an oil which was characterized as follows.

IR (neat) $\nu_{\text{max}}$: 3480 (OH), 1729(C=O), 1439, 1303, 1246, 1215, 742 cm$^{-1}$.
**1H NMR (400 MHz)** δ: 7.45-7.05 (m, 8H, aromatic H), 4.73-4.55 (m, 2H, CH$_2$OH), 4.43 (s, 1H, CH), 3.87 (s, 3H, CO$_2$CH$_3$), 3.75 (s, 3H, CO$_2$CH$_3$), 3.50-3.30 (dd, 1H, $J = 6$ Hz and 8 Hz, D$_2$O exchangeable, CH$_2$OH) ppm.

**13C NMR (50 MHz)** δ: 169.84, 168.76 (2 x C=O), 149.91, 149.59, 134.73, 133.09, 127.90, 127.71, 127.49, 127.40, 126.10, 125.66, 120.02, 119.84 (aromatic C), 68.94, 67.97, 59.54, 56.32 (CH$_2$OH and quaternary C), 52.75, 52.52, 49.40 (2 x CO$_2$CH$_3$ and cyclopropyl CH) ppm.

**MS m/e (relative intensity):** 350 (M$^+$, 0.1), 318 (6), 274(7), 260 (30), 242 (11), 215 (100), 202 (15). Exact mass calculated for C$_{21}$H$_{18}$O$_5$: 350.1154. Found: 350.1156.

**Photolysis of 94 in the solid state**

Solid state photolyses were performed by using single crystals or powdered samples. Upon irradiation for 10-30 hr, the resulting solids were analyzed by GC and GC-MS.

**Photochemical Studies on Dimethyl 9,10-Dihydro-9-acetoxymethyl-9,10-ethenoanthracene-11,12-dicarboxylate (93c)**

**In Solution**

Analytical photoyses were carried out in acetone and benzene, the reaction mixture was analyzed by GC (DB-1 or DB-17 column).

On a preparative scale, the title compound (500 mg) in 250 mL of acetone was deoxygenated with nitrogen for 1 hr before and as well as during the irradiation. Upon photolysis to completion (35 min) by using the Hanovia medium pressure mercury lamp with a Pyrex filter in an
immersion well apparatus, the solvent was removed in vacuum. The resulting yellow oil (500 mg) was chromatographed on silica gel by using 30% ethyl acetate in petroleum ether (30-60°) as the eluting solvent. This afforded 430 mg (yield 86%) of the 4b-acetoxymethyl isomer 120 as a solid and 60 mg (yield 12%) of the 8b-acetoxymethyl isomer 124 as an oil.

Characterization of Dimethyl 4b-Acetoxymethyl-4b,8b,8c,8d-tetrahydro dibenzo[a,f]cyclopropa[c,d]pentalene-8b,8c-dicarboxylate (120)

The material from the preparative photolysis was recrystallized from methanol to afford colorless prisms, m.p., 137-139°C.

IR (KBr) \( \nu_{\text{max}} \): 1741 (C=O), 1462, 1438, 1364, 1296, 1230, 1044, 758, 742 cm\(^{-1}\).

\(^1\text{H} \) NMR (400 MHz) \( \delta \): 7.68-7.05 (m, 8H, aromatic H), 5.99, 4.29 (two d, 2H, J = 12 Hz, CH\(_2\)OCOCH\(_3\)), 4.39 (s, 1H, CH), 3.88, 3.72 (two s, 6H 2 x CO\(_2\)CH\(_3\)), 1.98 (3, 3H, CH\(_2\)OCOCH\(_3\)) ppm.

\(^{13}\text{C} \) NMR (75 MHz) \( \delta \): 179.79, 168.79, 167.13 (3 x C=O), 149.44, 148.72, 134.56, 132.39, 127.75, 127.70, 127.65, 127.55, 127.09, 125.83, 119.53, 119.48 (aromatic C), 68.64, 65.07, 53.68 (quaternary C), 60.53 (CH\(_2\)OCOCH\(_3\)), 52.63, 52.19, 49.30 (2 x CO\(_2\)CH\(_3\) and CH), 20.56 (CH\(_2\)OCOCH\(_3\)) ppm.

MS m/e (relative intensity): 392 (M\(^+\), 6), 350 (2), 318 (16), 290 (14), 273 (14), 260 (100), 229 (18), 215 (45), 202 (31). Exact mass calculated for C\(_{23}\)H\(_{20}\)O\(_6\): 392.1260. Found: 392.1259.

Anal. calcd. for C\(_{23}\)H\(_{20}\)O\(_6\): C, 70.40; H, 5.14. Found: C, 70.69; H, 5.22.
Characterization of Dimethyl 8b-Acetoxymethyl-4b,8b,8c,8d-tetrahydro-
dibenzo[a,f]cyclopropa[c,d]pentalene-4b,8c-dicarboxylate (124)

IR (neat) \( \nu_{\text{max}} \): 1737 (C=O), 1438, 1245, 1037, 745 cm\(^{-1}\).

\(^1\)H NMR (400 MHz) \( \delta \): 7.39-7.03 (m, 8H, aromatic H), 5.11 (s, 1H, CH), 5.81, 4.41 (two d, 2H, J = 13 Hz, CH\(_2\)OCOCH\(_3\)), 3.83, 3.77 (two s, 6H, 2 x CO\(_2\)CH\(_3\)), 1.99 (s, 3H, COCH\(_3\)) ppm.

MS m/e (relative intensity): 392 (M\(^+\), 10), 360 (21), 332 (27), 318 (27), 290 (97), 258 (62), 230 (93), 215 (40), 202 (100). Exact mass calculated for C\(_{23}\)H\(_{20}\)O\(_6\): 392.1260. Found: 392.1268.

Photolysis of 93c in the Solid State

Photolysis in the solid phase was performed using either single crystals or powdered the crystals. GC was used to monitor the reaction. The products from the solid state photolysis were characterized by means of GC retention time and GC-MS compared to those from the solution phase.

Preparative Photolysis of 3,5-Dihydro-1H-5,9b[1',2']-benzenonaphtho[1,2-c]furan-3-one (98)

A solution of 300 mg of the title compound in 300 mL of acetone was irradiated under nitrogen for 60 min. The solvent was removed in vacuum leaving 300 mg of a white solid, and recrystallization from acetone/hexane afforded 252 mg (yield 84%) of colorless prisms of compound 176, m.p., 243-244\(^\circ\)C.

IR (KBr) \( \nu_{\text{max}} \): 1762 (C=O), 1468, 1376, 1181, 1078, 998, 762, 745, 725, 710 cm\(^{-1}\).
\textsuperscript{1}H NMR (400 MHz) $\delta$: 7.35-7.10 (m, 8H, aromatic H), 5.08 (s, 2H, CH\textsubscript{2}), 3.96 (s, 2H, cyclopropyl CH) ppm.

\textsuperscript{13}C NMR (50 MHz) $\delta$: 175.82 (C=0), 150.85, 135.80, 127.93, 127.80, 125.51, 120.46 (aromatic C), 73.59 (CH\textsubscript{2}O), 65.59, 61.83 (quaternary C), 46.54 (CO\textsubscript{2}CH\textsubscript{3}) ppm.

MS m/e (relative intensity): 260 (M$^+\$, 8), 215 (100), 202 (31), 107 (20). Exact mass calculated for C\textsubscript{18}H\textsubscript{14}O\textsubscript{2}: 262.0994. Found: 262.0985.

Anal. calcd. for C\textsubscript{18}H\textsubscript{14}O\textsubscript{2}: C, 83.06; H, 4.65. Found: C, 82.97; H, 4.66.

Solid state photolysis gave a product that proved to be identical to that observed in solution (compound 176).

Photochemical Studies on Methyl 1-Methyl-3,5-dihydro-3-oxo-1H-5,9b[1',2']-benzenonaphtho[1,2-c]furan-4-carboxylate (97)

In Solution

Analytical photolyses of the methyl lactone-ester 97 in acetone, benzene and acetonitrile were performed and the photolysates were analyzed by GC and \textsuperscript{1}H NMR. In all cases, the same two photoproducts (compounds 168 and 170) were observed.

A preparative photolysis was carried out using 300 mg of the methyl lactone-ester 97 in 300 mL of acetone. After irradiation under nitrogen with the Hanovia medium pressure mercury lamp for 30 min, the solvent was removed in vacuum leaving 300 mg of a solid. Chromatography of this solid on silica gel by using diethyl ether/petroleum ether (30-60°) as the eluting solvent afforded 120 mg (95% pure) of crystalline
168 as the major photoproduct and 12 mg (86% pure) of crystalline 170 as the minor one; the remainder of the material was a mixture of the two photoproducts. Further purification of the mixture gave only a small amount of the major product. The two photoproducts were fully characterized as a pair of epimers. They were distinguished from one another by proton decoupling and NOE difference experiments.

Characterization of the major photoproduct 168

m.p. 222-224°C.

IR (KBr) $\nu_{\text{max}}$: 1762 (lactone C=O), 1729 (C=O), 1474, 1457, 1440, 1358, 1331, 1231, 1156, 1067, 766 cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.60-7.10 (m, 8H, aromatic H), 5.28 (q, 1H, J = 7 Hz, CHCH$_3$), 5.11 (s, 1H, CH(Ph)$_2$), 3.80 (s, 3H, CO$_2$CH$_3$), 2.15 (d, 3H, J = 7 Hz, CHCH$_3$) ppm.

$^{13}$C NMR (75 MHz) $\delta$: 169.33, 167.72 (2 x C=O), 147.60, 146.75, 132.26, 131.00, 128.77, 128.65, 127.64, 127.37, 125.78, 125.11, 122.84, 121.97 (aromatic C), 75.61, 55.48, 52.86 (CO$_2$CH$_3$, CH(Ph)$_2$ and CHCH$_3$), 69.7, 65.9, 58.3 (quaternary C), 20.47 (CHCH$_3$) ppm.

MS m/e (relative intensity): 332 (M$^+$, 15), 304 (21), 272(32), 262 (42), 244 (42), 229 (31), 215 (15), 202 (100). Exact mass calculated for C$_{21}$H$_{16}$O$_4$: 332.1049. Found: 332.1055.

Stereochemistry of this compound was determined by the proton decoupling and NOE difference experiments. See text for details.

Characterization of the minor photoproduct 170

m.p. 192-202°C.
IR (KBr) ν max: 1763 (lactone C=O), 1730 (C=O), 1475, 1440, 1353, 1331, 1231, 1171, 1156, 1067, 766 cm⁻¹.

¹H NMR (400 MHz) δ: 7.55-7.12 (m, 8H, aromatic H), 5.56 (q, 1H, J = 7 Hz, CHCH₃), 5.12 (s, 1H, CH(Ph)₂), 4.79 (s, 3H, CO₂CH₃), 1.55 (d, 3H, J = 7 Hz, CHCH₃) ppm.

GC-MS m/e (relative intensity): 332 (M⁺, 10), 272 (22), 262 (35), 245 (18), 229 (38), 215 (33), 202 (100). Exact mass calculated for C₂₁H₁₆O₄: 332.1049. Found: 332.1046.

Stereochemistry of this product was determined by the proton decoupling and NOE difference experiments. See text for details.

Photolysis of the Methyl Lactone-Ester 97 in the Solid State

Single crystals or powders of the methyl-substituted lactone 97 were irradiated using the Hanovia 450 W lamp with a Pyrex filter for 5-20 hours. The photolyzed solid samples were analyzed by GC, GC-MS and ¹H NMR. It was found that the photolysis of the methylated lactone in the solid formed another product in addition to the same two products formed in solution phase. The product ratio was determined based on GC and ¹H NMR area integration. By varying the time of irradiation, the product ratios at the different conversions were obtained. It was found that the ratios remained constant under the experimental conditions.

A preparative photolysis in the solid state was conducted using 1.0 g of the powdered lactone. After irradiation for 30 hours, GC showed that conversion of the starting material was ca. 90%. However, chromatography of the resulting yellow solid on silica gel by using 15-30% ethyl acetate/petroleum ether (30-60°) gave no separation of the
solid state photoprodut from the mixture. Further column chromatography on deactivated neutral alumina eluted with benzene/petroleum ether (30-60°) was also unsuccessful. Therefore, an independent preparation of the solid state photoprodut was carried out as described in the next paragraph.

Independent Preparation of the Solid State Photoprodut 171

The dibenzosemibullvalene aldehyde 118 (1.40 g, 4.02 mmoles), prepared previously, in 100 mL of anhydrous diethyl ether was kept stirring under nitrogen at -78°C for 15 min, whereupon 1.5 mL of methyl magnesium bromide available from Aldrich (3 M, ca. 4.5 mmoles) were added slowly. The resulting mixture was stirred at -78°C for 2 hr, and poured into cold dilute aqueous HCl. Diethyl ether was added to extract the products. The organic layer was separated and the aqueous layer was further extracted with diethyl ether. The combined ether extracts were washed, dried and concentrated in vacuum leaving 1.22 g of an oil. Chromatography of this oil on silica gel by using 20-25% ethyl acetate in petroleum ether (30-60°) as eluant gave two products (diastereomers 173 and 174) which are characterized below.

(a) Characterization of the Diastereomer 173

The material was obtained as an oil, 505 mg (yield 35%).

IR (neat) ν_max: 3450 (OH), 1734 (C=O), 1438, 1288, 1246, 1119, 754 cm⁻¹.

¹H NMR (400 MHz) δ: 7.45-7.05 (m, 8H, aromatic H), 5.19 (m, 1H, CH(OH)CH₃), 4.37 (s, 1H, cyclopropyl CH), 3.89, 3.74 (two s, 6H, 2 x
CO\textsubscript{2}CH\textsubscript{3}), 3.67 (m, 1H, D\textsubscript{2}O exchangeable, OH), 1.46 (d, 3H, J = 6 Hz, CH(OH)CH\textsubscript{3}) ppm.

\textsuperscript{13}C NMR (50 MHz) \(\delta\): 170.21, 168.92 (2 x C=O), 151.36, 149.98, 134.42, 132.64, 127.86*, 127.28, 127.15, 126.00, 125.63, 120.47, 120.13 (aromatic C), 72.32, 68.41, 55.28 (quaternary C), 65.12, 52.73*, 49.77, 21.03 (3 x CH\textsubscript{3} and 2 x CH) ppm.

* Possibly two carbons here.

MS m/e (relative intensity): 364 (M\textsuperscript{+}, 0.1), 332 (4), 301 (1), 288 (17), 273 (12), 260 (53), 245 (12), 229 (100), 215 (15), 202 (25). Exact mass calculated for C\textsubscript{22}H\textsubscript{2}O\textsubscript{5}: 364.1311. Found: 364.1316.

(b) Characterization of the Diastereomer 174

480 mg (yield 33%). This material was recrystallized from acetone/hexane affording colorless prisms, m.p. 138-141°C.

IR (KBr) \(\nu_{\text{max}}\): 3450 (OH), 1729 (C=O), 1475, 1438, 1286, 1247, 1159, 1120, 743 cm\textsuperscript{-1}.

\textsuperscript{1}H NMR (400 MHz) \(\delta\): 7.57-6.95 (m, 8H, aromatic H), 5.16 (m, 1H, CH(OH)CH\textsubscript{3}), 4.40 (s, 1H, cyclopropyl CH), 4.19 (m, 1H, D\textsubscript{2}O exchangeable, OH), 3.86, 3.80 (two s, 6H, 2 x CO\textsubscript{2}CH\textsubscript{3}), 1.35 (d, 3H, J = 7 Hz, CH(OH)CH\textsubscript{3}) ppm.

\textsuperscript{13}C NMR (50 MHz) \(\delta\): 170.68, 168.93 (2 x C=O), 151.07, 150.70, 134.05, 132.16, 128.05, 127.82, 127.24, 127.19, 126.45, 125.47, 120.10* (aromatic C), 72.32, 67.79, 55.25 (quaternary C), 65.72, 52.83, 52.76, 49.58, 19.33 (3 x CH\textsubscript{3} and 2 x CH) ppm.

* Possibly two carbons here.
MS m/e (relative intensity): 364 (M+, 0.6), 348 (0.8), 332 (8), 288 (27), 273 (11), 260 (78), 245 (9), 229 (100), 215 (14), 202 (26).

Exact mass calculated for C₂₂H₂₀O₅: 364.1311. Found: 364.1305.

Anal. calcd. for C₂₂H₂₀O₅: C, 72.51; H, 5.53. Found: C, 72.65; H, 5.49.

The two diastereomers were shown to undergo decomposition under the GC conditions forming the corresponding lactones by elimination of methanol. Diastereomer 173 was the precursor leading to dibenzosemibullvalene lactone 171, which was observed in the solid state photoreaction of 97. This was confirmed by the following acid-catalyzed cyclization and GC-MS comparison. Diastereomer 174 was transformed into the isomeric lactone 174 by cyclization under acidic condition.

Cyclization of the Diastereomer 173 to the lactone 171 (solid state photoproduct)

p-Toluenesulfonic acid (70 mg) in 60 mL of benzene was refluxed for 30 min, and water was removed by means of a Dean-Stark tube. Diastereomer 173 (350 mg) in 10 mL of benzene was added to the above hot solution. The resulting mixture was refluxed for an additional 20 min. The organic layer was washed with 5% aqueous NaHCO₃ twice, and then water. The dried benzene solution was concentrated in vacuum leaving 315 mg of an oil which solidified upon standing. Recrystallization from acetone/hexane afforded 195 mg (yield 61%) of colorless prisms of 171, m.p., 202-204°C.

IR (KBr) ν max: 1772 (lactone C=O), 1720 (C=O), 1473, 1433, 1386, 1338, 1299, 1238, 1219, 1198, 1162, 1133, 1098, 1060, 768, 742 cm⁻¹.
$^1$H NMR (400 MHz) $\delta$: 7.10-7.73 (m, 8H, aromatic H), 5.35 (q, 1H, J = 6 Hz, CHCH$_3$), 4.81 (s, 1H, cyclopropyl CH), 3.95 (s, 3H, CO$_2$CH$_3$), 1.89 (d, 3H, J = 6 Hz, CHCH$_3$) ppm.

$^{13}$C NMR (50 MHz) $\delta$: 171.35, 166.73 (2 x C=O), 151.93, 147.10, 135.12, 133.83, 128.63, 128.47, 127.92, 127.77, 127.74, 126.27, 123.23, 120.37 (aromatic C), 80.24 (CO$_2$CH$_3$), 70.19, 66.85, 57.12 (quaternary C), 52.94, 50.28 (CHCH$_3$ and cyclopropyllic CH), 20.46 (CHCH$_3$) ppm.

MS m/e (relative intensity): 332 (M$^+$, 2), 288 (15), 273 (10), 260 (45), 245 (11), 229 (100), 215 (14), 202 (22). Exact mass calculated for C$_{21}$H$_{16}$O$_4$: 332.1049. Found: 332.1052.

Anal. calcd. for C$_{21}$H$_{16}$O$_4$: C, 75.89; H, 4.85. Found: C, 75.79; H, 4.87.

The structure of this compound was confirmed by an X-ray diffraction analysis. The crystal data were as follows: C$_{21}$H$_{16}$O$_4$, monoclinic, space group P2$_1$/n, a = 8.1129 (9), b = 13.1445 (9), c = 15.646 (1)Å, $V = 1651.6$ (2)Å$^3$, Z = 4, $D_x = 1.34$ g/mL, R = 0.042. The details will be published elsewhere.

Cyclization of the Diastereomer 174 to the isomer 172.

The same procedures were followed as described above, 250 mg of diastereomer 174 in 8 mL of benzene was added to 60 mL of a hot benzene solution containing 60 mg of p-toluenesulfonic acid (water was removed by a Dean-Stark tube prior to the addition). The mixture was refluxed for 30 min. Upon workup, 250 mg of a solid was obtained; 185 mg of this solid was recrystallized from acetone/hexane to afford 100 mg (yield 44%) of colorless prisms of 172, m.p., 185-187°C.
IR (KBr) \( \nu_{\text{max}} \): 1774 (lactone C=O), 1727 (C=O), 1472, 1441, 1336, 1297, 1214, 1175, 1117, 1058, 1007, 741, 510 cm\(^{-1}\).

\(^1\)H NMR (400 MHz) \( \delta \): 7.59-7.11 (m, 8H, aromatic H), 5.39 (q, 1H, J = 6 Hz, CH\(\text{CH}_3\)), 4.88 (s, 1H, cyclopropyl CH), 3.94 (s, 3H, CO\(\text{OCH}_3\)), 1.77 (d, 3H, J = 6 Hz, CH\(\text{CH}_3\)) ppm.

\(^{13}\)C NMR (50 MHz) \( \delta \): 171.145, 166.70 (2 x C=O), 151.48, 147.29, 135.89, 132.68, 128.64, 128.23, 127.74*, 127.68, 126.14, 123.27, 120.18 (aromatic C), 80.18 (CO\(\text{OCH}_3\)), 70.12, 66.92, 56.75 (quaternary C), 52.83, 50.72 (CH\(\text{CH}_3\) and cyclopropyllic CH), 20.54 (CH\(\text{CH}_3\)) ppm.

* Possibly two carbons here.

MS m/e (relative intensity): 332 (M\(^+\), 2), 288 (21), 273 (12), 260 (57), 229 (100), 215 (36), 202 (50). Exact mass calculated for C\(_{21}\)H\(_{16}\)O\(_4\): 332.1049. Found: 332.1048.

Anal. calcd. for C\(_{21}\)H\(_{16}\)O\(_4\): C, 75.89; H, 4.85. Found: C, 76.00; H, 4.86.

Photochemical Studies on Dimethyl 9,10-Dihydro-9-chloromethyl-9,10-ethenoanthracene-11,12-dicarboxylate 93d

In Solution

Analytical photolyses were performed in benzene, acetone, acetonitrile and chloroform. In all runs, the photoreaction was monitored by GC (DB-1 or DB-17 column).

On a preparative scale, the title compound (1.0 g) dissolved in 250 mL of acetone was photolyzed for 4 hours under nitrogen a
atmosphere. The solvent was removed after irradiation and the resulting oil was chromatographed on silica gel by using 20-30% diethyl ether/petroleum ether (30-60°) as the eluting solvent; 674 mg (yield 67%) of colorless prisms obtained by recrystallization from chloroform/methanol were isolated as the major photoproduct (4b-isomer 194), and 260 mg (yield 26%) of a viscous oil were obtained as the minor one (8b-isomer 195). Both products were characterized as follows:

Characterization of Dimethyl 4b-chloromethyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[c,d]pentalene-8b,8c-dicarboxylate (194)

m.p. 144-145°C.

IR (KBr) $\nu_{\text{max}}$: 1736 (C=O), 1436, 1298, 1259, 1238, 1224, 759, 743 cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.70-7.00 (m, 8H, aromatic H), 4.68, 4.58 (two d, 2H, J = 12 Hz, CH$_2$Cl), 4.40 (s, 1H, cyclopropyl CH), 3.89, 3.78 (two s, 6H, 2 x CO$_2$CH$_3$) ppm.

$^{13}$C NMR (75 MHz) $\delta$: 168.72, 167.11 (2 x C=O), 149.40, 149.04, 134.56, 132.52, 127.82, 127.75* , 127.70, 127.20, 125.90, 119.52, 119.25 (aromatic C), 68.63, 67.42, 53.56 (quaternary C), 52.71, 52.52, 49.01 (cyclopropyl CH and 2 x CO$_2$CH$_3$), 41.35 (CH$_2$Cl) ppm.

* Possibly two carbons here.

MS m/e (relative intensity): 370 (M+2, 10), 368 (M$^+$, 31), 340 (19), 319 (27), 305 (100), 291 (32), 273 (23), 260 (72), 245 (22), 229 (38), 215 (78), 202 (65), 189 (28). Exact mass calculated for C$_{21}$H$_{17}$ClO$_4$: 368.0815. Found: 368.0815.

Anal. calcd. for C$_{21}$H$_{17}$ClO$_4$: C, 68.39; H, 4.65; Cl, 9.63. Found: C, 68.31; H, 4.65; Cl, 9.44.
Characterization of Dimethyl 8b-chloromethyl-4b,8b,8c,8d-tetrahydro-
dibenzo[a,f]pentalene-4b,8c-dicarboxylate (195)

IR (neat) \( \nu_{\text{max}} \): 1729 (C=O), 1437, 1247, 913, 742 cm\(^{-1}\).

\(^1\)H NMR (300 MHz) \( \delta \): 7.45-7.00 (m, 8H, aromatic H), 5.13 (s, 1H, CH), 4.75, 4.60 (two d, 2H, J = 12 Hz, CH\(_2\)Cl), 3.88, 3.80 (two s, 6H, 2 x CO\(_2\)CH\(_3\)) ppm.

\(^{13}\)C NMR (75 MHz) \( \delta \): 167.99, 167.85 (2 x C=O), 150.92, 150.00, 134.41, 134.30, 128.34*, 126.95*, 125.41, 125.11, 121.36, 121.19 (aromatic C), 67.2, 61.3, 59.0 (quaternary C), 56.21, 52.83, 52.50 (CH and 2 x CO\(_2\)CH\(_3\)), 42.16 (CH\(_2\)Cl) ppm.

* Possibly two carbons here.

MS m/e (relative intensity): 370 (M+2, 1.4), 368 (M\(^+\), 4.3), 336 (14), 308 (47), 274 (25), 249 (66), 215 (100). Exact mass calculated for C\(_{21}\)H\(_{17}\)ClO\(_4\): 368.0815. Found: 368.0816.

Photolysis of 93d in the Solid State

Solid state photolyses were performed using either single crystals or powders. The photoproducts were analyzed by GC and GC-MS. Although new photoproducts were observed by GC, the preparative photolysis in the solid state was not carried out due to the limited conversion of the solid sample. Instead, the minor products from the solid photolysis were isolated from a solution photoreaction in chloroform. 9-Chloromethyl dibenzobarrelene diester 93d (1.0 g) in 300 mL of chloroform was irradiated under nitrogen with the Hanovia 450 W lamp for 6 hours. The solvent was removed by evaporation in vacuum and the resulting oil was chromatographed on silica gel twice. The first column using ethyl acetate/petroleum ether (30-60\(^{\circ}\)) as the eluting
solvent gave 570 mg of the solution major product 194. The second column using diethyl ether/petroleum ether (30-60°) as eluant led to the partial separation of the two minor products corresponding to those from the solid state photolysis. By fractional crystallization from the diethyl ether/petroleum ether (30-60°), each product was obtained separately and characterized by spectroscopic methods and X-ray diffraction analyses.

Characterization of Dimethyl 5,5a,10,10a-Tetrahydro-cis-5-chloro-10-methenoindeno[2,1-a]indene-5a,10a-dicarboxylate (197)

m.p. 209-212°C.

IR (KBr) ν_{max}: 1743 (C=O), 1640 (C=C), 1459, 1434, 1242, 1221, 1047, 1015, 896, 769, 705 cm⁻¹.

¹H NMR (300 MHz) δ: 7.90-7.30 (m, 8H, aromatic H), 5.77 (s, 2H, C=CH₂), 5.50 (s, 1H, -CHCl-), 3.68, 3.65 (two s, 6H, 2 x CO₂CH₃) ppm.

MS m/e (relative intensity): 370 (M⁺, 2.7), 368 (M⁺, 7.5), 334 (14), 308 (24), 274 (63), 229 (16), 215 (100). Exact mass calculated for C₂₁H₁₇ClO₄: 368.0815. Found: 368.0808.

The structure of 197 was determined by an X-ray diffraction analysis. The space group, Pc or P2₁/c. R = 0.094. Details will be published elsewhere.

Characterization of Dimethyl 5,5a,10,10a-Tetrahydro-trans-5-chloro-10-methenoindeno[2,1-a]indene-5a,10a-dicarboxylate (196)

m.p. 158.5-159.5°C.
IR (KBr) \( \nu_{\text{max}} \): 1742 (C=O), 1642 (C=C), 1476, 1457, 1434, 1228, 1175, 1136, 1080, 1046, 1000, 913, 783, 768, 735 \text{ cm}^{-1}.

\(^1\text{H} \text{ NMR} \text{ (300 MHz)} \delta: \) 7.85-7.25 (m, 8H, aromatic H), 6.42, 6.13, 5.87 (three s, 3H, C=CH\(_2\) and -CHCl-), 3.66, 3.65 (two s, 6H, 2 x CO\(_2\)CH\(_3\)) ppm.

MS m/e (relative intensity): 370 (M+2, 7.5), 368 (M\(^+\), 20.2), 334 (6), 308 (100), 274 (34), 249 (36), 229 (37), (215 (98). Exact mass calculated for C\(_{21}\)H\(_{17}\)ClO\(_4\): 368.0815. Found: 368.0816.

The structure of compound 196 was also determined by an X-ray diffraction analysis. The space group, PT, \( R = 0.045 \). Details will be published elsewhere.

Photolysis of Racemic and Optically Active Dimethyl 9,10-Dihydro-9-(\(\alpha\)-N-acetylamino-\(\alpha\)-methyl)acetoxy-9,10-ethenoanthracene-11,12-dicarboxylate (93b)

Analytical photolyses were performed in acetone and acetonitrile. Although two regioisomeric photoproducts (each regioisomer gave two diastereomers) were formed, they could not be distinguished from each other under the GC conditions (DB-1 column, oven temp = 260°C).

Characterization of these photoproducts relied on \(^1\text{H} \text{ NMR}. The title compound 93b (20 mg, either racemic or optically active) in 10 mL of acetone was photolyzed using the Hanovia medium pressure mercury lamp with a Pyrex filter until over 95% of the starting material was consumed. Removal of the solvent left an oil which was dissolved in CDCl\(_3\) and subjected to \(^1\text{H} \text{ NMR analysis}. In another run, the sample (ca. 5 mg) in CDCl\(_3\) was irradiated to more than 99% conversion. Then the
sample solution was analyzed by $^1$H NMR directly. It was shown that the photoreactions in the two runs had the same NMR spectra. Refer to the previous text for the spectroscopic details. Preparative photolysis was also carried out using 200 mg of compound 93b, however, separation of the photoproducts by column chromatography was unsuccessful.

Photoreactions in the solid state were conducted using both single and powdered crystals (optically active). In each case, the solid sample (2-20 mg) was irradiated with the Hanovia 450 W lamp for 20-40 hr and the resulting sample was dissolved in CDCl$_3$ and analyzed by $^1$H NMR.

Photolysis of the Racemic and Optically Active Dimethyl 9,10-Dihydro-9-(α-phenyl-α-methoxy)acetoxymethyl-9,10-ethenoanthracene-11,12-dicarboxylate (93a)

The photolyses in solution and in the solid state were carried out in the same way as described in the case of compound 93b. $^1$H NMR techniques were used to analyze and characterize the photoproducts in each run. No further purification of the photoproducts was performed. See text for $^1$H NMR spectra.

Photolysis of Racemic and Optically Active Methyl 9,10-Dihydro-9-(α-phenyl-α-methoxy)acetoxymethyl-9,10-ethenoanthracene-11-carboxylate (99)

Both direct (in CDCl$_3$) and acetone-sensitized photolyses were carried out using the Hanovia 450 W lamp with a Pyrex filter. The photolysis was monitored by GC (DB-1 column) until 95% of the starting material was consumed. The photoproducts (a pair of diastereomers) were analyzed and characterized by $^1$H NMR and GC-MS. Crystalline samples were
irradiated for 40 hr (10% conversion) and the resulting solid was also analyzed by $^1$H NMR in deuterochloroform. See text for $^1$H NMR spectra.

GC-MS of the mixture of photoproducts. m/e (relative intensity): 440 ($M^+$, 0.3), 215 (23), 121 (100).

Photochemical Studies on Racemic Methyl 9,10-Dihydro-9-(α-phenyl-α-methoxy)acetoxymethyl-9,10-ethanoanthracene-12-carboxylate (100)

Analytical photolyses was carried out in acetone, acetonitrile and deuterochloroform. In all three solvents, it was observed by GC (DB-1 column) and $^1$H NMR that one photoproduct was formed. In a preparative run, the racemic sample 100 (150 mg) in 15 mL of acetone was irradiated using the Hanovia lamp with a Pyrex filter for 5 hr. Removal of the solvent left a gum which solidified on standing. Recrystallization of the solid from chloroform/methanol afforded 95 mg (yield 63 %) of colorless crystals, m.p., 118-121°C.

IR (KBr) $\nu$$_{max}$: 1739 (C=O), 1716 (C=O), 1459, 1438, 1330, 1301, 1240, 1215, 1181, 1131, 1098, 764, 726 cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.50-6.90 (m, 8H, aromatic H), 5.30 (two d, 2H, J = 11 Hz, CH$_2$OCOR), 4.69 (s, 1H, OCOCH(Ph)OMe), 3.76 (two d, 2H, J = 7 Hz, cyclopropyl CHCH), 3.46, 3.34 (two s, 6H, CO$_2$CH$_3$ and OCOCH(Ph)OCH$_3$) ppm.

$^{13}$C NMR (50 MHz) $\delta$: 170.62 (C=O), 149.27, 149.16, 136.02, 135.11, 135.01, 128.44, 127.25, 127.21, 127.01, 126.97, 124.88, 124.81, 119.59 (aromatic C), 82.23 (OCOCH(Ph)OCH$_3$), 62.76, 62.65, (quaternary C), 61.60 (CH$_2$OCO), 57.33, 51.63, 46.30, 46.12 (cyclopropyl CHCH, CO$_2$CH$_3$ and PhCHOCH$_3$) ppm.
MS m/e (relative intensity): 440 (M⁺, 1), 290⁻ (1), 215 (24), 121 (100). Exact mass calculated for C₂₈H₂₄O₅: 440.1624. Found: 440.1629.
Anal. calcd. for C₂₈H₂₄O₅: C, 76.35; H, 5.49. Found: C, 76.48; H, 5.52.

C. Quantum Yields and Quenching Studies

Purification of Solvents and Reagents

Quantum yield measurements and quenching studies were conducted in benzene in all cases. Benzene was made thiophene-free by known procedures prior to the study. Valerophenone, used as the actinometer, was distilled and stored in the dark at low temperature. The starting materials and their photoproducts used in the measurements were purified by recrystallization from a suitable solvent. No further purification was made on the alkanes, n-C₁₄H₃₀ and n-C₂₄H₅₀ from Aldrich Chemical Co., which were used as internal standards.

GC Detector (FID) Response Calibrations

The relative response of the GC detector to the internal standards and photoproducts whose quantum yields of formation were under study was calibrated. Both the internal standard and the photoproduct were weighed accurately and dissolved in benzene. This sample solution was injected into the GC 4-5 times and the GC area ratio of the two peaks was averaged. The GC response of n-C₁₄H₃₀, the internal standard, and acetophenone (purified by distillation), which is the photoproduct from the actinometer valerophenone, were measured on the Carbowax 20M column.
The GC response of each photoproduct and $n$-$C_{24}H_{50}$ was performed on DB-1 and DB-17 columns.

**Apparatus**

A merry-go-round apparatus was used in the determination of the quantum yields and quenching studies, and the whole setup was immersed in a water bath. The temperature was kept at 16-18°C by circulating water. The Hanovia medium pressure mercury lamp (450 W) was used as a light source, and the 313 nm line from the lamp was isolated by a combination of the filter solution (0.002 M aqueous $K_2CrO_4$ containing 5% $K_2CO_3$, wt/wt) and 7-54 Corning glass filters.

**Preparation of the Sample Solutions**

Valerophenone actinometry, of which the quantum yield of acetophenone formation had been established in the literature, was used for the calculation of the number of photons emitted by the lamp ($\Phi = 0.3$ at a concentration of 0.1 M of valerophenone in benzene). A solution of 0.1 M valerophenone in benzene containing 1.0 mg/mL of tetradecane was prepared prior to the photolysis.

The sample solution was prepared in such a way that the concentration of the substrate was high enough to ensure optical opacity at 313 nm. The solution contained the internal standard of tetradodecane (1.0 mg/mL).
Irradiations

Both the sample and the actinometer solutions were irradiated under the same photolysis conditions. For each set, the sample and actinometer solutions were duplicated in Pyrex tubes (3.0 mL each). All the solutions were degassed by three freeze-pump-thaw cycles and sealed with paraffin films. The photolyses were monitored by GC and the conversion was kept below 10%. Afterwards, the number of photons emitted by the lamp and the number of moles of the photoproduct formed in the photolysis was calculated from the GC area ratios.

Calculation of Quantum Yields

Quantum yields (Φ) were calculated by the following equation:

\[
\Phi = \frac{\text{moles of given species formed}}{\text{moles of photons absorbed by the system}}
\]

In each experiment, the quantum yields at various conversions of the starting material were calculated. A plot of each calculation against the percentage conversion gave a straight line, and the quantum yield at zero percent conversion was obtained from the intercept of the line. Three independent measurements were performed for each substrate. Finally, the average value of the quantum yield (Φ) was determined from the three runs.

Quenching Studies

The same procedures as in the quantum yield measurement were followed except that a certain amount of quencher (2,5-dimethyl-2,4-
hexadiene or 1,3-cyclohexadiene) was added to each of the sample solutions. In each quenching experiment, a series of the sample solutions containing a different amount of the quencher was irradiated and the ratio of $\Phi_o/\Phi$ was calculated for each quencher concentration where $\Phi_o =$ quantum yield without the quencher, and $\Phi =$ quantum yield in the presence of the quencher. The $\Phi_o/\Phi$ value was plotted against the concentration of the quencher, $[Q]$, and a straight line was obtained by the Stern-Volmer equation where $k_q$ is the quenching rate constant and $\tau$ is the lifetime of the excited state of the substrate. From the slope ($k_q\tau$), the lifetime value can be calculated if $k_q$ value is assumed to be a rate constant of diffusion ($5 \times 10^{-9} \text{ M}^{-1}\text{s}^{-1}$ in benzene).

$$\frac{\Phi_o}{\Phi} = 1 + k_q\tau[Q]$$
REFERENCES


107. George, M. V., personal communication to J. R. Scheffer.


