SOLUTION AND CRYSTALLINE STATE PHOTOCHEMISTRY OF
2,3-DIACYL-SUBSTITUTED BENZOBARRELENES

by

Melvin Peng-Kwun Yap

B.Sc., University of British Columbia, Canada, 1986

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in
THE FACULTY OF GRADUATE STUDIES
(DEPARTMENT OF CHEMISTRY)

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April 1992

© Melvin Peng-Kwun Yap, 1992
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of CHEMISTRY

The University of British Columbia
Vancouver, Canada

Date June 23/92
ABSTRACT

A series of 2,3-diacyl-substituted benzobarrelenes was synthesized and their photochemistry investigated in the crystalline state and in solution media. The differences in photoreactivity and product selectivity between these compounds in the two phases were determined, and structure-reactivity correlations were established based on X-ray crystallographic data.

The photochemistry of the title series is multiplicity-dependent; benzocyclooctatetraene is formed through the singlet excited state and benzosemibullvalenes are products of the triplet excited state. Regioisomeric benzosemibullvalenes are derived from the different "di-π-methane" rearrangement pathways taken.

Solution phase, triplet-state photoisomerizations of a number of symmetrically disubstituted benzobarrelenes gave two benzosemibullvalenes—1,2-disubstituted and 2a,6c-disubstituted. Selectivity is controlled predominantly by electronic effects.

The use of a benzoyl substituent as one of the acyl groups enhances intersystem crossing, thereby enabling the substrate to achieve the triplet excited state through direct irradiation. Photolyses of several unsymmetrical benzoyl/ester benzobarrelenes in the solid state gave strikingly unusual regioselectivities between the 1,2-disubstituted and the 2a,6c-disubstituted products. The presence of specific lattice interactions was determined to be the major factor responsible; electronic effects were shown to play a much less significant role. Photochemical investigation of the benzoyl/methyl ester system was also conducted in polymer matrix media to show variation in product
selectivity.

Ammonium and metal ion salts of benzobarrelene-2,3-dicarboxylic acid were photolyzed in solution and the crystalline phase; their triplet product selectivities were recorded to further support the dominance of specific lattice interaction effects over electronic effects.

Discovery of a rare "tri-π-methane" rearrangement in some dibenzo-barrelenes prompted the design and synthesis of dimethyl 1,4-dihydro-1,4,5,8-tetramethyl-1,4-ethenonaphthalene-2,3-dicarboxylate. This successfully underwent the tri-π-methane rearrangement in both solution and solid states. The novel selectivity was rationalized in terms of intramolecular steric effects rather than on the basis of electronic stabilizing effects.

Many benzosemibullvalene photoproducts were found to undergo [1,3] shifts from a secondary photolysis; coincidentally, these rearrangements lead to regioisomeric benzosemibullvalenes. As a result, many exist in unusual photostationary states. It was found that benzosemibullvalenes require a carbonyl substituent adjacent to the bond cleaved in order for the [1,3] shift reaction to take place.
TABLE OF CONTENTS

TITLE PAGE .......................................................... i
ABSTRACT .................................................................. ii
TABLE OF CONTENTS ............................................... iv
LIST OF FIGURES ...................................................... vi
ACKNOWLEDGEMENT ................................................. xiii
DEDICATION ............................................................. xiv

INTRODUCTION ......................................................... 1
  I. History ............................................................. 2
  II. The Excited State .............................................. 3
  III. The Di-π-Methane Rearrangement ....................... 8
  IV. The Topochemical Principle ................................ 17
  V. Solid State Reactivity ........................................ 19
  VI. Photochemical [1,3] Sigmatropic Shifts .................. 27
  VII. Photochemistry of Benzobarrelenes .................... 32
  VIII. Object of Research ......................................... 38

RESULTS AND DISCUSSION ....................................... 44
  PART I. Preparation of Starting Materials .................. 45
  PART II. Characterization of Disubstituted Benzosemibullvalene Photoproducts ......................... 57
  PART III. Photochemistry of Symmetrically Disubstituted Benzobarrelenes ............................... 73
    A. Photochemistry of Dimethyl 1,4-Dihydro-1,4-etheno-naphthalene-2,3-dicarboxylate (29) ........... 73
    B. Photochemistry of 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid (40) ................. 82
C. Photochemistry of 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Anhydride (41).................. 94

D. Photochemistry of 2,3-Dibenzoyl-1,4-dihydro-1,4-ethenonaphthalene (42)................................. 102

PART IV. Photochemistry of Unsymmetrically Disubstituted Benzobarrelenes............................... 109

A. Photochemistry of Methyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (43).......... 109

B. Photochemistry of Ethyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (44).......... 129

C. Photochemistry of Isopropyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (45).... 135

PART V. Photochemistry of Benzobarrlene Salts (48-54)............. 147

PART VI. Photochemistry of Dimethyl 1,4,5,8-Tetramethyl-1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (47) 157

PART VII. Photochemical [1,3] Shifts in Benzosemibullvalenes.. 171

EXPERIMENTAL................................................................. 172

General Procedures...................................................... 175

I. Synthesis of Starting Materials................................. 179

II. Photochemistry of Substrates...................................... 205

A-D. Photochemistry of Symmetrically Disubstituted Benzobarrelenes........................................ 205

E-G. Photochemistry of Unsymmetrically Disubstituted Benzobarrelenes..................................... 222

H. 1,4-Dihyro-1,4-ethenonaphthalene-2,3-dicarboxylate Salts............................................... 245

I. Dimethyl 1,4,5,8-Tetramethyl-1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate.................. 246

III. Quantum Yield Studies............................................ 252

REFERENCES............................................................... 255
LIST OF FIGURES

INTRODUCTION

Figure 0.01 Energy Diagram for Selected Transitions................. 4
Figure 0.02 Energy Diagram for General Molecular Photophysical Processes.............................................. 5
Figure 0.03 1-Benzoyl-4-(a-naphthyl)-bicyclo[2.2.2]-octane (3) and a Rigid Benzophenone-Naphthalene Donor-Acceptor System (4).............................. 7
Figure 0.04 Di-π-Methane Mechanism Represented in 1,4-Pentadiene (6)............................................................... 9
Figure 0.05 Examples of Acyclic Di-π-Methane Systems............. 10
Figure 0.06 Examples of Cyclic Di-π-Methane Systems.............. 11
Figure 0.07 Examples of Initial Bond Formation Selectivity in the Di-π-Methane Rearrangement.............................. 14
Figure 0.08 Examples of Secondary Bond Cleavage Selectivity in the Di-π-Methane Rearrangement....... 16
Figure 0.09 Photochemistry of Trans Cinnamic Acid in Solution and Crystalline States............................... 18
Figure 0.10 Cohen's Concept of the Reaction Cavity................. 20
Figure 0.11 Example of a Unimolecular Solid State Reaction................................................................. 22
Figure 0.12 Photodimerization of Benzylidenecyclo- pentanone (17).............................................................. 23
Figure 0.13 Enantioselective Transformation of Dibenzo- barrelene Diisopropyl Ester (18)................................. 24
Figure 0.14 Lattice Environment of Dibenzobarrelene Diisopropyl Ester 18 .................................................. 26
Figure 0.15 Symmetry Diagrams Describing the Woodward-Hoffmann Theory of Orbital Overlap for [1,3] Shifts........... 28
Figure 0.16 Photochemical [1,3] Shifts............................... 29
Figure 0.17 Photochemical [1,3] Shifts............................... 30
Figure 0.18 Some Benzosemibullvalenes Studied for the [1,3] Sigmatropic Shift................................. 31
PART I. PREPARATION OF STARTING MATERIALS

Figure 1.01 Synthesis of Benzobarrelene Diester 29 from a Diels-Alder Reaction......................... 45

Figure 1.02 Derivation of Benzobarrelene Dimethyl Ester 29................................................. 46

Figure 1.03 NMR Spectra of Benzobarrelene 29 and Partially Deuterated Benzobarrelene 29-D......................... 48

Figure 1.04 Preparation of 2,3-Dibenzoyl-1,4-dihydro-1,4-ethenonaphthalene (42)................................. 49

Figure 1.05 Spectra of Symmetrical Benzobarrelenes 40 and 41.................................................. 51

Figure 1.06 a) Preparation of Benzoyl Esters 43, 44, and 45. b) Monodeuterated Benzoyl Methyl Ester (43-D)............ 53

Figure 1.07 NMR Spectra of Benzoyl Esters 43 and 45.................................................. 54

Figure 1.08 Synthesis of Tetramethyl Benzobarreline Diethyl Ester 47 ........................................... 56
PART II. CHARACTERIZATION OF DISUBSTITUTED BENZOSEMIBULLVALENE PHOTOPRODUCTION

Figure 2.01  
a) Structure of Pentalene.  
b) Structure of Benzosemibullvalene or 2a,2b,6b,6c-Tetrahydrobenzo[a]cyclopropan-cd]pentalene  

Figure 2.02  
NMR Spectra of 2a,6c-Disubstituted Benzosemibullvalenes 29a and 40a  

Figure 2.03  
NMR Spectral Expansions of 2a,6c-Disubstituted Benzosemibullvalenes 29a and 40a  

Figure 2.04  
NMR Spectral Expansions of 1,6c-Disubstituted Benzosemibullvalenes 29b and 43c  

Figure 2.05  
NMR Spectral Expansions of 1,2-Disubstituted Benzosemibullvalenes 40b and a Mixture of 43d and 43e  

Figure 2.06  
Methyl 2-Benzoyl Cis-2-butene-3-carboxylate (65)  

Figure 2.07  
Complexation of 1,2-Disubstituted Benzosemibullvalenes to Eu(hfc)3  

Figure 2.08  
Plots of Change in Chemical Shift (Δν) Against the Mole % of Eu(hfc)3 Added for Compounds 43d and 43e  

Figure 2.09  
NMR Spectrum and Expansion of Methyl 6c-Benzoyl-2a,2b-dihydrobenzo[a]cyclopropan-cd]pentalene-6b-carboxylate (43f)  

Figure 2.10  
X-ray Crystal Structure of Compound 43f  

Figure 2.11  
a) NMR Spectral Expansion of Methyl 6c-Benzoyl-2a,6b-dihydrobenzo[a]cyclopropan-cd]pentalene-2b-carboxylate (43g).  
b) Decoupling at 4.52 ppm  

PART III PHOTOCHEMISTRY OF SYMMETRICALLY DISUBSTITUTED BENZOBARRELENE

Figure 3.01  
Photochemistry of Compound 29 Reported by Grovenstein et al. in 1969  

Figure 3.02  
Mechanistic Study for Benzocyclooctatetraene 29c Formation, Performed by Bender and Brooks in 1975  

Figure 3.03  
Complete Photochemistry of Benzobarrelene 29  

Figure 3.04  
Mechanism of Benzosemibullvalene 29a and 29b Formation  
Figure 3.05  Mechanism of Benzosemibullvalene 29e Formation
from Benzocyclooctatetraene 29c. .......................... 79

Figure 3.06  NMR Spectrum of Compound 29c Reaction Mixture
Showing Signals of Cyclobutene 29d. .................... 80

Figure 3.07  Photoproducts from 1,4-Dihydro-1,4-etheno-
naphthalene-2,3-dicarboxylic Acid (40). ................. 82

Figure 3.08  Proton NMR spectra of a) 41d in DMSO-d6.
b) 41d-D in DMSO-d6. ................................. 85

Figure 3.09  Mechanisms of Benzosemibullvalenes 40a and
40b Formation .......................................... 86

Figure 3.10  a) Reaction Mixture Proton NMR Spectra of
Benzophenone Sensitization of 40-D. .................. 88
b) Table of Bond "a" and "b" Lengths from
X-ray Analysis. ........................................ 90

Figure 3.11  a) Solid State Infrared Spectrum of Diacid 40.
b) Simple Representation of the Reaction Cavity of
Diacid 40 Showing the Hydrogen Bond Anchors. ....... 92

Figure 3.12  Hydrogen Bonding Effects on the Photochemistry
of 66. ....................................................... 93

Figure 3.13  Photochemistry of Benzobarrelene Anhydride 41...... 95

Figure 3.14  NMR Spectrum of Anhydride 41 Reaction Mixture
from Direct Photolysis. .................................. 96

Figure 3.15  Plot of Anhydride Photoproduct Composition
as a Function of Starting Material Conversion. ......... 97

Figure 3.16  Pathways to Photoproduct Formation from
Anhydride 41. ............................................. 99

Figure 3.17  Photochemistry of Dibenzoyl Benzobarrelene 42...... 103

Figure 3.18  Characterization of Dibenzoyl Benzosemibull-
valene 42c in a Mixture with 42a, by NMR. .......... 104

Figure 3.19  Mechanisms to Photoproduct Formation from
Dibenzoyl Benzobarrelene 42. ............................ 105

Figure 3.20  Graph of Quantum Yield (Φ) of 42a versus
Starting Material 42 Conversion. ........................ 106
**PART IV. PHOTOCHEMISTRY OF UNSYMMETRICALLY DISUBSTITUTED BENZOBARRELENES**

| Figure 4.01 | Possible Di-π-Methane Rearrangement Pathways for 2-Benzoyl 3-Ester Benzobarrelenes | 110 |
| Figure 4.02 | Photochemistry of Benzoyl Methyl Ester Benzobarrelene 43 | 112 |
| Figure 4.03 | NMR Spectral Expansions of Compound 43 Reaction Mixture from Direct Solution Photolysis in CDCl₃ | 113 |
| Figure 4.04 | Plots of Quantum Yield versus Conversion for the Formation of Compounds 43a and 43h | 117 |
| Figure 4.05 | NMR Spectral Expansions of the Crystalline Reaction Mixture of Benzobarrelene 43 | 119 |
| Figure 4.06 | Tri-π-Methane Mechanism to Form Benzosemibullvalene 43f | 121 |
| Figure 4.07 | Radical Stabilization Approach to 1,2-Disubstituted Benzosemibullvalene Formation in the Solid State | 123 |
| Figure 4.08 | X-ray Crystal Structure Diagram Displaying the Conformation of Benzobarrelene 43 | 124 |
| Figure 4.09 | Motions Required for Benzosemibullvalenes 43d and 43h Formation | 125 |
| Figure 4.10 | Packing Diagram for Compound 43 | 127 |
| Figure 4.11 | Photochemistry of Benzobarrelene 44 | 129 |
| Figure 4.12 | Graph of Quantum Yield versus Conversion for Compounds 44a and 44c in Benzene | 131 |
| Figure 4.13 | Crystalline Conformation of Compound 44 from X-ray Analysis | 133 |
| Figure 4.14 | Packing Diagram of Benzobarrelene 44 Showing Intermolecular Contacts | 135 |
| Figure 4.15 | Photochemistry of Benzoyl Isopropyl Ester Benzobarrelene 45 | 136 |
| Figure 4.16 | Graph of Quantum Yield versus Conversion for Compounds 45a and 45c in Benzene | 139 |
| Figure 4.17 | Crystalline Conformation of Compound 45 from X-ray Analysis | 140 |
| Figure 4.18 | Motions Required in Relevant Di-π-Methane Pathways, Holding the Carbonyl Substituents Fixed | 142 |
Figure 4.19 Packing Diagrams of Benzobarrelene 45 from X-ray Analysis................................. 144
Figure 4.20 Table Summarizing Solution and Solid State Ratios in the Photochemistry of Compounds 43, 44, and 45...... 145

PART V. PHOTOCHEMISTRY OF BENZOBARRELENE SALTS
Figure 5.01 Photochemistry of Benzobarrelene Salts.............. 149
Figure 5.02 Photoproduct Ratios from Solution Phase Photochemistry of Benzobarrelene Salts............... 150
Figure 5.03 NMR Expansions of Salt 48 Before and After Reacidification, in CDCl3............................... 153
Figure 5.04 Photoproduct Ratios from the Solid State Study of Benzobarrelene Salts.............................. 154

PART VI PHOTOCHEMISTRY OF DIMETHYL 1,4,5,8-TETRAMETHYL-1,4-ETHENO-NAPHTHALENE-2,3-DICARBOXYLATE (47)
Figure 6.01 Photochemistry of Compound 47......................... 158
Figure 6.02 NMR Spectra (CDCl3) and Crystallographic Representations of Benzosemibullvalenes 47a and Benzocyclooctetraene 47b......................... 160
Figure 6.03 NMR Spectra of Compounds 47 and 47c in CDCl3...... 161
Figure 6.04 Proposed Structure for 47d with Analogy.............. 163
Figure 6.05 Proposed Mechanisms to Photoproduct Formation from Benzobarrelene 47............................. 165
Figure 6.06 Quantum Yield Graphs for the Formation of Photoproducts 47a and 47b in Benzene and in a 1:1 Mixture of Acetonitrile and Benzene....... 167
Figure 6.07 Crystal Structure of Benzobarrelene 47 with List of Bond Lengths and Angles....................... 168
Figure 6.08 Geometric Requirements for the Formation of [2+2] Cycloaddition Products from 47............... 170

PART VII. PHOTOCHEMICAL [1,3] SHIFTS IN BENZOSEMIBULLVALENES
Figure 7.01 Mechanism of [1,3] Shift Photoconversion............ 171
Figure 7.02 Benzosemibullvalenes Studied for Photo-
stationary States................................. 172
ACKNOWLEDGEMENTS

I wish to sincerely thank my research supervisor, Professor John R. Scheffer, for his support and guidance throughout the years; his novel ideas and constructive suggestions enabled me to overcome barriers that I never thought I could. His endless patience, friendship, and encouragement were invaluable in maintaining my enthusiasm in the program.

I would also like to thank Dr. Miguel Garcia-Garibay and Dr. Jianxin Chen for their assistance in the earlier part of the research, answering questions and responding to ideas no matter how ridiculous they may be. The warm surroundings provided by my co-workers made it a delight to be in graduate school. Also, I hope to some day return favors to Anna-dora Gudmunsdottir and Mardy Leibovitch for proofreading this thesis.

Special thanks to Dr. James Trotter, Dr. Steve Rettig, Dr. Phani Raj Pokkuluri, and Dr. Ray Jones for their detailed crystallographic work in this thesis. I greatly appreciate the help and kind assistance from the staff of the NMR, mass spectrometry, and elemental analysis laboratories.

Financial support from the University of British Columbia is gratefully acknowledged.
To my father and mother
INTRODUCTION
I. History

The study of organic photochemistry began about two centuries ago with the use of sunlight as the irradiation source. The popularity of this topic grew considerably in the early 1900s with the development of the mercury broad band arc lamp as an artificial light source. This meant that durations of photolysis were reduced to minutes and hours as opposed to days and weeks. Prior to this, lengths of photolysis depended not only on the absorption and reactivity of the compound but on the weather and season as well. Organic photochemistry is still expanding in many directions; one is in the region of organized media. The interaction of photons with organic molecules to cause a chemical reaction in an anisotropic environment is a more definitive term of the subject.

Types of organized media used in photochemistry are crystals, polymer matrices, zeolites, cyclodextrins, micelles, and monolayers. The unique characteristic common to these systems is their ability to dramatically alter, with respect to the solution state, the selectivity of photoproduct formation from regioisomers to stereoisomers as well as from unimolecular to bimolecular processes.

Interestingly, the first example of a reaction in an organized medium was not by photochemical means, even though it is currently the most widely used technique; in 1828, Friedrich Wohler synthesized urea from ammonium cyanate in a thermal solid state reaction.

Research in organized media did not bloom until about thirty years ago with the development of nuclear magnetic resonance spectroscopy, infrared spectroscopy, and most importantly, X-ray crystallography. Modern X-ray crystallography allows chemists to overcome two barriers in studies of photochemical structure-reactivity
relationships. The first is in the confirmation of photoproduct structures. The second and more vital is its use in the detailed visualization of the molecular reaction cavity.

Of the various organized media represented, the most extensive work has been done with the use of the crystalline phase. Molecules in a crystal are organized in such a manner that they are evenly close-packed among their neighbors. For most cases, the systematic repeating of each unit cell allows each molecule to feel the same constraining environment as its neighbors, thus the reacting molecule in the lattice would feel the same environmental influence so long as the lattice remains intact. This field of study was opened in the early twentieth century by pioneering scientists like Ciamician, Kohlshutter, Stobbe, and Senier. Although the progress of organic solid state photochemistry has advanced considerably since then and many review articles have recently been published, solid state photochemistry is still in the "discover-and-explain" stage as opposed to being used as a fully predictive synthetic tool. This is due primarily to the fact that crystal packing is unique to the molecule and cannot be predicted. It is thought that, ultimately, medium dependent photochemistry will have its main applications in the areas of asymmetric synthesis, materials science, and computers.

II. The Excited State

There are many aspects to the molecular excited state, and a complete summary would fill this text. The following will briefly
touch on some of the more relevant areas of this topic. Detailed reviews can be found in publications by Turro\textsuperscript{6} and de Mayo\textsuperscript{7}. Electrons in a molecular ground state exist in pairs according to their electron spin ($S_0$). Upon absorption of a photon, ultraviolet or visible radiation, an electron from the highest occupied molecular orbital (HOMO) is transferred to the lowest unoccupied molecular orbital (LUMO) (Figure 0.01). This excitation puts the molecule in the singlet excited state ($S_1$); spin-orbit coupling allows an electron to spin flip to the unpaired triplet excited state ($T_1$). Most photochemical reactions occur from either the $S_1$ or $T_1$ excited states.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{energy_diagram}
\caption{Energy Diagram for Selected Transitions.}
\end{figure}

The intention of the photochemist is to irradiate with low energy photons to selectively excite a HOMO electron to the LUMO. The use of broad band high energy photons would excite the HOMO to other unoccupied orbitals ($S_2$, $S_3$, ...) causing a cascade of decomposition modes. Conjugated molecules or molecules that possess heteroatoms with non-bonded electrons have lower HOMO / LUMO energy gaps and are therefore easier to selectively excite.
In the $S_1$ state, molecules have several methods of energy release. They can undergo:

a) Intersystem crossing - spin flip to the lower energy triplet state ($T_1$); this is forbidden but occurs through spin-orbit coupling.

b) Fluorescence - release energy in the form of light and return back to $S_0$; this process is allowed, and occurs at a rate of $10^6 - 10^{10}$ sec$^{-1}$.  

Figure 0.02 Energy Diagram for General Molecular Photophysical Processes.
c) Internal conversion - release vibrational energy in the form of heat and return to $S_0$; this is allowed as the spins of the two states are the same.

d) Reaction to give photoproduct(s).

Molecules in the triplet ($T_1$) state also have several modes of energy release. They can undergo:

a) Phosphorescence - release energy in the form of light and return to $S_0$; this is spin disallowed but occurs through spin-orbit coupling at a rate of $10^{-1} - 10^6$ sec$^{-1}$.

b) Intersystem crossing - release vibrational energy in the form of heat and return to $S_0$; this is spin forbidden but occurs through spin-orbit coupling.

c) Reaction to give photoproduct(s).

These commonly encountered photophysical processes are shown in Figure 0.02.

Quantum yield ($\Phi$) is the measure of process efficiency. Once a molecule is in an excited state, the probability that a selected decay route is taken is defined by the quantum yield. The sum of possible quantum yields for a defined state must equal one. For example, if a molecule is in the $S_1$ state of Figure 0.02, the $\Phi_{\text{fluorescence}}$, $\Phi_{\text{reaction}}$, $\Phi_{\text{intersystem crossing}}$, and $\Phi_{\text{internal conversion}}$ must add to one. However, chain-reaction processes can have values greater than one.

Another phenomenon worth mentioning is with triplet-triplet ($T_1$-$T_1$) energy transfer (triplet sensitization). This is the transfer of excited triplet energy from one system to another. The process usually occurs intermolecularly and a few criteria must be satisfied.
Firstly, the energy level of the excited donor triplet must be higher than the acceptor triplet. Secondly, the donor and acceptor must physically come together for energy to transfer. The efficiency of the second factor is ultimately dependent on the collision rate of the donor to the acceptor and the lifetime of the excited triplet donor.

Keller et al.\textsuperscript{8} in 1968 investigated this energy transfer intramolecularly to determine the effect of distance on the efficiency of energy transfer. The benzoyl-naphthyl system (3), benzophenone-naphthyl system (4) (Figure 0.03), and other systems were studied. Compound 3 was photolyzed ($\lambda > 350$ nm) such that only the benzoyl group was excited ($n-\pi^*$); the chromophore then transferred its energy through space to the naphthyl system where phosphorescence was observed. The efficiency of energy transferred was determined to be 100% with a calculated

---

\textbf{Figure 0.03} 1-Benzoyl-4-(\alpha-naphthyl)-bicyclo[2.2.2]octane (3) and a Rigid Benzophenone-Naphthalene Donor-Acceptor System (4).
7 Å separation between the donor and acceptor. The benzophenone group of compound 4 was selectively excited and the observed phosphorescence of the naphthalene moiety was compared to the decrease in phosphorescence of the benzophenone group. A 35% efficiency in the triplet sensitization over a ca. 15 Å space was concluded. This through distant excited state energy transfer was also recently studied by Garcia-Garibay in a solid state KBr medium and the sensitization distance was determined to be 12 Å.

III. The Di-π-Methane Rearrangement

One of the most thoroughly studied unimolecular rearrangements in organic photochemistry is the di-π-methane rearrangement. Without variation, this is the subject reaction of the thesis. The reaction was so named from the required presence of two π-bonds separated by an sp³ hybridized or "methane" carbon. A representation of the reaction is shown with one of the simplest of di-π-methane systems, 1,4-pentadiene (6), in Figure 0.04.

Howard Zimmerman proposed a stepwise mechanism with an initial bond formation across C₂ and C₄ to give the cyclopropyl intermediate 6a. This is followed by either bond cleavage of a, giving back starting material, or cleavage of b, proceeding to 1,3-biradical 6b. Simple ring closure of biradical 6b gives the vinylcyclopropane product 6c. More recently, Paquette proposed a viable alternative to this mechanism based on his study of substituted benzonorbornadienes. He suggested a [1,2] shift of one unsaturated
group followed by ring closure to give the product. The only difference between this mechanism and Zimmerman's is that biradical 6b is formed in only one step instead of two, as shown by the transition state in Figure 0.04. At this point, it can only be stated that biradical 6a is simply a representation and may not be a true intermediate; also in some cases, the steps may merge to a concerted process.

![Diagram of Di-π-Methane Mechanisms Represented in 1,4-Pentadiene (6).](ref. 11)

Figure 0.04 Di-π-Methane Mechanisms Represented in 1,4-Pentadiene (6).

The multiplicity of this reaction is found to be dependent on the type of di-π-methane system. Cyclic compounds undergo the di-π-methane rearrangement efficiently through their triplet excited state and inefficiently through their singlet states. On the other hand, acyclic systems rearrange via their singlet excited states more efficiently than their triplet states.
Compound 7 (Figure 0.05) is a typical example to the rule; direct photolysis results in a di-π-methane rearrangement to vinylcyclopropane 7a. Alternatively, triplet sensitization of 7 gives the trans-isomer in a reversible photostationary state. Likewise, diene 8 rearranges upon direct photolysis but is not reactive from triplet sensitization.

Figure 0.05 Examples of Acyclic Di-π-Methane Systems.
Barrelene (9) (Figure 0.06) is a cyclic di-π-methane system that rearranges to bullvalene (9a) upon triplet-sensitized photolysis.\textsuperscript{19} However, when directly irradiated, barrelene undergoes [2+2] cycloaddition followed by a thermal ring opening to give cyclooctatetraene (9b). Benzonorbornadiene (10) also undergoes the di-π-methane rearrangement upon triplet excitation to give the tetracyclic compound 10a.\textsuperscript{20} Direct photolysis yields the strained [2+2] product (10b), which readily reverts back to starting material.

![Chemical diagrams showing the transformation of barrelene and benzonorbornadiene](image-url)

**Figure 0.06** Examples of Cyclic Di-π-Methane Systems.
The multiplicity difference in reactivity was explained on the basis of the "free-rotor" effect. Acyclic systems do not rearrange through their triplet excited states because the double bond twisting permitted in non-rigid structures allows for fast triplet deactivation back to their ground states ($S_0$). The triplet states of rigid systems deactivate more slowly, thus facilitating efficient rearrangements. Although the rule applies in most cases, there have been reported instances where the opposite was true, i.e., cyclic compounds that rearrange through their singlet excited states and acyclic compounds through their triplet states.

Mentioned earlier in the mechanism to product formation was that the first intermediate can either proceed to product or revert back to starting material. This reversibility is discussed in a review by Zimmerman. He concluded from a study of azo barrelenes that triplet-mediated di-π-methane rearrangements tend to not be reversible.

In situations where more than one di-π-methane system exists with the same chromophore, opportunity arises for selectivity. Initial bonding can occur from different sites giving different photoproducts. However, this initial bonding is usually directed to the most stable intermediate as the energy barrier to its formation would most likely be lower. In many cases, this is the rate-limiting step of the rearrangement.

Compound 11 (Figure 0.07) can rearrange from either initial benzo-benzo bonding or initial benzo-vinyl bonding. However, the former pathway interferes with the aromaticity of two phenyl rings as opposed to the disruption of only one aromatic ring occurring in benzo-vinyl bonding. Consistent with the model, photoproduct 11c is the only product
observed. This result exemplifies the competition between pathways in which the disruption of aromaticity disfavors one but not the other. Alternatively, cyclohexadiene derivative 12 (Figure 0.07) selects the route through 12a over 12d on the rationale that the benzyl radical on 12a can delocalize through the aromatic ring. Dibenzobarrelene ester 13 (Figure 0.07) has four initial bonding possibilities. Based on the results of compound 11, benzo-benzo initial bonding may be excluded from the list of choices. This reduces the number of initial paths to two, with initial benzo-vinyl bonding on the ester side or on the unsubstituted side. The path through 13a, with a radical stabilized by the ester carbonyl, is preferred, giving dibenzosemi-bullvalene 13c as the only product.
Figure 0.07 Examples of Initial Bond Formation Selectivity in the Di-π-Methane Rearrangement.

Selectivity of the rearrangement is not solely incorporated in the initial step. Interestingly, in the second biradical formation
of Zimmerman's mechanism, the bond-breaking step provides another opportunity for selectivity. The theory for predicting the favored reaction pathway is as follows: the bond broken is dependent on the relative energy levels of the two branch-point products.\textsuperscript{14} From Zimmerman's notation, the more stable of the two biradicals formed from bond cleavage will be preferred. The basis of this rule stems from the theory that radical stability is dependent on efficiency of $\pi$-delocalization.

The proposed intermediate 14a (Figure 0.08) formed from the excitation of 14 can cleave any one of the three bonds a, b, or c. If bond c is broken then starting material will be regenerated, but if bond a or b is cleaved, the reaction will proceed to respective products. In 14a, owing to delocalization through the phenyl ring, the benzyl radical is less reactive than the cyclohexyl radical. As a result, bond b is cleaved to give compound 14c as the only product.\textsuperscript{23} The 1,4-diene 7 (Figure 0.05) is similar to bond a of the proposed biradical 7c favored for cleavage. Consequently, photoproduct 7a is the only di-$\pi$-methane product.\textsuperscript{15} Including the previous example, Zimmerman put forth a thorough investigation into substituent effects of the bond cleavage step in the di-$\pi$-methane rearrangement.\textsuperscript{26} Compound series 15 (Figure 0.08) represents only some of the many acyclic substituted 1,4-dienes used in his study. A methoxyl group in the meta position of a disubstituted aromatic ring is electron withdrawing, but if involved in resonance (i.e. in the ortho or para position) acts as an electron donor. The donating characteristic of the para substituted methoxyl group of p-15a reduces the ability of the aryl radical to delocalize. As a result, photoproduct p-15b from the homolytic cleavage of bond a occurs
with about three times the efficiency as compound p-15c from the breaking of bond b. On the other hand, the inductively electron-withdrawing effect of the methoxyl group in the meta position slightly stabilizes the aromatic radical in m-15a over the unsubstituted phenyl. Now the phenyl chromophore is less stable causing a slight preference for the cleavage of bond b over bond a. Results show a m-15c to m-15b quantum yield ratio of 0.086 : 0.072.  

Figure 0.08 Examples of Secondary Bond Cleavage Selectivity in the Di-π-Methane Rearrangement.
IV. The Topochemical Principle

This concept originated in the early days of solid state chemistry when Kohlshutter proposed in 1918 that "reactions in solids are dependent on the constraining three dimensional environment in which the molecules exist". However, it took just over forty years before this postulate was followed up. With the introduction of modern X-ray crystallography, Gerhard Schmidt and co-workers reinvestigated many solid state reactions using modern X-ray crystallographic techniques. The accumulated experimental results allowed them to establish some fundamental parameters for solid state reactivity. Of the systems reinvestigated by Schmidt et al., perhaps the most interesting is their study of trans-cinnamic acid.

Unsubstituted trans-cinnamic acid (5) is trimorphic (Figure 0.09) in that it possesses three known crystalline packing arrangements (α, β, and γ). Photolysis of trans-cinnamic acid in solution results in cis/trans isomerization; whereas photolysis of crystals of the α-form gives the [2+2] cycloaddition product 5b. The distance between the two double bonds (center-to-center) was established to be in the range of 3.6-4.1 Å from analysis of the unreacted crystal. The β-form photolyzes to give adduct 5c with a reaction distance ranging between 3.9-4.1 Å. The γ-form on the other hand, is unreactive as the determined separation is between 4.7-5.1 Å.

Without prejudice to the solid state, almost all modern media-dependent chemistry relies on this principle initially proposed by Kohlshutter and revitalized by Schmidt. As it will be seen, many of the theories later discussed are based on the Topochemical Principle.
Figure 0.09 Photochemistry of Trans Cinnamic Acid in Solution and Crystalline States.
V. Solid State Reactivity

Throughout the history of chemistry, scientists have recognized the organic crystalline phase as a means of reaction work-up. Compounds can be purified by recrystallization and are often stored as crystals, an easily handled, inert form. In a parallel manner, the properties of crystals are used in compound identification through their different appearances and melting points, and known compounds may be compared to their literature values for structural confirmation. Now it is becoming well accepted that the crystalline phase can also play an active role in chemical reactions. With the advent of modern X-ray crystallography, high resolution solid state $^{13}$C NMR, differential scanning calorimetry, and other techniques, the probe into solid state chemistry has facilitated many new findings.

The external crystal appearance is governed in part by the internal packing arrangement. Molecules in a crystal are systematically stacked in such a manner that every molecule feels the same intermolecular environment, but exceptions do exist. The repeating unit of molecules (unit cell) is classified according to its symmetry, and this classification is called the "space group". There are 230 possible space groups of which 65 are chiral. Each repeating unit in a chiral space group feels the same unsymmetrical environment as opposed to a symmetrical environment. As a result, crystalline chiral molecules must adopt chiral space groups due to their inherent lack of symmetry, and achiral molecules usually do not but may also have chiral space groups.

A molecule within a crystal lattice prevents neighboring molecules from infringing on it by basic steric interactions. This is
where the atoms of adjacent molecules feel each other's electrostatic charges and repel. Through these interactions the molecule has designed its own volume of space, molded to one of its conformational energy minima. Within this space, solid state photochemical reactions can occur. Cohen termed this space the "reaction cavity".32

In 1975, Cohen32 suggested that as a molecule reacts in a crystal, the physical geometry of the species changes while proceeding from reactant through transition state(s) to product. This is represented by the structures of Figure 0.10. Those reactions with minimal changes in geometry will proceed without much interference from the cavity walls (path a). However, reactions with transition state geometries incompatible with the reaction cavity will be slowed or even forbidden to occur (path b). This in turn will give rise to reaction selectivity differing from the solution phase.

The underlying factors responsible for crystalline state selectivity differ from reactant to reactant depending on specific
interactions of the substrate with the lattice. These interactions may either be direct, where a specific lattice group inhibits the movement of a substrate appendage required for reaction, or indirectly, where the lattice geometrically positions an atom or group of atoms properly for reaction by locking the molecule in the required conformation. Consequently, in this approach to understanding solid state selectivity, the reactant X-ray crystal structure data is examined for the presence or absence of specific steric interactions to explain any enhanced or retarded product formation. This "structure-reactivity correlation" is the most commonly used method of analysis, employed by leading solid state photochemists such as Lahav, McBride, Scheffer, and Ramamurthy.

In a study by Scheffer et al., it was found that β,γ-unsaturated ketone 16 photolyzes in benzene to give tetracyclic diketone 16c. Alternatively, photolysis in the crystalline phase gives the tricyclic isomer 16e as the only product. Compound 16c was postulated to come from a three-step process, initial C₄ to C₅ bonding to give 16a. The C₆ radical on 16a, owing to its conformational alignment with the C₂-C₃ double bond, bridges with C₂ to give 16b, and the rearrangement is completed with a 1,2-shift of C₄a to C₃ yielding the solution product (16c). Alternatively, the solid state product 16e is derived from initial C₃ to C₅ bonding, followed by the abstraction of the hydrogen atom on C₇ by the C₂ radical. It was reasoned that 4,5-bonding is favored over 3,5-bonding in solution because the reactant is an oxa-di-π-methane system; such systems easily undergo initial biradical formation to proceed to 16c. However, the large motion needed to form the C₂-C₆ bond forbids continuation
of this reaction in the crystalline phase. The initial 3,5-bonding route has minimal topochemical requirements and is therefore allowed.

It is not uncommon for a compound that is reactive photochemically in solution to be reactive in the solid phase as well. Usually solid state photoproduct conversion is limited. As a molecule is converted to product in the lattice, many reacted species retain or have an enhanced ability to absorb light, then the bulk will be unreacted due to poor photon penetration through the crystal.
Another common deterrent to bulk reactivity is that once a substrate is reacted, this new molecule has a three dimensional geometry different from the reactant and, as a result, generates a defect in the lattice. This defect promotes the scattering of light back to the surface and inhibits the bulk of the crystal from reacting. In most cases, prolonged photolyses result in the crystal forming cracks, becoming cloudy, and even melting on the surface. This problem is partially alleviated by irradiation in the tail of the absorption band to facilitate deeper penetration of light into the crystal. This bulk versus surface reactivity has been discussed in a recent study by Scheffer and co-workers.\(^{39}\)

Upon irradiation, some crystals can convert completely to a single photoproduct without loss of their crystalline appearance. This phenomenon is known as a "topotactic" or single crystal-to-single crystal reaction.\(^{40}\)

\[ \text{Figure 0.12 Photodimerization of Benzylidenecyclopentanone.} \]
Of the known bimolecular photochemical processes, by far the most commonly observed is the intermolecular [2+2] cycloaddition reaction. In 1980, Jones and Thomas et al.\textsuperscript{41} studied the solid state photochemical behavior of benzylidene cyclopentanone 17. Photolysis of crystalline compound 17 results in the complete conversion of starting material to the [2+2] adduct 17a with the retention of molecular crystallinity. Crystallographic analyses of compounds 17 and 17a reveal a remarkable similarity in crystal packing and cell dimensions allowing for favorable interconversion of pentanone derivative 17 to product 17a.

Asymmetric synthesis is another aspect to the study of the organic solid state. As mentioned earlier, 65 of the possible 230 crystal space groups possess chirality. Chiral crystal lattices exert an asymmetrical environment on the molecule. For photoreactions which generate a new chiral center(s), this temporary lattice chirality may influence a solid state reaction in such a manner that the product acquires this chirality in enantiomeric excess.

![Figure 0.13 Enantioselective Phototransformation of Dibenzobarrelene Diisopropyl Ester 18.](image-url)
Molecular chirality is not mandatory for crystallization into a chiral space group. Scheffer, Trotter, and co-workers\textsuperscript{42} noticed that dibenzobarrelene 18 has two crystalline morphologies. Recrystallization from ethanol gives prisms with the achiral space group Pcb\textalpha. However, if the compound is cooled from the melt, crystals having the chiral space group P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} appear. Photolysis of reactant 18 in solution or in a single Pcb\textalpha crystal gives a racemic mixture of dibenzosemibullvalene 18a through the di-\pi-methane rearrangement. The interesting aspect of this study is with the single crystal photolysis of the chiral P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} morphology; this leads to the formation of 18a with 100\% enantiomeric excess. The direction of optical rotation varies from run to run depending on the handedness of the chiral crystal chosen. The reaction pathways differ in the location of initial bonding. In Figure 0.14, if initial bonding forms on the M side from the anterior benzo group to the vinyl group of the molecule (dotted line), one enantiomer is obtained; and, if the bonding is on the P side from the anterior benzo to the vinyl, the other enantiomer is obtained. Crystallographic analysis (Figure 0.14) shows the steric crowding of the lattice on the latter bonding route (P side) while leaving the M side bonding (dotted line) relatively open.
Through the advancement of computer hardware and software, sophisticated calculations are now possible to assist in the understanding of molecular processes. Allinger's design of the Molecular Mechanics II (MM2) calculations allowed chemists to locate minimum energy conformations in molecules and intermediates. From this and other programs that stem from this design, molecular calculations have opened a new passage to the formulation of theories in solid state reactivity.

In a recent publication, Zimmerman and Zuraw established three parameters using the MacroModel program to predict crystalline phase reaction selectivity. Concerned were the starting material geometry, lattice dimensions, and the geometry of the intermediates or products directly following the branch point in the reaction pathway (termed the branch-point species). Change in motion ($\Delta M$) was the first parameter. This was calculated by superimposing the branch-point intermediate over
the starting material and adding all the non-hydrogen atomic displacement distances. Intuitively, the larger the displacement sum, the less efficient the solid state reaction. Volume requirement ($\Delta V$) was the next parameter. The branch-point species is superimposed over the reactant in a calculated best fit geometry and the non-overlapping volume of the branch-point species was reported as a percentage of the reactant volume. Therefore, small $\Delta V$ values should favor solid state reactivity. The third parameter was the lattice interference ($\Delta S$); this was determined by superimposing the branch-point species over the reactant molecule in the lattice and removing the reactant. The amount of overlap with the crystal lattice was then calculated and recorded as a percentage of the volume of lattice segment used. The volume of lattice segment chosen must be large enough to contain the entire superimposed species. Again, small $\Delta S$ values favour solid state reactivity. X-ray crystal structure coordinates were used wherever possible. These calculations were performed on a series of unsymmetrical di-$\pi$-methane systems to give encouraging results; however, more examples are needed to better establish the generality of this approach.

VI. Photochemical [1,3] Sigmatropic Shifts

Sigmatropic rearrangements are reactions where a sigma bond is cleaved and reformed elsewhere along a conjugated carbon chain. These reactions can be initiated either thermally or photochemically. The movement of the bond is described in a $[x,y]$ notation; the two chains are numbered starting from the atoms adjacent to the broken bond. Systematically $x$ and $y$ denote the positions along the chains.
where the new bond is formed. Such thermal and photochemical reactions are thought to be concerted pericyclic processes whereby the bonds form and break simultaneously with no detectable intermediates.

A set of orbital symmetry rules was proposed by Woodward and Hoffmann\(^{47}\) for predicting which sigmatropic rearrangements are favoured and which disfavored. Transitions occur from the highest occupied molecular orbital (HOMO). In thermal reactions, the [1,3] shift is forbidden to occur along the same surface as the symmetry of the interacting lobes must match. However, through inversion of configuration, this symmetry requirement is satisfied. Photochemical activation involves a slightly different scenario; an electron is promoted to the next orbital altering the symmetry of the HOMO (Figure 0.15). Now orbital symmetry allows [1,3] sigmatropic shifts to proceed with retention of configuration. In light of these predictions, retention of configuration should also occur with [1,7] shifts photochemically and [1,5] shifts thermally.

![Diagram](image)

**Figure 0.15** Symmetry Diagrams Describing the Woodward-Hoffmann Theory of Orbital Overlap for [1,3] Shifts.
As mentioned earlier, sigmatropic shifts are frequently analyzed as concerted pericyclic reactions; however, with photochemical \([1,3]\) shifts there have been many reports of biradical processes. A typical set of examples has been found with \(\beta,\gamma\)-unsaturated carbonyl compounds. Irradiation of compound 20 (Figure 0.16) leads to biradical 20a which then proceeds to give the \([1,3]\) shift product 20b in competition with a disproportionation reaction.\(^48\) Direct photolysis of compound 21 results in \(\alpha\)-cleavage to give \([1,3]\) shift product 21a and radical combination products, 21b and 21c.\(^56\) These \(\beta,\gamma\)-unsaturated carbonyls rearrange either through the \(S_1(n-\pi^*)\) or \(T_2(n-\pi^*)\) excited states.\(^49\)

![Figure 0.16 Photochemical [1,3] Shifts.](image-url)
The photochemical multiplicity of these reactions is predominantly singlet, but triplet states are not uncommon. This is exemplified in the triplet sensitization of bicyclic ketone 22 (Figure 0.17) to give [1,3] shift product 22d through biradical 22c.\textsuperscript{59} In contrast, direct photolysis of compound 22 leads to isomer 22b reversibly through ketene 22a. This ketene 22a is stable below -180 °C and gives an infrared band at 2118 cm\textsuperscript{-1}, characteristic of ketenes.\textsuperscript{51}

![Figure 0.17 Photochemical [1,3] Shifts.](image)

Turning to the benzosemibullvalene system, Bender and Wilson\textsuperscript{53} in 1976, uncovered a photochemical [1,3] shift reaction with compound 23. This interesting vinylcyclopropane to vinylcyclopropane rearrangement proceeded with direct or acetone sensitized photolysis. The authors suggested a triplet process, and no conclusion was made as to
whether a concerted process was involved. Bender et al., in a follow-up to this discovery, synthesized labelled benzosemibullvalene 24 and dimethyl benzosemibullvalene 25 (Figure 0.18) in an attempt to observe a similar [1,3] shift reaction. Direct or sensitized photolysis of either compounds 24 or 25 yielded no vinylcyclopropane to vinylcyclopropane rearrangement products. These results were rationalized by the necessity to have electron withdrawing groups on both sides of the cleaved C$_{2a}$-C$_{6c}$ bond in order for the reaction to occur.$^{55}$

Figure 0.18 Some Benzo-semibullvalene Derivatives Studied for the [1,3] Sigmatropic Shift.
VII. Photochemistry of Benzobarrelenes

In the study of the di-π-methane rearrangement of dibenzobarrelene derivatives, Scheffer et al.\(^5\) have found that some of these rearrangement pathways vary with the phase of the reacting dibenzobarrelene. Dibenzobarrelene systems can give different products depending on which of the four initial bonding modes is followed; note that the two initial benzo-benzo bonding pathways are omitted as they do not give feasible products. Consequently, the four possible products are all dibenzosemibullvalene derivatives, two regioisomers and their enantiomers.

![Diagram showing feasible initial bonding sites in the photochemistry of dibenzobarrelenes.](image)

**Figure 0.19 Feasible Initial Bonding Sites in the Photochemistry of Dibenzobarrelenes.**

The focus of the present investigation is on disubstituted derivatives of monobenzobarrelene. Di-π-methane rearrangements in mono-
benzobarrelene derivatives are much more complicated than in its dibenzo counterpart; there are now six feasible initial bonding sites (Figure 0.20). Also in the second bond-breaking step of the rearrangement, it is an energetic requirement for dibenzobarrelenes to regain aromaticity; with monobenzobarrelenes, that factor is not always present. As a result, the mono form may branch in the second step to give another host of possible photoproducts. The diversity of pathways available make this study more interesting and more challenging than the dibenzobarrelene systems.

Some of the products of Figure 0.20 may be structurally equivalent but be formed by different mechanisms. It must also be considered that products may arise from non-di-\(\pi\)-methane reactions as well as from secondary photoreactions.

The photochemistry of monobenzobarrelenes has been little studied compared to the dibenzo series. In 1963, Kitahonoki and Takano\(^{57}\) first reported the photochemistry of unsubstituted benzobarrelene (26) (Figure 0.21) by photolyzing it to benzosemibullvalene (28) in acetone. Four years later, Friedman\(^{58}\) showed that benzobarrelene gives benzocyclooctatetraene (27) upon direct irradiation. The mechanisms to these photoproducts were elucidated in a classical deuterium labelling experiment by Zimmerman et al.,\(^{59}\) in 1968. They concluded that the triplet benzosemibullvalene product is derived from a di-\(\pi\)-methane rearrangement with initial vinyl-vinyl bonding (Figure 0.21), and the cyclooctatetraene comes from a singlet-mediated [2+2] benzo-vinyl cycloaddition followed by an electrocyclic ring opening.
Figure 0.20 Possible Pathways in the Photochemistry of 2,3-Disubstituted Monobenzobarrelenes.
Congruent with the investigation of compound 26, Grovenstein et al.\textsuperscript{60} reported an investigation of the dimethyl ester derivative 29, Brewer and Heaney\textsuperscript{61} studied the tetrafluoro analog 30, and Bender\textsuperscript{62} studied naphthobbarrelenes 31 and 32 (Figure 0.22). Bender ultimately dedicated his career to the study of benzobarrelene derivatives and their photoproducts at the University of Lethbridge, Canada. Many of his techniques are creative and elegant in pioneering studies in this series. Benzobarrelenes 31-37 (Figure 0.22) are just some of the compounds synthesized and photolyzed by Bender through the years.

**Figure 0.21 Phototransformations of the Unsubstituted Benzobarrelene (26).**
Figure 0.22 List of Some Substituted Benzobarrelenes Previously Studied.
The established trends are that benzocyclooctatetraenes come from the singlet excited state. The initial intramolecular [2+2] cycloaddition is between the chromophore and the most easily disrupted π-system. For example, the chromophore of benzobarrelene 26 is the benzo-system; therefore, initial bonding is benzo-vinyl. Similarly, the diester vinyl is the chromophore for compound 34 and initial bonding is diester vinyl-vinyl.

Di-π-methane rearrangements of benzobarrelenes occur through the triplet excited state to give benzosemibullvalenes. Unlike the benzocyclooctatetraenes, initial bonding is between the two most easily broken double bonds. The longer triplet lifetimes allow for internal energy transfer to the two less stable π-systems for initial bond formation. Use of sensitizers also provokes the same initial bridging.

Recall that triplet sensitization of benzobarrelene 26 (Figure 0.21) gives initial vinyl-vinyl bonding instead of bonding to the benzo chromophore. With unsymmetrical benzobarrelenes, the side of initial di-π-methane bonding must also be considered; the side which can provide more stabilization to the radicals formed is the side that is favoured. This is exemplified with the 2-cyano derivative 33 (Figure 0.22). The initial bonding is vinyl-vinyl on the side opposite to the cyano group so that the cyano group can resonance stabilize one of the two newly formed radicals.

Only a small number of derivatives has been studied. Therefore, there is still much to be understood with respect to the solution behavior of benzobarrelenes. These proposed trends have yet to be fully tested. In addition, the many secondary photoproducts formed have opened
new areas of research as Bender has realized in his recent studies.\textsuperscript{67}

One of his latest investigations is with the photochemistry of 2,3-benzobicyclo[4.2.0]octa-2,4,7-triene derivative 39,\textsuperscript{68} a photoproduct of benzocyclooctatetraene 38a, which in turn is a singlet photoproduct of a benzobarrelene 38. Compound 39 undergoes a triplet di-\(\pi\)-methane rearrangement to afford benzosemibullvalene 39a.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure.png}
\caption{Photochemistry of 1-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (39).}
\end{figure}

VIII. Object of Research

In this thesis, disubstituted benzobarrelenes are synthesized and irradiated to assist in a better understanding of solution phase benzobarrelene photochemistry and, more interestingly, to provide the first reports\textsuperscript{69} of monobenzobarrelene photochemistry in the crystalline phase as well as in polymer medium.

For clarity, the Results and Discussion section is divided into
seven parts. The preparation of the starting materials is described in Part I of this thesis. The fundamental step in the synthesis of the benzobarrelenene ring system stems from a Diels-Alder addition of a naphthalene to an acetylene derivative. Substituent alterations can be done prior or subsequent to this addition.

One unique feature associated with this di-π-methane study is that all the products are disubstituted benzosemibullvalenes (Figure 0.20). Nuclear magnetic resonance spectroscopy (NMR) of these photoproducts is extremely informative, as the four protons on the disubstituted semibullvalene skeleton possess distinctive chemical shifts and coupling patterns. Part II of this thesis details the assignment of benzosemibullvalene regioisomers from spectroscopic techniques.

Part III of this thesis deals initially with dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (29, Figure 0.24). The photochemistry of this compound was investigated by Grovenstein in 1969. He reported the formation of a benzocyclooctatetraene derivative upon direct photolysis and a 5:3:2 ratio of three unidentified products from acetone sensitization. In this study, it was considered essential to determine the nature of these three triplet photoproducts in order to become familiar with this system and to proceed into the solid phase.

---

**Figure 0.24** Symmetrical Disubstituted Benzobarrelenes Studied.
Several other symmetrical disubstituted benzobarrelenes are also investigated in Part III to ascertain the effects of different substituent patterns on benzobarrelenene photochemistry. The substrates are shown in Figure 0.24. Favorable to the intentions, the last symmetrical system investigated, 2,3-dibenzoyl benzobarrelenene 42, unlike the others, efficiently intersystem crosses to give only triplet products in solution and the solid state.

The unsymmetrical benzobarrelenes studied in Part IV of this thesis are related to dibenzoyl derivative 42. The observation of its ease in intersystem crossing makes this an ideal system. If one of the benzoyl groups is replaced with an ester, the alkoxy group of the ester can easily be altered to little affect the solution photochemistry but dramatically reorganize the crystal packing. This in turn will hopefully demonstrate the effects of varying the crystal lattice on solid state selectivity. Upon noting the striking selectivity differences found in going from solution to the solid state, the series was also studied in polymer matrix media.

![Figure 0.25 Unsymmetrical Benzobarrelenes Studied.](image_url)
Varying the substituents on a molecule undoubtedly changes the crystal packing, which is what is desired in this study. Part V demonstrates the use of salts to alter crystal packing for essentially the same molecule. In theory, the solution photochemistry should not be affected significantly by simply altering the counterion. Different organic and inorganic salts of benzobarrelene dicarboxylic acid 40 were synthesized and photolyzed both in solution and in the solid state. The effects of the different crystal lattice environments on the solid state reactions can be directly measured from the different ratios of triplet products formed. In addition, some salts are synthesized in an attempt to deliberately affect intersystem crossing to enhance the formation of triplet photoproducts.

Figure 0.26 Salts of Benzobarrelene Dicarboxylic Acid.
The discovery of an unusual tri-\(\pi\)-methane\(^{70}\) rearrangement in Scheffer's group with the study of 9,10-dimethyl dibenzobarrelene 46\(^{71}\) (Figure 0.27) inspired an investigation of the generality of this rearrangement to other barrelene systems. A tri-\(\pi\)-methane rearrangement is a reaction which understandably involves three \(\pi\)-systems separated by a saturated carbon. In Part VI, the monobenzobarrelene analog of compound 46, dimethyl 1,4-dihydro-1,4,5,8-tetramethyl-1,4-ethenonaphthalene-2,3-dicarboxylate (47), was synthesized and irradiated.

Figure 0.27 Bridgehead Methylated Barrelene Dimethyl Esters.
Cumulatively, through this study it was noticed that many of the benzosemibullvalene photoproducts efficiently underwent secondary photochemical \([1,3]\) shifts. Although photochemical \([1,3]\) shifts are far from uncommon, few have been reported in the benzosemibullvalene system. Part VII briefly assesses these \([1,3]\) shifts in conjunction with the photostationary states in which they are found to frequently exist.
RESULTS AND DISCUSSION
PART I. PREPARATION OF STARTING MATERIALS

The basic structure of the starting materials possess the formal nomenclature of "1,4-dihydro-1,4-ethenonaphthalene," and the numbering is shown in Figure 1.01. The origin of this nomenclature stems from the naphthalene ring system, however, the skeleton is known more commonly as "benzobarrelene". Throughout the thesis, the two names will be used interchangeably.

Following the method of Grovenstein et al., dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (29) was prepared by the addition of dimethyl acetylenedicarboxylate to naphthalene in a thermal [4+2] cycloaddition reaction (Diels-Alder reaction).

![Synthesis of Benzobarrelene Diester 29 from a Diels-Alder Reaction.](image)

Figure 1.01 Synthesis of Benzobarrelene Diester 29 from a Diels-Alder Reaction.
It has been well recognized that naphthalenic systems are poor dienes for Diels-Alder addition. The preparation of compound 29 above requires heating in a sealed tube for 72 hours, and the reported yield of 25% is considered to be good. In light of this, many benzobarrelenes studied here were prepared through derivatization of diester 29. Synthesis of 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic acid (40) is achieved through the saponification of diester 29 (Figure 1.02). Extending from this, 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic anhydride 41 is prepared in a 24 hour dehydration of diacid 40 using oxalyl chloride. All three compounds (29, 40, and 41) are solids and can be easily purified by recrystallization.

Figure 1.02 Derivatization of Benzobarrelene Dimethyl Ester 29.
The partially deuterated versions of these starting materials were also prepared. The replacement of a bromo group with deuterium in a Grignard reaction gave 1-deuterionaphthalene\textsuperscript{74} from 1-bromo-naphthalene, in a ca. 95\% isotopic purity. The 1-deuterionaphthalene was used in place of naphthalene in the synthetic routes described in Figures 1.01 and 1.02. As a result, deuterium is evenly distributed over the 1,4,5, and 8 positions of the benzobarrelene ring. The NMR spectra of non-deuterated and selectively deuterated benzobarrelene 29 are provided in Figure 1.03. Notice that the C\textsubscript{1} and C\textsubscript{4} positions and the C\textsubscript{5} and C\textsubscript{8} positions are magnetically equivalent owing to the plane of symmetry present in the molecule.
Figure 1.03 NMR Spectra of Benzobarrelene 29 and Partially Deuterated Benzobarrelene 29-D in CDCl₃.
Synthesis of 2,3-dibenzoyl-1,4-dihydro-1,4-ethenonaphthalene (42) was accomplished through the Diels-Alder reaction of dibenzoylacetylene (57) with naphthalene (Figure 1.04). After 1 1/2 hours of heating in a sealed tube (180 °C), the alkyne was depleted to give a 19% yield of 42 after chromatography. Dibenzoylacetylene (57) was synthesized from the procedure of R.E. Lutz in 1951. Stemming from fumaryl chloride, two equivalents of benzene are added in a Friedel-Crafts reaction, catalyzed by anhydrous aluminum trichloride, to give trans-1,4-diphenyl-2-butene-1,4-dione (55). The vinyl group of ene-dione 55 is then reacted with bromine to give good yields of meso 2,3-dibromo-1,4-diphenylbutane-1,4-dione (56), and finally, 1,4-diphenyl-2-butyne-1,4-dione (57) is prepared from dibromide 56 by the addition of triethylamine in an elimination reaction.

Figure 1.04 Preparation of 2,3-Dibenzoyl-1,4-dihydro-1,4-ethenonaphthalene (42).
The $^1$H NMR spectra of symmetrical benzobarrenelene 40 and 41 are shown in Figure 1.05. Interestingly, the benzobarrelene skeleton carries a unique set of signals. The bridgehead (C$_1$ and C$_4$) protons resonate between 5-6 ppm with a doublet of doublets coupling pattern; this multiplicity comes from a strong (5 Hz) coupling to its vinyl neighbor along with a weaker (2 Hz) four bond distant coupling to the opposite vinyl. The vinyl protons resonate in the aromatic region; however, they can be distinguished from the aromatics by the coupling constants. In addition, the two groups of aromatic protons are easily differentiated by NMR integration of the deuterium labelled compounds shown in Figure 1.03.
Figure 1.05 $^1$H NMR Spectra of Symmetrical Benzobarrelenes 40 (DMSO-d$_6$) and 41 (CDCl$_3$).
The synthesis of unsymmetrical benzoyl methyl ester benzobarrelene 43 was achieved through further manipulation of the symmetrical benzobarrelene anhydride 41 (Figure 1.06). The anhydride ring was opened by reaction with dry methanol, and work-up gave 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic acid monomethyl ester (58). This acid ester was reacted with oxalyl chloride to give acyl chloride ester 59; this was immediately reacted with benzene in a Friedel-Crafts acylation catalyzed by anhydrous aluminum trichloride to yield the desired benzobarrelene 43. The ester side-chain can be easily altered under acidic conditions to give the corresponding ethyl and isopropyl esters (44 and 45, respectively). These benzoyl esters are highly crystalline making them ideal for solid state studies.

Selectively deuterated benzoyl methyl ester 43 was also prepared. This was done by taking the 1,4,5,8-labelled anhydride 41 through the described synthetic route (Figure 1.06). The resulting benzoyl methyl ester 43 was a monodeuterated mixture with the deuterium placed in the C1, C4, C5, and C8 positions. For simplicity, this mixture is represented diagrammatically as a single molecule with a 0.25 deuteration on the C1, C4, C5, and C8 positions (43-D).
The NMR spectra of unsymmetrical benzobarrelenes also contain a unique pattern of signals associated with the skeleton (Figure 1.07). The bridgehead (C\textsubscript{1} and C\textsubscript{4}) protons are no longer equivalent and resonate as two adjacent doublet of doublets between 5-6 ppm. Due to the lack of symmetry, the aromatic and vinyl proton signals overlap as a complex multiplet between 6.9-7.6 ppm and are therefore less informative.
Figure 1.07 NMR Spectra of Benzoyl Esters 43 and 45 in CDCl₃.
The amine salts of 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic acid (40) were prepared by dissolving the acid with a stoichiometric amount of an amine in ethyl acetate or acetonitrile. The solution was stirred under reflux for approximately one hour and the corresponding salt forms a precipitate which can be easily filtered. With amine double salts, a slight excess of the amine was used, and for inorganic salts, a stoichiometric amount of the cation as a hydroxide in water was added to the diacid in acetonitrile. Crystals of the derived salts were grown from suitable solvents. The salts prepared, shown in Figure 0.26, were characterized by analytical techniques such as NMR, IR, MS-DCI, C-H analysis, and mp.

The next substrate investigated in the thesis, dimethyl 1,4-dihydro-1,4,5,8-tetramethyl-1,4-ethenonaphthalene-2,3-dicarboxylate (47) was prepared from the Diels-Alder addition of dimethyl acetylene-dicarboxylate (DMAD) to 1,4,5,8-tetramethylnaphthalene (64) (Figure 1.08). DMAD is commercially available, but, naphthalene derivative 64 is not. The method devised by W.L. Mosby\textsuperscript{76} in 1952 was used to synthesize compound 64. The first step involves the reaction of anhydrous p-xylene with γ-valerolactone in the presence of anhydrous aluminum trichloride. The yield of the resulting 4-(2,5-dimethylphenyl)pentanoic acid (60) was 90%. Compound 60 is then treated with pyrophosphoric acid facilitating a dehydration ring closure to give 2,3-dihydro-4,5,8-trimethyl-1-naphthalone (61). The carbonyl group of ketone 61 was reacted with methyllithium, giving 1,2,3,4-tetrahydro-1,4,5,8-tetramethyl-1-naphthol (62) in 88% yield. This crude naphthol is then stirred
at room temperature in acidified tetrahydrofuran (THF) to give 1,2-dihydro-1,2,5,8-tetramethylnaphthalene (63) in a dehydration reaction. Finally, the 1,4,5,8-tetramethylnaphthalene (64) is formed from a catalyzed high temperature dehydrogenation of compound 63. The yield in this last step is 17%. Since 1952, several other synthetic routes to naphthalene derivative 64 have been reported. However, due to simple availability of reagents, the method of Mosby was used.

Figure 1.08 Synthesis of Tetramethyl Benzobarrelene Dimethyl Ester 47.
PART II. CHARACTERIZATION OF DISUBSTITUTED BENZOSEMIBULLVALENE PHOTOPRODUCTS

Most of the photoproducts synthesized in this thesis are benzosemibullvalenes, either from the di-\(\pi\)-methane rearrangement or from alternative mechanisms. Before embarking on discussions of elaborate reaction mechanisms, a strong foundation must be established with respect to the structural assignment of these photoproducts.

Benzosemibullvalene has the basic skeleton depicted in Figure 2.01. The proper Chemical Abstracts name is taken from the pentalene structure. Pentalene, in addition to a numbering system to describe the carbons, has an alphabetical system to represent the different carbon-carbon bonds of the ring system. The proper Chemical Abstracts name for benzosemibullvalene is \(2a,2b,6b,6c\)-tetrahydrobenzo[\(a\)]cyclopropa[\(cd\)]pentalene. The "\(2a,2b,6b,6c\)-tetrahydro" describes the position and number of the hydrogens on the pentalene skeleton. The "benzo[\(a\)]" indicates a benzo group at the a bond, and the "cyclopropa[\(cd\)]" denotes that the c and d bonds are involved in a cyclopropyl ring.\(^{80}\) Substituent descriptions are preceded by a number indicating their location on the benzosemibullvalene skeleton.

The disubstituted benzosemibullvalenes are most informatively characterized by nuclear magnetic resonance, infrared spectroscopy, and mass spectrometry. The NMR proton resonances on the benzosemibullvalene skeleton occur between 3.0 and 6.5 ppm; This region is relatively clear in the NMR spectrum, as the saturated hydrocarbon signals usually appear upfield of 3 ppm and aromatic protons appear downfield of 7 ppm. As a result, semibullvalene peaks are easily
distinguished and seldom suffer from overlap with other signals. Where possible, melting points and elemental analyses were taken. X-ray analyses were performed only in situations where the structures could not be firmly assigned from NMR techniques.

\[ \text{Figure 2.01 } \]
\[ a) \quad \text{Structure of Pentalene.} \]
\[ b) \quad \text{Structure of Benzosemibullvalene or 2a,2b,6b,6c-Tetrahydrobenzo[a]cyclopropa[cd]pentalene.} \]

A. Characterization of 2a,6c-Disubstituted-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene.

The proton NMR spectra of some 2a,6c-disubstituted benzosemibullvalenes are shown in Figures 2.02 and 2.03. The skeletal protons of the 2a,6c-disubstituted benzosemibullvalenes all have similar coupling and chemical shift patterns. The most shielded are H_{2b} and H_{6b}, giving rise to a singlet and a doublet (J = 3 Hz), respectively. The next most shielded signal comes from the C_2 vinyl proton as a doublet (J = 5 Hz), and the most deshielded proton on the semibullvalene skeleton is on C_1, a doublet of doublets (J = 5,3 Hz). The four aromatic protons resonate as a complex multiplet above 7 ppm. The chemical shifts from compound to compound vary slightly but the pattern and coupling constants remain similar.
Figure 2.02 Proton NMR Spectra of 2a,6c-Disubstituted Benzosemibullvalenes
29a in CDCl₃ and 40a in DMSO-d₆.
Figure 2.03 Proton NMR Expansions of 2a,6c-Disubstituted Benzosemi-bullvalenes 29a in CDCl\textsubscript{3} and 40a in DMSO-d\textsubscript{6}.
B. Characterization of 1,6c-Disubstituted-2b,6b(2aH)-dihydrobenzo[a]-
cyclopropa[cd]pentalenes.

The NMR spectral data for some 1,6c-disubstituted benzosemi-
bullvalenes are shown in Figure 2.04. Parallel to the situation of the
2a,6c-disubstituted analogs, the protons on the semibullvalene ring
resonate between 3.0 and 6.5 ppm, clear of the aromatic and saturated
hydrocarbon proton resonances. The semibullvalene NMR pattern of
1,6c-disubstituted benzosemibullvalene systems is also very
characteristic. Most shielded is the C^a proton doublet of doublets
(J = 8.3 Hz). Next is the C^b proton doublet (J = 8 Hz) followed by the
proton of C^b as a singlet. Considerably downfield is the C^2 vinyl
proton doublet (J = 3 Hz) at about 6 ppm. The aromatic protons of the
benzo group resonate as a complex multiplet above 7 ppm.
Figure 2.04 NMR Spectral Expansions of 1,6c-Disubstituted Benzosemibullvalenes 29b and 43c in CDCl₃.
C. Characterization of 1,2-Disubstituted-2a,2b,6b,6c-tetrahydrobenzo-[a)cyclopropa(cd)pentalenes.

NMR spectroscopy proved to be essential in the characterization of this set of photoproducts. Shown in Figure 2.05 are the NMR spectral expansions of some 1,2-disubstituted benzosemibullvalenes. The proton coupling pattern of this semibullvalene skeleton is consistently unique. The most shielded C2a proton signal is a doublet of doublets. However, the coupling strength to each of its neighbors (C2b and C6c) is the same (J = 6 Hz); as a result, the signal appears as a triplet. The doublet of doublets of the C2b proton also appears as a triplet from identical coupling to its neighbors (J = 6 Hz), slightly downfield of C2a. The doublet of doublet of doublets signal from the C6c proton also has the same coupling strength (J = 6 Hz) to all three of its neighbors, resulting in a quartet further downfield from the two triplets. Finally, the C6b proton doublet (J = 6 Hz) is most deshielded, at about 4.3 ppm.
Figure 2.05 NMR Spectral Expansions of 1,2-Disubstituted Benzosemi-bullvalenes 40b and a mixture of 43d and 43e.
The 1,2-disubstituted benzosemibullvalenes 43d and 43e are inseparable by column chromatography, and an expansion of the proton NMR is shown in Figure 2.05. From relative single proton signal intensities, the peaks of one compound can be easily distinguished from those of the other. The signal patterns of the two compounds clearly indicate that they are both 1,2-disubstituted benzosemibullvalene derivatives. However, ambiguity arises with respect to the relative positions of the methyl ester and the benzoyl groups.

![Substituted region of benzosemibullvalene](image)

**Figure 2.06 Relative Deshielding Capacities of the Benzoyl and the Methyl Ester Groups Determined from Compounds 65a and 65b.**

The assignment was based on NMR chemical shift data. It was noticed that the chemical shifts of H2a and H6b on the two benzosemibullvalenenes were distinctly different. One group has a stronger deshielding effect on the neighboring methine proton (H2a or H6b) than the other. Therefore, the determination of the relative deshielding strength between the benzoyl and the ester will provide
the answer. A model set of compounds (65a and 65b, Figure 2.06) was uncovered from a literature search; the magnetic environment of these compounds is very similar to the substituted region of the benzosemibullvalenes. The reported NMR of these compounds reveal that the benzoyle group has stronger deshielding properties; the methyl adjacent to the benzoyle on 65a is 0.10 ppm downfield of the methyl adjacent to the ester on 65b. Based on this result, the structures compounds 43d and 43e were assigned as shown in Figure 2.05.

Another interesting problem with the characterization of 1,2-disubstituted benzosemibullvalenes is the assignment of the C2a and C2b protons. Recall that both signals give rise to one proton triplets and have similar but not identical chemical shifts. This problem is solved by the use of a lanthanide shift reagent (Eu(hfc)3). It was reasoned from a similar study with cyclooctatetraene derivatives that the benzosemibullvalene would complex to the shift reagent as shown in Figure 2.07. The C2a and C2b protons are very close to each other and have similar orientations. Since the C2a proton is nearer to the site of complexation,
it should be more sensitive to additions of the shift reagent. From successive additions of the shift reagent to a maximum of 30 mole %, the changes in chemical shifts of each signal were recorded. These chemical shift changes ($\Delta \nu$) are plotted for both compounds, 43d and 43e, in Figure 2.08.

Figure 2.08 Plots of Change in Chemical Shift ($\Delta \nu$) Against the Mole % of Eu(hfc)$_3$ Added for Compounds 43d and 43e.
The slopes on the graphs of Figure 2.08 show large differences in sensitivity to the shift reagent. This allows for the assignment of the more sensitive triplet to \( H_{2a} \) and the less sensitive triplet to \( H_{2b} \). The confidence in this assignment is supported by the positive correlation between the other slopes to their established assignments. Consequently, the \( H_{2a} \) signals are more shielded than the \( H_{2b} \) signals in these 1,2-disubstituted benzosemibullvalenes.

D. Characterization of Other Disubstituted Benzosemibullvalenes.

The NMR spectrum and expansion of methyl 6c-benzoyl-2a,2b-dihydrobenzo[a]cyclopropa[cd]pentalene-6b-carboxylate (43f) are shown in Figure 2.09. The semibullvalene skeleton of 6b,6c-disubstituted benzosemibullvalene 43f also has an informative pattern of signals. The following signals are described going from most shielded to least shielded in progressive order. The \( H_{2a} \) doublet of doublets (\( J = 8.3 \) Hz) is the most shielded followed closely by the \( H_{2b} \) doublet (\( J = 8 \) Hz). Resonating further downfield is the vinyl \( H_2 \) doublet of doublets (\( J = 5.3 \) Hz) and the vinyl \( H_1 \) doublet (\( J = 5 \) Hz). The aromatic protons resonate above 7 ppm. These assignments were also supported by decoupling experiments. Although, the spectroscopic evidence from NMR led to the assignment of a 6b,6c-disubstituted benzosemibullvalene skeleton, the uncertainty as to whether the position of the substituents are correctly assigned or reversed still remained. Owing to the crystalline nature of the molecule, an X-ray analysis was performed by Dr. Pokkuluri to confirm the position of the substituents; an ORTEP\textsuperscript{82} diagram of the structure is shown in Figure 2.10.
Figure 2.09 NMR Spectrum and Expansion of Methyl 6c-Benzoyl-2a,2b-dihydrobenzo[a]cyclopropa[cd]pentalene-6b-carboxylate (43f) in CDCl₃.
The NMR spectrum in Figure 2.11 is that of methyl 6c-benzoyl-2a,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-6b-carboxylate (43g). The semibullvalene ring system shows H_{2a} as the most shielded signal appearing as a doublet (J = 3 Hz); next is the H_{6b} doublet (J = 2 Hz). The other two signals are further downfield. The proton on C_{2} is a doublet of doublets (J = 5,3 Hz); This is slightly upfield of the doublet of doublets (J = 5,2 Hz) from the C_{1} proton. Again, the aromatics resonate above 7 ppm. Through an understanding of the [1,3] photochemical shifts present in many of these benzosemibullvalene systems, and the fact that this compound (43g) is a product of compound 43f, the relative positions of the ester and the benzoyl groups can be assigned without another X-ray analysis.
Figure 2.11  a) NMR Spectral Expansion of Methyl 6c-Benzoyl-2a,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-2b-carboxylate (43g) in CDCl₃.

b) Decoupling at 4.52 ppm.
From examination of the many disubstituted benzosemibullvalene spectra in this section, the substituent locations give rise to characteristic patterns of signals in a clear region of the NMR spectrum. Although the substituents may be different, the location of these signals and their coupling constants stay relatively unchanged. This provides a vital asset in the study of the benzobarrelene systems, as NMR can be used to deduce the structure of the photoproducts easily.

As an extension, NMR is used in many studies for directly determining photoproduct ratios. The single proton signals of the different semibullvalene compounds rarely suffer from overlap with each other; therefore, it is possible to obtain a clear integration of the signals. Quantitative analysis by NMR has been well established to be very accurate with projected integration errors of ±3% on baseline-separated signals. This aspect proved to be quite effective because of the inherent instability that many of these benzosemibullvalenes have to the high temperature GC columns.
PART III. PHOTOCHEMISTRY OF SYMMETRICALLY DISUBSTITUTED BENZOBARRELENES

A. Photochemistry of Dimethyl 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (29).

The solution photochemistry of the title compound, dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (29), was first investigated by Grovenstein, Campbell, and Shibata\textsuperscript{60} over 20 years ago. They discovered that direct photolysis of benzobarrelene 29 gives complete conversion of starting material to dimethyl benzocyclooctatetraene-7,8-dicarboxylate (29c) and that acetone-sensitized photolysis gives three unidentified products in a 5 : 3 : 2 ratio.

Figure 3.01 Photochemistry of Compound 29 Reported by Grovenstein et al. in 1969.

In 1975, Bender and Brooks\textsuperscript{83} reinvestigated this compound in order to determine the mechanism of cyclooctatetraene 29c formation. Shown in Figure 3.02 are two possible routes, both initiate from a
photochemical \([2+2]\) intramolecular cycloaddition followed by a thermal ring opening. However, the routes differ with respect to the double bonds involved. Starting from 2-deuterionaphthalene, they prepared benzobarrelene 29 with deuterium labels at the \(C_7\) and \(C_9\) positions. Photolysis of this deuterated benzobarrelene gave benzocyclooctatetraene 29c with labels solely at the \(C_2\) and \(C_9\) positions, corresponding to the initial vinyl-vinyl bridging route. No mention was made of the acetone-sensitized photoreaction.

Figure 3.02 Mechanistic Study for Benzocyclooctatetraene 29c Formation Performed by Bender and Brooks\(^8\) in 1975.
In order to extend this investigation to the solid state, the solution photochemistry must be fully understood first. In accordance with the previous studies, direct photolysis (λ > 290 nm) was found to yield benzocyclooctatetraene 29c as the only product. However, benzophenone sensitization, where the benzophenone absorbs essentially all the incident radiation (λ > 330 nm), gives complete conversion to a 78% yield of a different product. This was subsequently characterized as dimethyl 2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-2a,6c-dicarboxylate 29a. This assignment is based mainly on the NMR spectral data (Figures 2.02 and 2.03).

Benzosemibullvalene 29a was photolyzed directly and under acetone sensitization to give another product at a maximum conversion of 52% by GC. This compound was determined, after chromatographic separation, to be dimethyl 2b,6b-dihydrobenzo[a]cyclo[cd]pentalene-1,6c-dicarboxylate 29b with the NMR spectrum shown in Figure 2.04.
Being aware of the possibility of secondary photoproducts, the solution phase photochemistry of benzocyclooctatetraene 29c was also investigated. Direct photolysis of compound 29c led to no detectable photoproducts by GC. On the other hand, acetone-sensitized photolysis of compound 29c gives, after work-up, 71% of another product. Based mainly on NMR data, this compound was identified as dimethyl 2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-2,6c(2aH)-dicarboxylate (29e).

Racemic benzosemibullvalene 29a is suggested to arise via a triplet-mediated di-\(\pi\)-methane photorearrangement. The selected path is through an initial vinyl-vinyl bonding followed by cleavage of bond \(a\) (Figure 3.04). Ring closure of this second biradical produces the observed species. Reflecting on the other di-\(\pi\)-methane
rearrangement possibilities of Figure 0.20, only the described route leads to compound 29a. It can be suggested that bond formation across the two vinyls is energetically less demanding than the disruption of aromaticity from initial benzo-vinyl bonding. With respect to the second bond-breaking step, cleavage of bond a gives a 1,3-biradical with one radical that can be comfortably delocalized onto an ester carbonyl and the other onto the benzene ring. On the other hand, cleavage of bond b gives a 1,3-biradical with one radical that can be delocalized onto the benzene ring but the other radical sits on a methylene position without any resonance stabilization. As a result, bond cleavage of a to form the more stable 1,3-biradical is favored. This leads to benzosemibullvalene 29a as the only observed product. In addition, photoproducts of this nature from similar benzobarrelenes are known.\textsuperscript{53}

\textbf{Figure 3.04} Mechanism of Benzosemibullvalene 29a and 29b Formation.
Benzosemibullvalene 29b is suggested to come from a photochemical [1,3] shift of 29a. The C2a-C6c bond of 29a is cleaved and reformed between the C1-C6c positions. The formation of photoprodudct 29b at a limiting conversion of 52% led to the suspicion of an interesting photostationary state. Pure benzosemibullvalene 29b was photolyzed directly in acetonitrile (λ > 260 nm) as well as from sensitization by acetone (λ > 290 nm) and benzene (λ > 260 nm); all three photolyses gave isomer 29a, and once again, a limiting conversion was obtained. However, the interconversion was noticeably slower in acetonitrile than in the other two solvents. The photostationary state ratios in acetone and benzene were investigated with a series of analytical photolyses. Degassed samples of pure compound 29a, compound 29b, and mixtures of the two were photolyzed. The reactions were monitored by GC to a steady state component ratio. These ratios were calibrated using an internal standard (octadecane).

After 13 runs, the arrived ratio of 29a : 29b in benzene is 7 ± 1 : 3 ± 1 and after three runs, the ratio of 29a : 29b in acetone is 8 : 2. This photoreaction is very likely triplet-mediated. With acetone (T1 = 79-82 kcal/mole) or benzene (T1 = 84.3 kcal/mole) sensitization, the reaction proceeds faster than from direct photolysis in acetonitrile. However, Benzophenone (T1 = 69 kcal/mole) is ineffective as a sensitizer. According to the literature, most photochemical [1,3] shifts occur through the singlet excited state, however, some [1,3] shifts have been reported to mediate through the T2 excited state. The observation that this reaction is enhanced upon use of higher energy sensitizers and retarded with lower energy sensitizers suggests a T2 mediated process.
Benzosemibullvalene 29e is believed to be a tertiary photoproduct of benzobarrelene 29. Upon direct excitation of the benzocyclooctatetraene photoproduct 29c, cyclobutene 29d is detected. Compound 29d is suggested to come from a [2+2] intramolecular cycloaddition, and upon triplet sensitization of this compound, photoproduct 29e can be arrived at from a di-\(\pi\)-methane rearrangement (Figure 3.05). The sequence of reactions to form 29e is not all together unknown; Bender\textsuperscript{87} is actively investigating this process with dimethyl and cyano substituted cyclooctatetraenes. Interestingly, the cyclobutene 29d is thermally unstable and readily reverts back to cyclooctatetraene 29c, thus accounting for the inability to detect its formation from GC monitoring. However, when compound 29c was photolyzed and directly analyzed by NMR, the spectrum (Figure 3.06) showed the formation of a new signal pattern corresponding to the cyclobutene.\textsuperscript{88}
Grovenstein's photolysis\textsuperscript{60} of benzobarrelene 29 in acetone was repeated in light of the three identified photoproducts (29\textit{a}, 29\textit{b}, and 29\textit{e}). The reaction (0.013 M) was monitored by GC for the formation of the three photoproducts. At low conversions, compounds 29\textit{a} and 29\textit{e} are formed in equal amounts. As conversion increases the signal of 29\textit{b} steadily rose. Conversely, the photoinstability of 29\textit{e} slowed its formation at higher conversions. The photolysis was discontinued after all benzobarrelene 29 had reacted.
and the final ratio of 29a : 29e : 29b was 65 : 25 : 9. It was also noticed from a series of similar analytical photolyses that the ratios varied not only with conversion but with the concentration of starting material. Reasoning that benzosemibullvalene 29e comes from an initial singlet process and the others from triplet processes, higher concentrations of starting material will allow for more direct absorption of incident radiation by the substrate, giving more singlet-mediated compound 29e. Benzobarrelene 29 is almost transparent to wavelengths above 330 nm; as a result, benzophenone sensitization using these long wavelengths gives no compound 29e.

Crystals of 29 were photolyzed with a medium pressure mercury lamp (λ > 290 nm) and a nitrogen laser (λ = 337 nm). Benzocyclooctatetraene 29c is the only product formed at a maximum conversion of 30% in both cases. Extended photolysis results in yellowing and surface melting of the crystals. The formation of benzocyclooctatetraene 29c displays crystalline state reactivity; however, this is the same product seen in direct solution photolyses, via a singlet-mediated [2+2] cycloaddition. The center-to-center distance of the two vinyl groups is 2.46 Å from X-ray crystal analysis and this is well within the established limiting distance of 4.1 Å for intermolecular [2+2] cycloadditions. Solution intramolecular [2+2] cycloadditions for acyclic non-conjugated dienes have a limiting double bond separation to 1,7-dienes. Greater diene separations result in only cis/trans isomerization.
B. Photochemistry of 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid (40).

Direct solution photolysis of diacid 40 gives complete conversion to benzocyclooctatetraene-7,8-dicarboxylic acid (40c) as the only product. However, this diacid photoproduct readily loses water in solution at room temperature to give the corresponding anhydride (41d, Figure 3.07).

![Figure 3.07 Photoproducts from 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid (40).]
Diacids are too polar to pass through the GC columns in the laboratory. Therefore, the reaction mixtures were monitored by NMR for the loss of starting material. The reaction mixture was concentrated under mild temperatures (T < 60 °C, to reduce anhydride formation) and the two cyclooctatetraenes separated by recrystallization from ethyl acetate. Diacid 40c forms clear yellow needles and anhydride 41d forms red-brown rods. The dehydration of diacid 40c can be easily detected, as the solution changes color from yellow to red-brown. Anhydride 41d was synthesized through diacid 40c by Grovenstein in effort to characterize diester 29c. However, only the results of a carbon-hydrogen analysis was provided in his report. The two cyclooctatetraenes were subsequently characterized by spectroscopic techniques.

An interesting feature of this anhydride formation was noticed during the melting point determination of the diacid 40c. Heating (rate = 1 °C/min) to 122 °C results in the formation of brown spots in the yellow crystal. At 130 °C, the crystal becomes completely red-brown and bulging is seen on the surface. No further change is seen until the crystal melts at 210 °C (mpAnhydride = 210-212 °C). This is a thermal solid state reaction, and although reactions of this nature are known, they are rather uncommon. Paul and Curtin proposed in a review of thermal organic solid state reactions that generally, reactions which occur in inert solvent at a reasonable rate 60-100 °C below the melting point of the reactant, can be made to occur in the solid. This proposal holds true for the above dehydration.

Benzophenone-sensitized photolysis (λ > 330 nm) of diacid 40
led to the formation of two photoproducts. Again the reactions were monitored by NMR for the loss of starting material. These two products were subsequently identified as 2a,2b,6b,6c-tetrahydrobenzo[a]cyclopropa[cd]pentalene-1,2-dicarboxylic acid (40b) and 2b,6b-dihydrobenzo-[a]cyclopropa[cd]pentalene-2a,6c-dicarboxylic acid (40a, Figure 3.08) in a ratio of 92 : 8, respectively. Owing to the inability of carboxylic acids to elute from silica gel columns, the mixture was treated with diazomethane and the resulting dimethyl esters (29a and 29f) separated and characterized. The NMR spectrum of dimethyl ester 29a is identical to the reported results (Figure 2.02). Likewise, the spectroscopic data for benzosemibullvalene 29f is consistent with the data for this compound originally reported by Grovenstein et al.\(^*\)\(^*\) in 1969.

Once separated, the diesters were hydrolyzed under basic conditions to give the corresponding pure diacids for characterization. The NMR spectra for compounds 40a and 40b are shown in Figures 2.02 and 2.05, respectively.

With regard to the mechanism of benzocyclooctatetraene formation, an experiment similar to that of Benders\(^*\)\(^*\) was performed. Benzobarrelene diacid 40 with deuterium labels on the C1, C4, C5, and C8 positions was photolyzed. Similar to the situation in Figure 3.02, there are two possible routes to the formation of benzocyclooctatetraene 40c. Owing to the facile interconversion of diacid 40c to the anhydride 41d, this anhydride was isolated and recrystallized for NMR analysis. The resulting spectrum (Figure 3.08) showed deuterium labels in the positions supporting only the initial vinyl-vinyl bonding route. Assignment of the vinyl protons were based on a shift reagent study performed by Bender\(^*\)\(^*\) on the dimethyl analog (29c).
Figure 3.08 Proton NMR spectra of a) Compound 41d in DMSO-d$_6$.

b) Deuterium Labelled 41d in DMSO-d$_6$. 
Benzosemibullvalene 40a (Figure 3.09) is suggested to come from a di-π-methane rearrangement with initial vinyl-vinyl bonding to give a cyclopropyl biradical (path i). This is followed by cleavage of bond a to give the product. This mechanism is the only di-π-methane route to 2a,6c-disubstitution (Figure 0.20) of benzosemibullvalene. Support also comes from similar results discussed with the dimethyl analog section (PART IIIA).

(heavy circled carbons denote locations of deuterium label)

Figure 3.09  Mechanisms to Benzosemibullvalenes 40a and 40b.
Benzosemibullvalene 40b, however, has two possible di-π-methane routes to its formation. The first possibility is through initial vinyl-vinyl bonding (path i, Figure 3.09), followed by radical cleavage of bond b, and biradical recombination gives compound 40b. The other route is from initial benzo-vinyl bonding (path ii) followed by the regeneration of aromaticity in the second step; subsequent biradical ring closure also gives product 40b. In order to determine which path is taken, benzobarrelene 40 was deuterium labelled in the C1, C4, C5, and C8 positions (Figure 3.09) and photolyzed under benzophenone sensitization. NMR analysis (Figure 3.10a) of the resulting mixture shows the diminution of the H2b (0.75H) signal supporting path i as the exclusive route to compound 40b. This is reasonable as the disruption of aromaticity in path ii would require much more energy.
Figure 3.10a Reaction Mixture Proton NMR Spectra from Benzophenone Sensitization of Deuterated Compound 40 in DMSO-d$_6$. 
It is interesting to note the increase in 1,2-disubstituted benzosemibullvalene diacid formation compared to its 2a,6c-disubstituted counterpart under triplet sensitization. Recall that the methyl ester analog favors the 2a,6c-disubstituted product exclusively over the 1,2-disubstituted product. Having established that the compounds both come from initial vinyl-vinyl bridging (path i, Figure 3.09), the reasons for the increase of bond b cleavage must be addressed. The branching step involved comes from the first biradical to the second biradical. Factors determining selectivity are not clearly understood as methods to measure biradical activation and stability have not been well established. However, the following discussion is an attempt to shed light on some possible considerations.

Examination of the second biradicals (BR1 and BR2, Figure 3.09) shows BR3 has both radicals located on delocalizable centers whereas BR2 has only one of the two radicals on a delocalizable center. As a result, this approach favors the formation of the 2a,6c-disubstituted benzosemibullvalene (40a). In accordance with this approach, dimethyl ester 29 forms the 2a,6c-disubstituted product exclusively from triplet sensitization. However, Weedon et al.\textsuperscript{91b} have found no preference in a study of [2+2] photocycloadditions for the formation of acyl radicals. Cristol\textsuperscript{91c}, on the other hand, reported findings of acyl radical selectivity in the di-\(\pi\)-methane rearrangement of dibenzobarrelenes.

The major difference between carboxylic acids and esters in this situation is that carboxylic acids are less efficient at stabilizing adjacent radicals as the carbonyls are involved in hydrogen bonding.\textsuperscript{96} The lowered efficiency of radicals to resonate onto the acid carbonyl should render both second intermediates (BR2 and BR3) comparable in their
abilities to form.

In addition, bond b may possibly be more easily cleaved than bond a. It has been reported that excited carbonyls adjacent to cyclopropane rings, similar to BRL, tend to favor β-cleavage (bond b) when other factors are not present. The only flaw in using this model is that the biradical considered (BRL) is in the ground state. Another idea that may be mentioned comes from crystallographic analyses of other 2,3-diacyl benzobarrelenes. It was consistently noticed that bond b is substantially longer than bond a (Figure 3.10b). This is a good indication of relative covalent bond strength. However, the major drawback is that it is unclear whether the relative bond strengths will remain unchanged in BRL.

$$\begin{array}{ccc}
\text{Compounds} & \text{bond a (Å)} & \text{bond b (Å)} \\
X = Y = \text{OCH}_3 & 29 & 1.520(1) & 1.542(8) \\
X = \text{Ph}, Y = \text{OMe} & 43 & 1.519(2) & 1.536(2) \\
X = \text{Ph}, Y = \text{OEt} & 44 & 1.517(3) & 1.532(3) \\
X = \text{Ph}, Y = \text{OiPr} & 45 & 1.522(3) & 1.536(3) \\
X = Y = \text{OCH}_3 & 47 & 1.530(4) & 1.540(3) \\
(C_1, C_4, C_5, C_8 = \text{CH}_3) & & & \\
\end{array}$$

Figure 3.10b Table of Bond "a" and "b" Lengths from X-ray Analysis.

In a solid state photochemical study, crystals of benzobarrelene 40 were photolyzed until they became yellow with slight melting on the
surface (4 and 15 hours). The resulting NMR spectra of the dissolved crystals showed no photoproducts. Although UV analysis and the change in physical appearance confirm that photons have been absorbed, no singlet or triplet photoproducts were detected. The excited energy is suggested to have dissipated from internal conversion, generating heat. Fluorescence may have also contributed to the deactivation as well.

Many acids exist in dimers through hydrogen bonding\(^{92}\) and as evidenced in the solid state infrared spectrum of the starting material (Figure 3.11a), compound 40 also is hydrogen bonded. Rather than a single absorption in the carbonyl region, there are several absorption bands arising from the symmetric and asymmetric stretching frequencies of the dimer.

In a crystalline environment, restricting the portion of the molecule that moves most in a reaction will in turn hinder the reaction. It is reasonable to assume that the portions of benzobarrelene 40 that move the most are the carboxylic acid substituents. Although, X-ray crystal data is not available, it can be reasonably proposed that the strong intermolecular hydrogen bonding binds the carbonyl appendages to the lattice such that reaction cannot take place. This situation is depicted in Figure 3.11b, where the anchoring of the acid groups prevents bond formation between the two vinyls.
Figure 3.11 a) Solid State Infrared Spectrum of Diacid 40.

b) Simple Representation of the Reaction Cavity of Diacid 40 Showing the Hydrogen Bond Anchors.
Support for this argument comes from a recent publication by Scheffer et al. on the photochemistry of ester/acid vinyl disubstituted dibenzobarrelene \( \text{66} \) (Figure 3.12). Focussing on the di-\( \pi \)-methane rearrangement, they found that intermolecular H-bonding of the acid essentially prevents initial bonding on the acid side (path ii) in the solid state. The H-bonds anchoring the acid group restricts the motion required in initial bond formation on the acid side. As a result, product \( \text{66b} \) from the initial ester side bonding (path i) is favored 95 : 5. In solution, however, intermolecular H-bonding plays a less significant role.

![Diagram of the reaction](image)

**Figure 3.12 Hydrogen Bonding Effects on the Photochemistry of Benzo-barrelene 66.**
C. Photochemistry of 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Anhydride (41).

Anhydrides are unstable to chromatographic separation on silica gel. In the photochemical study of anhydride 41, nuclear magnetic resonance was the key factor in the assignment of photoproduct structure and ratio.

On an analytical scale, anhydride 41 was photolyzed in ethyl acetate and benzene to give complete conversion to three products, independent of solvent. These three photoproducts were characterized as 2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-2a,6c-dicarboxylic anhydride (41a), naphthalene-2,3-dicarboxylic anhydride (41b), and 2a,2b,6b,6c-tetrahydrobenzo[a]cyclopropa[cd]-pentalene-1,2-dicarboxylic anhydride (41c, Figure 3.13) by NMR and GC-MS of the reaction mixture. The NMR spectrum of the reaction mixture is shown in Figure 3.14. No benzocyclooctatetraene 41d was detected.

In order to confirm the initial NMR assignments, a preparative scale photolysis was performed and the resulting mixture of anhydrides was converted to their corresponding dimethyl esters by reacting the photolysate first with methanol, then with diazomethane. The three diesters were separated by column chromatography on silica gel and independently characterized as benzosemibullvalene 29a, dimethyl naphthalene-2,3-dicarboxylate, and benzosemibullvalene 29f (Figure 3.13).
Figure 3.13 Photochemistry of Benzobarrelene Anhydride 41.
Figure 3.14  NMR Spectrum of Anhydride 41 Reaction Mixture from Direct Photolysis.
The reaction ratios were noticed to fluctuate with the conversion as some photoproducts undergo photodecomposition more rapidly than others. Direct quantum yield measurement of these anhydride products is too difficult as the products could not be purified for GC standardization. The next most effective method of accurate photoproduct ratio determination is to carefully monitor the reaction ratios as a function of conversion. This was done by GC and the resulting 20 readings were plotted in Figure 3.15. GC integration ratios of $41a$, $41b$, and $41c$ were standardized by NMR to be roughly $1 : 1 : 1$, respectively. At higher conversions, the error in GC integration may be substantially greater as the signal trace of $41b$ appears very broad and overlaps with the other two signals. A relative rate of formation of products $41a$, $41b$, and $41c$ was determined to be $25 : 19 : 56$ from the graph of Figure 3.15 at low conversion (ca. $10\%$).

![Figure 3.15 Plot of Anhydride Photoproduct Composition as a Function of Starting Material Conversion.](image-url)
Triplet sensitization using acetone gave complete conversion of starting material to benzosemibullvalenes 41a and 41c. However, compound 41c rapidly decomposes upon further photolysis. The ratio of the two at a low conversion (ca. 12%) is 36 : 64 of 41a to 41c, by GC. The confidence in this determined ratio is much greater as there is no interference of compound 41b in the GC.

Similar to the other systems, the two benzosemibullvalenes in this study are suggested to come from the triplet-mediated di-\(\pi\)-methane rearrangement (Figure 3.16). Benzosemibullvalene 41a comes from initial vinyl-vinyl bonding (path i) followed by bond a cleavage. Recall that 1,2-disubstituted benzosemibullvalenes can be formed from two di-\(\pi\)-methane routes, vinyl-vinyl bridging (path i) or benzo-vinyl bridging (path ii). Selectively labelled (C\(_1\), C\(_4\), C\(_5\), and C\(_8\) positions) starting material was photolyzed to determine the preference between the two routes. Again the labelled positions of compound 41c indicate that initial vinyl-vinyl bonding is the only pathway taken.
Figure 3.16 Pathways to Photoproduct Formation from Anhydride 41.

In both direct and triplet-sensitized photolyses, benzo-semibullvalene 41c is formed approximately twice as fast as the benzosemibullvalene 41a. The relative amount of 1,2-disubstituted product (41c) formed is even higher than in the diacid study. Both 41a and 41c come from the same initial biradical (BR1). The stability between the two secondary biradicals (BR2 and BR3) based on both radical delocalization and from MM2 calculations favors BR3, leading to the minor 2a,6c-disubstituted product (41a). It is suspected that there is a very delicate balance between the formation of these two benzosemi-
bullvalenes and subtle factors can drastically alter product selectivity. Also, the notion that the precursor (BR1) and both immediate branch-point species (BR2 and BR3) are biradicals further complicate the understanding of this selectivity. Anyhow, some suggestions are forwarded in attempt to rationalize the increase in 1,2-disubstituted product formation.

Recall in PART IIIB of this thesis that the tendency for bond b cleavage to BR2 maybe increased based on the observed β-cleavage of cyclopropane rings adjacent to excited carbonyls and on relative lengths of bond a and b in analogous compounds (Figure 3.10b). One major difference between this cyclic anhydride (41) and the dimethyl ester compound (29) is that the carbonyls of the anhydride are efficiently conjugated to each other by the rigid five-membered ring. On the other hand, the two methyl esters of 29 are shown from X-ray analysis to be too bulky for simultaneous conjugation to the adjacent vinyl. Perhaps the stabilization attained by the regeneration of this conjugation in BR2 formation contributes to the increase in 41c formation.

Turning to the formation of naphthalene-2,3-dicarboxylic anhydride (41b), it was noted that this product is not observed from the triplet sensitization of benzobarrelene 41; this indicates a singlet-mediated process. The benzobarrelenes in this study were synthesized by a Diels-Alder cycloaddition of an acetylene to a naphthalene; therefore, it seems reasonable that this naphthalene derivative is formed from a reverse [4+2] cycloaddition along with acetylene. Owing to its volatility, acetylene was not isolated. However, examination of the NMR spectrum in Figure 3.14 shows a 2-proton (relative to the
signal integration of naphthalene derivative 41b) singlet at 2.20 ppm. This signal may likely be from acetylene (2.3 ppm). Uncertainty arises as the solvent acetone has a singlet at 2.07 ppm. Reverse Diels-Alder reactions have been known to occur photochemically in other barrelene systems.

Crystals of anhydride 41 were photolyzed (λ > 260 nm) to give two products, benzosemibullvalenes 41a and 41c (13 hours); the crystal appearance changed from light yellow to cloudy dark yellow with cracks. NMR analysis of the reaction mixture showed a 38 : 62 ratio of 41a to 41c at 8% conversion. Again compound 41c is formed in almost twice the abundance of compound 41a. Thus there is little solid state selectivity in benzosemibullvalene formation. Although no X-ray analysis of the starting material was performed, it can be suggested that the anhydride portion of the molecule does not protrude from the barrelene skeleton enough to be affected by the lattice upon reaction.

It is interesting to note that the naphthalene derivative 41b was not detected in the solid state runs. A possible reason is that the eliminated acetylene is unable to leave the cage of the crystal lattice. The lattice is tight enough to hold the eliminated species in place for recombination to the naphthalene. This "cage effect," originally applied to solution systems also has relevance in the crystal lattice. For example, many Type I cleavages are made competitively unfavorable or drastically altered because the fragments are unable to leave the reaction cavity. In fact only a few decarbonylation reactions from the Type I process have been reported in the solid state and these are shown to have strong lattice cage effects.
D. Photochemistry of 2,3-dibenzoyl-1,4-dihydro-1,4-ethenonaphthalene (42).

In the study of 2,3-diacyl-substituted benzobarrelenes, the idea is that 2a,6c-disubstituted benzosemibullvalenes are generally favored in solution; however, the formation 1,2-disubstituted benzosemibullvalenes is increased from carbonyls with weaker radical stabilizing properties or from the cyclic anhydride where the carbonyls are rigidly fixed in a conjugated system to the adjacent vinyl.

It is necessary to synthesize another system to further investigate this. So far, two carbonyl systems that increase 1,2-disubstituted product formation and only one carbonyl system that gives only 2a,6c-disubstituted product formation have been studied. It would be appropriate to have another substrate that has bulky carbonyl side-chains and can efficiently delocalize adjacent radicals to enhance 2a,6c-disubstituted product formation. Also efficient intersystem crossing to the triplet is preferred as the subject reaction is triplet-mediated. Direct photolysis to the triplet excited state will also allow these di-\(\pi\)-methane reactions to be investigated in the solid state.

As a result, 2,3-dibenzoyl-1,4-dihydro-1,4-ethenonaphthalene (42) was synthesized. The benzoyl group is similar to acetophenone, a known triplet sensitizer that absorbs radiation above 330 nm. The intention is to excite the barrelene system to the triplet state through the benzoyl chromophore for a di-\(\pi\)-methane reaction.

Direct photolysis (\(\lambda > 330\) nm) of benzobarrelene 42 in benzene or acetonitrile gave 2a,6c-dibenzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]-pentalene (42a) as the only product independent of solvent (Figure 3.17). However, higher reaction conversions led to the formation of
1,6c-dibenzoyl-2b,6b(2aH)-dihydrobenzo[a]cyclopropa[cd]pentalene (42c) as a secondary photoprocess from compound 42a. Compound 42a and 42c are chromatographically inseparable; therefore, benzosemibullvalene 42c was characterized in a mixture with compound 42a. The NMR spectral expansion of the mixture is shown in Figure 3.18. The proton pattern in the NMR spectrum of the semibullvalene ring agrees with the reference patterns shown in PART II. On the other hand, benzosemibullvalene 42a was characterized through a benzophenone-sensitized reaction. An 18-molar excess of the sensitizer (absorbs ca. 75% of incident radiation) to benzobarrelene 42 gave complete conversion to compound 42a with only trace 42c detected. Benzophenone was removed easily by column chromatography.

Figure 3.17 Photochemistry of Dibenzoyl Benzobarrelene 42.
Figure 3.18 Characterization of Dibenzoyl Benzosemibullvalene 42c in a Mixture with 42a, by NMR.
Similar to the previous studies, the 2a,6c-disubstituted benzosemibullvalene 42a is suggested to form from a di-\(\pi\)-methane rearrangement through initial vinyl-vinyl bonding followed by bond a cleavage (Figure 3.19). This is formed as the only primary photoproduct from solution photolysis supporting the idea that carbonyls on 2,3-disubstituted benzobarrelenes that can efficiently stabilize adjacent radicals enhance the 2a,6c-disubstituted benzosemibullvalene formation over 1,2-disubstituted benzosemibullvalenes. The quantum yield for the formation of compound 42a is 0.10 (std. dev. = 0.04), determined from linear regression calculations outlined in the experimental section and graphed in Figure 3.20.

Figure 3.19 Mechanisms to Photoproduction Formation from Dibenzoyl Benzobarrelene (42).
Benzosemibullvalene 42c comes from a [1,3] photochemical shift of compound 42a, and again the two are in a photostationary state. The observation that this interconversion does not proceed with benzophenone sensitization indicates that this shift may be either a singlet or a higher energy triplet process. The 42a to 42c photostationary state ratio was determined to be 6 : 4.

\[ \Phi = 0.10 \text{ (std. dev.} = 0.04) \]

\[ 0 \quad x \quad 0.1 \quad x \quad 0.2 \quad x \quad 0.3 \]

% conversion

Figure 3.20 Graph of Quantum Yield ($\Phi$) of 42a versus Starting Material (42) Conversion.

Crystals of benzobarrelene 42 were photolyzed ($\lambda > 290$ nm) for 15 and 45 hours; the resulting unmelted yellow crystals were analyzed by NMR to show a 1 : 1 ratio of benzosemibullvalenes 42a and 42b at 8% and 14% conversion, respectively. Compound 42b was obtained pure from a preparative scale photolysis. Crystals of benzobarrelene 42 were crushed prior to photolysis to achieve a higher conversion (38%). After the reaction, the photolysate was passed through three
successive chromatography columns, the last of which yielded 9% of pure 42b.

Benzosemibullvalene 42b is suggested to come from a di-\(\pi\)-methane rearrangement with initial vinyl-vinyl bonding followed by bond cleavage as shown in Figure 3.19. The interesting feature of the solid state reactivity here is that compound 42b is not observed in solution.

Two approaches to explaining the results can be taken. The first approach relates to the solution determinants of photoproduct formation-electronic effects. The bulky benzoyl groups in the crystal lattice could be out of conjugation with the adjacent carbon-carbon double bond, thus lowering the ability of these groups to delocalize the radical during reaction. This factor could explain the formation of compound 42b in the solid state. The second approach involves the presence of specific interactions with the crystal lattice that can deter or enhance either of the two pathways; it is reasonable to imagine that the large benzoyl groups are required to move substantially during the reaction. As a result, selectivity could be affected by the crystal lattice. As described in the Introduction section, this is the most widely used method of explaining crystalline state reactivity. No X-ray crystal data was available in this case to test the validity of these two approaches. However, a more detailed investigation into the solid state behavior of 2,3-disubstituted benzo-barrelene will be discussed, using these two approaches, in PART IV of this thesis.

Concluding the solution study of benzosemibullvalene formation from the di-\(\pi\)-methane rearrangement, initial bridging of the 2,3-dicarboxyl
benzobarrelene is exclusively vinyl-vinyl in nature, as the disruption of aromaticity in benzo-vinyl bonding requires too much energy. More subtle is the selectivity exhibited in the second bond-breaking step of the reaction pathway. Generally, formation of 2a,6c-disubstituted benzosemibullvalenes are favored over the 1,2-disubstituted products; however, formation of the latter product is increased when carbonyls inefficient at delocalizing adjacent radicals or a cyclic anhydride are used as substituents.
PART IV. PHOTOCHEMISTRY OF UNSYMMETRICALLY DISUBSTITUTED BENZOBARRELENES

A. Photochemistry of Methyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (43).

Success in achieving triplet products from direct photolysis along with some interesting triplet-mediated solid state photochemistry in the dibenzoyl system, inspired the design of the next system for investigation. The objective was to study a similar system whereby substituents can be easily altered yet retain the ability to efficiently intersystem cross to the triplet excited state upon direct irradiation. As a result, methyl 2-benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (43) was synthesized. A benzoyl group is retained and the ester can easily be altered to study substituent effects on the di-π-methane rearrangement. However, it must be recognized that this is now an unsymmetrical benzobarrelene, prepared in racemic form. Furthermore, different regioisomers can also arise depending on the direction of initial bonding; this in effect doubles the number of possible benzosemibullvalene products from the di-π-methane rearrangement (Figure 4.01). Again, the solution photochemistry of this system must be understood first before the behavior in the crystalline state can be probed.
Figure 4.01 Possible Di-π-Methane Rearrangement Pathways for the 2-Benzoyl 3-Ester Benzobarrelene.
Direct photolysis of benzobarrelene 43 in benzene, methanol, acetonitrile, or hexanes gave six products independent of solvent. Overlapping of signals and thermal decomposition of the products from using the DB-1 and carbowax columns prevented accurate reaction product ratio determination by GC. However, the single proton signals of the semibullvalene products in the NMR are sufficiently separated for ratio determination by integration; this is shown in Figure 4.03, and the assignments are correlated with the spectra of pure samples. The photoproduct ratios were thus determined to be 50 : 25 : 17 : trace : 8 : trace of compounds 43a, 43b, 43h, 43c, 43d, and 43e.

Isolated from direct photolysis by column chromatography are methyl 2a-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-6c-carboxylate (43a) and methyl 6c-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-1(2aH)-carboxylate (43b); spectral data are consistent with the established patterns for these structures. Benzosemibullvalene 43a was noticed to possess two crystalline morphologies, needles and prisms, verified by their marked differences in melting points and carbonyl stretching frequencies (needles, MP = 106-107 °C, IR: ester C=O 1733 cm⁻¹, benzoyl C=O 1674 cm⁻¹ and prisms, MP = 113-114 °C, IR: ester C=O 1723 cm⁻¹, benzoyl C=O 1677 cm⁻¹).
Figure 4.02 Photochemistry of Benzoyl Methyl Ester Benzobarrelene 43.
Figure 4.03  NMR Spectral Expansions of the Benzoyl Methyl Ester Benzobarrelene 43 Reaction Mixture from Direct Solution Photolysis in CDCl₃.
Triplet-sensitized photolysis of benzobarrelene 43 was done on an analytical scale with a 10-fold molar excess of benzophenone as the sensitizer (absorbs ca. 85% of incident radiation). The photolysis ($\lambda > 330$ nm) was monitored by GC to show the initial formation of two major photoproducts, benzosemibullvalene 43a and methyl 6c-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-2a-carboxylate (43h). As the conversion increased, compound 43h began to diminish and other photoproducts were observed. Extended photolysis results in a similar GC trace to direct solution photolysis.

Benzosemibullvalene 43h was isolated from a different experiment, photolysis in polymer matrix media. On an analytical scale, starting material 43 was dissolved together with a 10-fold w/w excess of medium molecular weight poly[methyl methacrylate] (PMMA) in a minimum amount of methylene chloride. This mixture was spread over the surface of three Pyrex microscope slides and the solvent allowed to evaporate. The residual clear film housing the reactant was photolyzed ($\lambda > 290$ nm) at room temperature and conversion was monitored by GC until no starting material remained. The resulting ratio was 34 : 12 : 30 : 12 : 12 of 43a, 43b, 43h, 43d, and 43e. The experiment was repeated at -50°C to give a much slower reaction to the same ratio. The preparative scale procedure was same as above except that the inner surface of a large Pyrex tube was used as the support for the film. Flash column chromatography gave compound 43a in the first band followed by benzosemibullvalene 43h in the second band. The third band contained an inseparable mixture of isomers 43d and 43e. Interestingly, no compound 43b could be isolated, although
this compound was detected in the GC of the reaction mixture. This is because compound 43h thermally rearranges in the GC above 200 °C to give 43b; injections at 200 °C gave only partial rearrangement to 43b, and therefore the GC detection of 43b is an artifact of 43h decomposition.

Benzosemibullvalenes 43b and 43h were interconverted by photolysis ($\lambda > 290$ nm) in benzene and acetonitrile to confirm the existence of a photostationary state. The 8 : 2 ratio of compounds 43b and 43h is independent of solvent. Similarly, benzosemibullvalene 43a was photolyzed ($\lambda > 290$ nm) in benzene, acetonitrile, and acetone to give a maximum conversion of 20% by GC (corrected for detector response by NMR) to methyl 1-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-6c(2aH)-carboxylate (43c), shown in Figure 4.02. The reaction is solvent independent, but the rate of conversion in acetone was noticed to be slower. Photoproduct 43c was isolated from a larger scale photolysis in benzene followed by two successive chromatographic separations. Independent photolyses of compound 43c gave compound 43a with the same 8 : 2 ratio of 43a to 43c.

Compound 43a comes from a triplet-mediated di-$\pi$-methane rearrangement via initial vinyl-vinyl bridging on the benzoyl side of the double bond (path ii, Figure 4.01). This is followed by the cleavage of bond a to give the observed product. Similarly, benzosemibullvalene 43h comes from a di-$\pi$-methane rearrangement with initial vinyl-vinyl bond formation on the ester side (path i); subsequent cleavage of bond a gives the product.

Compound 43b is a photochemical [1,3] shift product of benzosemibullvalene 43h, from initial cleavage of C$_{2a}$-C$_{6c}$ bond.
The reaction proceeds on direct photolysis and acetone slows the reaction as it competes with the substrate for radiation. Therefore, this is probably a singlet-mediated process. Likewise, benzosemibullvalene 43c comes from a similar photochemical [1,3] shift of compound 43a. The reaction was also noticed to be slower in acetone, indicating a singlet reaction.

The suggested mechanisms are supported by a deuterium labelling experiment; photolysis of benzobarrelene 43 with deuterium labels placed on the C1, C4, C5, and C8 positions redistributes the labels to the C2b, C3, C6, and C6b positions on benzosemibullvalene 43a. This agrees with the proposed route in Figure 4.01. From the same NMR spectrum of the reaction mixture, the label distribution on compound 43b (C2b, C3, C6, and C6b) also supports the reaction sequence proposed.

In contrast, the 1,2-disubstituted benzosemibullvalenes (43d and 43e) are formed in trace amounts from direct photolysis of benzobarrelene 43. This agrees with the findings in PART III that carbonyl substituents such as benzoyl and ester favor the cleavage of bond a (Figure 4.01, paths i and ii) to form 2a,6c-disubstituted benzosemibullvalenes over the cleavage of bond b to give the 1,2-disubstitution.

The key method to assigning the relative substituent positions on compounds 43a and 43h comes not from NMR, but from IR analysis of their [1,3] shift isomers. Carbonyl stretching frequencies of α,β-unsaturated esters are about 30 wavenumbers lower than their saturated counterparts. Saturated esters have carbonyl stretching frequencies at about 1730 cm⁻¹; the ester of compounds 43a, 43c, and 43h have stretching frequencies at
1723 cm\(^{-1}\), 1726 cm\(^{-1}\), and 1718 cm\(^{-1}\), respectively. However, the ester carbonyl of compound 43b stretches at 1703 cm\(^{-1}\) indicating the presence of \(\alpha,\beta\)-unsaturation.

Quantum yields (\(\Phi\)) for the formation of primary photoproducts 43a and 43h were determined at different conversions and graphed (Figure 4.04). The results were extrapolated to zero conversion using linear least squares calculations to obtain the reported values. Using valerophenone actinometry, the quantum yields for formation of benzosemibullvalenes 43a and 43h are 0.14 (std. dev. 0.01) and 0.13 (std. dev. 0.02), respectively. The quantum yield values for the two di-\(\pi\)-methane rearrangement products are well within error limits of each other, indicating a lack of preference between the benzoyl side and the ester side for solution phase initial bonding.

Figure 4.04 Plots of Quantum Yield versus Conversion of Starting Material for the Formation of Benzosemibullvalenes 43a and 43h in Benzene.
Having established the solution phase photochemical behavior of benzobarrelene 43, this investigation can now be extended to the solid state. Crystals of benzobarrelene 43 were photolyzed and the resulting mixture analyzed by GC to show the formation of three photoproducts. NMR analysis of the reaction mixture showed a 17% conversion to compounds 43d, 43e, and 43f in a ratio of 50 : 30 : 20. NMR expansions of this mixture are shown in Figure 4.05. Higher conversions (ca. 20%) led to surface melting and detectable amounts of compound 43a began to form. On a preparative scale, crystals of 43 were photolyzed (λ > 290 nm) until the crystals were yellow but showed no sign of melting (ca. 18% conversion). The resulting mixture was chromatographed to give three partially overlapping bands; the first was rechromatographed to give methyl 6c-benzoyl-2a,2b-dihydrobenzo[a]cyclopropa[cd]pentalene-6b-carboxylate (43f, 5% yield). This is the first encounter with benzosemibullvalenes of this substitution pattern and therefore required extra effort for its conviction. The NMR spectrum along with details of the assignment are presented in PART II of this thesis. The structure was confirmed by an X-ray crystal analysis (Figure 2.10).
Figure 4.05 NMR Spectral Expansions of the Reaction Mixture from Photolysis of Benzobarrelene 43 in the Solid State.
The second chromatographic band was recovered starting material. The third band was rechromatographed to give an inseparable mixture of 1,2-disubstituted benzosemibullvalenes 43d and 43e. Consequently, the two were characterized together. The NMR spectrum of this mixture is shown in Figure 2.05 and details of this assignment are provided in PART II of the thesis.

Benzosemibullvalene 43f undergoes a photochemical [1,3] shift in solution to give compound 43g; they also exist in a photostationary state (Figure 4.02). The ratio of 43f to 43g is 2 : 8. Varying the solvent (benzene, acetonitrile, or acetone) in a series of analytical photolyses does not affect the ratio; however, the reaction was noticed to proceed slower with acetone, indicating a singlet-mediated reaction.

As shown in Figure 4.01 and mentioned periodically throughout the thesis, 1,2-disubstituted benzosemibullvalenes (43d and 43e) can come from two types of di-π-methane rearrangement, either initial vinyl-vinyl or initial benzo-vinyl bonding. For both cases, initial bridging on the benzoyl side of the double bond leads to compound 43e (paths ii and iii), and bridging on the ester side gives compound 43d (paths i and iv). Deuterium labels on C1 and C4 of the starting material will eventually find their way to the C2a and C6b positions if initial benzo-vinyl bonding occurs. Similarly, the labels will be located in the C2b and C6b positions of photoproducts 43d and 43e if initial vinyl-vinyl bonding is taken. After two successive chromatographic separations of the deuterated reaction mixture, NMR spectra were run in both CDCl3 and benzene-d6; the latter solvent was used to alleviate an overlapping signal. The results show initial vinyl-vinyl bridging was the only route taken (labels on C2b and C6b).
The 6b,6c-disubstituted benzosemibullvalene 43f is suggested to come from an unusual route, a "tri-\(\pi\)-methane" rearrangement;\(^7\) this reaction requires three vinyl groups separated by two methane carbons to proceed, shown in Figure 4.06. Instead of a bond being broken after initial bonding (route of the di-\(\pi\)-methane rearrangement), another bridge is formed to the third double bond. Finally, bond c of this polycyclic biradical is cleaved to directly give the observed product (43f). The \(C_1\) and \(C_4\) labelled benzobarrelene 43 rearranged to the \(C_{2b}\) and \(C_{6b}\) positions of the product supporting this tri-\(\pi\)-methane mechanism. However, there

![Figure 4.06 Tri-\(\pi\)-Methane Rearrangement Mechanism to Form Benzosemibullvalene 43f.](image-url)
is still uncertainty as to whether initial bond formation is vinyl-vinyl (path i, Figure 4.06), or benzo-vinyl (path ii). The likelihood that both bonds form at the same time is small, as Zimmerman has calculated that such process is energetically disfavored for barrelene itself.\textsuperscript{17}

The observed solid state results are very interesting from the fact that no 2a,6c-disubstituted benzosemibullvalenes are formed. Recall that the reaction pathways to 2a,6c-disubstituted benzosemibullvalenes differ from the 1,2-disubstitution in the second bond-cleavage step (Figure 4.01). Two approaches are forwarded to rationalize this observation.

The first approach relates to the relative stability of the two secondary 1,3-biradical intermediates (BR2 and BR3, Figure 4.07). If a carbonyl group is conformationally aligned to stabilize the adjacent radical of the initial intermediate (BR1) by delocalization, then the system that retains this delocalization after the second bond cleavage step will be more stable (BR2) than the system that loses this delocalization (BR3). As a result, the 2a,6c-disubstituted product from BR2 will be favored. However, if the carbonyl is held out of conjugation, then delocalization of the adjacent radical will not be possible and the 1,2-disubstituted product should also be formed, via BR3.

This rationale has several short-falls; if the carbonyls in the crystal were indeed out of conjugation, both 2a,6c-disubstituted and 1,2-disubstituted regioisomers should be formed, similar to the dibenzoyl 42 solid state results. Only 1,2-disubstitution products are seen here. Furthermore, X-ray crystal analysis of the starting material shows the benzoyl carbonyl is non-conjugated with the
vinyl group but the ester is nicely aligned for conjugation (Figure 4.08). This analysis would predict the formation of 1,2-disubstituted 43d from initial benzoyl side bridging and the formation of 2a,6c-disubstituted 43a from initial ester side bridging. Although this first approach seemed plausible in the rationalization to the solid state results of the dibenzoyl system (42), it is not supportive of the observation here.

Figure 4.07 Radical Stabilization Approach to 1,2-Disubstituted Benzosemibullvalene Formation in the Solid State.
The second approach to rationalizing the sole formation of 1,2-over 2a,6c-disubstitution in the solid state is from specific interactions of the substrate with the crystal lattice. As a unimolecular reaction proceeds from starting material through intermediate(s) to product, the three-dimensional geometry of the species changes within the lattice. Such changes that conform to the lattice environment will be allowed and those that do not, disallowed. First, the differences between the geometric requirements of the two reaction pathways must be understood. Figure 4.09 shows, based on molecular models, the motions required for the formation of compounds 43d (1,2-disubstituted) and 43h (2a,6c-disubstituted), from initial ester-side bridging. In order to emphasize the geometric changes with molecular motion, the models are drawn with the benzo-plane fixed for reference. The key items to watch for are the movements of the large carbonyl appendages, as they are intimately associated with to the bond-making and bond-breaking portion of the...
Figure 4.09 Motions Required for Benzosemibullvalenes 43d and 43h Formation.

molecule. These appendages are most likely to suffer from lattice interferences. Cleavage of bond b to form compound 43d causes a
slight shift of both ester and benzoyl groups to the left. Cleavage of bond a to give compound 43h maintains the benzoyl in the frontal downward position but pivots the ester tremendously upward and to the right, sweeping out a large volume of space. Clearly, formation of the favored solution products (2a,6c-disubstituted products) requires more movement than its 1,2-disubstituted counterpart. However, one must be aware that the described motions may be exaggerated, as the movements of the benzo-ring are not considered.

The next step is to examine the crystal lattice of the starting material for close contacts which may hinder or assist the required motions. The validity of the representation using the benzo ring as a fixed point of reference is supported; from the table of intermolecular distances less than 3.60 Å, there are many contacts above and below the benzo ring limiting its allowed motion during reaction. In association with the carbonyl appendages, four intermolecular contacts are found that would clearly inhibit the upward and outward movement of the two appendages with respect to the benzo-plane; these are shown with dotted lines in Figure 4.10. These interactions are suggested to deter the formation of 2a,6c-disubstituted benzosemibullvalenes in the solid state.

First the benzoyl carbonyl oxygen is involved in an H⋯O contact (2.70 Å) with the ortho-proton of a neighboring benzoyl phenyl group. This interaction prevents the ortho-proton and oxygen of the benzoyl group from moving upward and outward to form compound 43a. On the other side, the ether oxygen and the carbonyl carbon on the ester are in very close proximity to an aromatic hydrogen of an adjacent molecule, at 2.78 Å and 2.82 Å, respectively. The sum of van der Waals radii for H⋯O is 2.72 Å.
and for C···H is 2.90 Å. The directional influence of these contacts restricts the upward and outward movements required for the formation of compound 43h. As a result, the less motion-demanding formation of compounds 43d and 43e becomes competitively favorable. These described distances are very significant, as the closer the contact, the better the control in selectivity.

Figure 4.10 Packing Stereodiagram for Benzoyl Methyl Ester Benzo-barrelene 43.

Benzosemibullvalene 43f is the first observation of a tri-π-methane rearrangement in this study. In fact, very few tri-π-methane rearrangements have ever been observed. Photoproduct 43f is formed only in the solid state, thus some specific lattice effect must be enhancing the formation of this product. Recall, the substituted vinyl on the ester
side is required to bond to the benzo-ring in the described mechanism (Figure 4.06). Upon examination of the above intermolecular contacts, the ester carbonyl carbon is 2.82 Å away from an aromatic hydrogen of an adjacent molecule. This is well below the sum of van der Waals radii for C···H distance of 2.90 Å.\textsuperscript{79} The directionality of this interaction encourages the ester group to move toward the benzo ring. This interaction could, in turn, lower the activation parameters required for benzo-vinyl bridging, resulting in the formation of the tri-\(\pi\)-methane product 43f in the solid state. A similar interaction is not present on the benzoyl side and therefore, the reciprocal product is not observed.
B. Photochemistry of Ethyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (44).

The simple replacement of a methyl group with an ethyl group was done to study the effect of the crystal lattice on a slightly different molecule. Before the solid phase selectivity can be investigated, the solution photochemistry of ethyl 2-benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (44) must be thoroughly understood first (Figure 4.11).

![Diagram of photochemistry of ethyl 2-benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (44).](image)

*Figure 4.11 Photochemistry of Ethyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (44).*
Similar to the methyl analog, direct photolyses in benzene or acetonitrile led to two major and four minor photoproducts, independent of solvent. These were later identified by NMR to be compounds 44a, 44b, 44c, 44d, 44e, and 44f in a ratio of 45 : 32 : 10 : 10 : 3 : trace by NMR (Figure 4.11). On a preparative scale three bands were isolated from column chromatography. The first two bands were ethyl 2a-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-6c-carboxylate (44a) and ethyl 6c-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-1(2aH)-carboxylate (44b), respectively. The spectral patterns of these compounds were correlated to patterns in PART II for their assignment. The third band was a 1 : 7 : 2 inseparable mixture of benzosemibullvalenes 44c, 44d, and 44e; the latter two compounds were characterized from this mixture. Again, their assignments were based on NMR data.

Triplet-sensitized photolysis of compound 44 using an 80-fold molar excess of benzophenone (absorbs ca. 92% of incident radiation) gave two major products, benzosemibullvalenes 44a and 44c in a ratio of 48 : 52 by GC. Compound 44c was isolated from column chromatography for characterization.

The photostationary state between benzosemibullvalenes 44c and 44b was confirmed from independent photolyses of the two. The ratio of 44b to 44c is 8 : 2 by NMR. This interconversion is independent of solvent. Likewise, benzosemibullvalene 44a photolyzes (λ > 290 nm) to give the [1,3] shift product 44f in a photostationary state ratio of 9 : 1 = 44a : 44f by NMR. Benzosemibullvalene 44f, however, could not be separated from 44a and was, therefore, characterized in a mixture. These [1,3]-photochemical shifts initiate through the cleavage of the C2a-C6c bond. This is likely a singlet process as products are not formed
from the benzophenone sensitization ($\lambda > 330$ nm); also, the use of acetone as a sensitizer ($\lambda > 290$ nm) slows the reaction.

Benzosemibullvalenes 44a, 44c, 44d, and 44e are all products of the di-$\pi$-methane rearrangement (Figure 4.01). Compound 44a comes from initial vinyl-vinyl bridging on the benzoyl side (path i) followed by cleavage of bond a; similarly, compound 44e comes from the cleavage of bond b. Initial vinyl-vinyl bridging on the ester side (path i) followed by cleavage of bond a gives compound 44c, alternatively, cleavage of bond b gives compound 44d.

Similar to its methyl ester counterpart, initial bonding preferences between the ester side (path i) and the benzoyl side (path ii) were determined to be essentially the same from quantum yield measurements for the formation of compounds 44a and 44c, 0.072 (std. dev. = 0.004) and 0.064 (std. dev. = 0.015), respectively.

![Figure 4.12 Graph of Quantum Yield versus Conversion for Compounds 44a and 44c in Benzene.](image)
In the solid state study, crystals of benzobarrelene 44 were photolyzed (λ > 290 nm) until the crystals were slightly yellow but showed no sign of melting (2 hours). NMR analysis of the reaction mixture shows the formation of compounds 44a, 44c, 44d, and 44e at a ratio of 54 : 8 : 23 : 15, respectively at a conversion of ca. 47%. In another experiment, crystals were photolyzed for a longer period (5 hours) to show a similar ratio, 64 : 9 : 18 : 9 of 44a, 44c, 44d, and 44e at ca. 46% conversion.

The interesting feature of this study is the difference in solid state product selectivity from the methyl analog. Recall the methyl analog gave only 1,2-disubstituted benzosemibullvalenes from the di-π-methane rearrangement. In this case, a 2a,6c-disubstituted benzosemibullvalene (44a) is the major product over the other three di-π-methane rearrangement products. Two approaches to rationalizing the observed results are discussed; the first approach considers the relative ability of the carbonyl groups to resonance stabilize the initial radicals formed. The basis of this argument is described in PART III B. X-ray analysis of starting material 44 (Figure 4.13) shows that the ester is in conjugation with the vinyl group and that the benzoyl group is completely out of conjugation. Applying this approach, initial vinyl-vinyl bonding on the benzoyl side will allow the radical next to the ester carbonyl to be delocalized, favoring the 2a,6c-disubstituted product 44a. On the other hand, initial vinyl-vinyl bonding on the ester side will leave both radicals without resonance stabilization; this, therefore, should give both compounds 44d and 44c. The observed results seem quite consistent with this prediction as
compound 44a is the major product over 44e from benzoyl-side bridging, and compounds 44c and 44d are both formed from ester-side bridging.

The alternative approach comes from considering specific steric interactions of the substrate with the crystal lattice; the fewer interactions during rearrangement, the more favorable the product. The geometric requirements for these reactions are the same as for the benzoyl methyl ester compound (43) described in Figure 4.09. Formation of 2a,6c-disubstituted benzosemibullvalenes 44a and 44c requires an upward and outward movement of the appendage on the side of initial bonding, and the formation of 1,2-disubstituted benzosemibullvalenes 44d and 44e requires only a slight sideways shift of the appendages away from the side of initial bonding. The benzo-plane is assumed to be fixed in these
descriptions for simplicity; however, it must be kept in mind that the whole molecule can move during reaction.

Consistent with the model, examination of intermolecular distances less than 3.60 Å shows 13 of the total 19 interactions are associated with the benzo ring. This should, in effect, restrict movement of the benzo ring during reaction. A packing diagram of the starting material is shown in Figure 4.14; relevant contacts to the appendages are drawn with dotted lines. The ester carbonyl oxygen is involved in two contacts, with the ester-side bridgehead proton (2.59 Å) and the ester-side vinyl proton (2.72 Å) of an adjacent molecule. The sum of van der Waals radii for the O···H distance is 2.72 Å. The directionality of these interactions inhibits the upward and outward movement of the ester required for formation of compound 44c (Figure 4.09). As a result, very little compound 44c is produced in the solid state. On the other hand, there are no such interactions preventing the upward and outward movement of the benzoyl group, required in the formation of compound 44a. In fact, examination of the packing arrangement reveals two neighboring contacts pressing on the meta-proton of the benzoyl, one from the bicyclic bridging carbon on the ester-side (2.86 Å) and the other from the benzo-carbon beside it (2.92 Å). Recall that the sum of van der Waals radii for the C···H distance is 2.90 Å. These contacts are beneath the benzoyl and assist in the upward and outward movement giving enhanced compound 44a formation relative to the less motion-demanding 1,2-disubstituted products (44d and 44e). Recall, motions required for compound 44d formation are depicted in Figure 4.09. Again, this approach effectively explains the observed solid state selectivity.
Figure 4.14 Packing Stereodiagram of Benzobarrelene 44 Showing Selected Intermolecular Contacts.

C. Photochemistry of Isopropyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (45).

The isopropyl derivative was also studied with the idea that solid state photoreactivity may experience greater lattice control by the use of a more bulky side-chain group. Again, the solution photochemistry must be investigated first to ensure the completeness of the study.

Direct photolyses (λ > 330 nm) in benzene, acetonitrile, or methanol showed two major products and three minor products independent of solvent (Figure 4.15). The products were subsequently identified as
Figure 4.15  Photochemistry of Benzoyl Isopropyl Ester Benzobarrelene 45.

compounds 45a, 45b, 45c, 45d, and 45e in a ratio of 50 : 30 : 8 : 8 : 4, respectively by NMR integration of the reaction mixture. The photolysis was repeated on a larger scale and from column chromatography, isopropyl 2a-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-6c-carboxylate (45a) was isolated in the first band for characterization. NMR analysis agrees with the typical pattern for these structures, established in PART II. The second band contained a 7 : 3 mixture of
compounds 45b and 45c; trailing the second band were compounds 45d and 45e in another mixture.

Triplet-sensitized photolysis (\(\lambda > 330\) nm) was done using a 37-fold molar excess of benzophenone as sensitizer (absorbs ca. 93% of incident radiation). This is to prevent the formation of compound 45b, a secondary photoprocess. Chromatographic separation gave three bands; compound 45a eluted first (47% yield). Isopropyl 6c-benzoyl-2b,6b-benzo[a]cyclopropa[cd]pentalene-2a-carboxylate (45c) was isolated in the second band for characterization (37% yield). The third band was a 3 : 1 inseparable mixture of compounds 45d and 45e (9% yield). The structures of both compounds 45d and 45e were easily assigned by comparison with the NMR and IR spectra of the other 1,2-disubstituted benzosemibullvalenes described in PART II of this thesis.

Photolyses of benzosemibullvalene 45c in benzene, acetonitrile, or acetone gave compound 45b to a maximum conversion of 87% (9 : 1 = 45b : 45c), independent of solvent. The remaining 45c was inseparable by column chromatography, therefore, isopropyl 6c-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-1(2aH)-carboxylate (45b) was characterized in this mixture. These two compounds are interconverted by a [1,3] shift from initial cleavage of the \(C_{2a}-C_{6c}\) bond. A singlet excited state is suggested, as there is no interconversion with benzophenone (\(E_C = 69\) kcal/mole)\(^{85}\) and the rate of reaction is slowed from acetone photolysis. Benzosemibullvalene 45a was also found to exist in a photostationary state with compound 45f. The photolyses (\(\lambda > 290\) nm) were performed in benzene, acetonitrile, or acetone to afford a 9 : 1 ratio of 45a to 45f independent of solvent. The two compounds are also inseparable by column chromatography;
as a result, isopropyl 1-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]-pentalene-6c(2aH)-carboxylate (45f) was characterized by NMR from the mixture. These two compounds are also interconverted by a singlet-mediated photochemical [1,3] shift based on the same reasoning as above.

Referring to the di-\( \pi \)-methane pathways listed in Figure 4.01, the routes to photoproduct formation can be easily described. Benzosemibullvalenes 45a and 45e both come from initial vinyl-vinyl bonding on the benzoyl side (path ii); bond a cleavage gives compound 45a and bond b cleavage gives 45e. Similarly, benzosemibullvalenes 45c and 45d come from initial vinyl-vinyl bonding on the ester side (path i); the resulting cleavage of bond a gives 45c and cleavage of bond b yields 45d. Initial benzo-vinyl bonding can also give benzosemibullvalenes 45d and 45e (paths iii and iv). However, deuterium studies of analogous compounds in this thesis showed initial benzo-vinyl bonding is too energetically unfavorable to occur. Quantum yield values for the formation of compounds 45a and 45c were determined to be 0.072 (std. dev. = 0.007) and 0.071 (std. dev. = 0.006), respectively (Figure 4.16). This indicates no preference in the side of initial bonding, whether it is on the benzoyl side (path ii, Figure 4.01) or the ester side (path i).
Figure 4.16 Graph of Quantum Yield versus Conversion for Compounds 45a and 45c in Benzene.

In the solid state study, crystals of Benzobarrelene 45 were photolyzed ($\lambda > 290$ nm and $\lambda > 330$ nm) and the resulting unmelted sample was analyzed by NMR. Three compounds were detected, 45a, 45d, and 45e with a ratio of 10 : 45 : 45 at ca. 32% conversion. Photolyses to higher conversions (ca. 73%) causes surface melting; this is accompanied by an increase in compound 45a formation.

It is interesting to see again here the large difference in crystalline phase reaction selectivity compared to solution. The formation of 1,2-disubstituted benzosemibullvalenes is highly favored in the solid state. In an effort to explain the observed results, the same two approaches, used in PART IV-A and PART IV-B, are advanced and critically discussed. Recall that the first approach stems from conformational electronic effects, more specifically the degree of conjugation that the carbonyl has to the
α,β-unsaturation. If the carbonyl is co-planar to the vinyl then it can efficiently stabilize an adjacent radical by delocalization. As a result, bond a of the first intermediate will be cleaved (Figure 4.01), giving 2a,6c-disubstituted benzosemibullvalenes (45a and 45c). Carbonyls out of conjugation should give bond b cleavage to form 1,2-disubstituted benzosemibullvalenes (45d and 45e) as well as their 2a,6c-disubstituted counterparts.

Figure 4.17 Crystalline Conformation of Benzobarrelene 45 from X-ray Analysis.

The crystalline conformation of benzobarrelene 45 is shown in Figure 4.17. The ester carbonyl is in conjugation with the vinyl and the benzoyl carbonyl is almost completely out of conjugation.
with the vinyl. As a result, this approach would favor the 2a,6c-disubstituted product (45a) from path i (Figure 4.01) and the 1,2-disubstituted product (45d) from path ii. The observed results do somewhat show this trend; compound 45d is formed with no observation of its cleavage competitor 45c, and compounds 45a and 45e are both formed. However, isomer 45e is formed four times as much as 45a, opposite to the prediction.

The alternative approach is to examine the geometric demands of each reaction path and correlate these required motions with specific crystal lattice interactions from X-ray data. Holding the benzo-plane fixed, the movements of the bulky appendages are modelled in Figure 4.08. However, examination of the crystal packing in this structure reveals many contacts of the bulky isopropyl side-chain to the crystal lattice and relatively few associated with the benzo-ring. In fact, the table of intermolecular distances less than 3.60 Å shows all 25 interactions are associated with the two carbonyl appendages and only 2 involve the benzo ring. For this reason it is more realistic to model the largest region (carbonyl groups) fixed and observe motions of the next largest region (benzo-ring). These motions are shown in Figure 4.18. The formation of 1,2-disubstituted products requires only a slight sideways movement of the ring away from the side of initial bonding. Formation of 2a,6c-disubstituted products, on the other hand, requires a large upward twist of the benzo-ring on the opposing side to initial bonding. This simple change of reference still indicates that the motion requirements for 1,2-disubstituted benzo-semibullvalene formation are much less than for its 2a,6c-disubstituted counterpart.
Figure 4.18 Motions Required in Relevant Di-\(\pi\)-Methane Pathways, Holding the Carbonyl Substituents Fixed.
Examination of the below 3.60 Å lattice interactions to the benzo-ring shows no significant close contacts. The solid line of Figure 4.19 represents a CHO hydrogen bond (2.37 Å) between the two neighboring benzoyl groups. Further analysis of the packing diagram in Figure 4.19 shows the isopropyl group of an adjacent molecule is positioned directly above the benzo-ring. The dotted lines illustrate the relative positions of the two components the methyls are measured by X-ray analysis to be 3.64 Å and 4.51 Å from the benzo-plane. Recall the sum of van der Waals radii for the CH₃•••C distance is 3.70 Å. The location and distances of these methyl groups will clearly impede the upward twisting motion of the benzo-ring required in 2a,6c-disubstituted product formation (compounds 45a and 45c). On the other hand, the route to 1,2-disubstituted product formation (compounds 45d and 45e) will not shift the benzo-ring towards the isopropyl group, favoring its formation. This approach nicely rationalizes the observed selectivity for compounds 45d and 45e.
Figure 4.19 X-ray Packing Arrangement of Benzobarrelene 45 Shown from Two Different Faces.
The table in Figure 4.20 summarizes the results gathered in this PART of the thesis. The solution photochemical behavior of the three substrates is very similar. All favor the 2a,6c-disubstituted benzo-semibullvalenes greatly over the 1,2-disubstituted products. Factors controlling selectivity are consistent with the rationale based on electronic stabilizing effect provided by the carbonyls, suggested in PART III of the thesis. From the determined quantum yields,

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>( \begin{array}{c} \text{compound #} \text{ initial benzoyl-side bridging} \text{ initial ester-side bridging} \text{ initial ester-side bridging} \text{ initial benzoyl-side bridging} \ \text{E} = \text{CO}_2\text{Me} \text{B} = \text{benzoyl} \end{array} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>( \begin{array}{cccc} 43a \text{ (43c)<em>} &amp; 43b \text{ (43b)</em>} &amp; 43d &amp; 43e &amp; 43f ** \ \text{solution (%)} &amp; 34 &amp; 42 &amp; 12 &amp; 12 &amp; 0 \ \text{solid state (%)} &amp; 0 &amp; 0 &amp; 50 &amp; 30 &amp; 20 \ \text{(17% conversion)} &amp; &amp; &amp; &amp; &amp; \end{array} )</td>
</tr>
<tr>
<td>44</td>
<td>( \begin{array}{cccc} 44a \text{ (44f)<em>} &amp; 44c \text{ (44b)</em>} &amp; 44d &amp; 44e \ \text{solution (%)} &amp; 45 &amp; 42 &amp; 10 &amp; 3 \ \text{solid state (%)} &amp; 54 &amp; 8 &amp; 23 &amp; 15 \ \text{(47% conversion)} &amp; &amp; &amp; &amp; \end{array} )</td>
</tr>
<tr>
<td>45</td>
<td>( \begin{array}{cccc} 45a \text{ (45f)<em>} &amp; 45c \text{ (45b)</em>} &amp; 45d &amp; 45e \ \text{solution (%)} &amp; 50 &amp; 38 &amp; 8 &amp; 4 \ \text{solid state (%)} &amp; 10 &amp; 0 &amp; 45 &amp; 45 \ \text{(32% conversion)} &amp; &amp; &amp; &amp; \end{array} )</td>
</tr>
</tbody>
</table>

* the [1,3] shift product is included in this value.

** Tri-\( \pi \)-methane product.

Figure 4.20 Table Summarizing Solution and Solid State Product Ratios in the Photochemistry of Compounds 43, 44, and 45.
products from initial ester side bridging and initial benzoyl side bridging are formed at about the same rate.

With respect to the three solid state studies in this PART of the thesis, it is interesting to observe that all three, methyl, ethyl, and isopropyl derivatives, possess basically the same crystalline conformation. Consequently, the approach using conformational electronic effects predicts that all three substrates should show similar product distributions. This is not observed; only the ethyl derivative bore consistency with the model. On the other hand, the lattice interaction approach explained the results quite effectively in all three cases.

It is interesting to see that electronic effects, though dominant in solution chemistry, play a secondary role in product determination to specific lattice interactions in solid state selectivity. Further to this matter, such direct comparisons have had recent literature precedence. Scheffer, Trotter et al. also found this in a study of unsymmetrically substituted dibenzobarrelenes.
PART V. PHOTOCHEMISTRY OF BENZOBARRELENE SALTS

The three substrates studied in the previous part of this thesis all possess different lattice environments as shown from X-ray analysis. Lattice interactions in association with the required reaction geometry was determined to be the major factor governing reaction selectivity between the 1,2-disubstituted and 2a,6c-disubstituted di-π-methane products in the solid state. Examination of the geometric requirements for these two regioisomers (Figures 4.09 and 4.18) reveals that the 2a,6c-disubstituted benzosemibullvalene requires much greater motion for formation than its 1,2-disubstituted counterpart. Reflecting on the original concept by Cohen,32 discussed in the Introduction, those reactions with minimal changes in geometry will proceed without much interference from the surrounding lattice and vice-versa. Therefore, the likelihood of a di-π-methane rearrangement to 1,2-disubstituted benzosemibullvalenes should be greater than to its motion demanding 2a,6c-disubstituted competitor. In order to accumulate evidence to support or refute this, it would be ideal to design a method to achieve many different crystal arrangements while avoiding tedious synthetic routes and complicated separations of isomers. The salts of 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic acid (40) seem a logical choice. These compounds, shown in Figure 5.01, can be prepared by simply refluxing stoichiometric amounts of diacid 40 with an amine or metal hydroxide. Standard methods such as NMR, IR, and carbon-hydrogen analyses were used to characterize these compounds. Conveniently, most of these compounds are
crystalline with high melting temperatures. Again, the solution state photochemistry must be investigated first to ensure the completeness of the study. Photoproduct characterization is easily accomplished by conversion to their corresponding acids for reference.

Recall that in the direct solution photolysis of diacid 40 (Figure 3.08), the singlet-mediated [2+2] cycloaddition product (40c) is formed as the only product and triplet products (40a and 40b) are formed only from sensitization. Crystalline compound 40 gives no detectable products from photolysis.

The general procedure used in the study of the salts was to photolyze them in a suitable solvent and analyze the corresponding ratio of photoproducts by NMR signal integration. Photoproduct characterization is easily accomplished by conversion to their corresponding diacids for reference. In a similar fashion, solid state studies were carried out in nitrogen filled NMR tubes and the photoproduct ratios were determined by NMR analysis of the dissolved reaction mixture.
The solution results are listed in Figure 5.02 to show the relative ratios of cyclooctatetraene 40c, benzosemibullvalene 40a, and benzosemibullvalene 40b salts. The photolyses were carried out to incomplete conversion in order to minimize formation of secondary photoproducts. It was noticed that a greater proportion of triplet products are formed from direct photolysis of the amine salts than from direct photolysis of diacid 40.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Trial</th>
<th>Solvent</th>
<th>% starting material</th>
<th>% COT</th>
<th>% 1,2-sub</th>
<th>% 2a,6c-sub</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>1</td>
<td>CDCl₃</td>
<td>54</td>
<td>36</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(extracted)</td>
<td>(35)</td>
<td>(55)</td>
<td>(10)</td>
<td>(0)</td>
</tr>
<tr>
<td>2</td>
<td>CDCl₃</td>
<td>63</td>
<td>30</td>
<td>7</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CDCl₃</td>
<td>56</td>
<td>53</td>
<td>11</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>1</td>
<td>CDCl₃</td>
<td>43</td>
<td>47</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(extracted)</td>
<td>(19)</td>
<td>(70)</td>
<td>(11)</td>
<td>(0)</td>
</tr>
<tr>
<td>2</td>
<td>CDCl₃</td>
<td>64</td>
<td>31</td>
<td>5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>CDCl₃</td>
<td>37</td>
<td>53</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(extracted)</td>
<td>(15)</td>
<td>(70)</td>
<td>(15)</td>
<td>(0)</td>
</tr>
<tr>
<td>2</td>
<td>CDCl₃</td>
<td>62</td>
<td>31</td>
<td>7</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>1</td>
<td>DMSO-d₆</td>
<td>69</td>
<td>8</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(extracted)</td>
<td>(61)</td>
<td>(8)</td>
<td>(27)</td>
<td>(4)</td>
</tr>
<tr>
<td>2</td>
<td>DMSO-d₆</td>
<td>40</td>
<td>9</td>
<td>45</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>1</td>
<td>D₂O</td>
<td>83</td>
<td>11</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(extracted)</td>
<td>(87)</td>
<td>(11)</td>
<td>(0)</td>
<td>(2)</td>
</tr>
<tr>
<td>2</td>
<td>D₂O</td>
<td>72</td>
<td>28</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>1</td>
<td>D₂O</td>
<td>81</td>
<td>19</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(extracted)</td>
<td>(79)</td>
<td>(21)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>2</td>
<td>D₂O</td>
<td>58</td>
<td>42</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>1</td>
<td>CDCl₃</td>
<td>15</td>
<td>61</td>
<td>22</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(extracted)</td>
<td>(9)</td>
<td>(83)</td>
<td>(8)</td>
<td>(0)</td>
</tr>
<tr>
<td>2</td>
<td>CDCl₃</td>
<td>79</td>
<td>7</td>
<td>14</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.02 Photoprodut Ratios from the Solution Phase Photochemistry of Benzobarrelene Salts.

It has been reported that carbonyls of salts have a lesser capacity to resonance stabilize an adjacent radical than the carbonyls of carboxylic acids. This is because the carbonyls are more involved in delocalization of the existing negative charge.
An example of this effect in photochemistry is shown in Figure 3.12 with acid/ester 66. Photolysis of the sodium salt of 66 increases the formation of 66b, the product from a di-π-methane pathway that does not place a radical adjacent to the carbonyl of the salt.

The reduced ability to resonance stabilize an adjacent radical should, from the rational forwarded in PART III of this thesis, increase 1,2-disubstituted product formation relative to 2a,6c-disubstituted product formation. The ratio of 1,2- to 2a,6c-disubstitution should be greater than that of the diacid (4 : 6). The table of results (Figure 5.02) shows that selectivity between the two triplet products is consistent with the model by favoring the 1,2-disubstituted benzosemibullvalene over the 2a,6c-disubstituted benzosemibullvalene in all cases. These results, in turn, further support the proposed rational in PART III of this thesis.

In an effort to reduce the amount of singlet product formed from direct photolysis, mono-salt 54 was synthesized with the idea that a benzoyl analog could be selectively excited and internally transfer triplet energy to the barrelene reactant. With some success, photolysis ($\lambda > 330$ nm) gave enhanced triplet product formation.

Large metal cations have strong spin-orbit coupling effects and can assist in intersystem crossing to the triplet excited state. In light of this, heavy metal salts 52 and 53 were also synthesized and crystallized for photolysis; however, product ratios reveal a very low percentage of triplet product formation in comparison to the amine salts. This shows that the large metal cations used here are ineffective in facilitating intersystem crossing to the triplet of the substrates.

In order to confirm the photoproduct assignments, the reaction mixture was re-acidified, the counter cation extracted, and the
resulting diacid mixture analyzed by NMR. Figure 5.02 shows that the product ratio changes very little from pre-extraction to post-extraction. A typical NMR expansion of the reaction mixture and extracted mixture is shown in Figure 5.03. This region shows that the proton signals of the four compounds are well separated allowing for a clear integration to establish component ratios.

Turning to the underlying reason for this investigation, crystals or powders of all the salts were photolyzed with a medium pressure mercury lamp. Again, the ratios were determined by NMR and the signals can easily be identified by comparison with the solution results.
Figure 5.03 NMR Spectra of the Salt 48 Reaction Mixture in CDCl₃:

a) Before Extraction.

b) After Re-acidification.
Figure 5.04 Photoproduct Ratios from the Solid State Study of Benzo-barrelene Salts.

The solid state photoreactivity of these salts does support the hydrogen bonding theory of diacid 40 outlined in PART III-B of this thesis. Recall that diacid 40 gives no detectable photoproducts in the solid state and that the proposed reason for this stems from the anchoring of the acid protons to the lattice through hydrogen bonding (Figure 3.11). This hydrogen bonding is reduced in mono-salts and removed in disalts;

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>% starting material</th>
<th>% COT</th>
<th>% 1,2-sub</th>
<th>% 2a,6c-sub</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>crystal</td>
<td>85</td>
<td>12</td>
<td>3</td>
<td>0</td>
<td>brown, (mp = 164°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>74</td>
<td>21</td>
<td>5</td>
<td>0</td>
<td>no melt</td>
</tr>
<tr>
<td>49</td>
<td>crystal</td>
<td>88</td>
<td>4</td>
<td>8</td>
<td>0</td>
<td>brown, (mp = 187°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>84</td>
<td>4</td>
<td>12</td>
<td>0</td>
<td>no melt</td>
</tr>
<tr>
<td>50</td>
<td>crystal</td>
<td>67</td>
<td>20</td>
<td>13</td>
<td>0</td>
<td>brown, (decomp. = 90°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>66</td>
<td>22</td>
<td>12</td>
<td>0</td>
<td>melted</td>
</tr>
<tr>
<td>51</td>
<td>crystal</td>
<td>88</td>
<td>10</td>
<td>0</td>
<td>2</td>
<td>brown, (mp = 238°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>88</td>
<td>7</td>
<td>0</td>
<td>5</td>
<td>no melt</td>
</tr>
<tr>
<td>52</td>
<td>crystal</td>
<td>87</td>
<td>12</td>
<td>1</td>
<td>0</td>
<td>brown, (mp &gt; 300°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>83</td>
<td>15</td>
<td>2</td>
<td>0</td>
<td>no melt</td>
</tr>
<tr>
<td>53</td>
<td>crystal</td>
<td>73</td>
<td>27</td>
<td>0</td>
<td>0</td>
<td>brown, (mp &gt; 300°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14</td>
<td>86</td>
<td>0</td>
<td>0</td>
<td>no melt</td>
</tr>
<tr>
<td>54</td>
<td>solid</td>
<td>96</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>brown, (mp = 113°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>97</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>no melt</td>
</tr>
</tbody>
</table>
as a result, there is more movement allowed in the crystal lattice for reaction. Figure 5.04 shows that the crystalline salts studied are all reactive in the solid state.

Although crystal analysis data is not available for comparison, the finding that 1,2-disubstituted benzosemibullvalene formation is favored over its 2α,6c-disubstituted isomer in almost all cases is very supportive to Cohen's hypothesis\textsuperscript{32} that less motion demanding reaction pathways are generally favored over more motion demanding ones in the solid state.

Salts with the most interesting solid state behavior are those with ethylene diamine (51) and 3'-aminoacetophenone (54); In solution, benzobarrelene 51 forms the 1,2-disubstituted product seven times more efficiently than the 2a,6c-disubstituted compound (Figure 5.02); however, the solid state exclusively favors the formation of the latter (Figure 5.04). Without the aid of an X-ray analysis, it is imagined that specific lattice interactions are responsible for the reaction to select the more motion pathway over the lesser motion route. The chromophoric amino salt (54) was designed to internally triplet sensitize the reaction. Although a relatively larger amount of triplet products is formed from solution photolysis, the major product is still the singlet-mediated salt of cyclooctatetraene 40c. In the solid state, however, the only observed product is the triplet 1,2-disubstituted product. It is still not clear as to whether the cause of this triplet selectivity is from internal sensitization or from the lattice forbidding the singlet \([2+2]\) reaction in the solid state.
As seen cumulatively from this and other studies in this thesis, the benzobarrelene system provides a sensitive measure of lattice effects in solid state reactions. Slight steric factors can easily favor one reaction pathway over another. Such a system is useful for further structure-reactivity studies to enable scientists to develop a general system of quantitatively predicting the degree of solid state selectivity from a lattice design.
PART VI. PHOTOCHEMISTRY OF DIMETHYL 1,4-DIHYDRO-1,4,5,8-TETRAMETHYL-1,4-
ETHENONAPHTHALENE-2,3-DICARBOXYLATE (47)

The recent observation of a tri-\(\pi\)-methane\(^7\) rearrangement in bridgehead substituted dibenzobarrelenes\(^1\) urged the study of tetramethyl benzobarrelene 47 for the presence of this rearrangement. The replacement of bridgehead protons of some dibenzobarrelenes with other groups such as \(\text{CH}_2\text{Cl}\), Cl, methyl, or phenyl results in this unusual behavior. Photoproducts observed from the tri-\(\pi\)-methane rearrangement of dibenzobarrelenes are shown in Figure 0.27, products are cyclooctatetraenes with \(C_2\) axes of symmetry and pentalene-like compounds. The underlying reason for this isomerization being favored over the di-\(\pi\)-methane rearrangement was suggested to be due to steric effects combined with radical stabilization from the added tertiary centers; however, confidence in these rationales demands support. In an effort to better understand this phenomenon, the mono-benzo analog was synthesized to determine the generality of this reaction. The symmetrical 1,4,5,8-tetramethyl-naphthalene was used instead of 1,4-dimethylnaphthalene as the diene in the Diels-Alder synthesis of the bridgehead-substituted starting material. This compound was chosen in order to increase the yield of the desired adduct and to avoid a tedious chromatographic separation; dimethylnaphthalene would presumably add to dimethyl acetylenedicarboxylate to give a mixture of two regioisomers.

Direct photolysis of compound 47 (\(\lambda > 290\) nm) in benzene or acetonitrile to complete conversion led to two major photoproducts (47a and 47b, Figure 6.01). However, a secondary photoproduct (47c)
from compound 47b is observed at higher conversions (ca. 45%). This reaction behavior is independent of solvent. The three compounds were subsequently isolated by column chromatography from a preparative scale photolysis.

![Chemical Structure](image)

**Figure 6.01** Photochemistry of Dimethyl Tetramethylbenzobarrelene Diester (47).

Previous benzosemibullvalene ring systems described in this thesis were easily characterized by their signal patterns in the NMR spectrum. However, the replacement of these protons with methyls destroys the coupling, resulting in a series of singlets. Identification is, therefore, more challenging. The NMR spectra of the benzobarrelene starting material and its photoproducts are
shown in Figures 6.02 and 6.03. Various NMR techniques such as APT and NOE were employed; however, the structure of 47a was confirmed to be dimethyl 2a,2b-dihydro-1,2b,3,6-tetramethylbenzo[a]cyclopropa[cd]-pentalene-6b,6c-dicarboxylate and 47b was confirmed to be dimethyl 1,4,6,9-tetramethylbenzo[a]cyclooctene-5,10-dicarboxylate from X-ray analyses.

Photolyses of cyclooctatetraene 47b in benzene or acetone (λ > 290 nm) led to complete conversion to benzosemibullvalene 47c. The reaction in acetone was noticed to be much faster. With knowledge of the precursor structure and familiarity with the reaction sequence involved, compound 47c was assigned by NMR (Figure 6.03) to be dimethyl 2a,6c-dihydro-1,2a,3,6-tetramethylbenzo[a]cyclopropa[cd]pentalene-2b, 6b-dicarboxylate. This compound is suggested to be a tertiary photoproduct of benzobarrelene 47 and a secondary photoproduct of benzocyclooctatetraene 47b. A probable reaction sequence is that compound 47b undergoes an initial intramolecular [2+2] cycloaddition to form a cyclobutene (Figure 6.05). This cyclobutene is a di-π-methane system, and through absorption of another photon, undergoes the triplet-mediated reaction to the product. Recall this reaction sequence has been reported with many of Bender's studies as well as being observed with benzocyclooctatetraene 29d in PART IIIA of this thesis.
Figure 6.02  NMR Spectra (CDCl₃) and Crystallographic Representations of Benzosemibullvalenes 47a and Benzocyclooctatetraene 47b.
Figure 6.03  NMR Spectra of Benzobarrelene 47 and Benzosemibullvalene 47c in CDCl$_3$. 
Triplet-sensitization of benzobarrelene 47 using a two-fold molar excess of benzophenone ($\lambda > 330$ nm, substrate is transparent in this region) gave complete conversion of starting material to two products in an approximate ratio of $1 : 1.5 = 47a : 47d$. Compound 47d was unidentified as it is inseparable by column chromatography and readily decomposes to other unknown compounds upon standing. GC-MS on the reaction mixture shows the same parent mass as 47; however, attempts to quantify it using NMR on the mixture were unsuccessful. It is thought that this unknown triplet product (47d) may possibly be methyl 2b,6b-dihydro-2b,3,6,6b-tetramethylbenzo[a]cyclopropa[cd]pentalene-2a, 6c-dicarboxylate (Figure 6.04), the expected 2a,6c-disubstituted product from a di-$\pi$-methane rearrangement. Its apparent instability is understandable not only from the internal steric strain of the two pairs of methyl substituents Figure 6.04 but Scheffer's research group has found that semibullvalenes with substituents on all three available positions of the cyclopropyl ring (Figure 6.04) readily undergo secondary processes. This inherent instability may also be due to internal steric strain. Molecular modelling calculations show the C⋯C distances of the substituents on the ring to be very short (Figure 6.04), indicating a tremendous strain.
Crystalline phase photolysis of compound 47 using either a medium pressure mercury lamp or a nitrogen laser (λ = 337 nm) gave two products; compound 47a was formed as the major product, 10 : 1 (by NMR) over compound 47b at a ca. 11 % conversion. Higher conversions result in surface melting of the crystal.

Benzosemibullvalene 47a is suggested to come from the interesting tri-π-methane rearrangement shown in Figure 6.05. Recall that this product
is analogous to a minor product (43f) formed in the solid state photolysis of benzobarrelene 43 (Figure 4.06), but this time it is a major product from direct, triplet-sensitized, and crystalline phase photolysis of the starting material. As this product is formed in conjunction with differing photoproducts under both direct photolysis and triplet sensitization, it can be suggested that the reaction proceeds through both the singlet and triplet excited states. The initial bridge formation, vinyl-vinyl or benzo-vinyl, is still uncertain. However, both bonds are not likely to form at the same time as Zimmerman\(^{17}\) has pointed out that the energy requirement for such processes are highly unfavorable in the case of barrelene itself.

There are several differences between the tri-\(\pi\)-methane rearrangements of monobenzobarrelenes and dibenzobarrelenes. Primarily, unsymmetrical dibenzocyclooctatetraenes and pentalene-like compounds are the products from dibenzobarrelenes (Figure 0.27); correspondingly, benzosemibullvalenes are formed from monobenzobarrelenes (Figure 6.05). This is easily rationalized; once the tri-\(\pi\)-methane bridges are formed, the subsequent steps are selected along the potential energy surface such that, branch by branch, the most energetically favorable intermediates are formed. Two bond cleavages to regenerate aromaticity in the two benzo groups of the dibenzo-reaction are essential in the second step (Figure 0.27). The resulting biradical can then branch to give both the unsymmetrical cyclooctatetraene and the pentalene-like compound. In contrast, only one bond is required to break to regain aromaticity in the case of the mono-benzo system as there is only one aromatic ring disrupted; in the same step, the radicals can easily pair to form a benzosemibullvalene. A two bond cleavage to give the dibenzo-type
products requires too much energy.

The other major photoproduct from direct photolysis, benzocyclooctatetraene 47b, comes from a benzo-vinyl [2+2] intramolecular cycloaddition followed by a thermal ring opening (Figure 6.05). This reaction is singlet-mediated as the compound is not observed under triplet sensitization. No cyclooctatetraene from the vinyl-vinyl [2+2] reaction was detected.

Figure 6.05 Proposed Mechanisms to Photoproduct Formation from Benzo-barrelene 47.
Two rationales can be forwarded to explain the preference for the tri-\(\pi\)-methane rearrangement over the di-\(\pi\)-methane reaction. The first rationale is based on the possibility of a charge-transfer process whereby a \(\pi\)-electron of the benzo group donates to the disubstituted vinyl acceptor. This in essence would explain the selected benzo-vinyl bridging over vinyl-vinyl bridging; unsubstituted vinyls are extremely poor electron donors.\(^{113}\) If indeed a charge-transfer was involved, the reaction may be solvent dependent.\(^{114}\) Quantum yields for the formation of compounds 47a and 47b were determined in both benzene and a 1:1 mixture of acetonitrile and benzene (Figure 6.06) and showed no dependency to solvent polarity. Charge-transfer complexes commonly have characteristic absorption bands above 400 nm.\(^{115}\) An ultraviolet absorption study using a range of substrate concentrations exhibited no bands above 400 nm. Also charge-transfer complexes can have characteristic fluorescence spectra, a broad featureless band in the near UV-visible region.\(^{116}\) Fluorescence studies were also conducted to show a very weak emission bands at 335 nm, 350 nm, 367 nm, followed by a tail to 480 nm from excitation at 281 nm. The presence of a charge-transfer remains unsupported.
The second approach is from steric considerations. This is one of the methods used to rationalize the dibenzo results. Although steric effects were not emphasized in their rationale, this approach is thought to play a very large role toward product selectivity in this situation. X-ray analysis of the starting material shows that the bridgehead methyls and the benzo methyls are intramolecularly pushed against each other (Figure 6.07). The determined C-C distance for C_{11} to C_{18} is 2.963(5) Å and C_{16} to C_{17} is 3.013(6) Å. These are remarkably less than the sum of their van der Waals radii (3.40 Å). This strain was first noticed from the angles of the methyls on the aromatic ring, bent away from the bridgehead methyls. An added consequence of this strain is the lengthening of the C_{1}-C_{8a} and the C_{4}-C_{4a} bonds, 1.566(3) Å and 1.561(3) Å. A typical length for an sp^{3}-sp^{3} bond is 1.54 Å; sp^{3}-sp^{2} bonds are even shorter, 1.50 Å. From

---

Figure 6.06  Quantum Yield Graphs for the Formation of Photoproducts 47a and 47b in Benzene and a 1:1 Mixture of Acetonitrile and Benzene.
molecular models, the twisting of the molecule in tri-\(\pi\)-methane bridging reduces the steric strain on the methyls. Crystallographic analysis of the resulting product (47a) shows that the methyls are not as strained; only one methyl-methyl interaction is present, between the methyls on \(\text{C}_{2b}\) and \(\text{C}_3\) (dist. = 3.187(7) Å, Figure 6.02).

![Crystal Structure of Benzobarrelene 47](image)

**Intramolecular Atomic Distances**

<table>
<thead>
<tr>
<th>bond</th>
<th>distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_1-\text{C}_2)</td>
<td>1.538(3)</td>
</tr>
<tr>
<td>(\text{C}_1-\text{C}_8\text{a})</td>
<td>1.566(3)</td>
</tr>
<tr>
<td>(\text{C}_1-\text{C}_9)</td>
<td>1.530(4)</td>
</tr>
<tr>
<td>(\text{C}<em>1-\text{C}</em>{11})</td>
<td>1.521(4)</td>
</tr>
<tr>
<td>(\text{C}_3-\text{C}_4)</td>
<td>1.540(4)</td>
</tr>
<tr>
<td>(\text{C}_4-\text{C}_4\text{a})</td>
<td>1.561(3)</td>
</tr>
<tr>
<td>(\text{C}<em>4-\text{C}</em>{10})</td>
<td>1.530(4)</td>
</tr>
<tr>
<td>(\text{C}<em>4-\text{C}</em>{16})</td>
<td>1.531(4)</td>
</tr>
<tr>
<td>(\text{C}<em>5-\text{C}</em>{17})</td>
<td>1.501(5)</td>
</tr>
<tr>
<td>(\text{C}<em>8-\text{C}</em>{18})</td>
<td>1.504(4)</td>
</tr>
</tbody>
</table>

**Intramolecular Angles**

<table>
<thead>
<tr>
<th>angle</th>
<th>degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_4\text{a}) (\text{C}<em>4) (\text{C}</em>{16})</td>
<td>120.0(2)</td>
</tr>
<tr>
<td>(\text{C}_4\text{a}) (\text{C}<em>5) (\text{C}</em>{17})</td>
<td>127.3(3)</td>
</tr>
<tr>
<td>(\text{C}_7) (\text{C}<em>8) (\text{C}</em>{18})</td>
<td>116.4(2)</td>
</tr>
<tr>
<td>(\text{C}_8\text{a}) (\text{C}<em>8) (\text{C}</em>{18})</td>
<td>127.4(2)</td>
</tr>
<tr>
<td>(\text{C}_8\text{a}) (\text{C}<em>1) (\text{C}</em>{11})</td>
<td>118.5(2)</td>
</tr>
<tr>
<td>(\text{C}_9) (\text{C}<em>1) (\text{C}</em>{11})</td>
<td>110.2(2)</td>
</tr>
<tr>
<td>(\text{C}_{10}) (\text{C}<em>4) (\text{C}</em>{16})</td>
<td>110.2(3)</td>
</tr>
</tbody>
</table>

Figure 6.07 Crystal Structure of Benzobarrelene 47 Showing Selected Bond Lengths and Angles.
Similarly, these methyl-methyl interactions are thought to be responsible for formation of the observed benzocyclooctatetraene (47b). Although vinyl-vinyl cycloaddition does not disrupt benzo-aromaticity, it will, from molecular modelling calculations, thrust the bridgehead methyls towards the aromatic methyls thereby increasing tension (path i, Figure 6.08). This increased tension could easily deter the reaction by increasing the required activation energy for product formation. Benzo-vinyl cycloaddition, on the other hand, will relieve some steric strain (path ii). Consistent with crystallographic data, the calculated methyl-methyl distances from the modelling program are about 3.0 Å. Going to the vinyl-vinyl bridged species, the calculated methyl-methyl distances are reduced to about 2.9 Å; whereas, benzo-vinyl bridging increases the calculated methyl-methyl distances to about 3.1 Å. This reasonably explains the sole formation of the benzo-vinyl addition product (47b) over the vinyl-vinyl addition product.
Figure 6.08 Geometric Requirements for the Formation of [2+2] Cycloaddition Products from Benzobarrelene 47.
PART VII. PHOTOCHEMICAL [1,3] SHIFTS IN BENZOSEMIBULLVALENES

Departing slightly from the main focus of this thesis, an interesting phenomenon was noticed throughout the photochemical investigation of benzobarrelenes. The secondary photoprocess whereby the benzosemibullvalene undergoes a [1,3] shift to another benzosemibullvalene frequently occurred. A general description of these shifts was given in Section VI of the Introduction. However, the interesting feature here is that these shifts are found to be photochemically reversible resulting in unusual photostationary states. Shown in Figure 7.02 are some benzosemibullvalenes studied for this shift.

Consistent with the literature, these reactions proceed either through their singlet (S\textsubscript{1}) or higher energy triplet (T\textsubscript{2}) excited states. These [1,3] shifts come about from cleavage of the C\textsubscript{2a}-C\textsubscript{6c} bond followed by recombination between the C\textsubscript{1}-C\textsubscript{6c} positions of the initially cleaved species (Figure 7.01).

![Figure 7.01 Mechanism of [1,3] Shift Photoconversion.](image-url)
Figure 7.02 Photostationary States of Some Benzosemibullvalenes Studied.
It is interesting to note that the \([1,3]\) shift of benzosemibullvalene 29e leads to an identical compound; the interconversion is degenerate. Also noteworthy is the finding that photolysis of 1,2-disubstituted benzosemibullvalenes gave no substantial conversion.

Judging from the observed results along with some other benzosemibullvalenes\(^{120}\) studied by other groups, the \([1,3]\) shift of benzosemibullvalenes requires a carbonyl-containing substituent adjacent to the bond cleaved. This is understandable since after initial bond cleavage, a radical of the intermediate can be resonance stabilized by the adjacent carbonyl. In situations where the carbonyl substituent is at the \(C_6c\) position, isomerization still retains this carbonyl on the \(C_6c\) position for a reverse photoconversion. This, in turn, suggests an explanation for the photostationary states observed.
EXPERIMENTAL
GENERAL PROCEDURES

Melting Points (MP)

Melting points in degrees Celsius (°C), were determined on a Fisher-Johns hot stage apparatus and are uncorrected.

Infrared Spectra (IR)

Infrared spectra were measured on a Perkin-Elmer 1710 Fourier transform infrared spectrophotometer. Oily samples were prepared as a liquid film on a sodium chloride plate, background corrected for sodium chloride. Solid samples were prepared as pellets with potassium bromide (KBr), background corrected with a freshly prepared blank potassium bromide pellet. Pellets were prepared by grinding approximately 2 mg of sample with 100 mg of KBr and pressing the mixture in a Perkin-Elmer 186-0002 evacuated die with a Carver Model B laboratory press at 17,000 pounds per square inch (psi). All major peaks were reported. Absorption maxima ($\nu_{\text{max}}$) are reported in reciprocal centimeters (cm$^{-1}$) followed by signal intensity and assignment (if made) in parenthesis. Abbreviations: vs = very strong, s = strong, m = medium, br = broad.

Nuclear Magnetic Resonance Spectra (NMR)

Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on Bruker AC-200 (200 MHz), Varian XL-300 (300 MHz), and Bruker WH-400 spectrometers. The chemical shifts were recorded in the $\delta$ scale in parts per million (ppm) with tetramethyl silane (TMS) as the
internal standard at 0 ppm. Deuteriochloroform (CDCl₃) was used as the solvent unless otherwise stated. Signal multiplicity, number of protons, coupling constant(s) (J), and assignment are given in parenthesis. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet.

Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on the following instruments: Bruker AC-200 at 50 MHz, Varian XL-300 at 75 MHz, and Bruker WH-400 at 100 MHz for broad band proton (BB) decoupled and attached proton test (APT) experiments. Chemical shifts in ppm were reported from the signals of the BB decoupled spectra. The solvent was CDCl₃ unless otherwise stated. Assignment (if made) is in parenthesis following each δ.

Mass Spectra (MS)

Low and high resolution mass spectra were recorded with a Kratos MS-50 instrument. Gas chromatography mass spectra (GC-MS), low resolution and high resolution, were carried out on a Kratos MS-80RFA instrument. Ionization for the above was achieved by electron bombardment at 70 electron volts (EI). Desorption chemical ionization (DCI) spectra were done on a Delsi Nermag R10-10C spectrometer using ammonia as the CI gas. Fast atom bombardment (FAB) spectra were recorded on an AEI MS-9 mass spectrometer with Xenon bombardment on to an o-nitrobenzoic acid matrix of the sample. Mass to charge ratios (m/z) are reported with relative intensities in parenthesis.
Ultraviolet spectra (UV)

Ultraviolet spectra were measured on a Perkin-Elmer Lambda-4B UV/Vis spectrophotometer in acetonitrile (CH$_3$CN). The $\lambda_{\text{max}}$ is reported in nanometers followed by the extinction coefficient ($\epsilon$). Abbreviations: sh = shoulder.

Elemental Analyses (EA)

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

Crystallographic Analyses

All X-ray crystal structures were determined on a Rigaku 4-circle diffractometer by either Dr. J. Trotter, Dr. S.J. Rettig, Dr. P.R. Pokkuluri, or Dr. R. Jones of the UBC Department of Chemistry.

Chromatography

Gas chromatographic (GC) analyses were performed on a Hewlett Packard 5890 instrument fitted with a flame ionization detector. Signal integration was done with a Hewlett Packard 3392A attachment. Three fused silica capillary columns were used, a 15m x 0.25mm DB-1 column (J&W Scientific Inc.), a 15m x 0.25mm DB-17 column (J&W Scientific Inc.), and a 20m x 0.21mm carbowax column (Hewlett Packard).

Preparative column chromatographies were done by the Flash method$^{121}$ using 230-400 mesh silica gel (Merck). Eluting solvents are specified in each preparation.
Thin layer chromatography (TLC) was performed prior to each preparative column on pre-coated silica gel plates (type 5554, Merck).

**Solvents and Reagents**

Spectral grade solvents were used for photochemical experiments without further purification unless otherwise stated. Other solvents were purified according to known procedures\(^{122}\) prior to use. Reagents were used directly without further purification unless otherwise stated.

**Photochemical Light Sources**

Photolyses were carried out with either a 450 Watt Hanovia medium pressure mercury lamp or a PRA UV-12 nitrogen laser (337 nm). The desired wavelengths for the lamp were achieved by using Corex (\(\lambda > 260 \text{ nm}\)), Pyrex (\(\lambda > 290 \text{ nm}\)), or uranium glass (\(\lambda > 330 \text{ nm}\)) filter sleeves.

**Solution Photolyses**

Analytical photolyses were conducted in 0.2 ml quartz or Pyrex tubes and some preparative photolyses were performed in 10 ml Pyrex tubes, both sealed with ground glass caps. Samples were degassed by repeating the freeze-pump-thaw cycle twice and sealing under nitrogen. Larger scale preparative photolyses were carried out in an immersion well\(^{123}\) with the sample solution degassed by bubbling with nitrogen for 1/2 h prior to and during photolysis.
Solid State Photolyses

Analytical studies (4-10 mg) were conducted in NMR tubes evacuated and filled with nitrogen prior to photolysis. Preparative photolyses were conducted in 10 ml Pyrex phototubes evacuated and filled with nitrogen for crystalline photolyses. For larger conversions, the crystals were crushed between two Pyrex microscope slides as a sandwich and photolyzed without a nitrogen atmosphere (in all solid state photolyses performed in this thesis, the presence or absence of a nitrogen atmosphere makes no difference to the observed reactivity or product ratios).

I. SYNTHESIS OF STARTING MATERIALS

Dimethyl 1,4-Dihydro-1,4-ethenonapthalene-2,3-dicarboxylate (29)

Following the procedure of Grovenstein et Al., a mixture of naphthalene (108 g, 0.84 mole), dimethyl acetylenedicarboxylate (56 g, 0.44 mole), and hydroquinone (3 g, 27 mmoles) was sealed under vacuum in 8 heavy walled Pyrex tubes such that each tube was less than half full. The tubes were heated at 170-180 °C for 3 days in an explosion-proof oven. The dark brown reaction mixture was dissolved in 500 ml of chloroform and chromatographed on silica gel using ethyl acetate and petroleum ether (30-60 °C) (5 : 95 v/v) as the eluting solvent. The first band was naphthalene, and the second band was the desired compound 29. Recrystallization from methanol gave 14.5 g of colorless prisms (yield 12%).

MP: 105-106 °C (lit. 105.0-105.5 °C).
IR (KBr) $v_{\text{max}}$: 3070 (m, C-H), 1718 (vs, C=O), 1437 (s), 1307 (s), 1245 (vs, C=O), 1052 (s) cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.4-6.9 (m, 6H, aromatic and vinyl), 5.25 (dd, 2H, J = 4.3 Hz, bridgehead), 3.78 (s, 6H, methyl) ppm.

$^{13}$C NMR (75 MHz) $\delta$: 165.83 (C=O), 147.39, 144.59, 138.96, 124.37, 123.02, 52.15, 50.20 ppm.

MS (EI) m/e: 270 (M+, 30), 238 (16), 210 (96), 183 (67), 152 (100), 128 (55).

UV (CH$_3$CN): 230 sh ($\epsilon$ 5460), 275 ($\epsilon$ 1300) nm.

Anal. calcd. for C$_{16}$H$_{14}$O$_4$: C, 71.10; H, 5.22. Found: C, 71.22; H, 5.30.

The structure of this compound was confirmed by an X-ray diffraction analysis. The crystal data were as follows: C$_{16}$H$_{14}$O$_4$, tetragonal, space group $I\bar{4}$, $a = 18.572(4)\AA$, $c = 7.957 (7)\AA$, $V = 2744 (2)\AA^3$, $Z = 8$, $D_{X} = 1.31$ g/ml, $R = 0.034$. Details were published in a paper by J. Trotter.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid (40)

To a solution of 29 (21 g, 81 mmole) in 150 ml of ethanol was added 650 ml of 9.6 M NaOH(aq). The resulting solution was refluxed for 2 h, cooled to room temperature, and washed with 200 ml of diethyl ether to remove unreacted starting material. The basic aqueous layer was then neutralized with concentrated HCl(aq) to give a white precipitate. This was cooled to room temperature again and extracted twice with 500 ml of diethyl ether. The combined extracts were washed twice with 200 ml of water, dried
over MgSO₄, and evaporated under reduced pressure to give 17.0 g of diacid 40 as a white solid (yield 87%). Recrystallization from acetonitrile gave colorless prisms.

MP: 204-205 °C.

IR (KBr) \( \nu_{\text{max}} \): 3100-2300 (br, OH), 1700-1450 (s, C=O), 1279 (s, C-0) cm⁻¹.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \( \delta \): 10.00 (br s, 2H, OH), 7.4-6.9 (m, 6H, aromatic and vinyl), 5.26 (dd, 2H, J = 4.3 Hz, bridgehead) ppm.

\(^1\)H NMR (400 MHz, acetone-\(d_6\)) \( \delta \): 7.4-6.9 (m, 6H, aromatic and vinyl), 5.79 (dd, 2H, J = 4.3 Hz, bridgehead) ppm.

\(^1\)H NMR (400 MHz, CDCl₃) \( \delta \): 7.4-6.9 (m, 6H, aromatic and vinyl), 5.79 (dd, 2H, J = 4.3 Hz, bridgehead) ppm.

\(^13\)C NMR (75 MHz, DMSO-\(d_6\)) \( \delta \): 167.14 (C=O), 147.27 (C), 145.68 (C), 139.51 (CH), 124.34 (CH), 123.20 (CH), 50.16 (CH) ppm.

MS (EI) m/e: 242 (M⁺, 30), 224 (32), 198 (16), 180 (37), 152 (100), 128 (38). Exact mass calculated for \( \text{C}_{14}\text{H}_{10}\text{O}_4 \): 242.0579, found 242.0576.

UV (CH₃CN): 228 (\( \varepsilon \) 5700), 290 sh (\( \varepsilon \) 800) nm.


1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Anhydride (41)

To a solution of 40 (13.0 g, 53.7 mmole) dissolved in 500 ml of freshly distilled methylene chloride was added oxalyl chloride (17.4 ml, 0.20 mole). The solution was refluxed for 15 h in a nitrogen atmosphere. The solvent and excess oxalyl
chloride were evaporated and the remaining solid was recrystallized from a 1:4 mixture of benzene : hexanes to give 10.0 g of the product (yield 83%) as pale yellow needles.

MP: 129-130 °C.

IR (KBr) \( \nu_{\text{max}} \): 1838 (s, C=O), 1767 (s, C=O) cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)) \( \delta \): 7.4-7.0 (m, 6H, aromatic and vinyl), 5.29 (dd, 2H, \( J = 4,3 \) Hz, bridgehead) ppm.

\(^{13}\)C NMR (CDCl\(_3\)) \( \delta \): 160.30 (C), 159.92 (C), 143.67 (C), 139.58 (CH), 125.17 (CH), 124.40 (CH), 45.39 (bridgehead CH) ppm.

MS (EI) m/e: 224 (M+, 40), 180 (38), 152 (100), 128 (40), 76 (45). Exact mass calculated for C\(_{14}\)H\(_8\)O\(_3\): 224.0473, found 224.0472.

UV (CH\(_3\)CN): 246 (\( \varepsilon \) 17500) nm.

Anal. calcd. for C\(_{14}\)H\(_8\)O\(_3\): C, 75.00; H, 3.60. Found: C, 75.13; H, 3.60.

1,4-Diphenyl-2-butene-1,4-dione (55)\(^{75c}\)

Following the method of R.E. Lutz,\(^{75c}\) a benzene (180 ml) and anhydrous AlCl\(_3\) (35 g, 0.26 mole) solution, under nitrogen, was added 15.3 g (11 ml, 0.10 mole) of fumaryl chloride (from Aldrich) through a dropping funnel at a rate of 1-2 drops per second. The reaction mixture was heated to 50-60 °C at all times. After addition, the solution was refluxed for 10 min and then poured into an equal volume of acidified crushed ice. The benzene layer was washed 4 times with warm water, dried over Na\(_2\)SO\(_4\), filtered, and evaporated. The remaining product was recrystallized from ethanol to give 12.4 g of bright yellow needles (yield 53%).
MP: 108-110 °C (lit. 75c 109-110 °C).

IR (KBr) $v_{\text{max}}$: 1650 (m, C=O), 1446 (m), 1323 (m), 1294 (s), 705 (s) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 8.09 (m, 4H, ortho-aromatic), 8.01 (s, 2H, vinyl), 7.66-7.60 (m, 2H, para-aromatic), 7.56-7.49 (m, 4H, meta-aromatic) ppm.

MS (EI) m/e: 236 (M+, 22), 105 (100), 77 (42).

2,3-Dibromo-1,4-diphenylbutane-1,4-dione (56)$^{75b}$

Crystals of compound 55 (10.8 g, 45.8 mmoles) were dissolved in 115 ml of dry chloroform and to this was added dropwise an equimolar amount of bromine (7.32 g, 2.53 ml) under nitrogen. The reaction was stirred at room temperature for an additional 45 min and evaporated to a white solid. Recrystallization from ethanol : chloroform (1 : 5) gave 14.6 g of colorless prisms (yield 81%).

MP: 176-179 ºC (β form, lit.$^{75b}$ 179 ºC decomp.).

IR (KBr) $v_{\text{max}}$: 1681 (s, C=O), 1596 (m), 1446 (m), 1289 (s) cm$^{-1}$.

$^1$H NMR (300 MHz, Benzene-$d_6$) $\delta$: 7.86-7.78 (m, 4H, ortho-aromatic), 7.05-7.01 (m, 2H, para-aromatic), 6.98-6.90 (m, 4H, meta-aromatic), 6.15 (s, 2H, HCHBr) ppm.

MS (EI) m/e: 316 (0.1, M$^+$ - Br), 236 (19, M$^+$ - Br$_2$), 208 (11), 105 (100), 77 (79).

MS (DCI, NH$_3$) m/e: 414 (8, M + NH$_4^+$), 397 (7, M$^+$ + 1), 254 (15), 237 (27), 105 (100), 77 (23).
1,4-Diphenyl-2-butyne-1,4-dione (57)\textsuperscript{75a}

Dibromide 56 (13.5 g, 34.1 mmoles), triethylamine (11.1 ml, 80 mmoles), and 108 ml of dry benzene were refluxed under nitrogen for 4.5 h. The reaction was cooled to room temperature and the colorless crystals of triethylammonium bromide were filtered off. The resulting brown solution was evaporated to a solid and promptly recrystallized (to avoid polymerization) from methanol to give 4.4 g of brown crystals (yield 55%).

MP: 110-111 °C (lit.\textsuperscript{75a} 110-111 °C).

IR (KBr) \( \nu_{\text{max}} \): 1646 (s, C=O), 1592 (m), 1449 (m), 1317 (m), 1261 (s) cm\(^{-1}\).

\textsuperscript{1}H NMR (300 MHz) \( \delta \): 8.22-8.16 (m, 4H, ortho-aromatic), 7.73-7.66 (m, 2H, para-aromatic), 7.58-7.51 (m, 4H, meta-aromatic) ppm.

MS (EI) m/e: 234 (71, M\(^+\)), 206 (11), 178 (50), 129 (49), 105 (100), 77 (87).

2,3-Dibenzoyl-1,4-dihydro-1,4-ethenonaphthalene (42)

In a thick walled vacuum sealed Pyrex tube was placed compound 18 (500 mg, 2.14 mmoles), naphthalene (4.0 g, 31 mmoles), and hydroquinone (150 mg). The tube was heated to 180 °C for 1.5 h, cooled to room temperature, dissolved in chloroform, and chromatographed using an eluting mixture of diethyl ether and hexanes (1 : 9 v/v). The first band was unreacted naphthalene. Next came the desired product as a brown oil. This oil was treated with activated charcoal and celite in diethyl ether, filtered, and
evaporated to afford 146 mg of a colorless oil (yield 19%). Solidification from scratching in hexanes and recrystallization from benzene : hexanes (1 : 5 v/v) gave colorless prisms.

**MP:** 102-103 °C.

**IR (KBr)** $\nu_{\text{max}}$: 1649 (s, C=O), 1594 (m), 1273 (s) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.45-7.00 (m, 16H, aromatic and vinyl), 5.42 (dd, 2H, J = 4,3 Hz, bridgehead) ppm.

$^{13}$C NMR (50 MHz) $\delta$: 194.52 (C=O), 153.94 (C), 145.02 (C), 139.46 (CH), 137.87 (C), 132.77 (CH), 128.50 (CH), 128.21 (CH), 124.68 (CH), 123.41 (CH), 51.94 (CH, bridgehead) ppm.

**MS (EI) m/e:** 362 (M+, 49), 257 (36), 128 (55), 105 100), 77 (60).

Exact mass calculated for C$_{26}$H$_{18}$O$_2$: 362.1307, found 362.1305.

**UV (CH$_3$CN):** 255 ($\epsilon$ 21500) nm.

Anal. calcd. for C$_{26}$H$_{18}$O$_2$: C, 86.17; H, 5.01. Found: C, 85.97; H, 5.00.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid Monomethyl Ester (58)

A solution of anhydride 41 (9.1 g, 40.6 mmoles) in 300 ml of dry methanol was refluxed under nitrogen for 2 h. The methanol was evaporated and the resulting yellow oil was dissolved in 100 ml of methylene chloride and washed twice with 75 ml of water. The organic layer was dried over MgSO$_4$, filtered, and evaporated under reduced pressure to afford 10.8 g of a viscous oil (yield 100%).

**IR (liquid film)** $\nu_{\text{max}}$: 3400-2500 (br, OH), 1719 (s, C=O), 1637 (s), 1278 (C=O) cm$^{-1}$. 
$^1$H NMR (300 MHz) $\delta$: 7.3-6.9 (m, 6H, aromatic and vinyl), 5.89 (dd, 1H, $J = 5.2$ Hz, bridgehead), 5.60 (dd, 1H, $J = 5.2$ Hz, bridgehead), 4.00 (s, 3H, methyl) ppm.

$^{13}$C NMR (75 MHz) $\delta$: 166.50 (C=O), 166.05 (C=O), 148.25 (C), 146.19 (C), 145.38 (C), 145.26 (C), 139.47 (CH), 139.25 (CH), 124.29 (CH), 124.25 (CH), 123.15 (CH), 123.11 (CH), 52.20 (CH$_3$), 49.94 (CH), 49.79 (CH) ppm.

MS (EI) m/e: 256 (M+, 25), 212 (31), 196 (20), 179 (18), 152 (100), 128 (30). Exact mass calculated for C$_{15}$H$_{12}$O$_4$: 256.0736, found 256.0728.

**Methyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (43)**

To a solution of acid-ester 58 (5.5 g, 22 mmoles) in 180 ml of anhydrous methylene chloride was added dropwise oxalyl chloride (5.6 ml, 64 mmoles) and the reaction was refluxed for 1 h. The solvent was evaporated under reduced pressure and the crude acyl chloride, a yellow oil, was redissolved in 2.4 liters of dry benzene. Then approximately 4.4 g (33 mmoles) of anhydrous AlCl$_3$ (from Aldrich) was added in several portions directly to the solution. The reaction mixture was stirred at room temperature for 1 h 45 min under a nitrogen atmosphere. The deep red solution was then quenched with 300 ml of water and the total volume reduced to 1 liter. The solution was then washed with water (2 x 200 ml), dried over MgSO$_4$, filtered, and evaporated. The resulting oil was chromatographed and eluted with 10% diethyl ether in hexanes. The first major band was 1.4 g of the product as a white solid (yield 21%).
Recrystallization from hexanes gave prisms.

**MP:** 127-128 °C.

**IR (KBr) ν_{max}:** 1713 (s, ester C=O), 1667 (s, benzoyl C=O), 1244 (s, C-O) cm\(^{-1}\).

**\(^1^H\) NMR (400 MHz) δ:** 7.6-6.9 (m, 11H, aromatic and vinyl), 5.55 (dd, 1H, J = 6.2 Hz, bridgehead), 5.04 (dd, 1H, J = 6.2 Hz, bridgehead), 3.40 (s, 3H, methyl) ppm.

**\(^1^3^C\) NMR (75 MHz) δ:** 195.60 (benzoyl C=O), 164.14 (C), 159.27 (C), 145.41 (C), 144.12 (C), 141.97 (C), 140.27 (CH), 138.03 (CH), 135.69 (C), 133.39 (CH), 128.57 (CH), 128.52 (CH), 124.55 (CH), 124.34 (CH), 123.25 (CH), 123.07 (CH), 52.29 (CH), 51.61 (CH\(_3\)), 48.89 (CH) ppm.

**MS (EI) m/e:** 316 (M+, 11), 284 (11), 256 (12), 211 (12), 152 (20), 128 (90), 105 (100), 77 (39). Exact mass calculated for C\(_{21}\)H\(_{16}\)O\(_3\): 316.1100, found 316.1103.

**UV (Hexane):** 247 (ε 16890), 290 sh (ε 3220) nm.

**Anal. calcd. for C\(_{21}\)H\(_{16}\)O\(_3\):** C, 79.73; H, 5.10. Found: C, 79.75; H, 5.13.

The structure of this compound was supported by an X-ray diffraction analysis. The crystal data are as follows: C\(_{21}\)H\(_{16}\)O\(_3\), triclinic, space group P\(_{\bar{1}}\), \(a = 9.772\) (8)Å, \(b = 11.034\) (2)Å, \(c = 8.174\) (8)Å, \(α = 92.58(1)^{o}\), \(β = 111.50(8)^{o}\), \(γ = 97.96(1)^{o}\), \(V = 807.8(2)Å^3\), \(Z = 2\), \(D_x = 1.296\) g/ml, \(R = 0.042\).

**Ethyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (44)**

Crystals of 43 (400 mg, 1.27 mmole) were dissolved in 400 ml of dry ethanol and to this was added 4 ml of concentrated H\(_2\)SO\(_4\).
The solution was refluxed for 2 days and neutralized with saturated NaHCO$_3$(aq). The ethanol was evaporated under reduced pressure and the remaining solution extracted with diethyl ether, washed with water, dried over MgSO$_4$, filtered, and evaporated again. The remaining oil was chromatographed on silica gel using diethyl ether and hexanes (1 : 9 v/v) as the eluting solvent. The product eluted in the first band as a white solid (340 mg, 81%). This was followed closely by starting material 43. Recrystallization from hexanes gave colorless rods.

**MP:** 93.94 °C.

**IR (KBr) $\nu_{\text{max}}$:** 1708 (s, ester C=O), 1657 (s, benzoyl C=O), 1255 (s, C-O) cm$^{-1}$.

**$^1$H NMR (400 MHz) $\delta$:** 7.6-6.9 (m, 11H, aromatic and vinyl), 5.55 (dd, 1H, J = 6.2 Hz, bridgehead), 5.02 (dd, 1H, J = 6.2 Hz, bridgehead), 3.85 (q, 2H, J = 7 Hz, CH$_2$), 0.79 (t, 3H, J = 7 Hz, CH$_3$) ppm.

**$^{13}$C NMR (50 MHz) $\delta$:** 195.82 (benzoyl C=O), 163.91 (C), 158.74 (C), 145.66 (C), 144.36 (C), 142.11 (C), 140.52 (CH), 138.17 (CH), 136.03 (C), 133.51 (CH), 128.85 (CH), 128.63 (CH), 124.68 (CH), 123.36 (CH), 123.24 (CH), 61.04 (CH$_2$), 52.56 (bridgehead CH), 49.00 (bridgehead CH), 13.31 (CH$_3$) ppm.

**MS (EI) m/e:** 330 (M+, 15), 284 (16), 256 (15), 152 (10), 128 (17), 105 (100), 77 (20). Exact mass calculated for C$_{22}$H$_{18}$O$_3$: 330.1255, found 330.1251.

**UV (CH$_3$CN):** 251 ($\epsilon$ 16500) nm.

**Anal. calcd. for C$_{22}$H$_{18}$O$_3$:** C, 79.98; H, 5.49. Found: C, 80.10;
The structure of this compound was supported by an X-ray diffraction analysis. The crystal data are as follows: $C_{22}H_{18}O_{3}$, triclinic, space group $\overline{1}$, $a = 10.14(1)$ Å, $b = 11.28(2)$ Å, $c = 8.41(1)$ Å, $\alpha = 96.31(1)^\circ$, $\beta = 110.26(9)^\circ$, $\gamma = 95.62(1)^\circ$, $V = 886.8(2)$ Å$^3$, $Z = 2$, $D_x = 1.237$ g/ml, $R = 0.043$.

Isopropyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (45)

Compound 43 (400 mg, 1.27 mmole) dissolved in 200 ml of dry isopropanol was reacted with concentrated $H_2SO_4$ (1.2 ml) and stirred at reflux for 3 days. G.C. showed an equilibrium ratio (43:45) of 67:29. The reaction was neutralized with sat. $NaHCO_3$(aq) and the isopropanol evaporated. Extracting with diethyl ether, washing with water, drying over $MgSO_4$, filtering, and evaporating under reduced pressure gave a yellow oil. Chromatography of this oil on silica gel using a 1:9 (v/v) mixture of diethyl ether : hexanes as the eluent gave 108 mg of 45 in the first band (yield 25%). This was followed closely by starting material 43 (180 mg, 45% recovered). Recrystallization of 45 from hexanes gave needles.

MP: 77-78 °C.

IR (KBr) $\nu_{max}$: 1695 (s, ester C=O), 1666 (s, benzoyl C=O), 1270 (s, C-O), 711 (s) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.6-6.95 (m, 11H, aromatic and vinyl), 5.57 (dd, 1H, $J = 6.2$ Hz, bridgehead), 5.01 (dd, 1H, $J = 6.2$ Hz, bridgehead), 4.76 (septet, 1H, $J = 6$ Hz, $CH(CH_3)_2$), 0.79 (d, 3H, $J = 6$ Hz, methyl), 0.73 (d, 3H, $J = 6$ Hz, methyl) ppm.
$^{13}$C NMR (75 MHz) $\delta$: 196.07 (benzoyl C=O), 163.50 (C), 158.45 (C), 145.87 (C), 144.53 (C), 142.21 (C), 140.78 (CH), 138.24 (CH), 136.23 (C), 133.68 (CH), 129.10 (CH), 128.77 (CH), 124.80 (CH), 124.58 (CH), 123.46 (CH), 123.38 (CH), 69.13 (isopropyl CH), 52.69 (CH), 49.02 (CH), 21.19 (methyl), 21.14 (methyl) ppm. The above assignments were supported by an APT.

MS (EI) m/e: 344 (M+, 7), 284 (13), 256 (12), 128 (15), 105 (100), 77 (21). Exact mass calculated for C$_{23}$H$_{20}$O$_{3}$: 344.1412, found 344.1418.

UV (CH$_3$CN): 251 ($\epsilon$ 14500) nm.

Anal. calcd. for C$_{23}$H$_{20}$O$_{3}$: C, 80.21; H, 5.85. Found: C, 80.36; H, 5.90.

The structure was supported by an X-ray diffraction analysis. The crystal data are as follows: C$_{23}$H$_{20}$O$_{3}$, monoclinic, space group P2$_1$/c, $a = 7.402(3)$Å, $b = 20.013(5)$Å, $c = 12.556(3)$Å, $\beta = 93.32(2)^{\circ}$, $V = 1856.8(9)$Å$^3$, $Z = 4$, $D_X = 1.232$ g/ml, $R = 0.036$.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid, Diethylamine Monosalt (48)

Crystals of diacid 40 (300 mg, 1.2 mmoles), diethylamine (0.3 ml, 2.9 mmoles), and 15 ml of ethyl acetate were placed in a 50 ml round bottom flask. The solution was refluxed for 20 min and the salt, as a white precipitate was dissolved at reflux with a further addition of approximately 30 ml of ethyl acetate. The clear solution was slowly cooled to room temperature allowing for crystals to form. The resulting colorless rods were suction filtered.
(260 mg, yield 69%).

MP: 163-164 °C.

IR (KBr) $\nu_{\text{max}}$: 3058 (br s), 2772 (br s), 2507 (br m), 1700 (m), 1621 (s), 1524 (s), 1466 (s), 1371 (s) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 9.25 (br s, 2H, acid OH), 7.4-6.8 (m, 6H, aromatic and vinyl), 5.78 (dd, 2H, J = 4.3 Hz, bridgehead), 3.10 (q, 4H, J = 7 Hz, CH$_2$), 1.30 (t, 6H, J = 7 Hz, CH$_3$) ppm.

MS (EI) m/e: (no M+ peak) 242 (4), 224 (32), 198 (40), 180 (25) 152 (100), 128 (40).

MS (FAB) m/e: 316 (M + 1).

UV (CH$_3$CN): 223 sh ($\epsilon$ 9970), 290 ($\epsilon$ 1650) nm.

Anal. calcd. for C$_{18}$H$_{21}$O$_4$N: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.55; H, 6.81; N, 4.40.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid, Pyrrolidine Monosalt (49)

Diacid 40 (300 mg, 1.2 mmoles) and pyrrolidine (0.15 ml, 1.8 mmoles) were refluxed in 15 ml of ethyl acetate for 10 min to form a white precipitate. Approximately 75 ml of ethyl acetate was added at reflux to dissolve the product. This was allowed to cool slowly to form 230 mg of rods after filtration (yield 61%).

MP: 185-187 °C.

IR (KBr) $\nu_{\text{max}}$: 3011 (br s), 2790 (br m), 1578 (vs), 1463 (vs), 1360 (vs), 751 (s) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 9.58 (br s, 2H, acid OH), 7.34-6.88 (m, 6H, aromatic and vinyl), 5.72 (dd, 2H, J = 4.3 Hz, bridgehead), 3.34 (m,
4H, 2 × NCH₂), 2.05 (m, 4H, CH₂-CH₂-CH₂-CH₂) ppm.

MS (FAB) m/e: 314 (M + 1, 22), 72 (100).

UV (CH₃CN): 223 sh (ε 8050), 290 (ε 1280) nm.

Anal. calcd. for C₁₈H₁₉O₄N: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.87; H, 6.07; N, 4.40.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid, Pyrrolidine Disalt (50)

Diacid 40 (70 mg, 0.29 mmole) and pyrrolidine (41 mg, 0.58 mmole) in 4 ml of acetonitrile were refluxed for 45 min and cooled to give small white needles. The crystals were briefly suction filtered to give 80 mg of the salt (yield 70%). Prolonged suction filtration results in removal of one equivalent of pyrrolidine and subsequent melting of the crystals followed by their resolidification as the mono-salt.

MP: ≈ 90 °C (decomposition).

IR (KBr) ν max: 2979 (br s), 2773 (br m), 1558 (vs), 1464 (vs), 1386 (s), 716 (m) cm⁻¹.

¹H NMR (400 MHz, CDCl₃) δ: 7.30-7.20 (m, 2H, aromatic), 6.95-6.85 (4H, m, aromatic and vinyl), 5.50 (br s, 2H, bridgehead), 3.00 (m, 8H, 4 × NCH₂), 1.75 (m, 8H, 2 × CH₂CH₂) ppm.

MS (EI) m/e: (no M⁺) 242 (5), 224 (48), 198 (38), 180 (39), 152 (100), 128 (55), 70 (91).

MS (FAB) m/e: 385 (M + 1).

UV (CH₃CN): 223 sh (ε 6500), 290 (ε 2000) nm.
1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid Ethylenediamine Disalt (51)

Diacid 40 (300 mg, 1.2 mmole) and ethylenediamine (0.15 ml, 2.2 mmole) were refluxed in 20 ml of ethyl acetate for 1 h. The resulting precipitate was suction filtered to give 352 mg of a dry white powder (yield 97%). Recrystallization from water gave colorless needles. These crystals were insoluble in chloroform, acetone, benzene, and acetonitrile.

MP: 235-238 °C.

IR (KBr) \( v_{\text{max}} \): 3100 (br s), 1636 (s), 1559 (s), 1500 (s), 1455 (m), 1386 (s), 711 (m) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \( \delta \): 7.3-6.8 (m, 6H, aromatic and vinyl), 5.70 (dd, 2H, \( J = 4,3 \) Hz, bridgehead), 5.0-4.5 (very br s, 4H, \( 2 \times \text{NH}_2 \)), 2.78 (s, 4H, \( \text{CH}_2-\text{CH}_2 \)) ppm.

MS (EI) m/e: (no \( M^+ \) peak) 242 (5), 224 (31), 198 (37), 152 (100), 128 (48).

MS (FAB) m/e: 303 (\( M + 1 \)).

UV (CH\(_3\)CN): 223 sh (\( \epsilon 4160 \)), 290 (\( \epsilon 500 \)) nm.

Anal. calcd. for C\(_{16}\)H\(_{18}\)O\(_4\)N: C, 63.57; H, 6.00; N, 9.27. Found: C, 63.54; H, 6.00; N, 9.29.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid, Rubidium Disalt (52)

Acid 40 (200 mg, 0.8 mmole) was dissolved in 12 ml of acetonitrile and to this was added 0.1 ml of 50% (w/w) rubidium hydroxide in water (1.6 mmole, Aldrich). The solution was diluted to 17 ml, stirred
at reflux for 30 min, cooled, and filtered to give 271 mg of a white solid (yield 82%). Recrystallization by slow evaporation of methanol in an NMR tube gave colorless needles.

MP: > 300 °C.

IR (KBr) \( \nu_{\text{max}} \): 3400-3000 (br s), 1569 (vs), 1542 (vs), 1371 (vs) cm\(^{-1}\).

\(^1\)H NMR (300 MHz, CD\(_3\)OD) \( \delta \): 7.26-6.80 (m, 6H, aromatic and vinyl), 5.10 (dd, 2H, \( J = 4,3 \) Hz, bridgehead) ppm.

\(^1\)H NMR (300 MHz, D\(_2\)O) \( \delta \): 7.45-7.00 (m, 6H, aromatic and vinyl), 5.15 (dd, 2H, \( J = 4,3 \) Hz, bridgehead) ppm.

MS (FAB) m/e: 413 (M+1, 7), 411 (9), 238 (53), 85 (100).

UV (CH\(_3\)OH): 229 (\( \epsilon 11000 \)), 288 sh (\( \epsilon 1400 \)) nm.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid, Barium Disalt (53)

Diacid 40 (200 mg, 0.8 mmole) dissolved in 10 ml of acetonitrile and Ba(OH)\(_2\).8H\(_2\)O (252 mg, 0.8 mmole) in 4 ml of water were refluxed together for 3 h. The resulting precipitate was filtered to give 199 mg of a white powder (yield 66%).

MP: > 300 °C.

IR (KBr) \( \nu_{\text{max}} \): 1645 (m), 1559 (vs), 1455 (s), 1413 (s) cm\(^{-1}\).

\(^1\)H NMR (300 MHz, D\(_2\)O) \( \delta \): 7.5-7.0 (m, 6H, aromatic and vinyl), 5.16 (dd, 2H, \( J = 4,3 \) Hz, bridgehead) ppm.

MS (FAB) m/e: 379 (M\(^+\)+1, 29), 356 (20), 186 (22).

UV (H\(_2\)O): 228 sh (\( \epsilon 2200 \)), 265 (\( \epsilon 1900 \)) nm.
1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid, m-Aminoacetophenone Monosalt (54)

Crystals of diacid 40 (70 mg, 0.29 mmole) dissolved in 3 ml of acetonitrile and 3'-aminoacetophenone (50 mg, 0.37 mmole, Aldrich) in 2 ml acetonitrile were mixed together and stirred at room temperature for 20 min and then at reflux for another 20 min. The clear yellow solution was concentrated to a yellow oil, scratched to a solid in 1 ml of diethyl ether, and filtered to give 76 mg of an off-white solid (yield 70%). All attempts to recrystallize the solid have failed as the salt in solution dissociates and the amine slowly polymerizes to a dark brown oil.

MP: 111-113 °C.

IR (KBr) νmax: 2958 (br s), 2631 (br s), 1694 (s), 1579 (vs), 1445 (vs), 1359 (vs) cm⁻¹.

¹H NMR (300 MHz, CDCl₃) δ: 9.36 (br s, OH), 7.8-6.7 (m, 1OH, aromatic and vinyl), 5.65 (dd, 2H, J = 4.3 Hz, bridgehead), 2.55 (s, 3H, CH₃) ppm.

MS (FAB) m/e: 378 (M + 1, 4), 352 (6), 225 (13), 55 (54).

UV (CH₃CN): 230 (ε 37050), 252 sh (ε 11400), 333 (ε 3100) nm.

Anal. calcd. for C₂₂H₁₉O₅N: C, 70.02; H, 5.07; N, 3.71. Found: C, 70.13; H, 5.08; N, 3.75.

4-(2,5-Dimethylphenyl)-pentanoic Acid (60)

Anhydrous p-xylene (106 g, 1.00 mole, from Aldrich) and γ-valerolactone (47 ml, 0.50 mole, from Aldrich) were stirred under a nitrogen atmosphere and to this was added anhydrous
AICI₃ (70 g, 0.55 mole) as a solid over a period of 0.5 h. The solution was heated to reflux for 15 min and much HCl(g) evolved. The solution was then poured over acidified ice, diluted with diethyl ether, washed with dilute HCl(aq) (to remove Al(OH)₃), dried over MgSO₄, filtered, and evaporated to give 117 g of a light yellow solid (yield 90%). Recrystallization gave a white amorphous solid.

**MP:** 88-92 °C (lit. 76 113.5 °C).

**IR (KBr) v_max:** 3200-2600 (br s, OH), 1723 (s, C=O), 1460 (m), 1428 (m), 1286 (m), 1214 (m) cm⁻¹.

**¹H NMR (300 MHz) δ:** 7.1-6.8 (m, 3H, aromatic), 3.00 (m, 1H, CH₂-CH-CH₃), 2.30 (s, 3H, aromatic methyl), 2.27 (m, 2H, CH₂), 2.25 (s, 3H, aromatic methyl), 1.93 (m, 2H, CH₂), 1.22 (d, 3H, J = 8 Hz, CH-CH₃) ppm.

**MS (EI) m/e:** 206 (M+, 55), 146 (48), 133 (100), 117 (19), 105 (48), 91 (44), 77 (28).

2,3-Dihydro-4,5,8-trimethyl-1-naphthalenone (61)⁷⁶

In a 500 ml 2-neck flask was placed 100 g of 85% H₃PO₄ and to this was added, with stirring, 75 g of anhydrous P₂O₅ over 1 min. The temperature rose to ≈200 °C and the solid dissolved. The mixture was cooled to 170 °C and 58 g of acid 60 (0.282 mole) was added in several portions. After all the acid had dissolved, the reaction was stirred at 140 °C for 5 min more. The solution was then poured over ice, extracted with diethyl ether, washed with water, neutralized with sat. NaHCO₃, washed with water again, dried over MgSO₄, and filtered. The solvent
was removed to give 39.6 g of an oil (yield 74%).

IR (neat) $\nu_{\text{max}}$: 2929 (s, CH), 1677 (s, C=O), 1474 (m),
1263 (m) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.17 (d, 1H, J = 8 Hz, aromatic), 6.97
(d, 1H, J = 8 Hz, aromatic) 3.28 (m, 1H, CH$_2$-CH-CH$_3$), 2.57 (s, 3H,
aromatic methyl), 2.32 (s, 3H, aromatic methyl), 2.20 (m, 2H, CH$_2$),
1.95 (m, 2H, CH$_2$), 1.25 (d, 3H, J = 7 Hz, aliphatic methyl) ppm.

MS (EI) m/e: 188 (M+, 100), 173 (90), 160 (62), 145 (61), 132
(50), 117 (66), 91 (39).

1,2,3,4-Tetrahydro-1,4,5,8-tetramethyl-1-naphthol (62)$^{76}$

To ketone 61 (36 g, 0.19 mole) in 100 ml anhydrous diethyl ether under nitrogen was added dropwise with stirring at 0 °C was 285 ml of 1.4 M methyllithium in hexane (0.4 mole, from Aldrich). The reaction was warmed to room temperature and stirred for 45 min, poured into ice, extracted with diethyl ether, washed with water, and dried with MgSO$_4$. Removal of solvent gave 34 g of a cis/trans mixture of compound 62 as a white solid (yield 88%). A small portion was recrystallized to give colorless crystals.

MP: 87-89 °C (lit.$^{76}$ 93-95 °C).

IR (KBr) $\nu_{\text{max}}$: 3345 (vs, OH), 2941 (vs, CH), 1466 (s), 1124 (s),
812 (s) cm$^{-1}$.

$^1$H NMR (300 MHz, cis/trans mixture) $\delta$: 7.00-6.89 (m, 2H,
aromatic), 3.12 (m, 1H, CH$_2$-CH-CH$_3$), 2.61 (s, 3H,
aromatic methyl), 2.30 (s, 3H, aromatic methyl),
2.25-1.96 (m, 2H, CH$_2$), 1.95-1.65 (m, 2H, CH$_2$), 1.57 (s, 3H,
HO-C-CH₃), 1.22 (d, 3H, J = 5 Hz, CH-CH₃) ppm.

MS (EI) m/e: 204 (M⁺, 11), 189 (100), 171 (54), 156 (27).

Anal. calcd. for C₁₄H₂₀O: C, 82.30; H, 9.87. Found: C, 82.62; H, 9.82.

1,2-Dihydro-1,4,5,8-tetramethylnaphthalene (63)⁷⁶

The crude alcohol from above (31 g, 0.15 mole) was dissolved in 200 ml of tetrahydrofuran and to this was added 20 ml of conc HCl(aq). After stirring for 1 h, the reaction was neutralized with saturated NaHCO₃, extracted with ether and chromatographed on silica gel using petroleum ether (30-60 °C) as the eluting solvent. This gave 17 g of a colorless oil (yield 61%) in the first band.

IR (neat) νmax: 2963 (s, CH), 1456 (s), 813 (m) cm⁻¹.

¹H NMR (300 MHz) δ: 6.89 (s, 2H, aromatic), 5.77 (m, 1H, vinyl), 3.01 (m, 1H, CH₂-CH-CH₃), 2.41 (s, 3H, aromatic methyl), 2.28 (s, 3H, aromatic methyl), 2.19 (m, 3H, vinyl methyl), 2.10-2.00 (m, 2H, CH₂), 1.06 (d, 3H, J = 7 Hz, CH-CH₃) ppm.

MS (EI) m/e: 186 (M⁺, 43), 171 (100), 156 (60), 141 (26).

1,4,5,8-Tetramethylnaphthalene (64)⁷⁶

The alkene 63 (10 g, 54 mmoles) was placed in a 2-neck flask fitted with a condenser and a nitrogen inlet. To this was added 2 g of 10% palladium on activated charcoal (Aldrich) and the mixture heated to 280 °C in a sand bath for 5 h. During the reaction, a slow stream of nitrogen was flushed through the inlet to remove the H₂(g) evolved.
After the reaction, the sample was dissolved in methylene chloride, filtered, concentrated in vacuo, and twice recrystallized from methanol to give 1.7 g of colorless needles (yield 17%).

MP: 128-130 °C (lit. 131 °C).

IR (KBr) $v_{max}$: 2937 (m, CH), 1593 (m), 1463 (m), 816 (s) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.09 (s, 4H, aromatic), 2.82 (s, 12H, 4 x methyl) ppm.

MS (EI) m/e: 184 (M+, 100), 169 (86), 153 (27).

**Dimethyl 1,4-Dihydro-1,4,5,8-tetramethyl-1,4-ethenonaphthalene-2,3-dicarboxylate (47)**

Tetramethylnaphthalene 64 (1.7 g, 9.2 mmoles), dimethyl acetylenedicarboxylate (0.9 ml, 7.3 mmoles), and hydroquinone (0.15 g) were sealed under vacuum in a thick-walled Pyrex tube and heated at 180 °C for 2 h in an explosion-proof oven. The mixture was chromatographed on silica gel using diethyl ether and hexanes (1 : 9 v/v) as the eluting solvent. The first band was 0.9 g of tetramethylnaphthalene, and the second band was the product (47) as a white solid. Recrystallization from methanol gave 518 mg of colorless needles (yield 20%).

MP: 126-127 °C.

IR (KBr) $v_{max}$: 1728 (s, C=O), 1645 (m), 1606 (m), 1253 (s, C-O) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 6.59 (s, 2H, aromatic), 6.54 (s, 2H, vinyl), 3.73 (s, 6H, 2 x ester CH$_3$), 2.54 (s, 6H, 2 x aromatic CH$_3$), 2.21 (s, 6H, 2 x bridgehead CH$_3$) ppm.
\[^{13}\text{C}\text{ NMR (50 MHz) } \delta: 166.31 (\text{C=O}), 151.50 (\text{C}), 146.64 (\text{C}),
146.53 (\text{CH}), 130.57 (\text{C}), 129.32 (\text{CH}), 53.41 (\text{C bridgehead}), 51.91
(\text{ester CH}_3), 22.51 (\text{CH}_3), 21.09 (\text{CH}_3) \text{ ppm.}\]

\[^{\text{MS (EI) } m/e: 326 (M+, 20), 294 (43), 266 (98), 207 (100). \text{ Exact}}
\text{ mass calculated for } \text{C}_20\text{H}_22\text{O}_4: 326.1518, \text{ found 326.1525.}\]

\[^{\text{UV (CH}_3\text{CN): 236 (}\epsilon 2700), 281 (}\epsilon 975) \text{ nm.}}
\]

\[^{\text{Anal. calcd. for } \text{C}_20\text{H}_22\text{O}_4: } \text{C}, 73.60; \text{ H}, 6.79. \text{ Found: } \text{C}, 73.48;
\text{ H}, 6.73.}
\]

\[^{\text{The structure of this compound was supported by an X-ray}}
\text{diffraction analysis. Crystal data is as follows: } \text{C}_20\text{H}_22\text{O}_4, \text{ monoclinic,}
\text{ space group } P2_1/c, a = 12.643(9)\text{Å}, b = 9.288(1)\text{Å}, c = 15.153(9)\text{Å},
\beta = 105.696(5)^{\circ}, V = 1712.8(5)\text{Å}^3, Z = 4, \text{ D}_x = 1.265 \text{ g/ml, R} = 0.037.}
\]

\[^{\text{1-Deuterionaphthalene}^{74}}
\]

\[^{\text{Over a half hour period, 1-bromonaphthalene (40 g, 0.194 mole)}
\text{in 100 ml of anhydrous diethyl ether was added to magnesium turnings}
(8.0 \text{ g, 0.20 mole}) \text{ in 80 ml of anhydrous diethyl ether. The}}
\text{resulting mixture was refluxed for 1 h and cooled to 0 \text{°C. D}_2\text{O (10 ml,}}
0.05 \text{ mole) was added dropwise. After the addition, the reaction}}
\text{was stirred for 0.5 h further at room temperature and quenched with}
\text{acidified ice. The solution was diluted with 200 ml of diethyl ether, washed three times with water, dried over MgSO}_4,
\text{ filtered, and the solvent evaporated to give 24 g of a light yellow solid.}}
\text{Recrystallization first from methanol then from hexanes gave colorless}
\text{plates.}}
\]

\[^{\text{MP: 79-80 \text{°C (lit.}\text{74 80 \text{°C}).}}}\]
Mixture of Dimethyl 1 and 5-Deutero-1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (29-D)

The procedure was the same as for the non-deuterated preparation described earlier except that 6.0 g of 1-deuterionaphthalene (47 mmoles), 3.0 ml of dimethyl acetylenedicarboxylate (24 mmoles, from Aldrich), and 0.5 g of hydroquinone were placed in one Pyrex thick walled sealed tube. After recrystallization, 1.8 g of colorless prisms (yield 14%) were obtained.

MP: 105-106 °C.

IR (KBr) $v_{\text{max}}$: 1732 (s), 1714 (s), 1643 (m), 1238 (s) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.35-7.20 (m, 1.59H + 0.41D, H$_1$+H$_4$+H$_5$+H$_8$), 7.02-6.90 (m, 4.00H, H$_6$+H$_7$ + vinyl), 5.30-5.20 (dd, 1.47H + 0.53D, J = 4.3 Hz, bridgehead), 3.78 (s, 6.61H, 2 x methyl) ppm.

MS (EI) m/e: 271 (M$^+$, 51), 243 (13), 211 (77), 184 (63), 153 (100), 129 (56). Exact mass calculated for C$_{16}$H$_{13}$O$_4$D: 271.0955, found 271.0964.

Mixture of 1 and 5-Deutero-1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid (40-D)

The procedure was the same as for the non-deuterated
preparation described earlier except 6.9 g of 29-D was dissolved in 90 ml of ethanol and 75 g of NaOH in 250 ml water was used. After workup, 5.7 g of a white solid was obtained (yield 92%). Recrystallization from acetonitrile gave prisms.

MP: 208-209 °C.

IR (KBr) $v_{\text{max}}$: 3200-2200 (br m, OH), 1694 (s), 1618 (s), 1567 (vs), 1467 (s), 1280 (s), 1240 (s) cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 11.65 (br s, 1.18H, OH), 7.35-7.25 (m, 1.49H + 0.51D, H$_5$ + H$_8$), 7.05-6.90 (m, 4.00H, H$_6$ + H$_7$ + vinyl), 5.25 (dd, 1.55H + 0.45D, J = 4,3 Hz, bridgehead) ppm.

MS (EI) m/e: 243 (M$^+$, 19), 199 (57), 154 (100), 129 (33). Exact mass calculated for C$_{14}$H$_9$O$_4$D: 243.0641, found 243.0641.

Mixture of 1 and 5-Deuterio-1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Anhydride (41-D)

The same procedure used for the non-deuterated preparation was used here except that 4.8 g of 40-D (20 mmoles) in 135 ml of dry methylene chloride was reacted with 4.0 ml of oxalyl chloride (0.48 mole). Recrystallization from a 1:4 mixture of benzene and hexanes gave 3.4 g of light yellow needles (yield 76%).

MP: 128-129 °C.

IR (KBr) $v_{\text{max}}$: 1840 (m), 1771 (s, C=O), 870 (m) cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.40-7.30 (m, 1.44H + 0.56D, H$_5$ + H$_8$), 7.15-7.00 (m, 4.00H, H$_6$ + H$_7$ + vinyl), 5.29 (dd, 1.32H + 0.68D, J = 4,3 Hz, bridgehead) ppm.

MS (EI) m/e: 225 (M$^+$, 56), 181 (41), 153 (100), 129 (41).
Exact mass calculated for C_{14}H_{10}O_{3}D: 225.0536, found 225.0534.

Mixture of 1,4,5, and 8-Deuterio-1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid Monomethyl Ester (58-D)

The procedure was the same as for the preparation of compound 58 except that 1.00 g of anhydride 41-D was dissolved in 30 ml of dry methanol. The yield was 1.16 g (100%).

IR (liquid film) \( \nu_{\text{max}} \): 3400-2400 (br s, OH), 1718 (vs), 1636 (s), 1440 (s), 1278 (vs), 712 (m) cm\(^{-1}\).

\(^1\)H NMR (400 MHz) \( \delta \): 7.39-7.29 (m, 1.64H + 0.36D, H\(_5\) + H\(_8\)), 7.02-6.92 (m, 4.00H, H\(_6\) + H\(_7\) + vinyl), 5.90 (d, 0.82H + 0.18D, J = 5 Hz, bridgehead), 5.60 (d, 0.75H + 0.25D, J = 5 Hz, bridgehead), 3.99 (s, 3.24H, methyl) ppm.

MS (EI) m/e: 257 (M\(^+\), 6), 225 (10), 213 (18), 181 (19), 153 (100), 129 (34). Exact mass calculated for C_{15}H_{11}O_{4}D: 257.0798, found 257.0796.

Mixture of Methyl 1,4,5, and 8-Deuterio-2-benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (43-D)

The procedure was the same as for the non-deuterated preparation, except that 1.16 g of 58-D (4.51 mmoles) in 50 ml of dry methylene chloride, 3 ml of oxalyl chloride (34.4 mmoles), 600 ml of dry benzene, and approximately one molar equivalent of AlCl\(_3\) was used; the resulting white solid weighed 566 mg (yield 40%).

MP: 127-128 °C.

IR (KBr) \( \nu_{\text{max}} \): 1712 (s, ester C=O), 1667 (s, benzoyl C=O),
1242 (s, C-O), 702 (s) cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 7.60-6.95 (m, 10.80H + 0.20D, aromatic and vinyl), 5.54 (d, 0.67H + 0.33D, $J = 6$ Hz, bridgehead), 5.03 (d, 0.67H + 0.33D, $J = 6$ Hz, bridgehead), 3.40 (s, 3.00H, methyl) ppm.

MS (EI) m/e: 317 (M$^+$, 4), 285 (6), 129 (11), 105 (100), 77 (23). Exact mass calculated for C$_{21}$H$_{15}$O$_3$D: 317.1162, found 317.1153.
II. PHOTOCHEMISTRY OF SUBSTRATES

A. Dimethyl 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (29)

Direct Solution Photolysis

Analytical photolyses ($\lambda > 290$ nm) were performed in benzene, methanol, and acetonitrile. The reactions were monitored by GC (DB-1) which showed the formation of one product independent of solvent.

In a preparative run, a solution of 500 mg of 29 (1.9 mmole) in 100 ml of benzene was photolyzed ($\lambda > 290$ nm) in an immersion well setup to complete conversion, monitored by GC. The reaction mixture was directly recrystallized three times from a 2:1 mixture of hexanes and methanol to give white needles of dimethyl benzocyclooctene-7,8-dicarboxylate (29d).

MP: 77-78 °C (lit. $77.0-77.5$ °C).

IR (KBr) $\nu_{max}$: 1724 (s, C=O), 1435 (m), 1260 (s, C-O), 1149 (m), 1025 (m), 800 (m) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.30-7.00 (m, 4H, aromatic), 6.77 (d, 2H, $J = 12$ Hz, benzylic vinyl), 6.20 (d, 2H, $J = 12$ Hz, $\beta$-vinyl), 3.75 (s, 6H, 2 x methyl) ppm.

MS (EI) m/e: 270 ($M^+$, 11), 238 (14), 210 (77), 179 (32), 152 (100).

UV (CH$_3$CN) $\lambda_{max}$: 284 sh ($\epsilon$ 1820) nm.

Anal. calcd. for C$_{16}$H$_{14}$O$_4$: C, 71.10; H, 5.22. Found: C, 71.19; H, 5.24.
Benzophenone-Sensitized Photolysis

On an analytical scale, photolysis of an approximately 1:1 mass ratio of compound 29 to benzophenone in benzene through a uranium glass filter (λ > 330 nm) gave only one product by GC (DB-1).

A solution of 50 mg of compound 29 (0.18 mmole) and 0.40 g of benzophenone (2.2 mmole) in a 10 ml phototube of acetone was photolyzed with a medium pressure mercury lamp (λ > 330 nm). The reaction was monitored by GC until no starting material remained and chromatographed to give 39 mg of the product as a thick colorless oil (yield 78%), identified as dimethyl 2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-2a,6c-dicarboxylate (29a).

IR (neat) \( \delta \): 1730 (s, C=O) cm\(^{-1}\).

\(^1\)H NMR (300 MHz) \( \delta \): 7.5-7.1 (m, 4H, aromatic), 5.82 (dd, 1H, J = 5,3 Hz, H_1), 5.36 (d, 1H, J = 5 Hz, H_2), 4.49 (d, 1H, J = 3 Hz, H_6b), 4.48 (s, 1H, H_2b), 3.85 (s, 3H, methyl), 3.70 (s, 3H, methyl) ppm.

MS (EI) m/e: 270 (M^+, 37), 238 (14), 210 (94), 183 (90), 152 (100). Exact mass calculated for C_{16}H_{14}O_4: 270.0892, found 270.0892.

UV (CH_3CN) \( \lambda_{max} \): 278 (\( \epsilon \) 1100) nm.

Acetone-Sensitized Photolysis of Compound 29

The photolysis was analytically performed in acetone using a Pyrex filter sleeve (λ > 290 nm). The reaction was monitored by GC to show 2 major photoproducts with retention times corresponding to compounds 29a and 29e. At low conversion their ratio was approximately 1:1, but as conversion increased, 29e decomposes quickly, 29a decomposes slowly, and a new peak arose in the GC with a retention time corresponding to compound 29b. Compounds 29e and 29b will be
characterized later.

On a preparative scale, compound 29 (1.50 g, 5.6 mmoles) in 425 ml of acetone was photolyzed ($\lambda > 290$ nm) in an immersion well to complete conversion. GC showed photoproducts 29a, 29e, and 29b in a ratio 65:25:9 respectively. Chromatography eluting with pet. ether (30-60 °C) and diethyl ether 93:7 (v/v) gave two bands. The first was an inseparable mixture of 29e and 29b, followed by 0.96 g of 29a (yield 64%). The identity of these compounds was confirmed by NMR spectroscopic comparison of the mixtures to their full characterizations, described later.

Solid State Photolysis

Crystals of compound 29 were photolyzed analytically through Pyrex glass for 2, 6, and 9 h to afford one product, cyclooctatetraene (COT) 29c at 30%, 16%, and 25% conversion respectively. In all cases, the crystals turned yellow and were sticky on the surface. Compound 29 and COT 29c were inseparable by TLC.

Laser photolysis ($\lambda = 337$ nm) of the crystals in an NMR tube for 1 h also resulted in yellowing and slight surface melting. GC showed a 15% conversion to product 29c.

Photochemical Interconversion of Compounds 29a and 29b

Compound 29a was photolyzed analytically in acetone ($\lambda > 290$ nm), acetonitrile ($\lambda > 260$ nm), and benzene ($\lambda > 260$ nm). All three photolyses gave one major product at a maximum conversion of 52% by GC. The reaction in acetonitrile was found to proceed much more slowly than the other two reactions.
In a preparative run, compound 29a (0.64 g, 2.4 mmoles) in 200 ml of benzene was irradiated through a Corex filter (λ > 260 nm) in an immersion well for 13 h. The sample was subsequently chromatographed using an ethyl acetate and petroleum ether (30-60 °C) (1 : 19 v/v) solution as the eluting solvent. The first band contained 59 mg of dimethyl 2b,6b-dihydrobenzo[a]cyclopropa[cd]-pentalene-1,6c(2aH)-dicarboxylate (29b) as a colorless oil (yield 9%).

IR (KBr) v_{max}: 1719 (s, C=O) cm^{-1}.

^1H NMR (300 MHz) δ: 7.4-7.1 (m, 4H, aromatic), 6.15 (d, 1H, J = 3 Hz, vinyl), 4.69 (s, 1H, H_6b), 3.89 (d, 1H, J = 8 Hz, H_2b), 3.72 (s, 3H, methyl), 3.71 (s, 3H, methyl), 3.43 (dd, 1H, J = 8, 3 Hz, H_2a) ppm.

MS (EI) m/e: 270 (M^+, 55), 210 (62), 183 (47), 152 (100), 84 (42). Exact mass calculated for C_{16}H_{14}O_4: 270.0892, found 270.0885.

The photostationary state ratio of the reaction was investigated by a series of analytical scale photolyses. Ratios were determined by GC, calibrated by co-injections with octadecane (n-C_{18}H_{38}) as the internal standard. It was calculated that the GC detector is 1.6 times more sensitive to 29b then 29a. Compound 29a, compound 29b, and mixtures of the two were photolysed: a) in acetonitrile (λ > 260 nm) but compound decomposition was too fast to establish an equilibrium. b) in benzene (λ > 260 nm) thirteen times to establish a 29a to 29b ratio of 7 ± 1 : 3 ± 1.84 c) in acetone (λ > 260 nm) three times to establish a 29a to 29b ratio of 8 : 2.

**Acetone-Sensitized Photolysis of Compound 29c**

On an analytical scale, solutions of 29c in acetonitrile,
benzene, and acetone were photolyzed ($\lambda > 290$ nm) for 10 h; compound 29e was the only peak seen on GC (subsequently characterized) at conversions of 15%, 22%, and 100% respectively.

On a preparative scale, cyclooctatetraene 29c (100 mg, 0.37 mmole) in 200 ml of acetone was irradiated through Pyrex ($\lambda > 290$) in an immersion well system. The reaction was monitored by GC to complete conversion and then chromatographed on silica using diethyl ether and low boiling petroleum ether (1:3 v/v) as the eluent. This afforded 71 mg of dimethyl 2b,6b-dihydrobenzo[a]-cyclopropa[cd]pentalene-2,6c(2aH)-dicarboxylate (29e) as a colorless oil (yield 71%).

IR (KBr) $\nu_{\text{max}}$: 1718 (s, C=O) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.4-7.1 (m, 4H, aromatic), 6.58 (d, 1H, J = 3 Hz, vinyl), 4.51 (d, 1H, J = 3 Hz, H$_6$b), 3.84 (d, 1H, J = 6 Hz, H$_2$a), 3.74 (d, 1H, J = 6 Hz, H$_2$b), 3.70 (s, 3H, methyl), 3.65 (s, 3H, methyl) ppm.

MS (EI) m/e: 270 (M$^+$, 34), 238 (19), 210 (92), 183 (58), 152 (78), 43 (100). Exact mass calculated for C$_{16}$H$_{14}$O$_4$: 270.0892, found 270.0889.

**Detection of Cyclobutene 29d**

Compound 29c (6 mg, 0.022 mmole) dissolved in an NMR tube was photolyzed: a) in acetone-$d_6$ ($\lambda > 290$ nm) to 10% conversion by GC and analyzed by NMR (300 MHz). Signals corresponding to 29c, 29d, and 29e were detected in a ratio of 74 : 14 : 12. This third compound 29d was thermally unstable and readily reverted back to cyclooctatetraene 29c on GC; b) in deuteriochloroform ($\lambda > 330$ nm)
for 3 days to show no conversion on GC, but NMR (300 MHz) shows a 83 : 17 mixture of 29c to the cyclobutene derivative 29d. From the NMR of the mixture, dimethyl cyclobuta[a]naphthalene-2,2a(8bH)-dicarboxylate (29d) was characterized; c) in benzene-d$_6$ ($\lambda > 330$ nm) to a 29c : 29d : 29e ratio of 75 : 16 : 9 characterized by $^1$H NMR of the mixture as well. Spectroscopic data for 29d are described below.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.3-7.0 (m, 4H, aromatic overlapping with 29c), 7.72 (s, 1H, H$_1$), 6.47 (d, 1H, J = 10 Hz, H$_4$), 6.22 (d, 1H, J = 10 Hz, H$_3$), 4.23 (s, 1H, H$_{8b}$), 3.78 (s, 3H, methyl), 3.76 (s, 3H, methyl) ppm.

$^1$H NMR (300 MHz, benzene-d$_6$, only non-overlapping peaks are reported) $\delta$: 6.40 (d, 1H, J = 10 Hz, H$_4$), 6.26 (d, 1H, J = 10 Hz, H$_3$), 4.04 (s, 1H, H$_{8b}$) ppm.

B. 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid (40)

Direct Solution Photolysis

Analytical photolyses through Pyrex ($\lambda > 290$ nm) were conducted in NMR tubes. Samples were dissolved in CDCl$_3$ (3 mg) and DMSO-d$_6$ (6 mg), photolyzed for 1.5 h, and analyzed by NMR. This showed the formation of 40c (subsequently characterized) as the only product at 50% and 5% conversion respectively.

On a preparative scale, diacid 40 (60 mg, 0.25 mmole) was photolyzed ($\lambda > 290$ nm) in ethyl acetate, using 3 x 10 ml phototubes, until the solution was bright yellow (1.75 h). The reaction mixture was concentrated to a volume of 5 ml at 60°C and allowed to crystallize. Clear brown rods were filtered (18 mg)
and identified as benzocyclooctene-7,8-dicarboxylic anhydride (41d) \(60\) (yield 32%).

**MP:** 210-212 °C.

**IR (KBr) \(\nu_{\text{max}}\):** 1767 (s, C=O), 1263 (s, C-O), 713 (s) cm\(^{-1}\).

**\(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\):** 7.35-7.25 (m, 2H, aromatic), 6.99 (d, 2H, J = 12 Hz, benzylic vinyl), 6.97-6.91 (m, 2H, aromatic), 6.19 (d, 2H, J = 12 Hz, \(\beta\)-vinyl) ppm.

**\(^1H\) NMR (300 MHz, DMSO-d\(_6\)) \(\delta\):** 7.36-7.28 (m, 2H, aromatic), 7.13 (d, 2H, J = 12 Hz, benzylic vinyl), 7.05-6.80 (m, 2H, aromatic), 6.19 (d, 2H, J = 12 Hz, \(\beta\)-vinyl) ppm.

**MS (EI) m/e:** 224 (M\(^+\) , 69), 180 (42), 152 (100), 76 (41).

Exact mass calculated for \(\text{C}_{14}\text{H}_8\text{O}_3\): 224.0474, found 224.0474.

**Anal. calcd. for \(\text{C}_{14}\text{H}_8\text{O}_3\):** C, 75.00; H, 3.60. Found: C, 74.95; H, 3.56.

The mother liquor was left to stand and clear yellow needles formed. This was filtered to give 20 mg of benzocyclooctene-7,8-dicarboxylic acid (40c) crystals (yield 33%).

**MP:** Cracks and turns orange at 122-130 °C (dehydration), melts at 208-210 °C (anhydride melting point).

**IR (KBr) \(\nu_{\text{max}}\):** 3100-2400 (br s, OH), 1724 (s, C=O), 1624 (m), 1230 (s) cm\(^{-1}\).

**\(^1H\) NMR (400 MHz, DMSO-d\(_6\)) \(\delta\):** 12.95 (br s, 2H, 2 x OH), 7.4-7.0 (m, 4H, aromatic), 6.72 (d, 2H, J = 11 Hz, benzylic vinyl), 6.18 (d, 2H, J = 11 Hz, \(\beta\)-vinyl) ppm.

**MS (EI) m/e:** 224 (M\(^+\) - H\(_2\)O, 72), 180 (30), 152 (100), 84 (82), 66 (99).

**MS (DCI-NH\(_3\)) m/e:** 243 (M\(^+\) + 1, 11), 224 (100), 180 (47), 152 (90),
Benzophenone-Sensitized Photolysis

Samples of diacid 40 (ca. 5 mg) and benzophenone (ca. 30 mg) were dissolved in a phototube with 1 ml of acetone-d$_6$ and photolyzed ($\lambda > 330$ nm). Two products were detected by NMR, at 70% conversion and shown to be compounds 40b and 40a (ratio 87 : 13). The photolysis was repeated at lower conversion (19%), and a 92 : 8 ratio of 40b to 40c was determined by integration of the expanded NMR signals. Compounds 40b and 40a were characterized later.

On a preparative scale, a mixture of compound 40 (120 mg, 0.50 mmole) and benzophenone (900 mg) was dissolved with acetone in five 10 ml phototubes, photolyzed ($\lambda > 330$ nm) and monitored by NMR to almost complete conversion. The final component ratio of 40, 40c, 40b, and 40a by NMR was 10 : 2 : 78 : 10. The reaction mixture was transferred to diethyl ether, extracted with NaOH(aq), washed with diethyl ether (to remove benzophenone), reacidified with conc. HCl, extracted with diethyl ether, washed with water, dried over MgSO$_4$ and evaporated. To the remaining oil was added 5 ml of anhydrous diethyl ether and the solution treated with excess diazomethane in diethyl ether (prepared from Diazald, Aldrich). The diazomethane was added dropwise at room temperature until the solution stayed yellow; the reaction was stirred for another 20 min, quenched with water and the ethereal layer separated. Chromatography on silica gel, eluting with diethyl ether in hexanes (1 : 9 v/v) gave 11 mg of a 3 : 1 mixture of compounds 29a and 29c in the first band. The second band contained 40 mg of a white solid (yield 30%).
Recrystallization from hexanes gave colorless rods which were characterized as dimethyl 2a,2b,6b,6c-tetrahydrobenzo[a]cyclopropa[cd]pentalene-1,2-dicarboxylate (29f)\(^{60}\).

**MP:** 86-87 °C (lit.\(^{5}\) 86.5-87.0 °C).

**IR (KBr)** \(\nu_{\text{max}}\): 2927 (m, CH), 1729 (s, C=O), 1273 (s, C-O) cm\(^{-1}\).

**\(^1\)H NMR (400 MHz)** \(\delta\): 7.75-7.10 (m, 4H, aromatic), 4.23 (d, 1H, \(J = 6\) Hz, \(H_{6b}\)), 3.73 (s, 3H, methyl), 3.71 (s, 3H, methyl), 3.50 (ddd, 1H, \(J = 6,6,6\) Hz, \(H_{6c}\)), 3.29 (dd, 1H, \(J = 6,6\) Hz, \(H_{2b}\)), 3.00 (dd, 1H, \(J = 6,6\) Hz, \(H_{2a}\)) ppm.

**MS (EI) m/e:** 270 (M\(^{+}\), 32), 238 (45), 210 (100), 183 (48), 152 (100).

**Anal. calcd. for C\(_{16}\)H\(_{14}\)O\(_4\):** C, 71.10; H, 5.22. Found: C, 71.25; H, 5.27.

**Solid State Photolysis**

Crystals of 40 were photolyzed (\(\lambda > 290\) nm) in NMR tubes for 4 h and 15 h. These crystals turned yellow with slight melting. Analysis by NMR (400 MHz, DMSO-\(d_6\)) showed no photoproducts.

**Hydrolysis of Benzosemibullvalene 29f**

Compound 29f (26 mg, 9.6 x 10\(^{-5}\) mole) was stirred in 0.5 ml of ethanol for 10 min and to this mixture was added 0.2 g of NaOH in 4 ml water. The reaction was refluxed for 35 min, diluted to 10 ml with water, washed with diethyl ether, acidified with conc. HCl, extracted with ether, dried with MgSO\(_4\), filtered, and evaporated to afford 18 mg of a white solid (yield 77%). This was characterized as 2a,2b,6b,6c-tetrahydrobenzo[a]cyclopropa[cd]pentalene-1,2-dicarboxylic
Acid (40b).

MP: > 300 °C (decomposes slowly at approx. 150 °C).

IR (KBr) \( \nu_{\text{max}} \): 3200-2200 (br vs, OH), 1699 (s, C=O), 1601 (s), 1567 (s), 1484 (s), 1263 (s) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.25-7.05 (m, 4H, aromatic), 4.46 (d, 1H, \( J = 6 \) Hz, \( H_{6b} \)), 3.50-3.38 (m, 2H, \( H_{2b} + H_{6c} \)), 3.33 (dd, 1H, \( J = 6,6 \) Hz, \( H_{2a} \)) ppm.

\(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \): 9.4 (br s, 2H, \( 2 \times \) OH), 7.50-7.05 (m, 4H, aromatic), 4.20 (d, 1H, \( J = 6 \) Hz, \( H_{6b} \)), 3.46 (ddd, 1H, \( J = 6,6,6 \) Hz, \( H_{6c} \)), 3.34 (dd, 1H, \( J = 6 \) Hz, \( H_{2b} \)), 3.06 (dd, 1H, \( J = 6,6 \) Hz, \( H_{2a} \)) ppm.

MS (EI) m/e: 242 (M\(^+\), 16), 224 (55), 152 (100). Exact mass calculated for C\(_{14}H_{10}O_4\): 242.0579, found 242.0588.

Hydrolysis of Benzosemibullvalene 29a

Compound 3 (730 mg, 2.7 mmoles) was dissolved in 15 ml of ethanol and to this was added 5.6 g of NaOH in 100 ml of water and the solution refluxed for 40 min. The cooled solution was washed with diethyl ether, acidified with conc. HCl, extracted with diethyl ether, washed with water, dried over MgSO\(_4\), filtered, and evaporated to give 402 mg of a white solid (yield 61\%). Recrystallization from acetonitrile gave white crystals, characterized as 2b,6b-dihydrobenzo[a]cyclopropa-[cd]pentalene-2a,6c-dicarboxylic acid (40a).

MP: 178-181 °C.

IR (KBr) \( \nu_{\text{max}} \): 3200-2400 (br s, OH), 1697 (s, C=O), 1445 (m), 1299 (m) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 10.3-9.8 (br s, 2H, OH), 7.5-7.1
(m, 4H, aromatic), 5.84 (dd, 1H, J = 5,3 Hz, H1), 5.40 (d, 1H, J = 5 Hz, H2), 4.56 (s, 1H, H2b), 4.55 (d, 1H, J = 3 Hz, H6b with partial overlap to H2b) ppm.

1H NMR (200 MHz, acetone-d6) δ: 11.6-11.0 (br s, 2H, OH), 7.6-7.1 (m, 4H, aromatic), 5.85 (dd, 1H, J = 5,3 Hz, H1), 5.40 (d, 1H, J = 5 Hz, H2), 4.50 (d, 1H, J = 3 Hz, H6b), 4.40 (s, 1H, H2b) ppm.

1H NMR (400 MHz, DMSO-d6) δ: 13.1-12.3 (br s, OH), 7.55-7.10 (m, 4H, aromatic), 5.78 (dd, 1H, J = 5,3 Hz, H1), 5.30 (d, 1H, J = 5 Hz, H2), 4.35 (d, 3H, J = 3 Hz, H6b), 4.24 (s, 1H, H2b) ppm.

MS (EI) m/e: (no M+ peak) 198 (7), 196 (8), 152 (20), 78 (100).

MS (DCI-NH3) m/e: 260 (M + NH4+, 12), 243 (M + 1, 43), 225 (19), 198 (100), 153 (78).


**Deuterium Labelling Study**

Crystals of 40-D (60 mg, 0.25 mmole) in three 10 ml phototubes of ethyl acetate were photolyzed (λ > 290 nm). The reaction was continued until the solution was bright yellow (3h), then evaporated and the product recrystallized from in a 5 : 1 (v/v) solution of ethyl acetate and hexanes to gave 33 mg of anhydride 41d-D as clear orange rods (yield 59%).

MP: 209-211 °C.

1H NMR (400 MHz, DMSO-d6) δ: 7.40-7.25 (m, 2.05H, aromatic H2 + H3), 7.15-6.95 (m, 3.12H + 0.88D, aromatic H1 + H4 and vinyl H5 + H10), 6.19 (m, 2.00H, vinyl H6 + H9) ppm.

In a triplet-sensitized experiment, compound 40-D (25 mg, 0.10
mmole) and benzophenone (10 mg) were dissolved with 1.5 ml DMSO-d₆ in an NMR tube. This was photolyzed (λ > 330 nm) for 45 min and directly analyzed by NMR (shown in Figure 3.10 of text).

C. 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Anhydride (41)

Direct Solution Photolysis

On an analytical scale, anhydride 41 was photolyzed (λ > 290 nm) in benzene and ethyl acetate to give three products (41a, 41b, and 41c) independent of solvent, whose ratios however, varied with conversion.

Anhydride 41 (15 mg, 6.7 x 10⁻⁵ mole) in 1 ml of CDCl₃ was photolyzed (λ > 290 nm) in a phototube until complete conversion to give an NMR (GC) ratio 47 (51) : 18 (13) : 24 (19) of 41a, 41b, and 41c, respectively.

From an analysis of the reaction mixtures, 41a was determined to be 2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-2a,6c-dicarboxylic anhydride.

¹H NMR (400 MHz, CDCl₃) δ: 7.5-7.0 (m, 4H, aromatic overlapping with 41c), 5.90 (dd, 1H, J = 6,3 Hz, H₁), 5.44 (d, 1H, J = 6 Hz, H₂), 4.57 (d, 1H, J = 3 Hz, H₆b), 4.45 (s, 1H, H₂b) ppm.

GC-MS (DB-1, EI) m/e: 224 (M⁺, 73), 198 (88), 180 (70), 154 (91), 126 (100), 76 (72). Exact mass calculated for C₁₄H₈O₃: 224.0474, found 224.0465.

Compound 41b was identified from the mixture as naphthalene-2,3-dicarboxylic anhydride⁹³.

¹H NMR (400 MHz, CDCl₃) δ: 8.57 (s, 2H, H₁ and H₄), 8.16
(m, 2H, H₅ and H₈), 7.82 (m, 2H, H₆ and H₇) ppm.

GC-MS (DB-1, EI) m/e: 198 (M⁺, 90), 154 (91), 126 (100), 98 (68), 87 (70), 77 (72), 63 (79).

From the above mixture, 4lc was characterized as 2a,2b,6b,6c-tetrahydrobenzo[a]cyclopropa[cd]pentalene-1,2-dicarboxylic anhydride.

¹H NMR (400 MHz, CDCl₃) δ: 7.5-7.1 (m, 4H, aromatic overlapping with 41a), 4.29 (d, 1H, J = 6 Hz, H₆b), 3.99 (ddd, 1H, J = 6,6,6 Hz, H₆c), 3.67 (dd, 1H, J = 6,6 Hz, H₂b), 3.01 (dd, 1H, J = 6,6 Hz, H₂a) ppm.

GC-MS (DB-1, EI) m/e: 224 (M⁺, 36), 198 (7), 180 (33), 152 (100), 126 (20). Exact mass calculated for C₁₄H₈O₃: 224.0473, found 224.0470.

Compound 41 was analytically photolyzed (λ > 290 nm) three times in ethyl acetate and the photoproduct ratios were monitored as a function of conversion and plotted graphically in the text. Ratios were recorded on GC (DB-1) with the temperature program: 150 °C for 1 min, rate of 5 °C/min to 230 °C for 1 min. The relative GC response of the compounds was calibrated from NMR integration.

Anhydride 41 (200 mg, 0.90 mmole) was dissolved in 500 ml of ethyl acetate and photolyzed (λ > 290 nm) to complete conversion. This solution was then stirred with 100 ml dry methanol for 10 h and evaporated. The resulting yellow oil was dissolved in anhydrous diethyl ether and treated at room temperature with excess diazomethane (from Diazald, Aldrich); diazomethane was added dropwise until the solution remained bright yellow indicating an excess of unreacted diazomethane. This was stirred for another 30 min before the reaction was quenched over acidified ice, diluted with diethyl ether,
dried with MgSO$_4$, filtered, and evaporated. Chromatography gave three bands. The first was 20 mg (yield 8%) of compound 3, followed by 43 mg of dimethyl naphthalene-2,3-dicarboxylate$^{94}$ (yield 20%).

MP: 51-53 °C (lit.$^{94}$ 52-54 °C).

IR (KBr) $\nu_{\text{max}}$: 1733 (s, C=O), 1717 (s, C=O), 1288 (s, C-O) cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.25 (s, 2H, H$^3 + H^4$), 7.91 (m, 2H, H$_5 + H_6$), 7.62 (m, 2H, H$_6 + H_7$), 3.95 (s, 6H, 2 x methyl) ppm.

MS (EI) m/e: 244 (64, M$^+$), 213 (100), 183 (33), 127 (81), 63 (75).

The third band was 21 mg (yield 9%) of compound 29f (previously characterized).

**Acetone-Sensitized Photolysis**

Anhydride 41 was photolyzed ($\lambda > 290$ nm) analytically in acetone and the reaction was monitored by GC to show complete conversion to two products (41a and 41c); prolonged photolysis resulted in the decomposition of 41c. The ratio of 41a to 41c at low conversion (12%) was 37 : 63 by GC with the response calibrated by NMR.

In an NMR study, compound 41 (15 mg) in 1 ml of acetone-d$_6$ was photolyzed ($\lambda > 290$ nm) to complete conversion and analyzed by NMR (GC) to show a 64 (72) : 36 (28) ratio of 41a to 41c.

**Solid State Photolysis**

On an analytical scale, crystals of 41 were photolyzed ($\lambda > 260$ nm) for 4 h and analyzed by GC. The crystals were cracked and turned dark yellow with no sign of melting. Two products were formed, 41a and 41c,
in a ratio of 2 : 5 at 7% conversion.

For NMR, crystals of 41 (approx. 10 mg) in an NMR tube were photolyzed until there was no further change in the appearance of the crystals (13 h). The dark yellow crystals were dissolved in CDCl3 and analyzed by NMR (GC) which showed a 41 : 41a : 41c ratio of 84 (92) : 4 (3) : 12 (5) respectively.

Deuterium Labelling Study

Compound 41-D (20 mg) in 2 ml of CDCl3 was photolyzed (λ > 290 nm) to complete conversion to 41a-D, 41b-D, and 41c-D. This mixture was transferred to an NMR tube and analyzed. The signals for 41a-D are described below.

$^1$H NMR (400 MHz) $\delta$: 7.5-7.1 (m, 3.50H + 0.50D, aromatic overlapping with 41c-D), 5.91 (m, 1.00H, $H_1$), 5.48 (d, 1.00H, $J = 6$ Hz, $H_2$), 4.57 (distorted s, 0.88H + 0.12D, $H_{6b}$), 4.42 (s, 0.63H + 0.37D, $H_{2b}$) ppm.

The signals for 41b-D are below.

$^1$H NMR (400 MHz) $\delta$: 8.59 (s, 1.11H + 0.89D, $H_1 + H_4$), 8.14 (m, 1.33H + 0.67D, $H_5 + H_8$), 7.82 (m, 2.00H, $H_6 + H_7$) ppm.

Below are the signals for 41c-D.

$^1$H NMR (400 MHz) $\delta$: 7.5-7.1 (m, 3.5H + 0.5D, aromatic overlapping with 41a-D), 4.30 (d, 0.56H + 0.44D, $J = 6$ Hz, $H_{6b}$), 4.00 (ddd, 1.00H, $J = 6,6,6$ Hz, $H_{6c}$), 6.64 (dd, 0.78H + 0.22D, $J = 6,6$ Hz, $H_{2b}$), 3.00 (dd, 1.00H, $J = 6,6$ Hz, $H_{2a}$).
D. 2,3-Dibenzoyl-1,4-dihydro-1,4-ethenonaphthalene (42)

**Direct Solution Photolysis**

Small samples of compound 42 were dissolved in benzene and acetonitrile for photolysis (\(\lambda > 330\) nm). The reaction was monitored by GC and shown to be solvent-independent with the formation of only one product (42a). Further photolysis caused the formation of a secondary photoproduct (42c).

In an NMR study, compound 42 was photolyzed (\(\lambda > 330\) nm) with CDCl\(_3\) in an NMR tube for 10 minutes and analyzed by NMR (GC) to a 42 : 42a ratio of 84 (92) : 16 (8).

On a preparative scale, a solution of 42 (35 mg, 9.7 x 10\(^{-4}\) mole) in 4 ml of benzene in a 10 ml phototube was photolyzed (\(\lambda > 330\) nm) to complete conversion. The resulting mixture of 42a and 42c was chromatographed twice, eluting with a diethyl ether : hexanes (1:9 v/v) solution. This gave 20 mg of an inseparable 75 : 25 mixture of 42a and 1,6c-dibenzoyl-2b,6b(2aH)-dihydrobenzo[a]cyclopropa[cd]pentelene (42c), from which the latter is characterized below.

\(^1\)H NMR (400 MHz) \(\delta\): 8.0-7.1 (m, 14H, aromatic overlapping with 42a), 6.08 (d, 1H, \(J = 3\) Hz, \(H_2\)), 4.90 (s, 1H, \(H_{6b}\)), 4.12 (d, 1H, \(J = 8\) Hz, \(H_{2b}\)), 3.78 (dd, 1H, \(J = 8,3\) Hz, \(H_{2a}\)) ppm.

GC-MS (DB-1, EI) m/e: 362 (M\(^+\), 2), 257 (3), 105 (100), 77 (31).

Exact mass calculated for C\(_{26}\)H\(_{18}\)O\(_2\): 362.1307, found 362.1295.

**Benzophenone-Sensitized Photolysis of Compound 42**

On an analytical scale, a small amount of compound 42 and a five-fold excess (w/w) of benzophenone were dissolved in benzene
and photolyzed (λ > 330 nm) to complete conversion. GC monitoring showed the formation of 42a; only trace amounts of 42c was detected.

On a preparative scale, a solution of 42 (27 mg, 7.5 x 10⁻⁵ mole) and benzophenone (300 mg, 1.7 mmole) in 8 ml of benzene was photolyzed (λ > 330 nm) to complete conversion. Chromatography on silica gel eluting with diethyl ether : petroleum ether (30-60 °C) (1 : 9 v/v) gave benzophenone in the first band. The second band consisted of 16 mg of 2a,6c-dibenzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentadecalene (42a) as a colorless oil (yield 59%).

IR (neat) vₘₐₓ: 1682 (s, C=O), 1599 (m), 1279 (s) cm⁻¹.

¹H NMR (400 MHz) δ: 8.0-7.1 (m, 14H, aromatic), 5.94 (dd, 1H, J = 5.2 Hz, H₁), 5.50 (d, 1H, J = 5 Hz, H₂), 4.63 (s, 1H, H₂b), 4.40 (d, 1H, J = 2 Hz, H₆b) ppm.

MS (EI) m/e: 362 (M⁺, 70), 105 (100), 77 (20). Exact mass calculated for C₂₆H₁₈O₂: 362.1307, found 362.1298.

Solid State Photolysis of Compound 42

Crystals of 42 were placed in an NMR tube and photolyzed (λ > 290 nm) for 15 h to give unmelted yellow crystals. Analysis by NMR indicated an 8% conversion to two products, 42a and 42b in a 1 : 1 ratio. In a longer photolysis (45 h), the unmelted yellow crystals were analyzed by NMR which showed a 14% conversion to another 1 : 1 ratio of 42a to 42b.

In a preparative study, crystals of 42 (43 mg, 1.2 x 10⁻⁴ mole) were crushed between two pairs of microscope slides and photolyzed (λ > 330 nm) for 20 h. The unmelted yellow crystals were analyzed by NMR which indicated a 42a : 42b ratio of 59 : 41 at 38% conversion.
Chromatography on silica gel using a 1:9 (v/v) mixture of diethyl ether to hexanes as the eluent gave three overlapping bands. The first band contained starting material 42; second band consisted of 42a and the third band was rechromatographed two more times under the same conditions as above to give 4 mg of 1,2-dibenzoyl-2a,2b,6b,6c-tetrahydrobenzo[a]cyclopropa[cd]pentalene (42b) as a colorless oil (yield 9%).

IR (neat) $v_{\text{max}}$: 1651 (s, C=O), 1597 (m), 1273 (s) cm$^{-1}$.

$^1$H NMR (400 MHz) δ: 7.6-6.7 (m, 14H, aromatic), 4.61 (d, 1H, J = 6 Hz, H$_{6b}$), 3.64 (ddd, 1H, J = 6,6,6 Hz, H$_{6c}$), 3.49 (dd, 1H, J = 6,6 Hz, H$_{2b}$), 3.23 (dd, 1H, J = 6,6 Hz, H$_{2a}$) ppm.

MS (EI) m/e: 362 (M$^+$, 5), 105 (100), 77 (44). Exact mass calculated for C$_{26}$H$_{18}$O$_2$: 362.1307, found 362.1312.

Photolysis of Benzosemibullvalene 42a

On an analytical scale, compound 42a was photolyzed (λ > 330 nm) in benzene. One product (42c) was detected by GC (DB-1) at a photostationary state composition of 59 : 41 = 42a : 42c.

E. Methyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (43)

Direct Solution Photolysis

Solutions of 43 in benzene, acetonitrile, hexanes, and methanol were analytically photolyzed (λ > 330 nm) to complete conversion, monitored by GC (DB-1). Two major photoproducts, subsequently shown to have structures 43a and 43b, were seen along with some minor products. The reaction was independent of solvent.
A solution of keto-ester 43 (25 mg) in 1 ml CDCl$_3$ was photolyzed as above to complete conversion, and the integrated NMR spectrum of the resulting mixture showed six products (43a, 43b, 43h, 43c, 43d, and 43e) at a ratio of 50 : 25 : 17 : trace : 8 : trace, respectively.

A solution of compound 43 (130 mg, 0.411 mmole) in 40 ml of benzene was placed in four 10 ml phototubes and photolyzed to complete conversion as monitored by GC. The benzene was evaporated and the resulting yellow oil chromatographed on silica gel using diethyl ether and hexanes (1 : 19 v/v) as the eluent. The first band contained 47 mg of a white solid (yield 36%). Recrystallization from hexanes gave two crystal morphologies, needles and prisms, of methyl 2a-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentane-6c-carboxylate (43a).

MP: (needles) 106-107 °C, (prisms) 113-114 °C.

IR (KBr, needles) $v_{\text{max}}$: 1733 (s, ester C=O), 1674 (s, benzoyl C=O), 1224 (s, C-O) cm$^{-1}$.

IR (KBr, prisms) $v_{\text{max}}$: 1723 (s, ester C=O), 1677 (s, benzoyl C=O), 1225 (s, C-O) cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 8.0-7.2 (m, 9H, aromatic), 5.93 (dd, 1H, J = 3.5 Hz, $H_1$), 5.27 (d, 1H, J = 5 Hz, $H_2$), 4.69 (d, 1H, J = 3 Hz, $H_{6b}$), 4.57 (s, 1H, $H_{2b}$), 3.45 (s, 3H, methyl) ppm.

MS (EI) m/e: 316 (M$^+$, 28), 256 (31), 228 (40), 152 (30), 105 (100), 77 (80). Exact mass calculated for C$_{21}$H$_{16}$O$_3$: 316.1100, found 316.1103.

UV (CH$_3$CN) $\lambda_{\text{max}}$: 244 (e 14000), 277 sh (e 3100) nm.


The second band contained 29 mg of a white solid (yield 22%).
Recrystallization from pentane gave prisms and this compound was identified as methyl 6c-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]-pentalene-1(2aH)-carboxylate (43b).

MP: 100-101 °C.

IR (KBr) \( \nu_{\text{max}} \): 1703 (s, ester C=O), 1663 (s, benzoyl C=O), 1253 (s, C-O) cm\(^{-1}\).

\(^1\)H NMR (300 MHz) \( \delta \): 7.7-7.2 (m, 9H, aromatic), 6.29 (d, 1H, \( J = 3 \) Hz, \( H_2 \)), 4.62 (s, 1H, \( H_{6b} \)), 4.07 (d, 1H, \( J = 8 \) Hz, \( H_{2b} \)), 3.72 (s, 3H, methyl), 3.66 (dd, 1H, \( J = 8.3 \) Hz, \( H_{2a} \)) ppm.

MS (EI) m/e: 316 (M\(^+\), 7), 284 (8), 180 (23), 152 (50), 105 (100), 77 (72). Exact mass calculated for C\(_{21}\)H\(_{16}\)O\(_3\): 316.1100, found 316.1106.

UV (CH\(_3\)CN) \( \lambda_{\text{max}} \): 244 (\( \epsilon = 16500 \)), 280 sh (\( \epsilon = 4900 \)) nm.

Anal. calcd. for C\(_{21}\)H\(_{16}\)O\(_3\): C, 79.73; H, 5.10. Found: C, 79.80; H, 5.10.

**Benzophenone-Sensitized Photolysis**

In a 0.2 ml analytical phototube, a benzene solution of 0.02 M in 43 and ca. 0.2 M in benzophenone was photolyzed through uranium glass (\( \lambda > 330 \) nm). GC showed the formation of two photoproducts (43a and 43h), however, extended photolysis gave similar results to direct irradiation.

**Solid State Photolysis**

Crystals of 43 were photolyzed (\( \lambda > 290 \) nm) in nitrogen filled Pyrex analytical phototubes. GC showed the formation of three new products: 43d, 43e, and 43f. Neither 43a nor 43b were detected at low conversions, but at conversions above ca. 20%, the
crystals began to melt and stick to the tube surface, and detectable amounts of compound 43a began to form.

In an NMR study, crystals (approx. 10 mg) of 43 were photolyzed in an NMR tube until the sample turned yellow but showed no sign of melting. NMR analysis of the reaction mixture at 17% conversion indicated a 43d : 43e : 43f ratio of 50 : 30 : 20.

On a preparative scale, crystals of 43 (291 mg, 0.921 mmole) were placed in three vials and photolyzed (λ > 290 nm) until the crystals were yellow but showed no signs of melting (18% conversion by GC). The crystals were dissolved in benzene and chromatographed on silica gel using a solvent system of hexanes and diethyl ether, 92:8 (v/v), to give three overlapping bands. The first band was rechromatographed as above to give 13 mg of methyl 6c-benzoyl-2a,2b-dihydrobenzo[a]cyclopropa[cd]pentalene-6b-carboxylate (43f, yield 4.5%). Recrystallization from hexanes gave colorless needles.

MP: 162-163 °C.

IR (KBr) νmax: 1742 (s, ester C=O), 1668 (s, benzoyl C=O), 1285 (s, C-O) cm⁻¹.

H NMR (300 MHz) δ: 7.7-7.1 (m, 9H, aromatic), 6.06 (d, 1H, J = 5 Hz, H₁), 5.40 (dd, 1H, J = 5,3 Hz, H₂), 4.07 (d, 1H, J = 8 Hz, H₂b), 3.44 (dd, 1H, J = 8,3 Hz, H₂a), 3.12 (s, 3H, methyl) ppm. Spin decoupling experiments: irradiation of H₁ collapses H₂ to a doublet (J = 3 Hz); irradiation of H₂ collapses H₁ to a singlet and simplifies H₂a to a doublet (J = 8 Hz); irradiation of H₂a collapses H₂ to a doublet (J = 5 Hz) and collapses H₂b to a singlet; irradiation of H₂b simplifies H₂a to a doublet (J = 3 Hz).
MS (EI) m/e: 316 (M+, 12), 284 (13), 256 (20), 152 (20), 105 (100), 77 (35). Exact mass calculated for C_{21}H_{16}O_3: 316.1100, found 316.1098.

UV (CH_3CN) λ_{max}: 240 (ε 9500), 280 sh (ε 1760) nm.

Anal. calcd. for C_{21}H_{16}O_3: C, 79.73; H, 510. Found C, 79.73; H, 5.16.

The assigned structure was also supported by an X-ray crystal structure determination. The crystal data are as follows:

C_{21}H_{16}O_3, orthorhombic, space group Pbca, a = 33.023(2) Å, b = 11.210(1) Å, c = 8.637(2) Å, V = 3197(1) Å^3, Z = 8, D_x = 1.314 g/ml, R = 0.042.

The second band was 190 mg of recovered starting material and the third band was rechromatographed as above to give 26 mg of an inseparable oily mixture of photoproducts 43d and 43e (75 : 25). Compound 43d was characterized as a mixture with 43e.

IR (neat, 1:1 mixture with 43e) ν_{max}: 1714 (s, ester C=O), 1673 (s, benzoyl C=O), 1267 (s, C=O) cm⁻¹.

^1^H NMR (300 MHz, CDCl_3) δ: 7.6-6.8 (m, 9H, aromatic overlapping with 43e), 4.40 (d, 1H, J = 6 Hz, H_6b), 3.62 (ddd, 1H, J = 6,6,6 Hz, H_6c slightly overlapping with 43e), 3.45 (s, 3H, methyl), 3.40 (dd, 1H, J = 6,6 Hz, H_2b), 3.00 (dd, 1H, J = 6,6 Hz, H_2a) ppm. The peaks of 43d can be distinguished from those of 43e by analyzing several spectra with different compositions of 43d and 43e, varying from 1:1 to 4:1, respectively. Spin decoupling experiments: irradiation of H_2b modifies H_6c and H_2a; irradiation of H_2a modifies H_2b and H_6c; irradiation of H_6b modifies H_6c; irradiation of H_6c collapses H_6b to a singlet and H_2a to a doublet (J = 6 Hz) and H_2b to a doublet (J = 6 Hz). Lanthanide shift reagent studies were also performed to distinguish
H$_{2a}$ from H$_{2b}$. It was reasoned that H$_{2a}$, being closer to the site of shift reagent complexation (the carbonyl substituents), should be more strongly deshielded than H$_{2b}$.

Successive additions of 0, 4, 10, 20, and 30 mole % of Eu(hfc)$_3$ (from Aldrich) to the NMR mixture of 43d and 43e showed a greater shift at $\delta$ 3.00 compared to that at $\delta$ 3.40. Therefore these signals were assigned to H$_{2a}$ and H$_{2b}$ respectively. The results are presented graphically in the text.

GC-MS (EI, DB-1) m/e: 316 (M$^+$, 10), 284 (40), 179 (10), 152 (15), 105 (100), 77 (69). Exact mass calculated for C$_{21}$H$_{16}$O$_3$: 316.110, found 316.1097.

The spectral data for 43e are from mixtures with 43d and are described below.

IR (neat, 1:1 mixture with 43d) $\nu_{\text{max}}$: described above.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.6-6.8 (m, 9H, aromatic overlapping with 43d), 4.35 (d, 1H, $J = 6$ Hz, H$_{6b}$), 3.58 (ddd, 1H, $J = 6,6,6$ Hz, H$_{6c}$ slightly overlapping with 43d), 3.33 (dd, 1H, $J = 6,6$ Hz, H$_{2b}$), 3.18 (dd, 1H, $J = 6,6$ Hz, H$_{2a}$ overlapping with methyl), 3.17 (s, 3H, methyl overlapping with H$_{2a}$) ppm. Spin decoupling experiments: irradiation of H$_{2b}$ modifies H$_{2a}$ and H$_{6c}$; irradiation of H$_{2a}$ modifies H$_{2b}$ and H$_{6c}$; irradiation of H$_{6b}$ modifies H$_{6c}$; irradiation of H$_{6c}$ collapses H$_{6b}$ to a singlet and modifies H$_{2a}$ and H$_{2b}$. A shift reagent study was performed as above to assign H$_{2a}$ and H$_{2b}$ (see text).

GC-MS (EI, DB-1) m/e: 316 (M$^+$, 5), 284 (7), 152 (8), 105 (100), 77 (38). Exact mass calculated for C$_{21}$H$_{16}$O$_3$: 316.1100, found 316.1103.
Photolysis of Compound 43 in Poly[methyl methacrylate] (PMMA) Film

Compound 43 (3 mg, 1 x 10⁻⁵ mole) was dissolved along with 30 mg of medium molecular weight poly(methyl methacrylate) (from Aldrich) in 2 ml of methylene chloride and spread over three microscope slides. The solvent was evaporated under vacuum for 24 h, and the resulting clear films were photolyzed at 20 °C through a Pyrex filter (λ > 290 nm). For monitoring the reaction, portions of film were dissolved in CH₂Cl₂ and methanol was added to precipitate the PMMA prior to GC analysis. Irradiation to complete conversion gave five products (43a, 43b, 43h, 43d, and 43e) in a GC ratio of 34 : 12 : 30 : 12 : 12, respectively. A low temperature photolysis (-50 °C) gave similar results, but the rate was much slower.

On a preparative scale, a solution of 43 (200 mg, 0.63 mmole) and 2.0 g of medium molecular weight PMMA (from Aldrich) in 30 ml of CH₂Cl₂ was poured into a 24 x 5 cm Pyrex vacuum-safe tube and spread evenly over the inner surface. The solvent was removed by flushing with nitrogen for 30 min followed by pumping on a vacuum line for 50 hr. The tube was sealed under nitrogen and photolyzed (λ > 290 nm) at 20 °C. The tube was rotated every 15 min and the reaction monitored by GC to a maximum conversion of 93%. The polymer was dissolved in 100 ml of CH₂Cl₂ and 75 ml of methanol was added. The solvent was evaporated until approximately 75 ml remained, at which point most of the polymer had precipitated. The mixture was stirred for another 30 min to precipitate the rest of the polymer and the solution was filtered and evaporated to a yellow oil. Chromatography on silica gel using hexanes-diethyl ether, 9:1 v/v, as the eluent gave three major bands. The first band consisted
of 61 mg of 43a (yield 31%). The second band contained 27 mg of a white solid (yield 14%). Recrystallization from hexanes gave prisms which were characterized as methyl 6c-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa-
[cd]pentalene-2a-carboxylate (43h).

MP: 129-130 °C.

IR (KBr) νmax: 1718 (s, ester C=O), 1676 (s, benzoyl C=O),
1287 (s, C-O) cm⁻¹.

¹H NMR (300 MHz) δ: 7.9-7.1 (m, 9H, aromatic), 5.91 (dd, 1H,
J = 5.2 Hz, H₁), 5.64 (d, 1H, J = 6 Hz, H₂), 4.55 (s, 1H, H₂b),
4.30 (d, 1H, J = 2 Hz, H₆b), 3.70 (s, 3H, methyl) ppm.

MS (EI) m/e: 316 (M⁺, 25), 284 (49), 256 (25), 152 (15), 105
(100), 77 (30). Exact mass calculated for C₂₁H₁₆O₃: 316.1100,
found 316.1105.

UV (CH₃CN) λmax: 245 (ε 25800), 278 sh (ε 3900) nm.

Anal. calcd. for C₂₁H₁₆O₃: C, 79.73; H, 5.10. Found: C, 79.82;

The third band contained a 3 : 1 mixture of compounds 43d to
43e as indicated by GC.

Photostationary State of Benzosemibullvalenes 43a and 43c

Crystals of 43a were dissolved in benzene, acetonitrile, and
acetone to make up approximately 0.01 M solutions, and analytically
photolyzed (λ > 290 nm). The reactions monitored by GC to show
the formation of one compound, subsequently characterized
as 43c. The reaction was independent of solvent, except that
the rate of reaction in acetone was noticeably slower. In all three
cases, the 43a : 43c ratio after prolonged irradiation (corrected for
detector response by NMR) was 8 : 2. Independent analytical photolysis of compound 43c led to the same ratio.

On a preparative scale, a solution of 50 mg (0.16 mmole) of compound 43a in 40 ml of benzene was photolyzed in four 10 ml phototubes through a Pyrex filter (λ > 290 nm) to a time-invariant 43a : 43c ratio of 83 : 17. The solvent was concentrated to a yellow oil and chromatographed on silica gel using diethyl ether and hexanes (1 : 9 v/v) as the solvent. Two overlapping bands were eluted, compound 43a first, followed by 43c. A partial separation of 43c from 43a was achieved, and the pure 43a isolated (32 mg) was rephotolyzed and chromatographed as above to give partial separation of 43c again. The fractions of 43c were combined and rechromatographed as above to give complete separation resulting in 12 mg of a white solid (yield 24%). Recrystallization from hexanes gave colorless needles of methyl 1-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]penatalene-6c(2aH)-carboxylate (43c).

MP: 100-101 °C.

IR (KBr) \( \nu_{\text{max}} \): 1726 (s, ester C=O), 1639 (s, benzoyl C=O), 1329 (s), 1267 (s, C-O), 1213 (s) cm\(^{-1}\).

\(^1\)H NMR (300 MHz) \( \delta \): 7.6-7.1 (m, 9H, aromatic), 5.95 (d, 1H, \( J = 3 \text{ Hz, } H_2 \)), 4.96 (s, 1H, \( H_{6b} \)), 3.97 (d, 1H, \( J = 8 \text{ Hz, } H_{2b} \)), 3.74 (s, 3H, methyl), 3.54 (dd, 1H, \( J = 8,3 \text{ Hz, } H_{2a} \)) ppm.

MS (EI) m/e: 316 (M\(^+\), 20), 284 (4), 256 (10), 152 (13), 105 (100), 77 (45). Exact mass calculated for \( C_{21}H_{16}O_3 \): 316.1100, found 316.1100.

Anal. calcd. for \( C_{21}H_{16}O_3 \): C, 79.73; H, 5.10. Found: C, 79.63; H, 5.21.
Photostationary State of Benzosemibullvalenes 43f and 43g

Crystals of 43f were dissolved in benzene, acetonitrile, and acetone to make up approximately 0.01 M solutions and analytically photolyzed (λ > 290 nm). GC monitoring of the reaction indicated the formation of one volatile product, subsequently shown to have the structure 43g, at a photostationary state ratio of 43f : 43g = 2 : 8. Independent analytical photolysis of 43g in benzene also led to this ratio, but prolonged photolysis caused irreversible decomposition of the sample. The results were the same in all three solvents, except that the rate of reaction was noticeably slower in acetone.

Photoproduct 43g was isolated by photolysis of a solution of 7.5 mg (0.025 mmole) of 43f in 1 ml of CDCl₃. The photolysis was halted at a 43f : 43g ratio of 57 : 43 in order to avoid photodecomposition. The mixture was chromatographed on silica eluting with diethyl ether and hexanes (1 : 9 v/v). Compound 43f eluted first followed closely by 43g. Pure 43f was rephotolyzed and chromatographed as above. The two pure portions were combined to give 3 mg of a colorless oil (yield 40%) of methyl 6c-benzoyl-2a,6b-dihydrobenzo[a]cyclopropa[cd]-pentalene-2b-carboxylate (43g).

IR (neat) ν_max: 1728 (s, ester C=O), 1675 (s, benzoyl C=O), 1264 (s, C=O) cm⁻¹.

¹H NMR (300 MHz) δ: 7.9-7.1 (m, 9H, aromatic), 5.87 (dd, 1H, J = 5,2 Hz, H₁), 5.42 (dd, 1H, J = 5,3 Hz, H₂), 4.27 (d, 1H, J = 2 Hz, H₆b), 4.24 (d, 1H, J = 3 Hz, H₂a), 3.73 (s, 3H, methyl) ppm. Spin decoupling experiments: irradiation of H₁ collapses H₂ to a doublet (J = 3 Hz) and collapses H₆b to a singlet; irradiation of H₂ collapses H₁ to a doublet (J = 2 Hz) and collapses H₂a to a singlet.
Photostationary State of Benzosemibullvalenes 43h and 43b

Crystals of 43h were dissolved in benzene and acetonitrile to make up approximately 0.01 M solutions and analytically photolyzed (λ > 290 nm). GC indicated a photostationary state composition of 43h : 43b = 2 : 8. This was verified by an independent photolysis of compound 43b under identical conditions. Compound 43h rearranges thermally to 43b in the GC above 200 °C.

Photolysis of Benzosemibullvalenes 43d and 43e

A 1 : 1 mixture of compounds 43d and 43e was dissolved in benzene, acetone, and acetonitrile to make up approximately 0.02 M solutions and analytically photolyzed (λ > 290 nm). GC showed the formation of a new peak with a maximum conversion of 4% relative to the starting materials. Insufficient conversion prevented its isolation or identification.

Photolysis of Deuterated 43 (43-D) in CDCl₃

Compound 43-D (10 mg) dissolved in 1 ml of CDCl₃ was photolyzed (λ > 330 nm) to complete conversion. Compounds 43a-D and 43b-D were analyzed in the reaction mixture by NMR for the sites of deuteration. The results for 43a-D are described.

¹H NMR (300 MHz, only non-overlapping signals are reported) δ: 5.90 (dd, 1.00H, J = 5,3 Hz, H₁), 5.27 (d, 0.89H, J = 5 Hz, H₂), 4.69 (d, 0.59H + 0.31D, J = 3 Hz, H₆b), 3.57 (s, 0.63H +
Photolysis of Deuterated 43 (43-D) in the Solid State

Crystals of 43-D (54 mg, 0.17 mmole) were crushed between two pairs of microscope slides and photolyzed (λ > 290 nm). The resulting yellow solid was dissolved in 1 ml of CDCl₃ and analyzed by NMR. Spectral expansion and integration of the reaction mixture was done. Signals of compound 43f-D are reported below.

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, only non-overlapping signals are reported)}
\end{align*}
\]

\(\delta: 6.06 \text{ (d, 0.68H + 0.32D, } J = 5 \text{ Hz, } H\textsubscript{1}),
5.40 \text{ (dd, 1.00H, } J = 5,3 \text{ Hz, } H\textsubscript{2}),
4.07 \text{ (d, 0.76H + 0.24D, } J = 8 \text{ Hz, } H\textsubscript{2b}),
3.13 \text{ (s, 2.88H, methyl) ppm.}
\]

The mixture was chromatographed on silica using a 9 : 1 (v/v) mixture of hexanes to diethyl ether as the eluting solvent. This gave three overlapping bands; the first was 43f-D, the second was starting material, and the third was 10 mg of a 57 : 43 mixture of compounds 43d-D and 43e-D. The third band was rechromatographed as above and analyzed by NMR. Spectral data for 43d-D are described.

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, only non-overlapping bands are reported)}
\end{align*}
\]

\(\delta: 4.40 \text{ (d, 0.67H + 0.33D, } J = 6 \text{ Hz, } H\textsubscript{6b}),
3.45 \text{ (s, 3.07H, methyl),}
3.40 \text{ (dd, 0.80H + 0.20D, } J = 6,6 \text{ Hz, } H\textsubscript{2b}),
3.00 \text{ (dd, 1.00H, } J = 6,6 \text{ Hz, } H\textsubscript{2a}),
3.45 \text{ (s, 3.12H, methyl) ppm.}
\]

Results for 43e-D are below.
$^1$H NMR (300 MHz, CDCl$_3$, only bands non-overlapping with 43d-D are reported) $\delta$: 4.35 (d, 0.57H + 0.43D, J = 6 Hz, H$_{6b}$), 3.33 (dd, 0.71H + 0.29D, J = 6,6 Hz, H$_{2b}$), 3.22-3.16 (m, 4.00H, H$_{2a}$ + methyl) ppm.

The solvent was evaporated and redissolved in benzene-d$_6$ to analyze the signals of H$_{2a}$ and H$_{2b}$ of compound 43e-D again.

$^1$H NMR (400 MHz, benzene-d$_6$, only signals of H$_{2a}$ and H$_{2b}$ are reported) $\delta$: 2.86 (dd, 0.71H + 0.29D, J = 6,6 Hz, H$_{2b}$), 2.80 (dd, 1.00H, J = 6,6 Hz, H$_{2a}$) ppm.
F. Ethyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (44)

Direct Photolysis

In an analytical study, crystals of 44 were dissolved in benzene and acetonitrile for photolysis (λ > 290 nm). The reactions were monitored to complete conversion to give two major photoproducts and three minor photoproducts independent of solvent. However, overlapping peaks prevented proper GC integration at high conversion.

In an NMR study, compound 44 (approx. 10 mg) in 1.5 ml of CDCl₃ were photolyzed (λ > 330 nm) to complete conversion to give five products 44a, 44b, 44c, 44d, 44e, and 44f in a ratio of 46 : 35 : 4 : 11 : 4 : trace, respectively.

On a larger scale, compound 44 (28 mg, 8.5 x 10⁻⁵ mole) was dissolved in 1.5 ml of CDCl₃ and photolyzed (λ > 330 nm) in a phototube to complete conversion. Integration of the NMR expansion showed a 44a, 44b, 44c, 44d, 44e, and 44f ratio of 45 : 32 : 10 : 10 : 3 : trace, respectively. Chromatography on silica gel with diethyl ether and hexanes (1:9 v/v) as eluent gave 8 mg of a white solid (yield 29%) in the first band. Recrystallization from hexanes gave prisms of ethyl 2a-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[c]pentalen-6c-carboxylate (44a).

MP: 73-74 °C.

IR (KBr) νmax: 1724 (s, ester C=O), 1677 (s, benzoyl C=O), 1239 (s, C-O) cm⁻¹.

¹H NMR (300 MHz) δ: 8.05-7.15 (m, 9H, aromatic), 5.91 (dd, 1H, J = 5, 2 Hz, H₅), 5.27 (d, 1H, J = 5 Hz, H₅), 4.68 (d, 1H, J = 2 Hz,
Hgb, 4.57 (s, 1H, H2a), 3.88 (q, 2H, J = 7 Hz, methylene), 0.96 (t, 3H, J = 7 Hz, methyl) ppm.

MS (EI) m/e: 330 (M+, 52), 284 (8), 257 (9), 105 (100), 77 (40). Exact mass calculated for C22H18O3: 330.1255, found 330.1255.

Anal. calcd. for C22H18O3: C, 79.98; H, 5.49. Found: C, 80.05; H, 5.46.

The second band contained 2.5 mg of ethyl 6c-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-1(2aH)-carboxylate (44b) as a colorless oil (yield 9%).

IR (neat) v_max: 1709 (s, ester C=O), 1666 (s, benzoyl C=O), 1248 (s, C-O) cm⁻¹.

1H NMR (300 MHz) δ: 7.6-7.1 (m, 9H, aromatic), 6.29 (d, 1H, J = 3 Hz, Hg), 4.61 (s, 1H, Hgb), 4.25-4.10 (m, 2H, methylene), 4.06 (d, 1H, J = 8 Hz, Hgb), 3.66 (dd, 1H, J = 8,3 Hz, H2a), 1.30 (t, 3H, J = 7 Hz, methyl) ppm.

MS (EI) m/e: 330 (M+, 15), 284 (40), 257 (10), 225 (40), 180 (20), 152 (50), 105 (100), 77 (60). Exact mass calculated for C22H18O3: 330.1255, found 330.1260. More compound 44b was synthesized later for this characterization from the photolysis of compound 44c.

The third band was a 5 mg of an inseparable 1 : 7 : 2 mixture of 44c, 44d, and 44e, from which the latter two were characterized. Spectral data for ethyl 1-benzoyl-2a,2b,6b,6c-tetrahydrobenzo[a]-cyclopropa[cd]pentalene-2-carboxylate (44d) are as follows:

1H NMR (300 MHz) δ: 7.6-7.0 (m, 9H, aromatic overlapping with 44c and 44e), 4.40 (d, 1H, J = 6 Hz, H6b), 3.90 (m, 2H, methylene overlapping with 44e), 3.60 (ddd, 1H, J = 6,6,6 Hz, H6c overlapping with
44e), 3.41 (dd, 1H, J = 6.6 Hz, H2b), 3.00 (dd, 1H, J = 6.6 Hz, H2a), 0.85 (t, 3H, J = 7 Hz, methyl) ppm. Peaks of 44d were distinguishable from those of 44e by studying other mixtures with different ratios.

GC-MS (EI, DB-1) m/e: 330 (M+, 1), 213 (8), 180 (4), 152 (20), 105 (100), 77 (20). Exact mass calculated for C22H18O3: 330.1256, found 330.1253.

Data for ethyl 2-benzoyl-2a,2b,6b,6c-tetrahydrobenzo[a]cyclopropa[cd]pentalene-1-carboxylate (44e) are below.

1H NMR (300 MHz) δ: 7.6-7.0 (m, 9H, aromatic overlapping with 44c and 44d), 4.45 (d, 1H, J = 6 Hz, H6b), 3.90 (m, 2H, methylene overlapping with 44d), 3.60 (ddd, 1H, J = 6,6,6 Hz, H6c overlapping with 44d), 3.33 (dd, 1H, J = 6,6 Hz, H2b), 3.20 (dd, 1H, J = 6,6 Hz, H2a), 0.66 (t, 3H, J = 7 Hz, methyl) ppm.

GC-MS (EI, DB-1) m/e: 330 (M+, 2), 213 (8), 180 (4), 152 (17), 105 (100), 77 (22). Exact mass calculated for C22H18O3: 330.1256, found 330.1259.

Benzophenone-Sensitized Photolysis

In an analytical study, crystals of 44 and excess benzophenone were dissolved in benzene and photolyzed (λ > 330 nm). GC monitoring indicated complete conversion to 44a and 44c in a single inseparable GC (DB-1) peak. However, at column temperatures > 200 °C, compound 44c converts completely to 44b. The ratio of 44a to 44c (44b) was 48 : 52 as established by GC (DB-17).

On a preparative scale, benzobarrelene 44 (163 mg, 0.49 mmole) and 7 g (38 mmoles) of benzophenone in 140 ml of benzene were photolyzed
(λ > 330 nm) in an immersion well to complete conversion. The resulting solution was chromatographed on silica gel with hexanes and diethyl ether (9 : 1 v/v) as the eluent. The first band was benzophenone. The second band was 58 mg of photoproduct 44a (yield 36%), and the third band contained 57 mg of ethyl 6c-benzoyl-2b,6b-dihydrobenzo[a]-cyclopropa[cd]pentalene-2a-carboxylate (44c) as a colorless oil (yield 35%).

IR (neat) v_max: 1717 (s, ester C=O), 1675 (s, benzoyl C=O), 1278 (s, C=O) cm⁻¹.

¹H NMR (400 MHz) δ: 7.9-7.1 (m, 9H, aromatic), 5.90 (dd, 1H, J = 6.2 Hz, H₁), 5.64 (d, 1H, J = 6 Hz, H₂), 4.51 (s, 1H, H₂b), 4.29 (d, 1H, J = 2 Hz, H₆b), 4.12 (q, 2H, J = 7 Hz, methylene), 1.12 (t, 3H, J = 7 Hz, methyl) ppm.

MS (EI) m/e: 330 (M⁺, 28), 284 (65) 256 (30), 226 (25), 152 (49), 105 (100), 77 (60). Exact mass calculated for C₂₂H₁₈O₃: 330.1255, found 330.1262.

A small amount of compounds 44d and 44e (ca. 8 mg) were detected in the tail of the compound 44c band.

Solid State Photolysis of Compound 44

Crystals of 44 (9 mg, 2.7 x 10⁻⁵ mole) were photolyzed (λ > 290 nm) in an NMR tube for two hours and the unmelted, slightly yellow crystals were dissolved in CDCl₃ for NMR analysis. The ratio of the four primary photoproducts 44a, 44c, 44d, and 44e was 54 : 8 : 23 : 15 respectively at a conversion of 47%. The above experiment was repeated in a 5 h photolysis and the 44a, 44c, 44d, and
Photolysis of Benzosemibullvalene 44a

On an analytical scale, small samples of compound 44 were dissolved in benzene (λ > 330 nm), acetonitrile (λ > 330 nm), and acetone (λ > 290 nm) for photolysis. GC monitoring indicated one volatile product independent of solvent at a maximum conversion of ca. 10%.

Compound 44a (5 mg, 0.015 mmole) in 1 ml of CDCl₃ was photolyzed (λ > 290 nm) and the equilibrium ratio was analyzed by NMR (GC) to be 92 (92) : 8 (8) for 44a and 44f. The product, ethyl 1-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-6c(2aH)-carboxylate (44f) was characterized as a mixture with 44a as described below.

\[^1\text{H} \text{NMR (400 MHz)} \delta: 8.0-7.0 \text{ (m, 9H, overlapping with 44a), 5.94 (d, 1H, J = 3 Hz, H₂), 4.96 (s, 1H, H₆b), 4.20 (q, 2H, J = 7 Hz, methylene), 3.97 (d, 1H, J = 8 Hz, H₂b), 3.52 (dd, 1H, J = 8,3 Hz, H₂a), 1.30 (t, 3H, J = 7 Hz, methyl) ppm.}]

\[\text{GC-MS (EI, DB-1) m/e: 330 (M^+, 11), 256 (5), 152 (12), 105 (100), 77 (25). Exact mass calculated for C}_{22}\text{H}_{18}\text{O}_3: 330.1255, \text{ found 330.1266.}]

Photostationary State of Benzosemibullvalenes 44b and 44c

On an analytical scale, small samples of photoproduct 44c were photolyzed (λ > 290 nm) in benzene, acetonitrile, and acetone. The reaction was monitored by GC to show the formation of compound 44b, as the only product, independent of solvent. The maximum conversion
was ca. 85\%.

Compound 44c (5 mg) was dissolved in CDCl₃ and photolyzed (\(\lambda > 290\) nm) to equilibrium and analyzed by NMR (GC). This indicated 83 (82) : 17 (18) composition of compounds 44b and 44c. Independent analytical photolysis of 44b gave the same ratio.

G. Isopropyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (45)

Direct Solution Photolysis of Compound 45

Crystals of 45 were photolyzed analytically (\(\lambda > 330\) nm) in benzene, acetonitrile, and methanol to complete conversion. GC monitoring showed two major products and three minor products, and the reaction was independent of solvent. The GC (DB-1) ratios were typically 50 : 30 : 7 : 10 : 3 of 45a, 45b, 45c, 45d + 45e, and 45f respectively (use of the DB-17 resulted in other overlaps). These assignments were verified later.

On a larger scale, crystals of 45f (20 mg, 5.8 \times 10^{-5} \text{ mole}) were dissolved in 1.5 ml of CDCl₃ and photolyzed (\(\lambda > 330\) nm) to complete conversion. NMR analysis showed a 45a : 45b : 45c : 45d : 45e ratio of 50 : 30 : 8 : 8 : 4. The reaction mixture was chromatographed on silica gel eluting with a 1 : 9 (v/v) mixture of diethyl ether to hexanes. The first band consisted of 5 mg of a white solid (yield 26 \%). Recrystallization from hexanes gave colorless prisms of isopropyl 2a-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentane-6c-carboxylate (45a).
MP: 78-79 °C.

$^1$H NMR (300 MHz) $\delta$: 8.1-7.2 (m, 9H, aromatic), 5.91 (dd, 1H, $J = 5.2$ Hz, $H_1$), 5.26 (d, 1H, $J = 5$ Hz, $H_2$), 4.75 (septet, 1H, $J = 6$ Hz, isopropyl methine), 4.69 (d, 1H, $J = 2$ Hz, $H_{6b}$), 4.56 (s, 1H, $H_{2b}$), 1.04 (d, 3H, $J = 6$ Hz, methyl), 0.65 (d, 3H, $J = 6$ Hz, methyl) ppm.

MS (EI) m/e: 344 (M+, 36), 302 (6), 258 (21), 105 (100), 77 (20). Exact mass calculated for $C_{23}H_{20}O_3$: 344.1412, found 344.1408.

Anal. calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 79.89 H, 5.75.

The second band was an inseparable mixture of 45b and 45c (6.5 mg) overlapping with trace amounts of 45d and 45e. This was rechromatographed as above to remove 45d and 45e, giving 2 mg of 45b and 45c. From this mixture, isopropyl 6c-benzoyl-2b,6b-dihydrobenzo-[a]cyclopropa[cd]pentalene-1(2aH)-carboxylate (45b) was characterized as a 45b : 45c = 7 : 3 mixture.

IR (neat, 30% of 45c) $\nu_{max}$: 1705 (s, ester C=O), 1666 (s, benzoyl C=O), 1249 (s, C-O) cm$^{-1}$.

$^1$H NMR (300 MHz) $\delta$: 7.7-7.1 (m, 9H, aromatic overlapping with 45c), 6.28 (d, 1H, $J = 3$ Hz, $H_2$), 5.04 (septet, 1H, $J = 6$ Hz, isopropyl methine), 4.60 (s, 1H, $H_{6b}$), 4.04 (d, 1H, $J = 8$ Hz, $H_{2b}$), 3.66 (dd, 1H, $J = 8.3$ Hz, $H_{2a}$), 1.28 (d, 3H, $J = 6$ Hz, methyl), 1.23 (d, 3H, $J = 6$ Hz, methyl) ppm.

GC-MS (DB-1, DCI) m/e: 345 (M$^+$+1, 22), 285 (100), 105 (95). Exact mass calculated for $C_{23}H_{20}O_3$: 344.1412, found 344.1408.
Benzophenone-Sensitized Photolysis of Compound 45

Crystals of 45 (2 mg) and an approximately 10-fold molar excess of benzophenone were dissolved in benzene and photolized (λ > 330 nm) to complete conversion. GC showed the formation of compounds 45a and 45c as the photoproducts.

On a preparative scale, compound 45 (57 mg, 1.5 x 10^(-4) mole) and 1.0 g (5.5 mmoles) of benzophenone were photolized (λ > 330 nm) in 40 ml of benzene to complete conversion. Chromatography on silica gel using a 1 : 9 (v/v) mixture of diethyl ether to hexanes as eluent gave four bands. The first was benzophenone. The second contained 25 mg of compound 45a (yield 47%). The third band consisted of 20 mg of isopropyl 6c-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-2a-carboxylate (45c) as a colorless oil (yield 37%).

IR (neat) ν_max: 1718 (s, ester C=O), 1677 (s, benzoyl C=O), 1283 (s, C-O) cm^{-1}.

^1H NMR (300 MHz) δ: 7.9-7.0 (m, 9H, aromatic), 5.90 (dd, 1H, J = 5,2 Hz, H1), 5.65 (d, 1H, J = 5 Hz, H2), 4.96 (septet, 1H, J = 6 Hz, isopropyl methine), 4.46 (s, 1H, H2b), 4.28 (d, 1H, J = 2 Hz, H6b), 1.15 (d, 3H, J = 6 Hz, methyl), 1.01 (d, 3H, J = 6 Hz, methyl) ppm.

MS (EI) m/e: 344 (M^+, 3), 284 (8), 180 (12), 152 (19), 105 (100), 77 (27). Exact mass calculated for C_{23}H_{20}O_{3}: 344.1412, found 344.1406.

The forth band contained 5 mg of a 3 : 1 mixture of photoproducts 45d and 45e; these two compounds were characterized in the solid state study.
Solid State Photolysis of Compound 45

Crystals of 45 in an analytical phototube were photolyzed (λ > 330 nm) until the crystals were yellow but not melted. GC (DB-17) analysis showed a 44 : 44 : 12 ratio of 45d, 45e, and 45a at a 27% conversion. The photolysis was repeated with a Pyrex filter sleeve (λ > 290 nm) until the crystals started to melt. GC (DB-17) showed a 73% conversion to a 40 : 40 : 20 ratio of 45d, 45e, and 45a.

On a preparative scale, crystals of 45 (65 mg, 1.9 x 10⁻⁴ mole) were photolyzed (λ > 290 nm) for 4 h in two NMR tubes with rotating every 15 min. The unmelted yellow crystals were analyzed by NMR to show a 32% conversion and a 45d : 45e : 45a ratio of 45 : 45 : 10. The reaction mixture was chromatographed twice on silica gel eluting with diethyl ether and hexanes (1 : 9 v/v). The resulting inseparable mixture of 45d and 45e (7.8 mg, yield 12%) were characterized together. Data for isopropyl 1-benzoyl-2a,2b,6b,6c-tetrahydrobenzo[a]cyclopropa[cd]pentalene-2-carboxylate (45d) is described.

IR (neat, 50:50 mix with 45e) νmax: 1707 (s, ester C=O), 1672 (s, benzyol C=O), 1270 (s, C-0) cm⁻¹.

¹H NMR (300 MHz) δ: 7.6-6.7 (m, 9H, aromatic overlapping with 45e), 4.78 (septet, 1H, J = 6 Hz, isopropyl methine overlapping with 45e), 4.41 (d, 1H, J = 7 Hz, H₆b), 3.61 (ddd, 1H, J = 7,7,7 Hz, H₆c overlapping with 43), 3.40 (ddd, 1H, J = 7,7 Hz, H₂b), 3.00 (dd, 1H, J = 7,7 Hz, H₂a), 1.01 (d, 3H, J = 6 Hz, methyl), 0.66 (d, 3H, J = 6 Hz, methyl) ppm.

GC-MS (DB-17, DCI isobutane) m/e: 345 (M⁺ + 1, 100), 285 (35).
Exact mass (EI) calculated for C_{23}H_{20}O_{3}: 344.1412, found 344.1405.

Characterization of isopropyl 2-benzoyl-2a,2b,6b,6c-tetrahydrobenzo[a]cyclopropa[cd]pentalene-1-carboxylate (45e) is given below.

IR (neat, 50:50 mix with 45d) v_{max}: see above.

{\textsuperscript{1}H} NMR (300 MHz) δ: 7.6-6.7 (m, 9H, aromatic), 4.62 (septet, 1H, J = 6 Hz, isopropyl methine overlapping with 45d), 4.33 (d, 1H, J = 7 Hz, H_{6b}), 3.58 (ddd, 1H, J = 7,7,7 Hz, H_{6c} overlapping with 45d), 3.31 (dd, 1H, J = 7,7 Hz, H_{2b}), 3.20 (dd, 1H, J = 7,7 Hz, H_{2a}), 0.88 (d, 3H, J = 6 Hz, methyl), 0.44 (d, 3H, J = 6 Hz, methyl) ppm.

GC-MS (DB-17, DCI isobutane) m/e: 345 (M^+ + 1, 100), 285 (52).

Exact mass (EI) calculated for C_{23}H_{20}O_{3}: 344.1412, found 344.1418.

Photolysis of Benzosemibullvalene 45a

Small amounts of compound 45a were dissolved in benzene, acetonitrile, and acetone. Photolysis (λ > 290 nm) showed a solvent-independent reaction to form one product (45f) at a 13% maximum conversion by GC.

On a larger scale, 10 mg of 45a were dissolved in 1 ml of CDCl_{3} and photolyzed (λ > 290 nm) to equilibrium. The mixture was analyzed by NMR (GC) to give a 45a to 45f ratio of 88 (91): 12 (9). Isopropyl 1-benzoyl-2b,6b-dihydrobenzo[a]cyclopropa[cd]pentalene-6c(2aH)-carboxylate (45f) was characterized in this mixture.

{\textsuperscript{1}H} NMR (300 MHz) δ: 7.9-7.1 (m, 9H, aromatic), 5.94 (d, 1H, J = 3 Hz, H_{2}), 5.06 (septet, 1H, J = 6 Hz, isopropyl methine), 4.94 (s, 1H, H_{6b}), 3.95 (d, 1H, J = 8 Hz, H_{2b}), 3.50 (dd, 1H, J = 8,3 Hz, H_{2a})
ppm. Methyls of the isopropyl are hidden beneath 45a.

GC-MS (DB-1, EI) m/e: 344 (M+, 8), 302 (8), 284 (8), 257 (10), 152 (13), 105 (100), 77 (19). Exact mass calculated for C_{23}H_{20}O_{3}: 344.1412, found 344.1400.

Photolysis of Benzosemibullvalene 45c

On an analytical scale, compound 45c was dissolved in benzene, acetonitrile, and acetone. The solutions were photolyzed (λ > 290 nm) to give one product (45b), independent of solvent, at an equilibrium conversion of 87%. It was also noticed that compound 45c rearranges to 45b in the gas chromatography column (DB-17) at temperatures above 220 °C.

H. 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate Salts

Direct Solution Photolysis of Salts 48-54

A standard procedure for analytical photolysis of the prepared salts (48-54) was adopted. The salt (5 - 10 mg) was dissolved with a suitable deuterated solvent (1 ml) in a 10 ml Pyrex phototube. The sample was degassed by repeating the freeze-pump-thaw cycle twice. The ratios of photoproducts (determined by NMR) were reported in the text.

On a preparative scale, the standard procedure for salts 48-54 was to dissolve 10 - 30 mg of the salt in a suitable deuterated solvent (3 ml) in a 10 ml Pyrex phototube. The degassed sample was photolyzed and the resulting mixture analyzed directly by NMR. The
ratios were reported in the text. The mixture was then diluted with diethyl ether, acidified with HCl (aq), washed with water, dried over MgSO₄, filtered, evaporated, and redissolved in CDCl₃. The resulting mixture of reported diacids was analyzed by NMR (400 MHz) and the signals correlated to confirm our assignments.

**Solid State Photolysis of Salts 48-54**

Crystals or powders (approx. 10 mg) of salts 48-54 were placed in a nitrogen-filled NMR tube and photolyzed. After irradiation the sample was dissolved in a suitable solvent and analyzed by NMR. The product ratios and resultant sample appearances were tabulated in the text. For each salt, the same procedure was repeated using several different photolysis times.

I. Dimethyl 1,4-Dimethyl-1,4,5,8-tetramethyl-1,4-ethenonaphthalene-2,3-dicarboxylate (47)

**Direct Solution Photolysis of Compound 47**

On an analytical scale, crystals of compound 47 were photolyzed (λ > 290 nm) in benzene and acetonitrile. GC monitoring showed the formation of two products, 47b and 47a, independent of solvent at an approximate 1 : 1 ratio. At higher conversions the ratio changed; 47b started to diminish and the formation of a secondary photoproduct was seen (47c).

In an NMR study, crystals of 47 dissolved in 1.5 ml CDCl₃ were photolyzed (λ > 290 nm) for 30 min. The mixture was
analyzed by NMR (GC) to a 47b : 47a ratio of 43 (41) : 57 (59) at 9% conversion.

A preparative reaction was performed with 250 mg (0.77 mmole) of compound 47 in five 10 ml phototubes, using benzene as solvent, and photolyzed (λ > 290 nm) to 95% conversion. Chromatography of the mixture on silica gel using a diethyl ether and hexanes (1 : 9 v/v) solvent system gave three bands. The first band contained 23 mg of dimethyl 2a,6c-dihydro-1,2a,3,6-tetramethylbenzo[a]cyclopropa[cd]-pentalene-2b,6b-dicarboxylate (47c) as a white solid (yield 9%). Recrystallization from hexanes gave colorless prisms.

MP: 94-98 °C.

IR (KBr) ν max: 1730 (vs, C=O), 1274 (s, C-O), 1244 (s) cm⁻¹.

^1^H NMR (400 MHz) δ: 6.95 (AB quartet, 2H, J = 14.8 Hz, aromatic), 5.08 (s, 1H, H₂), 3.82 (s, 3H, ester methyl), 3.78 (s, 3H, ester methyl), 3.36 (s, 1H, H₆c), 2.21 (s, 3H, aromatic methyl), 2.19 (s, 3H, aromatic methyl), 1.78 (s, 3H, methyl on C₁), 1.25 (s, 3H, methyl on C₂a) ppm. The above assignments were supported by NOE studies.

^1^C NMR (50 MHz) δ: 171.0 (C=O), 170.5 (C=O), 148.3 (C), 147.1 (C), 134.5 (C), 133.9 (C), 129.4 (CH), 129.3 (CH), 128.2 (CH), 120.3 (CH), 73.5 (C), 65.1 (C), 53.0 (C), 52.1 (CH₃), 51.7 (CH₃), 47.4 (CH₃), 19.4 (CH₃), 19.2 (CH₃), 13.8 (CH₃), 12.0 (CH₃) ppm. The assignments were based upon an APT.

MS (EI) m/e: 326 (M⁺, 55), 294 (74), 267 (63), 235 (41), 207 (100). Exact mass calculated for C₂₀H₂₂O₄: 326.1518, found 326.1512.

Anal. calcd. for C₂₀H₂₂O₄: C, 73.60; H,6.79. Found: C, 73.50; H, 6.76.
The second band was 58 mg of dimethyl 1,4,6,9-tetramethylbenzo-
cyclooctene-5,10-dicarboxylate (47b) as a white solid (yield 23%). Recrystallization from methanol gave colorless rods.

MP: 204-207 °C.

IR (KBr) \( \nu_{\text{max}} \): 1711 (s, C=O), 1620 (m), 1239 (s, C-O) cm\(^{-1}\).

\(^1\)H NMR (400 MHz) \( \delta \): 6.98 (s, 2H, aromatic), 5.88 (s, 2H, vinyl), 3.65 (s, 6H, ester methyls), 2.21 (s, 6H, aromatic methyls), 2.06 (s, 6H, vinyl methyls) ppm. These assignments were supported by NOE studies.

\(^{13}\)C NMR (100 MHz) \( \delta \): 167.4 (2 x C=O), 148.5 (2 x C), 138.4 (2 x C), 133.1 (2 x C), 133.0 (2 x CH), 129.7 (2 x C), 128.5 (2 x CH), 51.6 (2 x ester CH\(_3\)), 19.7 (2 x CH\(_3\)), 19.6 (2 x CH\(_3\)) ppm. The above assignments were based on an APT.

MS (EI) m/e: 326 (M\(^+\), 35), 294 (80), 267 (64), 235 (43), 207 (100). Exact mass calculated for C\(_{20}\)H\(_{22}\)O\(_4\): 326.1518, found 326.1518.

Anal. calcd. for C\(_{20}\)H\(_{22}\)O\(_4\): C, 73.60; H, 6.79. Found: C, 73.70; H, 6.72.

The structure of this compound was confirmed by an X-ray diffraction analysis. The crystal data are as follows: C\(_{20}\)H\(_{22}\)O\(_4\), orthorhombic, space group Pbca, a = 17.716(2)Å, b = 15.298(2)Å, c = 13.210(3)Å, V = 3580(2)Å\(^3\), Z = 8, D\(_x\) = 1.211 g/ml, R = 0.046.

The third band was dimethyl 2a,2b-dihydro-1,2b,3,6-tetramethyl-
benzo[a]cyclopropa[cd]pentalene-6b,6c-dicarboxylate (47a) mixed with some unreacted starting material (47). The mixture was rephotolyzed and chromatographed as above to give 33 mg of 47a as a white solid (yield 13%). Recrystallization from hexanes gave colorless prisms.
MP: 104-105 °C.

IR (KBr) $v_{\text{max}}$: 1734 (s, C=O), 1435 (m), 1272 (s, C=O) cm$^{-1}$.

$^1$H NMR (400 MHz) $\delta$: 6.92 (s, 2H, aromatic), 5.04 (d, 1H, $J = 2$ Hz, H$_2$), 3.83 (s, 3H, ester methyl), 3.67 (s, 3H, ester methyl), 3.04 (d, 1H, $J = 2$ Hz, H$_{2a}$), 2.41 (s, 3H, aromatic methyl), 2.25 (s, 3H, aromatic methyl), 1.94 (s, 3H, methyl), 1.81 (s, 3H, methyl) ppm. The above assignments were supported by NOE studies.

$^{13}$C NMR (100 MHz) $\delta$: 171.1 (C=O), 169.5 (C=O), 146.7 (C), 145.9 (C), 137.0 (C), 132.9 (C), 130.4 (CH), 129.4 (CH), 128.3 (CH), 120.0 (CH), 70.0 (C), 68.3 (C), 53.0 (C), 51.9 (ester CH$_3$), 51.0 (ester CH$_3$), 20.7 (CH$_3$), 19.8 (CH$_3$), 17.3 (CH$_3$), 13.9 (CH$_3$) ppm. These assignments were based on an APT experiment.

MS (EI) m/e 326 (M$^+$, 35), 294 (27), 266 (100), 207 (84). Exact mass calculated for C$_{20}$H$_{22}$O$_4$: 326.1518, found 326.1527.

Anal. calcd. for C$_{20}$H$_{22}$O$_4$: C, 79.60; H, 6.79. Found: C, 73.80; H, 6.86.

The structure of this compound was confirmed by an X-ray diffraction analysis. The data are as follows: C$_{20}$H$_{22}$O$_4$, orthorhombic, space group Pca2$_1$, $a = 7.325(9)$Å, $b = 14.781(1)$Å, $c = 15.535(1)$Å, $V = 1681.9(5)$Å$^3$, Z = 4, $D_x = 1.289$ g/ml, $R = 0.045$. Details will be published elsewhere.

**Benzophenone-Sensitized Photolysis**

In an analytical study, compound 47 was dissolved with an approximately 2-fold w/w excess of benzophenone in benzene and photolyzed ($\lambda > 330$ nm) to complete conversion. GC monitoring showed
two products, 47a and 47d, at a 32 : 68 ratio.

On a larger scale, crystals of 47 (80 mg, 0.25 mmole) and benzophenone (200 mg) in 8 ml of benzene were photolyzed (λ > 330 nm) to 92% conversion to 47a and 47d in a 40 : 60 ratio. Chromatography on silica gel using diethyl ether and hexanes (1 : 19 v/v) as the eluent separated benzophenone from 47a and 47d. The two photoproducts could not be separated and therefore 47d could not be identified.

From the mixture, the following GC-MS data could be obtained:

GC-MS (DB-1, EI) m/e: 326 (M+, 12), 266 (100), 235 (14), 207 (80), 193 (29).

When left to stand, it was noticed that 47d readily converted to other inseparable products.

Solid State Photolysis of Compound 47

Crystals of 47 (8 mg) were photolyzed (λ > 290 nm) in an NMR tube for 15 h. The crystals remained colorless but were slightly sticky on the surface. NMR analysis showed the formation of one major photoproduct (47a). The ratio of 47 : 47a : 47b was 89 : 10 : 1. The photolysis was repeated for 45 h and the colorless, slightly sticky crystals had a 47 : 47a : 47b ratio of 79 : 20 : 1.

Crystals of 47 were photolyzed (λ > 330 nm) for 4 days to give by NMR a 47 : 47a : 47b ratio of 94 : 6 : trace.

Crystals were also photolyzed with a nitrogen laser (λ = 337 nm) for 5 h. NMR analysis of the unmelted colorless crystals in CDCl₃ showed a 47, 47a, and 47b ratio of 76 : 23 : 1.
Photolysis of Cyclooctatetraene 47b

On an analytical scale, crystals of 47b (5 mg) were dissolved in benzene and acetone. Photolysis ($\lambda > 290$ nm) with GC monitoring showed the formation of compound 47c. The acetone reaction was much faster than the benzene reaction.
III. QUANTUM YIELD STUDIES

Apparatus

A merry-go-round apparatus\textsuperscript{123} was used in a large water bath to maintain an even photolysis at a constant temperature (20 \( \pm \) 3 °C). The 450 W Hanovia medium pressure mercury lamp was used as the light source. The 313 nm line from the lamp was isolated by a filter combination of a 7-54 Corning glass plate\textsuperscript{123} and an aqueous solution of 0.002 M \( \text{K}_2\text{Cr}_2\text{O}_7 \) containing 5% \( \text{K}_2\text{CO}_3 \) (wt/wt) circulated through a Pyrex cooling jacket.

Purification of Solvents and Reagents

Benzene was used as the solvent unless otherwise specified. Benzene was made thiophene-free by successive washes with concentrated sulfuric acid followed by distillation over sodium metal.\textsuperscript{122} Valerophenone, used as the actinometer, was checked for acetophenone prior to use (< 0.3% by GC). The starting materials and their photoproducts were purified by chromatography and recrystallization. The alkane internal standards (from Aldrich) were used with no further purification.

Internal Standards and GC Detector (FID) Responses

Each alkane internal standard chosen was such that its GC signal was close but did not overlap with the starting material or its photoproducts.

Tetradecane (\( \text{n-C}_{14}\text{H}_{30} \)) was the internal standard for the valerophenone actinometry. Tetracosane (\( \text{n-C}_{24}\text{H}_{50} \)) was the internal
standard for the photoproducts of starting materials 42, 43, and 47. Tricosane \((n-C_{23}H_{48})\) was the internal standard for the photoproducts of 45, and octacosane \((n-C_{28}H_{58})\) internally standardized the study of starting material 44. Detector responses were measured from several injections \((n > 3)\) of an accurately weighed mixture of photoproduct and internal standard.

**Actinometry**

Valerophenone actinometry was used. The quantum yield of acetophenone from valerophenone has been established to be \(\Phi = 0.3\) with an opaque concentration \((0.1 \text{ M})\) of valerophenone in benzene.\(^{124}\) The excitation wavelength was the mercury 313 nm line. Two 3 ml benzene solutions of 0.1 M valerophenone and 1 g/ml of tetradecane were degassed by repeating the freeze-pump-thaw cycle twice under nitrogen. These solutions, in 10 ml Pyrex phototubes, were placed alongside the test samples in the merry-go-round apparatus and monitored by GC (carbowax column, 15 m, average of two injections).

**Irradiations**

Two 3 ml test samples were prepared for each starting material. An opaque concentration at 313 nm, determined by UV studies, was prepared. Internal standards were added and their concentration in the test samples was approximately 5% of the starting material. The samples were photolyzed alongside the actinometer solutions and monitored by GC (DB-1, 15 m, two injections per sample point) to no more than 10% photoproduct formation.
Calculation of Quantum Yields

After correcting for the various responses, the quantum yields were calculated from the following equation:

$\Phi = \frac{\text{# moles photoproduct}}{\text{# moles photons absorbed}}$

The quantum yield of each photoproduct was calculated at different conversions and graphed (in text). The straight line was extrapolated to zero conversion to determine the reported value. These values were determined by linear least squares calculations performed on one of B. Clifford's undergraduate laboratory computers. The error limits are reported as standard deviations, in parentheses.
REFERENCES


   b) Scheffer, J.R.; Trotter, J.; Garcia-Garibay, M.; Wireko, F. Mol.
   d) Scheffer, J.R.; Garcia-Garibay, M.; Nalamasu, O. in "Organic
      Photochemistry", Padwa, A., Marcel Dekker, New York, 1987, Ch. 8,
      Vol. 4.


9. Garcia-Garibay, M.; Scheffer, J.R.; Trotter, J.; Wireko, F.

10. For a review see: Hixson, Mariano, and Zimmerman Chem. Rev. 1973, 73,
    pp 531-551.


    b) Zimmerman, H.E.; Binkley, R.W.; Givens, R.S.; Sherwin, M.A. J. Am.

    8032.


      1969, 91, 1028.

49. Turro, N.J. "Modern Molecular Photochemistry", Benjamin/Cummings,


    Wiley Interscience, New York, 1977, 408.

      1963, 85, 2616.


56. a) Evans, S.V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J.R.;
    b) Garcia-Garibay, M.; Scheffer, J.R.; Trotter, J.; Wireko, F.
    c) Garcia-Garibay, M.; Scheffer, J.R.; Trotter, J.; Wireko, F.
    d) Scheffer, J.R.; Trotter, J.; Garcia-Garibay, M.; Wireko, F.


    90, 6096.

    1969, 34, 2418.


69. To the best of the author's knowledge, there has been no other reports on the photochemistry of benzobarrelenes in organized media.

70. The subject reaction is more appropriately termed "tri-\pi-dimethane". However, the text term is used in order to be consistent with previous literature reports.


82. ORTEP is an acronym for Oak Ridge Thermal Ellipsoid Program (1964), revised in 1976. This is a crystallographic drawing program showing vibrational motions.


84. After thirteen runs, the ratio of 29a/29a+29b was established to be 0.675 (std. dev. = 0.05). The error in this ratio was taken to be 0.1 (2 x std. dev.) for 95% certainty. This error of approx. 15% provides an idea of the precision in subsequent ratio determinations.


88. Characteristic signal patterns were provided through personal correspondence with C.O. Bender, Univ. Lethbridge, Alta. Canada.


95. The following bond distances were determined by J. Trotter and his crystallography group in support of this thesis. The numbers in parentheses are standard deviations of the least significant figure.


101. For examples see:


103. Several values for acetylene have been reported:
    b) $\tilde{\delta} = 2.3$; Cooper, J.W. "Spectroscopic Techniques for Organic Chemists", Wiley, New York, 1980, p 64.


112. a) Doctoral Thesis of Pokkuluri, P.R., University of British Columbia, 1990, p 70.


