A PHOTOCHEMICAL STUDY OF DIBENZOBARRELENE AMIDES AND ESTER-AMIDES: SOLUTION AND SOLID STATE REARRANGEMENTS

By

Alistair Graham McLeod Rattray

B.Sc., University of Guelph, 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

MARCH 1992

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ABSTRACT

The photochemical reactions of various dibenzobarrelene acyl derivatives has been investigated in solution and in the solid state. These derivatives consisted of monoamides, symmetrical diamides, mixed ester-amides, and mixed ester-thioesters. The two types of reactions found in the irradiation of these systems were the di-π-methane rearrangement and/or hydrogen abstraction.

Photolysis of dibenzobarrelene monoamides in solution and in the solid state gave a symmetrical dibenzosemibullvalene photoproduct. Two monoamides (R,R = Bz and R,R = iPr) gave ring-fused spiro β-lactam analogues of the starting materials in addition to the semibullvalene product. These two amides also gave an ethano-bridged monosubstituted amide photoproduct as did a third monoamide (R,R = Et). Photolysis of all monoamides in the solid state resulted in the formation of semibullvalenes only. X-ray crystallographic analysis of the diethyl and the di-*iso*-propyl starting materials were performed in order to correlate the lack of hydrogen abstraction in solid state irradiations with the geometric constraints of the crystalline starting material. An X-ray crystallographic analysis of the dibenzyl amide-derived β-lactam was also performed in order to establish the relationships between the various stereochemical centres in the molecule.

A series of symmetrical diamides was prepared and photolyzed in solution and in the solid state. All diamides gave a single semibullvalene photoproduct upon irradiation in solution. Two of the starting materials (N,N-dimethyl and N,N-diethyl) also reacted rapidly and efficiently in the solid state to give the semibullvalene product, whereas two others (N-methyl and N-ethyl) were found to be very unreactive in the solid state.

Photolysis of a series of mixed ester-amides in all cases except two (A = $CONBz_2$ and A = $CON(iPr)_2$) gave a semibullvalene product. The reaction was found to be regioselective, with the amide group ending up on a benzylic carbon. Only in one

instance (A = $CONMe_2$) was a small amount of the semibullvalene product with the opposite orientation of the acyl groups formed. Two ester-amide starting materials (A = $CONEt_2$ and A = $CON(iPr)_2$) gave an ethano-bridged ester monosubstituted amide product. One ester-amide starting material (A = $CONBz_2$) gave a β-lactam as the sole product from irradiation. Photolysis in the solid state had little effect on this series of compounds.

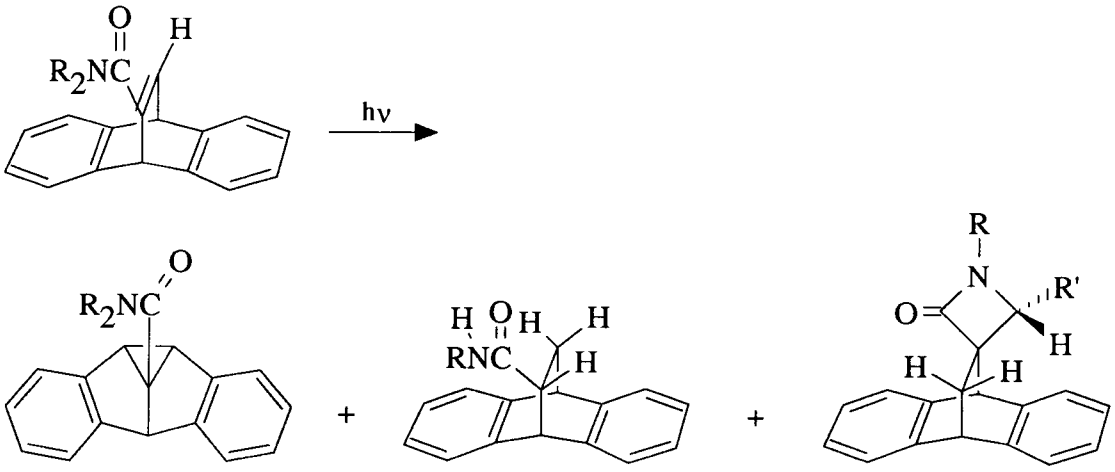
A methyl ester-phenyl adduct was prepared and photolyzed in order to distinguish between two possible explanations for the observed regioselectivity in the di-π-methane rearrangement of the mixed ester-amides. This material was found to give a single semibullvalene product which was determined by X-ray crystallographic analysis to have the ester group in the benzylic position.

An unsymmetrical diamide (A = CONHMe; A' = $CONEt_2$) was prepared and photolyzed in order to compare its photochemical behaviour to mixed diesters. This starting material was found to give significant amounts of both regioisomeric semibullvalenes, as well as a hydrogen abstraction product.

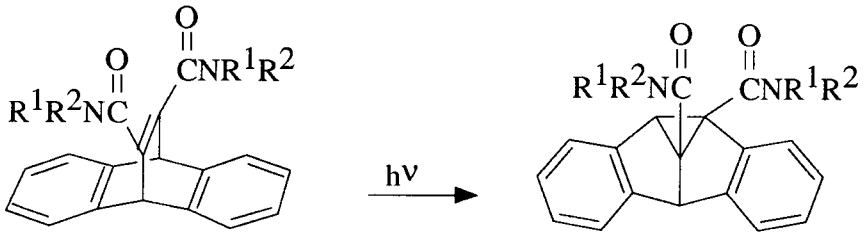
Finally a mixed thionoester-ester and a mixed thioloester-ester were prepared and photolyzed. Both starting materials gave a single semibullvalene photoproduct that X-ray crystallographic analyses determined had the esters attached to benzylic carbons. These results were rationalized on the basis of the relative stabilities of the possible biradical intermediates. This approach was also applied to the ester-amide series of compounds and allowed for the ordering of the various acyl derivatives for their ability to direct the regioselectivity of the di-π-methane rearrangement. This order was found to be;

$$H << CO_2^- \ (<) \ CONR_2 < CO_2R \ , \ CO_2H < CSOR, \ COSR$$

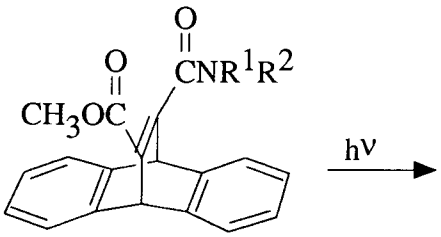
i) Monoamides

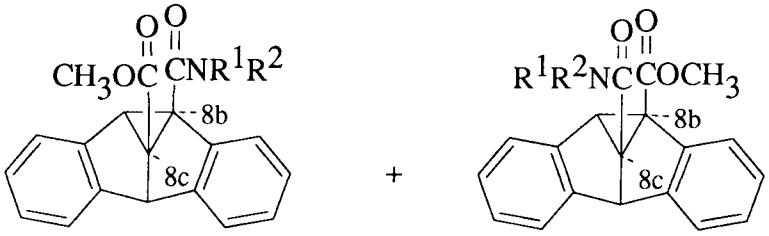


ii) Symmetrical Diamides



iii) Ester-amides





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ABBREVIATIONS

A	Amide, Amine
Ar	Aromatic
bp	Boiling Point
Bz	Benzyl
cm^{-1}	Wavenumbers
COSY	(Homonuclear) Correlated Spectroscopy
δ	Chemical Shift in ppm
d	Doublet (NMR)
E	Ester, ether
eqs	Equivalent
Et	Ethyl
EtOAc	Ethyl Acetate
glc	Gas-Liquid Chromatography
h	Hours
Hz	Hertz
iPr	Isopropyl
IR	Infrared Spectrum
J	Coupling Constant (Hz) (NMR)
lit	Literature Reference
LUMO	Lowest Unoccupied Molecular Orbital
M	Moles/Litre
m	Multiplet (NMR)
M^+	Molecular Ion (MS)
Me	Methyl

mg	Milligrams (10^{-3} grams)
mmol	Millimoles (10^{-3} moles)
mp	Melting Point
MS	Mass Spectrum
NBMO	Non-Bonded Molecular Orbital
NMR	Nuclear Magnetic Resonance
^{o}C	Degrees Celsius
PET	Petroleum Ether (bp = 35-60^{o})
Ph	Phenyl
ppm	Parts Per Million (NMR)
q	Quartet (NMR)
s	Singlet (NMR)
SOMO	Singularly Occupied Molecular Orbital
t	Triplet (NMR)
tlc	Thin Layer Chromatography
UV	Ultraviolet
W	Watts

ACKNOWLEDGEMENTS

I would like to thank Dr. J. R. Scheffer for the opportunity to be part of his research group and for all of his help over the years. I would also like to convey my admiration of his dedication to the field of solid state organic photochemistry. I have learned much of great value from my experiences in his laboratory.

I am very much indebted to the members of the X-ray crystallographic analysis laboratory, Drs. J. Trotter, Steve Rettig, and Ray Jones. They are responsible for all X-ray structures in this thesis and their contributions to this study have been invaluable. As well, thanks are due to the members of the NMR laboratory, the Mass-Spec lab and the guys in the various shops of the chemistry department. Without their assistance and friendliness, the last five years would have been a lot longer.

I would like to thank and express my appreciation to Dr. Martha Kline and Mardy Leibovitch for proof-reading this thesis. Their promptness and thoroughness, in addition to their comments and suggestions, were a great help and very much appreciated.

I would also like to express my gratitude to Dr. G. Eigendorf of the Mass-Spec lab for the opportunity to work in his lab, and for his patience and guidance during my tenure there.

Lastly, to the guys in the lab and everyone who contributed to making my time at U.B.C. very much enjoyable, whether on the soccer field or over the many cups of coffee- Thanks.

Facile credo, plures esse Naturas invisibiles quam visibilies in rerum universitate. Sed horum [sic] *omnium familiam quis nobis enarrabit? et gradus et cognationes et discrimina et singulorum munera? Quid agunt? quae loca habitant? Harum rerum notitiam semper ambivit ingenium humanum, nunquam attigit. Juvat, interea, non diffiteor, quandoque in amino, tanquam in tabula, majoris et melioris mundi imaginem contemplari: ne mens assuefacta hodiernae vitae minutiis se contrahat nimis, et tota subsidat in pusillas cogitationes. Sed veritati interea invigilandum est, modusque servandus, ut certa ab incertis, diem a nocte, distinguamus.*

T. Burnet, *Archaeol. Phil.* p.68, (1692)

Nothing is really work unless you would rather be doing something else.

J. M. Barrie, (1860-1937), Kirriemuir, Scotland.

To Mum and Dad for all their love and support

INTRODUCTION

I: Prefatory Remarks

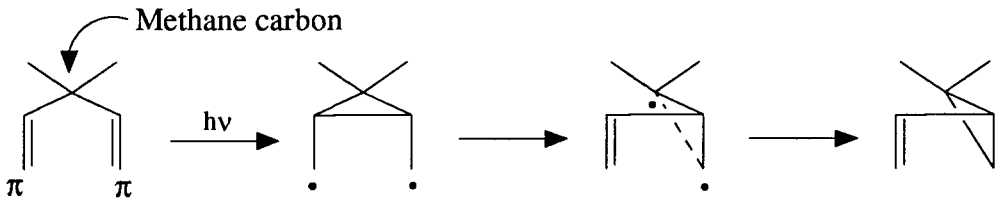
Photochemical processes have had a hand in the shaping of the chemical environment of the earth ever since sunlight was able to penetrate the prebiotic atmosphere.[1] The action of light on the mixture of organics present on early earth was essential in providing conditions under which life might arise. Billions of years of the production of oxygen in the most fundamental of photochemical reactors, the plant, was necessary for the development of higher life forms.[2] All of which is intended to show that photoreactions have the ability to cause changes which can be unique and inherently different from those that are possible through thermal processes. Furthermore, because of the ubiquitous nature of light and light-initiated reactions, a thorough comprehension of its interactions with matter is essential to any integrated overview of the fundamentals of chemistry.

In a more pragmatic vein, there are many areas where the knowledge gained from the study of various photochemical systems might have applications in current fields of technology. In particular, some of the studies on photochemistry in organized media are being found to have great promise in the fields of computers and electronics, for example the development of optical wave-guides, in the area of information storage and retrieval and in materials science in general. This is not to say that the present study is an attempt to develop commercial applications of photochemistry. It is rather an attempt to increase the base of knowledge of the factors that govern the behaviour of molecular species under the influence of light. In this way the principles of molecular photochemistry might be put on a more comprehensive level and further developments approached in a more systematic fashion.

II: The Di-π-methane Rearrangement

A: General Mechanism

The principal photoreaction studied in the present thesis is the di-π-methane rearrangement, one of the most general and thoroughly studied of all organic photoreactions.[3] This reaction is named as such because of the observation that compounds possessing a 1,4 diene unit separated by an sp^3-hydridized carbon, or methane carbon, can be converted upon absorption of a photon of light into products containing a vinylcyclopropyl moiety. The π-bonds involved in the rearrangement may be isolated or conjugated and can be part of either cyclic or acyclic systems. The proposed mechanism[4] for the di-π-methane rearrangement, first put forth in 1967 by H. E. Zimmerman, postulates that the initial step upon absorption of a photon of light is 2,4-bonding of the two π-bonds, generating a 1,4-biradical. This is followed by bond reorganization to a second, 1,3-biradical and subsequent ring closure to the vinylcyclopropyl unit. This mechanism has been detailed in Figure I for the simplest case of 1,4-pentadiene. It should be noted, however, that the exact nature of the biradical species, whether they are true intermediates or simply approximations of transition states along the reaction pathway, is still in some doubt[5], especially in instances where one of the π-bonds is part of an aromatic ring.[6] It can be said, though, that this mechanism has been very successful in predicting and rationalizing a large number of examples of the di-π-methane rearrangement.



1,4-Diene Vinylcyclopropane

Figure I: Mechanism of the Di-π-methane Photorearrangement

B: Reaction Multiplicity

As mentioned, the di-π-methane rearrangement has been shown to occur with both cyclic and acyclic systems. Further to this, the reaction has been shown to be multiplicity-dependent with the multiplicity being contingent on the molecular structure.[7] In general, acyclic substrates undergo the di-π-methane rearrangement from singlet excited states, whereas cyclic systems predominantly react from triplet excited states. This dependency is a result of alternate possible reaction pathways and how the structure of a molecule, in particular the diene unit, is suited for each of the available reactions. The most important of the competing pathways are cis-trans isomerization[8] and cycloaddition reactions.[9] A comparison of the rate constants for each of these processes:[3a]

Singlet state: $^1k_{CA} > {}^1k_{DPM} > {}^1k_{CT}$

Triplet state: $^3k_{CT} > {}^3k_{DPM} > {}^3k_{CA}$

Where: CA = Cycloaddition reactions

DPM = Di-π-methane rearrangement

CT = Cis-trans isomerization

shows that in the triplet state an acyclic compound will undergo cis-trans isomerization before the di-π-methane rearrangement, whereas a cyclic compound, being unable to cis-trans isomerize, can readily rearrange. Thus the di-π-methane rearrangement of acyclic

diene systems generally occurs from the singlet excited state and is often in competition with cycloaddition reactions.

An interesting example of the differential reactivity of a substrate based on the multiplicity of the excited state is that of barrelene (**1**) in Figure II.[4]

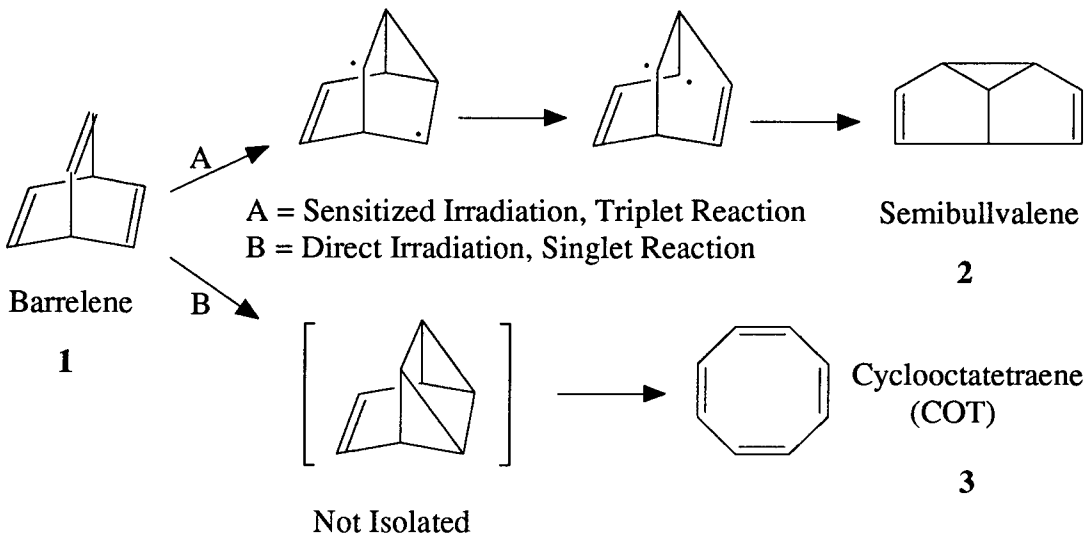


Figure II: The Multiplicity-Dependent Photochemistry of Barrelene

Zimmerman and co-workers found that acetone-sensitized irradiation of barrelene gave di-π-methane rearrangement-derived semibullvalene (**2**). However, direct irradiation of barrelene resulted in a cycloaddition reaction which produced cyclooctatetraene (COT) (**3**). This is one of the earliest examples of the di-π-methane rearrangement and still stands as one of the most elegant demonstrations of a multiplicity dependent photoreaction of a di-π-methane system.

C: Reaction Regioselectivity

In addition to the possibility of a variation in products arising from different excited states, it also possible to obtain regioisomeric products when the two π-bonds involved in the photorearrangement are not symmetrically substituted, as shown in Figure III.[3a]

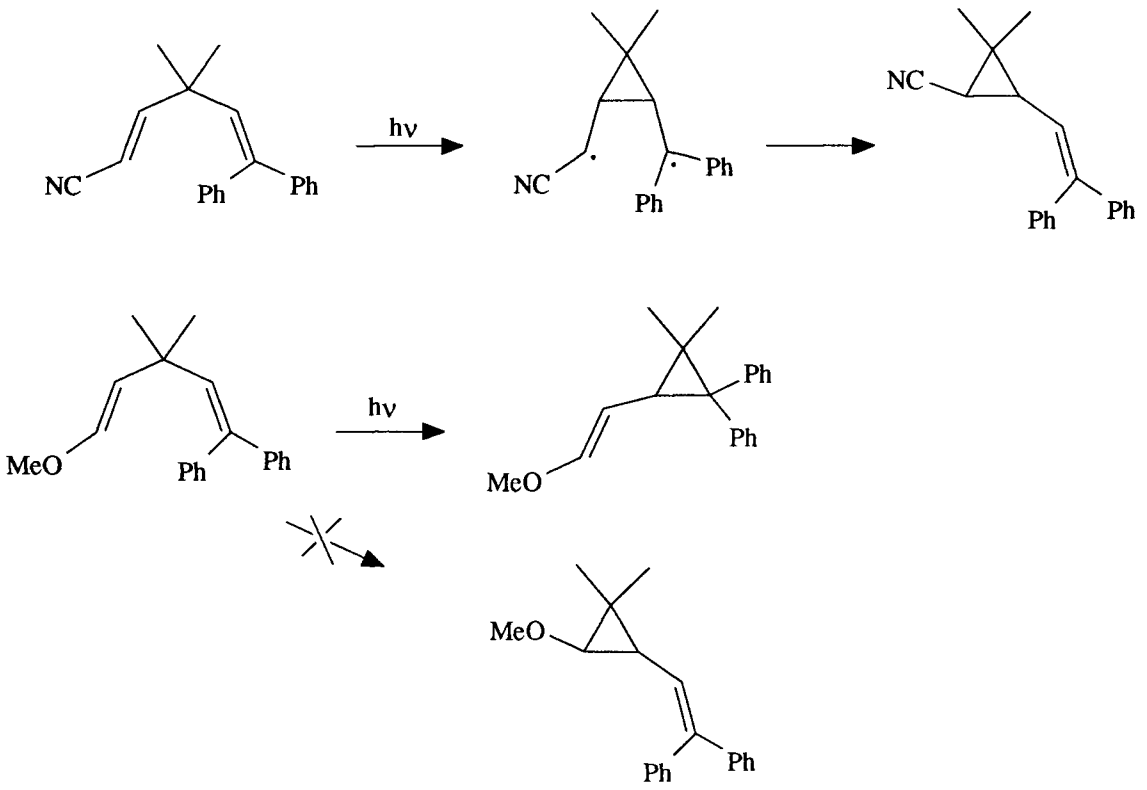


Figure III: Regioselective Di-π-methane Rearrangements

The regioselectivity has been correlated with the different stabilities of the two possible biradical species that can be produced in the initial step of the reaction mechanism.[3] Reactions involving an aromatic π-bond as part of the diene unit proceed in such a manner as to regenerate aromaticity in the final product. Additionally, the formation of the product derived from the most stable biradical intermediate was found to be favoured. Thus electron withdrawing groups generally end up on the cyclopropyl ring of the product while electron donating groups are attached to the product double bond.

It is also possible to obtain regioisomers when the ends of the π-bonds or the bridgehead carbons of the substrate involved in the rearrangement are unsymmetrically substituted, as is found for compounds **4** and **6**. This results in two different biradicals possible which, depending on the proximity and influence of the substituent, might be fairly close in energy giving a distribution of products[10], as illustrated in Figure IV.

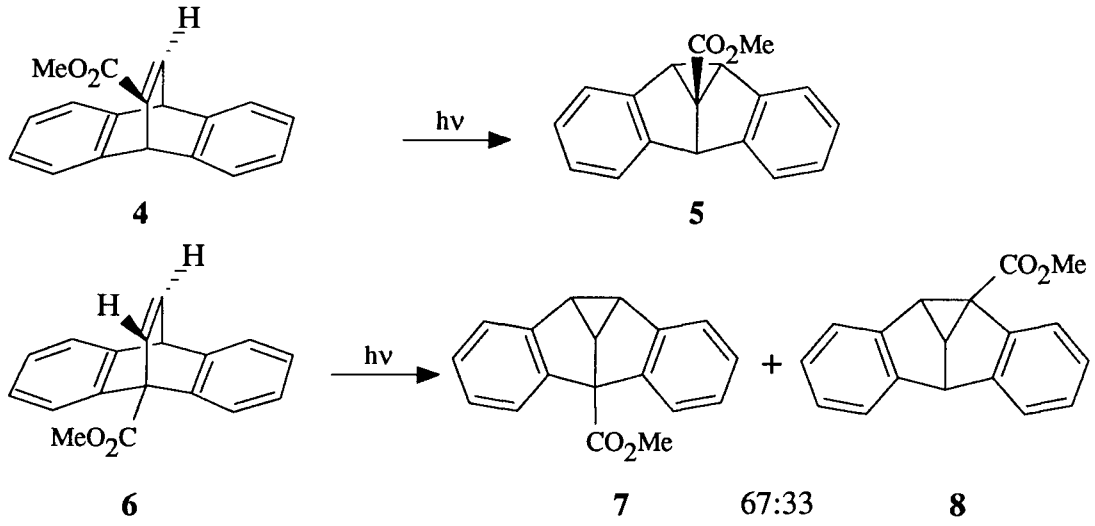


Figure IV: Regioselectivity in Dibenzobarrelene Systems

D: Substituted Dibenzobarrelenes

The study of the barrelene class of compounds has been expanded to include photoreactions of benzobarrelenes[11,12], dibenzobarrelenes[13], and notably to various ester derivatives of the same[10,14,15]. In 1966, E. Ciganek demonstrated that solution irradiation of the dimethyl dibenzobarrelene diester derivative **9** resulted in a dibenzosemibullvalene product **10**.[10] The mechanism postulated for this transformation is consistent with Zimmerman's proposal and involves bond formation between a bridging vinyl carbon and an adjacent aromatic ring carbon, referred to as vinyl-benzo bridging (Figure V). More recent studies[16] by Scheffer, Trotter and co-workers examined the photolysis of this dibenzobarrelene diester as well as other diester derivatives in the crystalline state. Among their findings, it was demonstrated that the di-π-methane rearrangement of these dibenzobarrelenes can also occur readily in the solid state, and some rather ingenious structure-reactivity correlation experiments involving X-ray crystallography and the photoreactivity of chiral crystals of a dibenzobarrelene diester were carried out.[16]

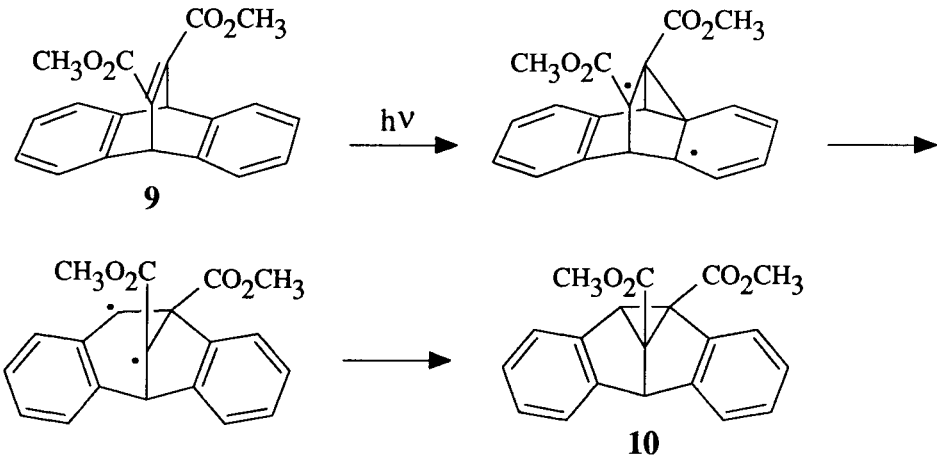


Figure V: Photorearrangement of Dimethyl Dibenzobarrelene Diester.

E: Hydrogen Bonding and the Di-π-methane Rearrangement

Among the dibenzobarrelene acyl derivatives which have been previously studied is the mixed acid-isopropyl ester of 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylic acid[17] **11**. The ratio of the two regioisomers resulting from di-π-methane rearrangement of this compound was found to be dependent on the type of hydrogen bonding that was present in the sample. Termed "Prototopic Control", Scheffer and co-workers demonstrated that it is possible to reverse the regioselectivity of the reaction simply by adjusting the reaction conditions in such a manner as to selectively obtain the starting material in a predominantly intramolecular or intermolecular bonded form.

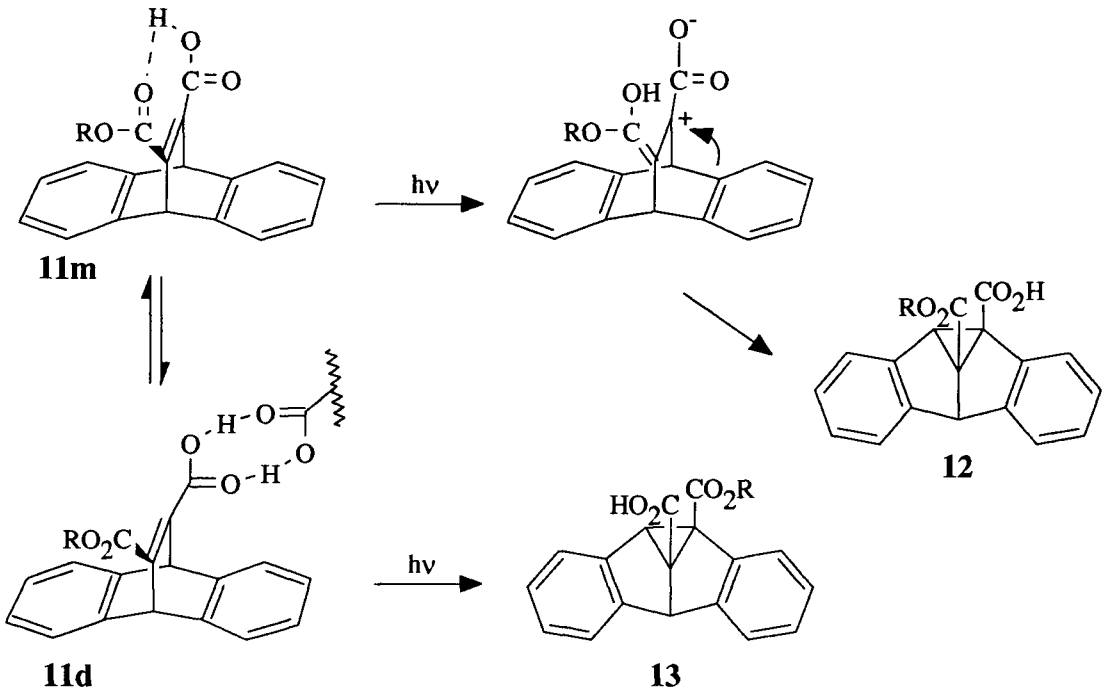
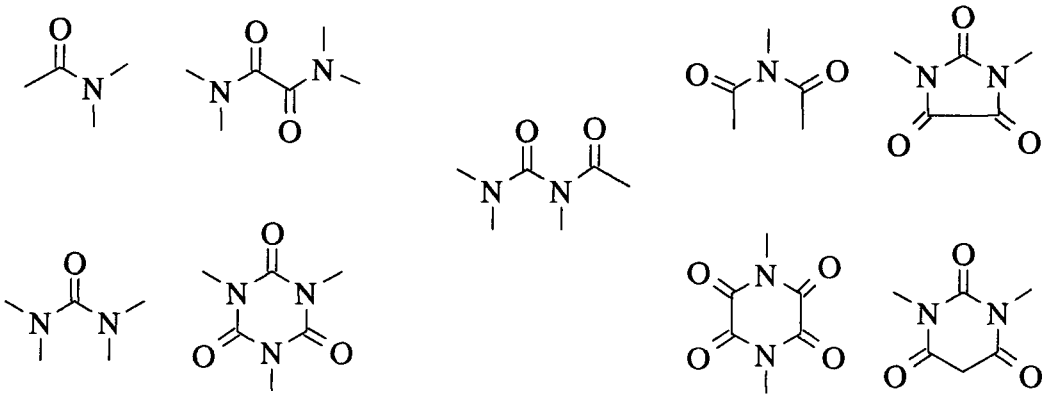


Figure VI: Prototopic Control of the Di-π-methane Photorearrangement

It has been shown that intramolecularly hydrogen bonded systems such as **11m** are able to transfer a proton from one carboxylic oxygen to the other *via* an excited state charge transfer interaction.[18] This then leads to a regioselective, positive charge initiated 1,2-aryl shift to give the corresponding semibullvalene **12** in a manner similar to the well documented ground state carbocationic rearrangements of dibenzobarrelenes.[19] When the vinyl acid substituent is the reaction site in the dimeric species **11d**, the acid functionality is required to undergo substantial displacement during vinyl-benzo bonding which causes disruption of the hydrogen bonds. With the ester group at the reaction site, hydrogen bonding is maintained throughout the reaction pathway and therefore the regioisomeric photoproduct **13** predominates. Solid state infrared spectroscopic measurements indicated that the dimer was the exclusive species in the crystal accounting for the almost exclusive formation of photoproduct **13** in the solid state.

III: Photochemistry of Nitrogen and Sulphur Acyl Derivatives

A: General Photochemistry of Nitrogen Compounds



Unreactive | Weakly Reactive | Reactive

Figure VII: Photoreactivities of Nitrogen-Containing Carbonyl Compounds

Figure VII summarizes the photochemical reactivities of a variety of nitrogen-containing carbonyl compounds.[20] Of primary interest is the photoreactivity of amides, discussed here in the instance of a saturated amide. The photochemical behaviour[21] of the amide functional group (Figure VIII) is principally confined to the α-cleavage (type I) process *via* either CO-N or CO-C cleavage. Type II cleavage (β-cleavage) is at best a minor process in comparison, unlike esters which readily undergo both processes.[21]

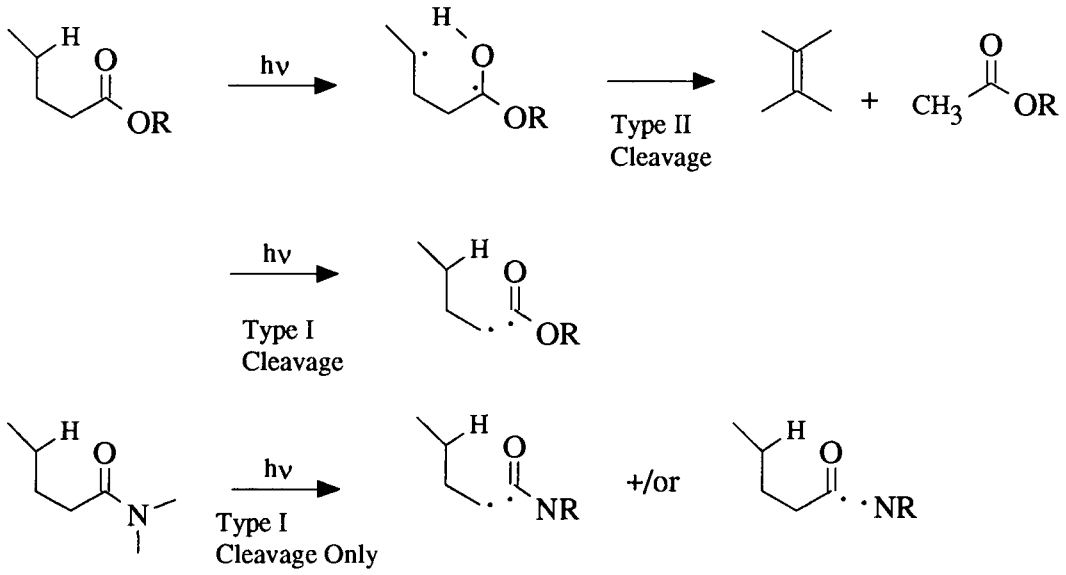


Figure VIII: Cleavage Processes in Esters and Amides

This reactivity difference can be rationalized in view of the fact that type II processes occur most efficiently when the reactive carbonyl n,π^* state is electrophilic. In the case of the ester, the ether oxygen withdraws electron density from the carbonyl oxygen atom through the σ-bond framework while at the same time donating electron density *via* the π framework. Since σ withdrawal is more efficient than π donation for oxygen, the net result is make to the carbonyl oxygen electron deficient and the n,π^* state electrophilic. With amides the relationship is exactly the opposite resulting in π donation being more efficient than σ withdrawal. Thus amides are predicted to have nucleophilic n,π^* states and therefore be nonreactive in type II processes. These conclusions have been confirmed by molecular orbital calculations.[20b]

However the introduction of unsaturation adjacent to the amide, whether it be a carbonyl group to make an oxo-amide or a carbon-carbon double bond to give an unsaturated amide, brings about increased possibilities of alternate reaction pathways.

B: Photochemistry of N,N-Dialkyl-oxoamides

Aoyama and co-workers[22] have found that the mechanism of hydrogen abstraction in the type II reaction of β-oxoamides and aminoketones is markedly different from such typical Norrish type II substrates as aromatic ketones. The principal effect of this difference is the interaction of the excited carbonyl with the amino or amido group and consequent electron transfer from the nitrogen to the carbonyl group prior to hydrogen transfer. The efficiency of electron transfer depends on the ionization potential of the nitrogen group. However, in the case of β-oxo-amides, it was found that by controlling the extent of substitution at the 2-position, the mechanistic pathway could be altered (Figure IX).[22]

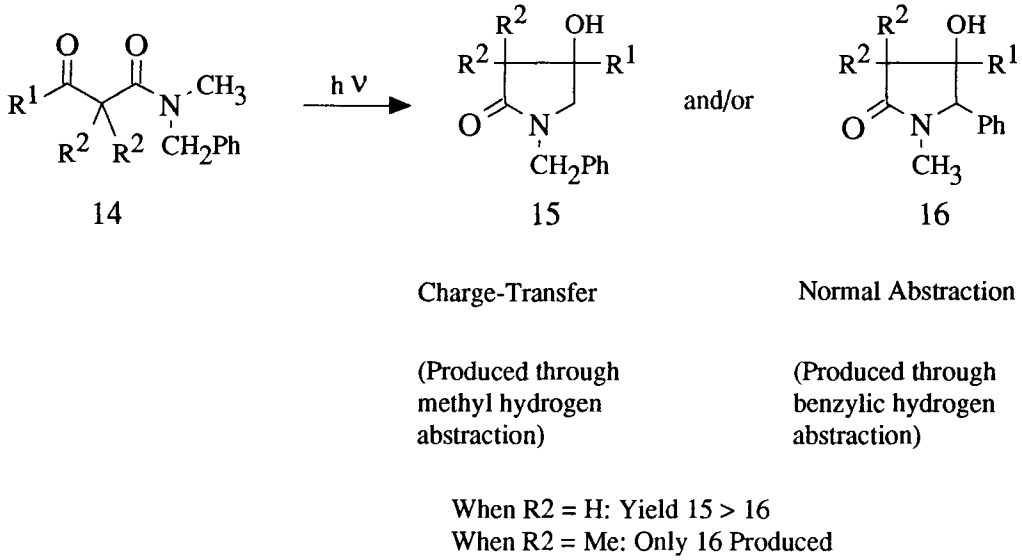


Figure IX: Photochemistry of β-Oxo-amides

Thus β-oxo-amides **14** with no substituents at the 2-position photocyclized mainly through electron transfer from the amide nitrogen to the carbonyl followed by γ-proton transfer and closure to give **15**. This charge transfer mechanism involves reaction through singlet excited states. The introduction of two methyl groups at the 2-position resulted in cyclization *via* normal hydrogen abstraction from the n,π* triplet state to give

16. The reason for the reaction difference is that the introduction of methyl substituents in the 2-position increases the contribution of the triplet state. This is thought to because the enol form of **14** acts as a quencher for the reactive keto-form triplet so that cyclization may proceed only from the singlet state of the keto-form.

Movement of the carbonyl one carbon closer to the amide functionality produces an α-oxo-amide (**17**). Irradiation results in a complete nullification of the charge-transfer mechanism of hydrogen abstraction.[23]

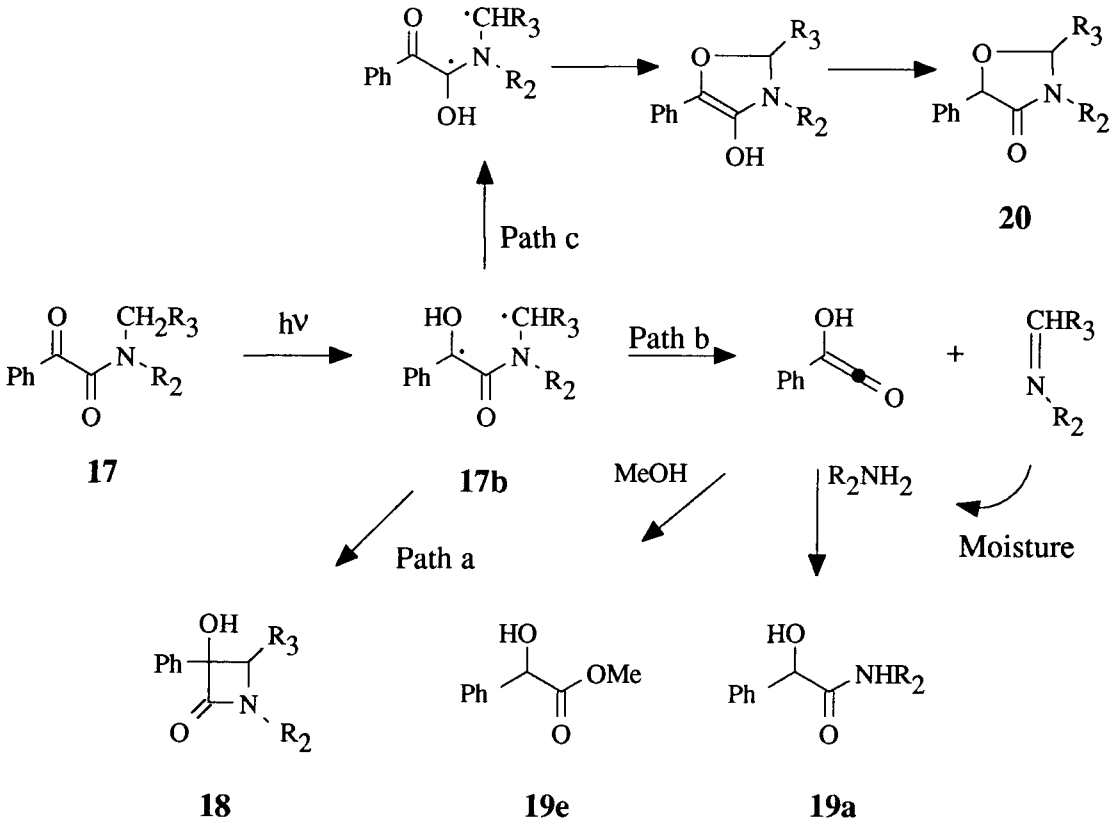


Figure X: Photoreactions of N,N-Dialkyl α-Oxo-amides

The primary reaction step in the irradiation of these α-oxo-amides is γ-hydrogen abstraction by the ketone carbonyl oxygen to give a biradical **17b**. This biradical can then undergo three types of reaction; i) Type II cyclization (path a) to produce a β-lactam **18**, ii) Type II elimination (path b) followed by addition of a nucleophile to the ketene

intermediate to give a mandelic acid derivative (**19a** and **19e**), and iii) 1,4-hydrogen shift (path c) followed by cyclization to afford the oxazolidin-4-one **20** (Figure X). The product distribution in solution irradiations was found to be dependent on substituents and solvent, with only dibenzyl-oxo-amides in aprotic solvents giving β-lactams.

In an unprecedented example[24] of a type II reaction of a nitrogen-containing carbonyl compound in the crystalline state, Aoyama was able to show that the selective formation of β-lactams from the irradiation of an α-oxoamide was a result of the crystal lattice restraints on the molecular motion of the biradical intermediate formed by γ-hydrogen abstraction (Figure XI). Furthermore, because the crystals of the achiral starting material were found to be in a chiral space group, irradiation in the solid state produced optically active β-lactams in high optical and chemical yields. X-ray analysis[25] of the starting oxoamide **21** and the lactam product **22** determined that, because of the bulky substituents in compound **21**, the carbonyl group approaches the isopropyl group in the crystal. A bond is formed between the carbon atoms of the two groups upon irradiation, resulting in the formation of the lactam. The chirality of the β-lactam is brought about by the twist of the carbonyl group of **21** from the amide plane, the sense of which depends on the chirality of the starting crystal.[25] This type of result, where optical activity is generated without the imposition of an external chiral source by man, holds great interest as a possible mechanism for the origin of optically active compounds on earth.[26]

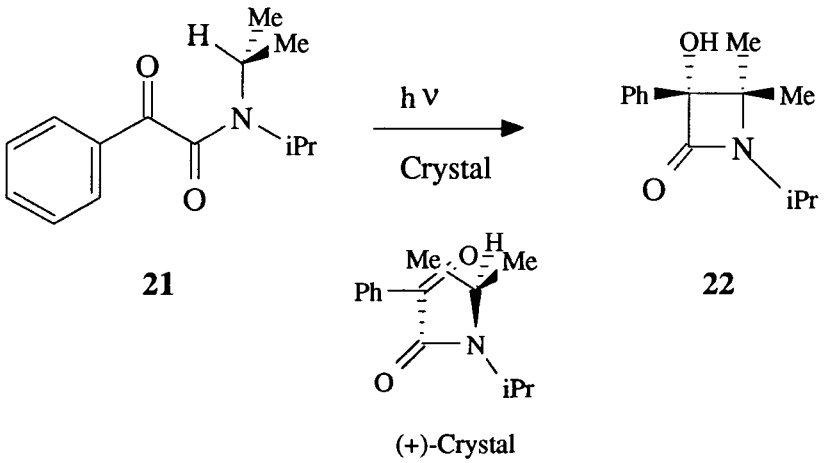
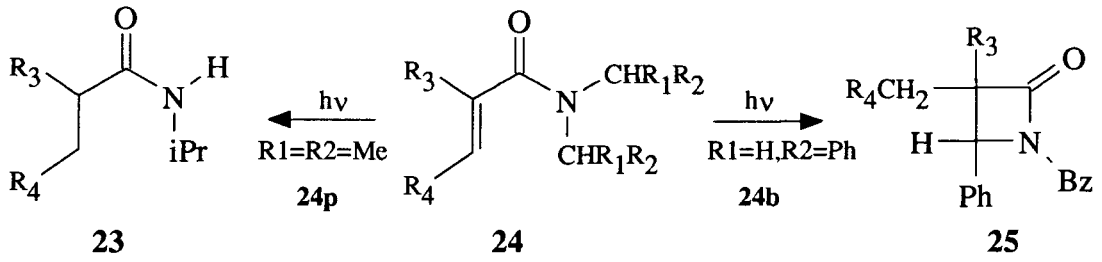


Figure XI: Solid State Photochemistry of N,N-Dialkyl α-Oxo-amides

C: Photochemistry of N,N-Dialkyl-α,β-Unsaturated Amides

In addition to the steric and electronic effects that amides can exert, α,β-unsaturated amides have been shown to participate directly in photorearrangements.[27] Aoyama and co-workers[28] were able to show that the irradiation of certain amides resulted in intramolecular hydrogen abstraction by the β-carbon atom. N,N-dibenzyl-α,β-unsaturated amides **24b** were found to undergo cyclization to the corresponding 2-azetidinones **25** while N,N-diisopropyl amides **24p** gave the N-isopropyl saturated amide **23**.[28] Hydrogen abstraction is followed by fragmentation to give a ketene and an imine. The difference in reaction products between the dibenzyl and the di-*iso*-propyl adducts is a result of the relative reactivities of the imine intermediates. The less reactive imine from **24p** undergoes hydrolysis to give a primary amine. This can then react with the ketene to give **23**. Irradiation of N,N-dimethyl and diethyl amides gave neither 2-azetidinones nor N-monosubstituted amides.



23 **24** **25**

R3, R4 = H or Me

Figure XII: Hydrogen Abstraction Products of N,N-Dialkyl α,β-Unsaturated Amides

Hydrogen abstraction, or the transfer of a hydrogen from one atom to another, is one of the most general of all photoreactions.[29] In most cases this occurs intramolecularly from an sp^3-hybridized carbon to an sp^2-hybridized atom such as oxygen, carbon or nitrogen. This type of reaction is found much less frequently to involve hydrogen atom abstraction by a carbon centre than oxygen. The reasons for this are partly due to the fact that the transfer of a hydrogen atom between two carbon centres is more nearly thermoneutral than the transfer from a carbon atom to an oxygen atom. Photoexcitation of an alkene followed by hydrogen abstraction is much rarer than the analogous reaction with a carbonyl compound, partially because of dissipation of the excited state energy of an alkene by alternate reaction routes such as cis-trans isomerization. Alkenes which do undergo photochemical hydrogen abstraction are generally cyclic, which restricts the ability to cis-trans isomerize, and conjugated to carbonyl groups, which will stabilize by resonance any radical which is produced by abstraction.[29]

Ideally, the transition state for the abstraction of a hydrogen atom would comprise of the adoption of a linear geometry by the three atoms immediately involved, to provide optimal orbital overlap.[30] Generally, however, this arrangement is only approximated due to geometric constraints. Experimentally, there has been shown to be a remarkable correlation between hydrogen abstraction distances and the sum of the van der Waals

radii of the abstracting and abstracted atoms. Thus, for the abstraction of a hydrogen atom by a vinyl carbon centre, the C-H sum of 2.9 angstroms is taken to be the optimal distance for reaction.[29]

D: Photochemistry of Thio-Esters

The replacement of the carbonyl oxygen in an ester group with a sulphur atom produces a thio-ester referred to as a thiono-ester. Likewise the replacement of the ester alkoxy oxygen with a sulphur atom produces a thiolo-ester. The reactions of thio-esters have not been as extensively investigated as their oxygen analogs, especially in the area of photochemistry.[31] However their widespread use in industrial settings as synthetic starting materials for dyes and photosensitizers as well as other diverse areas such as vulcanization accelerators, plastic modifiers and fungicides[32], requires that a comprehensive knowledge of the photochemical behaviour of these functional groups is acquired.

The electronic properties of thio-esters are governed by two basic principles: i) the sulphur atom is less inclined than oxygen to form double bonds and ii) the electronegativity of sulphur is approximately midway between that of carbon and oxygen.[33] In the tautomeric equilibrium between thiolocarboxylic acids and thionocarboxylic acids, these two principles are in opposition. The reluctance of the sulphur atom to form double bonds means that protonation will occur on the sulphur, involving its bonding electrons in two σ-bonds. However, the higher electronegativity of the oxygen atom makes the oxygen a more basic site for protonation. On the basis of infrared and ultraviolet studies, it has been shown the equilibrium lies very much to the thiolocarboxylic acid side and as such, apparently the first effect prevails.[33]

Photochemically, the excitation of the thiocarbonyl group of thiono-esters has proven to be fertile grounds for photoreactions.[32] However, a systematic knowledge of the photochemical behaviour of this group is still needed. The reaction products formed

upon irradiation depend on the type of irradiation and the reaction conditions, with dimerizations, polymerizations, rearrangements, fragmentation and desulphurization all being observed.[32] Irradiation of the π,π^* absorption of thiono-esters **26** has been used in the production of asymmetric alkenes[34] **28** (Figure XIII).

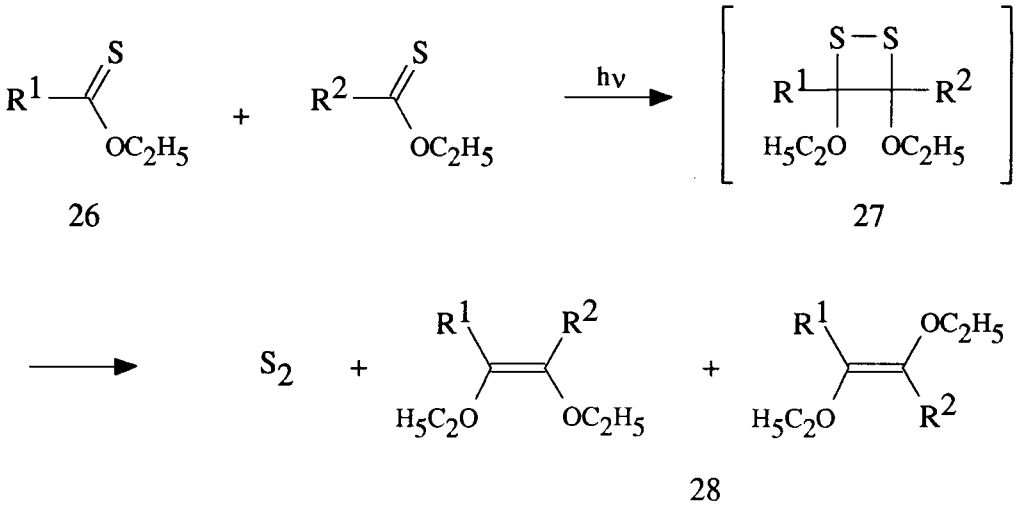
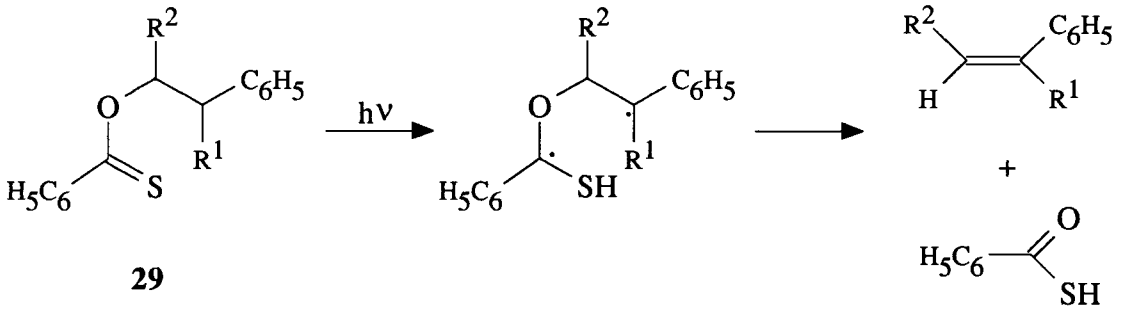


Figure XIII: Formation of Olefins from Thiono-ester Irradiation

Mechanistically, this desulphurization has been proposed to proceed *via* the unstable 1,2-thiethane **27.** However, attempts to confirm this by trapping diatomic sulphur were not successful.[34]

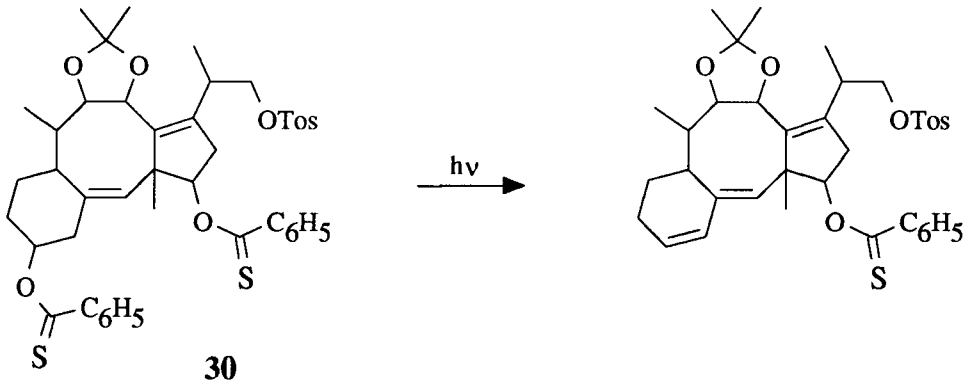
Irradiation of the n,π^* band of aryl thiono-esters **29** resulted in the elimination of olefinic derivatives (Figure XIV). However when the hydrocarbon portion of the thio-ester is of the alkyl type, the reactants tend to oligomerize or polymerize. This elimination process is said to be governed by the same factors as the Norrish Type II photoreaction of phenyl ketones.[35] Thus only compounds having a lowest triplet state of n,π^* configuration are reactive.



29

Figure XIV: Olefin Elimination in the Photolysis of Thio-esters

This photolytic elimination has proven to be a successful synthetic method for the dehydration of certain alcohols under very mild conditions.[36] Thus the bis-(thiobenzoic O-ester) **30** is able to undergo selective photochemical cleavage involving the elimination of only one of the thiobenzoic ester moieties to give a double bond in the desired position (Figure XV).



30

Figure XV: Photolytic Cleavage of Thiobenzoic Acid in Synthesis

IV: Photochemistry in the Solid State

The majority of our knowledge of the chemistry of organic materials has been derived from the study of these substances in solution. There are distinct reasons why solution reactivity has been more amenable to study than reactions in more organized media such as crystals, polymers, host-guest complexes and micelles. It is generally easier to handle reagents and control reaction conditions when the reaction mixture is a

homogeneous solution rather than a mixture of phases or of a particulate nature. As well, analysis of reaction intermediates and products by the more traditional methods have typically involved use of a solvent. However, with the advent of more technologically advanced methods of analysis such as X-ray diffraction analysis, magic angle spinning ^{13}C NMR and FT-IR, the barriers to in-depth information on structural information such as molecular conformation and spatial distribution of molecular components has been greatly reduced. These techniques provide detailed information on the molecular structure and packing arrangement of starting materials and products leading to a greater ability to interpret structure-reactivity relationships. But the reasons for resorting to organized media extend beyond purely analytical matters: reactions in organized media open up a whole new branch of chemistry involving many new and distinct reactions.[37]

One of the most fundamental of all laboratory techniques in organic chemistry is the recrystallization of a compound to remove impurities and to obtain the compound in a stable form. It was this inherent stability of the crystal that led to the belief that, upon obtaining a substance in the crystalline state, it was no longer susceptible to reaction.[38] In the last four decades, however, solid state organic chemists have dispelled this notion with a rapidly growing array of reactions in crystalline materials that have led to a vastly increased understanding of structure-reactivity relationships and the mechanisms therein.[37] Crystals have the highest degree of order of all organized media. As a result of the high degree of order in crystals, it is to be expected that molecular movement within the crystal might be considerably restricted. One of the goals of solid state organic chemistry is to use this control of molecular movement along the reaction coordinate to attain reactions of high regio- and stereoselectivity.

A number of review articles[37] have appeared in recent years detailing many instances of differential reactivity in solution and in the solid state. Figure XVI outlines a few examples where the photoproduct obtained is directly dependent on the reaction medium.

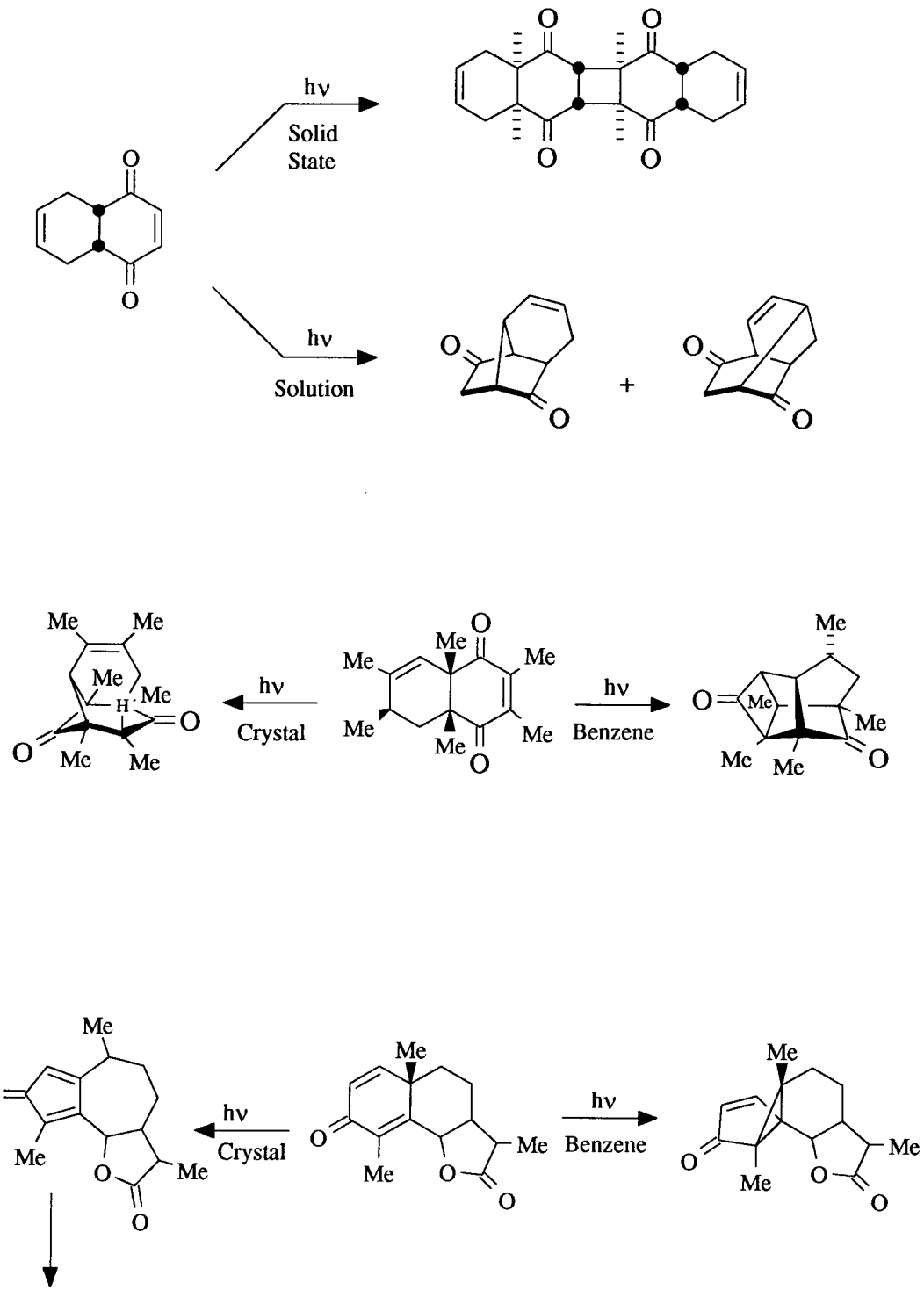


Figure XVI: Differential Photoreactivity in Solution and Solid State

The primary conceptual tenet in solid state reactivity is that of the Topochemical Postulate.[39] First proposed in 1918 by Kohlschutter[40], this axiom dictates that reactions in the solid state are constrained by the closely packed periodic three dimensional arrangement of the surrounding molecules. In solution, such constraints are not present, resulting in the reactions being governed primarily by factors such as steric and electronic effects. The topochemical postulate was put on a sound experimental basis by Schimdt and co-workers[41] in the 1960's with the examination of the $2\pi + 2\pi$ photodimerizations of crystalline *trans*-cinnamic acid derivatives (Figure XVII).

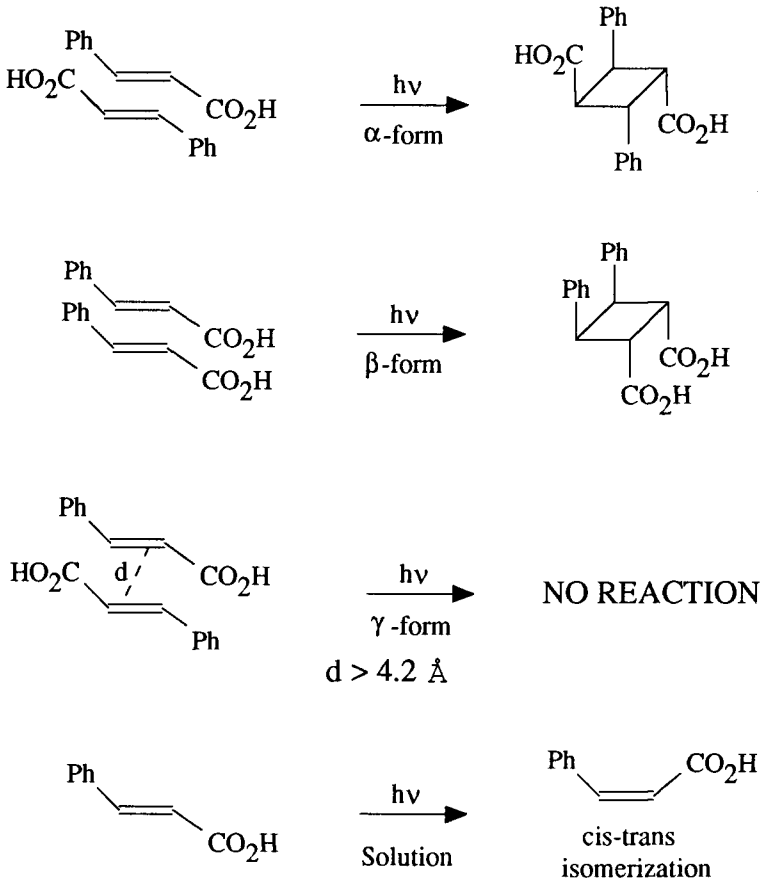


Figure XVII: Reactivity of Polymorphic Crystalline *trans*-Cinnamic Acids.

Making extensive use of X-ray crystallographic analysis, Schimdt's work[41,42] determined that the relatively fixed distances and orientations of reactive centres are fundamental to controlling solid state reactions and that the reactions proceed with a

minimum of atomic and molecular motion. One of the most important consequences of Schimdt's ideas was the development of the concept that reactions in the solid state, such as dimerizations, have an upper limit on the distance between the centres of reaction beyond which the reaction will not take place. This concept has been demonstrated to have applicability to a range of reactions in the solid state including hydrogen abstraction reactions.[29]

It should be noted that photoreactions are not the only type of reactions that can be studied in the solid state. Thermal reactions, such as the reaction of a crystal with a gas or the grinding together of two or more solid reactants, are also feasible and in fact have been reported[43]. However there are inherent problems with these types of reactions which can be controlled to a degree in photochemical reactions. The crystal's integrity can usually be maintained during irradiation, while thermal reactions often result in melting, causing loss of environmental control of the reaction. The grinding together of samples does not lend itself to analysis by X-ray methods and is in fact questionable as to whether it represents a true solid state reaction.

Molecular species in solution are in an isotropic environment giving rise to many conformations for flexible organic molecules. This is a consequence of the fast equilibria that exist between these conformations. In crystals, however, organic molecules generally adopt single conformations which represent minimum energy arrangements.[44] This high degree of order in crystals coupled with the fact that reactions are highly conformationally sensitive leads to the expectation that reactions in the crystalline state might be more selective than those in isotropic media such as in solution. But in addition to conformational concerns, it also is necessary to consider the packing arrangement of the reacting molecules in the crystal. The environment around the reaction centres in crystals consists of a regular arrangement of the neighbouring molecules. It is therefore likely that the packing arrangement will exert a greater influence on the course of reaction than will the isotropic environment of a solution.

V: Objectives of Present Research

The central purpose of this research is not only the study of the photoreactions of dibenzobarrelene adducts (Figure XVIII; page 26) but also to use the dibenzobarrelene system as a template or model with which to probe the influence of different media or determine the effect on reaction regioselectivity of modifying the substituents on the dibenzobarrelene bridge π-bond. This is not to say that the dibenzobarrelene system has been randomly selected; there are several features possessed by substituted dibenzobarrelene systems that make them desirable for study. Many of the substrates are crystalline solids, which allows one to examine their reactivity in the solid state and possibly examine the X-ray structure to develop structure-reactivity correlations. The fact that most substituted dibenzobarrelenes have relatively high melting points avoids problems of crystal melting which would cause confusion of the results from reactions possible only in liquid phases. The synthesis of these substrates is generally easy and readily modified to produce a series of compounds to study. Additionally, the photochemistry of some dibenzobarrelenes has been studied[16,17] and is relatively well understood. As such, this provides a basis on which to build in trying to further some of the fundamental principles of organic photochemistry.

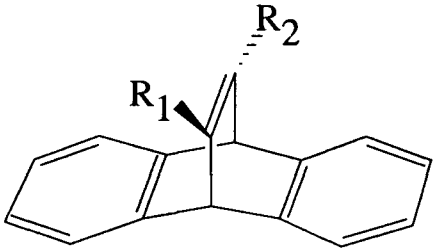
While much work has been done on the examination of the various aspects of the di-π-methane rearrangement of dibenzobarrelene esters and diesters[10,16,17], little has been done to extend these studies into the area of other acyl substituents. Initial objectives in the present research were to determine the viability and generality of the di-π-methane rearrangement of amide-substituted dibenzobarrelenes. It should be pointed out that in order to gain insight from the examination of the solid state reactivity of dibenzobarrelene amides, it is necessary that the reactivity in an isotropic medium be well understood. As such, the primary focus of the thesis is to detail photoreactivity in solution, with the solid state results being treated in a much more empirical sense, rather than as a systematic examination of crystal lattice effects. The approach taken was

principally one of product analysis of solution photoreactions and subsequent comparison with crystalline reactivity in most cases. Where a difference in reactivity existed, X-ray analyses of the starting material or photoproduct of interest were performed if possible, in order to establish basic structure-reactivity correlations. However this aspect of the thesis must be considered secondary to the main goal of comparing the changes in reactivity as a result of the variation in the types of acyl substituent present in the dibenzobarrelene.

Aside from the purely academic interest in such reactions, this area of research can be, and has been, extended to situations of possible utilitarian concern. With many of the present-day pharmaceuticals being biosynthetically derived, the possibility of the presence of amide functionalities, arising from the incorporation of amino acids, is significant. In such cases, knowledge of the photoreactions which might occur is essential so as to assess the stability of the drug.[44] Barbituric acids (barbiturates), well-known for their hypnotic and sedative effects, possess a chromophore consisting of two nitrogen atoms and three carbonyl groups and have been shown to undergo photochemical hydrolysis, Norrish type I cleavage and hydrogen abstraction.[20] Additionally, in a report which did not outline procedures or details, dibenzocyclopropapentalene amine derivatives were prepared *via* photochemical methods.[46] These compounds were examined extensively for use as antidepressants.

Amides, as a discrete functionality, are considered to be photochemically unreactive. However, as a substituent on a double bond which is part of a di-π-methane system, the amide functionality can have an indirect effect by exerting some sort of directional influence on the course of the reaction: thereby contributing to the determination of the regiochemistry of the products. Alternatively, it can have a direct effect by active participation of the alkyl portion of the amide in a reaction. The main

focus of this thesis is an examination of these effects in various dibenzobarrelene systems in the solid state and in solution.



Part 1: R_1 = CONR'R. R_2 = H.
Part 2: R_1 = R_2 = CONR'R.
Part 3: R_1 = CONR'R. R_2 = CO_2CH_3.
Part 4: R_1/R_2; Amide, Ester, Thioester.

Figure XVIII: Series of Substituted Dibenzobarrelenes Studied

In the first part of the thesis, the photoreactivity of dibenzobarrelene monoamides is considered. The photochemistry of the methyl ester analog was studied in solution in 1966 by Ciganek[10] and found to result in the formation of a single di-π-methane rearranged product. By determining the feasibility of the di-π-methane rearrangement of the monoamide series of compounds, it was hoped to extend the generality of this photorearrangement to amide substituted di-π-methane systems. Furthermore, the determination that the products from such a rearrangement were of the same regiochemistry as what Ciganek found would lend further credence to the rationale behind their formation. It was also thought that, in addition to the di-π-methane rearrangement, the possibility of the involvement of the alkyl portion of the amide in a photoreaction might lead to interesting and unusual products. Finally, an investigation of the photoreactions, or lack thereof, in the solid state might give some insight into the influence that crystal packing exerts on the availability of reaction pathways to the excited dibenzobarrelene monoamide.

The second part of the thesis deals with extending the concepts outlined for the monoamides to a series of symmetrically substituted dibenzobarrelene diamides. One fundamental difference between these amides and corresponding esters is the ability of amides possessing a hydrogen atom on the nitrogen to hydrogen bond. Several fully substituted and partially substituted amides were studied both in solution and in the solid state to determine whether this ability to hydrogen bond affects the course of the photoreaction.

The third part of the thesis deals with an examination of the photoreactivity of dibenzobarrelene ester-amides. As seen in the section on reaction regioselectivity, any time the bridgehead vinyl bond is unsymmetrically substituted, the possibility of the formation of two regioisomeric di-π-methane products is present. Thus, in addition to determining the effect of substituting an amide for an ester has on the types of reactions possible, it also becomes important to distinguish the factors that govern the distribution of the two possible regioisomeric photoproducts.

The photolysis of ester-amides in the solid state provides the opportunity to compare these systems to the monoamide series of compounds, and to determine whether product distribution is affected in a similar manner or whether the addition of the ester functionality alters solid state reactivity.

The last part of the thesis reports the photochemistry of an unsymmetrically substituted diamide as well as some dibenzobarrelene ester-thioesters. The unsymmetrical diamide is included as an attempt to ascertain whether its reactivity is analogous to that of an unsymmetrical diester and therefore results in a distribution of regioisomeric di-π-methane products. The thioesters were studied in order to compare the effect on the product distribution of substituting one of the ester functional groups of dimethyl dibenzobarrelene diester with a thiono-ester or a thiolo-ester.

RESULTS AND DISCUSSION

I: Synthesis of Starting Materials

A: Preparation of Dibenzobarrelene Monoamides

The synthesis of the parent ester (substrate **4**), from which all of the monoamide substrates studied were derived, was achieved by reaction between methyl propiolate and anthracene in the manner reported by Diels and Alder[47] (Figure XIX). However, instead of carrying out the reaction in refluxing xylenes as outlined in the literature, it was decided to perform the reaction without solvent in an evacuated sealed tube. The reason for this is simple; higher reaction temperatures attainable with the sealed tube mean shorter reaction times. This was found to be the case (6 h versus 7 days) with no concurrent loss of yield.

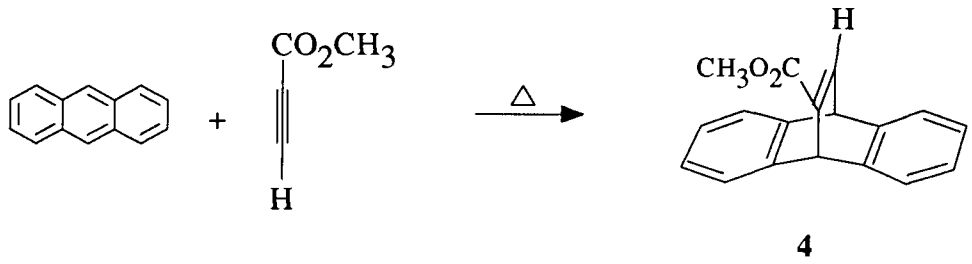


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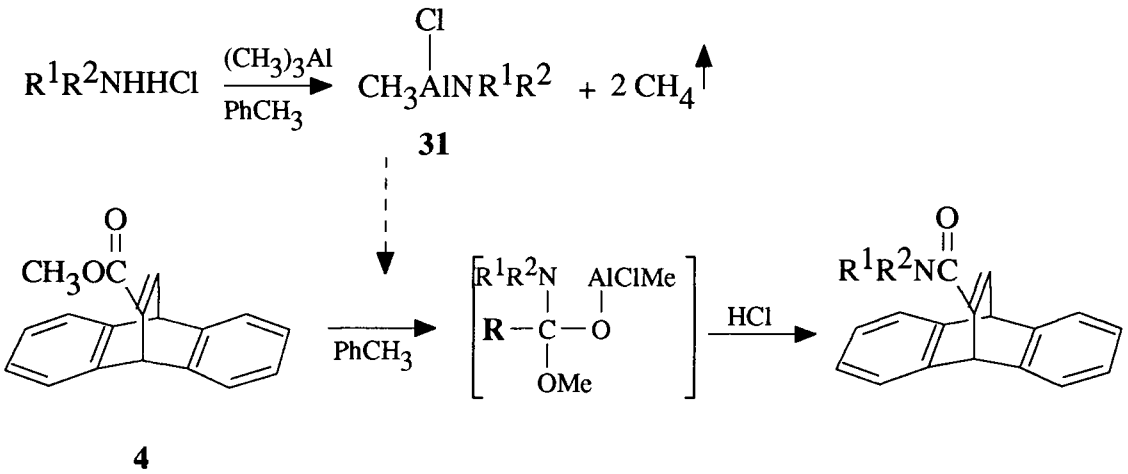
Figure XIX: Production of Dibenzobarrelene Methyl Ester

Weinreb aminolysis is a direct synthetic method for converting esters to amides using reagents derived from the reaction of trimethylaluminum with the corresponding amine hydrochloride.[48] There are several advantages in using this method to produce amides, most notable being that amides are afforded in high yields in short reaction times under relatively mild conditions. Additionally, the alkylaluminum reagents were found to be easy to handle and react very cleanly. Such was not the case when attempting to convert the ester to the desired carboxamide using the extremely volatile, low molecular weight amines required. The active species in these transformations is thought to be an alkylchloroaluminum amide species (**31** in Figure XX), which have been well

documented.[49] Although these aluminum reagents exist principally as dimers, their reactivity is readily explained by considering the Lewis acidity of the monomer, which is directly related to the tendency of the aluminum atom to build up an octet of electrons. Thus there is an association of the Lewis acid aluminum centre with a lone pair of electrons from an electronegative atom of the organic reactant. It has been shown by infrared spectroscopy that when an ester is reacted with the aluminum amide reagent, the aluminum is associated with the carbonyl oxygen.[49b]



32: $R^1 = R^2 = H$.[50]
33: $R^1 = R^2 = Me$.[51]
34: $R^1 = R^2 = Et$.
35: $R^1 = R^2 = Bz$.

Figure XX: Weinreb Aminolysis to Produce Monoamide Series of Compounds

The stock solutions of the aluminum reagents were prepared by the addition of commercially available 2 molar trimethylaluminum to a cooled slurry of the amine hydrochloride in toluene at 5°C. The mixture was allowed to warm to room temperature until the production of methane had ceased, which was on the order of 1-2 hours. These stock solutions could only be stored for 1-2 days before decomposition of the aluminum amide complex occurred. For safety reasons, toluene was substituted for benzene, used in the published procedure[47], in the formation of the aluminum complexes and in the

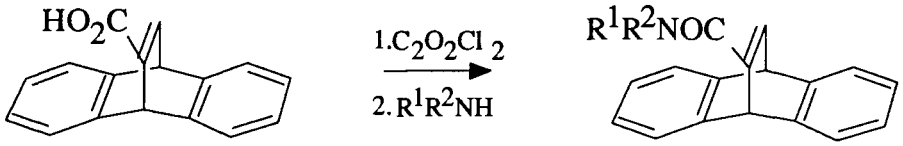
aminolyses. Toluene was chosen since the aluminum reagents are soluble only in aromatic solvents and not in alkane solvents.[49] This was found not to have a detrimental effect on the success of the reaction despite the higher reaction temperature.

Conversion of the ester to the amide was carried out by refluxing the ester in toluene with 2-3 equivalents of the aluminum amido reagent, except for the case of the ammonium chloride-aluminum complex, which required that the temperature be maintained at 50°C. This is a result of the innate instability of the unsubstituted amido reagent causing significant decomposition at higher temperatures. Quenching of the reaction mixture with HCl to destroy any residual reactive complex, followed by work-up, gave the essentially pure amide. Further purification by column chromatography was necessary in order to get the amide as pure as possible so as to expedite crystallization. The ease with which the dibenzobarrelene ester could be formed in conjunction with the versatility of the Weinreb aminolysis meant that a variety of amides were readily obtained.

The only member of this series of compounds that was not synthesized via a Weinreb aminolysis was the di-*iso*-propyl adduct, compound **37**. Attempts to produce this compound with the corresponding alkylaluminum reagent resulted in a very complex reaction mixture with a low yield of the desired product, even at lower temperatures. As di-*iso*-propyl amine does not have the same inherent handling problems as lower molecular weight amines and is readily purified, the di-*iso*-propyl adduct was produced by reaction of the acyl chloride derivative of the ester with di-*iso*-propyl amine. It is unclear why this particular amide should not be amenable to production by a Weinreb aminolysis, however it should be noted that complex formation is retarded with sterically hindered amines.[49]

Synthesis of the di-*iso*-propyl adduct was carried out by hydrolyzing the dibenzobarrelene ester **4** to the corresponding acid[52] **36** with ethanolic sodium

hydroxide, conversion to the acid chloride with oxalyl chloride and subsequent amination with di-*iso*-propyl amine (Figure XXI).

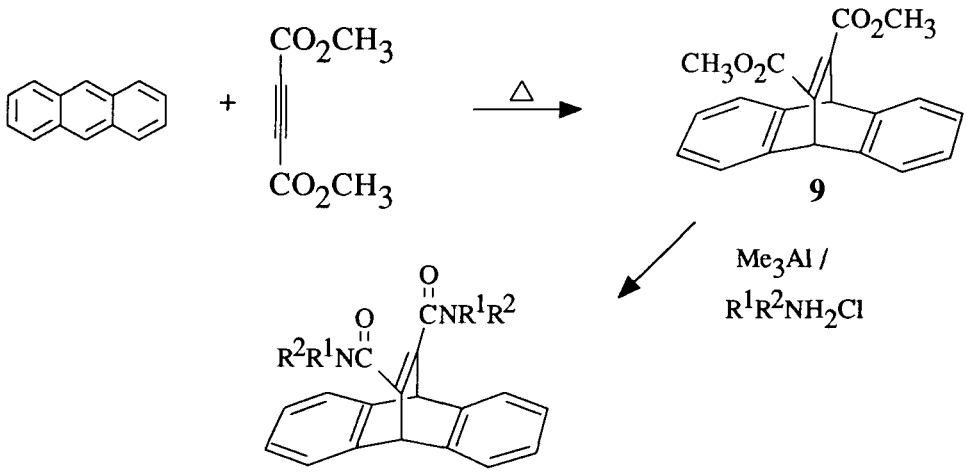


36 **37**: $R^1 = R^2 = iPr$

Figure XXI: Synthesis of the Di-*iso*-propyl Monoamide Derivative

B: Preparation of Symmetrical Dibenzobarrelene Diamides

The dibenzobarrelene diester[53] **9** was prepared in the same manner as the monofunctional analog, utilizing commercially available dimethyl acetylenedicarboxylate instead of methyl propiolate (Figure XXII). Again Weinreb aminolysis was found to be very effective in converting the diester to diamide, with the only modification needed being the doubling of the quantity of the aluminum reagent used, to take into account the presence of two esters instead of one.

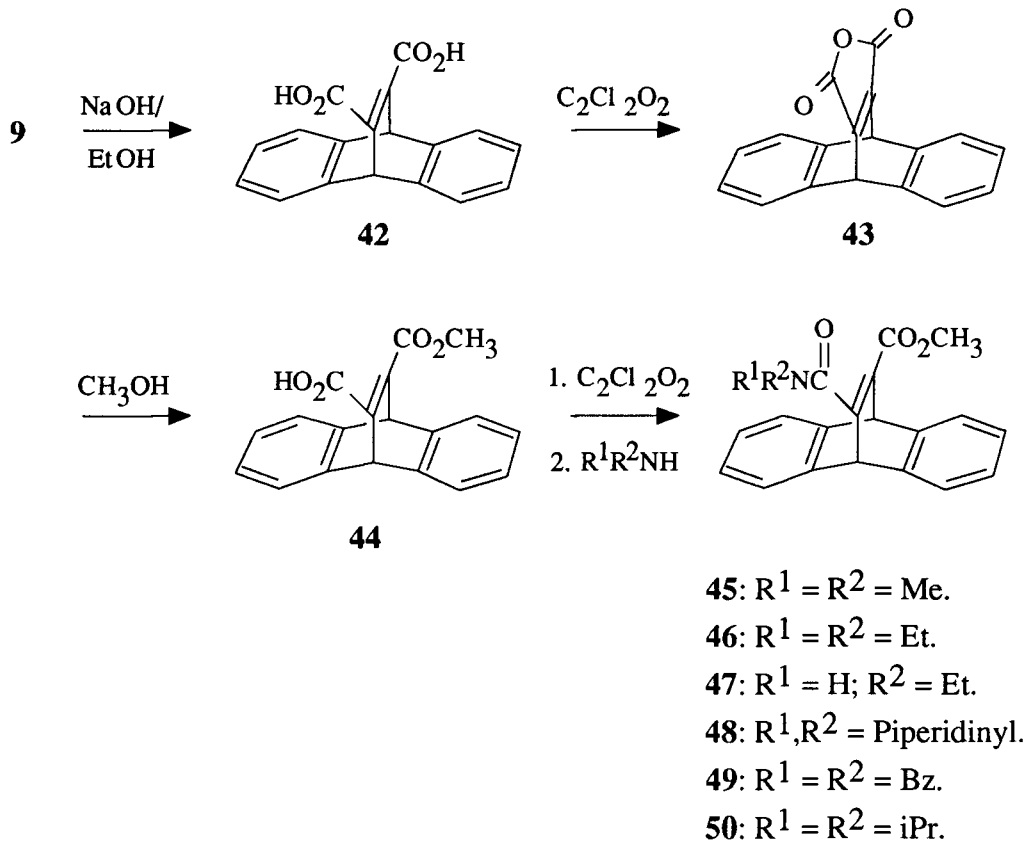


38: $R^1 = R^2 = Me.$
39: $R^1 = H; R^2 = Me.$
40: $R^1 = R^2 = Et.$
41: $R^1 = H; R^2 = Et.$

Figure XXII: Dibenzobarrelene Diamide Series of Compounds

C: Preparation of Dibenzobarrelene Ester-Amides

The synthesis of the ester-amide series of starting materials was based on chemical manipulation of the dibenzobarrelene diester (compound **9**, Figure XXIII) used to prepare the diamide series of compounds. In order to convert one of the ester moieties into an amide functionality selectively, it was necessary to obtain the corresponding monoacid of compound **9**. This was achieved by the following sequence of reactions. Hydrolysis of both ester functional groups with ethanolic sodium hydroxide led to the diacid[53] **42**. The conversion of the diacid to the acid anhydride[53] **43** was readily carried out by treatment of the diacid with oxalyl chloride. Mechanistically, this reaction is thought to proceed via a monoacyl chloride intermediate which reacts with the second acid group to eliminate HCl and form the cyclic anhydride. Treatment of the anhydride with anhydrous methanol resulted in the formation of the ring opened ester-acid, compound **44**. The ester-acid was subsequently treated with an excess of oxalyl chloride in anhydrous dichloromethane to produce the corresponding ester-acid chloride. Owing to the susceptibility to decomposition by moisture of this acyl chloride, it was not isolated but generated *in situ*. After removal of the solvent and excess oxalyl chloride, the reaction mixture was treated with the requisite amine. In order to maximize the yields of the ester-amides it was necessary to distill and dry the amines prior to use.



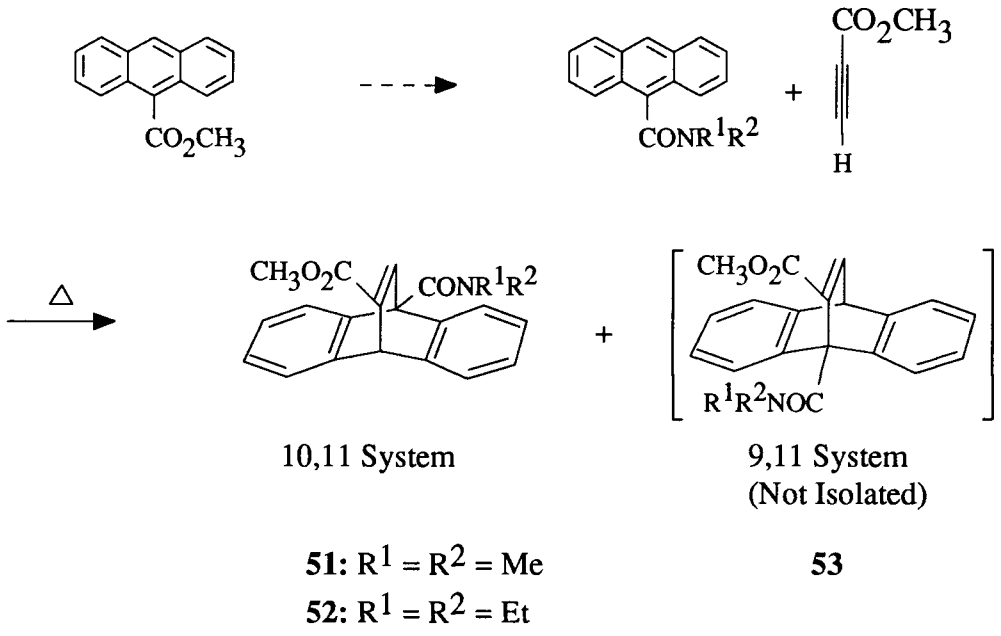
45: $R^1 = R^2$ = Me.
46: $R^1 = R^2$ = Et.
47: R^1 = H; R^2 = Et.
48: R^1,R^2 = Piperidinyl.
49: $R^1 = R^2$ = Bz.
50: $R^1 = R^2$ = iPr.

Figure XXIII: Dibenzobarrelene Ester-Amide Series of Compounds

This method for the production of the ester-amides generally proceeded cleanly and produced the desired compounds in high yields with a minimal amount of purification subsequently required. All of the ester-amides studied were relatively easily obtained in crystalline form by slow evaporation of a solution of the compound at ambient temperature.

D: Preparation of Dibenzobarrelene 10-Amide-11-Esters and Unsymmetrical Diamides

The preparation of the dibenzobarrelene 10-amide-11-esters was accomplished by Diels-Alder reaction between methyl propiolate and the requisite 9-anthracenecarboxamide (Figure XXIV). The 9-anthracenecarboxamides[54,55] were obtained from Weinreb aminolysis of the commercially available methyl 9-anthracenecarboxylate in the usual manner. The brown glassy material obtained after performing the Diels-Alder reaction in an evacuated sealed tube was found to be principally a single dibenzobarrelene adduct and unreacted anthracenecarboxamide. The assignment of the structure of the dibenzobarrelene obtained was based primarily on the ^{1}H NMR coupling between the bridgehead and vinylic protons.[56] The magnitude of the coupling has been found to be significantly different in 10,11-disubstituted systems (**51** and **52**) as opposed to 9,11-systems (**53**). Thus, in the allylically coupled 10,11 systems, a coupling constant in the range of a 1-2 Hertz is found, whereas for the vicinally coupled 9,11 system a value in the range of 7-8 Hertz is expected.[56] Based on these observations, the regiochemistry of the dibenzobarrelene adduct was assigned as a 10,11 system. Interestingly, when similar reactions involving 9-substituted anthracene esters and methyl propiolate were performed[57], adducts of both regiochemistry were isolated, albeit with the 10,11 adduct as the major product. It is probable that the steric influence that accounts for the selectivity in the case of the two ester reaction is augmented in the present case. The increased bulk of the amide functionality is probably sufficient exclude the head to head Diels-Alder reaction that results in the formation of the 9,11 system.



10,11 System

9,11 System
(Not Isolated)

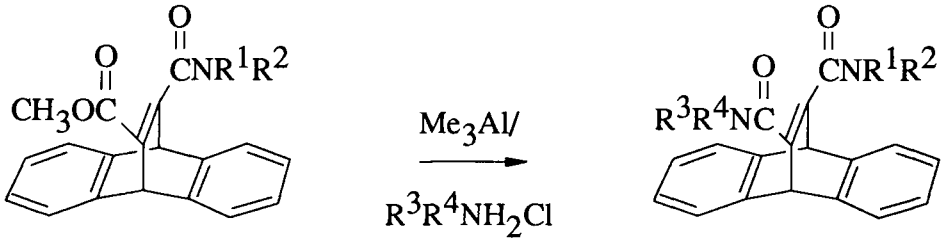
51: $R^1 = R^2 = Me$

52: $R^1 = R^2 = Et$

53

Figure XXIV: Formation of 10,11-Dibenzobarrelene Amide-Esters

The preparation of unsymmetrical dibenzobarrelene diamides, that is where the two amide functionalities on the bridgehead double bond differ in their alkyl components, is basically a combination of the two methods used to produce monoamides and the ester-amides. Since a Weinreb aminolysis acts upon esters only and not on other amides[48], it is possible to convert an ester moiety to an amide in the presence of a second, different amide, Figure XXV.



46 ($R^1 = R^2 = Et$)

54 (R^3 =H; R^4 = Me)

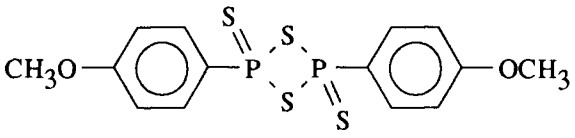
Figure XXV: Production of Unsymmetrical Dibenzobarrelene Diamides

Thus by subjecting a previously produced ester-amide to a Weinreb aminolysis using an aluminum amide complex derived from an amine hydrochloride differing in its

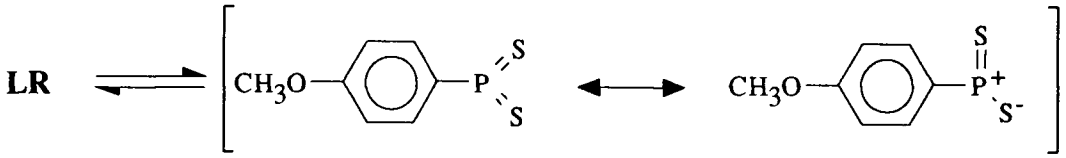
alkyl portion from the starting amide, one obtains an unsymmetrical dibenzobarrelene diamide, **54**. This procedure was also used to prepare a 10,11 analog of compound **54** by subjecting compound **52** to aminolysis with the methylamine hydrochloride-derived reagent to give the 10,11 unsymmetrical dibenzobarrelene diamide.

E: Preparation of Thiono-esters

Thiono-esters can be readily synthesized by the thiation of the ester carbonyl with the dimer of a thionophosphine sulphide, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulphide. This substance, designated Lawesson's Reagent[58] (**LR**) after the Danish chemist S.-O. Lawesson who pioneered its use, has demonstrated great versatility in the conversion of carbonyls to thio-carbonyls. The thiation of ketones, amides, esters, and thiocarboxylic S-esters[59] with **LR** produces the corresponding thiocarbonyl compounds, in many cases in nearly quantitative yield. Determination of the mechanistic aspects of this thiation reaction is complicated by the complex mixture of species present in the reaction mixture.[60] However, ^{31}P NMR studies have determined the presence of the tricoordinated, pentavalent phosphorus species **LR'**. (Figure XXVI)



LR (Lawesson's Reagent)



LR' **LR'**

Figure XXVI: Lawesson's Reagent and Intermediate Species

This intermediate can easily account for the conversion of the carbonyl to a thiocarbonyl in the manner illustrated in Figure XXVII. This mechanistic depiction must be considered, however, an oversimplification of the real situation, as phosphorus NMR studies of this reaction have indicated the presence of at least ten different phosphorus-containing species.

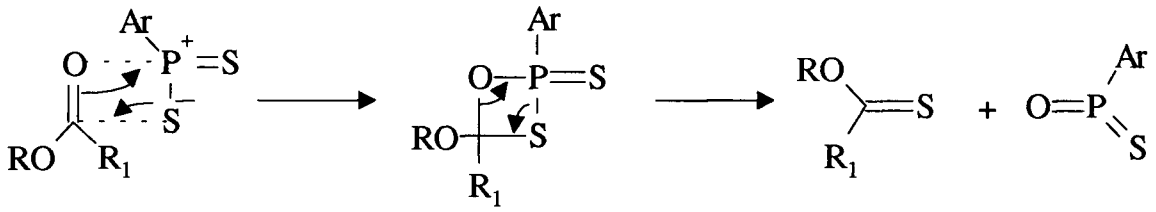
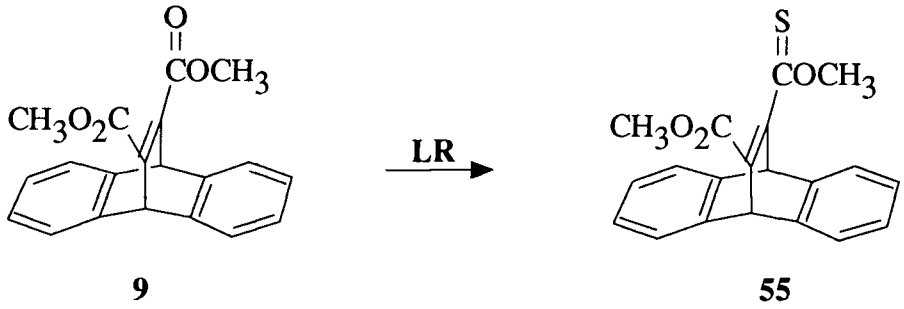


Figure XXVII: Mechanistic Possibilities of Thiation with **LR**

The mono-thiono analog of dibenzobarrelene diester **9** was readily prepared with Lawesson's Reagent in relatively high yield. The length of reaction was maintained such that contamination of the product mixture by the dithiono adduct was not a problem. Purification of the dibenzobarrelene thiono-ester (Compound **55** in figure XXVIII) afforded the product as bright yellow crystals. The rest of the adducts studied were generally found to be colourless or white solids.



9 **55**

Figure XXVIII: Production of Dibenzobarrelene Thiono-ester

II: Photochemical Reactions of Dibenzobarrelene Monoamides

A: Di-π-methane Rearrangement of Simple Monoamides

The reason for studying the dibenzobarrelene monoamides was not to look at the di-π–methane rearrangement *per se* but rather to attempt to determine the ease with which these amides might undergo the di-π-methane reaction and/or any other photoreactions. Additionally, by obtaining each of the starting materials in a crystalline form and subsequently subjecting them to reaction, the influence of the solid state medium on the type and availability of the various reaction pathways could be determined.

The first studies of the photochemistry of various functionalized dibenzobarrelene adducts were performed in 1966 by E. Ciganek.[10] From this work, Ciganek determined that, upon both direct and triplet sensitized irradiation, the dibenzobarrelenes all gave the corresponding semibullvalenes as photoproducts. In particular from his studies, the methyl dibenzobarrelene mono-ester **4** gave exclusively the semibullvalene regioisomer **A** shown in Figure XXIX.

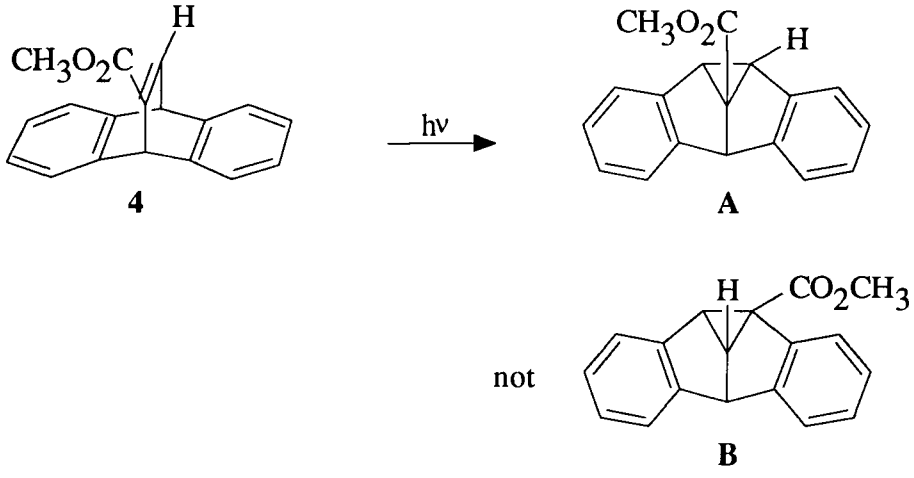


Figure XXIX: Di-π-methane Rearrangement of Dibenzobarrelene Methyl Ester

Regioselectivity of Photoproducts

The formation of the semibullvalene photoproduct obtained can be rationalized by examining the mechanism of the di-π–methane rearrangement for dibenzobarrelenes.[4] This mechanism was first postulated by H. E. Zimmerman after a study of the rearrangement of barrelene to semibullvalene. The structure of the observed product is determined by the initial bonding mode as shown in Figure XXX. The regiochemistry of the resulting semibullvalene can be rationalized by comparing the relative stabilities of the intermediates that result from the two possible pathways of aromatic attack by the bridging biradical. The photoreaction proceeds along the route which permits maximum π delocalization of the excited state biradical. Therefore intermediates with radical sites located so as to extend π delocalization with a substituent are preferred. In general this substituent effect is not associated with a particular excited state multiplicity, and holds true for both triplet and singlet reactions.[4]

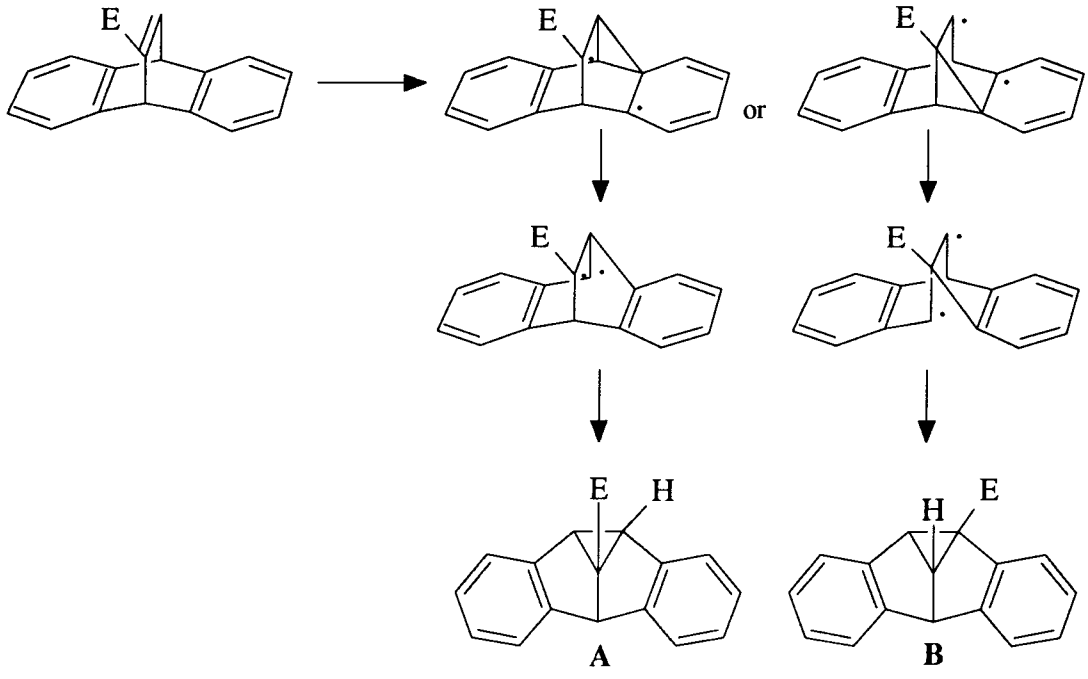


Figure XXX: Di-π-methane Rearrangement Mechanism

Semibullvalene Structural Elucidation

Photolysis in solution of all dibenzobarrelene monoamide substrates studied in this thesis resulted in the formation of a di-π-methane rearranged product. This result was found in a variety of solvents including acetone, acetonitrile, benzene and methanol, and in all cases it was determined that the photoproduct was of the same regiochemistry as observed in the photolysis of the dibenzobarrelene methyl ester **4**. Structural assignments of the photoproduct regioisomers were based primarily on their NMR spectra. The NMR signals of the pentalene ring hydrogens (Figure XXXI) of the dibenzosemibullvalene photoproducts typically appear as singlets in the region δ 3.5-4.8 ppm. In the event that the amide functionality ends up attached to a carbon adjacent to a benzene ring, the photoproduct is unsymmetrical and the three non-equivalent hydrogens of the pentalene ring system give three coupled peaks. When the amide functionality ends up on carbon-(8c), the product possesses a plane of symmetry and the NMR spectrum is found to be simplified. This means that the hydrogens of the pentalene system are represented by two singlets in the ratio 2:1. The more intense of the singlets, attributed to the hydrogens on carbons-(8b and 8d), was found further upfield in all cases. This is partly due to the proximity of a single phenyl group whereas the hydrogen on carbon-(4b) has the deshielding effect of two phenyl groups. More important, however, is the fact that carbons-(8b and 8d) are part of a cyclopropyl ring and therefore the attached hydrogens are more shielded.

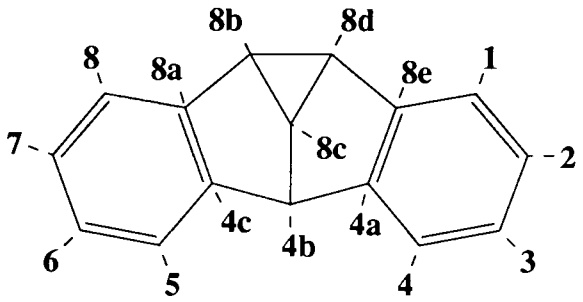
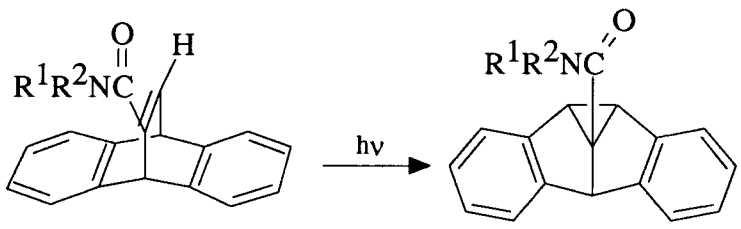


Figure XXXI: Numbering of the Semibullvalene Ring System

Photochemical Results for Adducts 32 and 33

The solution photolyses of both the unsubstituted[50] and the N,N-dimethyl[51] monoamides, compounds **32** and **33**, proceeded very cleanly and resulted in the production of a single photoproduct in each case. Samples containing 10 mg of starting material were completely converted to product in 1/2 h. Those products were determined to be the symmetrical di-π-methane rearrangement products. Additionally, photolyses of these substrates as powders and as single crystals gave rise to the same photoproduct as observed in their solution photolyses.



32: $R^1 = R^2 = H$ **56**: $R^1 = R^2 = H$

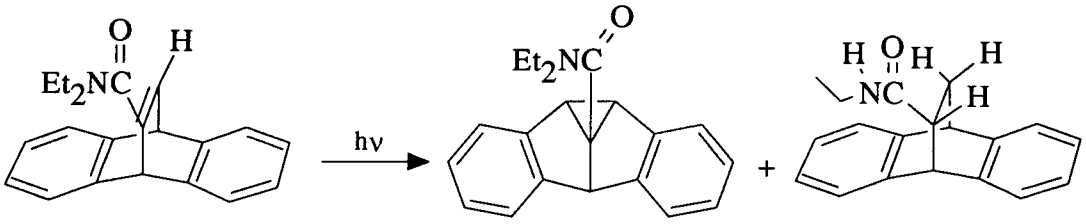
33: $R^1 = R^2 = Me$ **57**: $R^1 = R^2 = Me$

Figure XXXII: Photolysis of Simple Dibenzobarrelene Monoamides

The solid state photoreactions, like the solution photolyses, proceeded rapidly and were accompanied by very little yellowing. Thus the first attempt to determine the viability of the di-π-methane rearrangement of dibenzobarrelene amides in the solid state demonstrated that the reaction can and does proceed with great efficiency. Although no X-ray crystallographic evidence was obtained due to poor crystal quality, it might be said that the crystal lattices of these two substrates are such that there is little steric impediment of the reaction and therefore topochemical control does not result in any significant deviations in reaction pathway.

B: Hydrogen Abstraction Reaction of the Diethyl Adduct

Photolysis of the diethylamide adduct **34** in solution resulted in the formation of two products. The major photoproduct **58** was subsequently identified as the di-π-methane rearrangement-derived symmetrical semibullvalene. The second product, compound **59**, involved the reduction of the bridging double bond of the starting material with a concomitant loss of an ethyl group.



34 **58** **59**

Benzene	66	:	33
Acetone, MeCN	75	:	25
Solid State	100	:	0

Figure XXXIII: Photolysis of Dibenzobarrelene N,N-Diethyl Amide

Abstraction Product Elucidation

The structure assigned to the minor product **59** was supported by both mass spectrometry and infrared spectroscopy. The mass spectrum of the minor photoproduct had a parent ion that was 26 mass units less than the starting material, corresponding to the loss of C_2H_2. In addition, the most intense peak in the spectrum was at m/e 178 and can be attributed to anthracene. It is a general feature of the dibenzobarrelene systems studied in this thesis that their mass spectra show a significant anthracene peak, in contrast to the semibullvalenes, which have negligible anthracene peaks. Thus the presence of a significant 178 peak in the mass spectrum of the minor photoproduct can be taken as strong evidence that the product has maintained the dibenzobarrelene

skeleton. The infrared spectrum contains strong, sharp bands at 3248, 1639, and 1555 cm^{-1}. The first band, in conjunction with the carbonyl absorption at 1639 cm^{-1}, indicates the presence of a secondary amide. This assignment is further supported by the amide type II band[61] at 1555 cm^{-1} which is typical of an amide that is not fully substituted. The amide type II band in infrared spectroscopy is a combination of the N-H deformation band and the C-N stretching band.[61] The position of the carbonyl band indicates that the amide is attached to a saturated carbon.[56]

The principal means of assigning a structure to the photoproduct, however, was by NMR spectroscopy. Integration of the proton spectrum of the photoproduct (Figure XXXIV) shows the presence of 19 hydrogens in the structure, a loss of 2 from the starting material. Eight of the hydrogens can be accounted for in the aromatic region. A further 5 hydrogens can be assigned to the signals at δ 3.12 and 0.96 ppm, and attributed to the ethyl group. The coupling to the methylene signal at δ 3.12 ppm by the amide proton peak at δ 4.84 ppm is evident in the methylene signal but is obscured in the broadened N-H peak. Assignment of the δ 4.84 ppm peak to the amide proton was confirmed by the addition of D_2O and subsequent loss of signal intensity. Of the remaining 5 hydrogen signals, two occur in the region with which dibenzobarrelene bridgehead protons are typically associated. These two peaks, a doublet at δ 4.54 ppm and an overlapping doublet of doublets at δ 4.38 ppm, can be accounted for by the bridgehead proton adjacent to the amide substituted carbon (H_a), and the bridgehead adjacent to the bridge methylene (H_b), respectively. As might be expected, the electron-withdrawing influence of the amide group causes the doublet to appear downfield of the doublet of doublets. The remaining three signals are all doublets of doublets of doublets (ddd) as each of the protons is surrounded by three non-equivalent neighbours.

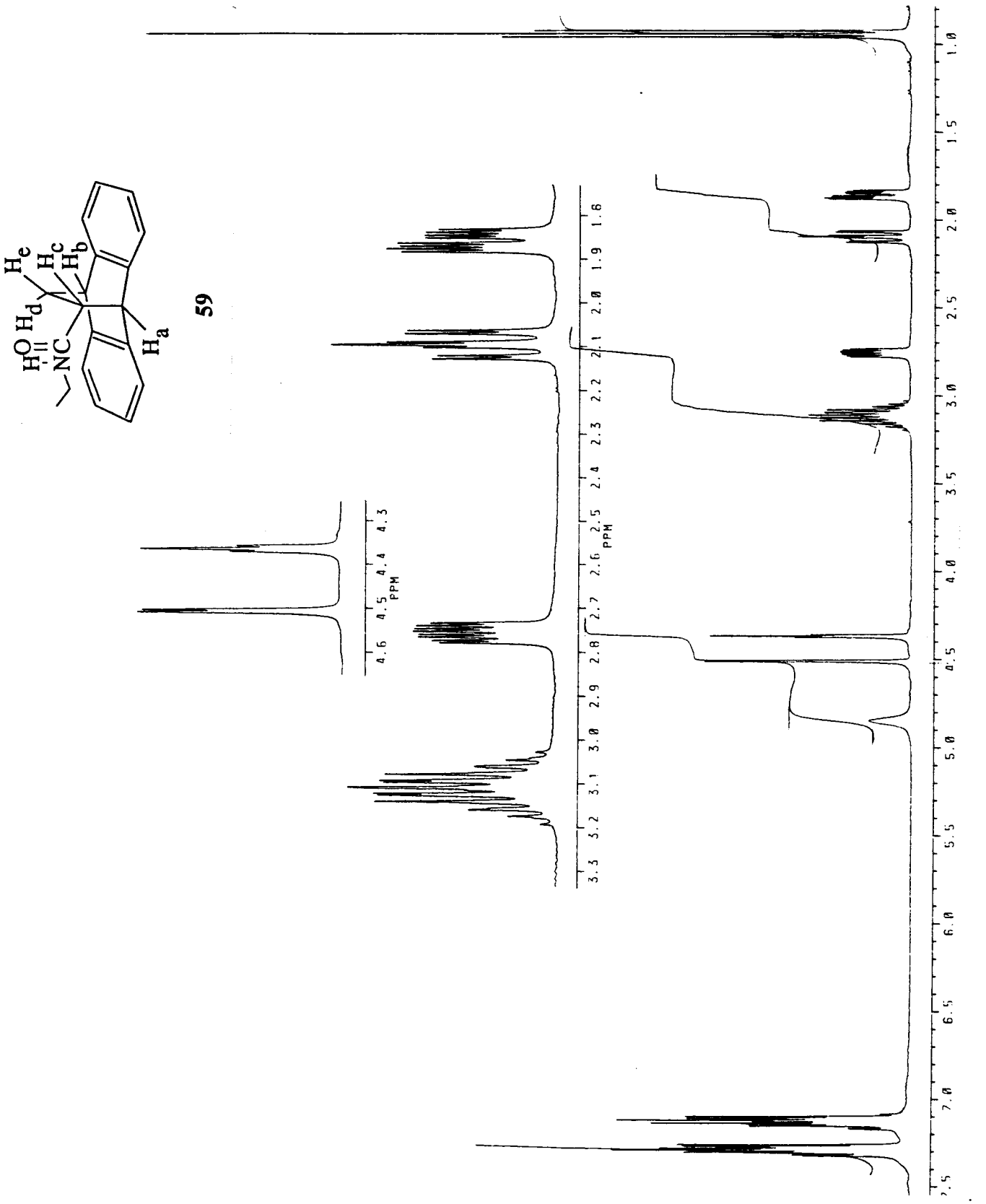
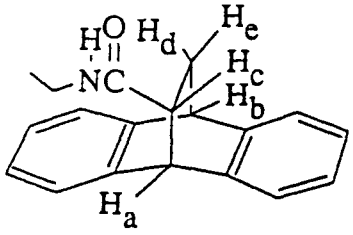


Figure XXXIV: Proton NMR Spectrum of Monoethyl Amide Photoproduct 59

The signal furthest downfield at δ 2.76 ppm can be assigned to the proton geminal to the amide moiety (H_c), as again the deshielding influence of the amide would be felt most strongly by the hydrogen that is closest. The last two proton signals are assigned to the geminal hydrogens of the bridge methylene (H_d and H_e). This assignment is supported by the size (J_{de} = 13 Hz) of the coupling constant between these two signals. Coupling constants between geminal hydrogens are typically in the range of 10-16 Hz. The exact assignments of these two peaks can be inferred from the Karplus relationship[56] which predicts that H_d would have a larger coupling constant with H_c than would H_e. Based on this assumption, it is possible to assign the signal at δ 2.10 ppm to H_d and the signal at δ 1.86 ppm to H_e. However these assignments must be treated with caution, as vicinal coupling constants also depend on the nature of the substituents in the molecule.

Confirmation of the relative couplings between the various proton signals was supported by a proton NMR COSY spectrum (Figure XXXV). This NMR technique establishes connectivity patterns by subjecting the sample to a series of sequenced electromagnetic pulses. The result of this pulse sequence is a two dimensional spectrum that shows peak cross-sections at the intersection points of coupled hydrogen signals. Thus from the COSY spectrum of compound **59**, it can be determined, for example, that the hydrogen signal at δ 2.76 ppm (assigned to H_c) is coupled to the peaks at δ 4.38 ppm (H_a), δ 2.10 ppm (H_d), and the peak at δ 1.86 ppm (H_e). In addition, carbon-13 NMR attached proton test experiments indicated the presence of four saturated carbons with an odd number of protons attached, and the presence of two saturated carbons with an even number of protons attached. All of the NMR data is consistent with the assigned structure **59**.



59

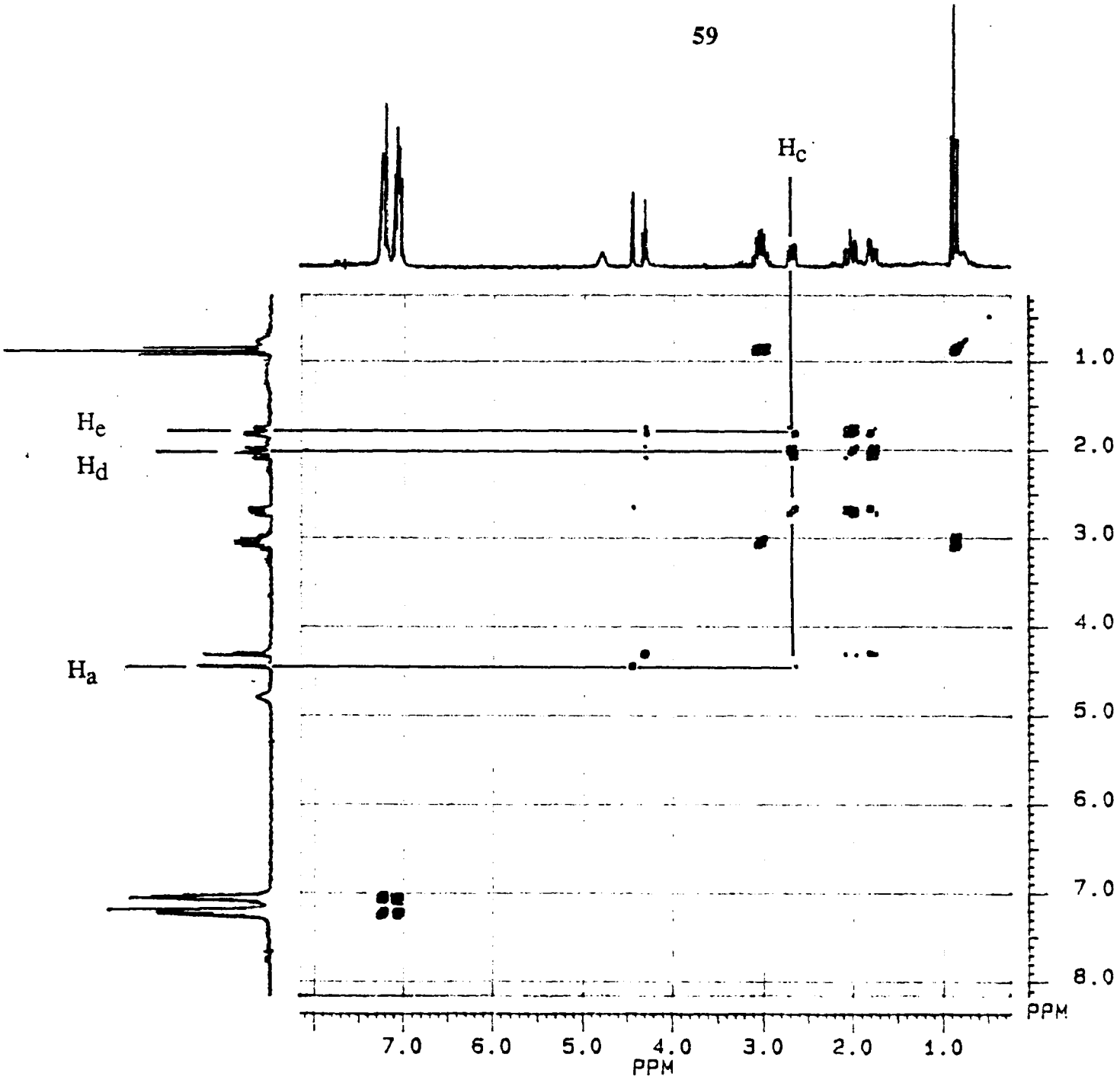


Figure XXXV: COSY Spectrum of Photoproduct **59**

Hydrogen Abstraction Mechanism

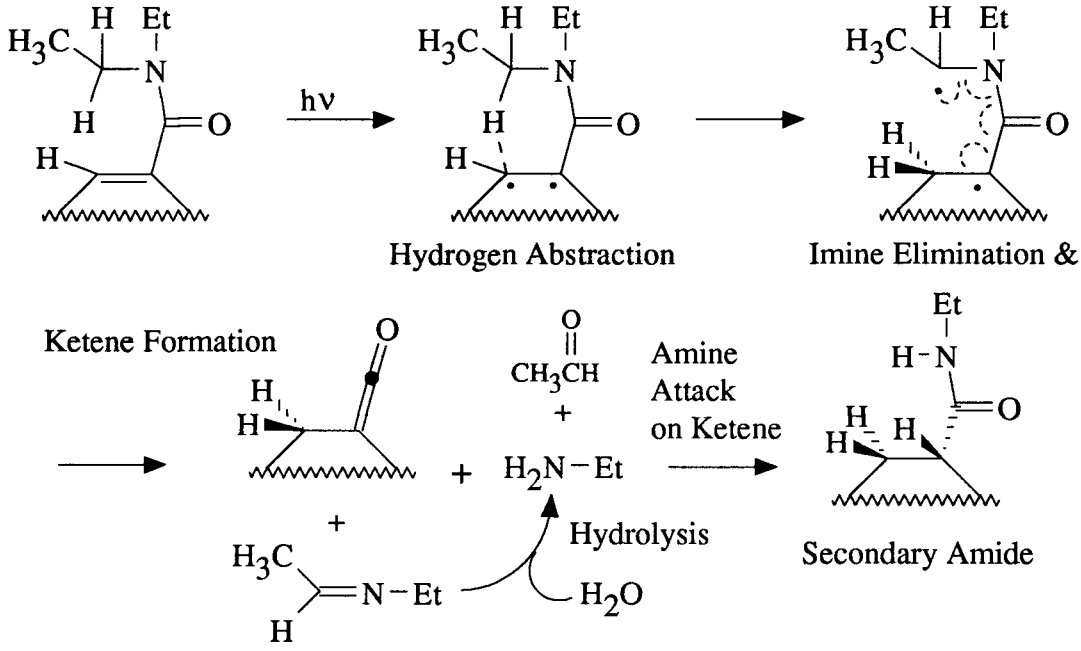


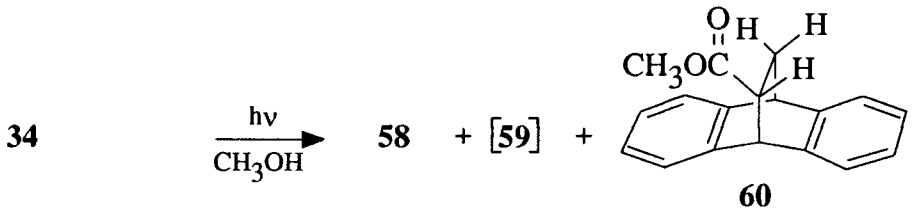
Figure XXXVI: Mechanism for the Formation of Mono-substituted Amide **59**

The formation of the photoproduct **59** may proceed *via* intramolecular hydrogen abstraction by the vinylic carbon *beta* to the amide functionality and can be thought of as an example of a type II reaction of an aliphatic olefin. This type of reaction was first demonstrated (Figure XII; page 16) by Aoyama[28b] et al. in the photocyclization of N,N-bis(benzyl)methacryl-amide (**24b**) to a β-lactam **25** and the photodealkylation of N,N-di-*iso*-propylmethacrylamide **24p** to N-*iso*-propyl-*iso*-butyramide **23**. Interestingly, in no instance did they report the formation of N-monosubstituted amides from the irradiation of N,N-diethyl amides. It might be expected that diethyl amides would be less amenable to this type of reaction, as the radical which remains on the ethyl group would be considerably less stable than the analogous benzyl or isopropyl radical.

It can be speculated that the reason that the diethylamide **34** does undergo abstraction, unlike in the previous study[28b], is due to the structural rigidity of these amides. In the amides in this thesis, the olefinic bond which abstracts the hydrogen is

part of a ring system and is rigid, and therefore can not undergo cis-trans isomerization to dissipate the absorbed energy after excitation. In the study by Aoyama et al.[28b], all substrates studied were susceptible to this type of energy loss and as such, the abstraction process would have to be sufficiently rapid to compete with decay to the ground state. With this type of energy loss not available to the dibenzobarrelene diethylamides, it is possible that the excited state lifetime is sufficiently extended that the hydrogen abstraction process becomes competitive.

After hydrogen abstraction, cleavage of the C-N bond of the resulting biradical leads to fragmentation to ketene and imine. The imine is readily hydrolyzed to ethylamine which can then react directly with the ketene to give the N-monosubstituted amide **59** (Figure XXXVI). By photolyzing the diethyl adduct **34** in benzene, in a sealed NMR tube, it was possible to identify the presence of small amounts of acetaldehyde spectroscopically resulting from the hydrolysis of the imine. The proton NMR spectrum of the photomixture exhibited peaks at δ 2.20 and 9.80 ppm indicating the presence of acetaldehyde.[56b] Furthermore, the photolysis of the diethyl adduct in methanol resulted in the formation of a second minor photoproduct **60**, the saturated-bridge methyl ester analog of the starting material, as a result of the nucleophilic trapping of the ketene by the solvent.. This photoproduct was readily identified as a known compound[62], and similarities between **59** and **60** in NMR and mass spectral data lend credence to the structural assignment of compound **59**. Interestingly, compound **59** was not observed in the methanol photolyses. The reason for this will be made clear when the photolysis of the dibenzyl amide adduct, compound **35**, is discussed later. The ratio of the major photoproduct (**58**) to minor ester product (**60**) was 2:1.



Methanol 67 : 0 : 33

Figure XXXVII: Photolysis of Diethyl Amide Adduct **34** in Methanol

Solid State Photolysis of 34

Solid state photolysis of the starting material **34** was carried out on both powdered samples and on single crystals. Conversion of the starting material was kept to approximately 10 percent. At this point both the powder and crystalline material had become pale yellow. As well, some regions of the powdered sample had taken on a gummy appearance, indicating that the sample had started to melt. Any attempt to continue the photolysis beyond this point would likely have resulted in a loss of topochemical control. The samples were analyzed by dissolving them in deuterated chloroform and obtaining a proton NMR spectrum. NMR analysis of the reaction mixture centred on the region between δ 3.5-4.5 ppm. The reasons for this are two-fold: the signals of both photoproducts in this region are well separated sharp singlets or doublets and this region is generally devoid of extraneous peaks due to solvent or photo-decomposition products. Analysis of the solid state irradiations indicated that the sole product was the same as the major product **58** in the solution photolyses of the diethylamide **34**.

The mechanism by which the abstraction product **59** is thought to be formed dictates that the remote end of the bridgehead double bond must be able to come into close enough proximity to an α-hydrogen of the alkyl portion of the amide in order for hydrogen transfer to occur. α-Hydrogens can be defined as those hydrogens directly attached to the carbon bonded to the amide nitrogen. In solution, conformational

isomerization allows such an occurrence, and therefore, if the rate of hydrogen abstraction and fragmentation is comparable to the rate of the di-π-methane rearrangement, N-monosubstituted amide products are seen. In the crystal, however, the molecule is often frozen at or near in its lowest energy conformation. As the topochemical principle[40] dictates, reactions in crystals will occur with a minimal amount of atomic and molecular motion. As such, the hydrogen abstraction reaction will only be efficient if the conformation of amide **34** in the solid state, as deduced by X-ray crystallography, has the proper distance between the α-hydrogen and the remote end of the bridging vinyl bond.

Six-membered transition states for the abstraction of a hydrogen by carbon have been shown to involve C···H distances of 2.7-2.9 Å[63] (parameter d in Figure XXXVIII). Carbon has a van der Waals radius of 1.7 Å whereas hydrogen has a radius of 1.2 Å[64], giving a C···H sum of 2.9 Å. Studies comparing experimental abstraction distances and the sum of the van der Waals radii of the abstracting and the abstracted atoms have demonstrated a striking correlation. Thus, it has been proposed that the van der Waal radii sum may represent an upper limit to hydrogen abstraction. But distance is not the only criterion that determines the feasibility of hydrogen abstraction; it is also important to consider angular requirements.[63]

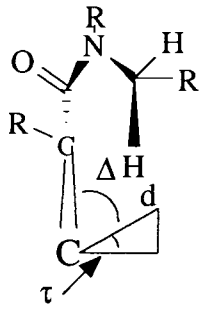


Figure XXXVIII: Definition of Angular Parameters d, τ and Δ

Figure XXXVIII details the geometric parameters involved in the six-membered transition state for hydrogen abstraction by carbon. The abstracting orbital is a p-orbital which, in the ground state, is orthogonal to the plane of the double bond. This requires that the abstracted hydrogen be positioned directly over the remote carbon of the double bond (τ and $\Delta = 90^{o}$). This can be contrasted with abstraction by an oxygen atom of a carbonyl where the abstracting orbital is the n-orbital. As such, the optimal angles for τ and Δ would be 0^{o} and $90\text{-}120^{o}$ respectively. This analysis assumes that the reactive excited state geometry is close to the ground state geometry as determined by X-ray crystallography.

X-ray crystallographic analysis (Figure XXXIX) of the diethylamide starting material **34** determined that the distance between carbon-(12) and the nearest abstractable hydrogen, H-(17), is 3.06 Å. This represents a degree of separation between the two reaction centres that is significantly greater that the sum of the van der Waal radii (3.06 *vs.* 2.90 Å). Consequently, the hydrogen abstraction reaction to produce the monosubstituted amide product **59** would not be expected to occur in the solid state. Thus only the di-π-methane rearrangement-derived product **58** is seen. It should be noted that in the X-ray structure of **34** there is disorder in the ethyl group pointing towards the bridging vinyl bond.

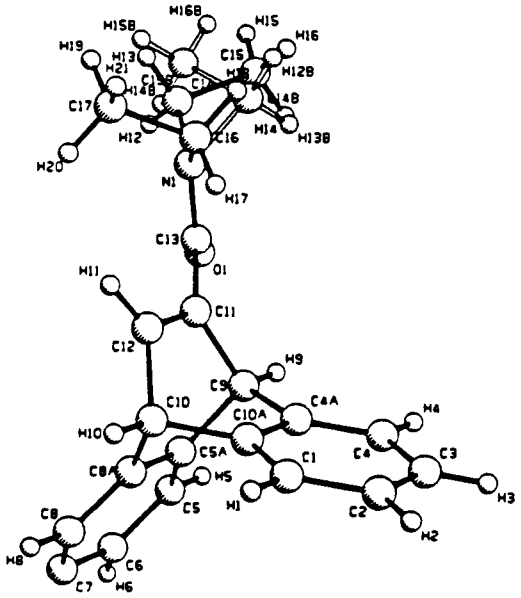
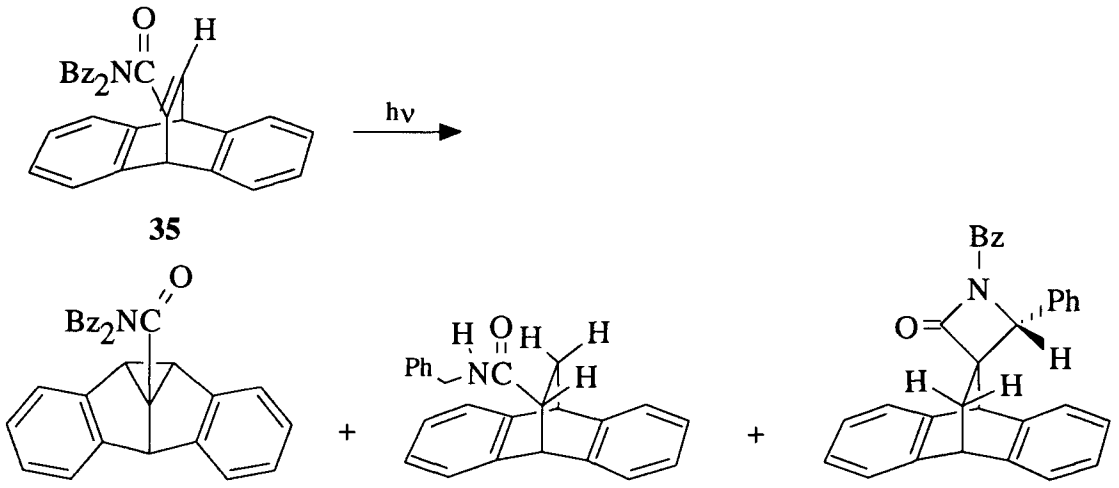


Figure XXXIX: X-ray Structure of Dibenzobarrelene Diethylamide **34**

C: Reactions of the Dibenzyl Amide Adduct

Irradiation of the dibenzylamide adduct **35** in solutions of acetone, acetonitrile and benzene resulted in the formation of three photoproducts. In this instance, however, the di-π-methane rearrangement-derived symmetrical semibullvalene, compound **61**, was found to be a minor photoproduct. A second minor photoproduct **62**, recovered in minute amounts, was found to be a benzyl amide analogous to the saturated-bridge secondary amide **59** recovered from the photolysis of the diethyl adduct **34**. The major product upon photolysis was determined to be a ring-fused β-lactam, compound **63**, as shown in Figure XL.



	61		62		63
Benzene	35	:	4	:	61
Acetone	39	:	4	:	57
MeCN	50	:	2	:	48
Solid State	85	:	0	:	15

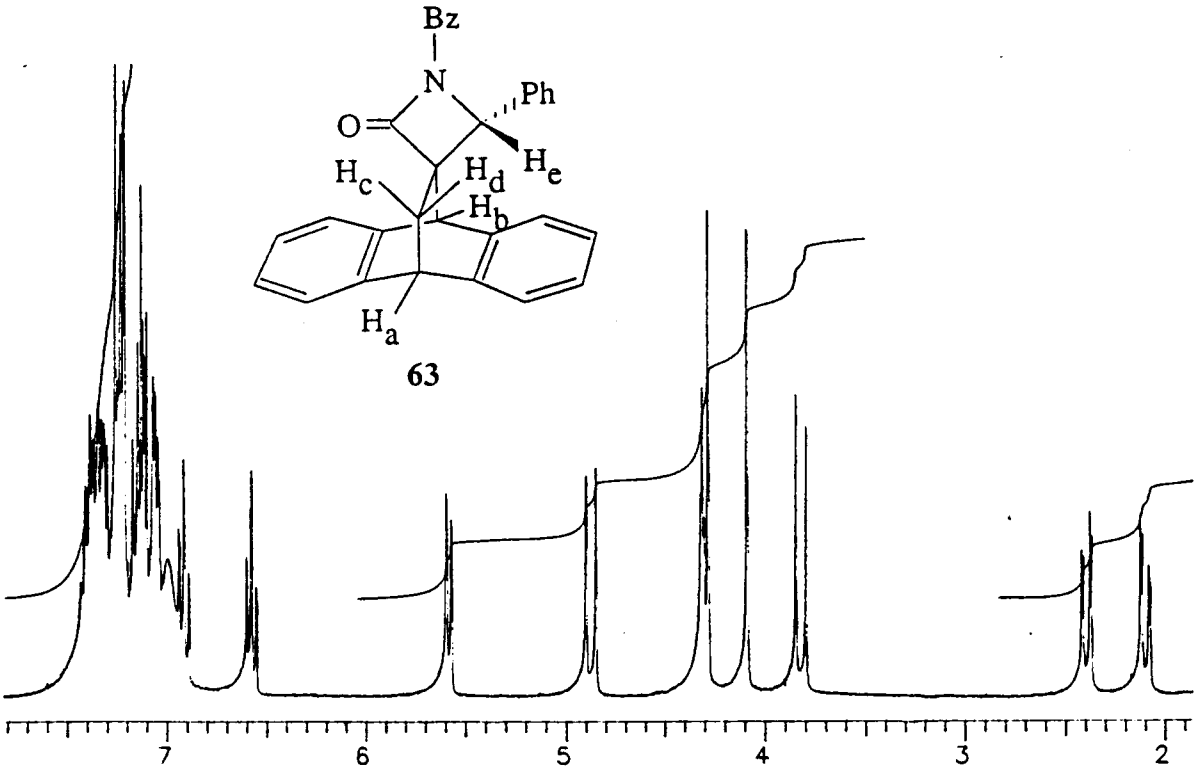
Figure XL: Photolysis of Dibenzobarrelene Dibenzylamide; Product Ratios

Lactam Structural Elucidation

Initial indications of the structure of the major product **63** came from infrared spectroscopy and mass spectrometry. The infrared spectrum was markedly devoid of bands except for a strong absorbance at 1758 cm^{-1}. This is well out of the usual range of amides and led to initial speculation that an ester had somehow been formed. However, mass spectrometry showed a parent mass of 427 mass units, the same as the starting material, indicating that nothing had been lost or added to the molecule. The only reasonable type of acyl compound that displays an infrared band in the experimentally determined region is a β-lactam.[56] Furthermore, the base peak in the mass spectrum corresponded to a mass of 178, again giving anthracene as a marker for the presence of a dibenzobarrelene compound. The first major fragmentation peak occurs at 294 mass units, corresponding to a loss of 133 mass units. This mass is equivalent to the loss of a O=C-N-Bz group.

Peak assignment of the proton NMR spectrum (Figure XLI) was initially made difficult by the appearance of a doublet at δ 5.58 ppm and a multiplet at δ 6.58 ppm. Out of 25 hydrogens in the β-lactam structure, 18 hydrogens are aromatic. These two peaks were in addition to peaks further upfield that already accounted for 7 hydrogens. This required these two peaks to represent aromatic hydrogens in a region outside the generally accepted range. However, decoupling experiments and connectivity patterns established by proton COSY NMR confirmed that the peaks in question were associated with aromatic protons in the molecule. This unusual chemical shift can be attributed to a close interaction between the phenyl ring directly attached to the lactam and the lactam benzyl group. This close interaction, as shown by the X-ray crystallographic structure depicted in Figure XLII, coupled with the anisotropic nature of the magnetic field around a phenyl group[65], results in two hydrogens being unusually shielded. Integration values for the two peaks and the main aromatic multiplet region accounted for 18 hydrogens,

peaks and 7 hydrogens to be assigned. Of the 7 remaining peaks, 2 are singlets corresponding to the bridgehead hydrogen adjacent to the lactam ring (H_b) and the methine hydrogen of the lactam ring (H_e). The geminal hydrogens of the benzyl methylene group can be assigned to the coupled peaks at δ 4.86 and 3.82, again based on the size of the coupling constant (J = 14.7 Hz). The 3 peaks left, all doublets of doublets, correspond to the bridgehead hydrogen H_a (δ 4.29) adjacent to the bridge methylene and to the geminal bridge methylenes H_c and H_d (δ 2.39 and 2.08). Again the couplings between the various aliphatic hydrogen signals were confirmed by the connectivity pattern observed from the COSY NMR spectrum. A carbon-13 attached proton test experiment indicated the presence of three aliphatic carbons each with an odd number of protons and three aliphatic carbons with zero or two protons attached. This is consistent with the proposed structure.



63

Figure XLI: Proton NMR Spectrum for β-Lactam **63**

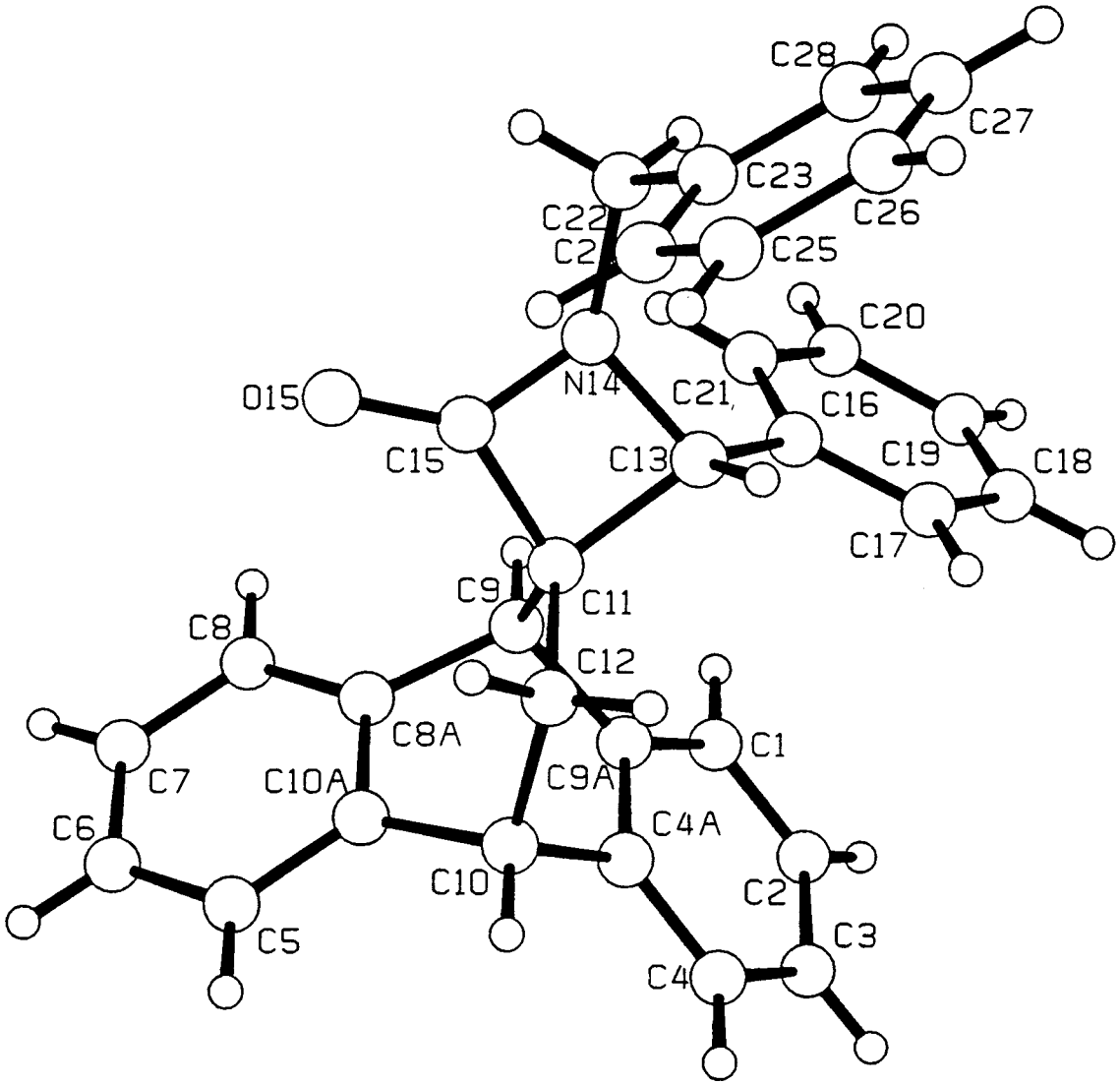


Figure XLII: X-ray Crystallographic Structure for β-Lactam **63**

Mechanism for β-Lactam Formation

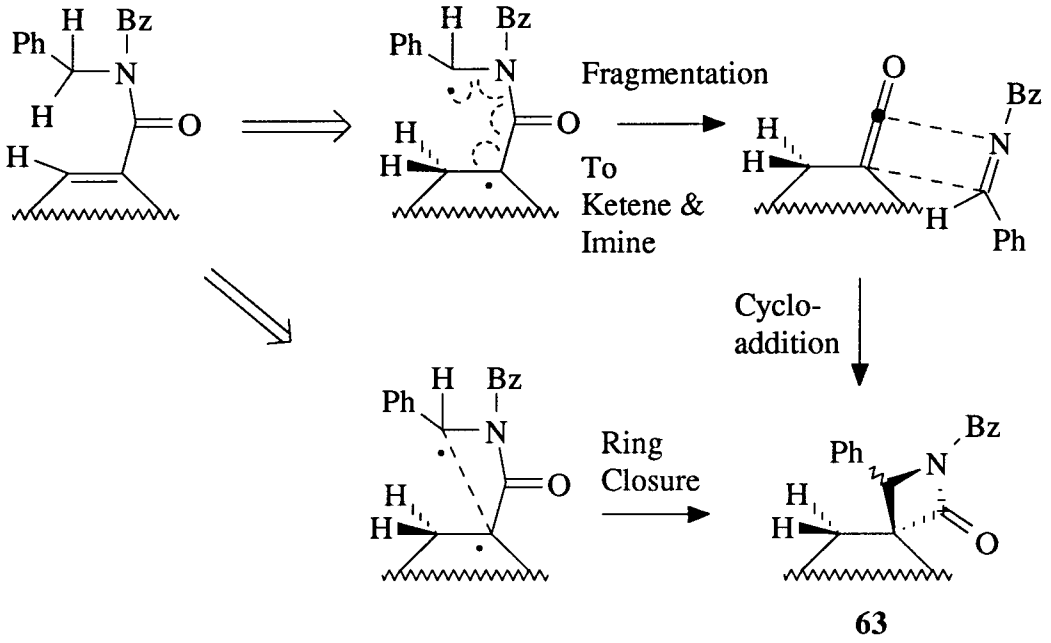


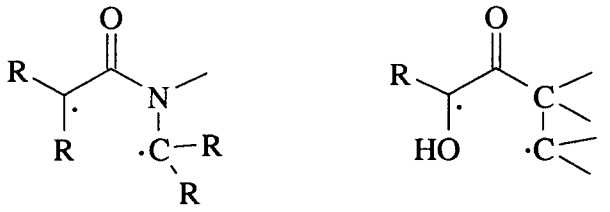
Figure XLIII: Mechanistic Possibilities For β-Lactam Formation

In Figure XLIII, two mechanistic possibilities[28b] for the formation of the β-lactam **63** are outlined. The first pathway, via a ketene intermediate, is necessary in order for the formation of a saturated-bridge monosubstituted amide photoproduct. In fact, this mechanism is in effect as small amounts of the reduced N-benzylamide adduct **62** were produced. However, this can not be taken as evidence that the lactam **63** was formed by the same mechanism. More informative is the fact that when the dibenzyl amide adduct **35** was irradiated in methanol, the result was a 1:1 mixture of the di-π-methane product **61** and the same saturated-bridge methyl ester (**60**) that was found in the methanol photolysis of the diethylamide adduct **34**. The presence of a trapping agent, such as methanol, is able to interfere with the formation of the lactam. Thus it can be surmised that the mechanism is not one of simple biradical closure but that a ketene is an intermediate in the formation of the lactam.

The reaction of ketenes with imines to produce β-lactams has been previously documented.[66] The possibility that the lactam is formed by closure and is in photochemical equilibrium with the imine-ketene pair, since photochemical cleavage of β-lactams to ketenes and imines is also known[67], can be discounted. This was on the basis of the an experiment involving the photolysis of the lactam in methanol and subsequent finding that the β-lactam **63** was photochemically inert. Thus both the monosubstituted amide and lactam photoproducts are produced *via* intramolecular hydrogen abstraction by the β-carbon of the bridging double bond, followed by cleavage of the C-N bond to give a ketene and an imine. The imine is readily hydrolyzed to a primary amine which can then attack the ketene to give the monosubstituted amide **62**. Alternatively, the imine can undergo a cycloaddition reaction with the ketene to give a lactam. This raises the question as to why the diethyl adduct gives exclusively the monosubstituted amide product from the hydrogen abstraction reaction whereas the dibenzyl adduct gives predominantly the β-lactam.

With few exceptions, cycloadditions of ketenes and imines have been limited to aromatic imines.[66] The diethyl-derived imine, being inherently less stable, is much more susceptible to hydrolysis than the dibenzyl-derived imine. Thus the rate of hydrolysis of the diethyl-derived imine relative to the rate of attack on the ketene is probably too large for any significant production of a β-lactam. In the case of the dibenzyl-derived imine, the rate of hydrolysis should be comparable to the rate of attack on the ketene resulting in the formation of both β-lactam and monosubstituted amide product.

A comparison of the behaviour of biradical **64**, analogous to the biradical formed in these abstraction reactions, with a similar biradical **65** (Figure XLIV) leads to some interesting observations. Biradical **64** undergoes cleavage with no cyclization whereas biradical **65** undergoes cyclization exclusively.[68] This would seem to be even more confusing considering that the amide CO-N bond is usually thought of as having partial double-bond character.[69]



64 **65**

Cleavage Cyclization

Figure XLIV: Comparison of 1,4-Biradical Reactivities

Despite the double bond character, the dissociation energy of the CO-N bond is considered to be comparable to the dissociation energy of the ordinary C-C bond. This is a result of the inherently weaker nature of the C-N bond (C-N, *ca.* 70 kcal mol^{-1}; C-C, *ca.* 85 Kcal mol^{-1}).[70] The failure of biradical **65** to undergo cleavage is thought to be due to the perpendicular relationship between the radical site adjacent to the carbonyl and the CO-C σ-bond. This orientation is due to the conjugation of the p-orbital of the radical with the carbonyl group. The conjugation of the C(α) p-orbital of biradical **64** with the amide carbonyl is presumed to be weak, based on studies that have shown that the radical-stabilizing effect of an ester carbonyl is very weak.[71] Thus, the configuration which prevents the cleavage reaction plays a lesser role in the chemistry of biradicals such as **64**.

Product Ratios

As was seen in Figure XL, the effect of going from a less polar solvent to a more polar one is to increase the amount of di-π-methane-derived semibullvalene, compound **61**, at the expense of both hydrogen abstraction products (**62** and **63**). In fact, in acetonitrile the product distribution has changed such that the semibullvalene product and the lactam product are produced in essentially equal amounts. The mechanism for the hydrolysis of the imine to produce the primary amine, in the case of the formation of the monosubstituted amide, involves extensive charge separation. Additionally, in the

formation of both abstraction products, the reaction of the nitrogen compound with the ketene is thought to be a nucleophilic attack[72] involving some degree of charge separation. The trend of moving from a less polar to a more polar solvent should be to stabilize the transition state in these reactions as a result of better solvation. From this it might be expected that increasing polarity would actually increase the amount of abstraction products formed, if attack on the ketene is the product determining step. If hydrogen abstraction, involving no charge separation at all, is the product determining step, then one would expect no change in the rate from a solvent effect. At the same time, the di-π-methane rearrangement mechanism involves no separation of charges and again should not be influenced by a change in solvent. In order to explain the observed trend, the solvent effect must work against the abstraction reaction either by slowing the reaction before the product determining step or by diminishing the amount of abstraction intermediate, ketene or imine, which is able to go on to product. However the product ratios vary only slightly and as such, the presence of a solvent effect is not definite.

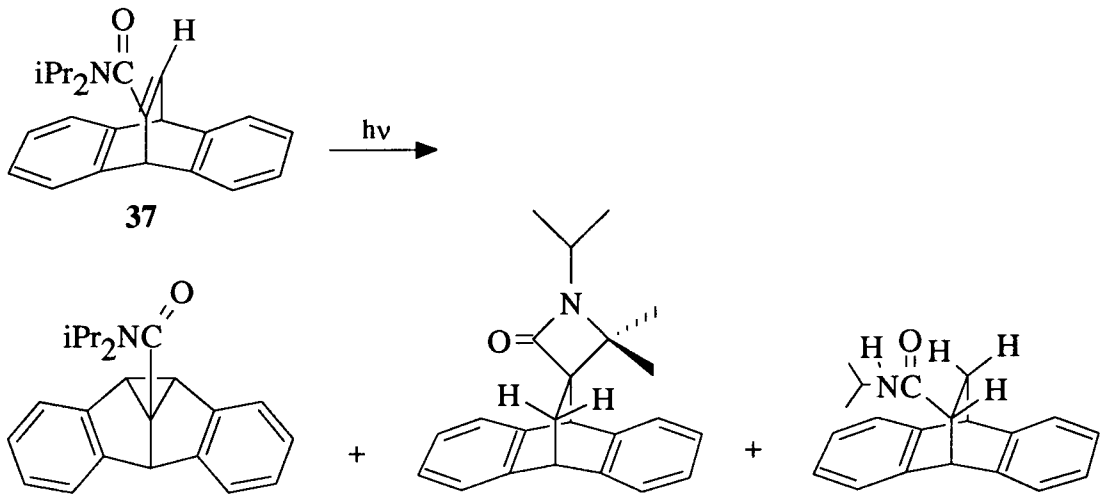
Solid State Results

Solid state photolysis of the dibenzyl adduct **35** resulted in the predominant formation of the di-π-methane product **61**. The abstraction-derived β-lactam product **63** was also detected (15%). This shows that the starting material must be packed in the crystal in such a manner as to allow for interaction between a benzyl methylene hydrogen and the β-carbon of the bridgehead double bond and that the orientation of the amide carbonyl with the bridging radical is favourable for ketene formation. Due to the poor quality of the dibenzylamide adduct crystals, an X-ray crystallographic study of this starting material could not be carried out. The fact that the ratio of abstraction product to semibullvalene has changed much to the favour of the semibullvalene seems to indicate that the di-π-methane rearrangement is less affected by topochemical control than the abstraction reaction.

As the di-π-methane rearrangement would seem to involve a much greater re-organization of the dibenzobarrelene skeleton than the abstraction reaction, topochemical restriction of the abstraction reaction must act principally on the benzyl substituents of the amide. This control could be exerted in two ways. The orientation of the benzyl methylene hydrogens in dibenzyl adduct **35**, with respect to the bridging double bond, is determined by the crystal packing. It is feasible that the benzyl methylene hydrogen to be abstracted and the β-carbon of the bridging vinyl bond are at the separation limit for reaction to occur. Topochemical control would impede movement that would reposition the reacting centres so as to make the reaction more efficient. Thus in the excited state the starting material is not as readily able to adopt the configuration needed for abstraction to occur. Alternatively, the abstraction readily occurs but the orientation of the amide carbonyl and the bridgehead radical in the solid state results in a considerably slower rate of ketene formation. In order for ketene formation to be efficient, the alignment of the O-C-N atoms and the bridging carbon-carbon bond must approach co-planarity.[73] This allows for maximum overlap of the p-orbitals involved in the formation of the ketene.

It is also possible that abstraction and ketene formation are occurring readily and that, once formed, the imine is diffusing into the crystal lattice before reaction with the ketene can take place. The diminishment of the abstraction product in the solid state would be a result of alternate reaction pathways of the ketene rather than an inherently less viable reaction.

D: Reactions of the Di-*iso*-propyl Adduct



Benzene	29	:	8	:	63
Acetone	57	:	17	:	26
MeCN	31	:	8	:	61
Solid State	100	:	0	:	0

Figure XLV: Photolysis of Dibenzobarrelene Di-*iso*-propylamide; Product Ratios

Irradiation of the di-*iso*-propylamide adduct **37** in solutions of acetone, acetonitrile and benzene resulted in the formation of three photoproducts (Figure XLV). As with the dibenzylamide adduct **35**, irradiation produced a di-π-methane rearrangement-derived semibullvalene **66**, an abstraction-derived β-lactam **67** and an abstraction-derived saturated-bridge monosubstituted amide **68**. Irradiation in benzene and acetonitrile gave essentially the same results: the major product was the saturated-bridge *iso*-propylamide accompanied by half as much semibullvalene and a small amount of β-lactam. Photolysis in acetone deviated significantly in that the percentages of the semibullvalene **66** and the monosubstituted amide **68** were essentially reversed. There was also an increase in the amount of β-lactam **67** produced, mostly at the expense of the monosubstituted amide.

Structural Assignment

Structural assignment of the various photoproducts was based on similar analyses as in the case of previous starting materials. The semibullvalene **66** was identified primarily by its characteristic mass spectrum and symmetrical proton NMR. The monosubstituted amide **68** showed bands in its infrared spectrum at 3305, 1645 and 1542 cm^{-1} characteristic of a saturated secondary amide. The base peak of the mass spectrum was again 178 mass units, indicating the presence of the dibenzobarrelene skeleton.

A comparison of the proton NMR spectra of the β-lactam **67** and the monosubstituted amide **68**, shown in Figure XLVI and XLVII respectively, reveals the similarities of the two products. From the position of the bridgehead methylene hydrogen signals (δ 4.60 and 4.34 ppm for **68**; δ 4.48 and 4.36 ppm for **67**), it can be determined that both products have maintained the dibenzobarrelene skeleton.

Comparing the NMR spectrum of the β-lactam **63** derived from the dibenzobarrelene dibenzylamide **35**, shown in Figure XLI, to that of the β-lactam **68** derived from the di-*iso*-propyl adduct in Figure XLVII (page 65), it can be seen that the two aromatic peaks in the dibenzyl adduct-derived β-lactam **63** spectrum, upfield from the usual aromatic region, do not have counterparts in the second spectrum. This fact and the similarities in the rest of the spectra lends weight to the assignment of these two peaks to the aromatic protons of the lactam ring phenyl group.

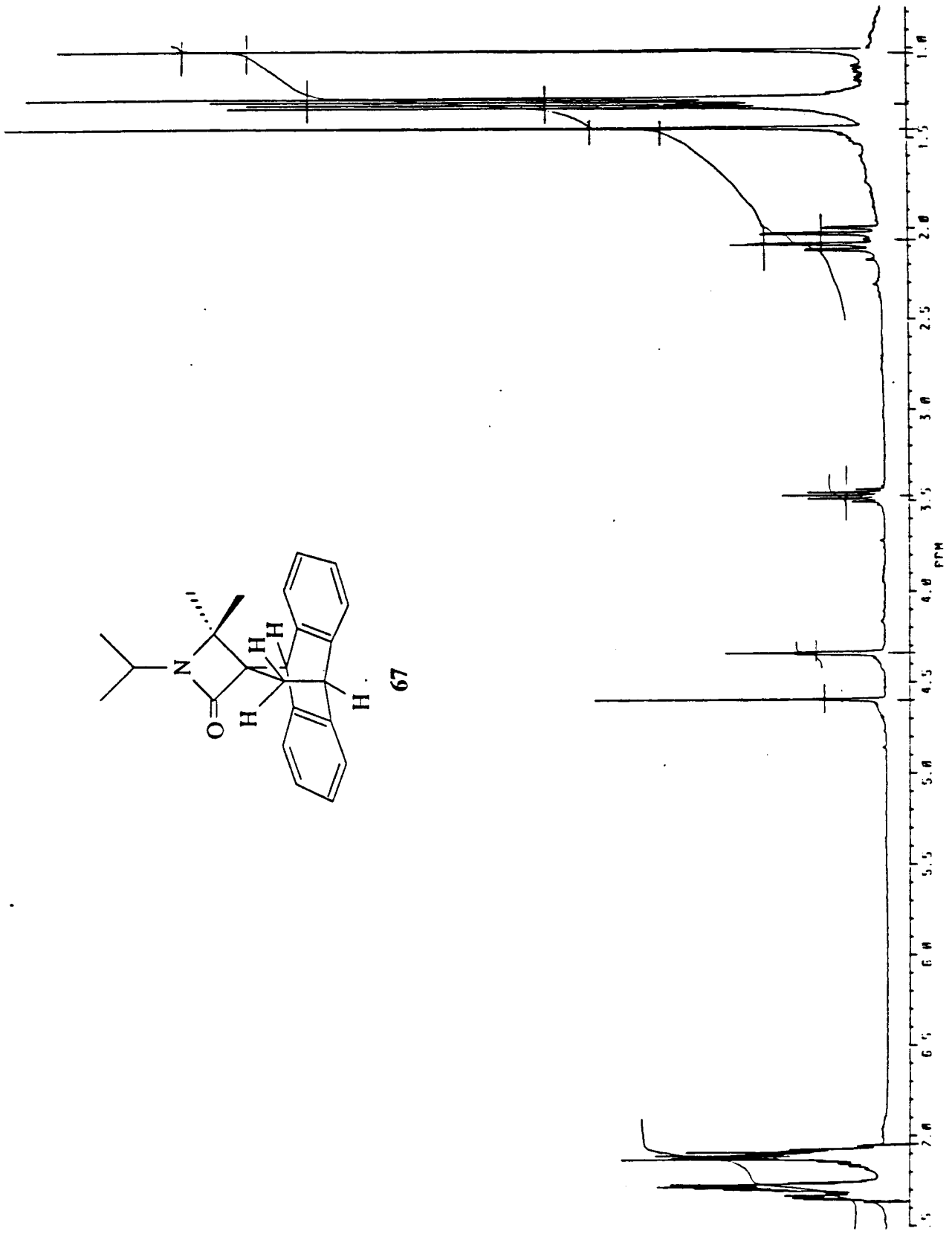


Figure XLVI: Proton NMR Spectrum of β-lactam Photoproduct **67**

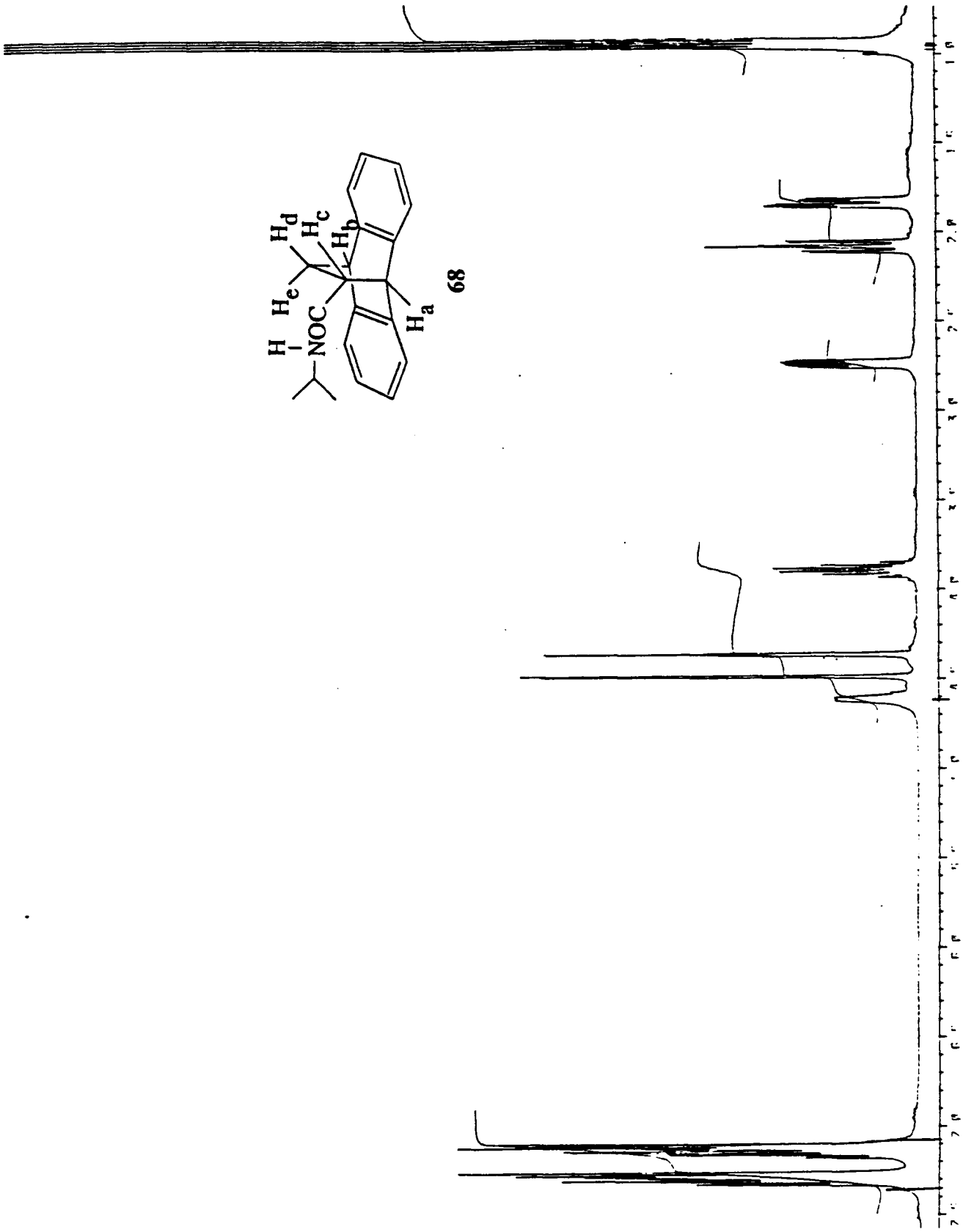


Figure XLVII: Proton NMR Spectrum of Monoamide Photoproduct 68

Mechanistic Considerations

Mechanistically, the formation of the monosubstituted amide **68** and the lactam **67**, upon photolysis of the di-*iso*-propyl starting material **37**, should be expected to occur in the same manner as for the dibenzyl photoproducts.[28b] However, as noted earlier, the cycloaddition of ketenes and imines have been limited to aromatic imines with few exceptions.[66] This then raises the question of whether the β-lactam **68** formed from the di-*iso*-propyl adduct **37** is perhaps produced by an alternate mechanism such as simple ring closure of the biradical. Again the presence of a ketene intermediate in the formation of the lactam is confirmed by the irradiation of the starting material in methanol. The only photoproducts of this photolysis are the symmetrical semibullvalene **66**, produced by the di-π-methane rearrangement, and the bridgehead-reduced methyl ester **60** found in the methanol photolyses of both the diethyl and dibenzyl adducts (compounds **34** and **35**). The ratio of semibullvalene to ester is 60:40, roughly the same as di-π-methane product to abstraction products when the photolysis is carried out in benzene and acetonitrile. Instead of producing any monosubstituted amide **67** or lactam **68**, the ketene intermediate in the methanol photolyses is completely trapped by the solvent.

In all of the solvents studied, the relative amounts of the di-π-methane reaction and the abstraction reactions are roughly equal, except for acetone. In acetone, the di-π-methane product **66** predominates, accompanied by a slight increase in amount of β-lactam **67** formed. Generally when one sees that the photochemistry of a substrate deviates upon photolysis in acetone versus other solvents, the inclination is to attribute the change to triplet sensitization of the substrate. In other words, instead of the substrate absorbing a photon of light directly, it achieves an excited state by energy transfer from an excited acetone molecule. There are several reasons why acetone will act as a triplet sensitizer unlike other common solvents. A sensitizer must be excited by the irradiation being used. For most solvents the wavelength of photolysis is too long to be absorbed. However, acetone has its n->π* absorption maximum in the region of 270-280 nm,

which is within the limits of irradiation through Pyrex. Furthermore, acetone is capable of transferring its absorbed energy to excite dissolved reactant molecules. However, a look at the kinetic scheme in Figure XLVIII;

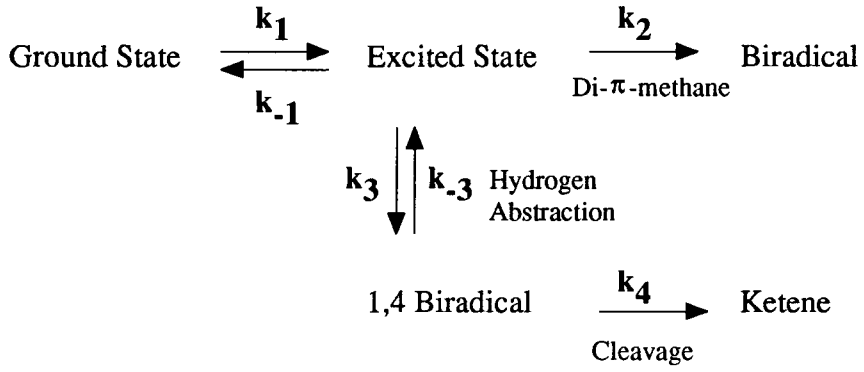


Figure XLVIII: Kinetic Scheme for the Irradiation of Monoamide Adducts

shows that since both the di-π-methane product and the abstraction products are derived from the same excited state, the only effect that sensitization can have is achieve this excited state more rapidly. Once created, however, sensitization will have no effect on the rates of formation of the various products from the excited state, as both products are a result of reaction from triplet states. The reason for the different product ratios in acetone can not be due to sensitization of the starting material.

Solid State Results

Irradiation of single crystals and powdered samples of the starting amide **37** resulted in the formation of a single photoproduct, the semibullvalene. An examination of the X-ray structural diagram of the di-*iso*-propyl adduct **37** in Figure XLIX shows that the isopropyl groups are oriented in such a manner as to put the amide methine hydrogen H(13) outside the predicted limit for abstraction by the β-carbon of the bridging double bond. The distance from H(13) to C(12) was calculated to be 3.13 Å. As in the case of the solid state irradiation of the diethyl amide **34**, this exceeds the sum of the van der

Waal radii for carbon and hydrogen (2.90 Å).[64] As such the only reaction pathway viable for the di-*iso*-propyl adduct **37** in the solid state is the di-π-methane reaction.

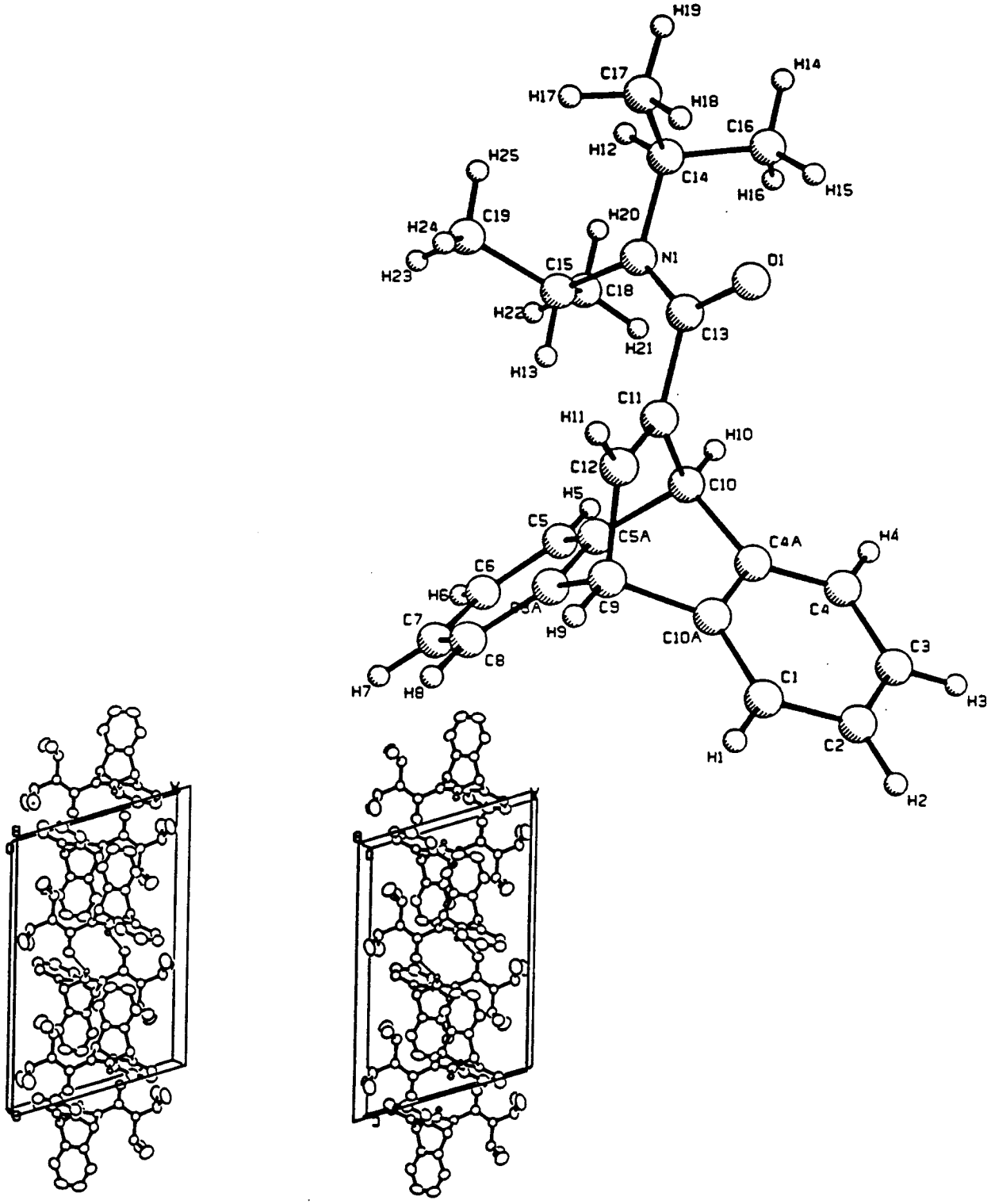


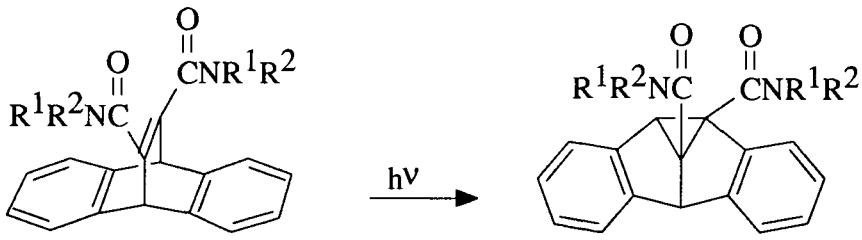
Figure XLIX: X-ray Structure of Dibenzobarrelene Di-*iso*-propylamide **37**

Abstraction Products Distribution

A comparison of the photoproduct ratios of the di-*iso*-propyl adduct **37** to those of the dibenzyl adduct **35** shows that the percentage of di-π-methane product has remained roughly constant. What has changed is the relative amounts of lactam to monosubstituted amide. In fact, one can include the diethyl adduct **34** results to show that the ratio of monosubstituted amide to lactam is a semi-quantitative measure of the efficiency with which the imine produced will be hydrolyzed. This in turn can be related to the relative stabilities of the imines involved. The aromatic imine that results from the irradiation of the dibenzyl adduct **35** cyclizes at a faster rate than hydrolysis and amine attack on the ketene. Thus more of β-lactam **63** is produced than of the monosubstituted amide **62**. The di-*iso*-propyl amide adduct **37** produces a small amount of lactam **68** indicating that the rate of hydrolysis of the di-*iso*-propyl-derived imine and amine attack on the ketene is slightly less than the rate of ketene attack by the imine. Lastly, the diethyl adduct **34**, which produced no detectable amounts of β-lactam, produces an imine that results in reaction with the ketene only after being hydrolyzed to a primary amine.

III: Photochemical Reactions of Symmetrical Dibenzobarrelene Diamides

The symmetrical dibenzobarrelene diamide series of compounds (Figure L) was chosen for study for several reasons. Dibenzobarrelene diesters and acids have been extensively studied[10,14,15,17] both in solution and in the solid state. These studies have yielded many insights into the di-π-methane photorearrangement as well as contributing much to the understanding of basic fundamental processes in solid state photochemistry. By extending these studies to amides, it was hoped to determine if and how diamides might react differently from diesters, particularly in the solid state. Additionally, because amides have two sites of substitution, whereas esters have only one, it becomes possible to compare the effect of varying the alkyl substituent and the degree of hydrogen bonding present.



38: R^1, R^2 = Me
39: R^1 = H; R^2 = Me
40: R^1,R^2 = Et
41: R^1 = H; R^2 = Et

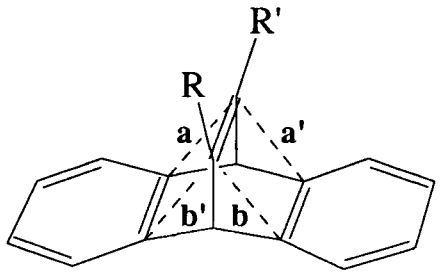
69: R^1, R^2 = Me
70: R^1 = H; R^2 = Me
71: R^1, R^2 = Et
72: R^1 = H; R^2 = Et

Figure L: Photolysis of Symmetrical Diamide Adducts

A: N,N-Dimethyl and N-Methyl Adducts

The first two symmetrical diamides chosen for study were the N,N-dimethyl diamide adduct **38** and the N-methyl diamide adduct **39**. The main difference in the two substrates, other than the obvious reduction by two in the number of methyl groups, is the presence of a hydrogen on each nitrogen in the N-methyl adduct which is available for hydrogen-bonding. As previously discussed, by varying the concentration of the

dibenzobarrelene mixed ester-acid substrate and therefore the type of hydrogen-bonding present, Scheffer et al[17] were able to direct the regiochemistry of the resulting di-π-methane photorearrangement. This type of effect would not necessarily be seen with these substrates because of the symmetrical nature of the starting materials. When the bridgehead double bond of a dibenzobarrelene adduct is unsymmetrically substituted, as with the mixed ester-acid and the monoamide adducts, there are two possible products resulting from four aromatic ring attack pathways (Figure LI).



When R is the same as R': a = b and a' = b'
while a/a' and b/b' lead to enantiomers.
When R and R' are not the same:
(a,a') give enantiomers of one product
(b,b') give enantiomers of its regioisomer

Figure LI: Product Formation in the Di-π-methane Rearrangement

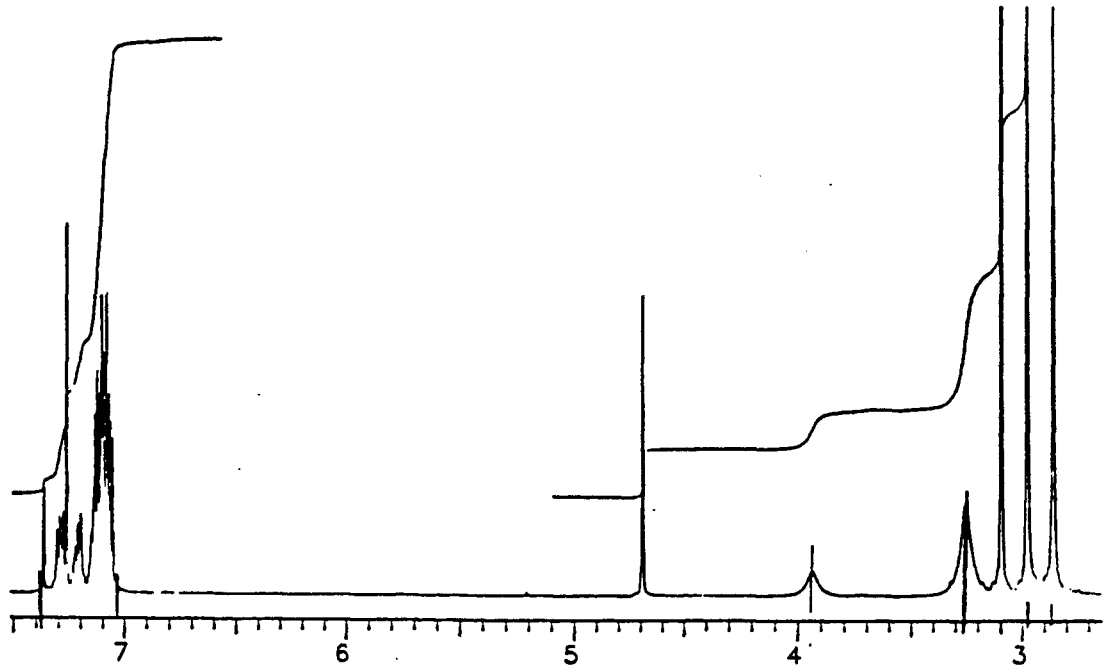
However, the photolysis of symmetrically substituted dibenzobarrelenes can not produce regioisomeric semibullvalenes, only enantiomers, and as such the directing influence of the hydrogen bonding would not be observable, unless optically active products are formed. It is possible, though, that other hydrogen-bonding effects might be found in solid state photolyses, due to the increased lattice strength of the crystal.

Both the N-methyl diamide **38** and N,N-dimethyl diamide **39** adducts were found to be only slightly soluble in all the solvents used for photolysis. As a result, it was not possible to study the photolysis of these compounds over as wide a range of concentrations as other substrates. Photolyses were performed primarily on saturated

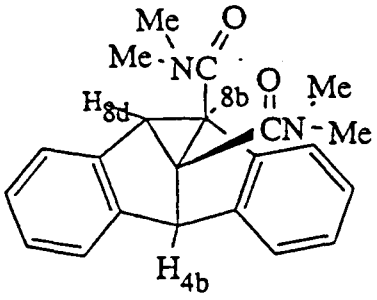
solutions of both diamide adducts. Irradiation of dilute samples were also carried out with no change in results. Both the N-methyl and N,N-dimethyl adducts gave only one photoproduct upon irradiation. These photoproducts were determined to be derived from a di-π-methane rearrangement of the starting materials.

The infrared spectrum of the N,N-dimethyl photoproduct **69** displayed a single broad absorption at 1636 cm^{-1} indicating the presence of a saturated amide. The interpretation of the proton NMR spectrum of the N,N-dimethyl photoproduct **69** is straightforward except for one feature. As expected, the spectrum has an aromatic region, two pentalene singlets, and four methyl singlets. But as seen in Figure L, one of the pentalene singlets and one of the methyl singlets is broadened. When proton NMR spectra are run at low temperature, this broadening is eliminated.

The peak position of the pentalene singlet identifies it as the hydrogen on carbon-(8d). This assignment is made based on its upfield position relative to the second pentalene hydrogen signal and its lower number of adjacent phenyl substituents. Phenyl substituents have a deshielding effect on the cyclopropapentalene hydrogens.



Ambient Temperature



69

-40°C

Figure LII: NMR spectra of N,N-Dimethyl Diamide Photoproduct 69

The broadened methyl singlet can not be as readily identified. Looking at the photoproduct, there is no obvious methyl which one could say should have an unusual interaction with the pentalene hydrogen. Two possible explanations for the broadening of these peaks are quadrupolar interactions and conformational equilibrium.

For a nucleus to be NMR active, such as hydrogen and carbon, it must have a spin angular momentum, I, greater than zero.[74] NMR active nuclei that spin in an ellipsoidal manner ($I > 1/2$) possess a quadrupole moment and as such can exhibit quadrupolar effects in the NMR spectra of other active nuclei. For example, nitrogen ($I = 1$) has a quadrupolar moment that can result in broadening of the signal, in the proton spectrum, of a hydrogen attached to the nitrogen. This effect is seen throughout this thesis in the proton spectra of the secondary amides, where the O=C-N-**H** signal is always broad. This broadening is a result of the rate of nuclear spin transitions among the spin states of the nitrogen. If the rate of transitions among the spin states of nitrogen is much faster than the rate of proton transitions, the proton "sees" only the average electronic moment of the nitrogen(i.e. it sees only one spin state). Thus the nitrogen and the hydrogen are no longer coupled and the proton signal will be sharp. If, however, the rate of transitions among the spin states of nitrogen is of the same order of time required for proton transitions, both the spin states of hydrogen "see" all the spin states of nitrogen and nuclear quadrupole broadening results. However, as quadrupole broadening is not temperature dependent, this effect can not account for the broadening in the NMR of photoproduct **69**. Additionally, the hydrogens involved in the broadening are six bonds apart so that the broadening is likely caused by a through-space effect. Again this is not consistent with a quadrupolar interaction.

Because four distinct methyl peaks are seen, the rotation about the CO-N bond must be very slow on the NMR time scale. In order to explain the signal broadening in the spectrum of **69** by conformational equilibrium, some sort of steric interaction

between one of the methyl groups and the pentalene hydrogen involved must occur. Since the remaining methyl peaks are sharp, this interaction must not affect the NMR environment of the other methyl groups. Models of the photoproduct do indicate the possibility of an interaction between one of the methyls of the amide group attached to carbon-(8b) and the hydrogen attached to carbon-(8d). As well, temperature dependent NMR experiments exhibit peak sharpening at higher temperatures. This would be consistent with the relief of a steric interaction by an increase in the rotation about the C-N double bond.

In contrast, the proton NMR of the N-methyl photoproduct **70** exhibits well defined signals for the both the methyl hydrogens and the cyclopropapentalene hydrogens. The infrared spectrum of the dimethyl product indicates the presence of considerable hydrogen-bonding, as evidenced by a broad medium-strength band in the N-H region. There is a certain degree of amide proton not involved in hydrogen-bonding as shown by two sharp bands in the same region.

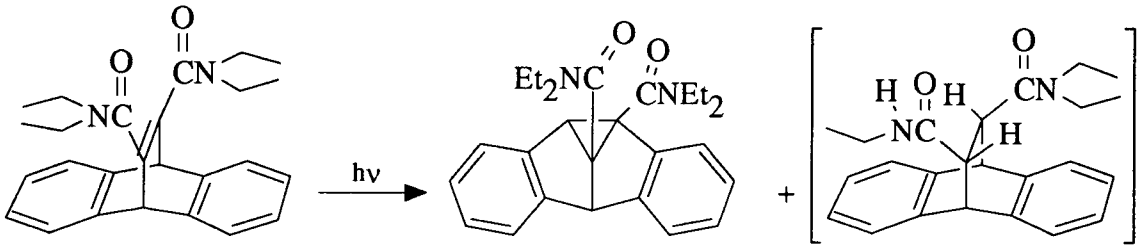
Solid state irradiations of the N-methyl and N,N-dimethyl diamide adducts (compounds **38** and **39**) were performed on both powdered and crystalline samples. The N,N-dimethyl adduct reacted readily to give the same photoproduct **69** that was obtained in solution. These reactions could be carried out to high degrees of conversion (> 70%) without concurrent melting of the crystals or powder. On the other hand, irradiation of crystals or powders of the N-methyl starting material **39** resulted in very little reaction. Extended photolyses, on the order of several days, produced the solution photoproduct with a degree of conversion that was at best seven percent.

The difference in solid state reactivity of these two adducts is possibly due to the contribution of the strong hydrogen-bonding forces in the crystals of the N-methyl diamide (**38**). If the starting material molecules are rigidly held in the crystal lattice by hydrogen bonds, their ability to undergo the atomic motions necessary for the di-π-

methane rearrangement could be severely impeded. The rate of reaction may be sufficiently slowed that processes involving decay of the excited state back to the ground state become more important. Attempts to grow crystals of the two starting materials for X-ray crystallographic analyses were unsuccessful in both cases. The poor solubility of the two diamides in all solvents tried resulted in inferior crystals of limited size. Therefore, X-ray crystallographic evidence on the extent of hydrogen bonding was not obtainable.

B: N,N-Diethyl and N-Ethyl Adducts

The study of the symmetrical N,N-diethyl dibenzobarrelene diamide **40** was carried out for several reasons. The photolysis of the N,N-diethyl adduct in solution and in the solid state might provide further information regarding the reactivity pattern seen with the methyl diamide adducts. Additionally, it was thought that, since there are two diethyl amide groups present in the molecule, the hydrogen abstraction reaction which produces a saturated-bridge monosubstituted amide, as seen with the diethyl monoamide adduct **34**, might play a greater role, both in the solution reactions and in the solid state.



40 **71** **71a**

Figure LIII: Possible Products from Photolysis of N,N-Diethyl Diamide Adduct **40**

Surprisingly, the photolysis of the N,N-diethyl adduct in solution resulted in the formation of only a single photoproduct, the N,N-diethyl semibullvalene **71**. The

photoreaction was performed in acetone, acetonitrile and benzene with no evidence of any abstraction product **71a**. The photolyses were accompanied by a significant yellowing of the photolysate solution, unlike the methyl adduct irradiations.

The reason for the lack of abstraction product formation is not immediately obvious. The yellowing of the photolysate and the presence of many minor peaks in the glc analyses of the reaction mixture indicates that the some of the starting material is being photodecomposed. It is possible that steric interactions between the two amide groups impede the adoption of the correct conformation for hydrogen abstraction. The N,N-diethyl diamide adduct **40** undergoes the di-π-methane rearrangement rapidly, as indicated. If hydrogen abstraction and ketene formation were sufficiently slow and the rate of the di-π-methane rearrangement sufficiently fast, abstraction products would not be seen.

The final symmetrical diamide starting material studied was the N-ethyl diamide adduct **41**. This material, like the two methyl diamides studied, displayed limited solubility in the solvents used for photolyses. Irradiation of solutions of the N-ethyl adduct resulted in the formation of a single photoproduct. This product was subsequently identified as the di-π-methane rearrangement-derived semibullvalene **72**. Again, as with the photolyses of the methyl adducts, the photoreaction was very clean and accompanied by very little yellowing of the photolysate solution.

In the proton NMR spectrum, all the pentalene, methylene, and methyl signals appear as sharp peaks, with the only broad peaks being the amide proton signals at δ 6.48 and 6.42. The infrared spectrum indicated the presence of both free and hydrogen bonded amides.

Solid state irradiations of crystals and powdered samples of the N-ethyl adduct **41** resulted in the formation of the semibullvalene product **72** found in solution photolysis.

However, as in the case of the dimethyl adduct overall rate was very slow, amounting to ten percent after several days of irradiation.

Again the reduced reactivity in the solid state can be attributed to the presence of strong hydrogen bonds within the crystal lattice of the starting material. The larger nature of the amide's alkyl substituents could account for the slight increase in reactivity by adding an element of disruption to the crystal packing, perhaps reducing the effectiveness of the hydrogen bonds. However, as with the dimethyl starting material **39**, an X-ray crystallographic analysis of the crystal packing could not be performed due to poor crystal quality.

IV: Photochemical Reactions of Dibenzobarrelene Ester-Amides

By converting one of the ester moieties of the dimethyl dibenzobarrelene diester **9** to an amide one obtains a difunctional ester-amide adduct. The photolysis of this sort of adduct allows one to compare the influence the respective groups have on the type of reactions that can occur and on the products formed. As seen in previous sections of this thesis and in the literature[10,14,15], dibenzobarrelene systems substituted with one or two esters readily undergo the di-π-methane photorearrangement, as do some of their amide analogs. However, there are no reports in the literature of di-π-methane systems that offer a direct comparison between the influence an ester has on this photoreaction *vs.* the influence of an amide.

In an effort to minimize the variables in the study, it was decided to maintain the same alkyl substituent on the ester throughout the series of compounds while the substituents on the amide were varied. The reasons for this are twofold. Previous studies[16] of dibenzobarrelene mixed diesters found that the photolysate obtained upon irradiation generally consisted of a mixture of the two possible regioisomers from the di-π-methane rearrangement. From this, it was determined that in solution photolyses the influence of the simple esters did not vary much as one progressed through the series of methyl, ethyl, propyl and butyl esters. As well, in addition to comparing the relative ester and amide substituent effects on the di-π-methane rearrangement, the influence of the ester group on the extent of the direct participation of the amide alkyl groups in photochemical hydrogen abstraction reactions can be judged.

A: Di-π-methane Reactions of Ester-Amides

The first two ester-amide adducts chosen for study, compounds **45** and **47** (Figure LIV), were selected specifically for their expected lack of photoreactions involving the amide alkyl groups. This allows for an unambiguous assessment of the relative influences

of the two functional groups on the di-π-methane rearrangement. From the studies on the dibenzobarrelene monoamides and symmetrical diamides, it was determined that dimethylamides and ethylamides were among those amides that did not produce any hydrogen abstraction products upon irradiation and provided the least amount of solubility problems.

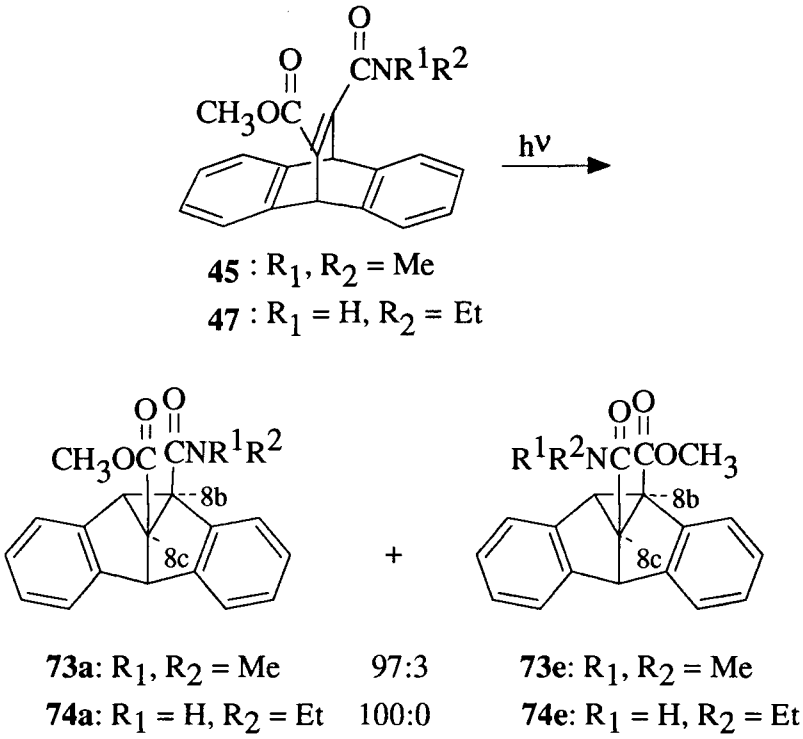


Figure LIV: Photolysis of Simple Dibenzobarrelene Ester-Amides

Photolysis of the methyl ester/dimethyl amide starting material, compound **45**, in various solvent systems resulted in the rapid formation of two photoproducts. The photoreaction proceeded cleanly and efficiently with a slightly yellow amorphous solid being recovered after concentration of the photolysate. The two photoproducts, **73a** and **73e**, were found to be regioisomeric products of the di-π-methane reaction. The product ratio (97:3) was heavily in favour of the structure with the amide functional group attached to the carbon (C-8b) adjacent to a phenyl ring (Figure LIV).

Photoproducts Structure Determination

Identification of the two photoproducts as semibullvalenes was facilitated by the similarities in their spectra to other semibullvalenes. Infrared spectra of the two photoproducts exhibited very little differences in the bands that corresponded to a saturated ester (1728 vs. 1724 cm^{-1}), as well as in the bands that corresponded to a saturated amide (1646 vs. 1646 cm^{-1}).[56] However, because all of the aliphatic signals in the proton NMR spectra are singlets, assignment of the location of the amide and ester functionalities is totally dependent on signal position. The similarity in product structures does not allow for this with any degree of certainty without an independent means of confirmation.

There are literature reports[16] on the identification by proton NMR of reaction product ratios of the regiomeric mixtures that resulted from the photolysis of a series of dibenzobarrelene mixed methyl ester/alkyl ester adducts. Centring on the ester methyl signals of the product mixtures, the spectra clearly exhibited two sharp and well resolved singlets at δ 3.70 and 3.85 ppm that were assigned respectively to the methyl ester groups attached to carbon-(8c) and carbon-(8b). This assignment is consistent with the ester methyl attached to a carbon adjacent to a phenyl ring (carbon-8(b)) being more deshielded and thus having an NMR signal that is further downfield. This correlation was found to hold over a series of ten mixed diester photoproduct mixtures. Several independently confirmed examples of the methyl esters of semibullvalene ester-amides conforming to this pattern would be needed before any reliance could be placed in structural assignment by this type of analysis.

Mass Spectra Analysis

A second method of assigning structures to mixed diester semibullvalene regioisomers was developed based on the fragmentation patterns obtained from mass

spectra.[75] The fragmentation pattern in the high mass range was characterized by the loss of the two ester substituents, either as molecular or as radical fragments. The key to the mass spectral behaviour is that the nature of these fragments depends on the location of the ester group on the two non-equivalent cyclopropyl positions of the semibullvalene. The following correlations were noted:

1) Ester substituents at carbon-(8b) (the benzylic cyclopropyl carbon) can be lost to give $[M - (R\text{-}OH)]^+$, where R is the alkyl portion of the ester, or more typically lost as $[M - (R\text{-}OH + C{=}O)]^+$,

2) Ester substituents at carbon-(8c) are typically lost as $[M - (R\text{-}O\cdot)]^+$ or as $[M - (R\text{-}O\cdot + C{=}O)]^+$,

3) Ester substituents at carbon-(8b) possessing abstractable γ-hydrogens may also undergo the McLafferty rearrangement. This fragmentation pathway is not seen for substituents at carbon-(8c) even when hydrogens available for abstraction are present.

A consideration of the mechanisms thought to be involved in these fragmentations offers an explanation for these observations.

The mechanism by which the loss of alcohol molecules and alkoxy radicals is thought to occur is one that involves a double hydrogen atom transfer between the two ester functional groups.[76] This requires that a hydrogen atom is first abstracted by the carbonyl oxygen of the ester group at carbon-(8c) and that the same hydrogen is transferred as a proton to the alkoxy oxygen of the ester group at carbon-(8b), resulting in the loss of the protonated alkoxy group as a molecular fragment (Figure LV).

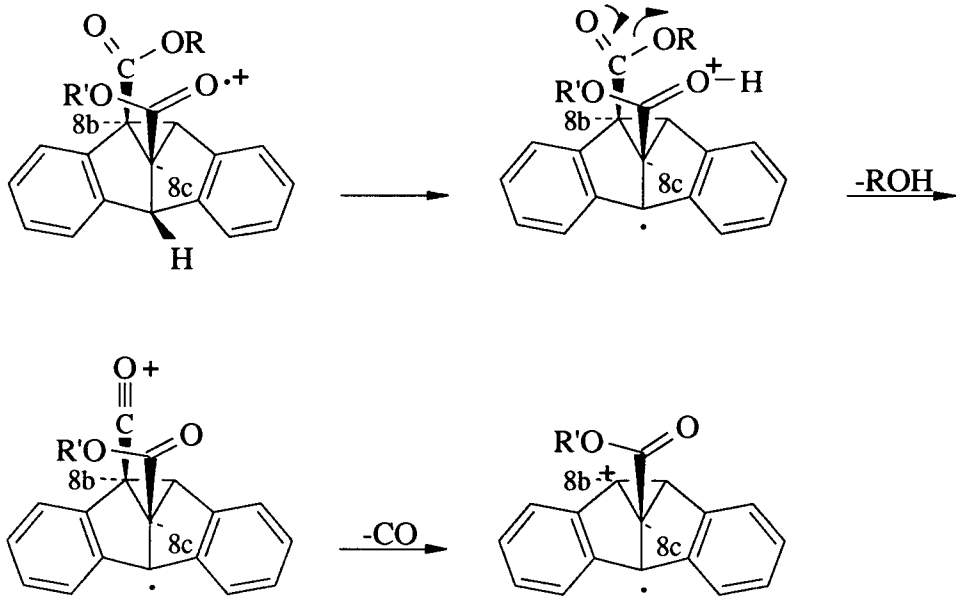


Figure LV: Stereospecific Fragmentation Of Semibullvalene Mixed Diesters

Of the two cyclopropapentalene hydrogens available for abstraction, the one most likely to be involved in this process is the bisbenzylic hydrogen attached at carbon-(4b). This hydrogen can be presumed to be more reactive due to the stabilizing influence of the two benzo groups. The lesser reactivity of the hydrogen attached to carbon-(8d) would explain why hydrogen transfer from the ester at carbon-(8b) to the ester at carbon-(8c) does not occur to any great extent.

The ester group at carbon-(8c) also fragments, in competition with the hydrogen abstraction and transfer, by normal α-cleavage to yield $[M - RO\cdot]^+$ and $[M - (RO\cdot + C{=}O)]^+$ ions. The lack of M^{c}Lafferty rearrangement at the ester group at carbon-(8c) is likely a result of being a relatively slower process compared to other fragmentation pathways, such as abstraction of hydrogen-(4b) or α-cleavage.

There are several points that have to be considered in any attempt to apply these fragmentation pattern findings to the analysis of dibenzosemibullvalene ester-amide regioisomers. In the case where the amide group is attached to carbon-(8c), the ability of the amide carbonyl to abstract the hydrogen at carbon-(4b) and subsequently transfer the

hydrogen to the ester attached to carbon-(8b) will be of primary importance if the pattern is to hold. Where the amide group is attached to carbon-(8b) and the ester attached to carbon-(8c), the ability of the amide functional group to accept an abstracted hydrogen atom and fragment to give the molecular amine and carbon monoxide determines whether or not this type of analysis will apply.

Attempts to apply this type of analysis to the photoproducts of the irradiation of the dibenzobarrelene methyl ester/dimethyl amide adducts were a partial success. The proposed structure for the major photoproduct **73a**, with the amide group attached to carbon-(8b), would be expected to exhibit a fragmentation pattern in the mass spectrum that involved the loss of molecular dimethylamine and carbon monoxide, as well as peaks resulting from the loss of methoxy and carbomethoxy radicals. What was found in the mass spectrum of **73a** was a fragmentation pattern that clearly showed the peaks resulting from the loss of the radical fragments but with no indication of the peaks arising from molecular loss of amine. The first significant fragmentation peak after the parent ion at 333 mass units occurs at 302 mass units, corresponding to the loss of a methoxy radical. A fragment loss of 59 mass units to give a peak at 274 mass units can be attributed to a carbomethoxy radical.

From the proposed structure for the minor photoproduct **73e**, with the ester group attached to carbon-(8b) (in the benzylic position) and the amide attached to carbon-(8c), one would expect a fragmentation pattern involving the loss of molecular methanol and carbon monoxide, accompanied by peaks derived from the loss of dimethylamino and dimethylamido radicals. In fact, what are seen are peaks which correspond to the loss of molecular methanol (32 mass units) and methanol plus carbon monoxide (60 mass units for a peak of 273 mass units). Again, however, the peak that should have arisen due to the fragmentation of the amide group to give the dimethylamino radical was not seen.

In both mass spectra, the predominant method of fragmentation of the amide group is α-cleavage. This is clearly seen as a peak at 261 mass units, corresponding to

the loss of the dimethylamido radical (72 mass units). It would therefore seem that of the two conditions set out for use of this method of analysis, only one has held true: the amide group might well be able to abstract and transfer the hydrogen attached to carbon-(4b), resulting in the desired ester fragmentation; however, when the amide itself is in the role of receiving the abstracted hydrogen, its behaviour does not conform to expectation. There are several reasons why the amide group might undergo α-cleavage instead of fragmenting like the ester. It is possible that α-cleavage occurs at too fast a rate to allow for the observation of the $[M - (Me_2N\text{-}H)]^+$ ion, or the transfer of the proton from the ester to the amide may not be efficient enough for any significant amounts of the fragmentation to occur.

An assessment of the utility of this type of analysis to dibenzobarrelene ester amide regioisomers could not be made without more examples. Of all the ester amides investigated in this study, the dibenzobarrelene methyl ester/dimethyl amide adduct **45** was the only one to give a mixture of dibenzosemibullvalenes upon irradiation. The structural assignments made above really would hold no weight without independent confirmation.

Alternate Synthesis of Photoproduct 73a

With this in mind, an alternate synthetic pathway to the major photoproduct, **73a**, from photolysis of methyl ester/dimethyl amide adduct **45**, was devised. The reason for choosing the major photoproduct as a synthetic target was simple: it involved an easier synthetic route. The synthetic routes to both photoproducts involved a Weinreb aminolysis on one of either methyl 9-anthracenecarboxylate or on methyl propiolate and subsequent Diels-Alder reaction between the isolated amide and its corresponding ester reactant (Figure LVI).

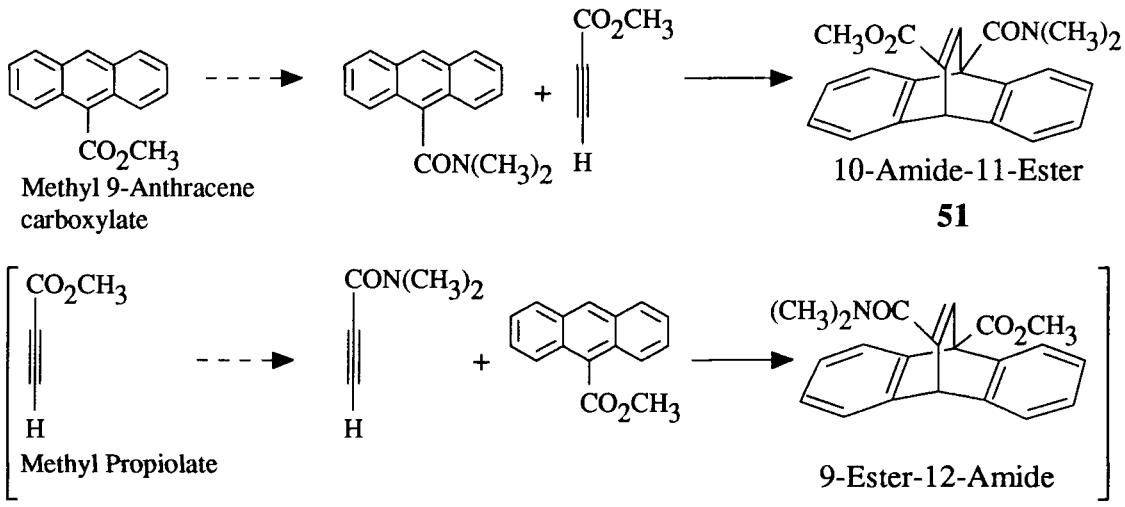
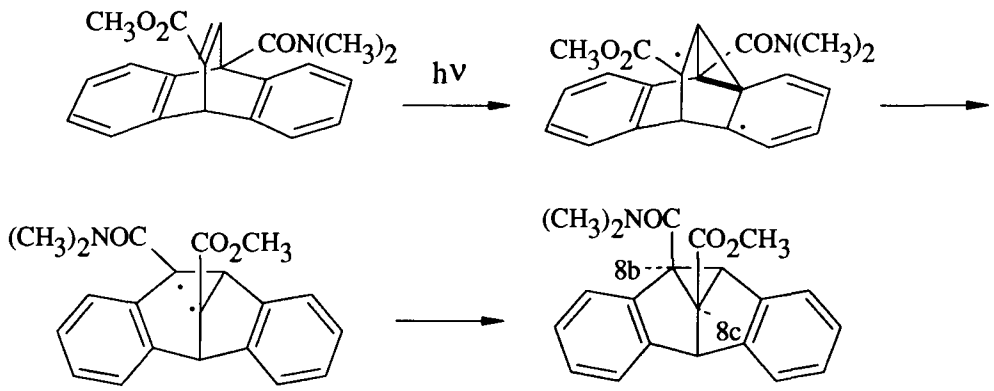


Figure LVI: Substrates for Alternate Synthesis of Photoproducts from **45**

The anthracenecarboxylate and its amide derivative, being solids, were much easier to handle than attempting to chemically manipulate the noxious acetylenic ester. When efforts were made to convert the acetylenic ester to the amide, the result was an extremely complex reaction mixture probably due to reaction between the aluminum amide complex and the triple bond.

The Diels-Alder reaction between methyl propiolate and N,N-dimethyl 9-anthraceneamide resulted in the recovery of the 10-amide-11-ester adduct **51** only. The corresponding 9-amide-11-ester adduct, formed by a head-to-head addition of the reactants (see Figure XXIV; page 36), was not isolated. The regioselectivity of this Diels-Alder reaction is likely a consequence of steric interaction between the acyl groups of the reactants.

The photolysis of one of the two dibenzobarrelene adducts in Figure LVI should lead to one and only one of the photoproducts of the methyl ester/dimethyl amide **45**. As shown in Figure LVII, the photolysis of the 10-amide-11-ester **51** was expected to lead to a dibenzosemibullvalene product with the amide attached to carbon-(8b) and the ester attached to carbon-(8c), *i.e,* compound **73a**.



73a

Figure LVII: Photolysis of 10-Amide-11-Ester Adduct **51**

As discussed with the dibenzobarrelene monoamide series of compounds, the first step in the di-π-methane mechanism[4], after excitation, is aromatic ring attack to give the most stable biradical intermediate. The fact that vinyl monosubstituted dibenzobarrelenes esters/amides rearrange with complete regioselectivity to give a semibullvalene substituted at carbon-(8c) has been interpreted in terms of the odd-electron centre stabilization by the carbon group on the proposed biradical intermediates. This results in a biradical with one radical stabilized by a cyclohexadienyl ring system and the other stabilized by the acyl group. The next step in the mechanism is the homolytic cleavage of the bold-face bond in the second structure of Figure LV. This re-establishes the aromaticity in the benzene ring, giving a second biradical. Biradical closure gives the semibullvalene product.

The irradiation of the 9-carbomethoxy dibenzobarrelene (**6**) gave a 67:33 mixture of semibullvalene regioisomers (see Figure IV page 7).[10] This result was interpreted by Hixson et al.[3b] as arising from the reluctance of the rearranging molecule to position the electronegative carbomethoxy group at an incipient cyclopropyl site that is gaining substantial s character. This results in the acyl substituent favouring attachment to the bisbenzylic carbon-(4b) in the semibullvalene product, with attachment to the benzylic carbon-(8b) being less important. Thus the effect of the vinyl substituent and the

bridgehead substituent in 10-amide-11-ester adducts is to favour initial bond formation at opposite ends of the bridging vinyl bond. However, as seen in Figure IV, the influence of a vinyl substituent is stronger than the influence of a bridgehead substituent. As such, photolysis of this starting material, compound **51**, should give a semibullvalene product that results from initial bond formation to the end of the vinyl bond *beta* to the ester. This photoproduct would have the amide attached to carbon-(8b) and the ester to carbon-(8c).

The photolysis of the 10-amide-11-ester adduct **51** was carried out and resulted in the formation of the semibullvalene photoproduct **73a** (Figure LVII). This product was found to be spectroscopically (IR, MS, NMR) and physically (mp) identical to the major photoproduct from the irradiation of the dibenzobarrelene 11-(methyl ester)/12-(dimethyl amide) adduct, compound **45**.

The single photoproduct from the irradiation of the 11-(methyl ester)/12-(ethyl amide) adduct, compound **47**, was also found to have the amide group attached to the benzylic carbon-(8b). This was determined by analysis of the fragmentation pattern in the mass spectrum of **47** and by the position of the ester methyl signal in the proton NMR spectrum. In fact, in all the ester-amides that reacted via the di-π-methane rearrangement, except for the methyl ester/dimethyl amide case discussed above, the only regioisomer formed was that with the amide located adjacent to the phenyl ring (attached to carbon-(8b)).

B: Regioselectivity of the Di-π-methane Reaction of Ester-Amides

Any explanation of the regioselectivity observed in the di-π-methane rearrangement of dibenzobarrelene ester-amides must be based on the different ways in which the amide and ester groups might be influencing the di-π-methane photoreaction. As such a more in-depth analysis of the mechanism of the di-π-methane rearrangement with respect to these ester-amides is needed.

Radical Intermediate Stabilization Theory

Irradiation of a dibenzobarrelene ester-amide results in initial excitation by the absorption of a photon of light, forming an excited state. As seen in the section above, this excited state can undergo bond formation between one of the two bridge radicals and a phenyl ring to give a ground state biradical intermediate. However, unlike the vinyl monosubstituted dibenzobarrelene adducts, there are two biradical intermediates that are possible in the case of the ester-amides. Both biradical intermediates are resonance stabilized by an acyl substituent; one by an ester and one by an amide. It is possible to rationalize the regiochemistry of the photoproducts from the di-π-methane rearrangement of these ester-amides based on the relative stabilities of these two biradical intermediates.

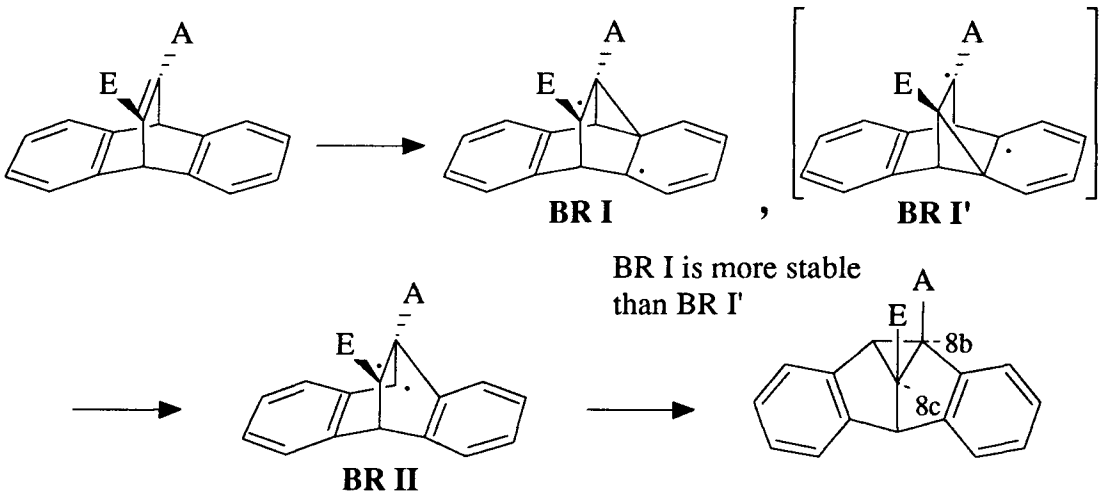


Figure LVIII: Product Formation as a Result of Radical Stability

This type of radical stability comparison has been rationalized previously on the basis of a simple perturbation molecular orbital argument. Garcia-Garibay et al.[17b] studied the photochemistry of dibenzobarrelene mixed acid-esters and found that when the acid was dissociated the ester was a better radical stabilizer than the carboxylate anion.

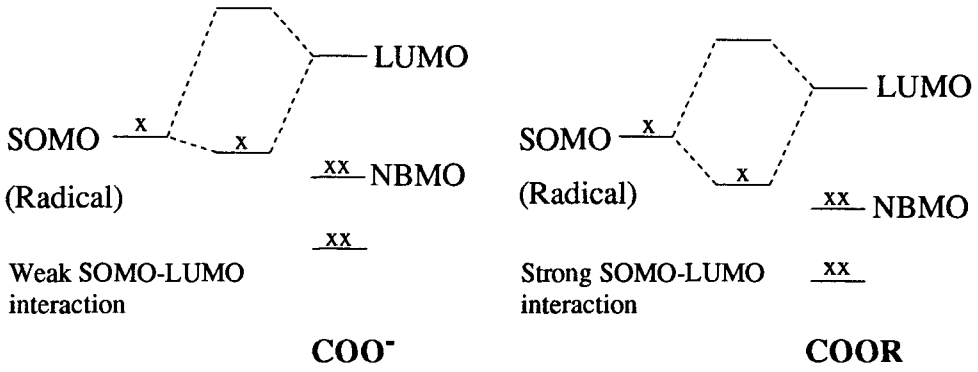
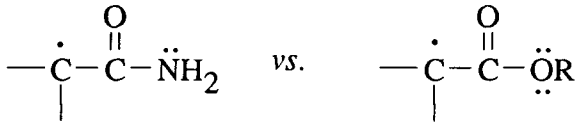


Figure LIX: PMO Diagrams for Carboxylate Ion and Ester

Qualitatively, it might be expected that a radical centre would have a more favourable resonance interaction with an adjacent ester group than with a carboxylate ion. The carbonyl group of the latter, having a very strong resonance interaction with the anionic oxygen, is presumably less "available" for resonance with the unpaired electron of the radical. The stabilizing interaction between a singly occupied p-orbital on a methylene group and the LUMO of either the COO^- or the COOR fragment should be less favourable in the former case owing to the higher LUMO energy of the carboxylate anion (greater SOMO-LUMO separation). The greater the energy difference between the SOMO and LUMO orbitals, the weaker is the interaction between the orbitals. A weaker interaction is manifested as a lesser degree of stabilization.

This argument can be applied to the case of the ester-amides. In this instance what is now being considered is the relative radical stabiliting abilities of an amide *vs.* an ester:



The amide nitrogen is less electronegative than the ester oxygen and as such the nitrogen is better able to donate a lone pair of electrons than oxygen. Thus resonance in the amide between the carbonyl and nitrogen is a much more important process than in the ester carbonyl and alkoxide oxygen. The strong resonance interaction between the amide carbonyl and nitrogen would mean that again the carbonyl is less "available" for

resonance with the unpaired electron of the radical. As a result the energy difference between the radical SOMO and the amide LUMO would be greater than the corresponding interaction involving a radical and an ester.

Data regarding the various radical-stabilizing abilities of the carboxylate anion, ester group and the amide group is very scarce. It is reasonable, however, to suggest that the effect of the amide group would be intermediary to that of the carboxylate ion and the ester. The effect of replacing the alkoxide oxygen of the carboxylate anion with an amino group would be to change the coefficients and therefore the size of the molecular orbitals involved in the resonance. This would alter the effectiveness of orbital overlap and would result in a less efficient resonance. Resonance involving atoms of the same kind (i.e. a carbonyl and anionic oxygen) is more efficient than resonance involving different atom types (i.e. carbonyl and amide nitrogen).[73] Additionally, there is no charge separation in the major resonance structures of the carboxylate anion group, whereas with an amide resonance involving the nitrogen entail a dipolar resonace structure. Dipolar resonance structures are less important than neutral or monopolar ones.

Radical Attack Theory

There is an alternate way to explain the observed regioselectivity. Although the photon that produces the excited state is absorbed by the bridging vinyl bond chromophore, the energy of excitation is associated with the molecule as a whole.[77] At least part of the time the energy of excitation can be thought of as residing with one of the phenyl rings. As such, the initial step of the di-π-methane rearrangement might be thought of as free radical addition of a cyclohexadienyl radical to a difunctional alkene, the bridging vinyl bond (Figure LX).

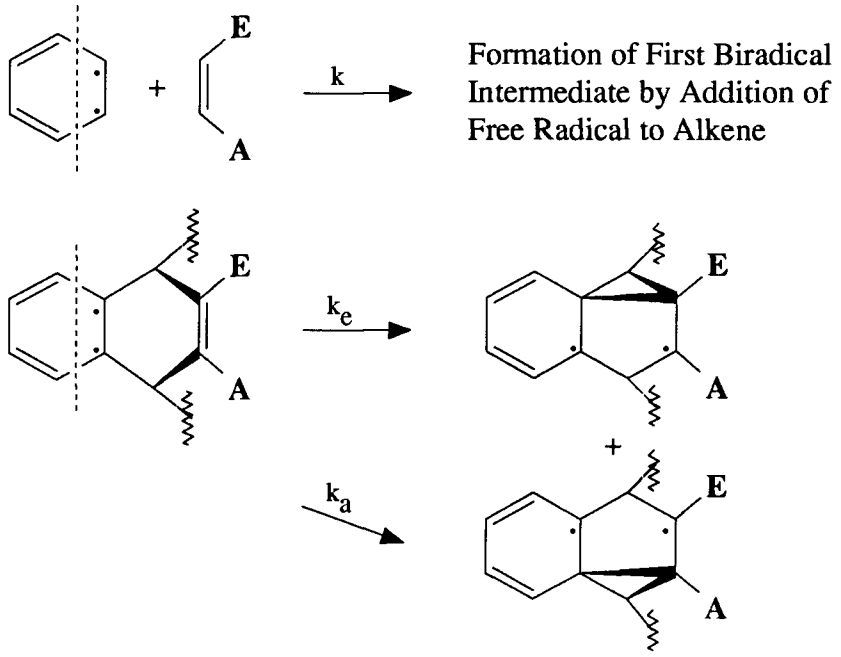


Figure LX: Additon of Free Radicals to Functionalized Alkenes

In this view, the formation of the first biradical intermediate of the di-π-methane rearrangement would be governed by the relative rates of addition of a free radical to different ends of the same alkene (k_e vs. k_a).[78] As seen in Figure LXI, the rate of addition of radicals increases with the electron-withdrawing ability of the substituent Z of the alkene.[79] This assumes that the formation of the first biradical intermediate (BR I) is irreversible, since if initial bond formation were reversible, product distribution would be governed by thermodynamic factors.

$$R^{\cdot} + H_2C{=}CHZ \xrightarrow{k_{rel}} RCH_2\text{-}{}^{\cdot}CHZ$$

where R is a cyclohexyl ring system

Z =	k_{rel} (at 20°C)
CHO	34
CN	24
$COCH_3$	13
CO_2CH_3	6.7
$CONH_2$	1.1
Ph	1.0
Cl	0.12
H	0.015

Figure LXI: Table of Relative Rates of Addition of a Radical to Functionalized Alkenes

Studies in radical additions, most notably by Giese et al.[79], have determined that the rate of addition of alkyl radicals to alkenes is controlled by steric and polar effects. The stabilities of the educts (that is the intermediates involved in the addition of a radical to a molecular species) and products are of only limited importance, since the transition states for these exothermic reactions occur very early along the reaction coordinate. Furthermore, in these additions substituents at the remote end of the reacting alkene (β-substituents) exert mainly polar effects on the rate of addition of free radicals. Radical-stabilizing and space-filling β-substituents influence the rate of addition only slightly. Substituents at the reacting centre of the alkene (α-substituents) exert both polar and steric effects on the rate of addition of free radicals. The polar α-effect is somewhat smaller than the β-polar effect.[79]

Comparing the relative rates of addition to a β-substituted amido-alkene and a β-substituted ester-alkene in Figure LXI, it can be seen that the rate of addition to the ester-substituted alkene is six times faster than to the amide-substituted alkene. Applying this

result to the dibenzobarrelene ester-amide system, one can predict that the photoproduct that would result from the di-π-methane rearrangement, if this is an appropriate mechanistic view of the reaction, would involve initial bond formation at the amide-substituted radical centre. This is consistent with the experimental results from the photolyses of dibenzobarrelene ester-amides.

In this consideration, the substituent attached to the carbon where initial bond formation occurs acts as an α-substituent and as a result can exert polar and steric effects. Steric effects can be discounted as the source of the regioselectivity in the di-π-methane rearrangement, as bulkier amides would be expected to give more of the dibenzosemibullvalene product with the ester attached to carbon-(8b). This was not found to be so. Additionally, the group that acts as an α-substituent is bonded to a carbon atom whose hybridization changes from sp^2 to sp^3 during the reaction. Thus, the stabilizing influence of the α-substituent on the bridging vinyl bond is removed during formation of the C-C bond to give the first biradical intermediate. If this hybridization change is manifested in the transition state for the free radical addition reaction, the substituent that is better able to stabilize the bridging vinyl bond (i.e. the ester) will exert a greater rate-reducing effect.[80] Whichever end of the double bond that experiences a greater rate reducing effect, will not be involved in initial bond formation. Thus the polar α-effect would act in conjunction with the β-polar effect, resulting in initial bond formation to the bridging vinyl carbon with the amide substituent.

The addition of a radical to an alkene substrate, substituted with an amide and two esters, has been studied. Porter et al.[81c] studied the addition of cyclohexyl radicals to various α,β-unsaturated amides. Among their findings was the result that addition to the substrate in Figure LXII was exclusively to the site of amide attachment.

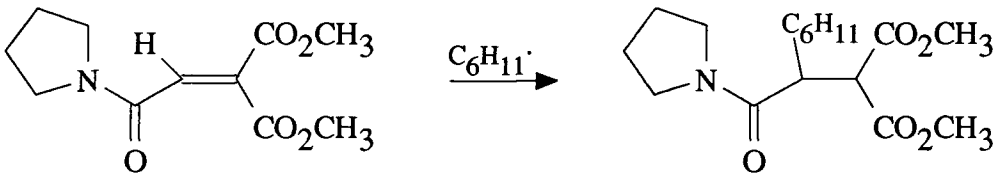


Figure LXII: Radical Addition to a Trifunctional Alkene

The rationale employed by Porter et al. to explain these results was based on ground state steric arguments with regards to the preferred conformation of the acyl substituents. The conformation of amides is much less mobile than that of esters, with allylic strain favouring the Z conformation. Approach of the radical to the amide end of the alkene on a nucleophilic trajectory is favoured by a Z conformation. However, this result is not very applicable to the case of the ester-amides since it involves a vicinal diester and the cyclohexyl radical is able to adopt any attacking orientation. However, it does demonstrate how vital a role steric effects can play in determining the selectivity of a reaction.

Radical Stabilization *vs.* Radical Attack

The question remains, however, as to which of these two explanations (radical stabilization of the biradical intermediate *vs.* relative rates of radical attack) more accurately reflects the true principle behind the regioselectivity observed in the di-π-methane rearrangement of dibenzobarrelene ester-amides. Both hypotheses give the same prediction so that it is impossible to distinguish between them based on the present system. To distinguish between these explanations, what is needed is a system which gives opposite predictions of reaction regioselectivity.

It has been determined that free radicals are better stabilized by phenyl substituents than by carbonyl groups.[81] Consequently, if radical stability is the determining factor in di-π-methane regioselectivity, then in a dibenzobarrelene system possessing a bridging double bond substituted with a phenyl group and a methyl ester

(**74**)[82], one would expect that photolysis would result in the major product being formed with the ester group attached to carbon-(8b) (**75e** in Figure LXIII). Conversely, a comparison of the rates of radical addition in Figure LXI shows that addition to the remote carbon of an ester-substituted alkene will be approximately seven times faster than addition to the remote carbon of a phenyl-substituted alkene. As such, the same phenyl group/methyl ester substituted system would be predicted to give the dibenzosemibullvalene product with the phenyl group attached to carbon-(8b) (**75p** in Figure LXIII).

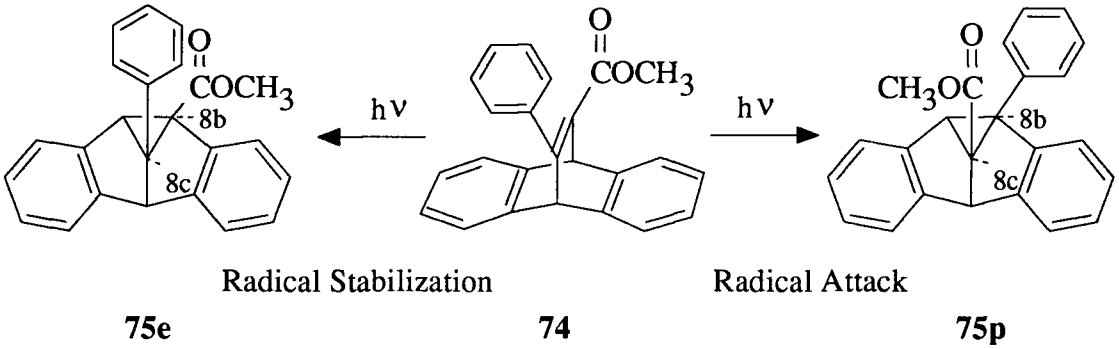


Figure LXIII: Predicted Photoproducts from the Irradiation of Adduct **74**

The preparation of compound **74**[82] was readily accomplished by converting 3-phenyl-2-propynoic acid to the methyl ester **76**[83] and heating the ester adduct with anthracene in an evacuated sealed tube (Figure LXIV).

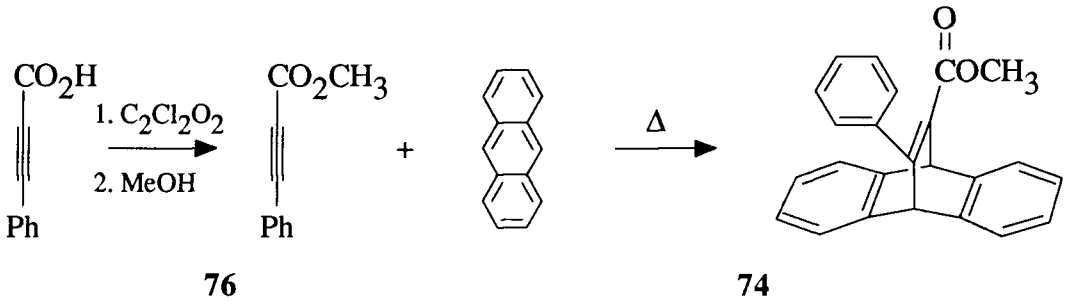


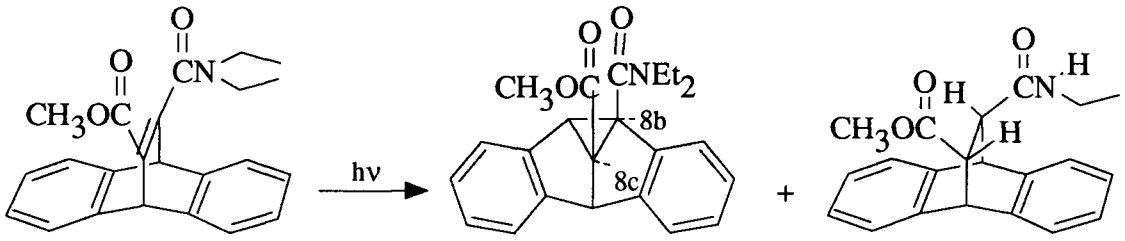
Figure LXIV: Preparation of Phenyl/Methyl Ester Adduct[82], Compound **74**

The irradiation of compound **74** rapidly gave rise to a single photoproduct in all solvents. The pure product was easily identifiable as a dibenzosemibullvalene derivative by its characteristic NMR spectrum. Although the upfield position of the ester methyl singlet (δ 3.58 ppm) suggested that the ester group was probably attached to carbon-(8b), the location of the ester group and the phenyl group could not be absolutely determined by spectroscopic analysis. Therefore an X-ray crystallographic analysis was performed on a crystal of the photoproduct. This verified the location of the ester group and confirmed the photoproduct structure as being that of compound **75e** in Figure LXIII.

From this result, it can be concluded that the guiding factors in the formation of the initial biradical intermediate in the di-π-methane rearrangement of dibenzobarrelenes are more in line with the concept of radical stabilization of biradical intermediates, rather than radical attack on the bridging vinyl bond. In hindsight this is perhaps not such an extraordinary finding. The approach of explaining the regioselectivity by free radical attack on the bridging vinyl bond is dependent on the assumption that one of the benzo groups will adopt biradical characteristics. While it is true that the energy of excitation is associated with the molecule as a whole, it is also generally accepted that this energy, for the most part, resides with the absorbing chromophore.[77] As such, the contribution that a dibenzobarrelene benzo-biradical electronic structure might represent to the overall reactivity of the system would be expected to be small.

C: Hydrogen Abstraction Reactions in Ester-Amide Systems

The irradiation of compound **46** in acetone, benzene and acetonitrile resulted in the formation of two photoproducts (Figure LXV). The photoreaction proceeded rapidly with very little photodecomposition of the starting material.



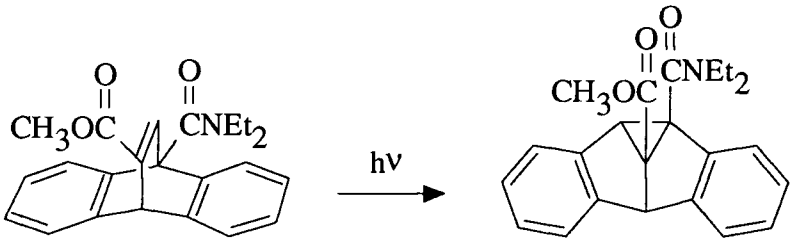
46	**77**		**78**
Solution	75	:	25
Solid State	100	:	0

Figure LXV: Photolysis of the Methyl Ester Diethyl Amide Adduct **46**

The proton NMR spectrum of the major product **77** displayed the typical dibenzosemibullvalene pattern of an aromatic region accounting for eight hydrogens, singlets at δ 5.10 and 4.40 ppm attributable to the pentalene hydrogens, a methyl ester singlet at δ 3.70 ppm, and ten hydrogens corresponding to two ethyl groups. The signal position of the methyl ester predicts that the ester should be attached to carbon-(8c). Additionally, the first significant fragmentation in the mass spectrum gives a peak at 302 mass units. This represents a loss of 59 mass units from the parent ion at 361 mass units, corresponding to the loss of a methoxy radical and carbon monoxide. An examination of higher mass fragmented peaks also reveals a peak at 330 mass units attributable to the loss of a methoxy radical. Applying the mass spectral analysis of dibenzosemibullvalene diesters to methyl ester/diethyl amide product, compound **77**, one would again predict that the ester would be attached to carbon-(8c) and the amide to the benzylic cyclopropyl

carbon. As in the photoproducts of compounds **45** and **47**, the major pathway of fragmentation of the amide group is α-cleavage.

As with the major photoproduct of the methyl ester/dimethyl amide adduct **45**, the dibenzobarrelene 10-(diethyl amide) 11-(methyl ester) analog of compound **46** was synthesized (**52**). Irradiation of this substrate gave a single photoproduct whose spectroscopic properties (NMR, MS, IR) and physical characteristics (mp) were identical to those of the major photoproduct of **46**.



52 **77**

Figure LXVI: Confirmation of the Structure of Photoproduct **77**

Structural Elucidation

Identification of the minor photoproduct (compound **78**) from the photolysis of compound **46** was based on the same sort of analysis as seen with the saturated-bridge monosubstituted amide photoproducts obtained from dibenzobarrelene monoamides. The infrared spectrum clearly indicated the presence of a saturated ester with a band at 1738 cm^{-1} and a saturated amide with a band at 1638 cm^{-1}. Furthermore, an amide type II band appears at 1546 cm^{-1} along with a band in the N-H region, clearly demonstrating the presence of a secondary amide. The mass spectrum of compound **78** has a base peak at 178 mass units, which as seen before, is a marker for the dibenzobarrelene skeleton.

A comparison of the proton NMR spectrum of compound **78** in Figure LXVII with the NMR spectrum (Figure XXXIV; page 45) of the analogous product from the photolysis of dibenzobarrelene diethyl amide (**34**) shows some interesting correlations.

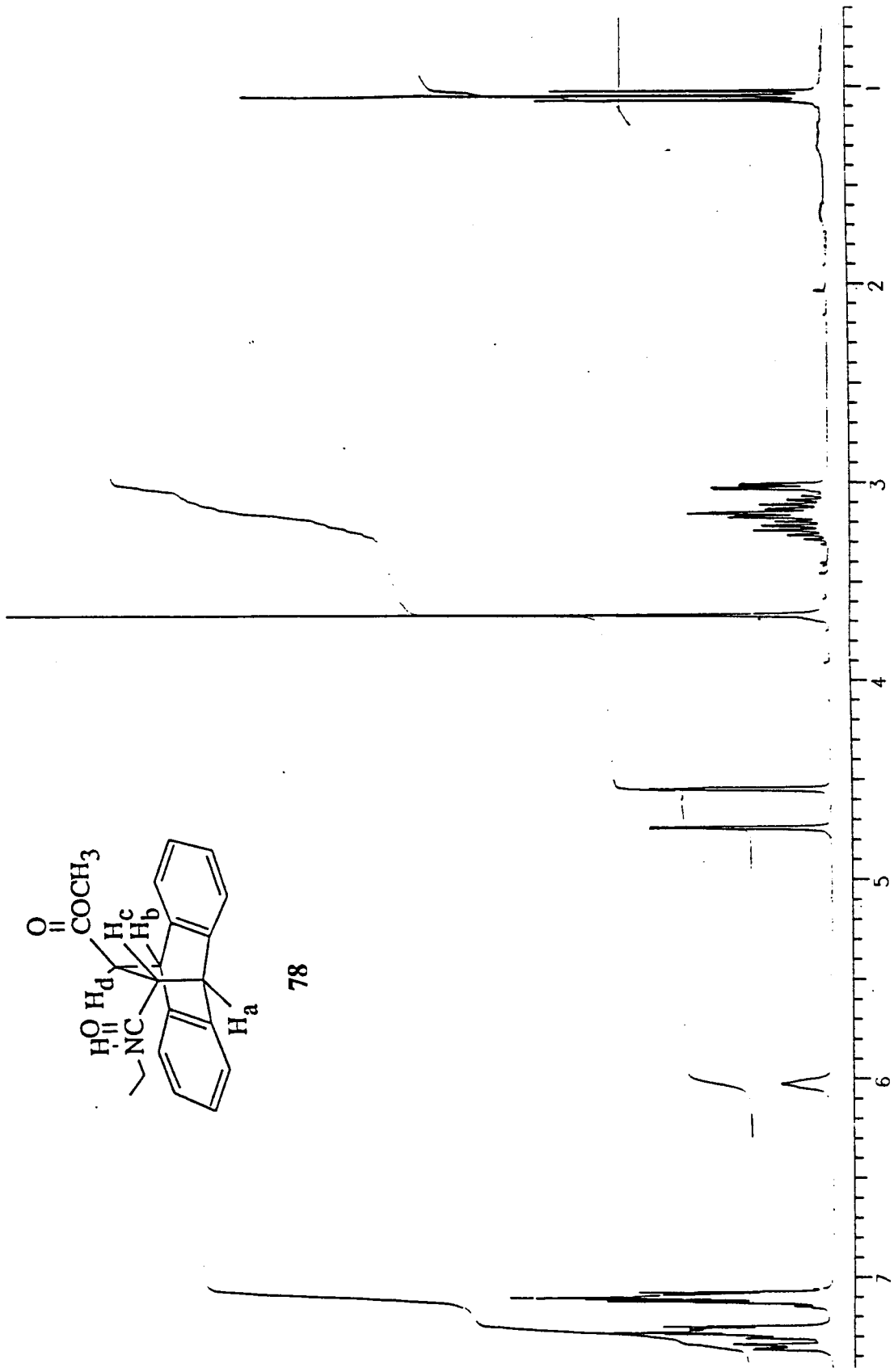


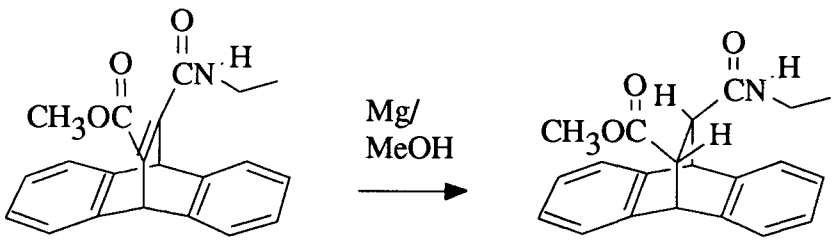
Figure LXVII: NMR Spectrum of Photoproduct **78**

Although the peak positions for the aromatic and ethyl hydrogens are essentially unchanged, the remaining peaks give structural information based on their change in position. The proton spectrum of ethyl amide photoproduct **59** (Figure XXXIV; page 45) has three multiplet peaks (ddd: δ 2.74 ppm ; 1.86 and 2.10 ppm) that were respectively assigned to the methine hydrogen geminal to the amide and to the bridging methylene hydrogens. In the NMR spectrum of the ester-amide photoproduct **78** (Figure LXVII), the multiplets in the region of δ 2.0 ppm have disappeared while two multiplets have arisen in the downfield region (δ 3.15 ppm and 3.03 ppm). This confirms the assignment of the multiplets in the upfield region of the spectrum of amide photoproduct **59** to the bridging methylene hydrogens (H_d and H_e). The signals for the bridgehead hydrogens (H_a and H_b) in the spectrum of ester-amide photoproduct **78** appear at δ 4.54 ppm and 4.84 ppm. A comparison of the peak positions of the bridgehead hydrogens adjacent to the site of acyl attachment in the monofunctionalized amide and ester photoproducts **59** and **60** allows one to assign the respective bridgehead hydrogen peaks. The proton spectrum of the saturated-bridge monoethyl amide **59** contains a peak at δ 4.54 ppm which can be assigned to the hydrogen adjacent to the site of amide attachment. Likewise the spectrum of the analogous methyl ester **60** contains a peak at δ 4.84 ppm attributable to the hydrogen adjacent to the site of ester attachment. These results allow one to assign the peaks at δ 4.52 ppm and 4.70 ppm in the spectrum of the ester-amide photoproduct **78** to the bridgehead hydrogens H_a (next to the amide group) and to H_b (next to ester group) respectively.

Methanol/Magnesium Reduction

In order to confirm the structure of the saturated-bridge ester-amide photoproduct, compound **78**, the following alternate synthesis was undertaken. The dibenzobarrelene methyl ester monoethyl amide adduct **47** was subjected to a methanol/magnesium reduction[84] of its bridging vinyl bond by dissolving **47** in

anhydrous methanol and adding ten equivalents of magnesium turnings at room temperature. After gas production had ceased, the excess magnesium was reacted with hydrochloric acid. The major product isolated from this reaction was spectroscopically and physically identical to compound **78** (Figure LXVIII).



47 **78**

Figure LXVIII: Methanol/Magnesium Reduction of Compound **47**

The mechanism by which this reduction is achieved is thought to involve a Birch-type radical anion formation followed by additional electron incorporation and finally a protonation. This last step could involve the protonation of a dienolate species, as experiments[84] performed in deutero-methanol using methyl cinnamate and ethyl crotonate revealed incorporation of deuterium into both positions of the double bond. Figure LXIX outlines this mechanism for the reduction of **47** as suggested by Hudlicky et al in the reactions of similar compounds.[84]

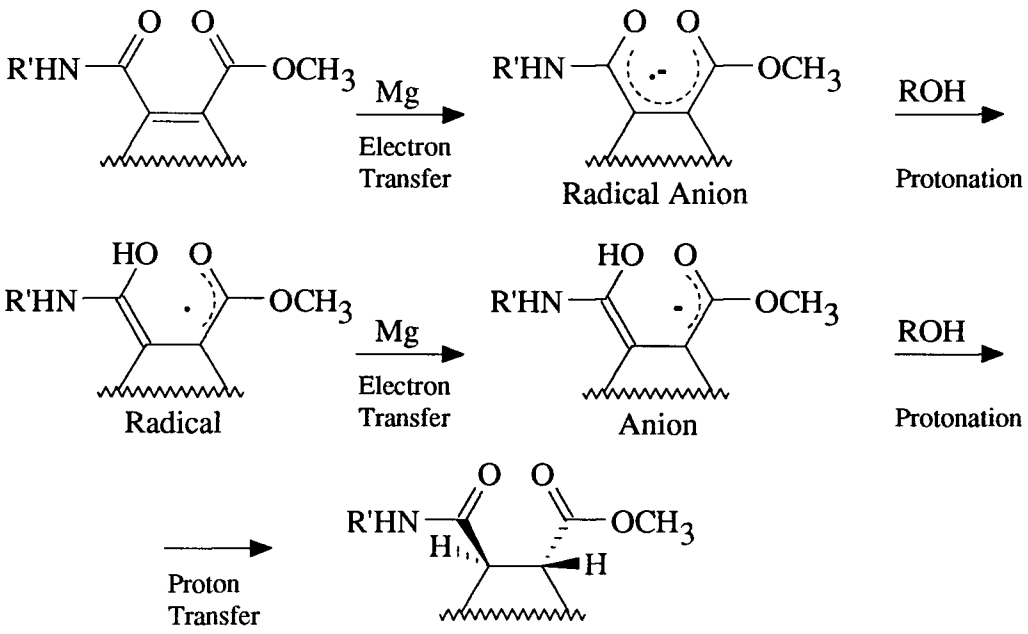


Figure LXIX: Mechanism of Methanol/Magnesium Reduction

These types of reductions are affected in a predictable manner by substituent groups.[85] Electron-releasing groups retard the electron transfer, whereas electron-withdrawing groups facilitate reduction. In the present case, the presence of an electron-deficient centre attached to either end of the bridging double bond greatly contributes to the ease of reaction. The methanol/magnesium reduction is, however, a very selective reaction. α,β-Unsaturated esters containing other functionalities subject to reduction can be selectively reduced to the corresponding saturated esters, in excellent yields in many cases.[84]

The protic nature of the reduction mechanism results in the formation of predominantly the most stable substituted alkane.[84] In a case such as the dibenzobarrelene system, where there is no free rotation about the bond connecting the carbons of acyl attachment, the major reduction product would have the two functional groups *trans* to one another. From this, it can be concluded that the minor product formed by the photolysis of compound **46**, being identical to the product from the reduction of **47**, will be *trans* as well,

Irradiation of 46 in Deuterated Methanol

The irradiation of the methyl ester diethyl amide adduct **46** in deuterated methanol (CH_3OD) gave rise to three products, as shown in Figure LXX, in addition to the dibenzosemibullvalene methyl ester/diethyl amide **77**. The ratio of di-π-methane product to hydrogen abstraction products was 3:1, the same as found in photolysis in acetone, acetonitrile or benzene. Of the three abstraction products isolated, **78d** was recovered only in trace amounts while the two diester products **79d** and **80d** were recovered in a ratio of 1:3.

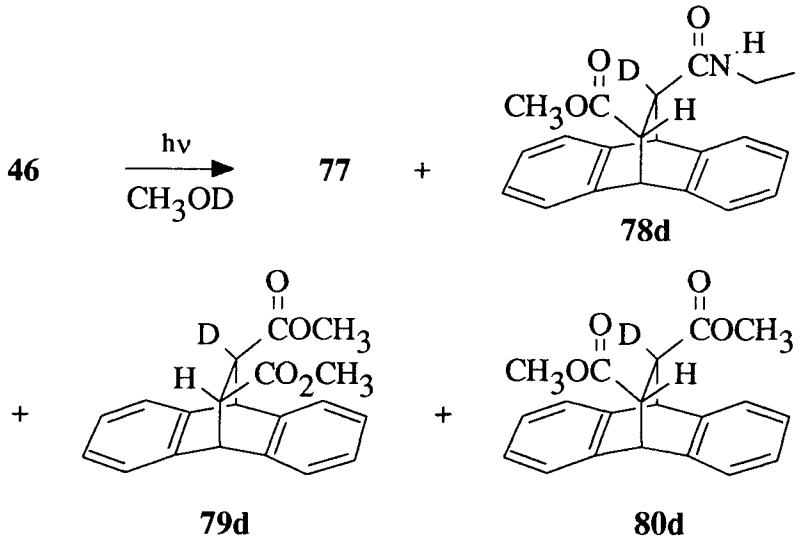
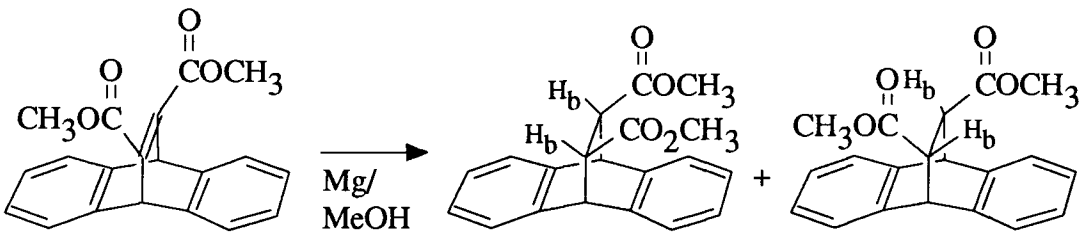


Figure LXX: Photolysis of Compound **46** in Deuterated Methanol

The non-deuterated analogs of compounds **79d** and **80d** are known compounds.[86] In order to confirm the structures of compounds **79d** and **80d**, as well as proving that the reduction reaction does proceed to give predominantly the trans product, dimethyl dibenzobarrelene diester **9** was subjected to methanol/magnesium reduction. Two products, compounds **79** and **80**, were obtained in a ratio of 1:4 (Figure LXXI).



9 **79** **80**

Figure LXXI: Non-deuterated Analogs of Compounds **79d** and **80d**

Structural assignments of the two products obtained were easily made by comparison of NMR spectra and melting points to the data in the literature.[86] A comparison of the deuterated products recovered from irradiation of **46** in deuterated methanol to the non-deuterated analogous recovered from the methanol magnesium reduction of **9** exhibits a few predictable changes in the spectroscopic data. In the proton NMR spectra of the deuterated products, the peak integration for the bridge hydrogens (H_b) was reduced by half. This was also accompanied by the splitting of the bridgehead hydrogens' signal into two separate peaks as a result of the molecular asymmetry introduced by the replacement of a bridge hydrogen with a deuterium. Interestingly, in the proton spectra of both the cis and trans non-deuterated adducts, the bridgehead and bridge hydrogen signals appear as singlets. In the deuterated adducts, the coupling between the bridge hydrogen and the bridgehead hydrogen further from the deuterium is now clearly seen (J = 2.4 - 2.7 Hz).

In addition to the two deuterated diester adducts recovered from the photolysis of compound **46** in deuterated methanol, a small amount of compound **78d** was isolated. Of note in the proton spectrum of this material is that deuterium incorporation is exclusively geminal to the amide group, within the detection limits of NMR spectroscopy. The proton spectrum, recorded at 400 MHz, contains not the smallest indication of the multiplet assigned to the hydrogen geminal to the amide. It is possible to conclude that

deuteration occurs adjacent to the amide and not the ester group based on the relative positions of the affected peaks in the spectrum.

What is of interest here is that any deuterated ethano-bridged methyl ester ethyl amide adduct **78d** is seen at all. In the dibenzobarrelene monoamide series of compounds, in all cases irradiation in methanol resulted in the only hydrogen abstraction product formed being the saturated-bridge methyl ester adduct **60**. The fact that no monosubstituted amides or any β-lactams were formed was taken as evidence that the mechanism by which the hydrogen abstraction products were formed must involve a ketene, and not a simple ring closure. However, the isolation of this deuterated adduct **78d** is not a negation of that reasoning. This then leads to two possibilities; either the ketene/hydrolyzed imine mechanism is not operative in this instance or there is some other influence at work here that is allowing for the formation of the deuterated adduct **78d**.

Theoretically, the reaction of the ketene with the solvent in these methanol photolyses should be in competition with the reaction of ketene with imine and/or amine. Therefore, rather than attempting to explain why both types of products (*i.e.* ethano-bridged diesters **79d** and **80d** and ethano-bridged ester amide **78d**) are seen in the photolysis of **46** in deuterated methanol, it would be more appropriate to speculate as to why no monosubstituted amide product is seen in the methanol photolyses of the dibenzobarrelene monoamides.

The only fundamental difference between the two types of compounds (*i.e.* dibenzobarrelene monoamides and ester-amide starting materials) is the presence of an ester group at the opposite end of the bridging vinyl bond. It can be speculated that hydrogen-bonding of the solvent by the ester group in the ester-amide adduct **46** might be expected to be extensive, creating a loosely held but considerable steric barrier to the approach of other solvent molecules. As a result, the imine and ketene produced by the photolytic cleavage of ester-amide **46** would not be as easily solvated as in the case of the

intermediates produced in the photolyses of monoamide adducts **34** (diethyl), **35** (dibenzyl) and **37** (di-iso-propyl) in methanol. These intermediates, lacking a second functional group to produce this hydrogen-bonded solvent shell, would be readily separated and solvated. The intermediates from ester-amide **46**, on the other hand, would be held in a type of solvent cage sufficiently long enough for the imine to be hydrolyzed and react with the ketene. However without any physical evidence to support this proposal, the idea of a solvent shell barrier is simply conjecture.

An indication of the necessity of water to the formation of the monosubstituted amide abstraction product **78** was carried out by photolyzing the ester-amide starting material **46** in anhydrous benzene. This should have resulted in the complete lack of formation of compound **78**. The results obtained saw the amount of monoethyl amide methyl ester product **78** reduced from 25% of the product mixture to approximately 6%. While showing the necessity of water to the formation of the monosubstituted amide products, this is also an indication of how efficient the hydrolysis of the imine is and of just how much water is left in a solvent after following conventional drying methods.

Solid State Photolysis of 46

Solid state irradiation of powdered and single crystal samples of compound **46** resulted in the production of the same two photoproducts, compounds **77** and **78**, as found in acetone, benzene and acetonitrile photolyses. The percentage of the second photoproduct was much reduced (10%) and diminished even further when efforts were made to keep the reaction mixture as dry as possible. This involved drying the powdered sample followed by placing the sample between two microscope slides and sealing in a polymer film, under a nitrogen atmosphere, prior to photolysis.

It is of interest to note that irradiations of the diethyl monoamide adduct **34** in both methanol and the solid state did not produce any monosubstituted amide whereas, in

the methanol and solid state photolyses of the methyl ester diethyl amide adduct **46**, a saturated-bridge methyl ester/monosubstituted amide product **78** did form. The methanol results were rationalized by postulating a hydrogen bonded solvent shell. Clearly if this were the only factor involved then the solid state irradiation of compound **46** should give only di-π-methane rearrangement-derived semibullvalene. The ability of abstraction products to form is conformation-dependent; the hydrogen abstraction step must not involve atomic motions that are too large as to disobey the topochemical principle while at the same time, the inter-atomic distance between the abstraction centres must not be of such magnitude that it represents a significant activation barrier.[40,41,42] However this in itself is not condition enough for reaction to proceed. As previously discussed, the angular orientation of the centres involved in hydrogen abstraction must also be taken into account.[63] The difference between the solid state reaction of the diethyl monoamide **34** and the methyl ester diethyl amide **46** lies in their respective abilities to undergo hydrogen abstraction and form a ketene, given the conformation in which they have crystallized. The crystal packing of monoamide **34** has been shown to be unfavourable for abstraction to occur. The packing of **46**, however, must be such that interatomic distances and angular requirements do not represent a significant barrier to either hydrogen abstraction or to ketene formation. Thus the abstraction product can form in solid state irradiations. However, it was not possible to obtain a crystal structure for **46**.

D: Photoreactions of More Complex Ester-Amides

Piperidine-derived Ester-Amide 48

The preparation of the dibenzobarrelene methyl ester piperidinyl-derived amide adduct, compound **48**, was undertaken in the hopes that the photolysis of this material might result in a higher yield of abstraction products. Additionally, the abstraction products that could form from the photolysis of compound **48** might be synthetically more interesting.

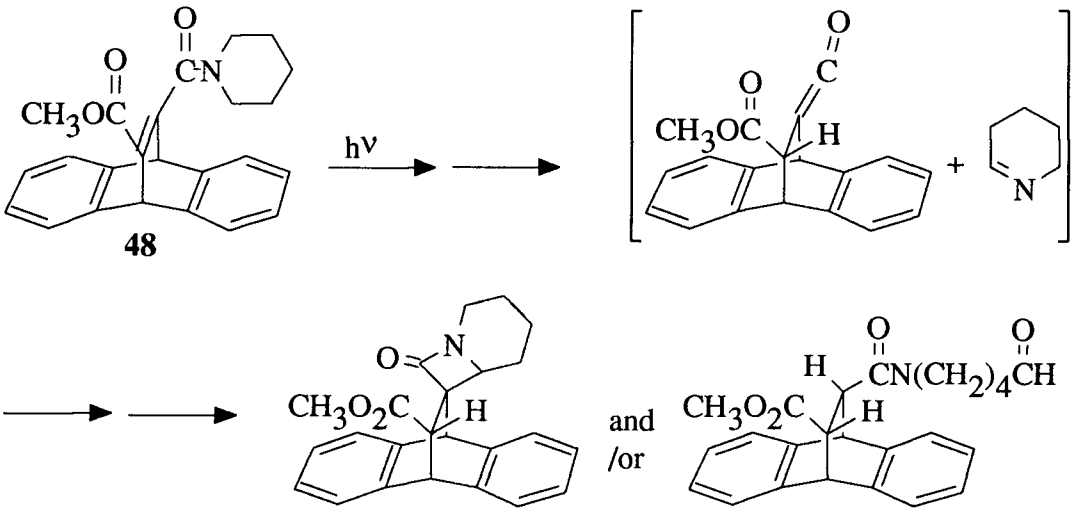
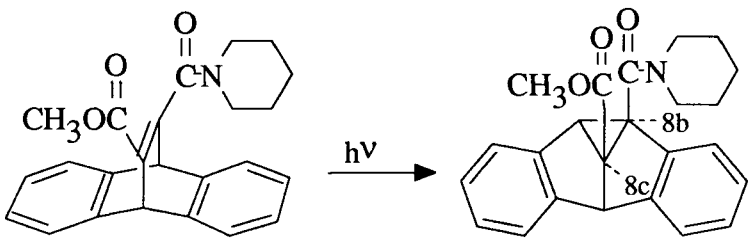


Figure LXXII: Possible Photoproducts from the Irradiation of Compound **48**

In Figure LXXII, the products from imine attack and imine-derived amine attack are depicted. If the photochemistry of compound **48** were such that these two products were produced in significant amounts, this could represent an easy route, after removal of the anthracene portion of the product *via* a retro-Diels-Alder reaction, to either a hetero-bicyclic ring system that might be found in natural products or a way of converting cyclic amines to more highly functionalized straight chain derivatives. However, as seen in Figure LXXIII, results do not always follow expectations.



48 **81**

Figure LXXIII: Photochemical Results from the Irradiation of Compound **48**

The photolysis of compound **48** in acetone, acetonitrile, benzene, and methanol all resulted in the very rapid formation of a single photoproduct. This photoproduct was identified as the dibenzosemibullvalene ester-amide compound **81**, arising from di-π-methane rearrangement of the starting material. The reaction proceeded very cleanly with no evidence of any abstraction products at all and little photodecomposition of the starting material.

The proton NMR spectrum of compound **81** is divided into roughly three sets of peaks: the aromatic region, the pentalene and ester singlets, and the amide methylene multiplets. From the methyl ester signal position at δ 3.72 ppm, one can determine the position of the amide functional group as being attached to carbon-(8b). In the mass spectrum, the loss of a fragment of 59 mass units from the parent ion (373 a.m.u. to 314 a.m.u.) corresponds to the loss of a carbomethoxy radical and places the methyl ester at carbon-(8c).

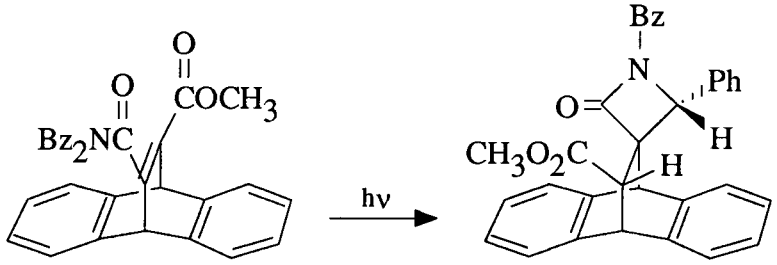
The lack of any reaction other than the di-π-methane rearrangement might be attributable to differences in the rates of reaction. The di-π-methane reaction is a very efficient reaction in the photolysis of compound **48**. On the other hand, the ability of the carbon *alpha* to the ester group to abstract a hydrogen from the amide group might be hampered by the rigid nature of the cyclic ring. Rigidity would make it very difficult for the molecule to adopt the proper orientation so that abstraction can occur. Furthermore,

once abstraction does occur the molecule would possibly be somewhat locked in a conformation from which ketene formation is unfavourable.

Solid state photolysis of powdered samples and single crystals of compound **48** gave the same photoproduct as in solution. The lack of abstraction products in the solid state can be attributed to an inability to adopt the proper conformation as in the solution photolysis.

Methyl Ester/Dibenzyl Amide

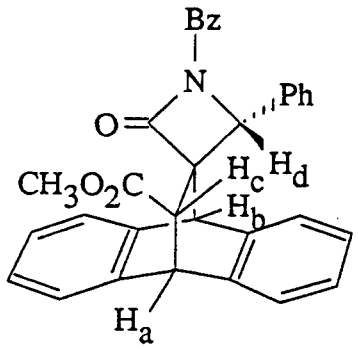
Photolyses of the methyl ester/dibenzyl amide adduct **49** in acetone, acetonitrile, and benzene all resulted in the formation of a single identifiable photoproduct, compound **82** (Figure LXXIV). The reaction of **49** was accompanied by significant yellowing of the photolysate, indicating extensive photo-decomposition of the starting material. This was confirmed by a proton NMR spectrum of the crude reaction mixture which exhibited a very complex pattern of peaks, yielding little useful structural information.



49 **82**

Figure LXXIV: Photoproduct from the Irradiation of Compound **49**

Structural elucidation of the photoproduct **82** was facilitated by its similarity to the β-lactam photoproduct from dibenzyl amide **35**. The infrared spectrum exhibited only a single broad band in the carbonyl region at 1747 cm^{-1}. Since β-lactam carbonyls absorb in the same region as esters, combined with the fact that the mass spectrum



82

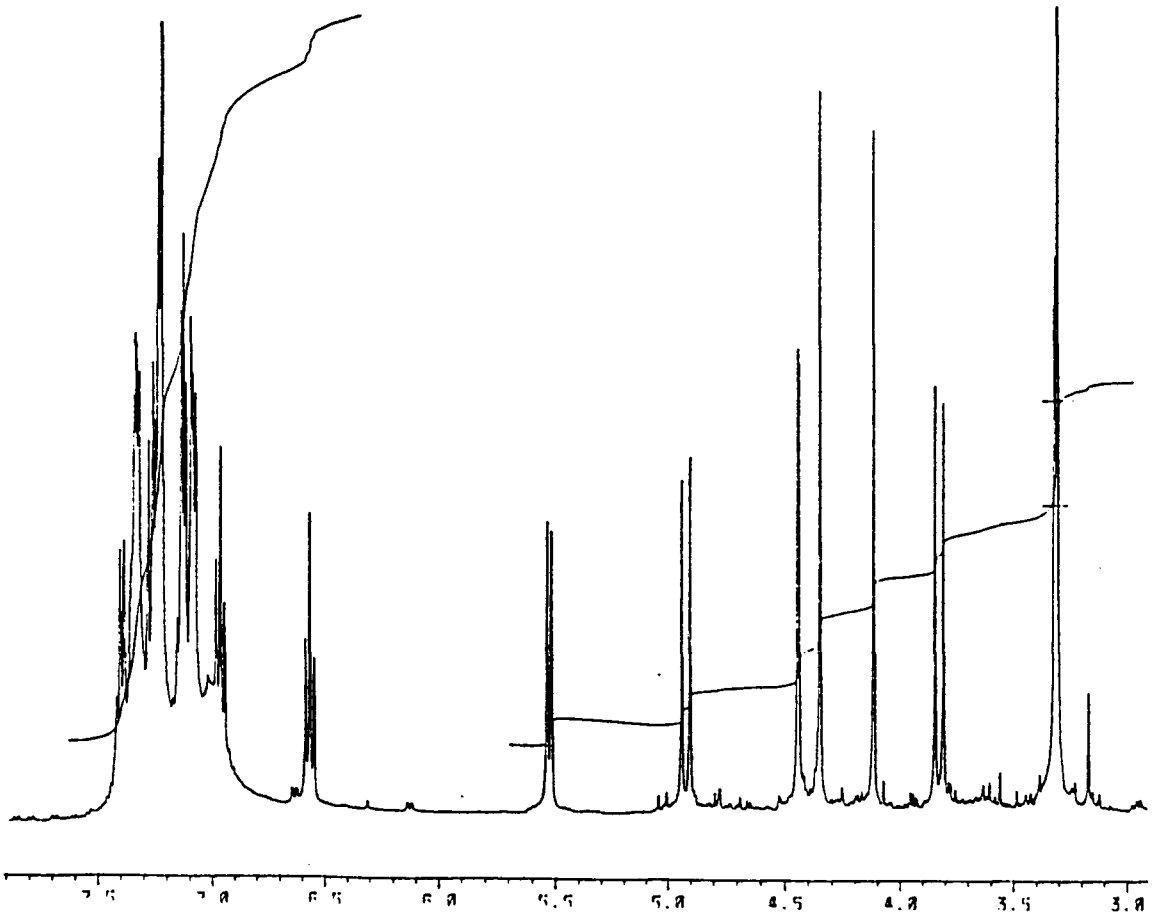


Figure LXXV: NMR Spectrum of Photoproduct **82**

indicated that the molecular weight of **82** was the same as **49**, the product was identified as a β-lactam/ester. As with previous abstraction products, the base peak in the mass spectrum was the anthracene peak at 178 mass units. Additionally, a peak at 352 mass units, corresponding to a loss of 133 a.m.u., is consistent with a retro [2+2] cycloaddition of the lactam ring.

Figure LXXV shows the proton NMR spectrum of compound **82**. What is of particular note here is the same peak pattern for the aromatic peaks as seen for the dibenzyl β-lactam **63** in Figure XLI (page 55). As such, the lactam ring phenyl group of **83** must be experiencing the same sort of phenyl/benzo ring interaction that resulted in two upfield aromatic signals in the spectrum of **63**. Thus, one can readily assign the stereochemistry of the lactam methine as being the same as for **63**. Also of note is the disappearance of the two doublets of doublets in the region δ 2-2.5 ppm and the appearance of two peaks at δ 3.3 ppm. This is consistent with the replacement of one of the ethano-bridge methylene hydrogens with a methyl ester group.

The stereochemistry of the ester with respect to the lactam can be tentatively assigned by considering the mechanism of formation. The lactam is thought to be formed by nucleophilic attack of the imine on the ketene. This reaction is presumably susceptible to steric hindrance. Thus attack from the side of the ketene where the ester group protrudes is restricted. Attack from the less sterically congested side of the ketene gives a lactam/ester product with the ester and the lactam carbonyl in a *cis* relationship (Figure LXXVI).

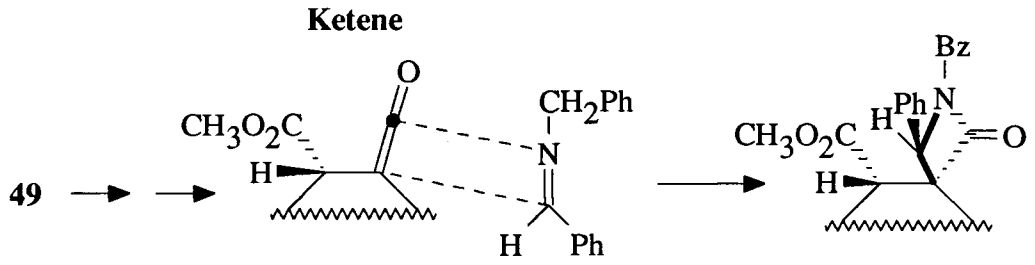
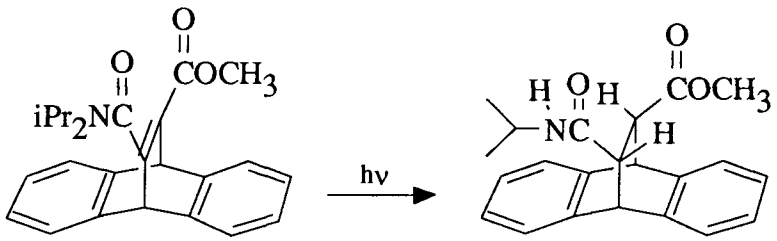


Figure LXXVI: Ester/Lactam Carbonyl Stereochemical Relationship in **82**

Solid state irradiations of **49**, carried out on both powders and single crystals, were found to give the same photoproduct **82** as observed in solution photolyses. The reasons for this and for the lack of any di-π-methane rearrangement products in solution or solid state reactions will be discussed later.

Methyl Ester/Di-iso-propyl Amide

The irradiation of the methyl ester/di-*iso*-propyl amide adduct **50** in acetone, acetonitrile and benzene resulted in the formation of a single photoproduct **83** (Figure LXXVII). Like the irradiation of compound **49**, the photolysis of this substrate was accompanied by significant decomposition. The product mixture from the photolysis of **50** was recovered as a viscous yellow oil.

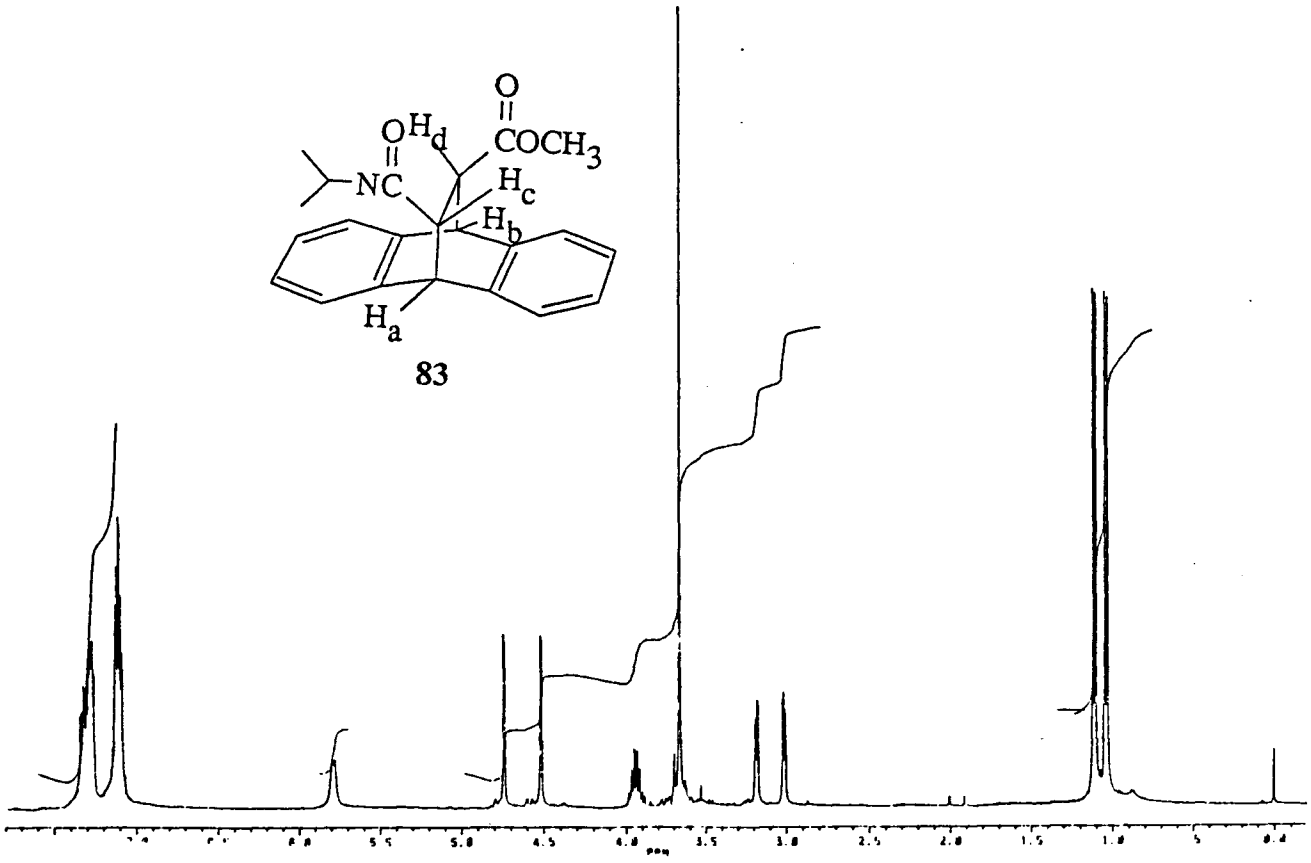


50 **83**

Figure LXXVII: Photoproduct from the Irradiation of Compound **50**

The infrared spectrum of photoproduct **83** displayed bands that were typical of an N-H (3330 cm^{-1}), a saturated ester (1733 cm^{-1}), a saturated amide (1644 cm^{-1}) and of a secondary amide (amide type II band at 1554 cm^{-1}). Identification of the photoproduct

83 was based primarily on its mass spectrum and its proton NMR spectrum. The mass spectrum of **83** exhibited a parent ion peak at m/e 349. This is consistent with the loss of C_3H_5 from the starting material. Once again, the base peak in the spectrum is at 178 mass units. The proton NMR spectrum of **83** is remarkably well resolved into coupled regions of aromatic, amide, bridgehead, methine, ester methyl, bridge and methyl protons (Figure LXXVI). The magnitude of the coupling (J = 5.6 Hz) between the ethano-bridge hydrogen peaks at δ 3.18 and 3.02 ppm indicate that the two functional groups in the saturated-bridge ester-amide **83** are *trans* to one another.[56]



83

Figure LXXVIII: Proton NMR Spectrum of Photoproduct **83**

The value of the coupling constant for **83** is consistent with the coupling constant found for the *trans*-monoethyl amide/methyl ester photoproduct **78** (J = 6.0 Hz).

Solid state irradiations performed on powdered samples and on single crystals of compound **50** resulted in the formation of the same photoproduct **83** as found in solution photolyses. The reaction could be carried out to 15% conversion without any noticeable yellowing or melting of the crystalline material.

What is most notable about the solution and solid state photolyses of compounds **49** and **50** is not the formation of the abstraction products but the complete lack of any di-π-methane rearrangement products. The product distribution of the abstraction products is as might be expected. The imine derived from di-*iso*-propyl adduct **50** is more readily hydrolyzed and produces a saturated-bridge, mono-*iso*-propyl amide **82**. The imine produced from the photolysis of the methyl ester/dibenzyl adduct **49** is hydrolyzed less rapidly and results in β-lactam **81**. However, all other starting materials studied in this thesis gave at least some semibullvalene photoproduct.

One notable feature common to the photolysis of both compounds **49** and **50** was the large degree of photodecomposition that accompanied the reactions. Irradiations were accompanied by extensive yellowing of the photolysate solution, indicating the production of many byproducts. This could be seen by the large number of spots observed in tlc analysis, as well as by the numerous peaks in the gc analysis. Proton NMR spectra of the reaction mixtures were of little help in trying to identify any of the decomposition products.

It is reasonable to suggest that the lack of di-π-methane rearrangement products is a result of very rapid hydrogen abstraction. If the rate of the di-π-methane reaction were sufficiently slow, no semibullvalene products could accumulate before consumption of the starting materials **49** and **50** by abstraction reaction. This, however, does not explain the extensive photodecomposition observed.

V: Photochemical Reactions of Miscellaneous Substrates

A: Unsymmetrical Diamides

The photochemistry of the unsymmetrical diamide compound **54** in Figure LXXIX was undertaken to determine whether dibenzobarrelenes with two different amide groups on the bridgehead double bond would behave in a similar fashion to dibenzobarrelene diesters. Unsymmetrical diesters have been shown to give a distribution of regioisomeric di-π-methane products.[16] The diamide also has the possibility of two regiosisomeric semibullvalene products, as well as the possibility of hydrogen abstraction products from the direct participation of the diethyl amide group.

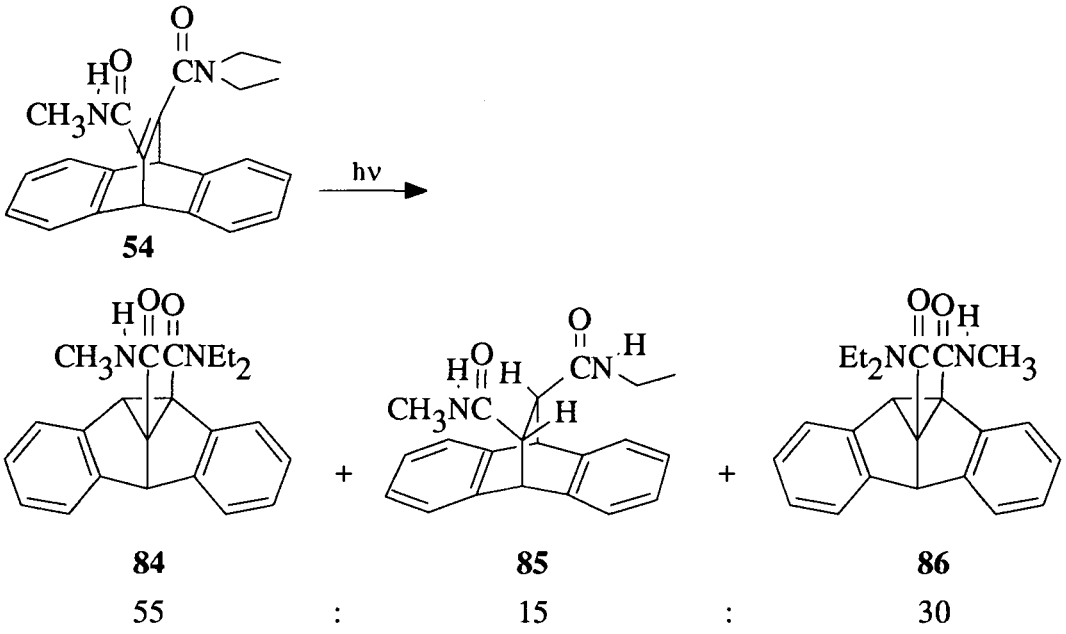


Figure LXXIX: Photolysis of Unsymmetrical Diamide Adduct **54**

The photolysis of compound **54** in solution resulted in the formation of three products. Separation of the major product, compound **84**, from the two minor products was easily achieved by column chromatography. The identification of this product was initially made difficult by its unusual NMR properties (Figure LXXX).

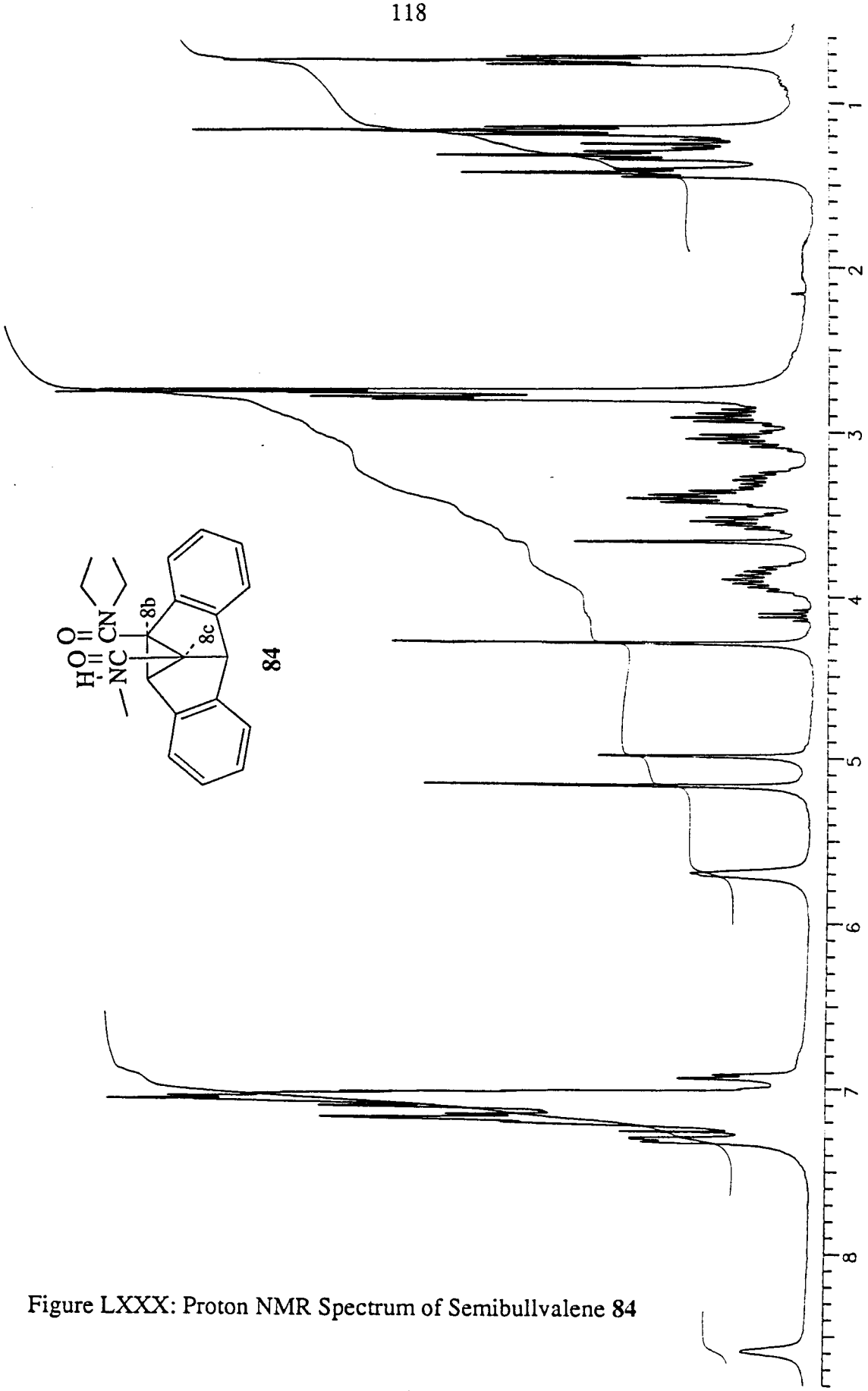


Figure LXXX: Proton NMR Spectrum of Semibullvalene **84**

Structure Confirmation of Compound 84

The NMR spectrum of compound **84** seems to indicate the presence of two compounds. The proton spectrum exhibits what appears to be a double set of peaks in the ratio of roughly 2:1. Attempts to determine the number of compounds present by further purification were not successful. Material that had been subjected to purification by column chromatography with various solvent systems was found to give the same spectrum with no variation in signal intensities. For this reason the photoproduct **84** was synthesized by an alternate method (Figure LXXXI).

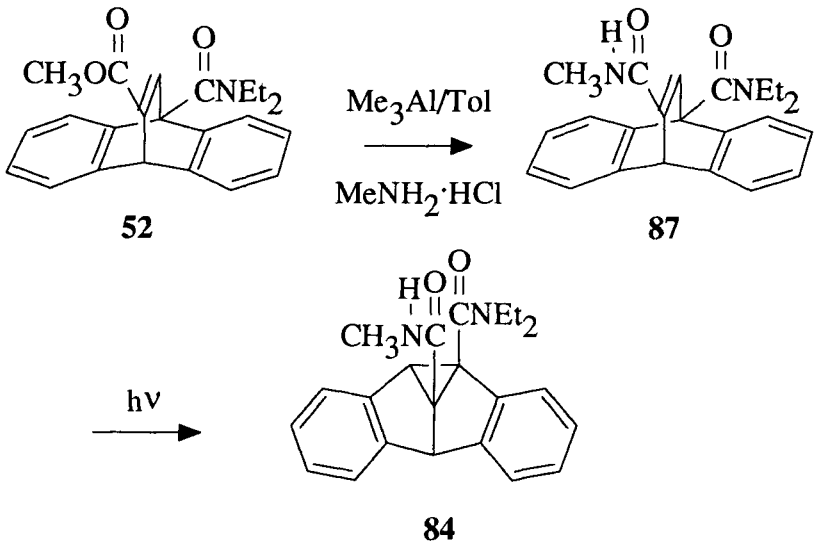
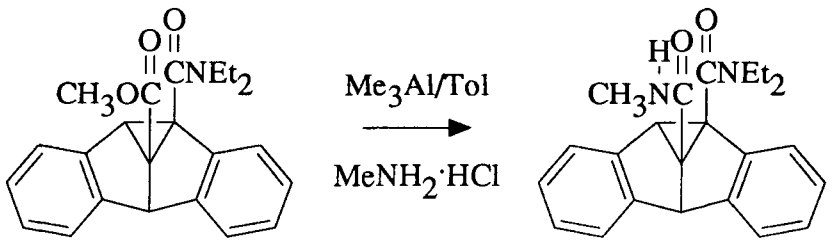


Figure LXXXI: Alternate Photochemical Preparation of Photoproduct **84**

As discussed earlier in this thesis, the photolysis of a 9,12-adduct such as compound **87** will likely give a only single regioisomer *via* di-π-methane rearrangement. Thus if the two sets of NMR peaks in the spectrum of compound **84** were due to a mixture of regioisomeric semibullvalenes, then the irradiation of compound **87** should give a product whose NMR spectrum consists of only one of the sets of peaks.

What in fact was found was that irradiation of the 9,12-adduct **87** gave a substance that was spectroscopically identical to the major photoproduct of compound

54, compound **84**. The proton NMR spectrum exhibited the same pattern of peaks with the two sets of peaks again in a ratio of 2:1. Melting point determinations for both compounds gave identical values of 228-229°C. This indicates that the photoproducts from compounds **54** and **87** are both composed of the same material and are semibullvalene-based. This does not rule out the presence of two different molecules in the photoproduct, however. It is possible that the irradiations of compounds **54** and **87** both give an initial photoproduct which is also photoreactive. This could lead to a second product and account for the double set of NMR peaks. Therefore a non-irradiative means of producing compound **84** was sought.



77 **84**

Figure LXXXII: Conversion of Photoproduct **77** to Compound **84**

The major photoproduct **77** from the irradiation of ester-amide **46** was subjected to a Weinreb aminolysis, using methylamine hydrochloride (Figure LXXXII). The ester-amide photoproduct had been fully characterized and did not have any unusual features in its NMR spectrum. The product isolated from this aminolysis was found to be spectroscopically identical to the original photoproduct from compound **54** and to the photoproduct from compound **87**. The only possible way that these three synthetic routes could produce two compounds in the same ratio is if the dibenzosemibullvalene diamide reacted thermally. Although this was thought to be unlikely, as semibullvalenes are generally found to be very stable, an X-ray crystallographic analysis was performed to determine absolutely whether the major photoproduct from compound **54** was a single compound or a mixture (Figure LXXXIII).

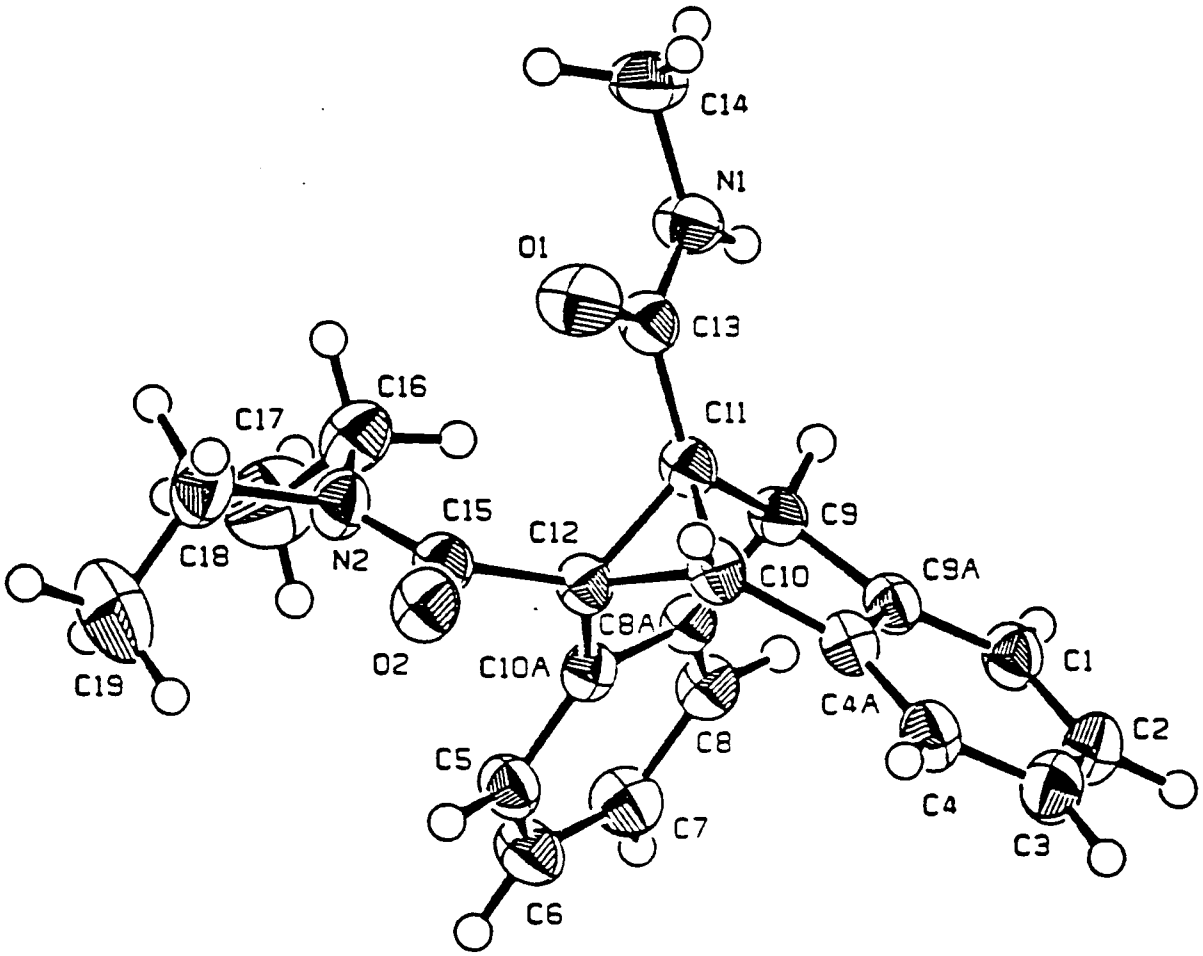


Figure LXXXIII: X-ray Crystallographic Structure of Photoproduct **84**

The X-ray crystallographic analysis was still not definitive proof that the photoproduct was a single compound. The possibility still existed that the photoproduct was a mixture of compounds and that recrystallization was simply selectively giving one compound. To test for this, a single crystal, taken from the same batch of crystals that the crystal for X-ray analysis was taken, was dissolved in deuterochloroform and its proton NMR spectrum run. The same peak pattern was observed showing that a single compound was in fact responsible for the dual set of peaks.

The reasons for this unusual spectroscopic behaviour are not readily evident. The phenomenon of conformational isomerism is often observed in NMR spectra as something that can produce two peaks for a single hydrogen.[56] This is a result of conformational isomerism that places the hydrogen in two magnetically different environments. In fact many of the amides in this study display this type of spectroscopic behaviour in the NMR signals of the alkyl portion of the amide group. As previously discussed, the photoproduct of the N-dimethyl diamide adduct **38**, compound **69**, has two sets of two chemically distinct methyl groups. However, because of restricted motion about the carbon-nitrogen bond, the methyl groups appear as four distinct signals. As with other instances of conformational isomerism, when high temperature NMR experiments are performed, one can see a coalescence of the two sets of peaks. This is because the equilibrium between the two magnetically distinct conformations has become fast on the NMR time scale.

This type of behaviour is observed in the proton spectra of compound **84**. When the spectrum of this compound is run at higher temperatures, the two sets of peaks do start to coalesce. Because coalescence is accompanied by broadening, a spectrum of compound **84** with a single set of peaks was not obtainable. However, to say that the two sets of peaks observed for compound **84** is due only to conformational isomerism would

be simple speculation. This type of behaviour was not observed with any other compounds in this study and as such must be treated as an interesting anomaly.

Minor Photoproducts from 54

The two minor photoproducts from the irradiation of compound **54**, compounds **85** and **86**, were recovered as a mixture after the separation of the major photoproduct by column chromatography. Compound **85** was obtained pure by successive recrystallizations of the mixture, while the mother liquor became enriched in compound **86**. The percentage of compound **86** had increased from 10% to 85% after a half dozen recrystallizations at which point **86** itself crystallized.

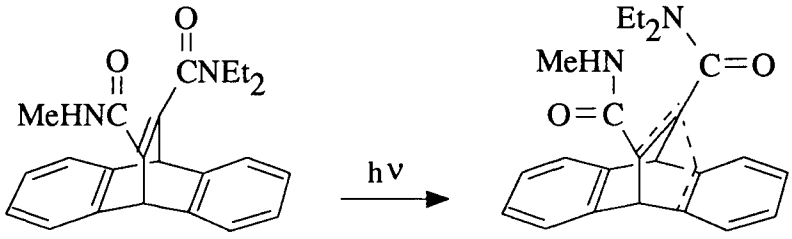
Compound **85** was found to be a hydrogen abstraction product with the two amide groups attached to the bridge *trans* to each other. The similarity between the two secondary amide groups was evident spectroscopically. Both the carbonyl position in the infrared spectrum and the proton NMR signal position of the adjacent bridge hydrogens were found to identical for the amides. The structure of compound **85** and the stereochemical relationship between the amide groups was confirmed by an alternate synthesis. This involved subjecting the abstraction product from the photolysis of the methyl ester/diethyl amide adduct **46**, compound **78**, to a Weinreb aminolysis. The material recovered from this reaction was shown to be spectroscopically and physically identical to compound **85**.

The third photoproduct from the irradiation of compound **54** was found to be a semibullvalene, regioisomeric with the major product (compound **86**). In this product the diethyl amide group is attached to carbon-(8c) and the methyl amide group to carbon-(8b). Both the NMR spectrum and the mass spectrum of compound **86** exhibited patterns typical of a dibenzosemibullvalene system.

Regioselectivity of Unsymmetrical Diamides

The photochemical behaviour of an unsymmetrical dibenzobarrelene diamide in the di-π-methane reaction can be likened to that of an analogous mixed diester. Given the similar electronic nature of the two amide substituents, it seems reasonable to suggest that the modest regioselectivity observed in the product ratio arises mainly from steric factors.[87] These factors can operate by either inhibiting one of the reaction pathways, that is a primary steric effect, or by influencing the resonance properties of the attached carbonyl groups; a secondary effect.[88]

A primary steric effect would operate such that the bulkier substituent, the diethyl amide group, occupies a sterically less demanding position in the transition state. This is reasonable considering that the most demanding steric interaction for the substituents is between themselves. The transition state, possibly resembling **BR** in Figure LXXXIV, would involve relief of this steric interaction. The substituents are separated from one another as the hybridization of the carbon substituted by the bulkier amide changes from sp^2 to sp^3, accompanied by lengthening of the bridging vinyl bond as it acquires single bond character. However the separation of the methyl and ethyl groups by the planar O=C-N groups and the bridging vinyl bond would seem to indicate that the interaction between the alkyl groups would be minimal.



54 **BR**

Figure LXXXIV: Relief of Steric Interaction by Bond Formation

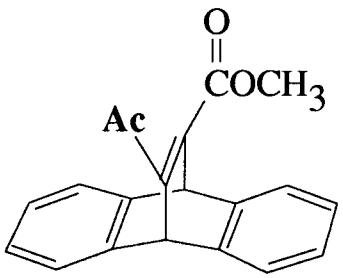
An alternate explanation for the observed regioselectivity is that the repulsive interactions between the alkyl groups may keep one of the adjacent carbonyl groups out of conjugation with respect to the vinylic double bond.[89] Theoretical models propose that the resonance stabilization of an α,β-unsaturated system should depend on the torsion angle, θ, defined by the mean planes of the two double bonds. The angular dependence of the resonance energy is suggested to vary as a function of $\cos^2\theta$ and will be maximized at 180^o and 0^o and minimized at 90^o.[90] Having one carbonyl group out of conjugation can be regarded as approaching the situation found with the dibenzobarrelene monoesters[10] where the ends of the bridging vinyl bond are substituted by a hydrogen and an ester (See Figure IV; page 7). The stereochemistry of the product in these cases was found to be completely determined by the formation of the product that proceeds through the more stable intermediate. Thus it is possible that the different degrees of conjugation between the two carbonyl groups and the bridging vinyl bond are responsible for the observed regioselectivity. This explanation of the observed regioselectivity requires that the diethyl amide carbonyl be out of conjugation. Being the bulkier of the two amides involved, one would expect a greater steric interaction between the ethyl groups of the diethyl amide group and the other amide group and/or the dibenzobarrelene phenyl groups.

It should be pointed out that these steric effects can not be solely responsible for the observed regioselectivity of the di-π-methane rearrangement of the ester-amides. In no instance with the mixed diester series of compounds were the effects found to be strong enough to cause complete selection of one semibullvalene regioisomer.[16] In the ester-amide series of compounds, except for a few percent of the opposite regioisomer in the case of the methyl ester/dimethyl adduct **45**, all semibullvalene products had the amide attached to carbon-(8b). Furthermore, adduct **45** has the least bulky alkyl substituents of all ester-amides studied and would thus be expected to be the least affected by steric interactions.

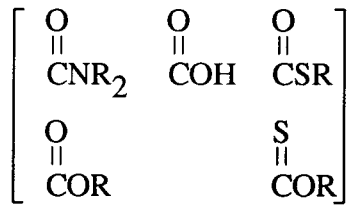
A comparison of the product ratios for the photolysis of the N-methyl/N'-diethyl amide **54** to those from the analogous methyl/ethyl diester[16,72] shows that regioisomer discrimination is somewhat more effective in the diamide irradiation. The product distribution of the two semibullvalene regioisomers from the photolysis of ethyl methyl dibenzobarrelene diester was weighed slightly in favour (54:46) of the regioisomer with the ethyl ester in the benzylic position (attached to carbon-(8b)). Although both adducts favour the reaction pathway that puts the larger substituent on the benzylic carbon, the effect in the diamide is more pronounced (55:30). This would seem to be in line with a steric argument; the diethyl amide, being bulkier than the ethyl ester, should exert a larger steric effect. However, an examination of the photolyses of other mixed diesters shows that as the steric bulk of one of the esters is systematically increased (ethyl, *n*-propyl, *i*-propyl, *s*-butyl, *i*-pentyl, t-butyl), the regioisomeric ratios of the semibullvalene photoproducts do not vary in a corresponding manner. In fact, the mixed diester with one of the larger size discrepancies in its two constituent ester groups (methyl vs. *iso*-pentyl) exhibited no regioisomeric discrimination at all. From this, it can be concluded that steric effects are of little importance in determining regioisomeric product distribution in the solution photolyses of difunctional dibenzobarrelenes.

B: Thioesters

To further compare the effects of different acyl derivatives on the di-π-methane rearrangement, two thioesters were prepared; a dibenzobarrelene thionoester-ester **55** and the corresponding thioloester-ester **88** (Figure LXXXV). The acid derivative substituents that have been compared against an ester group in the dibenzobarrelene system have up until now been limited to other esters and to the acid group itself. A previous section dealt with comparing amides against a methyl ester. In this section the effects of substituting one of the four oxygen atoms in dibenzobarrelene **9** for sulphur can be assessed. This would also allow the relative influence of the various acid derivatives on the di-π-methane photoreaction to be systematically ordered.



Ac =

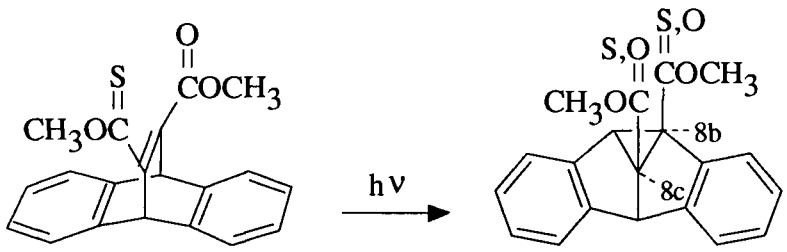


55: Ac = (S=C-OCH_3)
88: Ac = (O=C-SCH_3)

Figure LXXXV: Dibenzobarrelene Mixed Ester-Acyl Derivatives

Thionoester *vs.* Ester

Irradiation of the thionoester, compound **55**, in solution resulted in the formation of a single dibenzosemibullvalene photoproduct, compound **89**. These photolyses required rigorous degassing, as both the starting material and the photoproduct were susceptible to photooxidation. The bright yellow starting material gave a photoproduct that was essentially colourless. This is consistent with the disruption of the conjugation between the ester groups as a result of the rearrangement.



55 **89**

Figure LXXXVI: Irradiation of Mixed Thionoester-Ester **55**

The infrared spectra of the thionoester starting material and its photoproduct provide an interesting contrast between the bands of a carbonyl and a thiocarbonyl. Esters are generally seen to exhibit a carbonyl stretch anywhere from 1715 cm^{-1} to 1750 cm^{-1}, depending on the whether the ester is part of a conjugated system.[56] The thio-carbonyl band of thiono-esters, as seen for **55** (1271 cm^{-1}) and its photoproduct **89** (1248 cm^{-1}), typically occur in the region of 1000 cm^{-1} to 1300 cm^{-1}. It has been reported that a ratio of 1.34 to 1.60 for $\nu_{C=O}/\nu_{C=S}$ can be deduced from the relation between the stretching force constants of the carbonyl and the thiocarbonyl groups and the mass units of the atoms concerned.[91] The ratios of $\nu_{C=O}/\nu_{C=S}$ for the starting material **55** (1.34) and its photoproduct **89** (1.38) are in agreement with this relationship.

In order to confirm that the photoproduct **89** was a semibullvalene product, the photoproduct **90** from the di-π-methane rearrangement of the diester **9** was reacted with Lawesson's reagent[58] (Figure LXXXVII) This resulted in the recovery of a single product that was shown to be spectroscopically and physically identical to photoproduct **89**. However, since there are two possible sites of thiation, there are two possible products from the reaction of **90** with Lawesson's reagent (**LR**). These correspond to the two regioisomers that could result from the di-π-methane rearrangement of **89**. Thus, this synthesis was not able to distinguish between semibullvalene regioisomers.

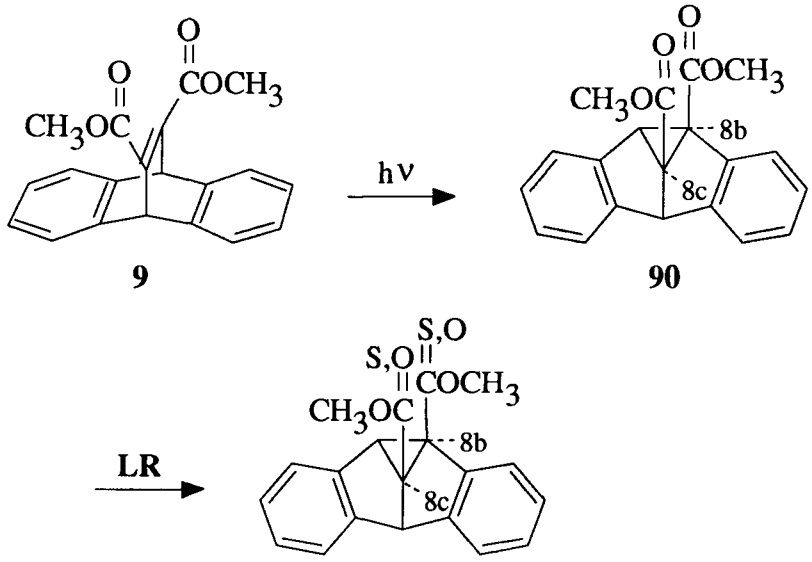


Figure LXXXVII: Conversion of Semibullvalene Diester to Photoproduct **89**

The same type of analysis of the mass spectrum[72] of compound **89** to determine the locations of the thioester and ester groups, as was done with mixed diesters, can be attempted. However the first fragment, which is almost equal in intensity to the base peak, corresponds to a loss of 33 mass units. This would seem to indicate the loss of S-H in an extremely efficient manner. It is doubtful that if the thioester were attached to carbon-(8c) that the second hydrogen transfer[73] could be made, thus reducing the reliability of this method. The mass spectrum also exhibits a peak at m/e 275, representing a loss of 59 a.m.u.. This can be assigned to the loss of a methoxy radical and carbon monoxide. If the double hydrogen transfer is in effect, then this indicates that the ester group is attached to carbon-(8c) and the thioester to carbon-(8b).

The proton NMR of compound **89** supports this assignment by the position of the methyl ester. As previously seen the methyl singlet of an ester group attached to carbon-(8c) typically appears around δ 3.80 ppm, whereas when the ester is attached to carbon-(8b) the peak appears δ 3.70 ppm. In the proton spectrum of compound **89**, the ester methyl signal appears at δ 3.83 ppm, indicating attachment to carbon-(8c). The assignment of this signal to the ester methyl is not definite however. The second methyl

singlet, attributable to the thioester methyl, appears at δ 4.08 ppm. These signal positions are too close to assign unequivocally.

To prove the structure, an X-ray crystallographic analysis was performed on a crystal of compound **89**. The structure was found to be of the opposite regiochemistry predicted (Figure LXXXVIII), with the ester attached to the benzylic carbon-(8b) (labelled C-12 in the X-ray diagram). Obviously the spectra of thiono-esters do not conform to the patterns observed in semibullvalene diesters.

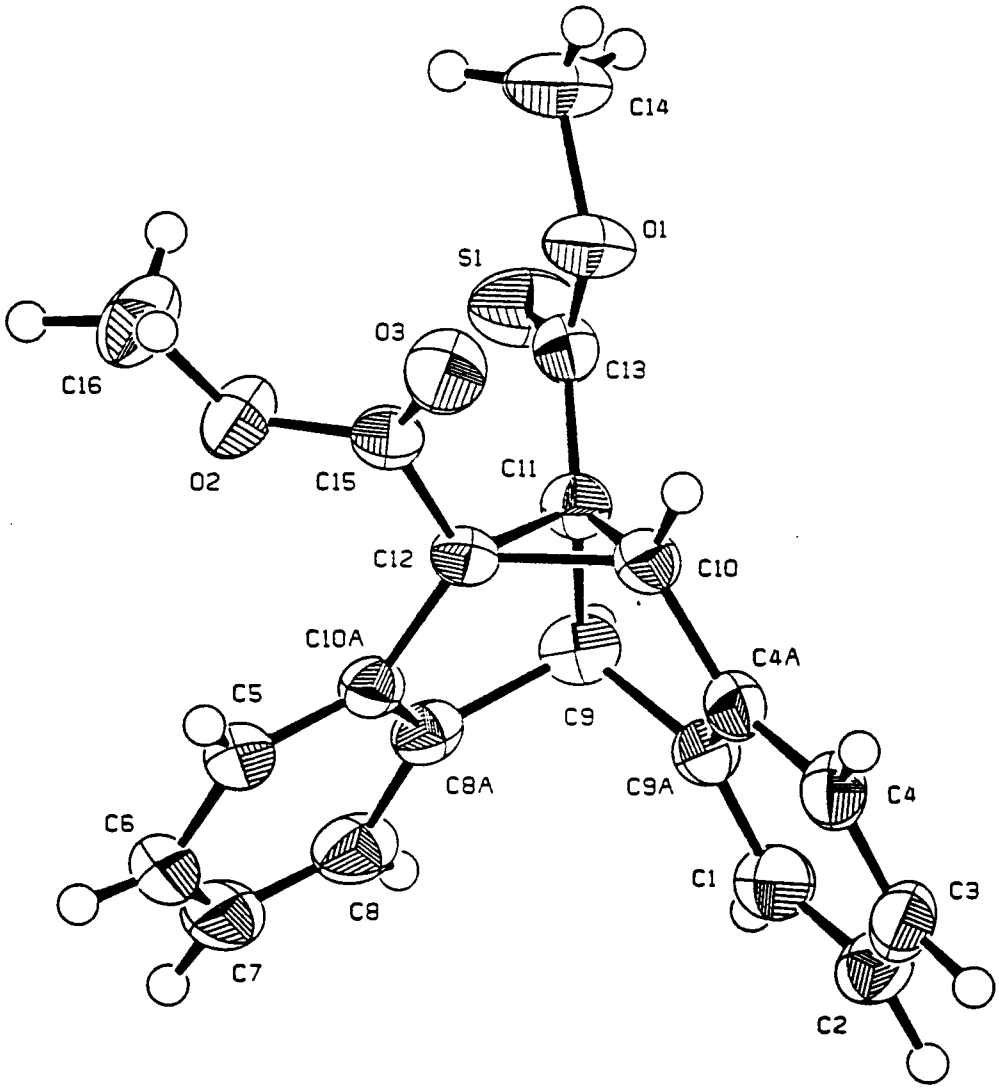


Figure LXXXVIII: X-ray Crystallographic Structure of Compound **89**

Regioselectivity in the Photoreaction of 55

The regioselectivity observed in the photolysis of compound **55** indicates that in the initial step of the di-π-methane rearrangement, bond formation occurs preferentially to the site of ester attachment. A comparison of the carbon-13 NMR signals of the two carbonyl carbons in the starting material **55** shows that the thio-carbonyl carbon (δ 211 ppm) is much more deshielded than the oxy-carbonyl carbon (δ 166 ppm).

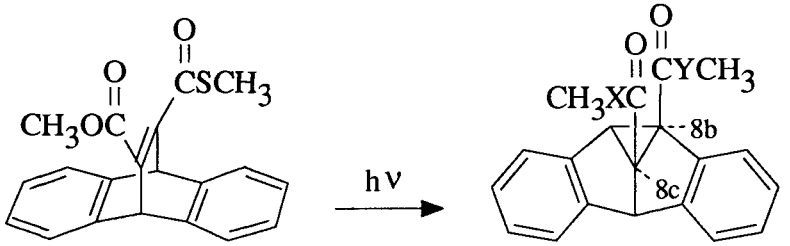
The properties of thiocarbonyl compounds as compared to the corresponding carbonyl compounds can be explained by considering simple molecular orbital calcualtions. Due to the higher electronegativity of the carbonyl oxygen and more extensive σ-bond overlap with the adjacent carbon atom, the p-orbital system of a carbonyl group is more stabilized than that of a thiocarbonyl. As the antibonding π*-level of the thiocarbonyl group lies energetically lower than that of the carbonyl group, the thiocarbonyl is the better π-acceptor. The different energies of the π*-levels are responsible for the greater polarizability of a thiocarbonyl group during interaction with π-donors or π-acceptors. Due to the small orbital overlap, the weak unstable C=S bond tends to rearrange to a more stable C-S bond.[92]

In the biradical which arises from the excitation **55**, the carbon-sulphur double bond is able to resonate with the adjacent radical centre. The resonance structure that results would have the radical located on the sulphur and a carbon-carbon double bond exocyclic to the bridge. Sulphur radicals are generally regarded as more stable than analogous alkoxide radicals.[93] The better orbital overlap between two carbon 2p orbitals, rather than between a carbon 2p and a sulphur 3p orbital, favours this resonance structure. Initial bond formation thus becomes more favourable adjacent to the less stable site of ester attachment. As such, in the semibullvalene product **89** the ester ends up attached to carbon-(8b) while the thiono-ester becomes attached to carbon-(8c).

The reasons behind the regioselectivity of the reaction of Lawesson's reagent on the semibullvalene diester **90** are unclear but are undoubtedly rate and probably sterically related. The fact that the thiation of **90** produced the same regioisomer as the photolysis of **55** is probably coincidental and not mechanistically connected.

Thioloester *vs.* Ester

Thiolo-ester **88** was produced by the reaction of the acid-chloride of ester-acid **44** with methanethiol. The photolysis of **88** yielded a single photoproduct **91** (Figure LXXXIX). Irradiations of **88** were accompanied by photooxidation, although tlc analysis indicated not as severely as compound **55**.



88 **91**

Figure LXXXIX: Irradiation of Thiolo-adduct, Compound **88**

The location of the ester and thiolo-ester groups in the semibullvalene photoproduct can be predicted based on the same type of analysis used to rationalized the regioselectivity in the photolyses of ester-amides. Again the regioisomer that results from the more stable biradical intermediate should be favoured. This can be determined by considering the relative abilities of the ester and thiolo-ester groups to stabilize an adjacent radical. A radical centre adjacent to a thiolo-ester should be better stabilized than one adjacent to an ester owing to a more favourable resonance interaction. The carbonyl group of the ester would presumably have a more favourable resonance interaction with the alkoxide oxygen than would the thiolo-ester with the sulphur because

of more effective orbital overlap. Thus the carbonyl group of the ester would be less "available" for resonance with the unpaired electron of the radical. The energy difference between the SOMO of the radical and the LUMO of the thiolo-ester would be less than for the SOMO-LUMO interaction of the radical and ester. Based on this analysis, one would predict that the ester should end up in the benzylic position (attached to carbon-(8b)) and the thiolo-ester attached to carbon-(8c).

The infrared spectrum of 88 exhibited two carbonyl bands; an ester band at 1708 cm^{-1} and a thiolo-ester carbonyl band at 1675 cm^{-1}. The lower wavenumber of the thiolo-ester band is consistent with the thiolo-carbonyl having more double bond character than the ester carbonyl bond. This might be a result of a less efficient resonance between the suphur and the carbonyl than in the case of the ester carbonyl and alkoxide oxygen.

The structure of the photoproduct was determined by X-ray crystallographic analysis to have the thiolo-ester attached to carbon-(8c) (XC).

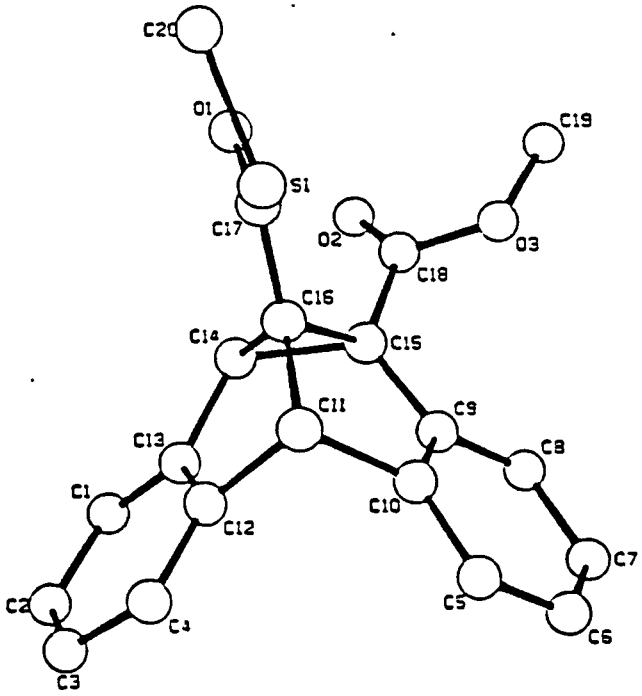


Figure XC: X-ray Crystallographic Diagram of Photoproduct **91**

VI: Concluding Remarks

This study has established the ability of dibenzobarrelene amide derivatives to undergo the di-π-methane photorearrangement both in solution and in the solid state. Furthermore, it was found that certain amides and ester-amides also participated in hydrogen abstractions in addition to the di-π-methane reaction. These abstraction reactions led to either bridge-saturated monosubstituted amide or ester-amide products, or to β-lactams.The mechanism of the abstraction reaction was investigated and it can be concluded that ketene intermediates are involved.

From the studies on the thio-esters and from the studies on the ester-amides, the various acid derivatives can be ordered based on their relative ability to direct the di-π-methane rearrangement. This ordering is observed to follow a trend in which the acid derivative better able to stabilize the adjacent radical ends up attached to carbon-(8c) of the semibullvalene system. This trend in all likelihood could be applied to other di-π-methane systems.

The following trend can be outlined in increasing order of the group which is best able to stabilize the radical adjacent to it:

$$H << CO2^{-} (<) CONR_2 < CO_2R < CO_2H < CSOR, COSR$$

From this one can predict how any combination of the above acid derivatives will effect the outcome of a di-π-methane system to which they are attached.

EXPERIMENTAL

I: General Experimental

Infrared Spectra (IR): Infrared spectra were run on a Perkin-Elmer 1700 Fourier transform infrared spectrometer, with the absorption maxima (ν_{max}) of the spectral bands reported in recriprocal centimetres (cm^{-1}). Liquid samples were run neat as a thin film between two sodium chloride plates. The spectra of solid samples were recorded by preparation of a KBr pellet by grinding 100-150 mg of KBr and 1-5 mg of sample together and compressing the mixture in a Perkin-Elmer evacuable die (186-0002) with a Carver laboratory press (Model B, 20,000 psi).

Nuclear Magnetic Resonance Spectra (NMR): Proton nuclear magnetic resonance (^1H NMR) spectra, unless otherwise noted, were recorded in deuterochloroform using tetramethylsilane (TMS) as the internal reference on a Brüker AC-200 (200 MHz), a Varian XL-300 (300MHz) and/or on a Brüker WP-400 (400 MHz) spectrometer at ambient temperature. Signal positions (δ) are given in parts per million (ppm) with the number of protons, multiplicity, coupling constants in Hertz (Hz), and assignments given in parenthesis following the signal position. The multiplicities of the signals have been abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 50.3 MHz on a Brüker AC-200 instrument using deuterochloroform as solvent and the middle peak of the solvent signal as internal reference. All spectra were run under broad band proton decoupling ^{13}C-^1H. Chemical shifts (δ) are reported in ppm. Assignments, where given, were supported by APT (attached proton test) ^{13}C spectra.

Mass Spectra (MS): Low and high resolution mass spectra were obtained on a Kratos MS 50 instrument operating at 70 eV. Coupled gas chromatography-mass spectral analyses (gc-ms) were performed on a Kratos MS 80RFA spectrometer connected to a

Carlo-Erba 4160 gas chromatograph. Intensities are recorded in brackets as percentages of the base peak. Molecular ions are designated as M^+.

Ultraviolet Spectra (UV): Ultraviolet spectra were recorded on a Perkin Elmer Lambda-4B UV/Vis spectrophotometer in acetonitrile or methanol. Wavelengths (λ) in nanometres (nm) are reported and extinction coefficients (ε) are given in brackets. Spectral grade solvents available from BDH were used without further purification.

Microanalysis: Elemental analyses were performed by the departmental microanalyst, Mr. P. Borda.

Melting Points (mp): Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected.

Gas Liquid Chromatography (glc): Gas chromatographic analyses were run on a Hewlett-Packard 5890 A gas chromatograph, using a 15 m x 0.25 mm fused silica capillary DB-1 (J&W Scientific Inc.) and a column head pressure (carrier gas: Helium) of 15 psi. The signal from a flame ionization detector was integrated by a Hewlett-Packard 3392 A integrator.

Chromatography: Analytical thin layer chromatography was performed on commercial pre-coated silica gel plates (E. Merck, type 5554) and the plates developed in the indicated solvent system. The developed plates were observed with UV light. Flash column chromatography[94] was carried out under 5-10 psi of N_2 pressure using 0.040-0.063 mm particle size silica gel (Merck 9385) slurry packed with the eluting solvent. Column size was determined by the amount of crude material to be purified.

Solvents and Reagents: Spectral grade solvents were used for spectroscopic and photochemical studies. Further purification was not necessary unless otherwise noted.

Reagents for the synthesis of starting materials were purified according to methods reported in the literature as indictated.

X-ray analysis: All X-ray crystal structures were determined on a Rigaku AFC6S 4-circle diffractometer using single crystal X-ray diffraction analysis, by Dr. Steve Rettig, Dr. Ray Jones and Dr. James Trotter of the UBC Chemistry Department. Stereoscopic diagrams were drawn with a locally modified version of the ORTEP program at a 50% probability level.

II: Synthesis of Starting Materials

A: Dibenzobarrelene Monoamides

Methyl 9,10-Dihydro-9,10-ethenoanthracene-11-carboxylate[47] (4)

A Carius tube containing 502 mg (2.81 mmol) of anthracene and 0.3 ml (1.2 eqs) of methyl propiolate (available from Aldrich) was sealed under vacuum and heated at 180°C for 6 h in a Kugelrohr oven. The resulting brown glass-like material obtained upon cooling was subjected to column chromatography using an eluting solvent system of petroleum ether (PET) and ethyl acetate (EtOAc, 80:20 v/v). The white solid recovered was recrystallized from chloroform/PET to give colourless crystals with mp = 180-181°C (lit;[47] 177-178°C). Spectroscopic data of **4** given below are in complete agreement with the literature values.[47]

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.90 (1, d, J = 6.0 Hz, Vinylic H), 7.45-6.85 (8, m, Ar-H), 5.68 (1, d, J = 6.0 Hz, Bridgehead H_9), 5.20 (1, s, Bridgehead H_{10}), 3.70 (3, s, $CO_2\mathbf{CH_3}$).

^{13}C NMR ($CDCl_3$, 50MHz): δ 165.2 (C=O); 149.6, 145.3, 144.5, 144.4 (Vinylic and Ar-C's, No H's); 125.1, 124.9, 123.7, 123.5 (Ar-C-H's); 51.8, 51.6, 50.4 (Bridgehead C's and $CO_2\mathbf{CH_3}$).

IR (KBr) ν_{max}: 1709 (C=O), 1615 (E-C=C), 1222 (C-O) cm^{-1}.

MS m/e (rel. intensity): 262 (M^+, 46.1), 203 (100), 202 (93), 178 (13), 101 (23).

Yield: 62.5% (lit;[47] = 66%).

Preparation of 9,10-Dihydro-9,10-ethenoanthracene-11-carboxamide[50] (32)

Preparation of the dibenzobarrelene monoamides, unless otherwise stated, followed the Weinreb[48] procedure for the conversion of esters to amides, as outlined below for the unsubstituted monoamide.

Preparation of 0.67 M Stock Solution of Aluminum Amide Reagent

A 2.0 M solution (2 ml) of trimethylaluminum in toluene (available from Aldrich) was slowly added to a suspension of 214 mg (4.0 mmol) of ammonium chloride in 4 ml of dry toluene at 5°C. After addition was complete, the mixture was allowed to warm to room temperature and stirred for 1-2 hrs until gas evolution had ceased. It was found that in order for the alkylaluminum amide reagents to react cleanly it was imperative that the amine hydrochlorides be recrystallized (ethanol) and dried on a high-vacuum line prior to use. As well, the glassware used for the stock solution of the aluminum amide reagent and for the aminolysis had to be flamed-dried and cooled in a desiccator before use. Stock solutions of the aluminum amide reagents generally could be stored in the freezer for up to 48 h before significant decomposition of the reactive species occurred.

Procedure for the Aminolysis of Compound 4

To a solution of 236 mg (0.90 mmol) of compound **4** in 10 ml of dry toluene was added 4.0 ml (2.7 mmol) of the ammonium chloride derived aluminum amide reagent. The solution was heated under nitrogen at 50°C for twelve hours at which point no starting material was observable by tlc. The reaction mixture was cooled and quenched with 5% HCl. The organic layer was removed and the aqueous layer washed three times with 20 ml of ethyl acetate. The organic extracts were combined, dried over magnesium sulphate and the solvent removed *in vacuo* to afford the crude amide. After column

chromatography (PET/EtOAc, 50:50), 150 mg of the amide was recovered for a yield of 68%. Recrystallization from chloroform gave colourless crystals with a melting point of 275-277°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-6.90 (9, m, Vinylic and Ar-H), 5.70 (1, d, J = 2.0 Hz, Bridgehead H_9), 5.48 (2, broad, exchanges with D_2O, CON**H$_2$**), 5.22 (1, d, J = 6.0 Hz, Bridgehead H_{10}).

^{13}C NMR (50 MHz, $CDCl_3$): δ 167.2 (C=O); 147.6, 145.3, 144.5, 143.3 (Vinylic and Ar-C's, No H's); 125.1, 124.8, 123.8, 123.3 (Ar-C-H's); 51.3, 50.4 (Bridgehead C's).

IR (KBr) ν_{max}: 3494 (Free N-H), 3284 (H-bonded N-H), 1673, 1651 (C=O), 1614 (A-C=C), 1459, 1406 cm^{-1}.

UV (CH_3CN) λ_{max}: 278.9 nm (ε = 3200), 271.1 (ε = 2800).

MS m/e (rel. intensity): 247 (M^+, 27.9), 203 (100), 178 (55.8). Calculated mass: 247.0998; found: 247.0995.

Analysis calculated for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.44; H, 5.15; N, 5.58.

Preparation of 9,10-Dihydro-N,N-dimethyl-9,10-ethenoanthracene-11-carboxamide[51] (33)

Preparation of alkyl substituted monoamides proceeded as for the primary amide with two notable differences:

i) instead of the three equivalents of amido reagent used in the primary amine hydrochloride case, with alkyl substituted reagents two equivalents were found to be sufficient;

ii) additionally, because the alkylated amide reagents were not as susceptible to decomposition, reactions were run at reflux instead of 50°C.

To prepare the dimethyl monoamide **33** from **4**, 248 mg (0.95 mmol) of the ester were reacted with 3.0 ml of the dimethylamine hydrochloride-derived aluminum amide reagent in 10 ml of dry toluene for a period of 8 h. The reaction mixture was cooled and 5% HCl added to quench any remaining reactive amido reagent. After extracting with ethyl acetate (3 x 25 ml), the organic layers were combined, dried with magnesium sulphate, filtered, and the solvent removed *in vacuo* to give a brown solid. The pure amide product was obtained (216 mg, 0.79 mmol) after purification by column chromatography (PET/EtOAc, 50:50) in a yield of 83%. Recrystallization from PET/EtOAc gave colourless crystals, mp = 130-132°C (lit;[51] 131-133°C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-6.94 (9, m, Vinylic and Ar-H), 5.38 (1, s, Bridgehead H_9), 5.20 (1, d, J = 7.5 Hz, Bridgehead H_{10}), 2.94 (6, broad, CON(CH_3)$_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.9 (C=O); 147.0, 145.4, 145.1, 140.6 (Vinylic and Ar-C's, No H's); 124.9, 124.7, 123.5, 123.1 (Ar-C-H's); 53.1, 51.1 (Bridgehead C's).

IR (KBr) ν_{max}: 1635 (C=O),1618 (A-C=C); 1458, 1397, 1181 cm^{-1}.

UV (CH_3CN) λ_{max}: 279.3 nm (ε = 3000), 271.4 (ε = 2400).

MS m/e (rel. intensity): 275 (M^+, 47.8), 203 (100.0), 178 (31.7), 72 (96.7). Calculated mass: 275.1310; found: 275.1305.

Preparation of N,N-Diethyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxamide (34)

The preparation of compound **34** was carried out in the same manner as for the dimethyl adduct, using 256 mg (0.97 mmol) of the starting ester and 3.0 ml of the diethylamine hydrochloride-derived aluminum reagent in 10 ml of dry toluene. The reaction was quenched after 8 h with 5% HCl. After extraction with ethyl acetate (3 x 50 ml), the organic layer was separated and dried with magnesium sulphate. After filtration and removal of the solvent, a yellowish-brown solid remained which was shown by IR to

be predominantly amide. The crude amide was subjected to column chromatography (PET/EtOAc, 80:20) to yield 207 mg (70% yield) of the pure amide. Recrystallization from ethanol gave colourless prisms (mp = 123.5-124°C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94-7.40 (9, m, Vinylic and Ar-H), 5.30 (1, d, J = 1.5 Hz, Bridgehead H_9), 5.18 (1, d, J = 6.0 Hz, Bridgehead H_{10}), 3.24 (4, broad, $CON(\mathbf{CH_2}CH_3)_2$), 1.08 (6, broad, $CON(CH_2\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.0 (C=O); 148.0, 145.4, 145.1, 138.3 (Vinylic and Ar-C's, No H's); 124.8, 124.7, 123.4, 123.1 (Ar-C-H's); 53.3, 51.0 (Bridgehead C's).

IR (KBr) ν_{max}: 1623, 1602 (C=O), 1474, 1457 cm^{-1}.

UV (CH_3CN) λ_{max}: 279.3 nm (ε = 3660), 271.4 (ε = 2720).

MS m/e (rel. intensity): 303 (M^+, 11.2), 203 (32.5), 202 (25.2), 178 (21.2), 100 (100). Calculated mass: 303.1623; found: 303.1615.

Analysis calculated for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 82.87; H, 6.94; N, 4.61.

The structure of this compound was also supported by an X-ray diffraction analysis. The crystal data were as follows: $C_{21}H_{21}NO$; orthorhombic; space group *Pbca;* a = 31.862 (3)Å, b = 11.088 (2)Å, c = 9.400 (3)Å; V = 3321 (2)$Å^3$; z = 8; D_{calc} = 1.214 g/cm^3; R = 0.037.

Preparation of N,N-Dibenzyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxamide (35)

Compound **35** was prepared via Weinreb aminolysis in the same manner as the dimethyl adduct **33**, using 306 mg (1.18 mmol) of the starting ester and 3.6 ml of the dibenzyl aluminum amide reagent in 12 ml of dry toluene. The reaction mixture was worked up after refluxing for 12 h and extracted with ethyl acetate (3 x 50 ml). Drying and removal of the solvent *in vacuo* was followed by purification of the resulting brown

viscous oil by column chromatography (Hexanes/EtOAc, 90:10). Recrystallization from PET/chloroform yielded small white crystals (459 mg, 1.23 mmol) for a yield of 92%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.84-7.34 (19, m, Vinylic and Ar-H), 5.48 (1, s, Bridgehead H_9), 5.06 (1, d, J = 6.4 Hz, Bridgehead H_{10}), 4.56 and 4.28 (2x2, broad, $CON(\mathbf{CH_2}Ph)_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.7 (C=O); 146.6, 14.5, 145.0, 140.1, 136.9 (Vinylic and Ar-C's, No H's); 128.9, 127.6, 125.0, 124.9, 123.6, 123.3 (Ar-C-H's); 53.3, 51.2 (Bridgehead C's); 47.9 ($CON(\mathbf{CH_2}Ph)_2$).

IR (KBr) ν_{max}: 1636 (C=O), 1456, 1256 cm^{-1}.

UV (CH_3CN) λ_{max}: 279.3 nm (ε = 3130), 271.2 (ε = 2630).

MS m/e (rel. intensity): 427 (M^+, 34.1), 336 (9.7), 249 (18.2), 203 (100). Calculated mass: 427.1936; found: 427.1944.

Analysis calculated for $C_{31}H_{25}NO$: C, 87.09; H, 5.89; N, 3.28. Found C, 86.78; H, 5.83; N, 3.21.

mp = 133-134°C.

Preparation of 9,10-Dihydro-N,N-di-(2-propyl)-9,10-ethenoanthracene-11-carboxamide (37)

Weinreb aminolysis to produce compound **37** was unsuccessful. Therefore the following alternate synthesis was used, involving the conversion of the dibenzobarrelene acid to the corresponding acid chloride and subsequently to the amide with di-*iso*-propyl amine.

9,10-Dihydro-9,10-ethenoanthracene-11-carboxylic acid[52] (36)

A solution of 30% NaOH (20 ml) to which ethanol (12 ml) had been added was placed in a 50 ml round bottom flask. Methyl 9,10-dihydro-9,10-ethenoanthracene-11-

carboxylate (Compound **4**; 807 mg, 3.08 mmol) was added and the resulting solution refluxed for two hours. After cooling, saturated sodium bicarbonate solution (80 ml) was added to the mixture which was then washed with diethyl ether (3 x 100 ml) to remove any residual ester present. The aqueous layer was then acidified dropwise with 1.0 M HCl and washed with diethyl ether (3 x 75 ml). After drying with magnesium sulphate, the organic layer was filtered, the solvent removed *in vacuo,* and the resulting acid obtained in 90% yield (690 mg, 2.77 mmol). The acid was subsequently recrystallized from acetonitrile.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (1, dd, J = 6.7 and 2.7 Hz, Vinylic H_{12}), 6.75-7.40 (8, m, Ar-H), 5.64 (1, d, J = 2.7 Hz, Bridgehead H_9), 5.26 (1, d, J = 6.7 Hz, Bridgehead H_{10}).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.9 (C=O); 152.4, 145.1, 144.0, 124.2 (Vinylic and Ar-C's, No H's); 125.0, 123.7, 123.6 (Ar-C-H's); 51.8, 50.1 (Bridgehead C's).

IR (KBr) ν_{max}: 3200 (OH), 1675 (C=O), 1610 (C=C-CO_2H), 1233 (C-O) cm^{-1}.

MS m/e (rel. intensity): 248 (M^+, 64.1), 203 (97.8), 178 (10.6).

mp = 248-250°C (lit;[52] 250°C).

Synthesis of Di-(2-propyl) Amide Adduct (37)

The preparation of compound **37** involved the addition of 568 mg (2.29 mmol) of acid **36**, 1.0 ml of oxalyl chloride and 50 ml of dichloromethane to a 100 ml flame dried round bottom and refluxing the reaction mixture under nitrogen overnight. The excess oxalyl chloride and solvent were then removed *in vacuo*. Freshly distilled di-*iso*-propyl amine (2 ml) was added along with 30 ml of anhydrous benzene and the resulting solution refluxed for 4 h. After cooling and filtering off the precipitated amine hydrochloride, 50 ml of diethyl ether were added to the reaction mixture. The mixture was washed with water and then 5% HCl solution to remove any residual amine. The

organic layer was subsequently washed with water, saturated sodium bicarbonate solution and then water again to remove any unreacted dibenzobarrelene acid. The organic layer was dried and the solvent removed, leaving a viscous oil. The pure amide (570 mg, 1.72 mmol) was obtained after column chromatography (PET/EtOAc, 90:10) in 75% yield. Recrystallization from chloroform/PET resulted in colourless prisms (mp = 186°C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94-7.38 (8, m Ar-H), 6.86 (1, dd, J = 1.6, 6.0 Hz, Vinylic H_{12}), 5.20 (1, d, J = 1.6 Hz, Bridgehead H_9), 5.15 (1, d, J = 6.0 Hz, Bridgehead H_{10}), 3.52 (2, broad, $CON(CH(CH_3)_2)_2$), 1.22 (12, broad, $CON(CH(CH_3)_2)_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.9 (C=O); 148.6, 14.5, 145.1, 135.9 (Vinylic and Ar-C's, No H's); 124.8, 124.7, 123.3, 123.1, (Ar-C-H's); 53.3, 50.8 (Bridgehead C's); 20.9 (Methyls).

IR (KBr) ν_{max}: 1619 (C=O), 1459, 1337, 1150 cm^{-1}.

UV (CH_3CN) λ_{max}: 279.4 nm (ε = 3980), 271.1 (ε = 2860).

MS m/e (rel. intensity): 331 (M^+, 59.7), 231 (46.6), 203 (100), 178 (45.4). Calculated mass: 331.1936; found 331.1940.

Analysis calculated for $C_{23}H_{25}NO$: C, 83.35; H, 7.60; N, 4.23. Found C, 83.26; H, 7.66; N, 4.15.

The structure of this compound was also supported by an X-ray diffraction analysis. The crystal data were as follows: $C_{23}H_{25}NO$; monoclinic; space group *P2$_1$/c;* a = 10.846 (1)Å, b = 10.788 (1)Å, c = 17.0467 (9)Å, β = 107.836(6)°, V = 1898.8 (4)Å^3; z = 4; D_{calc} = 1.159 g/cm^3; R = 0.037.

B: Symmetrical Dibenzobarrelene Diamides

Dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate[53] (9)

Compound **9** was prepared by placing 3.8 g (21.3 mmol) of anthracene and 3.8 ml (23.1 mmol) of dimethyl 2-butyne-1,4-dioate (dimethyl acetylenedicarboxylate; available from Aldrich) in a Carius tube, sealing under vacuum and heating at 180°C for 8 h. The resulting brown crystalline material was partially purified by column chromatography (PET/EtOAc, 80:20). Further purification was necessary by recrystallization from chloroform/ethanol to give a white solid (6.20 g, 19.4 mmol) in 91% yield. The spectroscopic data for this compound are in complete agreement with the published literature.[53]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96-7.42 (8, m, Ar-H), 5.48 (2, s, Bridgehead H_9 and H_{10}), 3.80 (6, s, $CO_2\mathbf{CH_3}$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 165.9 (C=O); 147.0, 132.8 (Ar-C's, No H's); 125.5, 123.8 (Ar-C-H's); 52.5, 52.4 (Bridgehead and methyl C's).

IR (KBr) ν_{max}: 1715, 1722 (2xC=O), 1636 (E-C=C-E), 1273 cm^{-1}.

MS m/e (rel. intensity): 320 (M^+, 71.2), 260 (100), 202 (76.6), 178 (49.7).

mp = 159.5-160.5°C (lit;[53] 160-161°C).

Preparation of 9,10-Dihydro-N,N,N',N'-tetramethyl-9,10-ethenoanthracene-11,12-dicarboxamide (38)

Preparation of the symmetrical dibenzobarrelene diamide series of compounds followed a synthetic procedure similar to that for the monoamides (i.e. via a Weinreb aminolysis) as outlined for compound **33**.

To a solution of dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (343 mg, 1.07 mmol) in 10 ml of dry toluene was added 6 ml (4.0 mmol, 2

eqs) of the dimethylamine hydrochloride-derived aluminum amide reagent (0.67 M). The reaction mixture was refluxed overnight at which point no starting material was observed by tlc. After cooling and subsequent quenching with 5% HCl, the aqueous layer was separated and washed (3 x 40 ml) with ethyl acetate. The organic extracts were combined, dried, filtered, and concentrated *in vacuo* to give the crude diamide. The pure amide was obtained after column chromatography (EtOAc/PET, 80:20) in a yield of 98% (363 mg, 1.05 mmol). White crystals (mp = 174-175^{o}C) were obtained upon recrystallization from ethanol.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98-7.40 (8, m, Ar-H), 5.20 (2, s, Bridgehead H_9 and H_{10}), 2.94 and 2.62 (2x6, 2 broad, 2xCON($\mathbf{CH_3}$)$_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.5 (C=O); 144.4, 143.5 (Vinylic and Ar-C's, No H's); 125.2, 123.4 (Ar-C-H's); 53.3 (Bridgehead C's); 38.1, 34.6 (2xCON($\mathbf{CH_3}$)$_2$).

IR (KBr) ν_{max}: 1625 (C=O), 1459, 1403 cm^{-1}.

UV (CH_3CN) λ_{max}: 279.6 nm (ε = 2880), 271.5 (ε = 2470).

MS m/e (rel. intensity): 346 (M^+, 9.6), 303 (100), 274 (21.4), 258 (10.0), 203 (33.4), 178 (81.6), 72 (84.7). Calculated mass: 346.1681; found 346.1688.

Analysis calculated for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.06; H, 6.37; N, 8.08.

Preparation of 9,10-Dihydro-N,N'-dimethyl-9,10-ethenoanthracene-11,12-dicarboxamide (39)

Compound **39** was prepared in the same manner as compound **33** using 304 mg (0.95 mmol) of starting diester **9**, 8 ml (2.7 eqs.) of the methylaluminum amide reagent solution and 10 ml of dry toluene. The reaction mixture was refluxed for 7 h after which time no starting material could be observed by glc. After quenching with 5% HCl and work-up in the usual manner, the solvent was removed *in vacuo* leaving a white

amorphous solid shown to be essentially the pure amide by proton nmr. Crystals of the pure amide (286 mg, 0.90 mmol) were obtained by recrystallization from ethanol (mp > 300°C) in a yield of 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00-7.44 (8, m, Ar-H), 6.84 (2, broad, 2xCONH(CH_3)), 5.58 (2, s, Bridgehead H_9 and H_{10}), 2.86 and 2.88 (2x3, 2s, 2xCONH(**CH_3**)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 167.8 (C=O); 146.0, 144.0 (Vinylic and Ar-C's, No H's); 125.4, 123.6 (Ar-C-H's); 53.5 (Bridgehead C's); 26.6 (CONH(**CH_3**)).

IR (KBr) ν_{max}: 3265 (N-H, Free and H-Bonded), 1625 (C=O), 1562 (Amide type II), 1406, 1162 cm^{-1}.

UV (CH_3OH) λ_{max}: 278.8 nm (ε = 2980), 270.4 (ε = 3060).

MS m/e (rel. intensity): 318 (M^+, 17.0), 261 (68.2), 230 (13.3), 204 (100), 203 (71.8), 178 (51.0), 58 (10.5). Calculated mass: 318.1368; found 318.1371.

Analysis calculated for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found; C, 75.30; H, 5.69; N, 8.81.

Preparation of 9,10-Dihydro-N,N,N',N'-tetraethyl-9,10-ethenoanthracene-11,12-dicarboxamide (40)

Compound **40** was prepared via Weinreb aminolysis starting with 1.03 g (3.2 mmol) of diester **9**, 20.0 ml (2 eqs.) of the diethylaluminum amide reagent, and 30 ml of dry toluene. The reaction mixture was heated at reflux for a period of 6 h. Glc analysis indicated at this point that none of the starting ester remained. The reaction mixture was quenched with 5% HCl and the aqueous layer extracted with ethyl acetate (3 x 50 ml). The combined organic fractions were dried, filtered and concentrated *in vacuo* to give a viscous yellow oil. The pure amide was obtained after purification by column

chromatography (EtOAc/Hexanes, 70:30) in 98% yield (1.26 g, 3.14 mmol). Recrystallization from acetonitrile gave colourless prisms (mp = 146-147°C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96-7.40 (8, m, Ar-H), 5.18 (2, s, Bridgehead H_9 and H_{10}), 3.38 and 2.90 (2x2, 2q, J = 7.5 Hz, $CON(\mathbf{CH_2}CH_3)_2$), 1.10 and 0.88 (2x3, 2t, J = 7.5 Hz, $CON(CH_2\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.0 (C=O); 144.4, 142.0 (Vinylic and Ar-C's, No H's); 125.0, 123.3 (Ar-C-H's); 53.2 (Bridgehead C's); 42.4, 38.6 ($CON(\mathbf{CH_2}CH_3)_2$); 14.6, 12.8 $CON(CH_2\mathbf{CH_3})_2$).

IR (KBr) ν_{max}: 1615 (C=O), 1460, 1292 cm^{-1}.

UV (CH_3CN) λ_{max}: 279.4 nm (ε = 3020), 271.4 (ε = 2370).

MS m/e (rel. intensity): 402 (M^+, 2.3), 331 (35.7), 302 (22.9), 262 (10.5), 202 (25.3), 178 (48.5), 72 (100). Calculated mass: 402.2307; found 402.2323.

Analysis calculated for $C_{26}H_{30}N_2O_2$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.80; H, 7.60; N, 7.00.

Preparation of N,N'-Diethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxamide (41)

The diethyl diamide was prepared by the addition of 356 mg (1.11 mmol) of the starting diester **9**, 7 ml (2.1 eqs) of the diethyl aluminum amide reagent, and 10 ml of dry toluene to a 25 ml round bottom flask and refluxing under nitrogen for 6 h. Tlc and gc analysis indicated that all the starting material had reacted completely. The reaction mixture was quenched with 5% HCl and the aqueous layer extracted with chloroform (3 x 50 ml). The organic layers were combined, dried and filtered. The solvent was removed *in vacuo* leaving a brown amorphous material which upon infrared analysis was determined to be the crude diamide. Purification by column chromatography (EtOAc/Hexanes, 80:20) resulted in the recovery of a white powdery material.

Recrystallization from ethanol produced small white crystals (mp > 300°C) in a yield of 94% (360 mg, 1.04 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92-7.40 (8, m, Ar-H), 6.60 (2, broad, CONHEt), 5.48 (2, s, Bridgehead H_9 and H_{10}), 3.26 (4, m, 2xCONH($\mathbf{CH_2}CH_3$)), 1.10 (2x3, 2t, J = 7.2 Hz, 2xCONH($CH_2\mathbf{CH_3}$)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 166.5 (C=0); 147.2, 144.1 (Vinylic and Ar-C's, No H's); 125.4, 123.6 (Ar-C-H's); 53.4 (Bridgehead C's); 34.8 (CONH($\mathbf{CH_2}CH_3$); 14.6 (CONH($CH_2\mathbf{CH_3}$).

IR (KBr) ν_{max}: 3448 (N-H, Free and H-bonded) 3271 (Free N-H), 1622 (C=O), 1554 (Amide type II), 1459 cm^{-1}.

UV (CH_3CN) λ_{max}: 278.7 nm (ε = 2730), 270.1 (ε = 2850).

MS m/e (rel. intensity): 346 (M^+, 7.3), 303 (17.7), 275 (32.9), 230 (23.3), 204 (100), 178 (59.4). Calculated mass: 346.1681; found 346.1679.

Analysis calculated for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.44; H, 6.35, N, 8.02.

C: Dibenzobarrelene Ester-Amides

9,10-Dihydro-9,10-ethenoanthracene-11,12-dicarboxylic acid[53] (42)

The hydrolysis of diester **9** to the diacid was carried out by addition of the diester (4.1 g, 12.8 mmol) to a mixture of 25 ml of 30% NaOH solution and 15 ml of ethanol. The mixture was heated to reflux until all the suspended material had dissolved and refluxed for a further two hours. After cooling to ambient temperature, the reaction mixture was washed with diethyl ether (2 x 50 ml) to remove any traces of the starting ester. The remaining aqueous solution was acidified by dropwise addition of concentrated hydrochloric acid resulting in the precipitation of the diacid. After precipitation was complete, the solution was washed with diethyl ether (3 x 100 ml) to recover the diacid. The organic layers were subsequently dried with magnesium sulphate, filtered, and the solvent removed *in vacuo*. This gave the essentially pure diacid as a slightly yellow solid (3.2 g, 11.1 mmol) in 87% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (2, broad, exchanges with D_2O, CO_2**H**), 7.04-7.56 (8, m, Ar-H), 6.00 (2, s, Bridgehead H_9 and H_{10}).

IR (KBr) ν_{max}: 3450-3600 (CO_2H), 1700 (C=O) cm^{-1}.

MS m/e (rel. intensity): 292 (M^+, 0.7), 248 (32.0), 230 (64.1), 202 (100), 178 (9.9).

mp = 214-215°C (lit;[53] 215-216°C).

9,10-Dihydro-9,10-ethenoanthracene-11,12-dicarboxylic acid anhydride[53] (43)

An excess of oxalyl chloride (6 ml) was added to a suspension of 4.6 g (15.8 mmol) of diacid **42** in 50 ml of dichloromethane. The reaction mixture was refluxed for 24 h under nitrogen and then cooled to ambient temperature. The solvent and excess

oxalyl chloride were removed *in vacuo* and the resulting solid recrystallized from ethyl acetate to give slightly yellow crystals (3.4 g, 12.4 mmol) in a yield of 78%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98-7.50 (8, m, Ar-H), 5.58 (2, s, Bridgehead H_9 and H_{10}).

IR (KBr) ν_{max}: 1843 (C=O, Antisymmetric stretch), 1788, 1767 (C=O, Symmetric stretch), 1637 (C=C) cm^{-1}.

MS m/e (rel. intensity): 274 (M^+, 58.4), 230 (52.2), 202 (100), 178 (55.5)

mp = 246°C (lit;[53] 247°C)

Methyl 9,10-Dihydro-9,10-ethenoanthracene-11-carboxylate-12-carboxylic acid (44)

A solution of 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylic acid anhyride (Compound **43**; 478 mg, 1.74 mmol) in 10 ml of freshly distilled methanol was refluxed for 3 h. The excess alcohol was removed *in vacuo*, the residue dissolved in diethyl ether (30 ml), washed with water and then saturated sodium bicarbonate solution (3 x 25 ml). The aqueous layer was acidified by dropwise addition of concentrated HCl. When the acid-ester had completely precipitated, it was extracted with diethyl ether (3 x 75 ml). The combined organic layers were dried with magnesium sulphate, filtered, and evaporated to dryness. The resulting white solid (460 mg, 1.5 mmol) was recrystallized from chloroform (mp = 214-215°C) in 86% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 11.96 (1, broad, exchanges with D_2O, $CO_2\mathbf{H}$), 7.00-7.48 (8, m, Ar-H), 6.06 (1, s, Bridgehead H), 5.80 (1, s, Bridgehead H), 3.98 (3, s, $CO_2\mathbf{CH_3}$).

IR (KBr): ν_{max} 3462 (CO_2H), 1704 (2xC=O), 1461, 1276, 1211 cm^{-1}.

MS m/e (rel. intensity): 306 (M^+, 3.5), 274 (24.6), 262 (20.4), 230 (33.4), 202 (100), 178 (36.7).

Analysis calculated for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.74; H, 4.90.

Preparation of Methyl 9,10-Dihydro-N,N-dimethyl-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (45)

A solution of the ester-acid **44** (0.86 mmol) and oxalyl chloride (0.5 ml) in 7 ml of anhydrous benzene was refluxed for 2 h. The solvent and excess oxalyl chloride were removed by rotary evaporation and left on a high-vacuum pump line for 2 h. Dimethyl amine (bp = 7.2°C) was stirred over sodium for 6 h, passed through a potassium hydroxide tube and condensed in a dry flask containing potassium. The amine was distilled into the flask (at 0°C) containing the acid chloride and 5 ml of dry benzene. The reaction mixture was allowed to warm to room temperature and stirred until no further reaction was evident by tlc. Diethyl ether was added (25 ml) and the resultant solution washed with water, saturated sodium bicarbonate solution and water again. The organic layer was dried over magnesium sulphate, filtered, and the solvent removed. The crude ester-amide was purified by column chromatography (PET/EtOAc, 60:40) resulting in the recovery of a white solid (233 mg, 0.70 mmol) in 83% yield. Recrystallization from ethanol gave colourless prisms, mp = 155-157°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98-7.42 (8, m, Ar-H), 5.70 (1, s, Bridgehead H_9), 5.18 (1, s, Bridgehead H_{10}), 3.74 (3, s, $CO_2\mathbf{CH_3}$), 3.04 and 2.50 (2x3, 2s, $CON(\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.7,164.2 (2xC=O); 156.2, 144.4, 143.4, 137.8 (Vinylic and Ar-C's, No H's); 125.5, 125.3, 123.7, 123.6 (Ar-C-H's); 54.8, 52.3, 50.5 (Bridgehead C's and $CO_2\mathbf{CH_3}$); 37.4, 34.2 ($CON(\mathbf{CH_3})_2$).

IR (KBr) ν_{max}: 1700 (E-C=O), 1641 (A-C=O), 1459, 1341, 1236 cm^{-1}.

UV (CH_3CN) λ_{max}: 278.5 nm (ε = 3140), 270.3 (ε = 3100).

MS m/e (rel. intensity): 333 (M^+, 46.6), 261 (46.1), 202 (36.6), 178 (61.9), 71 (100). Calculated mass: 333.1365; found 333.1357.

Analysis calculated for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.74; H, 5.92; N, 4.27.

Preparation of Methyl N,N-Diethyl-9,10-dihydro-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (46)

A suspension of the ester-acid **44** (343 mg, 1.12 mmol) and oxalyl chloride (0.5 ml) in dry benzene (10 ml) was refluxed for 2 h. The solvent and excess oxalyl chloride were removed by rotary evaporation and left on a high-vacuum pump line for 2 h. Diethyl amine was purified by fractional distillation from sodium and stored over molecular sieves (4 Å). Dry benzene (10 ml) was added to the flask containing the acid chloride, cooled, and 1.0 ml of the amine added. The reaction mixture was refluxed under nitrogen for 5 h. After the addition of 50 ml of diethyl ether, the mixture was washed with water, saturated sodium bicarbonate twice, and then water once again. The organic layer was dried with magnesium sulphate and concentrated *in vacuo* leaving the crude product as a yellow oil. The crude ester-amide was purified by column chromatography (PET/EtOAc, 80:20) and subsequently recrystallized from ethanol. Colourless prisms were obtained (mp = 166°C) in 78% yield (316 mg, 0.87 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96-7.42 (8, m, Ar-H), 5.70 (1, s, Bridgehead H_9), 5.14 (1, s, Bridgehead H_{10}), 3.70 (3, s, $CO_2\mathbf{CH_3}$), 3.50 (2, broad, $CON\mathbf{CH_2}CH_3$), 2.80 (2, q, J = 6.7 Hz, $CON\mathbf{CH_2}CH_3$), 1.18 and 0.90 (2x3, 2t, J = 6.7 Hz, $CON(CH_2\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.0, 164.4 (2xC=O); 144.5, 143.5, 137.2 (Vinylic and Ar-C's, No H's); 125.5, 125.2, 123.7, 123.6 (Ar-C-H's); 55.0, 51.9, 50.5

(Bridgehead C's and $CO_2\mathbf{CH_3}$); 41.9, 38.2 ($CON(\mathbf{CH_2}CH_3)_2$), 14.1, 12.4 ($CON(CH_2\mathbf{CH_3})_2$).

IR (KBr) ν_{max}: 1713 (E-C=O), 1631 (A-C=O), 1459, 1436, 1228 cm^{-1}.

UV (CH_3CN) λ_{max}: 278.6 nm (ε = 2970), 270.3 (ε = 2910).

MS m/e (rel. intensity): 361 (M^+, 9.6), 329 (13.2), 302 (1.8), 261 (18.9), 202 (23.0), 178 (38.1), 100 (41.2), 72 (100). Calculated mass: 361.1678; found: 361.1681.

Analysis calculated for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.28, H, 6.56, N, 3.88.

Preparation of Methyl 9,10-Dihydro-N-ethyl-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (47)

Preparation of the requisite acid chloride was carried out as for the dimethyl and diethyl adducts, using 318 mg (1.04 mmol) of the starting ester-acid **44** in 9.0 ml of dry benzene and 0.5 ml of oxalyl chloride and refluxing for 2 h. Ethylamine (bp = 16.6°C) was purified by fractional distillation from sodium into a flask containing molecular sieves (4 Å), which was cooled in a dry ice/acetone bath. After placing 5 ml of dry benzene in the flask containing the acid chloride, a solution of 1.10 mmol of ethylamine in 5 ml of benzene was added. In this instance it was crucial to regulate the amount of ethylamine added so as to prevent transamination of the ester group to give the diamide. The reaction mixture was stirred for 4 h after which 50 ml of diethyl ether was added. The mixture was washed with water, saturated sodium bicarbonate solution twice and water once more. Subsequent drying and removal of the solvent gave a brown solid, shown by infrared spectroscopy to be the crude ester-amide. The ester-amide was purified by column chromatography (PET/EtOAc, 70:30) and the product recrystallized from ethanol (mp = 195.5-196.5°C) giving small white crystals in 63% yield (220 mg, 0.66 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (1, broad, CONHEt), 7.00-7.48 (8, m, Ar-H), 5.88 (1, s, Bridgehead H_9), 5.69 (1, s, Bridgehead H_{10}), 3.84 (3, s, $CO_2\mathbf{CH_3}$), 3.36 (2, dq, J = 6.8, 8.0 Hz, $CON\mathbf{CH_2}CH_3$), 1.14 (3, t, J = 8.0 Hz, $CONCH_2\mathbf{CH_3}$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 166.5, 164.5 (2xC=O); 155.1, 144.1, 144.0, 140.9 (Vinylic and Ar-C's, No H's); 125.4, 125.3, 124.1, 123.5 (Ar-C-H's); 54.1, 52.7, 52.6 (Bridgehead C's and $CO_2\mathbf{CH_3}$); 34.7 ($CON\mathbf{CH_2}CH_3$); 14.4 ($CONCH_2\mathbf{CH_3}$).

IR (KBr) ν_{max}: 3307 (N-H), 1703 (E-C=O), 1650 (A-C=O), 1622 (C=C), 1542, 1459, 1436, 1293, 1229 cm^{-1}.

UV (CH_3CN) λ_{max}: 278.3 nm (ε = 3220), 270.0 (ε = 3430).

MS m/e (rel. intensity): 333 (M^+, 24.7), 262 (25.2), 230 (28.7), 202 (100) 178 (100). Calculated mass: 333.1365; found 333.1375.

Analysis calculated for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.33; H, 5.84; N, 4.08.

Preparation of Methyl 9,10-Dihydro-12-(N-piperidinylcarbonyl)-9,10-ethenoanthracene-11-carboxylate (48)

Preparation of the acid chloride was carried out as for the dimethyl and diethyl adducts, using 328 mg (1.07 mmol) of the starting ester-acid in 10 ml of dry benzene and 0.5 ml oxalyl chloride, and refluxing under nitrogen for 2 h. Piperidine was purified by fractional distillation from sodium immediately before use. After addition of 10 ml of dry benzene and 1.0 ml of freshly distilled piperidine to the flask containing the acid chloride, the reaction mixture was refluxed for 3 h. The reaction mixture was cooled to ambient temperature, diethyl ether (60 ml) added and the mixture washed with 5% HCl (50 ml) to remove any excess amine. The organic layer was then washed with saturated sodium bicarbonate solution and water to remove any of acid-ester starting material. The crude product was concentrated *in vacuo* to give a yellow oil. Purification by column

chromatography (PET/EtOAc, 50:50) yielded the pure amide (273 mg, 0.73 mmol) in 68% yield. Recrystallization from ethanol gave colourless prisms, mp = 194-195°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96-7.50 (8, m, Ar-H), 5.72 (1, s, Bridgehead H_9), 5.14 (1, s, Bridgehead H_{10}), 3.72 (3, s, $CO_2\mathbf{CH_3}$), 3.56 (2, broad, Ring methylene), 2.78 (2, broad, Ring methylene), 1.60 (4, broad, 2 Ring methylenes), 1.30 (2, broad, Ring methylene).

^{13}C NMR (50 MHz, $CDCl_3$): δ 167.0, 164.3 (2xC=O); 156.3, 144.4, 143.9, 137.5 (Vinylic and Ar C's, No H's); 125.5, 125.2, 123.7, 123.5 (Ar-C-H's); 55.0, 52.1, 50.5 (Bridgehead C's and $CO_2\mathbf{CH_3}$); 47.1, 42.1, 26.2, 25.5, 24.5 (Methylenes).

IR (KBr) ν_{max}: 1713 (E-C=O), 1632 (A-C=O), 1457, 1269, 1210 cm^{-1}.

UV (CH_3CN) λ_{max}: 278.5 nm (ε = 4300), 270.2 (ε = 4250).

MS m/e (rel. intensity): 373 (M^+, 0.1), 320 (52.5), 288 (14.3), 260 (100), 261 (62.8), 233 (34.8), 217 (17.9), 202 (66.8), 178 (40.9). Calculated mass: 373.1678; found: 373.1679.

Anaylsis calculated for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.30; H, 6.15; N, 3.68.

Preparation of Methyl N,N-Dibenzyl-9,10-dihydro-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (49)

In order to generate the acid chloride necessary for the preparation of ester-amide **49**, 20 ml of dry dichloromethane and 0.5 ml of oxalyl chloride were added to a 50 ml flask containing 517 mg (1.69 mmol) of dibenzobarrelene ester-acid **44**. The reaction mixture was refluxed overnight under nitrogen, at which point the solvent was removed *in vacuo* and the flask evacuated for a further 2 h on a vacuum line. To the flask containing the requisite acid chloride was added 10 ml of dry benzene and 0.5 ml of anhydrous dibenzyl amine (freshly distilled from sodium). The reaction mixture was

refluxed for 6 h at which time no further reaction was observed by glc. Residual amine was removed by washing with water and then 5% HCl (2 x 25 ml). Any residual acid was removed by washing with a solution of saturated sodium bicarbonate (2 x 25 ml) and then water. The organic layer was dried and the solvent removed giving a yellow oil. Purification was achieved by column chromatography (PET/EtOAc, 75:25). Combination of the fractions containing the product and subsequent slow evaporation of the solvent gave large colourless prisms (mp = 210-210.5^{o}). The product was obtained in 78% yield (641 mg, 1.32 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94-7.42 (18, m, Ar-H), 6.88 (2, broad, CON($\mathbf{CH_2}$Ph)), 5.70 (1, s, Bridgehead H_9), 5.24 (1, s, Bridgehead H_{10}), 3.98 (2, s, CON($\mathbf{CH_2}$Ph)), 3.48 (3, s, $CO_2\mathbf{CH_3}$).

13C NMR (50 MHz, CDCl3): δ 169.6, 164.2 (2xC=O); 155.0, 144.2, 143.4, 138.3, 136.5, 136.0 (Vinylic and Ar-C's, No H's); 129.3, 128.8, 128.5, 127.8, 127.6, 127.1, 125.4, 125.1, 123.6 (Ar-C-H's); 55.1, 52.0, 50.7 (Bridgehead C's and $CO_2\mathbf{CH_3}$); 50.3, 46.5 (CON($\mathbf{CH_2}$Ph)$_2$).

IR (KBr) ν_{max}: 1713 (E-C=O), 1618 (A-C=O), 1426, 1291, 1240 cm^{-1}.

UV (CH_3CN) λ_{max}: 279.0 nm (ε = 4390), 270.6 (ε = 4140).

MS m/e (rel. intensity): 485 (M^+, 17.3), 453 (7.0), 394 (30.7), 289 (59.8), 261 (76.5), 202 (53.2), 196 (73.1), 178 (74.1), 91 (100). Calculated mass: 485.1991; found 485.1995.

Analysis calculated for $C_{33}H_{27}NO_3$: C, 81.63; H, 5.60; N, 2.88. Found: C, 81.80; H, 5.60; N, 2.89.

Preparation of Methyl 9,10-Dihydro-N,N-di-(2-propyl)-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (50)

Formation of the acid chloride necessary for the preparation of ester-amide **50** was carried out in the same manner as for the dibenzylamide compound **49**, using 387 mg (1.26 mmol) of the starting acid-ester **44**, 0.5 ml of oxalyl chloride and 20 ml of dry dichloromethane. The reaction mixture was refluxed overnight under nitrogen. After removal of the solvent and excess oxalyl chloride, the flask was evacuated for a further 2 h on a vacuum line. Di-*iso*-propyl amine was purified by distillation from sodium prior to use. Dry benzene (10 ml) and 0.5 ml of the amine were added to the flask containing the acid chloride. The reaction mixture was refluxed until no further reaction was observed by tlc. After the addition of diethyl ether (50 ml), the mixture was washed with 5% HCl (50 ml) to remove any residual amine and then sodium bicarbonate solution (50 ml) and water to remove any residual acid. The solvent was removed *in vacuo* giving a brown solid which infrared spectroscopy indictated was crude amide. Purification by column chromatography (PET/EtOAc, 80:20) resulted in the recovery of a white amorphous solid (362 mg, 0.93 mmol) in 74% yield. Recrystallization from chloroform/PET gave fine white needles, mp = 184-185^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94-7.44 (8, m, Ar-H), 5.70 (1, s, Bridgehead H_9), 5.06 (1, s, Bridgehead H_{10}), 3.70 (3, s, $CO_2\mathbf{CH_3}$), 3.42 and 3.12 (2x1, 2 septet, J = 5.4 Hz, CON(C**H**$(CH_3)_2$)), 1.52 and 0.96 (2x6, 2 broad doublets, CON(C**H**$(CH_3)_2$)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.0, 164.8 (2xC=O); 157.4, 144.6, 141.2, 136.0 (Vinylic and Ar-C's, No H's); 126.6, 125.4, 123.6, 123.4 (Ar-C-H's); 55.0, 51.7, 50.4, 50.2, 45.6 (Bridgehead, Ester methyl and Amide methine C's); 22.0 20.0 (CON(CH(**CH_3**)$_2$)$_2$).

IR (KBr) ν_{max}: 1714 (E-C=O), 1631 (A-C=O), 1441, 1292, 1226 cm^{-1}.

UV (CH_3CN) λ_{max}: 279.2 nm (ε = 3040), 270.8 (ε = 2900).

MS m/e (rel. intensity): 389 (M^+, 11.6), 357 (23.1), 289 (37.1), 261 (78.1), 229 (22.7), 202 (79.0), 178 (100), 100 (78.9). Calculated mass: 389.1991; found 389.1998.

Analysis calculated for $C_{25}H_{27}NO_3$: C, 77.09; H, 6.99; N, 3.60. Found: C, 77.25; H, 7.00; N, 3.59.

D: Miscellaneous Funtionalized Dibenzobarrelene Adducts

a) Methyl Ester/Phenyl Adduct

The preparation of this compound was accomplished by converting phenylacetylenic acid to the corresponding ester, and reacting the ester and anthracene together in a Diels-Alder reaction.

Preparation of Methyl 9,10-Dihydro-12-phenyl-9,10-ethenoanthracene-11-carboxylate[82] (74)

i) Preparation of Methyl 3-Phenyl-2-propynoate[83] (76)

The alkyne ester dienophile was prepared by adding 501 mg of 3-phenyl-2-propynoic acid (3.42mmol), 10 ml of CH_2Cl_2 and 1 ml of oxalyl chloride to a 25 ml round bottom flask and, after the solid had dissolved, refluxing for 2 h. The solvent and excess oxalyl chloride were evaporated *in vacuo* to yield an orange oil assumed to be the corresponding acyl chloride. Freshly distilled methanol (15 ml), dried over molecular sieves (4 Å), was added to the flask and the reaction mixture refluxed for 2 h after the cessation of gas evolution. After this time (3 h) the solution was evaporated to dryness, dissolved in diethyl ether and washed with saturated sodium bicarbonate solution and then water. The organic layer was dried, filtered, and concentrated *in vacuo*. The resulting viscous oil was purified by column chromatography (Hexanes/diethyl ether, 96:4) to give the product in 78% yield (386 mg, 2.4 mmol). Spectroscopic data of **76** given below are in complete agreement with the literature values.[83]

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.60-7.20 (5, m, Ar-H), 3.80 (3, s, $CO_2\mathbf{CH_3}$).

IR (KBr) ν_{max}: 2227 (C-C Triple bond), 1708 (C=O), 1436, 1206 cm^{-1}.

MS m/e (rel. intensity): 160 (M^+, 46.4), 129 (100), 102 (59.4), 75 (41.1).

ii) Diels-Alder Reaction between Anthracene and Methyl 3-Phenyl-2-propynoate

A Carius tube containing 350 mg (2.19 mmol) of methyl 3-phenyl-2-propynoate and 400 mg (2.25 mmol) of anthracene was sealed under vacuum and heated in an oven at 180°C for 6 h. The desired dibenzobarrelene ester product was separated from the resultant brown viscous oil by column chromatography (Hexanes/EtOAc, 97:3), and recrystallized from ethanol to give white prisms (578 mg, 1.71 mmol) in 78% yield. The crystals had a melting point = 154.5-155°C (lit;[82] mp = 153.5-154.5°C) and the spectroscopic data of **74** given below are in complete agreement with the literature values.[82]

^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.98-7.48 (13, m, Ar-H), 5.86 and 5.28 (2, 2s, Bridgehead H_9 and H_{10}), 3.58 (3, s, $CO_2\mathbf{CH_3}$).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 166.1, 161.1 (2xC=O); 145.1, 144.1, 138.4, 136.6 (Vinylic and Ar-C's, No H's); 128.1, 127.8, 127.3, 125.3, 125.0, 123.6, 123.4 (Ar-C-H's); 60.1, 52.1, 51.5 (Bridgehead C's and $CO_2\mathbf{CH_3}$).

IR (KBr) ν_{max}: 1692 (C=O), 1637 (Ph-C=C-E), 1345, 1252 cm^{-1}.

MS m/e (rel. intensity): 338 (M^+, 25.0), 278 (34.1), 202 (4.6), 178 (100).

b) Unsymmetrical Diamides

The synthetic approach to unsymmetrical dibenzobarrelene diamides is essentially a combination of methods used to prepare the ester-amides and the symmetrical diamides. The ester functionality of an ester amide is converted via Weinreb aminolysis to a second, different amide functionality.

Preparation of N,N-Diethyl-9,10-dihydro-N'-methyl-9,10-ethenoanthracene-11,12-dicarboxamide (54)

Preparation of compound **54** involved 412 mg (1.14 mmol) of the ester-amide **46** as starting material, 10 ml dry of toluene and 3.5 ml of the methylamine hydrochloride-derived aluminum amide reagent (0.67 M). After refluxing the reaction mixture for 8 h under nitrogen, no starting material was observed by tlc. After quenching with 5% HCl, the organic layer was separated and the aqueous layer washed with ethyl acetate (3 x 20 ml). The organic extracts were combined, dried and the solvent removed leaving a solid brown residue. Purification by column chromatography (PET/EtOAc, 60:40) and subsequent recrystallization from ethanol gave colourless prisms (mp = 213-215°C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94-7.46 (8, m, Ar-H), 6.86 (1, broad, CON**H**Me), 5.72 and 5.08 (2x1, 2s, Bridgehead H_9 and H_{10}), 3.46 (2, broad, CON(**CH_2**CH_3)), 2.82 (2, q, J = 6.7 Hz, CON(**CH_2**CH_3)), 2.76 (3, d, J = 4.7 Hz, CONH(**CH_3**)), 1.14 and 0.98 (2x3, 2xt, J = 6.7 Hz, CON(CH_2**CH_3**)$_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.3, 165.9 (2xC=O); 147.5, 144.8, 143.8, 143.1 (Vinylic and Ar-C's, No H's); 125.5, 125.0, 123.9, 123.1 (Ar-C-H's); 53.8, 51.6 (Bridgehead C's); 42.4, 39.0 (CON(**CH_2**CH_3)$_2$); 26.1, 14.2, 12.6 (Methyls).

IR (KBr) ν_{max}: 3305 (N-H), 1659, 1638 (2xC=O), 1616 (A-C=C-A'), 1542 (Amide type II), 1459, 1409, 1287 cm^{-1}.

UV (CH_3CN) λ_{max}: 279.0 nm (ε = 2450), 270.9 (ε = 2270).

MS m/e (rel. intensity): 360 (M^+, 4.7), 289 (18.4), 260 (13.3), 230 (12.1), 203 (52.3), 178 (67.1), 100 (30.4), 72 (100). Calculated mass: 360.1838; found 360.1832.

Analysis calculated for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.68; H, 6.75; N, 7.70.

c) Thioesters

Preparation of Dimethyl 9,10-Dihydro-9,10-ethenoanthracene-12-carboxylate-11-thionocarboxylate (55)

Previously prepared compound **9** (dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate; 1.00 mg, 3.13 mmol) was added to a 50 ml round bottom flask along with 1.26 g (2 eqs) of Lawesson reagent[58] and 30 ml of toluene. The reaction mixture was refluxed for 3 days at which point the mixture was cooled and filtered. The solvent was removed *in vacuo* and the yellow oily residue purified by column chromatography (PET/EtOAc, 98:2) to give a bright yellow solid (854 mg, 2.54 mmol) in 81% yield. Recrystallization from ethanol gave small yellow prisms, mp = 139.5-141°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98-7.42 (8, m, Ar-H), 5.66 and 5.50 (2x1, 2s, Bridgehead H_9 and H_{10}), 4.06 and 3.72 (2x3, 2s, CSO**CH$_3$** and CO_2**CH$_3$**).

^{13}C NMR (50 MHz, $CDCl_3$): δ 211.0 (C=S); 166.1 (C=O); 154.8, 144.1, 143.9, 140.6 (Vinylic and Ar-C's, No H's); 125.5, 125.4, 124.2, 123.8, 123.4 (Ar-C-H's); 58.7, 56.2, 52.3, 52.2 (Bridgehead and methyl C's).

IR (KBr) ν_{max}: 1709 (C=O), 1606 (C=C), 1435, 1271 (C=S) cm^{-1}.

UV (CH_3CN) λ_{max}: 404.5 nm (ε = 1140), 320.0 (ε = 2830), 278.0 (ε = 5990), 270.2 (ε = 6220).

MS m/e (rel. intensity): 336 (M^+, 78.7), 303 (100), 275 (33.6), 261 (38.2), 202 (67.4), 178 (85.1); Calculated mass: 336.0820; found 336.0820.

Analysis calculated for $C_{20}H_{16}SO_3$: C, 71.41; H, 4.79; S, 9.53. Found: C, 71.24; H, 4.74; S, 9.57.

Preparation of 11,12-Dimethyl-9,10-dihydro-9,10-ethenoanthacene-12-carboxylate-11-thiolocarboxylate (88)

To prepare compound **88**, the acyl chloride of the ester-acid **44** was prepared by combining 506 mg (1.65 mmol) of compound **44**, 0.5 ml of oxalyl chloride and 30 ml of dry dichloromethane in a 50 ml flask, and refluxing overnight under nitrogen. The excess oxalyl chloride and solvent were removed *in vacuo* leaving a yellow oil, assumed to be the corresponding acid chloride. Dry dichloromethane (15 ml) and 1 ml of methanethiol (available from Eastman-Kodak) were added to the flask containing the acid chloride and the resultant mixture refluxed for 4 h under nitrogen. The excess methanethiol and solvent were removed and the residual oil dissolved in ethyl acetate, washed with water, saturated sodium bicarbonate solution and then once again with water. The organic layer was dried, filtered, and the solvent removed leaving a yellow viscous oil which, after column chromatography (Hexanes/EtOAc, 95:5) gave compound **88** in a pure form. Recrystallization from ethanol gave colourless prisms, mp = 129°C (407 mg, 1.21 mmol) in 73% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00-7.40 (8, m, Ar-H), 5.60, 5.44 (2, 2s, Bridgehead H_9 and H_{10}), 3.76 (3, s, $CO_2\mathbf{CH_3}$), 2.40 (3, s, $COS\mathbf{CH_3}$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 192.3 (O=C-S); 164.8 (O=C-O); 155.7, 144.0, 143.2, 142.8 (Vinylic and Ar-C's, No H's); 125.6, 125.4, 123.9, 123.8 (Ar-C-H's), 54.0, 52.4, 51.7 ($CO_2\mathbf{CH_3}$ and Bridgehead C's).

IR (KBr) ν_{max}: 1708 (O=C-O), 1675 (O=C-S), 1620 (C=C), 1459, 1239 (C-O) cm^{-1}.

UV (CH_3CN) λ_{max}: 295.2 nm (ε = 2020), 277.8 (ε = 3820), 268.6 (ε = 4240).

MS m/e (rel. intensity): 336 (M^+, 5.8), 308 (4.0), 289 (67.1), 261 (100), 246 (6.7), 229 (24.2), 218 (9.1), 202 (46.3), 178 (55.5). Calculated Mass: 336.0820; found 336.0816.

Analysis calculated for $C_{20}H_{16}SO_3$: C, 71.41; H, 4.79; S, 9.53. Found: C, 71.12; H, 4.78; S, 9.61.

III: Photochemical Procedures

A: General

Photolyses for analytical purposes, both in solution and in the solid state, were performed using a 450 W medium pressure Hanovia mercury lamp. Solution photolyses were systematically carried out in spectral grade solvents; benzene and acetonitrile for direct irradiations and acetone for triplet sensitized reactions. Additionally, some compounds were photolyzed in methanol. The concentration of the sample solution for analytical runs was generally 0.01 M, unless otherwise noted. All analytical samples were degassed via several freeze-pump-thaw cycles and sealed under nitrogen with paraffin film before irradiation. Solid samples were photolyzed either as single crystals in Pyrex or quartz tubes, or as powder sandwiched between two microscope slides. The photolyzed samples were generally analyzed by glc, glc/ms, IR, and/or proton NMR.

Preparative photolyses were performed by dissolving 0.1 to 1.0 g of the requisite compound in 250 ml of spectral grade solvent and placing it in a 250 ml quartz immersion well. Degassing was accomplished by bubbling nitrogen through the stirred solution for 30 minutes prior to and during the irradiation. The same light source as for analytical photolyses was used, and the desired wavelength achieved by use of a Pyrex glass filter. Reaction progress was monitored by glc analysis. The irradiation was stopped when less than 5% of starting material remained. The solvent was removed *in vacuo* and the photolysate purified by column chromatography, unless otherwise noted, followed by recrystallization from an appropriate solvent system. All irradiations were carried out at ambient temperature unless stated otherwise.

B: Photochemistry of Dibenzobarrelene Monoamides

Photolysis of 9,10-Dihydro-9,10-ethenoanthracene-11-carboxamide (32)

Analytical photolysis of compound **32** in acetone, acetonitrile, benzene, and methanol resulted in a rapid production (<1/2 h) of a single photoproduct. Solid state irradiation also resulted in the formation of the same product. The reaction proceeded very cleanly in both solution and in the solid state, accompanied by very little yellowing of the solution or the powder. Preparative scale irradiation of compound **32** was carried out in acetone resulting in essentially quantitative conversion to the photoproduct in less than an hour. Removal of the acetone *in vacuo* after the photolysis left a slightly yellow amorphous solid in the flask. Subsequent recrystallization from chloroform produced small white crystals (mp = 210-211.5°C) which were found to be:

4b,8b,8c,8d-Tetrahydro-dibenzo[a,f]cyclopropa[cd]pentalene-8c-carboxamide (56)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94-7.44 (8, m, Ar-H), 5.78 (2, broad, exchanges with D_2O, $CONH_2$), 4.74 (1, s, Pentalene H_{4b}), 3.74 (2, s, Pentalene H_{8b} and H_{8d}).

^{13}C NMR (50 MHz, $CDCl_3$): δ 173.3 (C=O); 149.7, 135.7 (Ar-C's, No H's); 126.9, 126.8, 124.9, 121.2 (Ar-C-H's); 54.7, 46.5 (Pentalene C-H's).

IR (KBr) ν_{max}: 3384, 3202 (H-bonded and free N-H), 1614, (C=O), 1459, 1437, 1346 cm^{-1}.

MS m/e (rel. intensity): 247 (M^+, 14.8), 229 (41.9), 203 (100), 202 (59.5). Calculated mass: 247.0998; found: 247.0994.

Analysis calculated for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.65; H, 5.26; N, 5.67.

Photolysis of 9,10-Dihydro-N,N-dimethyl-9,10-ethenoanthracene-11-carboxamide (33)

Photolysis of compound **33** in acetone, acetonitrile, benzene, and methanol solution resulted in the formation of a single photoproduct. Photolysis in the solid state produced a single photoproduct as well which was shown by proton NMR to be identical to that which was produced in solution. Preparative scale irradiation was performed by dissolving 200 mg of the starting material in 250 ml of acetonitrile and photolyzing for 4 h. After removal of the solvent, the crude product was obtained as a yellow solid. The pure photoproduct was isolated after column chromatography (PET/EtOAc, 50:50), and recovered as a white powder in 90% yield. Recrystallization from chloroform/PET resulted in the formation of small colourless crystals (mp = 194-196^{o}C) which were identified as:

N,N-Dimethyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd]pentalene-8c-carboxamide (57)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.95-7.34 (8, m, Ar-H), 4.62 (1, s, Pentalene H_{8b}), 3.58 (2, s, Pentalene H_{8b} and H_{8d}), 2.88 (6, broad, $CON(\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 170.8 (C=O); 149.7, 136.3 (Ar-C's, No H's); 126.9, 126.7, 125.2, 121.1 (Ar-C-H's); 63.9 (Quaternary pentalene C); 57.3, 43.4 (Pentalene C-H's); 30.8 ($CON(\mathbf{CH_3})_2$).

IR (KBr) ν_{max}: 1631 (C=O), 1472, 1022 cm^{-1}.

MS m/e (rel. intensity): 275 (M^+, 29.4), 203 (100), 202 (53.4), 72 (81.4). Calculated mass: 275.1311; found: 275.1307.

Analysis calculated for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 83.04; H, 6.22; N, 5.11.

Photolysis of N,N-Diethyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxamide (34)

Solid state irradiations of compound **34** were performed on both a single crystal in the bottom of an NMR tube and on the powder that resulted from grinding several small crystals between two Pyrex microscope slides. In both cases the formation of only one product was observed. Analyses of these samples consisted of photolyzing to about 10 percent conversion of the starting material, as indicated by gc, and then dissolving the sample in deuterochloroform and obtaining a proton NMR spectrum.

This photoproduct was produced in solution as well and therefore isolated from solution irradiation *(vide infra)* of compound **34**. After purification, the pure product was recovered as an oil. It was subsequently obtained in crystalline form from chloroform/PET upon scratching with a glass rod, giving colourless prisms, mp = 171°C. Spectral data identified the photoproduct as:

N,N-Diethyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd]pentalene-8c-carboxamide (58)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.95-7.25 (8, m, Ar-H), 4.50 (1, s, Pentalene H_{4b}), 3.50 (2, s, Pentalene H_{8b} and H_{8d}), 3.20 (4, broad, $CON(\mathbf{CH_2}CH_3)_2$), 1.02 (6, broad, $CON(CH_2\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.6 (C=O); 149.6, 136.3 (Ar-C's, No H's); 126.8, 126.6, 125.2, 121.0 (Ar-C-H's); 63.8 (Quaternary pentalene C); 57.6, 43.3 (Pentalene C-H's).

IR (KBr) ν_{max}: 1630 (C=O), 1473, 1265 cm^{-1}.

MS m/e (rel. intensity): 303 (M^+, 8.8), 203 (30.2), 202 (25.7), 100 (100). Calculated mass: 303.1623; found: 303.1617.

Analysis calculated for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.29; H, 7.01; N, 4.59.

Photolysis in acetone, benzene, or acetonitrile produced, in addition to the major photoproduct, a second product **59**. The product ratio of compounds **58** and **59** in benzene was 2:1, whereas for acetone and acetonitrile the ratio was 4:1. Therefore, in order to maximize the yield of the minor photoproduct, preparative scale irradiation of compound **34** was carried out in benzene. Photoreaction of the starting material was accompanied by yellowing of the benzene solution. Removal of the benzene *in vacuo* left a viscous yellow film on the bottom of the flask. The two photoproducts were isolated from the crude reaction mixture by column chromatography (PET/EtOAc, 80:20). Compound **59** was recrystallized from chloroform to give white, powdery crystals (mp = 183-185^{o}C) and identified as:

9,10-Dihydro-N-ethyl-9,10-ethanoanthracene-11-carboxamide (59)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-7.34 (8, m, Ar-H), 4.84 (1, broad, CONHEt), 4.54 (1, d, J = 2.4 Hz, Bridgehead H_9), 4.38 (1, dd, J = 2.4, 2.4 Hz, Bridgehead H_{10}), 3.12 (2, m, CONH(**CH_2**CH_3)), 2.76 (1, ddd, J = 2.4, 4.8, 10.0 Hz, Bridge H_{11}), 2.10 (1, ddd, J = 2.5, 10.0, 12.8, Bridge H_{12} *cis* to H_{11}), 1.86 (1, ddd, J = 2.48, 4.8, 12.8 Hz, Bridge H_{12} *trans* to H_{11}), 0.96 (3, t, J = 8.0 Hz, CONH(CH_2**CH_3**)).

Assignments are supported by decoupling and COSY ^{1}H NMR experiments.

^{13}C NMR (50 MHz, $CDCl_3$): δ 173.4 (C=O); 143.8, 143.2, 142.9, 140.0 (Ar-C's, No H's); 126.4, 126.1, 126.0, 125.9, 125.4, 123.6, 123.4, 123.3 (Ar-C-H's); 47.6, 45.8, 43.9 (Bridge and bridgehead C-H's); 34.3, 32.3 (Methylenes); 14.7 (CONH(CH_2**CH_3**)).

IR (KBr) ν_{max}: 3248 (N-H), 1639 (C=O), 1555 (Amide Type II), 1459, 1256 cm^{-1}.

MS m/e (rel. intensity): 277 (M^+, 3.7), 203 (2.8), 178 (100). Calculated mass: 277.1467; found: 277.1465.

Analysis calculated for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.21; H, 6.73; N, 4.92.

Photolysis of compound **34** in methanol gave rise to a third photoproduct **60**. Again compound **58** was the major photoproduct, with a product ratio of 2:1, while compound **59** was not observed at all. Separation of compounds **58** and **60** was achieved by column chromatography (PET/EtOAc, 90:10). Colourless crystals of compound **60** were obtained by recrystallization with PET/EtOAc, mp = 105°C (lit;[62] 104°C) and were identified as:

Methyl 9,10-Dihydro-9,10-ethanoanthracene-11-carboxylate[62] (60)

^1H NMR (300 MHz, $CDCl_3$): δ 7.04-7.38 (8, m, Ar-H), 4.70 (1, d, J = 2.0 Hz, Bridgehead H_9), 4.36 (1, m, Bridgehead H_{10}), 3.62 (3, s, $CO_2\mathbf{CH_3}$), 2.90 (1, m, Bridge H_{11}), 1.96-2.24 (2, m, 2xBridge H_{12}).

^{13}C NMR (50 MHz, $CDCl_3$): δ 174.0 (C=O); 143.9, 143.6, 142.5, 140.0 (Ar-C's, No H's); 126.2, 126.1, 125.7, 124.7, 123.6, 123.4, 123.2 (Ar-C-H's); 51.9, 46.8, 44.0, 43.8 (Bridgehead, bridge and ester methyl C-H's); 30.8 (Bridge methylene).

IR (KBr) ν_{max}: 1730 (C=O), 1459, 1207 cm^{-1}.

MS m/e (rel. intensity): 264 (M^+, 15.9), 233 (2.0), 178 (100). Mass calculated: 264.1151; found: 264.1144.

Photolysis of N,N-Dibenzyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxamide (35)

After analysis of the irradiation of compound **35** in the solid state, both as crystals and as a powder, the photoreaction was shown to result in the formation of two products.

Photolysis of a single crystal of **35** was not feasible because of the very small nature of the crystals and therefore several small crystals of **35** were photolyzed. The major product of the solid state photolysis was shown to be identical by proton nmr and gc-ms to photoproduct **61** formed when **35** was photolyzed in solution *(vide infra)*. The minor photoproduct of solid state irradiation of compound **35** was found to be identical by proton NMR and gc-ms to compound **62** formed in the solution photolysis. Compounds **61** and **62** were therefore isolated, after purification by column chromatography (PET/EtOAc, 90:10), from acetone solution photolysis of **35**.

Recrystallization of compound **61** from PET/EtOAc gave colourless prisms, mp = 126.5-128^{o}C, and identified as:

N,N-Dibenzyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd]pentalene-8c-carboxamide (61)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92-7.40 (18, m, Ar-H), 4.54 and 4.34 (2x2, broad, CON($\mathbf{CH_2}$Ph)$_2$), 4.50 (1, s, Pentalene H_{4b}), 3.60 (2, s, Pentalene H_{8b} and H_{8d}).

^{13}C NMR (50 MHz, $CDCl_3$): δ 171.2 (C=O); 149.5, 136.9, 136.1 (Ar-C's, No H's); 128.7, 127.4, 126.9, 126.7, 125.3, 124.8, 121.1 (Ar-C-H's); 63.7 (Quaternary pentalene C); 57.1, 44.0 (Pentalene C-H's).

IR (KBr) ν_{max}: 1637 (C=O), 1361, 1232 cm^{-1}.

MS m/e (rel. intensity): 427 (M^+, 11.7), 336 (1.4), 203 (57.6), 202 (43.1), 178 (25.4), 91 (100). Calculated mass: 427.1938; found: 427.1936.

Analysis calculated for $C_{31}H_{25}NO$: C, 87.09; H, 5.89; N, 3.28. Found: C, 87.28; H, 5.97; N, 3.20.

The second photoproduct was recovered in trace amounts (< 5 mg) as a powder from the photolysis of compound **35** and was identified as;

N-Benzyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxamide (62)

^{1}H NMR (300 MHz, CDCl3): δ 6.92-7.46 (13, m, Ar-H), 6.30 (1, broad, exchanges with D_2O, CONHBz), 4.94 (1, d, J = 14.3Hz, CON**CH$_2$**Ph), 4.32 (1, s, Bridgehead H_9), 4.28 (1, s, Bridgehead H_{10}), 4.10 (1, t, J = 3.0Hz, Bridge H_{11}), 3.90 (1, d, J = 14.3Hz, CON**CH$_2$**Ph), 1.78 (1, dd, J = 3.0, 14.3Hz, Bridge H_{12}) 1.18 (1, dd, J = 3.0, 14.3Hz, Bridge H_{12}).

^{13}C NMR (50 MHz, CDCl3): δ 173.5 (C=O); 147.1, 143.8, 143.6, 142.0, 140.6 (Ar-C's, No H's); 131.0, 128.9, 128.4, 127.8, 127.2, 126.7, 126.0, 125.5, 123.9, 123.7, 123.3 (Ar-C-H's); 47.8, 45.4, 43.0, 41.8 (Methine C's); 33.8 (Methylene C).

IR (KBr): ν_{max}: 3320 (N-H), 1640 (C=O), 1550, 1448, 1238 cm^{-1}.

MS m/e (rel. intensity): 338 (M^+, 6.8), 203 (32.5), 178 (100). Calculated mass: 338.1545; found: 338.1561.

Analysis calculated for $C_{24}H_{20}NO$: C, 85.18; H, 5.96; N, 4.14. Found: C, 85.29; H, 6.14; N, 4.20.

In addition to the photoproducts described above, irradiation of compound **35** in acetone, benzene and acetonitrile resulted in the production of another compound, **63**. The ratio of compounds **61** and **63** range from approximately 40:60 in benzene, to 50:50 in acetonitrile. The amount of compound **62** produced never exceeded 4 percent of the product mixture. Irradiation of the dibenzyl dibenzobarrelene amide **35** on a preparative scale was carried out in acetone, using 300 mg of the starting material and 250 ml of spectral grade acetone. The solution was photolyzed for 6 h at which point only 4% of the starting amide remained and the solution had become distinctly yellow. Removal of

the solvent *in vacuo* gave a viscous yellow film in the flask. The three photoproducts were isolated, as described above, after column chromatography.

Compound **63** was recovered as a viscous oil which, upon crystallization from a mixture of petroleum ether and chloroform, gave white crystals, mp = 185-186°C, and identified as:

1-Benzyl-4-phenyl-azetidin-2-one-3-spiro-11'-(9',10'-dihydro-9',10'-ethanoanthracene) (63)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88-7.42, (16, m, Ar-H), 6.58 (1, ddd, J = 1.4, 7.6, 7.6 Hz, Ar-H), 5.58 (1, d, J = 7.6 Hz, Ar-H), 4.86 (1, d, J = 14.7 Hz, N**CH$_2$**Ph), 4.29 (1, dd, J = 2.2, 2.2 Hz, Bridgehead H), 4.27 (1, s, Lactam ring H), 4.08 (1, s, Bridgehead H), 3.82 (1, d, J = 14.7 Hz, N**CH$_2$**Ph), 2.39 (1, dd, J = 2.2, 13.0 Hz, Bridge H), 2.08 (1, dd, J = 2.2, 13.0 Hz, Bridge H).

Assignments are supported by decoupling and COSY ^{1}H NMR experiments and by ^{13}C NMR APT (attached proton test) experiments.

^{13}C NMR (50 MHz, $CDCl_3$): δ 172.1 (C=O); 144.1, 143.8, 139.9, 138.6, 135.8, 134.9 (Ar-C's, No H's); 128.7, 128.5, 128.4, 128.3, 127.6, 126.3, 125.8, 125.6, 125.1, 125.0, 124.0, 123.0, 122.6 (Ar-C-H's); 67.6 (Lactam ring C-H); 62.8 (Quaternary C); 46.3, 44.1 (Bridgehead C's); 44.0, 37.8 (Methylenes).

IR (KBr) ν_{max}: 1758 (Lactam C=O), 1459 cm^{-1}.

MS m/e (rel. intensity): 427 (M^+, 5.9), 294 (18.0), 203 (17.5), 178 (100). Calculated mass: 427.1936; found: 427.1937.

Analysis calculated for $C_{31}H_{25}NO$: C, 87.09; H, 5.89; N, 3.28. Found: C, 87.15; H, 5.96; N, 3.36.

The structure of this compound was also supported by X-ray diffraction analysis. The crystal data were as follows: $C_{31}H_{25}NO$; monoclinic; space group *P21/a;* a =

10.228 (3)Å, b = 32.818 (3)Å, c = 15.529 (3)Å; β = 99.79 (2)^{o}; V = 5212.5 (3)Å^{3}; Z = 4; D_{calc} = 1.106 g/cm^{3}; R = 0.053.

Photolysis of the dibenzyl amide adduct **35** in methanol solution resulted in the formation of the semibullvalene amide, compound **61**, as well as the bridgehead-reduced methyl ester, compound **60**, in a product ratio of 1:1. Assignment of the photoproduct structures was a result of proton NMR and GC-MS analyses.

Photolysis of 9,10-Dihydro-N,N-di-(2-propyl)-9,10-ethenoanthracene-11-carboxamide (37)

Irradiation of single crystals and powdered samples of the starting amide resulted in the formation of a single photoproduct, compound **66**. Samples were generally irradiated to about 10% conversion and then analyzed by proton NMR and gc-ms. Analytical solution photolyses indictated that the same photoproduct **66** was obtained in solution. This product was therefore isolated from solution irradiation *(vide infra)* of compound **37**. Recrystallization from chloroform/PET gave white crystals with mp = 244-246^{o}C. Photoproduct **66** was identified as:

N,N-Di-(2-propyl)-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd] pentalene-8c-carboxamide (66)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00-7.30 (8, m, Ar-H), 4.50 (1, s, Pentalene H_{4b}), 3.78 and 3.38 (2x1, broad, CON(C**H**$(CH_3)_2)_2$), 3.50 (2, s, Pentalene H_{8b} and H_{8d}), 1.42 and 1.06 (2x6, 2 broad, CON(CH(**C**$H_3)_2)_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.1 (C=O); 149.7, 136.5 (Ar-C's, No H's); 126.9, 16.6, 125.3, 121.0 (Ar-C-H's); 65.2 (Quaternary pentalene C); 57.7, 42.8 (Pentalene C-H's); 20.6 (Methyls).

IR (KBr) ν_{max}: 1629 (C=O), 1443, 1371, 1329, 1215 cm^{-1}.

MS m/e (rel. intensity): 331 (M^+, 14.9), 246 (18.6), 203 (46.9), 128 (63.4), 86 (100). Calculated mass: 331.1938; found: 331.1933.

Analysis calculated for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.35; H, 7.61; N, 3.94.

Analytical irradiation of compound **37** in acetone, acetonitrile and benzene solution resulted in the formation of three photoproducts. The ratio of the products **66**:**68** was 1:2 in benzene and in acetonitrile. In acetone photolyses, the ratio was essentially reversed. Compound **67** generally represented between 5-15% of the product mixture. Photolysis in acetone was accompanied by significant yellowing of the photolysate solution. Acetonitrile was chosen as the solvent for preparative irradiation because, although reaction time was much longer, the reaction was much cleaner. Subsequent removal of the solvent *in vacuo* left a yellow oil. Attempted separation of the three products by column chromatography (PET/EtOAc, 90:10) resulted in compound **66** being obtained pure while the other two photoproducts, compounds **67** and **68**, were obtained as a mixture. The fractions containing the mixture of photoproducts were combined and the solvent removed leaving a viscous colourless oil. The oil was dissolved in as small an amount of chloroform as possible and PET ether added. After scratching for a few minutes with a glass rod, a white solid appeared. The solid material was separated, recrystallized and determined to be:

9,10-Dihydro-N-(2-propyl)-9,10-ethanoanthracene-11-carboxamide (68)

^1H NMR (300 MHz, $CDCl_3$): δ 7.08-7.38 (8, m, Ar-H), 4.62 (1, broad, exchanges with D_2O, CON**H**($CH(CH_3)_2$)), 4.48 (1, d, J = 2.0 Hz, Bridgehead H_9), 4.36 (1, dd, J = 2.0, 2.0 Hz, Bridgehead H_{10}), 3.88 (1, m, CONH(C**H**($CH_3)_2$)), 2.74 (1, ddd, J = 2.0, 4.0, 8.1, Bridge H_{11}), 2.08 (1, ddd, J = 2.0, 8.1, 9.7, Bridge H_{12} cis to H_{11}),

1.84 (1, ddd, J = 2.0, 4.0, 9.7, Bridge H_{12} trans to H_{11}), 0.98 and 0.96 (2x3, 2d, J = 7.0 Hz, CONH(CH(**CH_3**)$_2$)).

Assignments are supported by COSY ^{1}H NMR and ^{13}C NMR APT (attached proton test) experiments.

^{13}C NMR (50 MHz, $CDCl_3$): δ 172.7 (C=O); 143.7, 143.2, 142.8, 140.0 (Ar-C's, No H's); 126.4, 126.1, 125.9, 125.8, 125.5, 123.5, 123.4, 123.3 (Ar-C-H's); 47.7, 45.8, 43.8, 41.2 (Methine C's); 32.4 (Methylene C's); 22.6, 22.5 (CONH(CH(**CH_3**)$_2$)).

IR (KBr) ν_{max}: 3305 (N-H), 1645 (C=O), 1542, 1458, 1235 cm^{-1}.

MS m/e (rel. intensity): 291 (M^+, 3.5), 203 (3.4), 178 (100). Calculated mass: 291.1624; found 291.1592.

Analysis calculated for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 8.20; H, 7.43; N, 4.77.

mp = 178-180°C

After several recrystallizations of the original mother liquor, the percentage of the third photoproduct had been raised to 85%. At this point the third photoproduct crystallized out of solution and was identified as:

4,4-Dimethyl-1-(2-propyl)-azetidin-2-one-3-spiro-11'-(9',10'-dihydro-9',10'-ethanoanthracene) (67)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04-7.38 (8, m, Ar-H), 4.60 (1, s, Bridgehead H_9), 4.34 (1, dd, J = 2.0, 2.0 Hz, Bridgehead H_{10}), 3.48 (1, m, NC**H**$(CH_3)_2$), 2.00-2.14 (2, m, 2xBridge H_{12}) 1.46 and 1.02 (2x3, 2s, Lactam methyls), 1.34 and 1.32 (2x3, 2d, J = 7.0 Hz, NCH(**CH_3**)$_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 170.3 (C=O); 145.2, 143.6, 140.6, 140.2 (Ar-C's, No H's); 126.1, 125.9, 125.6, 125.5, 125.3, 125.2, 123.2, 123.0 (Ar-C-H's); 63,5, 62.1

(Quaternary C's); 47.9, 44.2, 43.6 (Bridgehead and Bridge C-H's); 33.4 (Methylene); 25.8, 23.3, 22.3, 21.8 (Methyl C's).

IR (KBr) ν_{max}: 1745 (lactam C=O), 1459, 1347 cm^{-1}.

MS m/e (rel. intensity): 331 (M^+, 3.1), 246 (87.5), 215 (31.3), 203 (50.0), 202 (51.6), 178 (100). Calculated mass: 331.1938; found: 331.1949.

Analysis calculated for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.12; H, 7.44; N, 4.25.

mp = 154-155°C (Recrystallized from ethanol)

Irradiation in methanol resulted in the formation of the reduced bridge methyl ester adduct **60**, as found in methanol irradiations of other monoamides, as well as photoproduct **66** in a ratio of 3:2. Structural assignment was made on the basis of gc retention times, proton NMR data and gc-ms.

C: Photochemistry of Symmetrical Dibenzobarrelene Diamides

Photolysis of 9,10-Dihydro-N,N,N',N'-tetramethyl-9,10-ethenoanthracene-11,12-dicarboxamide (38)

Diamide **38** was found to be only slightly soluble in the solvents used for photolysis and it was not possible to obtain the usual concentration. Therefore saturated solutions of the tetramethyl diamide in acetone, acetonitrile, and methanol were prepared and irradiated. The starting material reacted cleanly to give a single photoproduct as evidenced by proton NMR and glc. Preparative photolysis was carried out in methanol due to the more limited solubility in the other solvents. After irradiating for several hours the starting material had essentially all reacted and the solution had remained colourless. Removal of the solvent *in vacuo* gave a white amorphous solid. Subsequent recrystallization from ethanol, gave small white crystals with mp = 265-266°C. The photoproduct was subsequently identified as:

4b,8b,8c,8d-Tetrahydro-N,N,N',N'-tetramethyl-dibenzo[a,f]cyclopropa[cd] pentalene-8b,8c-dicarboxamide (69)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04-7.38 (8, m, Ar-H), 4.70 (1, s, Pentalene H_{4b}), 3.96 (1, broad, Pentalene H_{8d}), 3.28 (3, broad, CON(**CH_3**)), 3.10, 2.98, and 2.88 (3x3, 3s, 3xCON(**CH_3**)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8, 168.2 (2xC=O); 149.9, 149.8, 135.5, 135.2 (Ar-C's, No H's); 127.7, 127.3, 127.2, 127.0, 125.3, 124.4, 121.8, 121.2 (Ar-C-H's); 68.1, 58.2 (Quaternary pentalene C's); 56.4, 46.2 (Pentalene C-H's); 38.2, 38.1, 35.8, 35.4 (Methyl C's).

IR (KBr) ν_{max}: 1636 (C=O), 1395 cm^{-1}.

MS m/e (rel. intensity): 346 (M^+, 10.9), 301 (27.0), 273 (38.1), 246 (33.1), 216 (11.1), 202 (71.9), 72 (100). Calculated mass: 346.1681; found 346.1679.

Analysis calculated $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.52; H, 6.42; N, 8.08.

Solid state irradiation of compound **38** was performed on both powdered samples sandwiched between two microscope slides and on several small crystals. Analysis by proton NMR and glc showed that the same rearrangement product **69** was readily formed. High degrees of conversion could be achieved (70%) without concurrent melting of the crystals or powder.

Photolysis of 9,10-Dihydro-N,N'-dimethyl-9,10-ethenoanthracene-11,12-dicarboxamide (39)

Irradiation of compound **39** in acetone, acetonitrile, and methanol solution all gave a single photoproduct. Preparative photolysis was carried out on a saturated acetone solution of **39**, as the limited solubility of the starting material precluded the possibility of obtaining the usual concentration for such photolyses. The photoreaction proceeded readily until all the starting material had reacted and was accompanied by significant yellowing of the solution. Removal of the solvent gave a yellow amorphous solid. Purification by column chromatography (EtOAc) yielded a white solid which after recrystallization from ethanol gave white powdery crystals, mp = 261-262°C. The photoproduct was identified as:

N,N'-Dimethyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd]pentalene-8b,8c-dicarboxamide (70)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00-7.30 (8, m, Ar-H), 6.46 (2, broad, 2xCONHMe), 5.30 (1, s, Pentalene H_{4b}), 4.60 (1, s, Pentalene H_{8d}), 2.96 and 2.86 (2x3, 2d, J = 6.0 Hz, 2xCONH($\mathbf{CH_3}$)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.1, 168.4 (2xC=O); 151.7, 150.1, 135.3, 132.7 (Ar-C's, No H's); 128.3, 127.4, 127.1, 126.7, 125.3, 125.3, 122.6, 121.4 (Ar-C-H's), 69.9, 58.8 (Quaternary pentalene C's); 56.2, 47.3 (Pentalene C-H's); 27.1, 26.3 (2xCONH$\mathbf{CH_3}$).

IR (KBr) ν_{max}: 3277 (N-H, Free and H-bonded), 1641 (C=O), 1563, 1517 (Amide type II) cm^{-1}.

MS m/e (rel. intensity): 318 (M^+, 2.4), 287 (3.7), 261 (73.9), 230 (35.3), 204 (100), 203 (88.4), 202 (85.2), 58 (28.0). Calculated mass: 318.1368: found 318.1368.

Analysis calculated for $C_{20}H_{18}N_2O_2$: C, 75.46; H, 5.70; N,8.80. Found: C, 75.67; H, 5.71; N, 8.83.

Solid state irradiation of diamide **39** was performed on powdered samples sandwiched between microscope slides and on single crystals, resulting in the production of **70**. Analysis by proton NMR and glc showed that the degree of conversion obtained was very small (7%), even upon extended photolysis.

Photolysis of 9,10-Dihydro-N,N,N',N'-tetraethyl-9,10-ethenoanthracene-11,12-dicarboxamide (40)

Analytical photolyses of compound **40** were carried out in solutions of acetone, acetonitrile and benzene. In all cases a single photoproduct was readily obtained. Preparative photolysis was carried out in an acetonitrile solution of **40**. The photoreaction was accompanied by a yellowing of the photolysate solution. Removal of the solvent *in*

vacuo resulted in the recovery of a viscous yellow oil. The pure amide photoproduct was obtained by column chromatography (PET/EtOAc, 70:30) as a colourless oil. Crystallization from acetonitrile gave prismic crystals with mp = 147-148°C. Spectral data identified the photoproduct as:

N,N,N',N'-Tetraethyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd] pentalene-8b,8c-dicarboxamide (71)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02-7.30 (8, m, Ar-H), 4.64 (1, s, Pentalene H_{4b}), 3.98 (1, broad, Pentalene H_{8d}), 3.82 (1, broad, (CON(**CH_2**CH_3)), 3.16-3.50 (6, m, (CON(**CH_2**CH_3)), 3.07 (1, dq, J = 7.2, 14.0Hz, (CON(**CH_2**CH_3)), 1.38 (3, broad, (CON(CH_2**CH_3**)), 1.23 (3, t, J = 7.2Hz, (CON(CH_2**CH_3**)), 1.14 (6, m, (2xCON(CH_2**CH_3**)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8, 168.8 (2xC=O); 154.8, 149.9, 135.6, 135.5 (Ar-C's, No H's); 127.6, 127.3, 127.2, 126.9, 125.0, 124.3, 121.6, 121.2 (Ar-C-H's); 68.8, 58.1 (Quaternary pentalene C's); 56.6, 45.6 (Pentalene C-H's); 45.0, 42.2, 39.6, 39.0 (2xCON(**CH_2**CH_3)$_2$), 13.6, 12.9, 12.3 (2xCON(**CH_2**CH_3)$_2$).

IR (KBr) ν_{max}: 1636 (C=O), 1461, 1256 cm^{-1}.

MS m/e (rel. intensity): 402 (M^+, 22.1), 329 (10.5), 301 (11.7), 258 (20.4), 230 (15.7), 202 (31.6), 126 (25.5), 100 (100), 72 (43.3). Calculated mass: 402.2307; found 402.2302.

Analysis calculated for $C_{26}H_{30}N_2O_2$: C, 77.58; H, 7.51; N, 6.96. Found; C, 77.42; H, 7.44; N, 7.05.

Irradiation of samples of crystals and powders of compound **40** resulted in the production of a single photoproduct shown by proton NMR to be the same semibullvalene product **71** as found in the solution photolyses.

Photolysis of N,N'-Diethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxamide (41)

Analytical photolyses of compound **41** resulted in the formation of a single product in each solvent. Preparative photolysis of compound **41** in acetone gave rise to single photoproduct **72**. Removal of the solvent and subsequent purification by column chromatography (PET/EtOAc, 50:50) yielded a white powder. Recrystallization from chloroform gave small, fine white crystals with mp = 197-198°C. The photoproduct was identified as:

N,N'-Diethyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd]pentalene-8c,8d-dicarboxamide (72)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00-7.32 (8, m, Ar-H), 6.48 and 6.42 (2x1, 2 broad, 2xCON**H**Et), 5.32 (1, s, Pentalene H_{4b}), 4.60 (1, s, Pentalene H_{8d}), 3.44 (2, m, CONH(**CH_2**CH_3)), 3.22 and 3.30 (2, 2m, CONH(**CH_2**CH_3)), 1.20 and 1.10 (2x3, 2t, J = 7.0 Hz, 2xCONH(CH_2**CH_3**)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.2, 167.6 (2xC=O); 151.8, 150.1, 135.3, 132.8 (Ar-C's, No H's); 128.2, 127.3, 127.1, 126.7, 125.3, 125.2, 122.6, 121.4 (Ar-C-H's); 69.8, 60.0 (Quaternary pentalene C's); 56.1, 47.0 (Pentalene C-H's); 35.3, 34.4 (2xCONH(**CH_2**CH_3)), 14.8, 14.2 (2xCONH(CH_2**CH_3**)).

IR (KBr) ν_{max}: 3326 (N-H, Free and H-bonded), 1645 (C=O), 1553 (Amide type II), 1474 cm^{-1}.

MS m/e (rel. intensity): 346 (M^+, 2.4), 275 (61.1), 246 (8.1), 230 (29.0), 204 (100), 203 (66.1), 202 (61.2). Calculated mass: 346.1681; found 346.1678.

Analysis calculated for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.29; H, 6.37; N, 8.00.

Solid state irradiation of crystals and powdered samples of compound **41** resulted in a very slow production of the semibullvalene **72** product found in solution irradiations. The photoproduct was shown to be the same product as found in solution by proton NMR and gc analyses.

D: Photochemistry of Dibenzobarrelene Ester-amides

Photolysis of Methyl 9,10-Dihydro-N,N-dimethyl-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (45)

Analytical photolysis of compound **45** in acetone, benzene, and acetonitrile proceeded rapidly and cleanly to produce two photoproducts in a ratio of 97:3 in all cases. Preparative photolysis was performed on an acetone solution of 506 mg of the starting material. The reaction was monitored by GC every 5 minutes in order to achieve complete conversion of the starting material without overexposing the photoproducts to the UV light. The acetone was removed *in vacuo* giving a slightly yellow amorphous solid. The two photoproducts were separated by column chromatography (PET/EtOAc, 50:50). The major photoproduct was recrystallized from ethanol to give small colourless crystals, mp = 148.5-150°C, and identified as:

Methyl N,N-Dimethyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd] pentalene-8b-carboxamide-8c-carboxylate (73a)

^{1}H NMR (400 MHz, $CDCl_3$): δ 700-7.44 (8, m, Ar-H), 5.14 (1, s, Pentalene H_{4b}), 4.44 (1, s, Pentalene H_{8d}), 3.78 (3, s, $CO_2\mathbf{CH_3}$), 3.08 and 2.52, (2x3, 2s, $CON(\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 170.4, 167.3 (2xC=O); 150.0, 148.5, 135.4, 134.6 (Ar-C's, No H's); 127.8, 127.3, 127.2, 126.8, 125.7, 124.5, 122.0, 121.1 (Ar-C-H's); 67.1, 60.0 (Quaternary pentalene C's); 54.9, 52.2, 49.4 ($CO_2\mathbf{CH_3}$, Pentalene C-H's); 37.2, 36.0 ($CON(\mathbf{CH_3})_2$).

IR (KBr) ν_{max}: 1728 (E-C=O), 1646 (A-C=O), 1438, 1397, 1238 cm^{-1}.

MS m/e (rel. intensity): 333 (M^+, 41.1), 274 (11.9), 261 (10.0), 202 (100), 72 (28.5). Calculated mass: 333.1365; found: 333.1365.

Analysis calculated for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.63; H, 5.91; N, 4.24.

The second photoproduct was recrystallized by dissolving it in a minimal amount of chloroform, adding petroleum ether and scratching the bottom of the flask with a glass rod. This product was identified as:

Methyl N,N-Dimethyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd] pentalene-8c-carboxamide-8b-carboxylate (73e)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (1, m, Ar-H), 7.08-7.48 (7, m, Ar-H), 4.70 (1, s, Pentalene H_{4b}), 4.42 (1, s, Pentalene H_{8d}), 3.92 (3, s, $CO_2\mathbf{CH_3}$), 3.00 and 2.80 (2x3, 2s, CON($\mathbf{CH_3}$)$_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.4, 167.8 (2xC=O); 149.9, 148.4, 135.6, 134.8 (Ar-C's, No H's); 128.0, 127.1, 126.9, 126.6, 125.8, 124.4, 122.2, 121.3 (Ar-C-H's); 67.0, 59.8 (Quaternary pentalene C's); 54.8, 52.0, 47.8 ($CO_2\mathbf{CH_3}$, Pentalene C-H's); 376.8, 36.4 (CON($\mathbf{CH_3}$)$_2$).

IR (KBr) ν_{max}: 1724 (E-C=O), 1646 (A-C=O), 1456, 1218 cm^{-1}.

MS m/e (rel. intensity): 333 (M^+, 44.7), 290 (5.8), 273 (17.5), 261 (57.8), 246 (11.3), 229 (19.5), 202 (95.6), 72 (100). Calculated mass: 333.1365; found 333.1357.

Analysis calculated for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.51; H, 5.98; N, 4.35.

mp = 142-143°C.

Solid state photolyses were carried out on both powdered samples sandwiched between microscope slides and single crystals of compound **45**. Analysis by proton NMR and gc indicated only the production of photoproduct **73a.** Because of crystal melting, conversion of the starting material was limited to 15%, and it is possible that the photoproduct **73e** was simply not detectable in the quantities in which it was produced.

Because the two photoproducts are regioisomers and therefore spectroscopically very similar, further experimental evidence was needed to distinguish the location of the amide and ester functionalities in the major and minor products. For this reason the following compound was synthesized and photolyzed:

Methyl 9,10-Dihydro-N,N-dimethyl-9,10-ethenoanthracene-9-carboxamide-12-carboxylate (51)

Preparation of N,N-Dimethyl-9-anthracenecarboxamide[54]

N,N-Dimethyl-9-anthracenecarboxamide[54] was produced via Weinreb aminolysis using 214 mg of methyl 9-anthracenecarboxylate as starting material. The ester was added to 10 ml of dry toluene and 2.0 ml of a 0.67 M solution of the dimethyl amine hydrochloride-derived aluminum amide reagent. The reaction mixture was refluxed under nitrogen overnight and subsequently quenched with 5% HCl. After working up in the usual manner, the crude product was purified by column chromatography (PET/EtOAc, 90:10) and recovered in essentially quantitative yield. The anthracene amide product was recrystallized from diethyl ether and petroleum ether to give a white solid with mp = 137.5-138.5°C (lit;[54] mp = 139°C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (1, s, Ar-H_{10}), 7.84-8.04 (4, m, Ar-H), 7.50 (4, m, Ar-H), 3.42 (3, s, CONC**H**$_3$), 2.70 (3, s, CONC**H**$_3$).

IR (KBr) ν_{max}: 1636 (C=O), 1498, 1445, 1164 cm^{-1}.

MS m/e (rel. intensity): 249 (M^+, 43.5), 205 (100), 177 (50.0).

Diels-Alder Reaction to Produce Compound 51

N,N-Dimethyl-9-anthracenecarboxamide[54] (303 mg, 1.22 mmol) and methyl propiolate (available from Aldrich) were added to a Carius tube and the tube sealed under vacuum. The Carius tube was heated for 6 h at 180°C. After cooling of the reaction

mixture, a brown glassy material was obtained. The crude product mixture was purified by column chromatography (PET/EtOAc, 60:40) resulting in the recovery of 82 mg of unreacted anthracene amide and 227 mg (68 % yield) of the desired product, compound **51**. The product was recrystallized from ethanol giving large crystals with mp = 180-181^{o}C, and spectral data as follows:

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (1, d, J = 2.0 Hz, Vinylic H_{11}), 6.98-7.58 (8, m, Ar-H), 5.66 (1, d, J = 2.0 Hz, Bridgehead H_{10}), 3.72 (3, s, $CO_2\mathbf{CH_3}$), 3.20 and 2.80 (2x3, 2s, $CON(\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 167.4, 165.3 (2xC=O); 151.5 (Vinylic C-H); 145.2, 144.5, 142.2 (Vinylic and Ar-C's, No H's); 125.9, 124.7, 124.1, 123.6 (Ar-C-H's); 62.7 (Quaternary bridgehead C); 51.8, 51.0 (Bridgehead C-H and $CO_2\mathbf{CH_3}$); 41.4, 36.6 ($CON(\mathbf{CH_3})_2$).

IR (KBr) ν_{max}: 1702 (E-C=O), 1637 (A-C=O),1459, 1440, 1212, 1170 cm^{-1}.

UV (CH_3OH) λ_{max}: 277.7 nm (ε = 5060), 270.3 (ε = 4960).

MS m/e (rel. intensity): 333 (M^+, 72.0), 274 (19.6), 261 (18.6) , 246 (13.6), 229 (16.8), 202 (55.3), 177 (9.4), 72 (100). Calculated mass: 333.1365; found 333.1372.

Analysis calculated for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.38; H, 5.60; N, 4.27.

The regiochemistry of the Diels-Alder adduct was principally determined by the magnitude of the proton NMR coupling constant between the bridgehead and the vinyl hydrogens, and by comparison to analogous diester systems.[56,57]

Photolysis of compound **44** in acetone, acetonitrile and benzene gave rise to a single photoproduct. Preparative irradiation was performed on a solution of 197 mg (0.59 mmol) of compound **44** in acetone. The reaction was monitered by gc and stopped when less than 3% of the starting material remained. At this point the solution had become slightly yellow. The solvent was removed *in vacuo* giving a viscous oil. Purification of

the photoproduct was achieved by successive recrystallizations from ethanol. Spectral (proton and carbon NMR, IR, MS) and physical data (mp, gc, tlc) indicated that this photoproduct was identical to compound **42**.

Photolysis of Methyl 9,10-Dihydro-N,N-diethyl-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (46)

The irradiation of compound **46** in acetone, benzene and acetonitrile gave rise to two photoproducts, as determined by glc. Preparative photolysis of 368 mg (1.02 mmol) of compound **46** in acetone produced a yellow oil after removal of the solvent. The two photoproducts were isolated in a ratio of 3:1 by subjecting the oil to column chromatography (PET/EtOAc, 80:20).

The major photoproduct was recrystallized from ethanol giving rise to white crystals, with mp = 150-151°C, and subsequently identified as:

Methyl N,N-Diethyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd] pentalene-8b-carboxamide-8c-carboxylate (77)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00-7.40 (8, m, Ar-H), 5.10 (1, s, Pentalene H_{4b}), 4.40 (1, s, Pentalene H_{8d}), 3.70 (3, s, $CO_2\mathbf{CH_3}$), 3.62, 3.36, 3.04, 2.84 (4x1, 4dq, J = 6.0, 14.9 Hz, $CON(\mathbf{CH_2}CH_3)_2$), 1.20 and 0.72 (2x3, 2t, J = 6.0 Hz, $CON(CH_2\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 170.5, 166.7 (2xC=O); 150.1, 148.3, 135.5, 134.8 (Ar-C's, No H's); 127.9, 127.2, 126.9, 125.6, 124.8, 122.0, 121.7, 121.0 (Ar-C-H's); 67.0, 60.3 (Quaternary pentalene C's); 54.9, 52.0, 49.5 (Pentalene C-H's and $CO_2\mathbf{CH_3}$); 41.4, 39.1 ($CON(\mathbf{CH_2}CH_3)_2$); 12.6, 12.3 ($CON(CH_2\mathbf{CH_3})_2$).

IR (KBr) ν_{max}: 1723 (E-C=O), 1641 (A-C=O), 1439, 1234 cm^{-1}.

MS m/e (rel. intensity): 361 (M^+,45.6), 302 (8.4), 262 (25.0), 202 (100), 100 (56.2), 72 (62.2). Calculated mass: 361.1678; found 361.1681.

Analysis calculated for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.36; H, 6.46; N, 3.72.

The structure of compound **77** was confirmed by the synthesis and photolysis of the following compound;

Methyl N,N-Diethyl-9,10-dihydro-9,10-ethenoanthracene-9-carboxamide-12-carboxylate (52)

Preparation of N,N-Diethyl-9-anthracenecarboxamide[55]

Following the procedure for Weinreb aminolysis, 6.0 ml (4.0 mmol) of a 0.67 M solution of the diethyl amine hydrochloride-derived aluminum amide reagent was added to 492 mg (2.06 mmol) of methyl 9-anthracenecarboxylate in 20 ml of dry toluene. The solution was refluxed under nitrogen until no starting material was observed by tlc (6 h). The reaction was quenched with 5% HCl and worked up in the usual manner. The product was isolated in quantitative yield after column chromatography (PET/EtOAc, 90:10). Recrystallization from diethyl ether and petroleum ether gave fine white crystals with mp = 160-162°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (1, s, Ar-H), 7.88-8.06 (4, m, Ar-H), 7.48 (4, m, Ar-H), 3.88 and 3.04 (2x2, 2q, J = 6.0 Hz, CON($\mathbf{CH_2}CH_3)_2$), 1.52 and 0.88 (2x3, 2t, J = 6.0 Hz, CON($CH_2\mathbf{CH_3}$)$_2$).

IR (KBr) ν_{max}: 1631 (C=O), 1434, 1267 cm^{-1}.

MS m/e (rel. intensity): 277 (M^+, 45.1), 262 (20.5), 205 (100), 177 (55.8). Calculated mass: 277.1467; found 277.1473.

Diels-Alder Reaction to Produce Compound 52

N,N-Diethyl-9-anthracenecarboxamide (513 mg, 1.85 mmol) and methyl propiolate (2 mmol) were sealed in an evacuated Carius tube and heated in an oven at 180°C for 6 h. The brown glassy material which was obtained was subjected to column chromatography (PET/EtOAc, 70:30) from which 136 mg of unreacted anthracene amide and 354 mg (0.98 mmol, 72% yield) of the desired product **52** were recovered. Compound **52** was recrystallized from ethanol to produce colourless prisms (mp = 173-175°C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (1, d, J = 1.9 Hz, Vinylic H_{11}), 7.00-7.50 (8, m, Ar-H), 5.68 (1, d, J = 1.9 Hz, Bridgehead H_{10}), 3.86 and 3.06 (2x2, 2d, J = 6.1 Hz, $CON(\mathbf{CH_2}CH_3)_2$), 3.68 (3, s, $CO_2\mathbf{CH_3}$), 1.46 and 1.06 (2x3, 2t, $CON(CH_2\mathbf{CH_3})_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 167.0, 165.4, (2xC=O); 152.0 (Vinylic C-H); 145.0, 144.6, 142.4 (Vinylic and Ar-C's, no H's); 126.0, 124.5, 124.2, 123.7 (Ar-C-H's); 63.0 (Quaternary bridgehead C); 51.8, 51.0 (Bridgehead C-H and $CO_2\mathbf{CH_3}$); 44.49, 39.7 ($CON(\mathbf{CH_2}CH_3)_2$), 13.2, 13.0 ($CON(CH_2\mathbf{CH_3})_2$).

IR (KBr) ν_{max}: 1713 (E-C=O), 1630 (A-C=O), 1437, 1277, 1217 cm^{-1}.

MS m/e (rel. intensity): 361 (M^+, 98.7), 302 (23.7), 290 (5.1), 262 (33.5), 202 (100), 100 (67.1), 72 (47.2). Calculated mass: 361.1678; found 361.1677.

Analysis calculated for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.60; H, 6.44; N, 4.00.

Isolation of the single photoproduct which resulted from preparative irradiation of compound **52** in acetone, was achieved by recrystallization from ethanol. This photoproduct was found to be spectroscopically (proton and carbon NMR, IR, MS) identical to compound **77**. The melting point of this photoproduct (150-151°C) also matched that of compound **77**.

The second product (mp = 210°C) from the irradiation of compound **46** was recrystallized from chloroform and identified as;

Methyl 9,10-Dihydro-N-ethyl-9,10-ethanoanthracene-12-carboxamide-11-carboxylate (78)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.40 (8, m, Ar-H), 5.97 (1, broad, exchanges with D_2O, CONHEt), 4.74 (1, d, J = 3.0 Hz, Bridgehead H_9), 4.55 (1, d, J = 3.0 Hz, Bridgehead H_{10}), 3.70 (3, s, $CO_2\mathbf{CH_3}$), 3.26 and 3.14 (2x1, 2xdq, J = 20.0, 7.0 Hz, CONH($\mathbf{CH_2}CH_3$)), 3.15 and 3.03 (2x2, 2xdd, J = 3.0, 6.0 Hz, Bridge H_{11} andH_{12}), 1.07 (3, t, J = 7.0 Hz, CONH($CH_2\mathbf{CH_3}$)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 174.1, 171.8 (2xC=O); 143.1, 142.0, 140.6, 140.3 (Ar-C's, No H's); 126.4, 126.3, 126.1, 126.0, 125.7, 124.9, 123.2, 123.1 (Ar-C-H's); 52.5, 49.2, 48.7, 46.9, 46.2 ($CO_2\mathbf{CH_3}$, Bridgehead and bridge C-H's); 34.4 (CONH($\mathbf{CH_2}CH_3$)); 14.9 (CONH($CH_2\mathbf{CH_3}$)).

IR (KBr) ν_{max}: 3440, 3301 (N-H, Free and H-bonded), 1738 (E-C=O), 1638 (A-C=O), 1546 (Amide type II), 1270 cm^{-1}.

MS m/e (rel. intensity): 335 (M^+, 15.5), 303 (12.7), 202 (20.4), 178 (100). Calculated mass: 335.1521; found: 335.1514.

Analysis calculated for $C_{21}H_{21}NO_3$: C, 75.19; H, 6.31; N, 4.18. Found: C, 75.05; H, 6.41; N, 3.90.

Proof of the structure of this photoproduct was achieved by the synthesis of mono-ethyl analog of the starting material, compound **47**, and subsequent magnesium/methanol reduction[84] of the bridging vinyl bond.

Methyl 9,10-Dihydro-N-ethyl-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (47)

The procedure for the preparation of this compound is outlined in the section on synthesis of ester-amide starting materials.

Magnesium/methanol Reduction of Compound 47

Using flamed-dried glassware, freshly distilled methanol and oven-dried magnesium turnings, the reduction was carried out by dissolving compound **47** in methanol and adding 10 eqs of magnesium turnings. The reaction mixture was allowed to stir at ambient temperature for two hours at which point effervescence had ceased. The reaction was monitored by glc and tlc as well. The excess magnesium was reacted with concentrated HCl, diethyl ether added (100 ml) and the reaction mixture washed with water. After drying with magnesium sulphate, filtration and removal of the solvent, the reaction mixture was dissolved in deuterochloroform. The product mixture was shown to contain predominantly compound **78** by NMR and glc-ms.

Solid state irradiation of powdered and single crystal samples of **46** resulted in the production of the same two photoproducts **77** and **78** as shown by proton NMR, glc-ms, and gc. The percentage of the second photoduct was much reduced and reduced even further when efforts were made to keep the reaction mixture as dry as possible by drying and sealing the sample, sandwiched between microscope slides, in a polymer film under nitrogen prior to photolysis.

Photolysis of Compound 46 in Deuterated Methanol (CH_3OD)

Photolysis of compound **46** in deuterated methanol (CH_3OD) gave rise to three products, in addition to the di-π-methane product, which were identified as:

Methyl 12-Deuterio-9,10-dihydro-N-ethyl-9,10-ethanoanthracene-12-carboxamide-11-carboxylate (78d)

^1H NMR (400 MHz, $CDCl_3$): δ 7.10-7.40 (8, m, Ar-H), 5.97 (1, broad, CONHEt), 4.74 (1, d, J = 3.0 Hz, Bridgehead H_9), 4.55 (1, s, Bridgehead H_{10}), 3.70 (3, s, $CO_2\mathbf{CH_3}$), 3.26 and 3.14 (2x1, 2xdq, J = 20.0, 7.0 Hz, CONH($\mathbf{CH_2}CH_3$)), 3.15 (2, d, J = 3.0, Hz, Bridge H_{11}), 1.07 (3, t, J = 7.0 Hz, CONH($CH_2\mathbf{CH_3}$)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 174.2, 171.8 (2xC=O); 143.1, 142.1, 140.6, 140.3 (Ar-C's, No H's); 126.4, 126.3, 126.2, 126.1, 125.8, 124.9, 123.3, 123.2 (Ar-C-H's); 52.4, 49.2, 48.7, 46.9, 46.2 ($CO_2\mathbf{CH_3}$, Bridgehead C-H's and Bridge C-H α to the ester); 34.4 (CONH($\mathbf{CH_2}CH_3$)); 29.7 (Bridge C-D α to Amide); 14.9 (CONH($CH_2\mathbf{CH_3}$)).

IR (KBr) ν_{max}: 3449, 3302 (N-H free and H-bonded), 1737 (E-C=O), 1636 (A-C=O), 1543 (Amide type II), 1295 cm^{-1}.

MS m/e (rel. intensity): 336 (M^+, 17.3), 304 (12.4), 203 (29.6), 178 (100). Calculated mass: 336.1583; found: 336.1577.

mp = 211-212°C.

Dimethyl *cis*-11-Deuterio-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (79d)

^1H NMR (300 MHz, $CDCl_3$): δ 7.08-7.38 (8, m, Ar-H), 4,75 (1, d, J = 2.7 Hz, Bridgehead H_{10}), 4.74 (1, s, Bridgehead H_9), 3.62 (6, s, $CO_2\mathbf{CH_3}$), 3.42 (1, d, J = 2.7 Hz, Bridge H_{12}).

^{13}C NMR (50 MHz, $CDCl_3$): δ 172.8 (C=O); 142.1, 140.3 (Ar-C's, No H's); 126.5, 126.4, 124.6, 123.8 (Ar-C-H's); 52.2, 47.8, 46.7 ($CO_2\mathbf{CH_3}$, C_9, C_{10}, C_{11} and C_{12}).

IR (KBr) ν_{max}: 1735 (C=O), 1262, 1219 cm^{-1}.

MS m/e (rel. intensity): 323 (M^+, 8.6), 291 (8.7), 262 (1.6), 203 (9.9), 178 (100), 114 (86.0). Calculated mass: 323.1267; found: 323.1265.

mp = 149°C

Dimethyl *trans*-11-Deuterio-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (80d)

^1H NMR (300 MHz, $CDCl_3$): δ 7.04-7.30 (8, m, Ar-H), 4.54 (1, d, J = 2.4 Hz, Bridgehead H_{10}), (1, s, Bridgehead H_9), 3.44 (3, s, $CO_2\mathbf{CH_3}$), 3.14 (1, d, J = 2.4 Hz, Bridge H_{12}).

^{13}C NMR (50 MHz, $CDCl_3$): δ 172.1 (C=O); 142.6, 140.2 (Ar-C's, No H's); 126.4, 126.2, 125.1, 123.8 (Ar-C-H's); 51.8, 47.3, 46.6 ($CO_2\mathbf{CH_3}$, C_9, C_{10}, C_{11} and C_{12}).

IR (KBr) ν_{max}: 1748 (C=O), 1272, 1214 cm^{-1}.

MS m/e (rel. intensity): 323 (M^+, 2.6), 292 (1.1), 203 (5.4), 178 (100). Calculated mass: 323.1258; found: 323.1267.

mp = 103.5-105°C

Magnesium/Methanol Reduction of Compound 9 to Give Non-deuterated Analog Compounds[86] 79 and 80

Using the procedure outlined for the reduction of compound **47**, 210 mg (0.66 mmol) of dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate was reacted with 172 mg (10 eqs) of magnesium turnings. After work-up and subsequent separation by column chromatography (PET/EtOAc, 85:15), 25 mg of the starting diester was

recovered along with 50 mg of compound **79** (27% yield) and 129 mg of compound **80** (70% yield). Spectral data[86], as well as melting point determinations, confirmed the assigned structures of compounds **79** and **80**.

Dimethyl *cis*-9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (79)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08-7.38 (8, m, Ar-H), 4.74 (2, s, Bridgehead H_9 and H_{10}), 3.62 (6, s, $CO_2\mathbf{CH_3}$), 3.42 (2, s, Bridge H_{11} and H_{12}).

^{13}C NMR (50 MHz, $CDCl_3$): δ 172.8 (C=O); 142.1, 140.3 (Ar-C's, No H's); 126.5, 126.4, 124.6, 123.8 (Ar-C-H's); 52.2, 47.8, 46.7 ($CO_2\mathbf{CH_3}$, Bridgehead and bridge C-H's).

IR (KBr) ν_{max}: 1732 (C=O), 1267, 1219 cm^{-1}.

MS m/e (rel. intensity): 322 (M^+, 7.5), 291 (2.5), 202 (9.7), 178 (100).

mp = 149-150°C (lit;[86] 150-150.5°C)

Dimethyl *trans*-9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (80)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04-7.30 (8, m, Ar-H), 4.52 (2, s, Bridgehead H_9 and H_{10}), 3.44 (3, s, $CO_2\mathbf{CH_3}$), 3.14 (2, s, Bridge H_{11} and H_{12}).

^{13}C NMR (50 MHz, $CDCl_3$): δ 172.1 (C=O); 142.6, 140.2 (Ar-C's, No H's); 126.4, 126.2, 125.1, 123.8 (Ar-C-H's); 51.8, 47.3, 46.6 ($CO_2\mathbf{CH_3}$, Bridgehead and bridge C-H's).

IR (KBr) ν_{max}: 1747 (C=O), 1271, 1239 cm^{-1}.

MS m/e (rel. intensity): 322(M^+, 5.5), 291 (3.1), 202 (8.7), 178 (100).

mp = 106.5-107.5°C (lit;[86] 107°C).

Photolysis of Methyl 9,10-Dihydro-N-ethyl-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (47)

Compound **47** was found to give upon irradiation only one photoproduct. Preparative photolysis was carried out in acetone which resulted in a yellow oil after removal of the solvent. Purification by column chromatography (PET/EtOAc, 70:30) and recrystallization from ethanol gave very small white crystals (mp = 169-170°C) identified as:

Methyl N-Ethyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd]pentalene-8c-carboxamide-8b-carboxylate (74a)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02-7.40 (8, m, Ar-H), 5.96 (1, broad, CONHEt), 5.08 (1, s, Pentalene H_{4b}), 4.58 (1, s, Pentalene H_{8d}), 3.72 (3, s, $CO_2\mathbf{CH_3}$), 3.42 (2, m, CONH($\mathbf{CH_2}CH_3$)), 1.20 (3, t, J = 7.0 Hz, CONH($CH_2\mathbf{CH_3}$)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 170.0, 166.6 (2xC=O); 150.5, 149.7, 135.2, 134.3 (Ar-C's, No H's); 128.1, 127.4, 127.2, 126.9, 125.5, 121.8, 121.3 (Ar-C-H's); 67.6, 60.3 (Quaternary pentalene C's); 55.5, 52.1, 48.2 (CO_2CH_3, Pentalene C-H's); 35.1 (CONH($\mathbf{CH_2}CH_3$)); 14.9 (CONH($CH_2\mathbf{CH_3}$)).

IR (KBr) ν_{max}: 3251 (N-H), 1718 (E-C=O), 1636 (A-C=O), 1549 (Amide type II), 1440, 1253 cm^{-1}.

MS m/e (rel. intensity): 333 (M^+, 100), 301 (13.4), 274 (14.9), 262 (35.9), 246 (17.4), 230 (25.1), 202 (74.3). Calculated mass: 333.1365; found 333.1361.

Analysis calculated for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.90; H, 5.72; N, 4.15.

Solid state irradiation of crystalline samples of **47** resulted in the production of a single photoproduct which was shown by proton NMR and gc to be the same as that in solution.

Photolysis of Methyl 9,10-Dihydro-12-(N-piperidinylcarbonyl)-9,10-ethenoanthracene-11-carboxylate (48)

Analytical photolysis of compound **48** in acetone, acetonitrile and benzene resulted in rapid reaction giving rise to a single photoproduct. Preparative scale photolysis was carried out in acetonitrile and monitored by gc. When only 5% of the starting material remained, irradiation was stopped and the solvent removed *in vacuo*. The resultant viscous oil was subjected to column chromatography (Hexanes/EtOAc, 60:40) with a white solid being subsequently isolated. Recrystallization from ethanol gave colourless crystals with mp = 199.5-200.5^{o}C, which were identified as:

8c-Methyl-8b-(N-piperidinylcarbonyl)-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclo propa[cd]pentalene-8c-carboxylate (81)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02-7.44 (8, m, Ar-H), 5.10 (1, s, Pentalene H_{4b}), 4.40 (1, s, Pentalene H_{8d}), 3.84 (1, m, Amide ring methylene), 3.72 (3, s, $CO_2\mathbf{CH_3}$), 3.50, 3.00, 2.86 (3x1, 3m, Amide ring methylenes), 1.60 (4, broad, Amide ring methylenes), 1.12 (2, m, Amide ring methylenes).

^{13}C NMR (50 MHz, $CDCl_3$): δ 170.4, 165.8 (2xC=O); 150.0, 148.3, 135.5, 135.0 (Ar-C's, No H's); 127.8, 127.2, 127.0, 126.8, 125.7, 124.6, 122.0, 120.0 (Ar-C-H's); 67.1, 60.0 (Quaternary pentalene C's); 54.9, 52.1, 49.3 ($CO_2\mathbf{CH_3}$ and Pentalene C-H's); 46.8, 43.5, 25.6, 25.4, 24.3 (Amide ring methylenes).

IR (KBr) ν_{max}: 1719 (E-C=O); 1646 (A-C=O); 1441, 1255, 1235 cm^{-1}.

MS m/e (rel. intensity): 373 (M^+, 41.3), 262 (18.4), 230 (19.7), 202 (84.0), 112 (57.9), 84 (100). Calculated mass: 373.1678; found 373.1676.

Analysis calculated for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 76.95; H, 6.21; N, 3.66.

Solid state photolysis of powdered samples and single crystals of the starting material **48** resulted in the production of a single photoproduct which was shown by proton NMR and gc-ms to be identical to compound **81**.

Photolysis of Methyl N,N-Dibenzyl-9,10-dihydro-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (49)

Analytical photolyses of compound **49** in acetone, acetonitrile, benzene, and methanol all showed the formation of a single photoproduct. Preparative irradiation was carried out on a solution of 250 mg of **49** in 250 ml of spectral grade acetonitrile. The reaction was allowed to proceed until 5% starting material was still unreacted at which point the solution had become quite yellow. Removal of the solvent *in vacuo* resulted in the recovery of a yellow oil. Proton NMR indicated that the reaction had been accompanied by significant decompostion. The photoproduct was purified by column chromatography (PET/EtOAc, 80:20). Recrystallization from diethyl ether gave prisms, mp = 172.5-174^{o}C. The photoproduct was identified as:

1-Benzyl-4-phenyl-azetidin-2-one-3-spiro-11'-(12'-methyl-9',10'-dihydro-9',10'-ethanoanthracene-12'-carboxylate) (82)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92-7.44 (16, m, Ar-H), 6.58 (1, t, J = 8.8 Hz, Ar-H), 5.50 (1, d, J = 8.8 Hz, Ar-H), 4.92 (1, d, J = 14.9 Hz, N**CH$_2$**Ph), 4.44 (1, d, J = 2.6 Hz, Bridgehead H_9), 4.36 (1, s, Bridgehead H_{10}), 4.22 (1, s, Ring NC**H**Ph), 3.82 (1, d, J = 14.9 Hz, N**CH$_2$**Ph), 3.32 (1, d, J = 2.6 Hz, Bridge H_{11}), 3.30 (3, s, CO_2**CH$_3$**).

Assignments are supported by ^{13}C APT and COSY ^{1}H NMR experiments.

^{13}C NMR (50 MHz, $CDCl_3$): δ 172.6, 170.6 (2xC=O); 143.1, 141.0, 139.9, 138.3, 133.4, 134.3 (Ar-C's, No H's); 128.7, 128.6, 128.5, 128.4, 127.6, 126.5, 126.3, 125.7, 125.3, 125.2, 124.8, 124.5, 122.9 (Ar-C-H's); 64.7 (Quaternary bridge C); 62.7

(Bridge C-H); 51.4, 49.9, 46.9, 46.6, (Bridgehead C-H's, $CO_2\mathbf{CH_3}$, Ring C-H); 44.3 ($N\mathbf{CH_2}Ph$).

IR (KBr) ν_{max}: 1747 (Lactam and ester C=O), 1455, 1157 cm^{-1}.

MS m/e (rel. intensity): 485 (M^+, 12.3), 352 (31.1), 291 (6.3), 262 (12.8), 261 (19.5), 215 (19.7), 203 (33.6), 202 (36.1), 178 (100), 91 (39.6), 84 (39.5). Calculated mass: 485.1991; found: 485.2003.

Analysis calculated for $C_{33}H_{27}NO_3$: C, 81.63; H, 5.60; N, 2.88. Found: C, 81.35; H, 5.64; N, 2.90.

Solid state irradiation of compound **48** was carried out on both powdered samples and on a single crystal. The samples were analyzed by dissolution in deuterochloroform and subsequent proton NMR experiments, in addition to analysis by glc. The samples were found to give the same photoproduct, **82**, as observed in solution irradiations.

Photolysis of Methyl 9,10-Dihydro-N,N'-di-(2-propyl)-9,10-ethenoanthracene-12-carboxamide-11-carboxylate (49)

Photolysis of compound **49** in acetone, acetonitrile and benzene resulted in the formation of a single photoproduct, accompanied by significant decomposition. Preparative photolysis of 300 mg of starting material in benzene solution (250 ml) was carried out and resulted in the solution turning quite yellow. Concentration of the photolysate solution *in vacuo* left a viscous yellow film in the flask. Purification of the reaction mixture by column chromatography (Hexanes/EtOAc, 80:20) resulted in the isolation of a colourless oil. Recrystallization of the photoproduct from ethanol gave white powdery crystals with mp = 276-277°C. Spectral data of the photoproduct identified it as:

Methyl 9,10-Dihydro-N-(2-propyl)-9,10-ethanoanthracene-12-carboxamide-12-carboxylate (83)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-7.48 (8, m, Ar-H), 5.78 (1, broad, CON**H**(iPr)), 4.74 (1, d, J = 2.2 Hz, Bridgehead H_9), 4.52 (1, d, J = 2.2 Hz, Bridgehead H_{10}), 3.94 (1, septet, J = 6.4 Hz, CONHC**H**$(CH_3)_2$), 3.66 (3, s, CO_2**CH_3**), 3.18 (1, dd, J = 2.2, 5.6 Hz, Bridge H_{11}), 3.02 (1, dd, J = 2.2, 5.6 Hz, Bridge H_{12}), 1.12 (3, d, J = 5.6 Hz, CONHCH(**CH_3**)), 1.06 (3, d, J = 5.6 Hz, CONHCH(**CH_3**)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 173.9, 171.0 (2xC=O); 143.0, 142.0, 140.5, 140.4 (Ar-C's, No H's); 126.3, 126.2, 126.1, 125.6, 124.9, 123.3 (Ar-C-H's); 52.4, 49.0, 48.8, 47.2, 46.3, 41.4 (Bridge, bridgehead, isopropyl methine and ester methyl C's); 22.9, 22.6 (CONHCH(**CH_3**)$_2$).

IR (KBr) ν_{max}: 3330 (H-bonded N-H), 3269 (Free N-H), 1733 (E-C=O), 1644 (A-C=O), 1554 (Amide type II), 1460, 1268, 1201 cm^{-1}.

MS m/e (rel. intensity): 349 (M^+, 3.2), 317 (2.0), 231 (1.9), 178 (100). Calculated mass: 349.1678; found: 349.1673.

Analysis calculated for $C_{33}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.57; H, 6.62, N, 3.88.

Solid state photolyses were performed on powdered samples and on single crystals of compound **49**. The reaction was carried out to approximately 15% conversion without any noticeable yellowing or melting of the solid material. Analysis by proton NMR and gc indicated that the only product in the solid state reaction was the same as in solution irradiations.

E: Photochemistry of Miscellaneous Dibenzobarrelene Adducts

Photolysis of Methyl 12-Phenyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxylate (74)

The irradiation of compound **74** was carried out in acetone, benzene, acetonitrile and methanol, rapidly giving rise to a single photoproduct in all cases. Preparative irradiation was performed in a solution of acetone. The reaction could not be monitored by tlc or gc because of the inability to distinguish the starting material from the photoproduct. Reaction progress had to be followed by removing aliquots at 5 minute intervals and running a proton NMR spectrum. In order to avoid difficulties separating the product from the starting material, the reaction mixture was irradiated until no starting material ester peak was observed in the NMR spectrum. After removal of the acetone, a yellow oil was obtained which was purified by column chromatography (PET/EtOAc, 95:5) to give the pure semibullvalene product. Recrystallization from ethanol gave colourless crystals, mp = 150.5-152^{o}C. The photoproduct was identified as;

Methyl 8c-Phenyl-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd] pentalene-8b-carboxylate (75e)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (13, m, Ar-H), 4.72 (1, s, Pentalene H_{4b}), 4.56 (1, s, Pentalene H_{8d}), 3.58 (3, s, $CO_2\mathbf{CH_3}$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 168.9 (C=O); 150.7, 150.5, 136.4, 136.3, 133.9 (Ar-C's, No H's); 128.3, 127.8, 127.6, 127.5, 127.2, 126.8, 125.6, 121.3 (Ar-C-H's); 73.0 (Quaternary pentalene C); 61.9 (Pentalene C-H); 55.7 (Quaternary pentalene C); 51.9, 48.3 (Pentalene C-H and $CO_2\mathbf{CH_3}$).

IR (KBr) ν_{max}: 1717 (C=O), 1474, 1224 cm^{-1}.

MS m/e (rel. intensity): 338 (M^+, 25.2), 279 (79.0), 278 (83.6), 202 (15.9), 178 (31.5), 138.2 (16.2). Calculated mass: 338.1307; found 338.1303.

Analysis calculated for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.38; H, 5.36.

The structure of this compound was also supported by X-ray diffraction analysis. The crystal data were as follows: $C_{24}H_{18}O_2$; orthorhombic; space group *Pbca;* a = 15.266 (2)Å, b = 16.262 (3)Å, c = 14.107 (2)Å, V = 3502.1 (7)$Å^3$; Z = 8; D_{calc} = 1.283 g/cm^3; R = 0.039.

Photolysis of N,N-Diethyl-N'-methyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxamide (54)

Photolysis of compound **54** in solution gave rise to three products in the ratio of 55:15:30 as determined by glc. Preparative photolysis on 350 mg of the starting material was performed in acetonitrile solution. The photolysis was accompanied by a slight yellowing of the solution. After removal of the solvent, the yellow residue which remained was subjected to column chromatography (PET/EtOAc, 60:40) which gave the major product in pure form and the two minor products as a mixture. The major product was recrystallized from ethanol to give colourless crystals (mp = 228-229°C), and identified as:

8b-(N,N-Diethyl)-8c-(N'-methyl)-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd]pentalene-8b,8c-dicarboxamide (84)

^1H NMR (300 MHz, $CDCl_3$): δ 8.54 and 5.62 (Broad, exchanges with D_2O, CONHMe), 6.90-7.38 (m, Ar), 5.00 and 5.18 (s, Pentalene H_{4b}), 3.66 and 4.30 (s, Pentalene H_{8d}), 2.92, 3.06, 3.30, 3.42, 3.54, 3.90 (m, methylenes), 2.78 and 2.82 (d, J = 4.2 Hz, CONHCH_3), 0.96, 1.18, 1.32, 1.44 (t, J = 7.0 Hz, CON(CH_2CH_3)$_2$).

The proton and ^{13}C NMR spectra of compound **84** consisted of a double set of peaks in the ratio of roughly 2:1. Variable temperature ^{1}H NMR indicated the two sets of peaks were beginning to coalesce at 60°C but severe broadening of the peaks at this temperature and higher made this observation somewhat tenuous.

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.8, 169.0, 167.5 (C=O's); 150.7, 150.2, 148.7, 135.6, 134.8, 134.4 (Ar-C's, No H's); 127.8, 127.2, 126.9, 126.7, 125.5, 124.7, 124.3, 122.3, 122.0, 121.7, 121.0 (Ar-C-H's); 68.8, 67.9, 59.8, 53.0 (Quaternary C's); 58.3, 55.8, 48.5, 46.6 (Pentalene C-H's); 42.8, 41.9, 39.4 (Methylenes); 26.3, 13.7, 12.7, 12.4 (Methyls).

IR (KBr) ν_{max}: 3307 (N-H), 1651, 1626 (C=O), 1542 (Amide type II), 1459, 1431, 1274 cm^{-1}.

MS m/e (rel. intensity): 360 (M^+, 57.1), 303 (68.1), 287 (10.8), 259 (25.7), 230 (57.2), 202 (80.5), 100 (100), 72 (73.8). Calculated mass: 360.1838; found 360.1835.

Analysis calculated for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.53; H, 6.76; N, 7.69.

In order to prove the structure of compound, the following compound was synthesized and then photolyzed.

9-(N,N-Diethyl)-9,10-dihydro-12-(N'-methyl)-9,10-ethenoanthracene-9,12-dicarboxamide (87)

Using previously prepared Methyl N,N-Diethyl-9,10-dihydro-9,10-etheno anthracene-9-carboxamide-12-carboxylate **52**, compound **87** was synthesized via Weinreb aminolysis. The starting ester-amide (96 mg, 0.27 mmol) was added to a flame-dried 10 ml round bottom flask to which 3 ml of dry toluene and 1.0 ml (2.5 eqs) of the methylamine hydrochloride-derived aluminum amide reagent had been transferred. The reaction mixture was refluxed overnight at which point tlc indictated that no starting material was left. After quenching and working up in the usual manner, the crude yellow

residue left was subjected to column chromatography (PET/EtOAc, 50:50) producing the pure amide in 78% yield (76 mg, 0.21 mmol). The product was recrystallized from ethanol giving colourless crystals (mp = 230-230.5°C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (1, d, J = 1.5Hz, Vinylic H_{11}), 6.98-7.52 (8, m, Ar-H), 5.86 (1, broad, CONHMe), 5.78 (2, d, J = 1.5Hz, Bridgehead H_{10}), 3.84 and 3.10 (2x2, 2q, J = 7.5Hz, CON($\mathbf{CH_2}CH_3)_2$), 2.78 (3, d, J = 4.6Hz, CONH($\mathbf{CH_3}$)), 1.44 and 1.16 (2x3, 2t, J = 7.5Hz, CON($CH_2\mathbf{CH_3}$)$_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 167.5, 165.4 (2xC=O); 148.1, 145.3, 142.7 (Vinylic and Ar-C's, No H's); 143.4 (Vinylic C-H); 125.9, 124.3, 124.2, 123.2 (Ar-C-H's); 62.4, 51.2; (Bridgehead C-H's); 44.5, 39.6 (CON($\mathbf{CH_2}CH_3)_3$); 26.3 (CONH($\mathbf{CH_3}$)); 13.1, 12.9 (CON($CH_2\mathbf{CH_3}$)$_3$).

IR (KBr) ν_{max}: 3321 (N-H), 1642, 1626 (2xC=O), 1604 (C=C), 1533 (Amide type II), 1459, 1427, 1279, 1257 cm^{-1}.

MS m/e (rel. intensity): 360 (M^+, 6.9), 303 (22.9), 230 (16.8), 202 (36.3), 100 (100), 72 (32.7). Calculated mass: 360.1838; found 360.1836.

Analysis calculated for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.53; H, 6.76; N, 7.69.

Photolysis of 9-(N,N-Diethyl)-12-(N'-methyl)-9,10-dihydro-9,10-ethenoanthracene-9,12-dicarboxamide (87)

Photolysis of compound **87** in acetone gave rise to a single product. The photoproduct was isolated from a preparative scale irradiation of 200 mg of the starting material in acetone. The oil which remained after removal of the solvent was subjected to column chromatography (PET/EtOAc, 60:40) giving the photoproduct as a white solid. This photoproduct was shown to be spectroscopically (^{1}H NMR, ^{13}C NMR, IR and MS) and physically (glc, tlc and mp) identical to compound **84**.

Because the possibility of a mixture of photoproducts being responsible for the double set of NMR peaks could not be completely ruled out by the above alternate preparation of compound **84**, a third synthesis was undertaken.

Conversion of Photoproduct 77 to 84 via Weinreb Aminolysis

Crystals (98 mg, 0.27 mmol) of the ester-amide photoproduct **77**, which were shown to be pure spectroscopically, were dissolved in 5 ml of dry toluene and reacted with 1.0 ml of the methylaluminum amide reagent. The reaction mixture was refluxed for 5 h and quenched when gc analysis indicated less than 5% starting material remained. The reaction mixture was worked up and the product purified by column chromatography (PET/EtOAc, 60:40). Again the product was shown to be spectroscopically (^{1}H NMR, ^{13}C NMR, IR and MS) and physically (glc, tlc and mp) identical to compound **84**.

Finally the structure of this photoproduct was determined by X-ray diffraction analysis. The crystal data were as follows: $C_{23}H_{24}N_2O_2$; monoclinic; space group $P2_1/n$; a = 8.766 (2)Å, b = 17.885 (2)Å, c = 12.612 (2)Å; β = 103.66 (1)^o; V = 1921.4 (4)Å^3; Z = 4; D_{calc} = 1.246 g/cm^3; R = 0.042.

The separation of the two minor photoproducts of the irradiation of compound **54** was accomplished by successive recrystallizations of the mixture which afforded compound **85** essentially pure while the mother liquor became enriched in compound **86**. After six recrystallizations the amount of compound **86** in the mother liquor had been raised from 10% to 85% at which point **86** crystallized out itself. Compound **85** was recovered as a fine white powder with a melting point above 300^{o}C and identified as:

***trans*-9,10-Dihydro-N-ethyl-N'-methyl-9,10-ethanoanthracene-11,12-dicarboxamide (85)**

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08-745 (8, m, Ar-H), 6.84 and 6.56 (2x1, 2 broad, CONHMe and CONHEt), 4.66 and 4.59 (2x1, 2s, Bridgehead H_9 and H_{10}), 3.20 (2, m, CONH($\mathbf{CH_2}CH_3$)), 2.81 (2, s, Bridge H_{11} and H_{12}), 2.74 (3, d, J = 4.6Hz, CONH($\mathbf{CH_3}$)), 1.06 (3, t, J = 7.0Hz, CONH($CH_2\mathbf{CH_3}$)).

^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1, 168.2 (2xC=O); 144.2, 143.2, 140.8, 140.0 (Ar-C's, No H's); 127.4, 126.8, 126.5, 125.9, 125.6, 125.0, 123.3, 122.9 (Ar-C-H's); 50.1, 49.2, 48.5, 47.0, 45.8 (CON$\mathbf{CH_3}$, Bridgehead and bridge C-H's); 32.8 (CONH($\mathbf{CH_2}CH_3$)); 15.6 (CONH($CH_2\mathbf{CH_3}$)).

IR (KBr) ν_{max}: 3309 (N-H), 1640 (C=O), 1553 (Amide type II) cm^{-1}.

MS m/e (rel. intensity): 334 (M^+, 7.6), 303 (3.8), 289 (2.7), 262 (3.4), 231 (4.6), 203 (9.5), 178 (100). Calculated mass: 334.1681; found: 334.1690.

Analysis calculated for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. Found: C, 75.15; H, 6.60; N, 8.36.

Conversion of Photoproduct 78 to 85 via Weinreb Aminolysis

The structure and stereochemistry of compound **85** were confirmed by reacting 46 mg (0.14 mmol) of compound **78** and 0.5 ml of methylamine hydrochloride aluminum amide reagent in 5.0 ml of dry toluene via a Weinreb aminolysis. The reaction was monitored by tlc and quenched after 6 h. After work-up in the usual manner, the product was isolated by column chromatography (EtOAc/PET, 70:30) and recovered as a white powder. The product was found to be spectroscopically and physically identical to compound **85**.

Compound **86** was subsequently recrystallized from ethanol (mp = 212-214°C) and its structure determined to be:

8c-(N',N'-Diethyl)-8b-(N-methyl)-4b,8b,8c,8d-tetrahydo-dibenzo[a,f]cyclopropa[cd]pentalene-8b,8c-dicarboxamide (86)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04-7.52 (8, m, Ar-H), 6.70 (1, broad, CONHMe), 4.62 (1, s, Pentalene H_{4b}), 4.40 (1, s, Pentalene H_{8d}), 3.62 (1, dq, J = 7.5, 8.0Hz, CON(CH**H**CH_3)), 3.04-3.28 (3, m, CON(**CH_2**$CH_3)_2$), 2.92 (3, d, J = 4.6Hz, CONH(**CH_3**)), 1.14 and 1.06 (2x3, 2t, J = 7.5Hz, CON(CH_2**CH_3**)$_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 169.4, 167.2, (2xC=O); 135.7, 135.2, 131.0, 130.8 (Ar-C's, No H's); 127.7, 127.3, 127.2, 126.2, 126.0, 121.7, 121.2 (Ar-C-H's); 58.8, 47.5 (CONH(**CH_3**), Pentalene C-H's); 42.0, 39.8 (CON(**CH_2**$CH_3)_2$); 14.0, 12.7 (CON(CH_2**CH_3**)$_2$).

IR (KBr) ν_{max}: 3343 (N-H), 1659, 1613 (2xC=O), 1532 (Amide type II), 1466, 1445, 1266 cm^{-1}.

MS m/e (rel. intensity): 360 (M^+, 9.3), 329 (16.1), 289 (1.6), 258 (16.2), 231 (17.7), 215 (5.8), 202 (32.2), 100 (93.1), 72 (100). Calculated mass: 360.1838; found 360.1831.

Analysis calculated for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.60; H, 6.69; N, 7.70.

Photolysis of Dimethyl 9,10-Dihydro-9,10-ethenoanthracene-12-carboxylate-11-thionocarboxylate (55)

Irradiation of ester-thionoester **55** in solution required rigorous degassing to minimize photooxidation of the starting material and photoproduct. Solutions of **55** were prepared in the usual concentration range and placed in 250 μl phototubes. The phototubes were placed on a high-vacuum line and subjected to six cycles of freeze-

pump-thaw degassing. Irradiation of the monothiono compound in each solvent system yielded a single photoproduct, along with some photooxidation. Compound **55** was irradiated on a preparative scale in benzene solution, using benzene which had been distilled under nitrogen. Nitrogen was also bubbled through the substrate solution for an hour before commencing and during irradiation. Concentration of the photolyzed material resulted in the recovery of a bright yellow oil. Purification of the photoproduct was accomplished by column chromatography (Hexanes/EtOAc, 98:2). The photoproduct was recrystallized from chloroform/hexanes to give colourless prisms, mp = 142.5-144^{o}C , and subsequently identified as:

Dimethyl 4b,8b,8c,8d-Tetrahydro-dibenzo[a,f]cyclopropa[cd]pentalene-8b-carboxylate-8c-carboxylate (89)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04-7.34 (8, m, Ar-H), 5.36 (1, s, Pentalene H_{4b}), 4.68 (1, s, Pentalene H_{8d}), 4.08 (3, s, $CSOCH_3$), 3.83 (3, s, CO_2CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ 215.4 (C=S); 168.6 (C=O); 134.8, 133.6, 130.0 (Ar-C's, No H's); 127.6, 126.9, 126.8, 125.6, 125.4, 121.5, 121.4 (Ar-C-H's); 60.9 (Quaternary pentalene C); 58.8, 58.3, 52.7, 51.7 (Ester methyls and Pentalene C-H's).

IR (KBr) ν_{max}: 1722 (C=O), 1437, 1248 (C=S) cm^{-1}.

MS m/e (rel. intensity): 336 (M^+, 36.0), 303 (98.5), 275 (27.9), 261 (57.0), 202 (100). Calculated mass: 336.0820; found 336.0820.

Analysis calculated for $C_{20}H_{16}SO_3$: C, 71.41; H, 4.79; S, 9.53. Found C, 71.66; H, 4.83; S, 9.56.

Confirmation of the photoproduct structure was achieved by the following alternate synthesis involving conversion of the photoproduct of dibenzobarrelene diester **9** to compound **89**.

An acetone solution of 400 mg of dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate, compound **9**, was photolyzed until about 5% of the starting material remained. The solvent was removed and the resultant yellow oil purified by column chromatography (PET/EtOAc, 80:20) giving a white solid. Spectral and physical data are in complete agreement with literature values.[10]

Dimethyl 4b,8b,8c,8d-Tetrahydo-dibenzo[a,f]cyclopropa[cd]pentalene-8c,8b-dicarboxylate[10] (90)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92-7.38 (8, m, Ar-H), 5.06 (1, s, Pentalene H_{8d}), 4.50 (1, s, Pentalene H_{4b}), 3.86 (3, s, C_{8b}-$CO_2\mathbf{CH_3}$), 3.66 (3, s, C_{8c}-$CO_2\mathbf{CH_3}$).

IR (KBr) ν_{max}: 1737, 1718 (2xC=O), 1248 (C-O) cm^{-1}.

MS m/e (rel. intensity): 320 (M^+, 27.6), 260, (89.2), 202 (100).

mp = 95-96°C (lit;[10] mp = 98-99°C).

The semibullvalene photoproduct **90** (256 mg, 0.80 mmol) was placed in a 25 ml round bottom flask. Two equivalents of Lawessons reagent[58] and 15 ml of toluene were added and the reaction mixture refluxed for two days. After cooling and filtering of the precipitated waste product, removal of the solvent *in vacuo* left a viscous yellow oil. A single semibullvalene monothiono-diester product was recovered by column chromatography (Hexanes/EtOAc, 98:2) giving a slightly yellow solid (215 mg, 0.64 mmol) in 80% yield. The spectral data and melting point determination indicated that this product was the same material as the photoproduct from the irradiation of compound **55**.

The structure of the photoproduct was also supported by X-ray diffraction analysis. The crystal data were as follows: $C_{20}H_{16}SO_3$; monoclinic; space group $P2_1/c$; a = 12.452 (2)Å, b = 16.182 (2)Å, c = 8.118 (2)Å, β = 90.68 (2)°; V = 1635.7 (5)Å^3; Z = 4; D_{calc} = 1.366 g/cm^3; R = 0.048.

Photolysis of Dimethyl 9,10-Dihydro-9,10-ethenoanthracene-12-carboxylate-11-thiolocarboxylate (88)

Analytical solution photolyses of ester-thioloester **88** required rigorous degassing to prevent photooxidation of the starting material and photoproduct. Solutions of **88** were prepared in the usual concentration range and transferred to 250 μl phototubes. The phototubes were placed on a high-vacuum line and subjected to six cycles of freeze-pump-thaw degassing. Irradiation of the monothiolo compound yielded a single photoproduct in each solvent system. Compound **88** was irradiated on a preparative scale in acetone solution, using acetone which had been distilled under nitrogen. Nitrogen was also bubbled through the substrate solution for an hour before commencing and during irradiation. After photolysis the solvent was removed *in vacuo* leaving a yellow oil. The photoproduct was purified by column chromatography (Hexanes/EtOAc, 95:5) and subsequently recrystallized from ethanol/chloroform to give colourless prisms (mp = 127°C). The photoproduct was identified as:

Dimethyl 4b,8b,8c,8d-Tetrahydro-dibenzo[a,f]cyclopropa[cd]pentalene-8c-carboxylate-8b-thiolocarboxylate (91)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04-7.36 (m, 8, Ar-H), 5.10 (1, s, Pentalene H_{4b}), 4.60 (1, s, Pentalene H_{8d}), 3.88 (3, s, $CO_2\mathbf{CH_3}$), 2.36 (3, s, $COS\mathbf{CH_3}$).

^{13}C NMR (50 MHz, $CDCl_3$): δ 194.2 (C=S); 168.8 (C=O); 149.7, 149.6, 134.6, 133.3 (Ar-C's, No H's); 130.0, 127.7, 127.1, 126.1, 125.6, 121.4, 121.3 (Ar-C-H's); 59.8 (Quaternary pentalene C); 56.3, 52.8, 50.9 ($CO_2\mathbf{CH_3}$ and Pentalene C-H's), 11.8 ($COS\mathbf{CH_3}$).

IR (KBr) ν_{max}: 1737 (O-C=O), 1651 (S-C=O),1246 cm^{-1}.

MS m/e (rel. intensity): 336 (M^+, 1.2), 261 (100), 229 (14.3), 202 (47.8). Calculated mass: 336.0820; found: 336.0823.

Analysis calculated for $C_{20}H_{16}SO_3$: C, 71.41; H, 4.79; S, 9.53. Found C, 71.05; H, 4.87; S, 9.50.

The structure of this compound was also supported by X-ray diffraction analysis. The crystal data were as follows: $C_{20}H_{16}SO_3$; monoclinic; space group $P2_1/n$; a = 7.911 (1)Å, b = 14.457 (1)Å, c = 14.813 (1)Å; β = 90.895 (9)^o; V = 1693.9 (3)Å^3; Z = 4; D_{calc} = 1.319 g/cm^3; R = 0.042.

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