SYNTHESIS AND PHOTOCHEMICAL TRANSFORMATIONS OF A FEW TETHERED BARRELENES

Thesis submitted to the
Cochin University of Science and Technology
In partial fulfilment of the requirements for the degree of

Doctor of Philosophy
In
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In the Faculty of Science
By

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Under the supervision of

Dr. P. A. Unnikrishnan

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July 2013

DECLARATION

I hereby declare that the work presented in the thesis entitled **"Synthesis and Photochemical Transformations of a few Tethered Barrelenes"** is the result of genuine research carried out by me under the supervision of **Dr. P. A. Unnikrishnan**, Assistant Professor of Organic Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-22, and the same has not been submitted elsewhere for the award of any other degree.

Kochi-22 **Eason M. Mathew**
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CERTIFICATE

This is to certify that the thesis entitled "Synthesis and Photochemical Transformations of a few Tethered Barrelenes" is a genuine record of research work carried out by **Mr. Eason M. Mathew**, under my supervision, in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for the award of any other degree.

Kochi-22
July 1, 2013

P. A. Unnikrishnan
(Supervising Guide)

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Eason M. Mathew

PREFACE

Dibenzobarrelenes undergo facile photorearrangement to the corresponding dibenzosemibullvalenenes under triplet sensitized irradiation through di-π-methane rearrangement whereas on direct irradiation dibenzocyclooctatetraenes are formed. Number and variety of organic molecules obtained by di-π-methane rearrangement is incredible and makes it particularly synthetically useful. Such photoproducts are not readily available by alternate routes. Besides, di-π-methane rearrangement of appropriate dibenzobarrelene derivatives finds application in the alignment of nematic liquid crystals.

It is observable from the literature that generalization is possible for the observed regioselectivity of di-π-methane rearrangements of numerous acyclic, cyclic and bicyclic 1,4-dienes. The reaction regioselectivity of such compounds has been predicted from mechanistic point of view. However, there are conflicting reports on the effect of electronic and steric factors on the regioselectivity observed with barrelene-semibullvalene photorearrangement.

We have designed few barrelene molecules in such a way that the structural features of these compounds will enable them to undergo intriguing triplet state mediated di-π-methane rearrangement. Our strategy involved the preparation of dibenzobarrelenes appended with a fused ring systems, thereby restricting the rotational freedom of the bridgehead substituent. We describe these systems as ‘tethered barrelenes’. These tethered barrelenes enabled us to examine the effect of orientation and the nature of the bridgehead-substituents in controlling the regioselectivity of di-π-methane rearrangement in a more systematic fashion. In this background, the thesis entitled "***SYNTHESIS AND PHOTOCHEMICAL TRANSFORMATIONS OF A FEW TETHERED BARRELENES***" reveals our attempts to explore the factors controlling the regioselectivity of di-π-methane rearrangement displayed by dibenzobarrelenes. Moreover, we have observed interesting dark reactions of suitable substituted tethered dibenzosemibullvalenes in a few cases.

The thesis is divided into five chapters. The first chapter briefly introduces regioselectivity of di-π-methane rearrangement, some photochemical transformations of dibenzobarrelenes and an application of di-π-methane rearrangement. The definition of the research problem is given at the end of this chapter. The second chapter deals with the synthesis of the barrelenes through intramolecular Diels-Alder reactions of anthracene derivatives appended with suitable acetylenic substituents. Photochemical transformations of tethered ethers and tethered esters are given in the third and fourth chapters respectively. The fifth chapter describes di-π-methane rearrangement of tethered sulfides and one tethered sulfone. Major outcomes are given at the end of the thesis.

The structural formulae, schemes, tables and figures are numbered chapter-wise as each chapter of the thesis is as an independent unit. All new compounds are fully characterized on the basis of their spectral and analytical data including the single crystal X-ray analysis in many cases. A comprehensive list of references is given at the end of each chapter.

List of Abbreviations

br	: broad
C	: centigrade
DCM	: dichloromethane
DEPT	: distortionless enhancement by polarisation transfer
DMF	: dimethylformamide
d	: doublet
FT IR	: fourier transform infrared
g	: gram
h	: hour
GC-MS	: gas chromatography-mass spectrometry
HCl	: hydrochloric acid
Hz	: hertz
IMDA	: intramolecular Diels-Alder
m	: multiplet
Me	: methyl
mg	: milligram
min	: minute
mL	: millilitre
mp	: melting point
nm	: nanometre
NMR	: nuclear magnetic Resonance
ORTEP	: oak ridge thermal ellipsoid plot program
KBr	: potassium bromide
Ph	: phenyl
KOH	: potassium hydroxide
NaOH	: sodium hydroxide
s	: singlet
Sens.	: sensitized
SN	: substitution
t	: triplet
THF	: tetrahydrofuran
TLC	: thin layer chromatography
XRD	: X-ray diffraction

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CHAPTER 1

PHOTOISOMERIZATIONS AND PHOTOCHEMICAL REARRANGEMENTS – A SHORT INTRODUCTION

1.1. Abstract

This chapter portrays a general idea on photoisomerizations and rearrangements which delivers the milieu for the present study. It describes a few aspects of the di-π-methane rearrangements followed by an application.

1.2. Introduction

Sun light has been used as a radiation source in order to induce chemical reactions before the development of sophisticated instruments. Nowadays photochemical reactions are carried out more carefully in a controlled manner and narrower bands of electromagnetic radiations have been employed to investigate photochemical reactions systematically.

In synthetic organic photochemistry, a structurally simple molecule might be transformed by the process of irradiation into a rather complex structure, which could be otherwise difficult to synthesize. In this thesis, synthesis and photochemical transformations of a few dibenzobarrelene derivatives have been investigated. The molecules under study are designed in such a way that their structure enables them to undergo intriguing photochemical transformations including triplet state mediated di-π-methane rearrangement and singlet state mediated electrocyclic reactions.

Dibenzobarrelene derivatives decorated with thiazole and thiophene units have attracted continuing interest over the years since they exhibit various biological activities and have found application in drug development for various diseases. For example, a thiazole derivative **1**, a thiophene derivative **2**[1] and 4-substituted-5-(arylazo)thiazole derivatives **4** and **5**[2] show antibacterial activity against two strains of bacteria namely *Bacillus thuringiensis* and *Escherichia coli*.

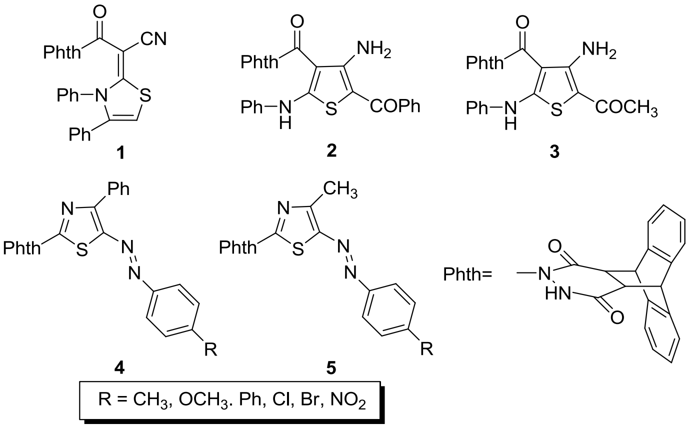


Figure 1.1

Since the emphasis of our studies is more on the photochemical transformations of the bicyclic systems, this chapter is dedicated to a short introduction to photoisomerizations and rearrangements.

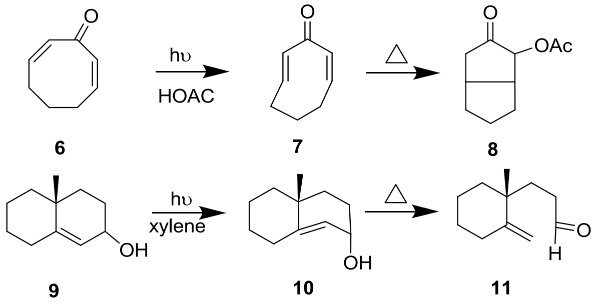
1.3. Classification of Photochemical Rearrangements

The primary photochemical rearrangements may be classified into four reaction types, *cis-trans* isomerizations, sigmatropic rearrangements, electrocyclic reactions and intramolecular cycloadditions. In a broad sense all four of these classes may be considered as special cases of pericyclic reactions.

1.3.1. *Cis-trans* isomerizations

A compound with an olefinic linkage when absorb a photon may get excited to the singlet or triplet excited state followed by a twisting motion about the double bond until a critical geometry is reached and radiationless transition to the ground state occurs. This often results in *cis-trans* geometric isomerization.[3] Photosensitization may also result in *cis-trans* geometric isomerization and it is one of the most general photoreactions of ethylenes and other unsaturated linkages capable of such isomerizations, (e.g., C=N, N=N).

Cyclic compounds with double bonds may undergo many photoreactions which seem to be overall linear additions, cycloadditions, electrocyclic reactions, rearrangements, etc., but in reality, they are photoinducd *cis-trans* isomerizations followed by reaction of a reactive *trans*-cyclic isomer. For example, the solvent addition reaction of **6** involves highly reactive *trans*-cyclic intermediate **7** through an initial photochemical *cis*-*trans* isomerization which results in the formation of **8** *via* secondary thermal reactions.[4,5] Similarly, fragmentation reaction of **9** involves highly reactive *trans*-cyclic intermediate **10** which proceeds to **11** (Scheme 1.1) through secondary thermal reactions.[6]



Scheme 1.1

Photochemical *cis*-*trans* isomerizations of 1,3-dienes have a definite place in the theoretical development and practice of mechanistic organic photochemistry. 1,3-Dienes are capable of accepting triplet energy efficiently[7] which result in the *cis*-*trans* isomerization. Thus the observation of photosensitization may be employed as diagnostic of triplet energy transfer. Over and above 1,3-dienes are often triplet quenchers.

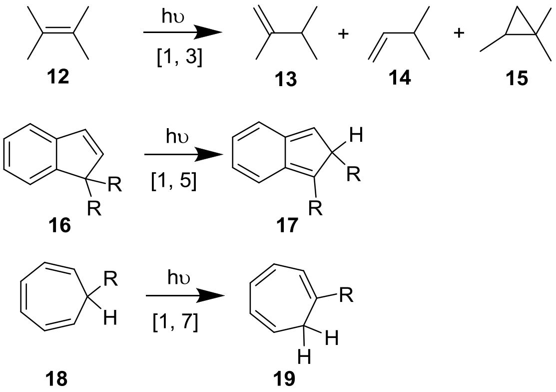
Dienes are ideal triplet quenchers in many cases. For example, with alkyl ketones, 1,3-dienes can quench first triplet state from 10^2 to 10^4 times faster than they quench first singlet state.[8] Adducts of ketones and dienes resulting from triplet quenching are formed with low quantum yield.[9,10]

1.3.2. Sigmatropic Rearrangements

The photoisomerizations, in which a sigma bond is shifted from a given position along a chain of carbon atoms to a new position by rearrangement of the carbon skeleton or position of a substituent, are termed sigmatropic rearrangements.[11] Carbon skeleton shifts or hydrogen shifts are the most important sigmatropic rearrangements.

On the basis of number of atoms involved in the rearrangement, sigmatropic rearrangement is classified as [i,j], where i and j represent the number of carbon atoms intervening between old and new sigma bonds. Each of the atoms of the sigma bond being broken in the reactant is assigned the number 1 and then carbon-connected atoms are counted until the two positions of the new sigma bonds [i,j] of the product are located. When a hydrogen atom is migrated, the sigmatropic rearrangement is of the [1,j] variety as there are no carbon atoms intervening the old and new bonds for half of the rearrangement. Generally [1,3] and [1,7] sigmatropic rearrangements do not occur upon triplet sensitization and thus they are expected to occur exclusively through singlet excited state.

For example, direct irradiation of tetrasubstituted alkene **12** results in the formation of **13**, **14** and **15** through [1,3] sigmatropic rearrangements.[12,13] Irradiation of indenes **16** results in [1,5] sigmatropic rearrangement to give isoindenes **17** which have been trapped chemically and detected spectroscopically.[14,15] Many cycloheptatrienes, on the other hand, undergo eight-electron [1,7] sigmatropic rearrangement of a hydrogen or alkyl groups and thus cycloheptatriene **18** undergoes eight-electron [1,7]sigmatropic rearrangement of the hydrogen to yield **19** (Scheme 1.2).[16]

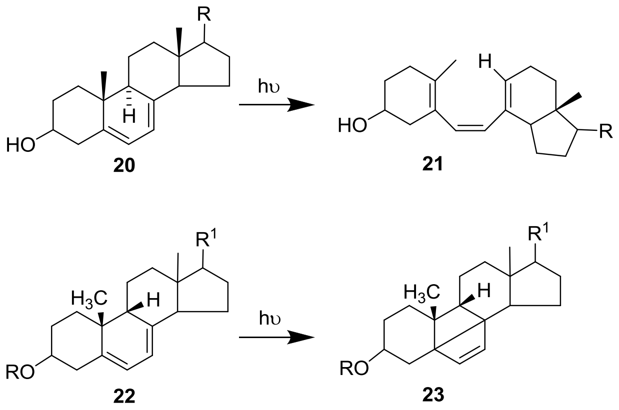


Scheme 1.2

Since we are interested in di-π-methane rearrangement which is a [1,2] sigmatropic rearrangement of 1,4 dienes (or equivalent structures) to vinyl cyclopropanes, a few aspects of the rearrangement will be described later.

1.3.3. Electrocyclic Reactions

An electrocyclic reaction may be defined as the ring closure or ring opening reaction in which formation or breakage of a single bond occurs between the termini of a conjugated π system. Electrocyclic reaction is a special type of positional isomerization as the position of π-bonds and σ bonds changes during the reaction. A new σ bond is formed during electrocyclic ring closure and a σ bond is broken during electrocyclic ring opening reactions. Most of the electrocyclic ring closures occur from singlet excited state and do not occur upon triplet sensitization For example, on irradiation, ergosterol **20** results in the formation of the hexatriene **21** (previtamin D) through electrocyclic ring opening while **22** undergoes elecrocyclic ring closure to yield the cyclobutene **23** (Scheme 1.3).[11] Electrocyclic reactions are classified electronically or structurally on the basis of ring closing reaction, by indicating the number and type of electrons involved in a formal one-step reaction, or by the new ring size formed. For example, isomerization of 1,3-butadiene to cyclobutene is represented as electrocyclic π^4 or σ^2+π^2 or [4].

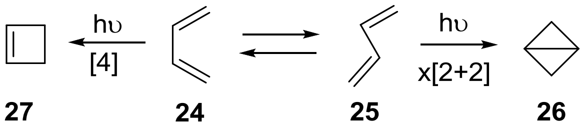


Scheme 1.3

1.3.4. Intramolecular cycloadditions

Intramolecular cycloaddition of a conjugated system is a reaction in which two or more rings are formed by making two new σ bonds. It differs in type from electrocyclic reactions that involve only one new σ bond. On the basis of the π-electron components formally involved in making the two new σ bonds and by the number of atoms contributed to the new rings by the component systems, intramolecular cycloadditions are classified. For example, 1,3-butadiene isomerizes to bicyclobutane through intramolecular cycloaddition which involves 2π systems of two atoms each.[17,18] Thus it is represented as a $\pi^2 + \pi^2$ or x[2+2] cycloaddition where the label x is placed to serve as a reminder that bonding occurred from a terminal atom to an internal atom. Intramolecular cycloadditions commonly occur in singlet states.

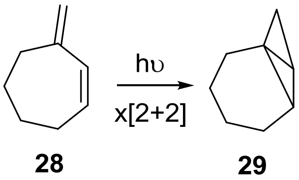
There is a competition between intramolecular cycloaddition reactions of conjugated polyenes and [n]electrocyclic reactions. For example, in the case of 1,3-butadiene, x[2+2] reaction competes with [4] electrocyclic ring closure.



Scheme 1.4

From structural considerations, it is expected that x[2+2] reaction results from s-*trans* conformer **25** of 1,3-butadiene, whereas [4] reaction results from s-*cis* conformer **24**. Even though the major conformer of 1,3-butadiene is s-*trans* form, cyclobutene **27** is the major product on irradiation as the efficiency of the formation of bicyclobutane **26** is low (Scheme 1.4).

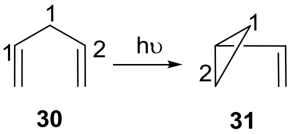
On the other hand, in the case of **28**, x[2+2] reaction results from s-*trans* conformer **28** to give **29**[18] on irradiation and [4] reaction is completely inhibited because of constraint of the 1,3-diene to the s-*trans* conformation (Scheme 1.5).



Scheme 1.5

1.4. The di-π-methane rearrangement

Zimmerman first noted the generality of di-π-methane rearrangement which is a [1,2]sigmatropic rearrangement of 1,4 dienes (or equivalent structures).[19-21] When molecules with two π moieties bonded to a saturated single sp^3-hybridized carbon atom as in **30** are photolyzed, di-π-methane rearrangement occurs leading to a π-substituted cyclopropane **31** (Scheme 1.6). Even though the second double bond is not required formally to ensure an overall [1,2] sigmatropic rearrangement, 1,4-dienes employ it also in the rearrangement.



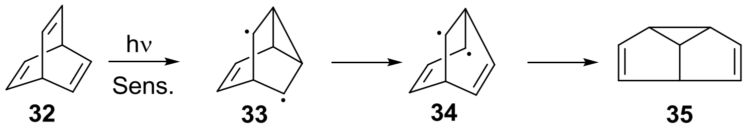
Scheme 1.6

Variety of organic molecules obtained by di-π-methane rearrangement is incredible and makes it a particularly useful synthetic tool. Such photoproducts are generally not readily available by alternate routes.

1.4.1 Mechanistic Aspects

It is intriguing that one basic mechanism can account for so many transformations which on a first glance do not seem to be related. The same basic mechanism is applicable not only to that of di-π-methane rearrangements which proceed by way of singlet excited states but also to those which proceed *via* triplet excited states. The rearrangements produced by singlet excited state are found among those occurring upon direct irradiation without the use of an added sensitizer, whereas triplet rearrangements are effected by addition of a sensitizer which itself is converted into a triplet species by absorbing light, and then sensitizing the reactant molecule to the triplet state. The mechanism of di-π-methane rearrangement may be explained with the aid of representative examples.

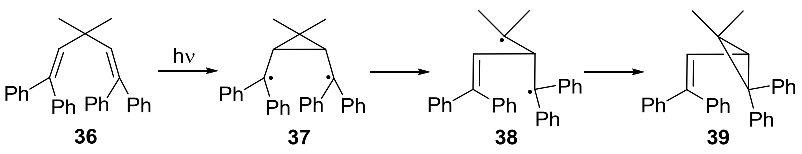
At first glance, photoisomerization of barrelene to semibullvalene does not appear to be straightforward. As barrelene satisfies the basic requirement of two π-bonds attached to a sp^3-hybridized carbon, the photoisomerization of barrelene to semibullvalene points to the potential generality of di-π-methane rearrangement. The occurrence of more than two vinyl groups attached to two bridgehead carbons poses no problem and either of the two bridgehead carbons may be considered as the methane carbon. The basic mechanism applied to barrelene (**32)** is depicted in Scheme 1.7.[20]



Scheme 1.7

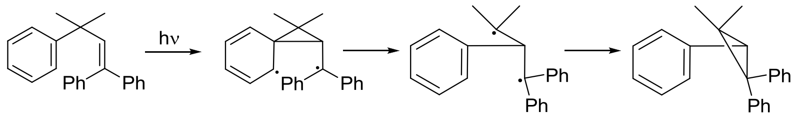
The diradical species (**33** and **34**) may help to understand and predict reaction courses, regioselectivity, and general reaction trends. Nevertheless, in general, such diradical species may be either real reaction intermediates or transition states. In the case of barrelene, there are reports about the experimental evidence of triplet diradical **34** as intermediate and theoretical efforts[22-24] show this to be the case for triplet diradical **33** as well. Also it needs to be mentioned that the barrelene to semibullvalene rearrangement is a triplet reaction.

A similar mechanism is shown for diene **36** as an example of an acyclic di-π-methane rearrangement (Scheme 1.8).[25] However, this happens without the use of a sensitizer and is known to be a singlet process. Moreover, diradicals **37** and **38** are species along the mechanistic pathway.



Scheme 1.8

In a third example, compound **40**, has an aryl group as one of the π-components differing it from compound **36**. This occurs by a perfectly similar mechanism with a variation that aromatic ring is participating in the bridging process (Scheme 1.9).[26] Again; rearrangement is ensued by the singlet excited state.



40 **41** **42** **43**

Scheme 1.9

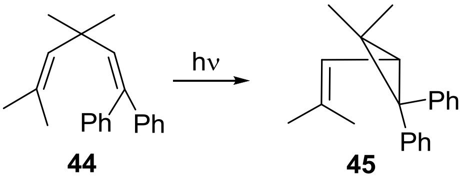
The three examples given above exemplify the di-π-methane rearrangements of bicyclic and acyclic systems. Moreover, they demonstrate reactions which proceed through triplet excited states on sensitization as well as reactions proceeding *via* singlet excited state on direct irradiation (*i.e.* without use of a sensitizer). Nevertheless, all reactions occurring without addition of a sensitizer need not proceed by way of the singlet excited state, as the initially formed singlet in some cases will convert itself to the triplet by “intersystem crossing” and the triplet then rearranges.

The mechanism certainly gives an idea about the reaction regioselectivity, reaction multiplicity and stereochemistry.

1.4.2 Reaction Multiplicity

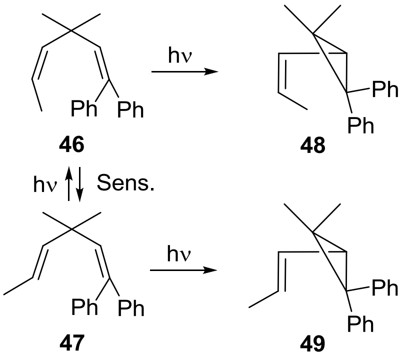
The question of reaction multiplicity is a practical matter in the di-π-methane rearrangement. Thus, some molecules require a sensitizer while others are unreactive when a sensitizer is employed. The most common sensitizers include ketones such as acetophenone, benzophenone and xanthone. The function of the sensitizer is to make the triplet excited state of the di-π-methane reactant with certainty. When a sensitizer is not used, it is more likely to observe the reaction of the singlet excited state but sometimes the initially formed excited singlet will convert itself to the triplet faster than it reacts and this point has to be checked experimentally.

A classic example of di-π-methane rearrangement is found in the reaction of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**44**), studied by Zimmerman and Pratt.[27] This 1,4-diene rearranged readily upon direct irradiation to give corresponding vinyl cyclopropane **45** (Scheme 1.10). Moreover, the reaction showed remarkable regioselectivity. The analogous sensitized reactions, using benzophenone or acetophenone triplet sensitizers under conditions in which energy transfer to the diene takes place, failed to give detectable amount of products.



Scheme 1.10

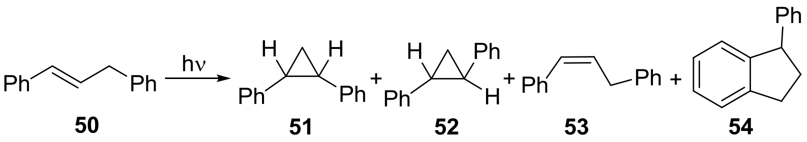
Similar results were noted by Zimmerman and Mariano for 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**36**) (Scheme 1.8) which also rearranged efficiently from its singlet excited state but not from its triplet state to the corresponding vinyl cyclopropane **39**. Zimmerman and Mariano concluded that di-π-methane rearrangement of **36** occurs efficiently only through singlet excited state manifold and the singlet was the favoured excited state employed by acyclic di-π-methane systems in general. Zimmerman and Pratt[28] conducted another investigation on the photochemistry of *cis* and *trans*-1,1-diphenyl,3,3-dimethyl-1,4-hexadiene (**46** and **47**) and the dependence of the reaction course and stereochemistry on multiplicity. Rearrangement of the *cis* and *trans* isomers proceeded only upon direct irradiation and the reaction showed extreme regiospecificity and striking stereospecificity. The *cis* isomer gave exclusively the *cis*-1-propenylcyclopropane **48** and *trans* isomer gave exclusively the *trans*-propenyl product **49** (Scheme 1.11). Due to slow competing *cis*-*trans* interconversion of the reactants, this stereospecificity was noticeable only at low conversions.



Scheme 1.11

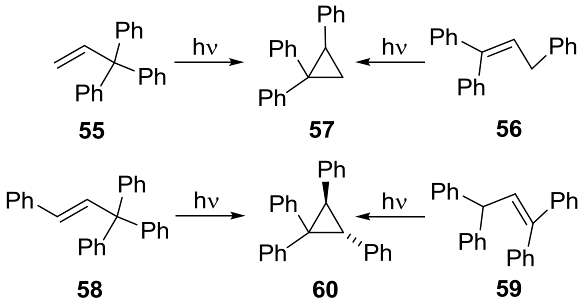
The triplet-sensitized irradiation is significantly different from the direct irradiation (*i.e.*, singlet reactions) of dienes **46** and **47**. The triplet-sensitized photolyses could not produce vinyl cyclopropane products, but, instead, led to efficient *cis-trans* isomerization, interconverting **48** and **49**. This may be used to explain the inertness of the di-π-methanes towards triplet manifold as acyclic 1,4-dienes are able to efficiently dissipate their triplet energies by *cis*-*trans* isomerization pathways. In the case of **36** and **44**, this deactivation pathway, by isomerization about π-bonds, was disguised because of its degeneracy. Thus the current example along with other di-π-methane rearrangements in acyclic and monocyclic system has validated the proposal by Zimmerman and Mariano that, in systems where free rotation about unconstrained π-bonds can bring about efficient deactivation from their triplet excited states, di-π-methane rearrangements can occur through the singlet excited state.

The photochemistry of various substituted 3-phenylpropenes has been extensively examined by Griffin and coworkers.[29,30] They studied di-π-methane system containing phenyl and vinyl moieties in an acyclic arrangement. In all of these examples direct irradiation effected the rearrangement which involved phenyl migration to yield cyclopropane products. When *trans*-1,3-diphenylpropene (**50**) was irradiated in benzene or cyclohexane (direct irradiation), a mixture of *cis*- and *trans*-1,2-diphenylcyclopropane (**51** and **52**), *cis*-1,3-diphenylpropene (**53**) and phenylindan **54** were formed at low conversions (Scheme 1.12).



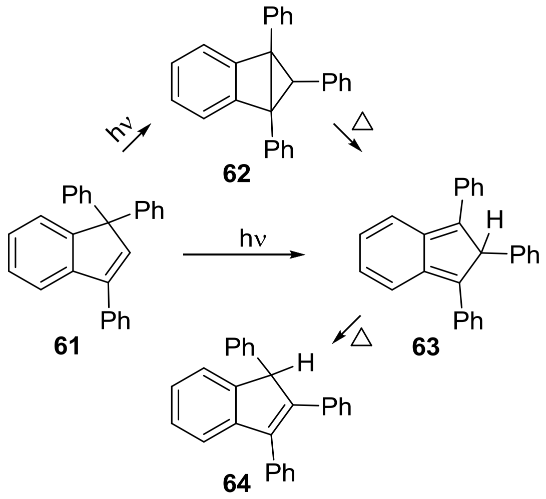
Scheme 1.12

Generality of this rearrangement is further illustrated in the photolysis of 3,3,3-triphenylpropene (**55**) and 1,1,3-triphenylpropene (**56**), both yielding product mixtures in which 1,1,2-triphenylcyclopropane (**57**) is the major product. Correspondingly, irradiation of 1,3,3,3-tetraphenylpropene (**58**) and 1,1,3,3-tetraphenylpropene (**59**) gave the stereoisomers of 1,1,2,3-tetraphenylcyclopropane (**60**) as major components (Scheme 1.13).



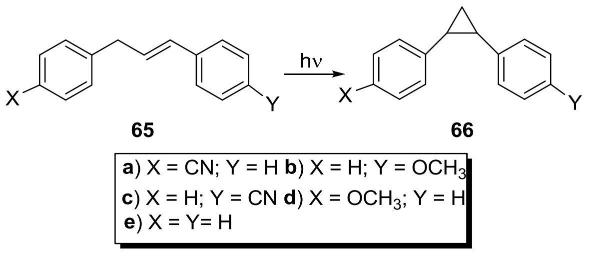
Scheme 1.13

A final example in the series showed by Griffin and co-workers demonstrates the remarkable conversion of 1,1,3-triphenylindene (**61**) to 1,2,3-triphenylindene (**64**) (Scheme 1.14). The product in this case may be formed by direct irradiation followed by a secondary thermal process involving a 1,5-hydrogen shift in isoindene **63** as suggested by Griffin. It may involve a potential transient intermediate **62**, and thus the reaction is either a normal di-π-methane type or a reaction where pathway is diverted once phenyl migration is completed.



Scheme 1.14

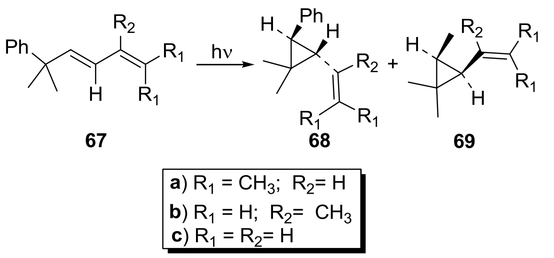
It is significant to mention that, although the general di-π-methane rearrangement pathway easily describes the nature of the molecular reorganization in all of these systems, mechanisms which comprise photoinduced 1,2-hydrogen shifts can equally well explain the structural aspects of the conversions of **50** and **56** to their respective cyclopropanes, as reported by Griffin. Yet, in the case of **50**, Hixon has shown that it is certainly phenyl which migrates. Moreover, although these investigations were primarily qualitative in nature and, thus, did not explain the multiplicities of 3-phenylpropene excited states undergoing reaction, correlated systems have shown to undergo analogous reactions exclusively from their singlet manifold. Hixson[31] has shown that direct irradiation of a series of *para*-substituted 1,3-diphenylpropenes **65a-e** gave 1,2-diarylcyclopropanes **66a-e** as the major products (Scheme 1.15) while triplet-sensitized irradiation gave no detectable amounts of **66a-e** and showed extensive *cis-trans* isomerization.



a) X = CN; Y = H **b**) X = H; Y = OCH_3
c) X = H; Y = CN **d**) X = OCH_3; Y = H
e) X = Y= H

Scheme 1.15

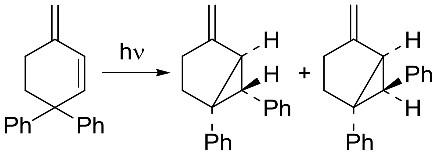
Hence, the observations of singlet di-π-methane rearrangement and triplet *cis-trans* isomerization in the case of 3-phenylpropene systems supplement further evidence to the suggested multiplicity control of the fate of acyclic di-π-methane excited states. More evidence for this generalization is found in the transformation on direct irradiation of the 1-phenyl-2,4-pentadienes **67**, through a phenyl migration, to a mixture of of *cis*- and *trans*-1-phenyl-2-vinylcyclopropanes **68** and **69** (Scheme 1.16), as reported by Hammond and Kristinsson.[32]



a) $R_1 = CH_3$; R_2= H
b) R_1 = H; R_2= CH_3
c) $R_1 = R_2$= H

Scheme 1.16

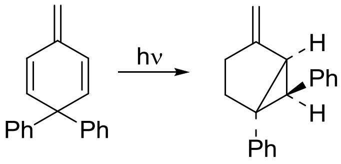
Di-π-methanes which have one of the two π-moieties in a six-ring system and lack structural constraints barring free rotation about all the π-bonds also experience rearrangement to their respective π-substituted cyclopropane products efficiently only from their singlet excited states. For example, the unsensitized rearrangement of 1-methylene-4,4-diphenyl-2-cyclohexene (**70**) leads to a mixture of the *cis*- and *trans*-bicyclic olefins **71** and **72**, in which the *trans* diastereoisomer is the majority (Scheme 1.17).[33] The triplet sensitized photolysis of this exocyclic methylene di-π-methane system did not give detectable amounts of products, showing the triplet **70** to be unreactive.



70 **71** **72**

Scheme 1.17

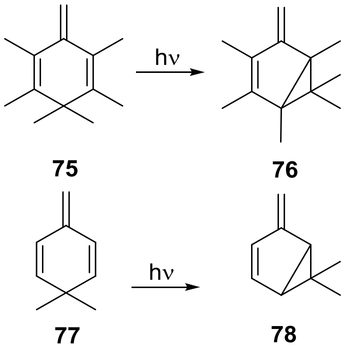
Likewise, irradiation of the triene analogue, 1-methylene-4,4-diphenyl-2,5-cyclohexadiene **73** gives *trans*-bicyclic diene **74** as the major product as it endures rearrangement through phenyl migration only in the singlet manifold (Scheme 1.18).[34]



73 **74**

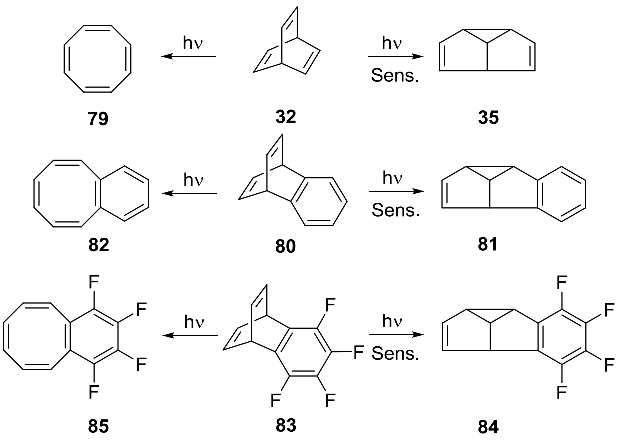
Scheme 1.18

Similar behaviour is shown by irradiation of 1-methylene-cyclohexa-2,5-dienes (**75**) and (**77**) to give **76** and **78** respectively which involves vinyl-vinyl bonding (Scheme 1.19).[35,36]



Scheme 1.19

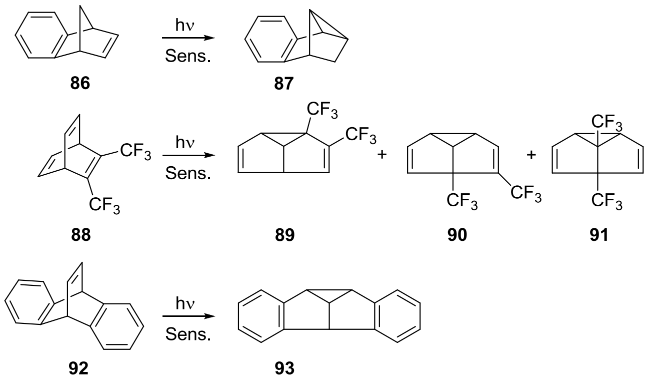
The difference between di-π-methane reactivity of various bicyclic systems like barrelene (**32**), which contains both π-moieties within rigidly structured environments and the acyclic and exocyclic methylene monocyclic systems is dramatic in that in the former the triplet multiplicity is prerequisite for rearrangement. The rearrangement of barrelene by di-π-methane pathway to semibullvalene (**35**) solely with acetone sensitization has been reported by Zimmerman and coworkers. On the other hand cyclooctatetraene (**79**) is the major product of direct irradiation. The analogous rearrangement is shown by benzobarrelene (**80**) in which rearrangement to benzosemibullvalene (**81**) takes place from the triplet while benzocyclooctatetraene (**82**) is formed on direct irradiation.[37] There are a number of similar examples, each illustrating the general phenomenon of preferred triplet multiplicity for di-π-methane rearrangement in structures which do not allow free rotation about the π-bonds (rigid constrained systems). Characteristics of these include the observations of Brewer and Heanley[38] in the acetone-sensitized transformation of tetrafluorobenzobarrelene **83** to the corresponding semibullvalene **84** while direct irradiation leads to the corresponding cyclooctatetraene **85** (Scheme 1.20).



Scheme 1.20

Similar observations have been reported by Edman[39] in acetophenone-sensitized transformations of benzonorbornadiene **86** to the benzotricycloheptene **87**; by Liu[40] where 2,3-bistrifluoromethyl-barrelene (**88**) experienced sensitized conversions to the three semibullvalenes **89-91**; and by Ciganek[41] and Friedman[42] in which dibenzobarrelene (**92**) underwent efficient sensitized rearrangement to dibenzosemibullvalene **93** (Scheme 1.21).

Since we are also looking at the isomerization of dibenzobarrelene derivatives, these aspects will be described later.



Scheme 1.21

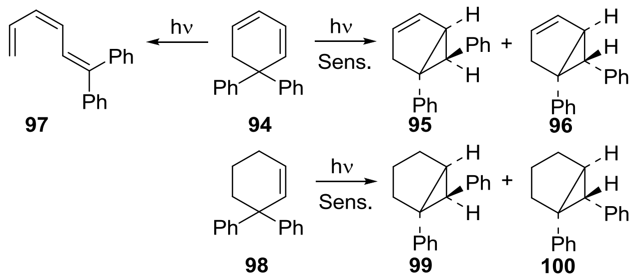
There are several factors which govern the structure-multiplicity relationships generally applicable in the case of di-π-methane rearrangement (Table 1.1).

Di-π-methane Structural feature	***Singlet excited state***	***Triplet excited state***
Presence of a free π-moiety	Efficient	Inefficient
Absence of a free π-moiety	Inefficient	Efficient

Table 1.1

In acyclic and methylene monocyclic di-π-methane systems, triplet excited states seem to have more efficient pathways for dissipation of the excited-state energy than for isomerization to π-substituted cyclopropanes. Free rotation about nonconstrained π-bonds is one of the efficient ways for the energy dissipation. Zimmerman and Pratt[27] directly observed such energy dissipation in the photochemistry of *cis* and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**46** and **47**) where *cis-trans* isomerization actually happened. In contrast, rapid di-π-methane rearrangements are always open to appropriately substituted singlets of flexible di-π-methane systems. Additionally, competing singlet reactions are normally not accessible in these types of systems. But whenever there is an availability of a more efficient alternate pathway, isomerization to π-substituted cyclopropanes does not become observable. Such alternate singlet pathways are shown by barrelene like systems in which an electrocyclic [2+2] addition followed by a retrocycloaddition proceed to the cyclooctatetraene products. At the same time, due to the rigid structure, the triplet excited states of such bicyclic systems cannot dissipate energy by free rotation. Thus they prefer rearrangement to π-substituted cyclopropanes.

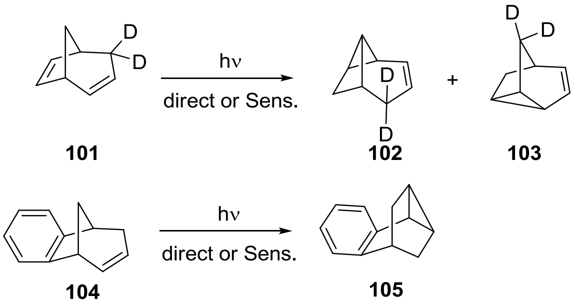
The rationalization of the structure-multiplicity relationships based on the presence or absence of structural features which give mechanisms for energy degradation appears to be sensible taking into account the observations of Dauben,[43] Zimmerman[44] and Swenton.[45] In Scheme 1.17, it has been shown that the triplet excited state of the monocyclic di-π-methane containing an exocyclic methylene **70**, expected to be formed by benzophenone sensitization, was inert and this could be attributed to free-rotor deactivation about the exocyclic π-bond. In concurrence with this view the structurally interrelated endocyclic diene **94** and monoolefin **98** upon sensitized irradiation were noted to undergo di-π-methane rearrangement to the corresponding π-substituted cyclopropane products **95**, **96** and **99**, and **100**, respectively (Scheme 1.22). This significant restoration of triplet di-π-methane reactivity is rationally ascribed to the absence of any exocyclic π-bonds in cyclohexene **98** and cyclohexadiene **94**, thus excluding the possibility of the alternate pathway for triplet energy dissipation by simple stereoisomerization. Moreover, the singlet photochemistry of 5,5-diphenylcyclohexadiene (**94**) underlines the importance of considering competing and more efficient types of reactions. In this case, direct irradiation leads to the formation of the triene **97** from the singlet through a facile electrocyclic ring opening.



Scheme 1.22

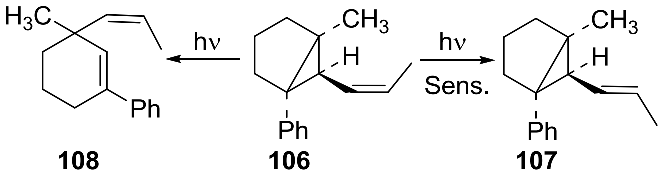
Even though the generalizations of the structure-multiplicity relationships develop from numerous examples of di-π-methane photochemistry in acyclic, monocyclic and bicyclic systems, there are several exceptions to the generalization. For example an interesting observation is reported in the rearrangement of 4,4-

dideuteriobicyclo[3.2.1]octa-2,6-diene (**101**) which isomerizes to a mixture of tricyclic olefins **102** and **103** upon both direct as well as sensitized irradiation (Scheme 1.23).[46] Similar observations are reported by Hahn and Rothman[47] in the photochemistry of benzo analogue **104** which rearranges to benzotricyclooctane **105** upon both direct and sensitized irradiation.



Scheme 1.23

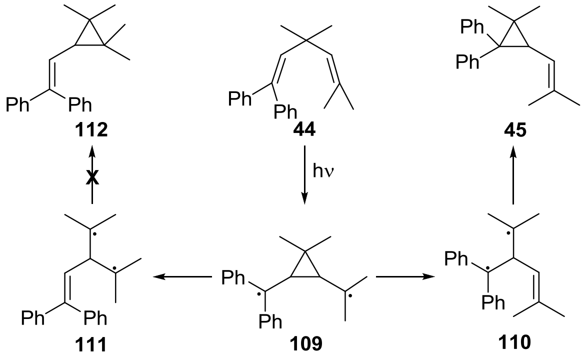
An exception of another type was reported by Mariano and Ko[48] in which presence of a free rotor does not prevent di-π-methane triplet reactivity. Thus singlet and triplet di-π-methane reactivity of 1-phenyl-3-methyl-3-(*cis*-1-propenyl)cyclohexene (**106**) result in the formation of **108** and **107** respectively (Scheme 1.24).



Scheme 1.24

1.4.3 Regioselectivity

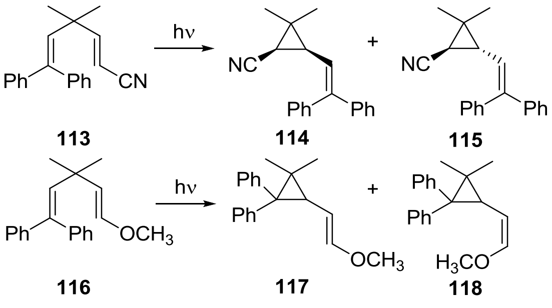
When di-π-methane reactants are unsymmetrically substituted it needs to predict which one of the two π-systems will result in the photoproduct. Fortunately, reaction regioselectivity can be predicted from mechanistic point of view. A classic example is found in the direct irradiation of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**44**), studied by Zimmerman and Pratt. The regioselectivity observed is established on the basis of the preferential cyclopropane ring opening of **109** (diradical 1) to **110** (diradical 2) leading to the formation of corresponding vinyl cyclopropane **45** (Scheme 1.25).[49] The ring opening may give rise, either to a less delocalized odd electron center, with dimethyl substitution as in **111** or to a more stable and delocalized odd electron center, with diphenyl substitution as in **112**. As expected, the opening proceeds to afford the more stable of the two, alternate 1,3-diradicals, the one with benzhydryl delocalization. So in these systems, the regioisomer which has the less delocalizing group on the residual double bond is preferably formed as a result of di-π-methane rearrangement.



Scheme 1.25

The regioselectivity of aryl-vinyl di-π-methane systems may be predicted more easily. For example, in the reaction of 3-methyl-1,1,3-triphenyl-1-butene (**40**) shown earlier (Scheme 1.9), the odd-electron center which is involved in the three-membered ring opening is the one which restores aromaticity. In diradical **41**, the three membered ring opening takes place utilizing the odd electron which is in the six-membered ring leading to the restoration of aromaticity of the benzene ring. If the benzhydryl odd electron was encompassed in the three-membered ring opening, not only would the benzhydryl delocalization be gone astray, but also the driving force of aromaticity would not be earned.

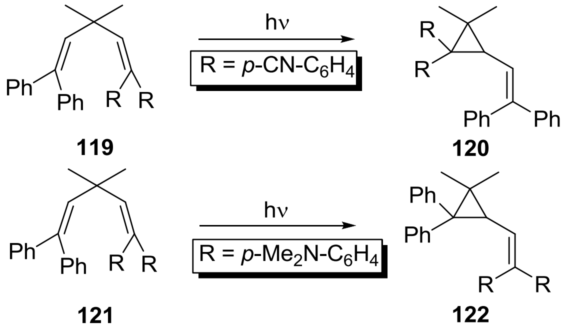
There is still another kind of situation. It arises from the presence of electron donors and/or acceptors on one or both of the π-moieties and a general rule may be developed for such situation. The rule states that there is a strong tendency for electron donors to be found on the residual π-bond of the photoproduct and for electron withdrawing groups to appear on the product three membered rings. Representative examples are depicted in Schemes 1.26 and 1.27.



Scheme 1.26

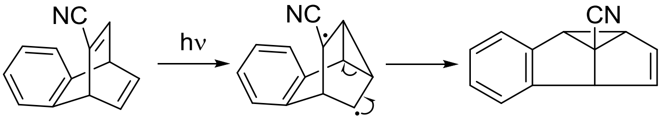
On direct irradiation of **113** (Scheme 1.26), the double bond bearing the cyano substituent (electron withdrawing group) is found on the cyclopropyl ring of the photoproduct. Conversely, on direct irradiation of **116**, the enol ether methoxy group which is an electron donor appears on the surviving double bond of photoproduct as shown in Scheme 1.26.

It has been observed that generalization[50] is possible in the case where the electron donating or withdrawing groups are *para* substituents on an aryl group. For example when di-π-methane reactant **119** with an electron withdrawing *para* substituent is irradiated, it will be rearranged to **120** (Scheme 1.27) in which *p*-cyanophenyl group appears on the three membered ring of the photoproduct[51]. On the other hand, irradiation of di-π-methane reactant **121** with an electron donating *para* substituent results in the formation of **122** (Scheme 1.27) in which *p*-(N,N-dimethylamino) phenyl group is found on the double bond of the photoproduct[52].



Scheme 1.27

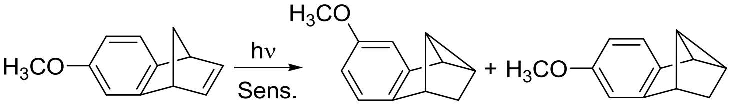
A further question arises when there are three π-systems bonded to a single methane carbon. These might be termed as a tri-π-methane reactants. Although there is a possibility of three non-equivalent bridges, only two π-systems can participate in the rearrangement. For example, in the cases of benzobarrelene,[53,54] 2,3-naphthobarrelene,[55] and 2,3-anthracenebarrelene,[56] bonding occurs preferentially between the vinyl bridges rather than between benzo and vinyl bridges. Nevertheless, one exception has been reported in the rearrangement of 1,2-naphthobarrelene where α-naphtho-vinyl bridging is preferred. The mechanistic details are known for all these reactions.[53-57] A different but still related variation in regioselectivity is found in systems where the two π-moieties are bonded to methane carbons at both ends. In these systems, there is a choice of at which end of the molecule the π-π bridging will preferably take place. Such a system has been reported by Bender[58] in the rearrangement of 2-cyanobarrelene **123**. The regiochemistry can be predicted by taking into account the more delocalized of the cyclopropyldicarbinyl diradicals **124** which can be formed on π-π bridging (Scheme 1.28). It is observed that the initial bridging that occurs between two vinyl bridges leaves the cyano group at an odd electron center. Although, benzo-vinyl bridging could also lead to a cyano-stabilized diradical, it has been ruled out by Bender using isotopic labelling, and in any case such bridging would lead to the same product in the unlabelled example here. Additionally, although there are two three-membered ring-opening possibilities, the odd electron not stabilized by the cyano group is the one utilized. The observed product **125** may be predicted by this reasoning.



123 **124** **125**

Scheme 1.28

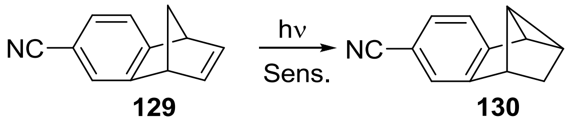
Another example of this type is found in the photochemistry of substituted benzonorbornadienes. Paquette[59,60] has reported that the regiochemistry is governed in similar manner. Therefore in the case of methoxybenzonorbornadiene **126** benzo vinyl bridging takes place away from the methoxy group and **127** and **128** are formed in the ratio 7:1 (Scheme 1.29).



126 **127** **128**

Scheme 1.29

As expected, in the case of cyanobenzonorbornadiene **129**, benzo-vinyl bridging occurs proximate to the cyano group to give the product **130** (Scheme 1.30). The regioselectivity is analogous to that described with electron-donating and electron-withdrawing substituents on acyclic π-methane systems. Thus regiochemistry may be generalized as, electron-withdrawing groups demand positioning themselves in conjugation with the carbinyl centers of the cyclopropyldicarbinyl diradicals (diradical1) and electron donors avoid positioning themselves in conjugation with the carbinyl centers of the cyclopropyldicarbinyl diradicals. A lot of examples of di-π-methane rearrangements of acyclic, cyclic and bicyclic 1,4-dienes have been reported in literatures.[61-87]



Scheme 1.30

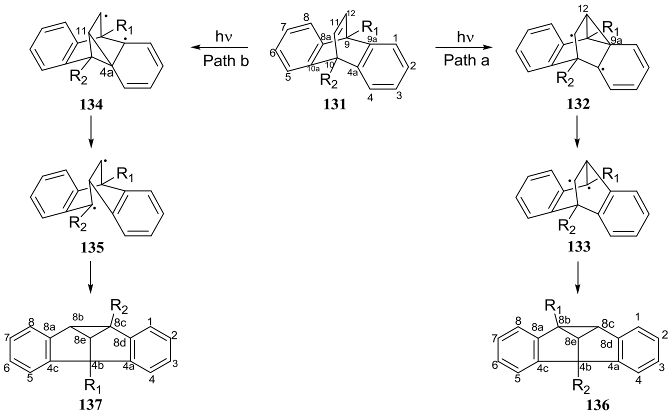
Since the primary focus of our investigation is on the photochemistry of dibenzobarrelenes, a brief summary of available literature is included in this section. Regioseltivity is a primary concern here too, but a universally-accepted generalization for the regiochemistry of unsymmetrical dibenzobarrelene systems is yet to be evolved. A few reports on the photochemistry of dibenzobarrelenes is collected hereunder.

1.5. Isomerization of Dibenzobarrelenes

Triplet state mediated di-π-methane rearrangement offer a variety of exciting synthons which could lead to complex synthetic targets. These synthons are formed as primary and secondary photoproducts. It is well known that dibenzobarrelenes give dibenzosemibullvalene through triplet state mediated pathway and dibenzocyclooctatetraenes *via* singlet state mediated pathway. Out of the two pathways, 11,12-dibenzoyl-substituted dibenzobarrelenes prefer triplet state mediated pathway due to the presence of two benzoyl groups.

1.5.1. Dibenzosemibullvalenes

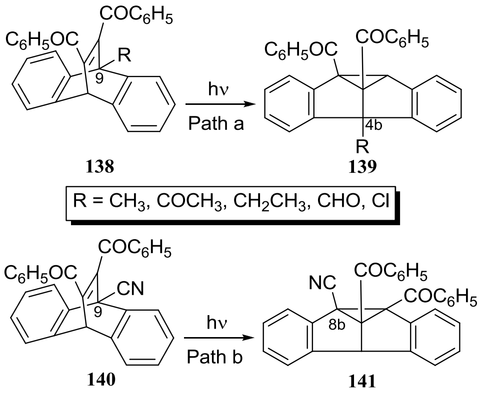
Triplet state mediated isomerization of dibenzobarrelenes results in the formation of dibenzosemibullvalene. The di-π-methane route for the isomerization of dibenzobarrelenes involves initial benzo-vinyl bridging to form diradical intermediates. The four possible pathways for the benzo-vinyl bridging proceed to the same product if the dibenzobarrelenes are symmetrically substituted. The presence of a bridgehead substituent makes the dibenzobarrelenes unsymmetrical and the di-π-methane pathway, when there are substituents at both the bridgehead positions, is depicted in Scheme 1.31.



Scheme 1.31

In Path a, interaction of the vinyl group and phenyl group results in benzo-vinyl bridging (C(12)-C(9a) bridging) to form the diradicals **132** and **133** and ultimately transformed into 8b-substituted dibenzosemibullvalene **136**. On the other hand, Path b involves benzo-vinyl bridging (C(11)-C(4a) bridging) leading to diradical intermediates **134** and **135**, which would finally be transformed to 4b-substituted dibenzosemibullvalene **137**. Similarly, interaction of the vinyl group and phenyl group results in benzo-vinyl bridging (C(12)-C(8a) bridging) and (C(11)-C(10a) bridging) to form the corresponding diradical intermediates, which would then give the enantiomers of the dibenzosemibullvalene **136** and **137**.

For example, photoisomerizations of a few 9-substituted-11,12-dibenzoyldibenzobarrelenes to the corresponding dibenzosemibullvalene are illustrated in the Scheme 1.32.[88-90]



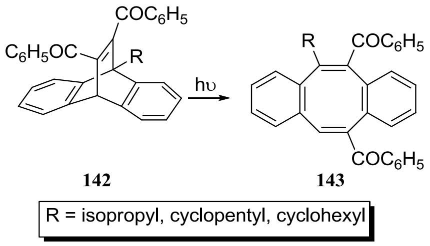
Scheme 1.32

It shows that when the bridgehead substituent is alkyl groups or halogens 4b-substituted dibenzosemibullvalenes are almost exclusively generated. On the other hand, when the bridgehead substituent is an electron withdrawing substituent such as cyano group, the 8b-substituted semibullvalene predominates (scheme 1.32).

1.5.2. Dibenzocyclooctatetraene

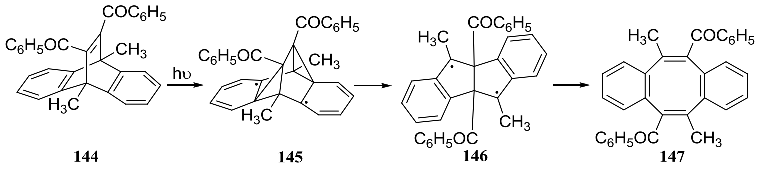
Three distinct pathways are available for the photochemical isomerization of dibenzobarrelenes to the corresponding cyclooctatetraenes. Dibenzocyclooctatetraenes are the products obtained by direct irradiation of dibenzobarrelenes. Based on the observations on the photochemistry of similar benzo- and naphthobarrelene systems, it has been proposed that dibenzocyclooctatetraenes are formed through the singlet excited states of dibenzobarrelenes and it involves intramolecular [2+2] cycloaddition.

Even though 11,12-dibenzoyl-substituted dibenzobarrelenes prefer triplet state mediated pathway, irradiation of a few 9-alkyl-substituted 11,12-dibenzoyldibenzobarrelenes results in the formation of corresponding dibenzocyclooctatetraenes (Scheme 1.33).[91] The reaction is expected to occur *via* an electrocyclic [2+2] addition followed by a retrocycloaddition and finally a rearrangement to the dibenzocyclooctatetraenes **143**.



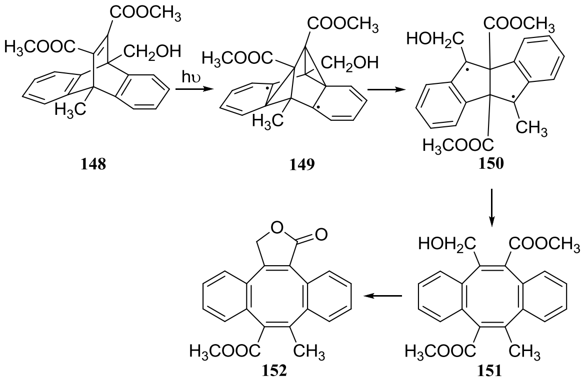
Scheme 1.33

The bridgehead substituted dibenzobarrelenes might undergo photorearrangement *via* tri-π-methane route leading to 1,4-diradical intermediates, which subsequently proceed to dibenzocyclooctatetraenes. For example, irradiation of 11,12-dibenzoyl-9,10-dimethyl-substituted dibenzobarrelene (**144**) in benzene in the absence of oxygen gives corresponding dibenzocyclooctatetraene **147** as the major product (Scheme 1.34).[92] Excitation of **144** would proceed to diradical intermediate **145** *via* tri-π-methane route[93] and then to benzylic 1,4-diradical **146** which finally results in the formation of dibenzocyclooctatetraene **147**. When isopropyl, cyclopentyl or cycloheptyl groups occupy the bridgehead position, substantial amounts of dibenzocyclooctatetraenes are formed through analogous tri-π-methane route.



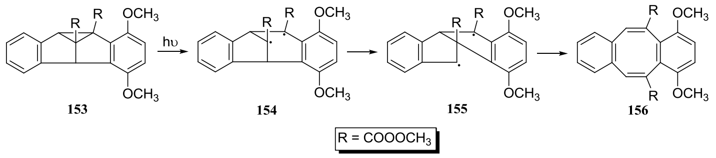
Scheme 1.34

A similar example has been observed in the phototransformation of dimethyl 9-hydroxymethyl-10-methyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**148**) in which tri-π-methane rearrangement leads to the formation of corresponding dibenzocyclooctatetraene **151** and it is ultimately transformed into the dibenzocyclooctatetraene lactone **152** (Scheme 1.35).[94]



Scheme 1.35

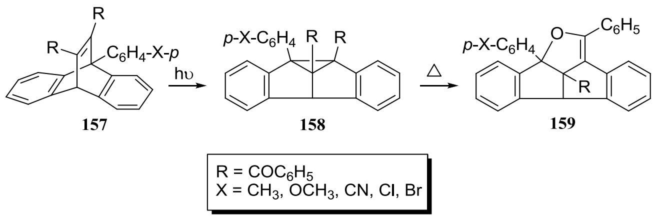
Dibenzocyclooctatetraene may be formed as a secondary photoproduct from the dibenzosemibullvalene. For example, dibenzosemibullvalene **153** undergoes further rearrangement into the dibenzocyclooctatetraene **156** (Scheme 1.36).[95] It has been proposed that cleavage of the σ bond in the dibenzosemibullvalene **153** proceeds to give the 1,3-diradical **154**, which then undergoes an aryl 1,2-shift to give the 1,4-diradical **155** and further transformation results in the formation of dibenzocyclooctatetraene **156**.



Scheme 1.36

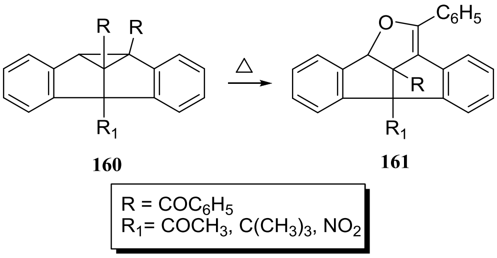
1.5.3. Dibenzopentalenodihydrofurans

Dibenzopentalenodihydrofurans are formed exclusively by facile thermal isomerization of suitably substituted dibenzosemibullvalenes. The easiness of isomerization depends on the nature and position of the substituents. For example, irradiation of 9-aryl-substituted dibenzobarrelenes **157** results in the formation of corresponding 8b-aryl substituted 11,12-dibenzoyl-dibenzosemibullvalenes **158** only at low temperatures. At ambient conditions, dibenzosemibullvalenes **158** undergo thermal isomerization to dibenzopentalenodihydrofurans **159** so that only **159** could be isolated as the photoproduct (Scheme 1.37).[96] These isomerizations would occur either through a concerted pathway, involving a [1,3]sigmatropic shift or through a 1,3-diradical intermediate.



Scheme 1.37

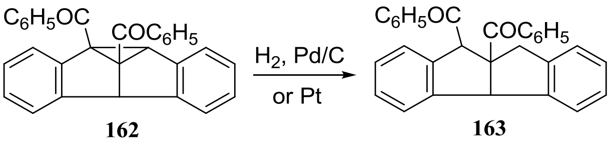
Likewise, some of the 4b-substituted dibenzosemibullvalenes **160** undergo facile thermal isomerization to the corresponding dibenzopentalenodihydrofurans **161** (Scheme 1.38). However, here dibenzoemibullvalenes **160** are stable under ambient experimental conditions and thermal isomerization occurs only at elevated temperatures (100-200 °C).



Scheme 1.38

1.5.4. Dibenzopentalenes

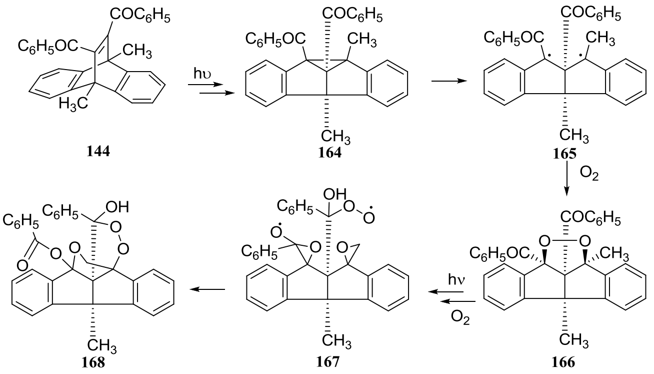
The conversion of the dibenzosemibullvalenes to dibenzopentalenes cannot be achieved by direct photolysis. However, dibenzopentalene **163** is formed from the corresponding dibenzosemibullvalene **162** by hydrogenation with 5% Pd on charcoal (Scheme 1.39).[88] Hydrogenolysis results in the cleavage of the σ bond in the cyclopropane ring to form the corresponding dibenzosemibullvalene.



Scheme 1.39

1.5.5. Oxygen Heterocycles

We have already seen that irradiation of 11,12-dibenzoyl-9,10-dimethyl-substituted dibenzobarrelene **144** in benzene gives corresponding dibenzocyclooctatetraene **147** as the major product (Scheme 1.34). Moreover, a dibenzopentalene derivative and a small amount of hexacyclic peroxycarbinol are also formed along with **147**. The structure of hexacyclic peroxycarbinol **168** has been established on the basis of X-ray crystallographic analysis[92] and the conversion of dibenzobarrelene **144** to **168** is intriguing. It is proposed that di-π-methane rearrangement leads to the formation of corresponding dibenzosemibullvalene **164** which is further transformed into a new 1,3-diradical **165** through the cleavage of cyclopropane ring in **164**. Further transformations of the endoperoxide **166**, formed by combining **165** with oxygen would result in the formation of **168** (Scheme 1.40).



Scheme 1.40

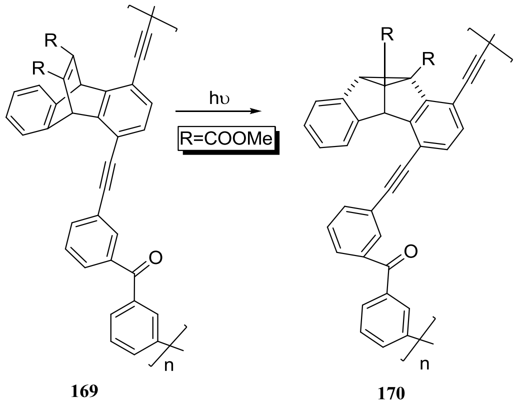
1.6. Application of the di-π-methane rearrangement

Di-π-methane rearrangement of a designed polymer finds application in the alignment of nematic liquid crystals.[97] The strong coupling of the liquid crystal directors to dibenzobarrelene groups is responsible for the alignment mechanism. The isomerization occurs in the presence of a triplet sensitizer and is found to be regiospecific.

In the majority of technologies, a uniform alignment of liquid crystal phases is necessary which has been traditionally achieved by unidirectional rubbing of polymeric substrates.[98] As this method can result in damage of sensitive electronic components that are part of integrated devices[99], noncontact alignment methods have been developed in which axis selective photochemical transformations are proposed in majority of the cases.[99,100] Photochemical reactions comprise isomerization of unsaturated centers and photochemically allowed cycloaddition reactions. Swager and coworkers[97] has recently employed di-π-methane rearrangement in the alignment of nematic liquid crystals as the transformation generates large shape changes in the molecular structure of the reactant.

Triptycene derivatives have been used to enhance the alignment of liquid crystal molecules through minimization of internal free volume and similarly substituted dibenzobarrelenes could also offer strong director field interaction with liquid crystal phases. The sensitized irradiation of substituted dibenzobarrelene **169** results in the formation of corresponding dibenzosemibullvalenes **170** (Scheme 1.41) which is expected to have diminished internal free volume,[101,102] thus the alignment preferences of dibenzobarrelenes are eliminated.

For efficient isomerization, a triplet sensitizer is incorporated adjacent to the di-π-methane substrate. Such a design enhances the rapid energy transfer between the substrate and the sensitizer. The key point in photoisomerization is that only the molecular locations which absorb light can undergo rearrangement.



169 **170**

Scheme 1.41

The proposed photoalignment mechanism is illustrated in Figure 1.2. Here, the benzophenone units are selectively excited by polarized light with transition dipole moments oriented parallel to the electric vector of the exciting light. The subsequent rapid intersystem crossing to the first triplet state followed by rapid energy transfer to the adjacent di-π-methane units result in the selective rearrangement of dibenzobarrelenes. As a result, the dibenzobarrelene molecules residing in the plane perpendicular to the exciting light would not undergo isomerization and thus can strongly influence the liquid crystal directors. Because of diminished internal free volume, dibenzosemibullvalenes are incapable of strong interaction with liquid crystal directors and the rest of the dibenzobarrelenes govern the alignment.

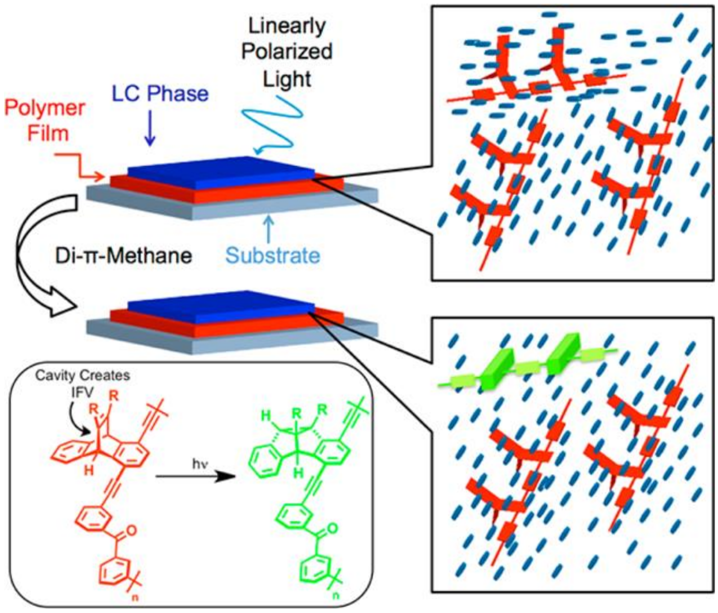


Figure 1.2[97]

1.7 Definition of the research problem

From a careful analysis of the literature it can be noted that although generalization is possible for the regioselectivity of di-π-methane rearrangements of numerous acyclic, cyclic and bicyclic 1,4-dienes, there are conflicting reports on the effect of electronic and steric factors on the regioselectivity observed with barrelene-semibullvalene photorearrangement. George and coworkers[103] have examined photoisomerization of several 9-substituted-11,12-dibenzobarrelenes. Scheffer and coworkers[104-113] also have investigated the photorearrangements of several dibenzobarrelenes in the solid and solution state. Their results are not conclusive enough to establish structural features that decide the regioselectivity of barrelene-semibullvalene photorearrangement.

We have designed our barrelene molecules in such a way that they can undergo triplet state mediated di-π-methane rearrangement. Our strategy involved the preparation of dibenzobarrelenes appended with a fused ring systems, thereby restricting the rotational freedom of the bridgehead substituent. This enabled us to examine the effect of such a tethering and the nature of the bridgehead-substituents in controlling the regioselectivity of di-π-methane rearrangement in a more systematic fashion. Intramolecular Diels-Alder reactions of anthracene derivatives appended with suitable acetylenic substituents provide a convenient route for the synthesis of target barrelenes.[114] We propose to examine secondary transformations of photoproducts in a few representative examples.

General representation of the tricyclic systems selected by us is given in Figure 1.3. We propose to “bind” the bridgehead and vinyl position of the barrelenes through ether, ester, sulfide and sulfone bridges. Such binding essentially is equivalent to tethering since the geometry of the molecule is controlled by the bridge. Consequently, we coined a novel term – *tethered barrelenes* – to describe our targets. Depending on the nature of the bridge, we label our targets as tethered ethers, esters, sulfides or sulfones respectively.

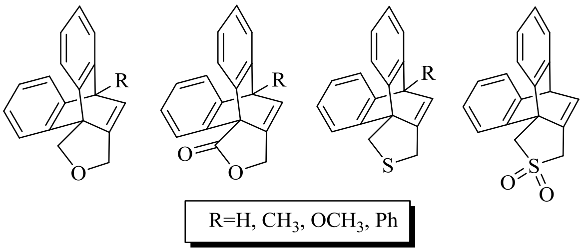


Figure 1.3

1.8 Objectives

1. Synthesis of tethered barrelenes
    - Tethered esters
    - Tethered sulfides and Tethered sulfone
    - Tethered ethers
2. Direct photolysis of the tethered barrelenes
    - Irradiation of tethered ester
    - Irradiation of tethered ether
3. Sensitised photolysis of the tethered barrelenes
    - Sensitized irradiation of tethered esters

   - Sensitized irradiation of tethered sulfides
   - Sensitized irradiation of tethered sulfone
   - Sensitized irradiation of tethered ethers
4. Regioselectivity in the photorearrangement of the tethered barrelenes
5. Single crystal X-Ray crystallographic analysis of substrate structure
6. Secondary transformations of suitable primary photoproducts
7. Novel insight into the mechanism for such transformations

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CHAPTER 2

SYNTHESIS OF A FEW TETHERED ESTERS, SULFIDES, SULFONES AND ETHERS

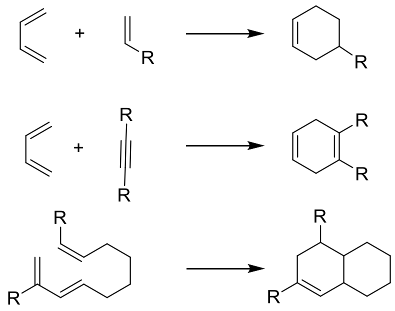
2.1. Abstract

Dibenzobarrelenes or 9,10-ethenoanthracenes are known to undergo interesting photochemical rearrangements. The present work is a systematic study of photorearrangement of tethered dibenzobarrelenes. This chapter deals with our endeavours on the synthesis of various substrates, including bridgehead-substituted tethered barrelenes using intramolecular Diels-Alder reactions.

2.2. Introduction

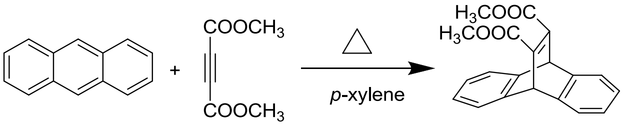
Howard E. Zimmerman and Robert M. Paufler[1] first reported the synthesis of bicyclo[2.2.2]octa-2,5,7-triene in 1960 using α-pyrone and methyl vinyl ketone as the basic starting materials. They suggested the name ‘barrelene’ for the compound because of the barrel shaped electron cloud. Dibenzobarrelene and its derivatives have been synthesized by various procedures.[2-5] In the present study, intramolecular Diels-Alder reaction was adopted for the synthesis of the required tethered dibenzobarrelenes.[5]

In Diels-Alder reaction[6], a 1,3-diene (diene) reacts with an olefinic or acetylenic compound (dienophile) resulting in the formation of a six-membered ring containing one or two double bonds (Scheme 2.1). This provides an unparalleled strategy for the regioselective and stereospecific synthesis of a variety of valuable compounds.



Scheme 2.1

Since its formulation, Diels-Alder reaction has been used for the synthesis of monocyclic as well as polycyclic compounds. A number of polycyclic aromatic hydrocarbons like anthracenes may react with appropriate dienophiles by a 1,4-addition leading to the synthesis of bicyclic compounds (Scheme 2.2).



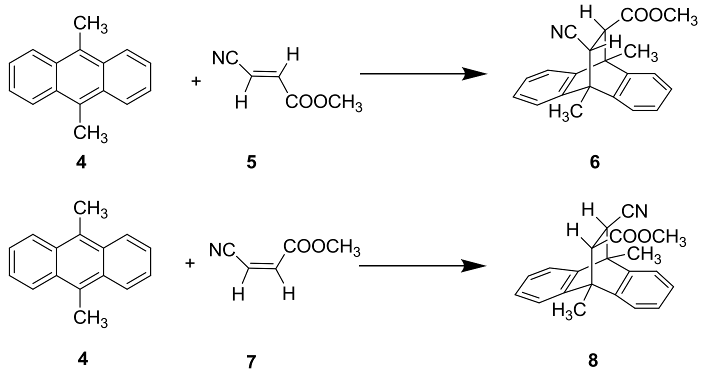
1a **2** **3**

Scheme 2.2

The diene component in Diels-Alder reaction may be open chain or cyclic and it can have many different kinds of substituents. For Diels-

Alder reaction to occur, the diene must be in the s-*cis* conformation.[7] Cyclopentadiene, cyclohexadiene, cycloheptadiene and anthracene are some examples of dienes that are permanently in the s-cis conformation and exceptionally good at Diels-Alder reaction. But cyclic dienes that are permanently in the s-*trans* conformation will not undergo Diels-Alder reaction at all.[8] Ethylenic and acetylenic groups have been used mainly as active dienophiles in Diels-Alder reaction.

According to the "*cis* principle", the addition of a dienophile to a diene is purely *cis* addition. The relative positions of substituents are retained in the adduct and *cis* addition can be readily explained by synchronous formation of the bonds between the two components in a one-step reaction.[9] *Cis* or *trans*-dienophiles react with dienes to give 1:1 adducts in which the *cis* or *trans* arrangement of the substituents in the dienophile is retained, showing the stereoselective nature of Diels-Alder reaction. An illustrative example is shown for the reactions of isomeric methyl-β-cyanoacrylates **5** and **7** with 9,10-dimethylanthracene (**4**) (Scheme 2.3).[10]



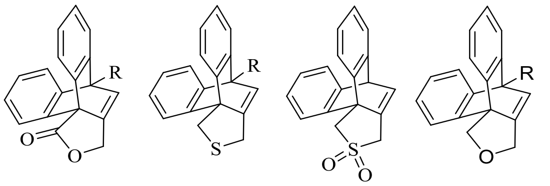
Scheme 2.3

With intramolecular Diels-Alder reactions, in addition to the six-membered ring formed by [4+2]cycloaddition, the product contains a second ring. In contrast to intermolecular Diels-Alder reaction, the two reacting functionalities are part of the same molecule in intramolecular Diels-Alder reaction (IMDA), thus exhibiting increased reaction rates under milder conditions. It is one of the most efficient modes to synthesize a variety of interesting bridged polycyclic compounds. These reactions accrue advantages in terms of ease of reaction, regioselectivity, stereoselectivity and introduction of multiple stereocentres in properly designed systems. Thus, IMDA reaction offers a simple and direct approach to the synthesis of complex structures.

IMDA reactions of anthracene derivatives appended with suitable acetylenic substituents provide a convenient route to ‘tethered barrelenes’ (a tether connecting bridgehead and vinylic carbons of a dibenzobarrelene). When tethering is effected by incorporating an ester, sulfide, sulfone or ether in the barrelenes, such barrelenes are called ‘tethered esters, tethered sulfides, tethered sulfones or tethered ethers’ respectively in the thesis. We have also synthesised tethered barrelenes with different substituents like methyl, methoxy and phenyl at the other bridgehead position.

2.3. Results and Discussion

We implemented IMDA reactions[5] for the synthesis of our target molecules (Figure 2.1). Appropriate 9-substituted anthracenes can undergo IMDA in which anthracene and acetylene are employed as the reactive diene and dienophile respectively. In a single step, two rings are formed (often obtained as fused bicyclic adducts), and the cyclisation often occurs under mild conditions.



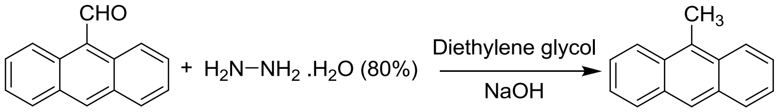
9 10 11 12

a) R=H **b**) R=CH_3 **c**) R=OCH_3 **d**) R=Ph

Figure 2.1

2.3.1 Synthesis of 9-substituted anthracenes

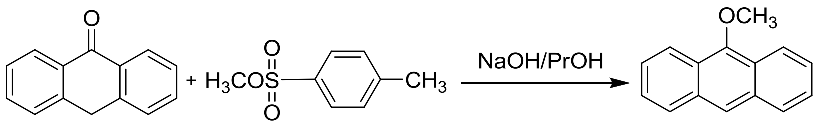
9-Methylanthracene[11-13] was prepared by modified Wolff-Kishner reduction of 9-anthraldehyde with diethylene glycol, sodium hydroxide and 80% hydrazine hydrate (Scheme 2.4).



13a **14** **1b**

Scheme 2.4

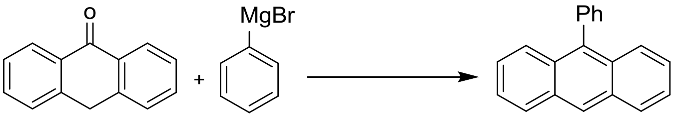
9-Methoxyanthracene[14,15] was prepared by refluxing anthrone with methyl-*p*-toluensulfonate in 2-propanol with 20% NaOH followed by column chromatography (Scheme 2.5).



15 **16** **1c**

Scheme 2.5

9-Phenylanthracene$^{16-19}$ was prepared by Grignard reaction of anthrone with phenylmagnesium bromide in tetrahydrofuran. Product **1d** was purified by column chromatography (Scheme 2.6).

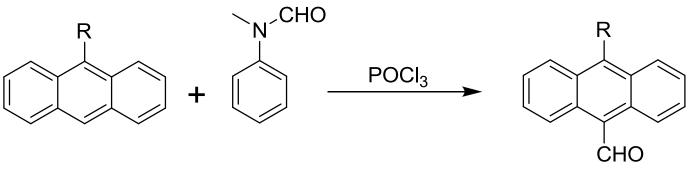


15 **17** **1d**

Scheme 2.6

2.3.2. Formylation of 9-substituted anthracenes

Formylation of **1** was carried out by a known procedure^{20} in which **1** was dissolved in *o*-dichlorobenzene and then heated with *N*-methylformanilide and phosphorous oxychloride. The reaction mixture was then treated with sodium acetate-water mixture (Scheme 2.7).



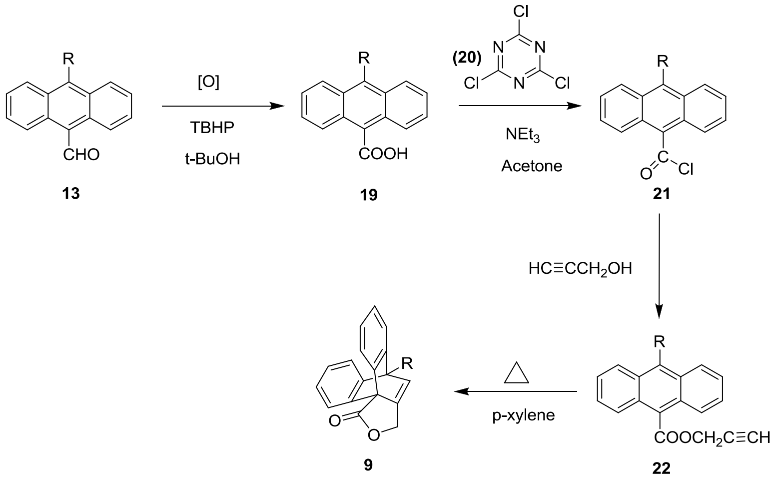
1 **18** **13**

a) R=H **b**) R=CH_3 **c**) R=OCH_3 **d**) R=Ph

Scheme 2.7

2.3.3. Synthesis of tethered esters

Aldehydes **13** were oxidized to corresponding acids[21,22] **19** by refluxing in *t*-butanol with *t*-butyl hydroperoxide (TBHP) and SeO_2**.** Acids **19** were stirred with cyanuric chloride[23,24] in acetone in the presence of triethylamine followed by reaction with propargyl alcohol to get **22**. Acetylene appended anthracenes **22** were refluxed in *p*-xylene to obtain corresponding tethered esters **9** (Scheme 2.8). The products obtained were purified by column chromatography.



a) R=H **b**) R=CH_3 **c**) R=OCH_3 **d**) R=Ph

Scheme 2.8

The structures of tethered esters **9** were established on the basis of analytical results and spectral data. The ^1H NMR spectrum of **9a** (Figure 2.2), for example showed a one proton doublet at δ 6.75, assigned to vinylic proton, whereas the bridgehead proton appeared as a doublet at δ

5.21. The eight aromatic protons appeared as a multiplet from δ 6.95-7.45 and a doublet due to two protons at δ 4.98 was assigned to methylene protons. The ^{1}H NMR spectrum of **9b** and **9c** showed a singlet due to three protons at δ 2.23 and δ 3.94, assigned to methyl and methoxy protons respectively and the aromatic protons and vinylic proton appeared as a multiplet in the δ 6.94-7.70 region in **9d**.

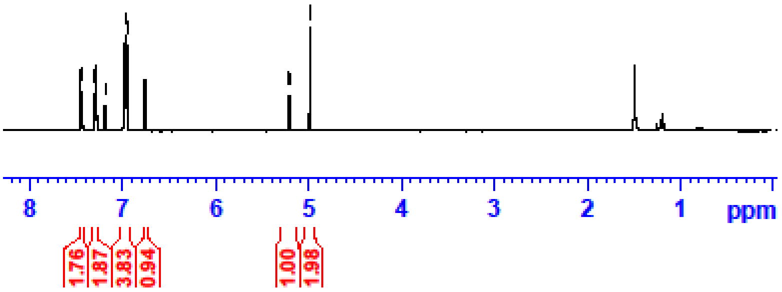


Figure 2.2 ^{1}H NMR spectrum of 9a

The ^{13}C NMR spectrum of **9a** (Figure 2.3) showed signals at δ 171.13, 146.98, 144.59, 142.52, 129.81, 125.53, 124.86, 123.54, 121.19, 68.16, 59.62 and 52.22. Of these, the signal at δ 171.13 has been assigned to C=O group of the ester, whereas the eight signals from δ 121.29-146.98 were assigned to aromatic and vinylic carbons. The three aliphatic carbons appeared in the δ 52.22-68.16 region. Likewise, ^{13}C NMR spectrum of **9a** and **9c** showed signals at δ 15.49 and δ 88.53, assigned to methyl and methoxy carbons respectively and the aromatic carbons and vinylic carbons appeared from δ 121.05-149.10. ^{13}C NMR spectrum of 9d was also in agreement with the expected structure.

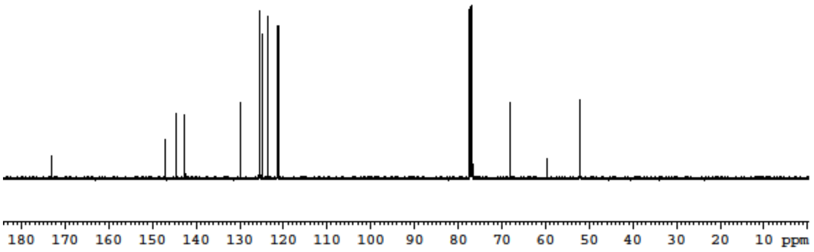
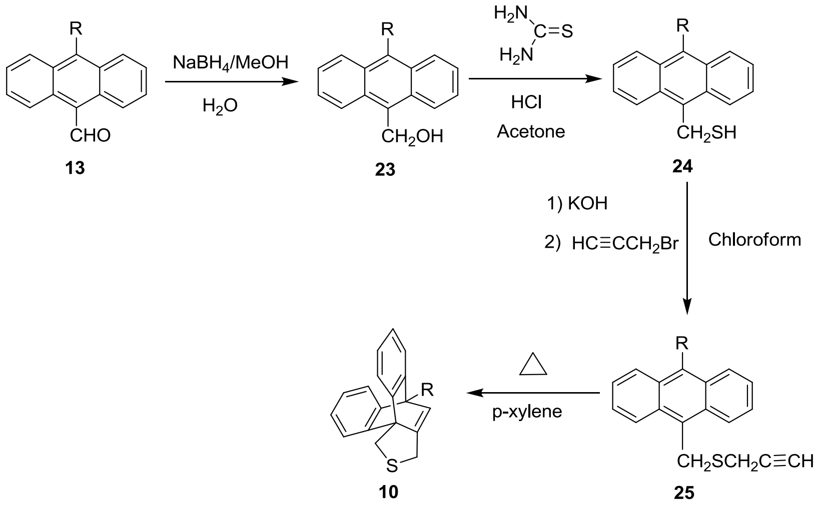


Figure 2.3 ^{13}C NMR spectrum of 9a

In the IR spectrum, the C=O stretching is obviously affected by adjacent C-C stretching. In esters with a six membered ring, the C-C-C bond angle is near 120°. When the angle is less than 120°, there will be ring strain (e.g., five membered ring) and interaction with C-C bond stretching increases the energy required to produce C=O stretching and thus stretching frequency is increased. Therefore the carbonyl absorption of saturated δ-lactones (six membered ring) occurs in the same region as straight-chain, unconjugated esters while saturated γ-lactones (five membered ring) absorb at higher frequency (1760-1795 cm^{-1}) than esters or δ-lactones[25]. The C=O stretching vibration of **9a**, **9b**, **9c** and **9d** thus occurred at 1764 cm^{-1}, 1778 cm^{-1}, 1769 cm^{-1} and 1778 cm^{-1} respectively while C=O stretching vibration of **22a** occurred at 1708 cm^{-1} (straight chain).

2.3.4. Synthesis of tethered sulfides

Aldehydes **13** were reduced to corresponding alcohols[26] **23** by sodium borohydride dissolved in a mixture of methanol and water. The reduction product **23** and two equivalents of thiourea were dissolved in acetone and 5N HCl was added to it and stirred overnight. The precipitate formed was treated with sodium hydroxide to get the thiol **24**.[27] Anthracenethiols **24** dissolved in chloroform were mixed with KOH dissolved in methanol followed by addition of propargyl bromide and the mixture was stirred overnight to obtain **25**. Anthracene derivatives appended with acetylinic substituents **25** were refluxed in *p*-xylene to obtain corresponding tethered sulfides **10** (Scheme 2.9). The products were purified by column chromatography.



a) R=H **b**) R=CH_3 **c**) R=OCH_3 **d**) R=Ph

Scheme 2.9

Structure of tethered sulfides **10** was established on the basis of analytical results and spectral data. ^{1}H NMR spectrum of **10a** (Figure 2.4), for example showed a doublet due to one proton at δ 6.66, assigned to vinylic proton, whereas the bridgehead proton appeared as a doublet at δ 5.09. The eight aromatic protons appeared as a multiplet from δ 6.65-7.30 and a singlet due to two protons at δ 3.98 and a doublet due to two protons at δ 3.57, assigned to methylene protons. ^{1}H NMR spectrum of **10b** and **10c** showed a singlet due to three protons at δ 2.16 and δ 3.90, assigned to methyl and methoxy protons respectively and the aromatic protons and vinylic proton appeared as a multiplet from δ 6.89-7.71 in **10d**.

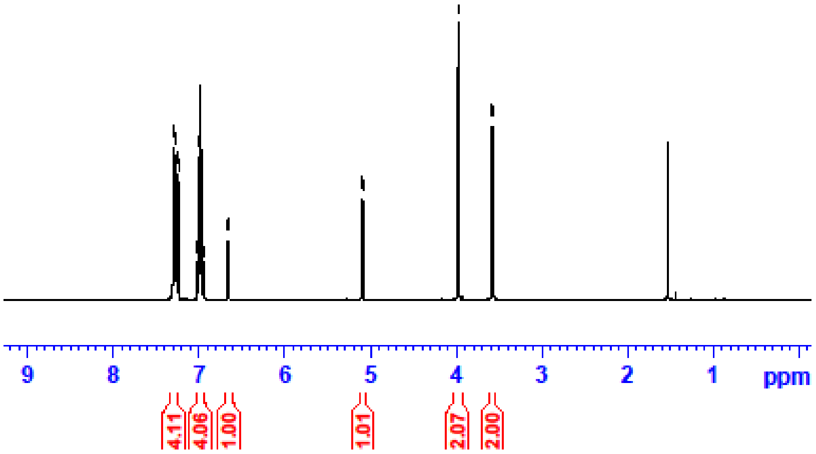


Figure 2.4 ^{1}H NMR spectrum of 10a

^{13}C NMR spectrum of **10a** (Figure 2.5) showed several signals at δ 155.39, 147.64, 145.81, 128.90, 124.62, 124.29, 122.98, 120.00, 64.22, 51.65, 33.46, 30.76. Of these the eight signals from δ 120.00-155.39 were assigned to aromatic and vinylic carbons. The four aliphatic carbons appeared from δ 30.76-64.22. ^{13}C NMR spectrum of **10b** and **10c** showed a signal at δ 15.70 and δ 86.28, assigned to methyl and methoxy carbons respectively and the aromatic carbons and vinylic carbons appeared from δ 119.93-157.48 in **10d**.

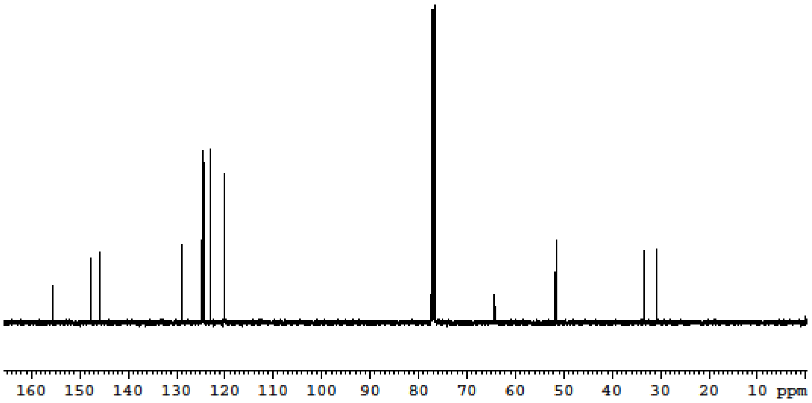
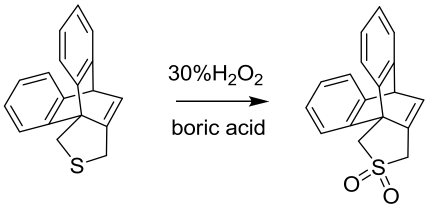


Figure 2.5 ^{13}C NMR spectrum of 10a

2.3.5. Synthesis of tethered sulfone

Tethered sulfide **10a** was oxidized by stirring with 30% hydrogen peroxide[28] and boric acid [29-32] as the catalyst resulting in the formation of tethered sulfone **29** (Scheme 2.10).



10a **11**

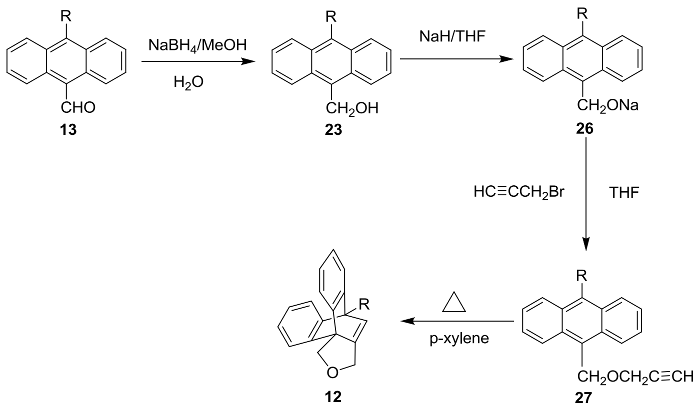
Scheme 2.10

Structure of tethered sulfone **11** was established on the basis of literature precedence, analytical results and spectral data. In the IR spectrum, sulfones generally show strong absorption bands at 1350-1300

cm^{-1} region due to asymmetric SO_2 stretching. The asymmetric SO_2 stretching of **11** occurred at 1318 cm^{-1}. Mass spectrum was also in agreement with the structure.

2.3.6. Synthesis of tethered ethers

Aldehydes **13** were reduced to the corresponding alcohols **23**. Sodium salts of **23** on reaction with propargyl bromide afforded the corresponding propargyl ethers **27**. Anthracene derivatives appended with acetylinic substituents **27** were refluxed in *p*-xylene to obtain corresponding tethered ethers **12** (Scheme 2.11). The products were purified by column chromatography.



a) R=H **b**) R=CH_3 **c**) R=OCH_3 **d**) R=Ph

Scheme 2.11

Structure of tethered ethers **12** was established on the basis of analytical results and spectral data. ^1H NMR spectrum of **12a** (Figure

2.6), for example showed a doublet due to one proton at δ 6.61, assigned to vinylic proton, whereas the bridgehead proton appeared as a doublet at δ 5.16. The eight aromatic protons appeared as a multiplet from δ 6.97-7.29 and a singlet due to two protons at δ 4.99 and a doublet due to two protons at δ 4.41), assigned to methylene protons. ^{1}H NMR spectrum of **12b** and **12c** showed a singlet due to three protons at δ 2.19 and δ 4.00, assigned to methyl and methoxy protons respectively and the aromatic protons and vinylic proton appeared as a multiplet from δ 6.90-7.24 in **12d**.

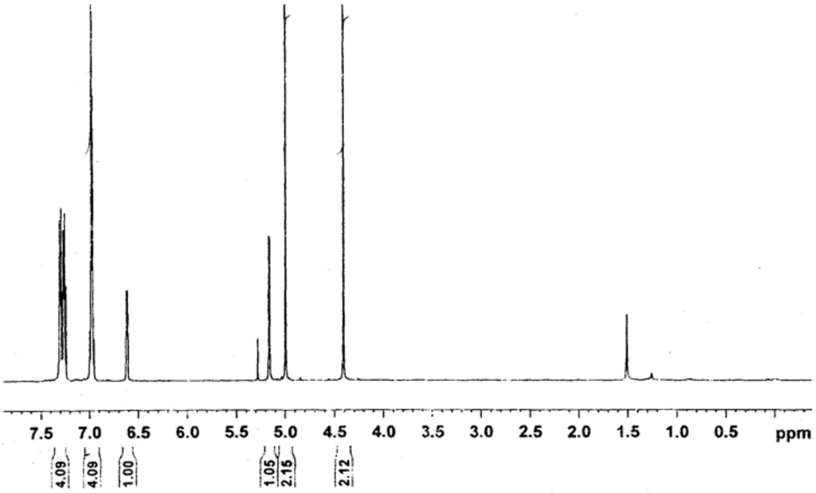


Figure 2.6^{1}H NMR spectrum of 12a

^{13}C NMR spectrum of **12a** (Figure 2.7) showed signals at δ 154.91, 147.25, 145.18, 125.71, 124.67, 124.30, 123.05, 120.02, 67.52, 66.45, 62.11 and 52.00. Of these the eight signals from δ 120.02-154.91 were assigned to aromatic and vinylic carbons. The four aliphatic carbons appeared from δ 52.00-67.52. ^{13}C NMR spectrum of **12b** and **12c** showed a signal at δ 14.71 and δ 87.95, assigned to methyl and methoxy carbons respectively. ^{13}C NMR spectrum of **12d** was also in agreement with the proposed structure.

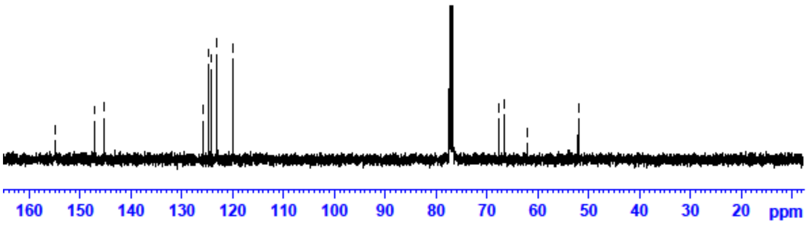


Figure 2.7 ^{13}C NMR spectrum of 12a

2.3.7. Conclusion

Intramolecular Diels-Alder reaction of anthracene derivatives appended with suitable acetylenic substituents were effectively utilized for the efficient synthesis of the required tethered barrelenes.

2.4. Experimental Section

2.4.1. General Techniques

All reactions were carried out utilizing oven dried glasswares. Except otherwise specified, all the solvents were used directly without any further purification. When further purification was needed, known methods and procedures were followed in each case. All the reagents were purchased from either *Sigma-Aldrich* or *Spectrochem Chemicals* and were used without further purification. Progress of the reaction and chromatographic separations were monitored by dried silica gel TLC plates (Aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was achieved by exposure to UV lamp and iodine vapours. Separation and purification of compounds were done by column chromatography using silica gel (*Spectrochem Chemicals*, 60-120 mesh). The products were further purified by recrystallization from suitable solvent systems. Solvent eluted from the column chromatography was concentrated using *Heidolph, IKA or Buchi* rotary evaporators. Melting points were determined on a *Neolab* melting point apparatus and are uncorrected. Infrared spectra were recorded on *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario EL III)*. Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*).

2.4.2. 9-Substituted anthracenes

2.4.2.1 9-Anthraldehyde (13a)

9-Anthraldehyde was prepared by a known procedure[20] (92% yield, mp 98 °C).

2.4.2.2 9-Methylanthracene (1b)

9-Methylanthracene[13] was prepared by a modified Wolff-Kishner reduction reaction in which 9-anthraldehyde (10.0 g, 48 mmol), diethylene glycol (70 mL), sodium hydroxide (5 g) and hydrazine hydrate (80%, 10 mL)) were heated at 120 °C for 2h initially and then increasing the temperature to 200 °C for 3h. HCl (5N, 50 mL) was added to the reaction mixture after cooling and the precipitate was filtered and dried to obtain 8.7 g of **1b** (93% yield, mp 77 ^{o}C).

2.4.2.3 9-Methoxy anthracene (1c)

9-Methoxyanthracene was prepared using a known procedure[15] (81% yield, mp 95 ^{o}C).

2.4.2.4 9-Phenylanthracene (1d)

9-Phenylanthracene was prepared by a known procedure[16] (65% yield, mp 151 ^{o}C).

2.4.3. General procedure for the synthesis of tethered esters 9

Formylation[27-28] of **1** was carried out by a known procedure. Aldehydes **13** (50 mmol) were dissolved 70 mL of *t*-butanol and stirred at 75 ^{o}C with *tert*-butyl hydroperoxide (4.80 mL, 50 mmol) and Se(IV) oxide (0.28 g, 2.5 mmol) (48-70h). Solid residues were filtered off and filtrate was evaporated. The residue was dissolved in dichloromethane (120 mL) and stirred with 5N HCl (200 mL) at room temperature for 4h. The aqueous and organic layers were separated and from the aqueous layer, the acids were extracted with dichloromethane. The organic solutions were collected and dried over anhydrous sodium sulfate and solvents were evaporated to obtain corresponding acids **19** in 20-30% yields. Triethylamine (0.70 mL, 5 mmol) was added to a solution of **19** (5 mmol) and cyanuric chloride (0.92 g, 5 mmol) in acetone and stirred at room temperature for 1h to get the corresponding acid chloride **21**. Propargyl alcohol (0.30 mL, 5 mmol) was added into it and the mixture was stirred for 4h. The products obtained were washed with sodium bicarbonate and extracted with dichloromethane. Esters **22** were purified by silica gel column chromatography using a mixture of hexane and DCM as eluents. Pure products were obtained in 70-80% yields. Anthracene derivatives appended with acetylinic substituents **22** (5 mmol) were refluxed in *p*-xylene (10 mL) (48-64h) to generate corresponding barrelenes **9** that were purified by silica gel column chromatography using a mixture of hexane and dichloromethane as eluents (80-90% yields).

2.4.4. General procedure for the synthesis of tethered sulfides 10

Alcohols **23** (20 mmol) and two equivalents of thiourea (3 g, 40 mmol) were dissolved in acetone (50 mL) and 5N HCl (5 mL) was added to it and stirred overnight. The precipitate formed was filtered and treated with sodium hydroxide (10%, 30 mL) solution and stirred at room temperature for 2h. Acidification with 5N HCl (25 mL) yielded **24** in 85-95% yields. To a solution of anthracenethiols **24** (5 mmol) dissolved in chloroform (20 ml), KOH (0.20 g, 5 mmol) dissolved in methanol was added at 0 ^{o}C followed by propargyl bromide (0.38 mL, 5 mmol) and stirred overnight. Reaction mixture was concentrated, washed with water and extracted with dichloromethane. Thioethers **25** were purified by silica gel column chromatography using a mixture of hexane and DCM as eluents. IMDA reaction of 25 was effected by refluxing in *p*-xylene (10 mL) (5-10h) to obtain corresponding barrelenes **10** in 70-80% yields after recrystallization from suitable solvents.

2.4.5. Synthesis of tethered sulfone 11

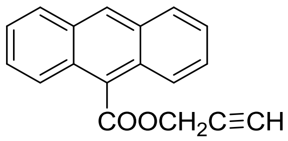
Tethered barrelene **10a** (200 mg, 0.76 mmol) was dissolved in DMF (5 mL) and stirred with hydrogen peroxide (30%, 2 mL) and boric acid (0.006 g, 0.1 mmol) for 12h to obtain corresponding sulfone **11**.

2.4.6. General procedure for the synthesis of tethered ethers 12

Anthracenemethanols **23** were converted to the corresponding sodium salts **26**. Propargyl bromide was added to it and stirred at room temperature for 2h followed by refluxing in THF for 4h to obtain **27**. Propargyl ethers **27** were refluxed in *p*-xylene (10 mL) (12 h to 20 h) to obtain the corresponding barrelenes **12.** The products were purified by silica gel column chromatography using a mixture of hexane and DCM as eluents followed by recrystallization from suitable solvents and structures were confirmed by spectral and analytical data.

2.4.7. Spectral and analytical data of target compounds

2.4.7. 1 Compound 22a



mp: 90-93 °C.

IR ν_{max} (KBr): 1708 (C=O stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 8.46-7.39 (m, 9H), 5.12 (d, 2H, J = 2.4 Hz), 2.56 (t, 1H, J = 2.4 Hz).

^{13}C NMR ($CDCl_3$): δ167.76, 129.91, 128.82, 127.63, 127.60, 126.14, 125.45, 124.50, 123.83, 76.45, 74.54, 51.85.

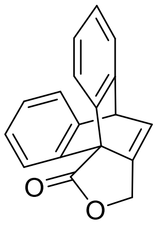
MS: *m/z* 260.

Elemental analysis calculated for $C_{18}H_{12}O_2$: C: 83.06, H: 4.65. Found: C: 83.04, H: 4.63.

2.4.7. 2 Compound 9a

mp: 232-235 °C.

IR ν_{max} (KBr): 1764 (C=O stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out



of plane bending).

^{1}H NMR (CDCl$_3$): δ 7.45-6.95 (m, 8H), 6.75 (d, 1H, *J* = 6 Hz), 5.21 (d, 1H, *J* = 5.6 Hz). 4.98 (d, 2H, *J* = 2.4 Hz).

^{13}C NMR (CDCl$_3$): δ173.13, 146.98, 144.59, 142.52, 129.81, 125.53, 124.86, 123.54, 121.19, 68.16, 59.62, 52.22.

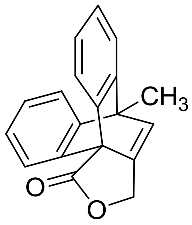
MS:- *m/z* 260.

Elemental analysis calculated for

$C_{18}H_{12}O_2$: C: 83.06, H: 4.65.

Found: C: 83.04, H: 4.63.

2.4.7.3 Compound 9b



mp: 175-178 °C.

IR ν_{max} (KBr): 1778 (C=O stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR (CDCl$_3$): δ 7.52-7.01 (m, 8H), 6.43 (t, 1H, *J* = 2.4 Hz), 5.03 (d, 2H, *J* = 2.4 Hz), 2.23 (s, 3H).

^{13}C NMR (CDCl$_3$): δ173.26, 147.57, 146.90, 143.50, 134.03, 125.27, 124.59, 120.83, 120.67, 68.04, 59.17, 51.33, 15.49.

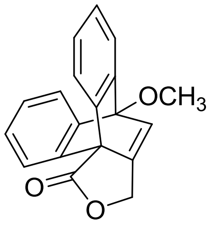
MS: *m/z* 274.

Elemental analysis calculated for

$C_{19}H_{14}O_2$: C: 83.19, H: 5.14.

Found: C: 83.17, H: 5.12.

2.4.7.4 Compound 9c



mp: 200-202 °C.

IR ν_{max} (KBr): 1769 (C=O stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.44-6.93 (m, 9H), 4.99 (d, 2H, *J* = 2 Hz), 3.94 (s, 3H).

^{13}C NMR ($CDCl_3$): δ172.62, 145.81, 144.89, 140.89, 127.98, 125.45, 124.91, 120.81, 120.74, 88.53, 67.99, 57.97, 55.27.

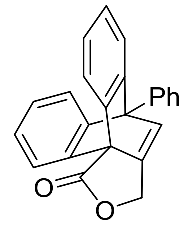
MS: *m/z* 290.

Elemental analysis calculated for

$C_{19}H_{14}O_3$: C: 78.61, H: 4.86.

Found: C: 78.59, H: 4.84.

2.4.7.5 Compound 9d



mp: 274-276 °C.

IR ν_{max} (KBr): 1778 (C=O stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR (CDCl$_3$): δ 7.70-6.94 (m, 14H), 5.11 (d, 2H, *J* = 2.4 Hz).

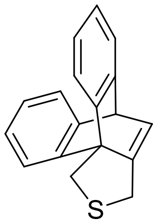
^{13}C NMR (CDCl$_3$): δ 173.13, 149.10, 147.28, 142.91, 134.58, 130.07, 129.56, 128.73, 127.93, 124.95, 124.92, 123.85, 121.05, 68.17, 61.34, 59.86.

MS: *m/z* 336.

Elemental analysis calculated for $C_{24}H_{16}O_2$: C: 85.69, H: 4.79.

Found: C: 85.67, H: 4.77.

2.4.7.6 Compound 10a



mp: 129-132 °C.

IR ν_{max} (KBr):-1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR (CDCl$_3$): δ 7.30-6.95 (m, 8H), 6.66 (d, 1H, *J* =6 Hz), 5.09 (d, 1H, *J* =6

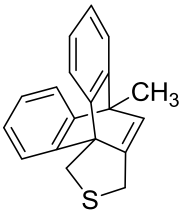
Hz), 3.98 (s, 2H), 3.57 (d, 2H, *J* = 1.6 Hz).

^{13}C NMR ($CDCl_3$): δ 155.39, 147.64, 145.81, 128.90, 124.62, 124.29, 122.98, 120.00, 64.22, 51.65, 33.46, 30.76.

MS: *m/z* 262.

Elemental analysis calculated for $C_{18}H_{14}S$: C: 82.40, H: 5.38, S: 12.22. Found: C: 82.38, H: 5.40, S: 12.22.

2.4.7.7 Compound 10b



mp: 112-114 °C.

IR ν_{max} (KBr): 2965 (-C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

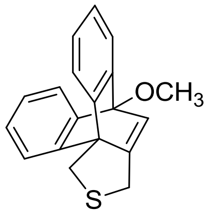
^{1}H NMR ($CDCl_3$): δ 7.29-7.00 (m, 8H), 6.29 (t, 1H, *J* = 2 Hz), 3.98 (s, 2H), 3.58 (d, 2H, *J* = 2 Hz), 2.16 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 156.01, 149.91, 146.84, 133.30, 124.39, 124.04, 120.04, 119.64, 63.68, 49.97, 33.52, 31.02, 15.70.

MS: *m/z* 276.

Elemental analysis calculated for $C_{19}H_{16}S$: C: 82.56, H: 5.83, S: 11.61. Found: C: 82.54, H: 5.83, S: 11.63.

2.4.7.8 Compound 10c



mp: 153-156 °C.

IR ν_{max} (KBr): 2936 (-C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

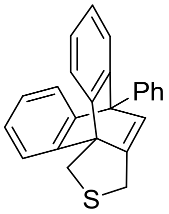
^{1}H NMR ($CDCl_3$): δ 7.39-6.91 (m, 8H), 6.79 (t, 1H, *J* = 2 Hz), 3.90 (s, 3H), 3.88 (s, 2H), 3.54 (d, 2H, *J* = 2 Hz).

^{13}C NMR ($CDCl_3$): δ 153.14, 146.64, 143.27, 125.90, 123.54, 123.35, 118.99, 118.59, 86.28, 61.84, 53.93, 32.67, 29.83.

MS: *m/z* 292.

Elemental analysis calculated for $C_{19}H_{16}OS$: C: 78.05, H: 5.52, S: 10.97. Found: C: 78.03, H: 5.50, S: 10.95.

2.4.7.9 Compound 10d



mp: 218-221 °C.

IR ν_{max} (KBr):1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.71-6.89 (m, 14H), 4.06 (s, 2H), 3.66 (d, 2H, *J* = 1.6 Hz).

^{13}C NMR ($CDCl_3$):- δ 157.48, 150.11, 146.16, 135.53, 130.25, 128.62, 128.51, 127.52, 124.37, 124.06, 123.18, 119.93, 63.87, 60.03, 33.94, 31.22.

MS: *m/z* 338.

Elemental analysis calculated for $C_{24}H_{18}S$: C: 85.17, H: 5.36, S: 9.47. Found: C: 85.15, H: 5.36, S: 9.49.

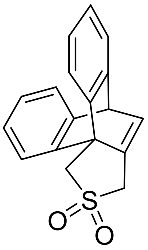
2.4.7.10 Compound 11

mp: 129-132 °C.

IR ν_{max} (KBr): 1318 (asymmetric SO_2 stretch, 1300-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.26 -6.87 (m, 9H), 5.09 (d, 1H, *J* =6 Hz), 4.10 (s, 2H), 3.80 -3.73 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 148.34, 145.63,



144.35, 134.42, 133.35, 119.47, 119.02, 118.73, 58.48, 53.96, 50.53, 50.29.

MS: *m/z* 294.

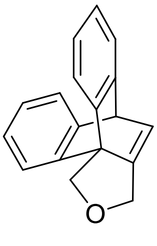
Elemental analysis calculated for $C_{18}H_{14}O_2S$: C: 73.44, H: 4.79, S: 10.89.

Found: C: 73.42, H: 4.77, S: 10.87.

2.4.7.11 Compound 12a

mp: 198-1200 °C.

IR ν_{max} (KBr): 2880 (-C-H stretch), 1350-1000 (C-O stretch) and 750-690 cm^{-1} (aromatic out of plane bending).



^{1}H NMR ($CDCl_3$): δ 7.29-6.97 (m, 8H), 6.61 (d, 1H, *J* = 6 Hz), 5.16 (d, 1H, *J* = 6 Hz), 4.99 (s, 2H), 4.41 (d, 2H, *J* = 2 Hz).

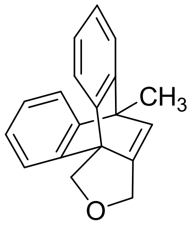
^{13}C NMR ($CDCl_3$): δ 154.91, 147.25, 145.18, 125.71, 124.67, 124.30, 123.05, 120.02, 67.52, 66.45, 62.11, 52.00.

MS: *m/z* 246.

Elemental analysis calculated for $C_{18}H_{14}O$: C: 87.78, H: 5.73.

Found: C: 87.76, H: 5.7.

2.4.7.12 Compound 12b



mp: 139-142 °C.

IR ν_{max} (KBr): 2925 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.32 -6.99 (m, 8H), 6.25 (d, 1H, *J* = 2.4 Hz), 5.00 (s, 2H), 4.42 (d, 2H, *J* = 2.4 Hz), 2.19 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 154.53, 148.51, 145.19, 128.97, 123.40, 123.01, 119.09, 118.62, 66.53, 65.58, 60.51, 49.43, 14.71.

MS: *m/z* 260.

Elemental analysis calculated for $C_{19}H_{16}O$: C: 87.66, H: 6.19.

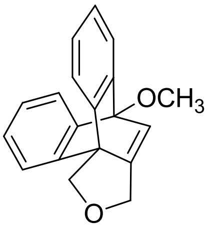
Found: C: 87.64, H: 6.17.

2.4.7.13 Compound 12c

mp: 155-158 °C.

IR ν_{max} (KBr): 2940 (-C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.49-6.98 (m, 8H), 6.83 (s, 1H), 5.00 (s, 2H), 4.56 (s, 2H),



4.00 (s, 3H).

^{13}C NMR (CDCl$_3$): δ 153.78, 147.35, 143.66, 124.63, 124.38, 123.75, 120.14, 119.66, 87.95, 67.66, 66.61, 60.60, 55.08.

MS: *m/z* 276.

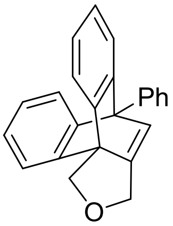
Elemental analysis calculated for $C_{19}H_{16}O_2$: C: 82.58, H: 5.84.

Found: C: 82.56, H: 5.82.

2.4.7.14 Compound 12d

mp: 233-236 °C.

IR ν_{max} (KBr): 2863 (-C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).



^{1}H NMR (CDCl$_3$): δ 7.24-6.90 (m, 14H), 5.09 (s, 2H), 4.49 (s, 2H).

^{13}C NMR (CDCl$_3$): δ 157.06, 149.800, 145.56, 135.56, 130.28, 128.52, 127.53, 125.42, 124.36, 124.08, 123.24, 119.85, 67.84, 66.72, 61.83, 60.56.

MS:- *m/z* 322.

Elemental analysis calculated for $C_{24}H_{18}O$: C: 89.41, H: 5.63.

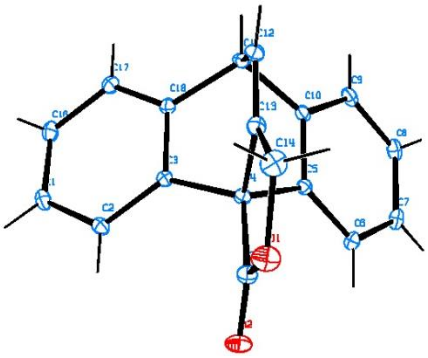
Found: C: 89.39, H: 5.61.

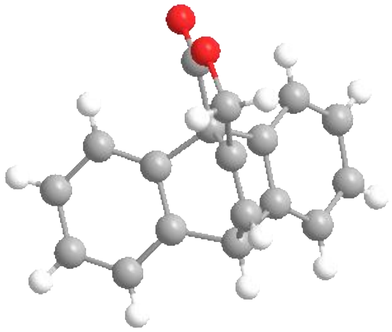
2.4.8. *ORTEP* diagrams and corresponding ball & stick models of target compounds

2.4.8. 1 Compound 9a

Crystal system: Monoclinic

Space group : P21/C

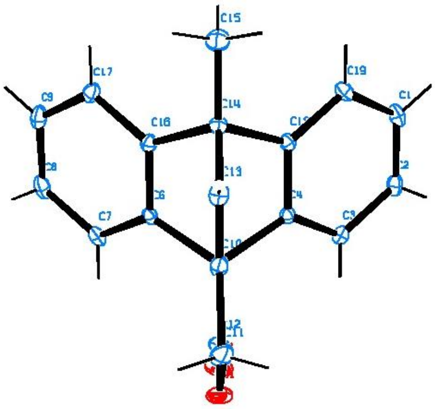


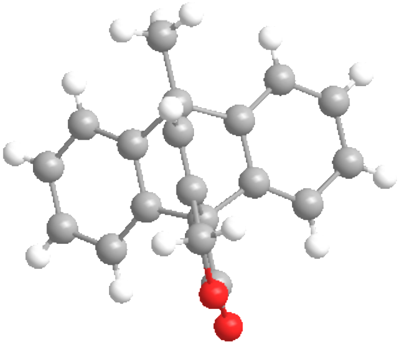


2.4.8. 2 Compound 9b

Crystal system: Orthorhombic

Space group : Pbcn

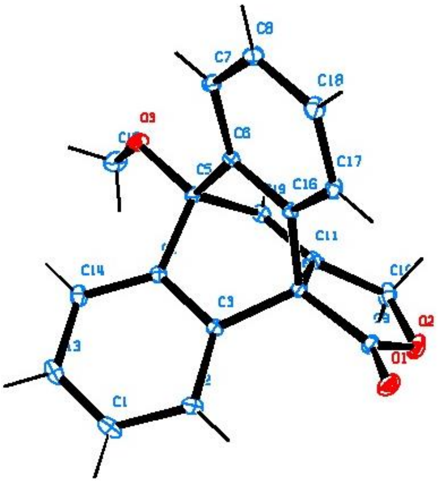


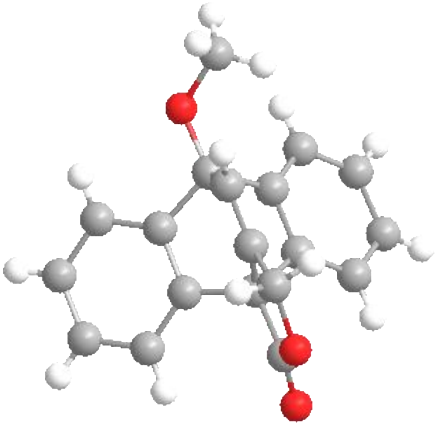


2.4.8. 3 Compound 9c

Crystal system: Triclinic

Space group : P-1

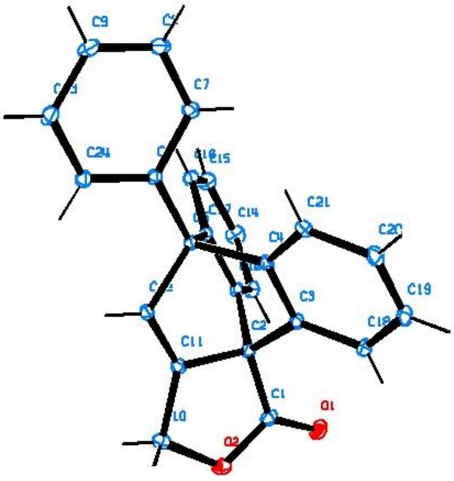


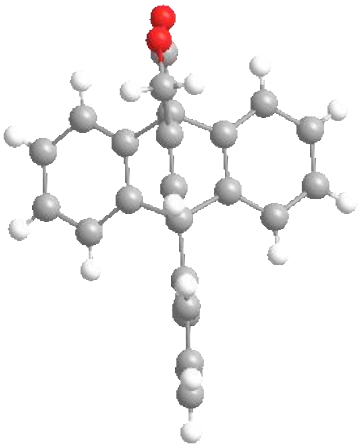


2.4.8. 4 Compound 9d

Crystal system: Triclinic

Space group : P-1

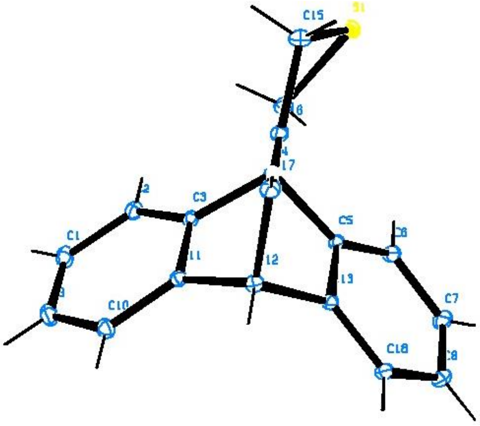


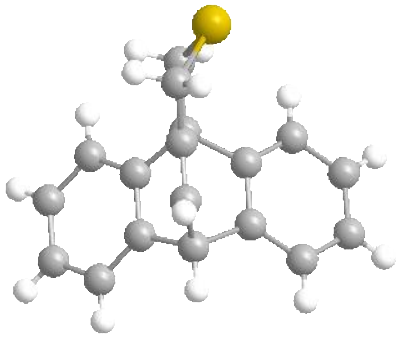


2.4.8. 5 Compound 10a

Crystal system: Triclinic

Space group : P-1

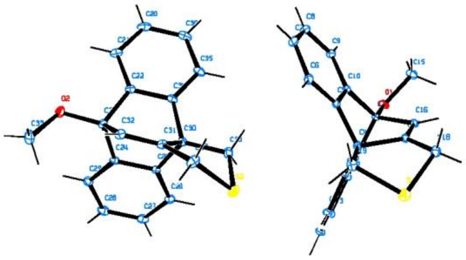


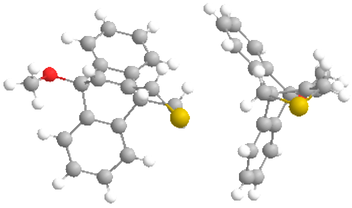


2.4.8.6 Compound 10c

Crystal system: Monoclinic

Space group : P21/C

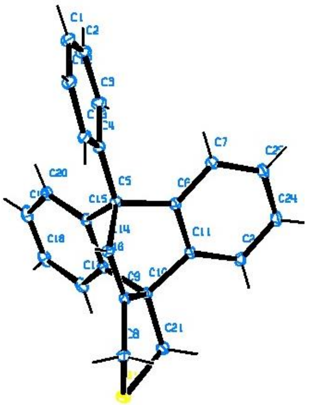


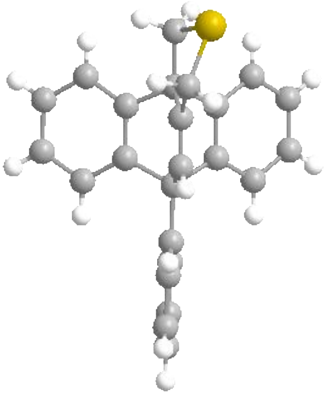


2.4.8.7 Compound 10d

Crystal system: Orthorhombic

Space group : Pbca

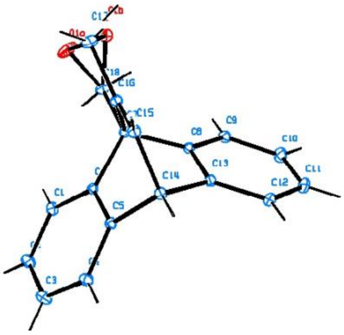


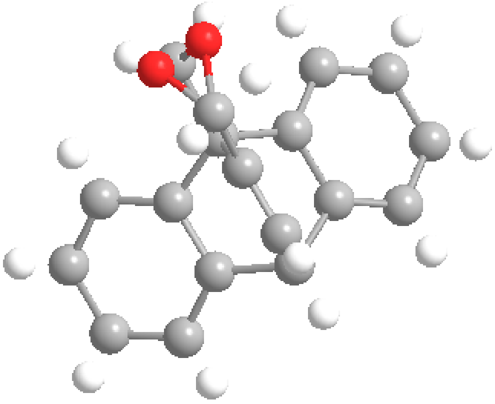


2.4.8.8 Compound 12a

Crystal system: Monoclinic

Space group : P21/C

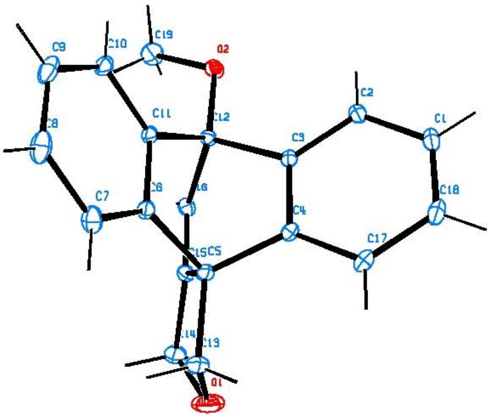


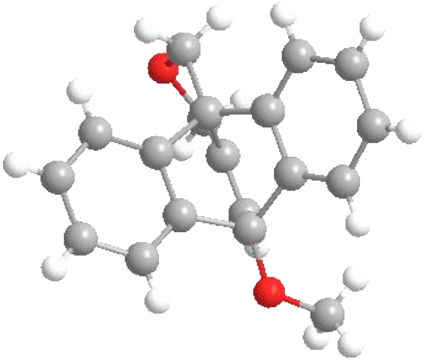


2.4.8.9 Compound 12c

Crystal system: Monoclinic

Space group : P21/n

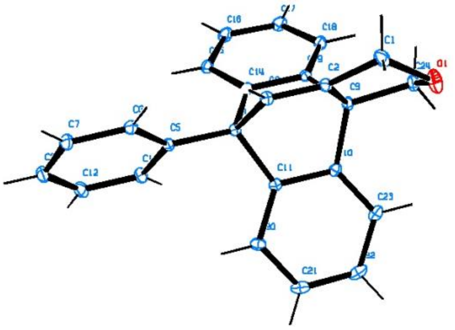


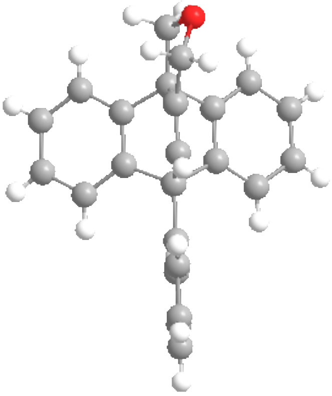


2.4.8.10 Compound 12d

Crystal system: Monoclinic

Space group : P21/n





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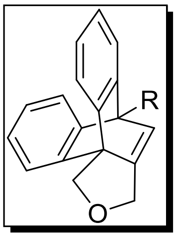
PHOTOCHEMICAL TRANSFORMATIONS OF THE TETHERED BARRELENES

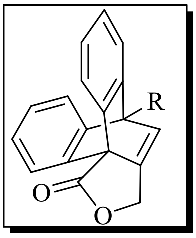
We are interested in the photochemical transformations of the following tethered barrelenes whose synthesis has been described in Chapter 2. Photochemical transformation of thethred barrelenes synthesized by us will be discussed in subsequent chapters as indicated below.

Chapter 3



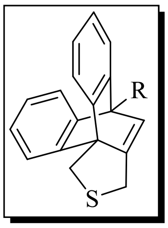
Tethered ethers

Chapter 4

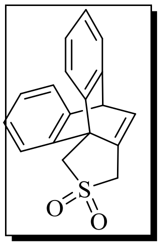


Tethered esters

Chapter 5



Tethered sulfides



Tethered sulfone

CHAPTER 3

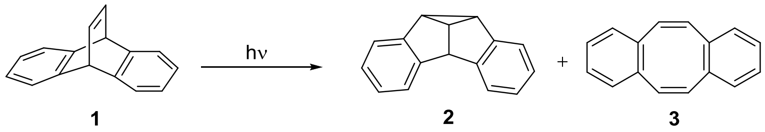
PHOTOCHEMICAL TRANSFORMATIONS OF THE TETHERED ETHERS

3.1. Abstract

This chapter describes the photochemical transformations of a few bridgehead-substituted tethered ethers. Irradiation of tethered dibenzobarrelene derivatives in dry acetonitrile led to the formation of the corresponding dibenzocyclooctatetraenes. On the other hand, irradiation of these compounds in dry acetone gave the corresponding 4b-substituted tethered dibenzosemibullvalenes in near-quantitative yields.

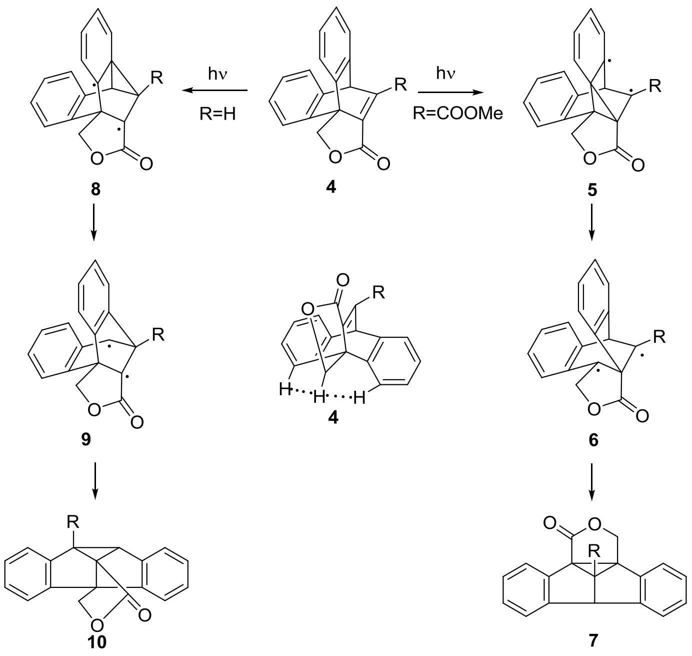
3.2. Introduction

As dibenzobarrelenes are rigid cyclic systems, only triplet states are involved as the reactive states in their di-π-methane rearrangement[1] and their singlet excited states generally undergo cycloddition reaction leading to the generation of the corresponding dibenzocyclooctatetraenes. Thus under triplet sensitized irradiation, dibenzobarrelenes **1** undergo facile photorearrangement to the corresponding dibenzosemibullvalenenes[2] **2**, whereas on direct irradiation dibenzocyclooctatetraenes[3] **3** are formed (Scheme 3.1).



Scheme 3.1

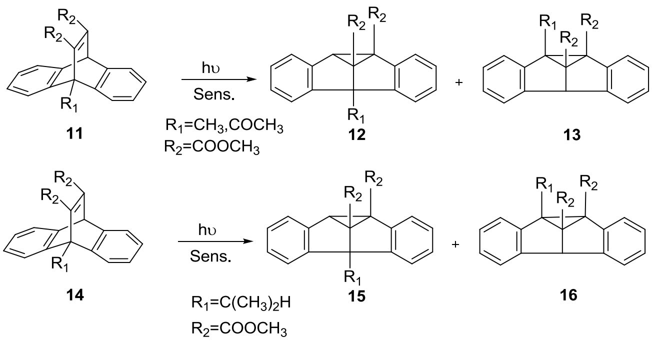
In the case of unsymmetrically substituted dibenzobarrelenes, photochemical rearrangement can lead to more than one dibenzosemibullvalene regioisomers. There are various factors that govern the regioselectivity of di-π-methane rearrangement of dibenzobarrelenes. According to Scheffer[4-14], the steric crowding and electronic factors work against each other and the regioselectivity is mainly controlled by the relief of steric crowding in sterically crowded molecules like dibenzobarrelenes (9,10-ethenoanthracene) derivatives. For example, in compound **4**[5], as the rotational freedom of the bridgehead methylene group is restricted, fixed non-bonding interaction is introduced between the methylene hydrogen atoms and the adjacent aromatic hydrogen atoms. It is clear from the X-ray crystallography that the H···H distance in this compound is lower than the sum of the van der Waals radii for the two hydrogen atoms. So the preferred pathway for the di-π-methane rearrangement should be the one that most effectively alleviates the unfavourable H···H interactions Thus, photoproduct **7** is sterically favoured over the photoproduct **10** for compound **4** (Scheme 3.2). The steric crowding and radical stability work against each other in compound **4** (when R=H) and radical stabilization effect clearly controls the regioselectivity. The odd electron stabilization by either ester carbonyl or lactone carbonyl and steric crowding work in compound **4** (when R=$COOCH_3$) and sterically favoured product **7** is formed as the photoproduct exclusively.



Scheme 3.2

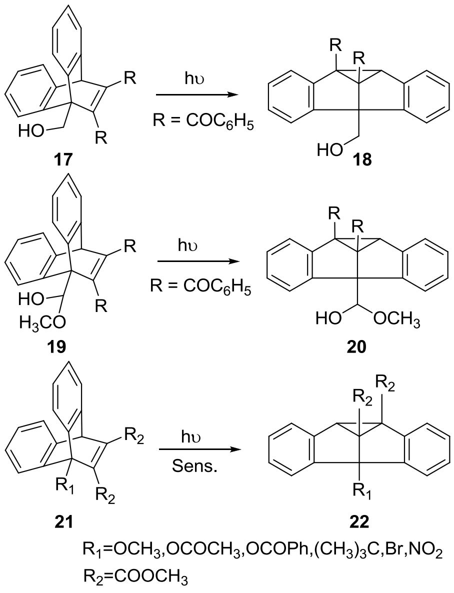
The photochemistry of a large number of barrelene derivatives has been investigated. It has been established that direct irradiation of dibenzobarrelene leads to dibenzocyclooctateraenes and sensitized irradiation leads to dibenzosemibullvalenes. When there is a substituent at the bridgehead position in the dibenzobarrelene derivatives, the sensitized irradiation gives dibenzosemibullvalenes, either a mixture of two 4b- and 8b-regioisomers or any one of the regioisomer exclusively through di-π-methane rearrangement.

Scheme 3.3 shows formation of both regioisomers in the sensitized irradiation of dibenzobarrelenes with different bridgehead substituents.[15]



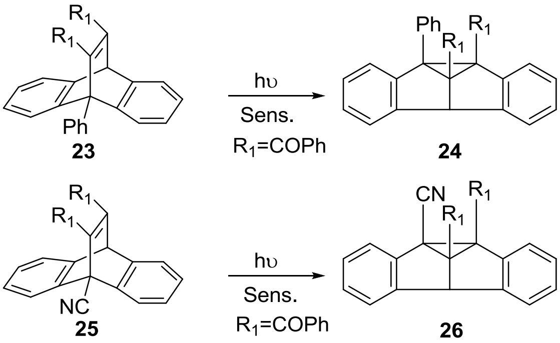
Scheme3.3

A few examples for exclusive formation of 4b-regioisomer on sensitized irradiation of dibenzobarrelenes with different bridgehead substituents is shown in Scheme 3.4.[15-17]



Scheme 3.4

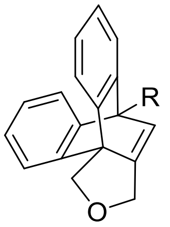
Similarly, there are reports on exclusive formation of 8b-regioisomer on sensitized irradiation of dibenzobarrelenes having bridgehead substituents. A few of these are collected in Scheme 3.5.[17,18]



Scheme 3.5

In general, dibenzobarrelenes with bridgehead substitution by nitro group, methoxy group and halogens exclusively afford the 4b-substituted dibenzosemibullvalenes and dibenzobarrelenes with substituents such as cyano and aryl groups give the 8b-substituted dibenzosemibullvalenes. Dibenzobarrelenes with substituents such as methyl group give both 4b- and 8b-substituted dibenzosemibullvalenes. Interestingly, several examples of bridgehead-substituted dibenzobarrelenes undergoing tri-π-methane rearrangement are also reported in literature.[19-21]

From the above discussion it is clear that irradiation of dibenzobarrelenes with different bridgehead substituents offers a variety of products with remarkable regioselectivity/chemoselectivity controlled by the nature of bridgehead substituents. Unfortunately, observed regioslectivity and/or chemoselctivity in these transformations have been justified on a case-to-case basis and as is customary of this approach, a few of the justifications are even contradictory in nature. Though it is clear that both steric and electronic factors have definite role in establishing regioslectivity, the extent to which these factors control regioslectivity is not yet conclusively established. We reasoned that examination of tricyclic systems may be more appropriate in this regard. Accordingly, we synthesized several tricyclic systems with ether, ester, thioether and sulfone linkages between bridgehead and 9- positions of dibenzobarrelenes and examined regioselectivity of their triplet mediated transformations to the corresponding dibenzosemibullvalenes. Based on the nature of the linker, we describe such barrlenes as ether, ester, thioether and sulfone tethered barrelenes. Selection of tether length is also in accordance with a definite plan. Creation of a five membered ring will not change the geometry of the bridgehead tetrahedral carbon since the internal angle of even a planar five-membered ring is near-identical with tetrahedral angle. However, at the vinyl position, some amount of angle strain will be induced. We anticipate relief of angle strain at the vinyl position to exert significant control over regioselectivity in barrelene-semibullvalene rearrangement. In this chapter, we describe photochemical transformations of ether-tethered dibenzobarrelenes **27** having different substituents such as methyl, methoxy and phenyl located at the other bridgehead position. It may be noted that the ether bridge will induce permanent H···H interaction while exerting minimal electronic effects. Our selection of the “second” bridgehead substituent is also in accordance with a definite plan. Bridgehead methyl substituent largely favours generation of 4b-substituted isomer while a bridgehead phenyl substituent should essentially drive regioselectivity towards the generation the corresponding 8b-substituted isomer. It is interesting to examine whether such trends are maintained in the case of tricyclic systems as well.



27

a) R=H **b**) R=CH_3 **c**) R=OCH_3 **d**) R=Ph

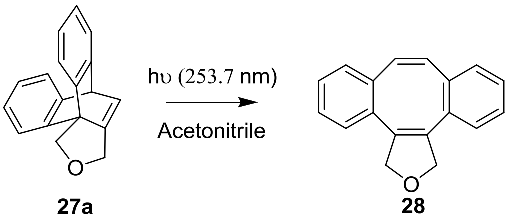
Figure 3.1

3.3. Results and Discussion

A few tethered ethers **27** were synthesized[22] (Figure 3.1) with a view to study the photochemical transformations of bridgehead-substituted tethered dibenzobarrelenes. As expected, direct irradiation of **27** led to the formation of tethered cyclooctatetraene and sensitized irradiation led to the formation of tethered dibenzosemibullvalenes. Through sensitized irradiation, we can investigate the effects of bridgehead-substituents in controlling the regioselectivity of tethered dibenzobarrelenes.

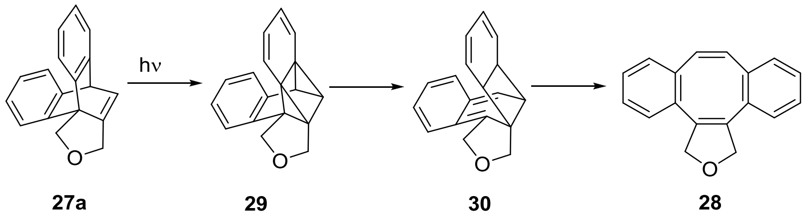
3.3.1. Direct Irradiation

Irradiation of tethered barrelene **27a** in dry acetonitrile (253.7 nm) under argon atmosphere gave corresponding tethered cyclooatatetraene **28** (Scheme 3.6), the structure of which was established on the basis of ^{1}H NMR spectra and literature precedence.[23]



Scheme 3.6

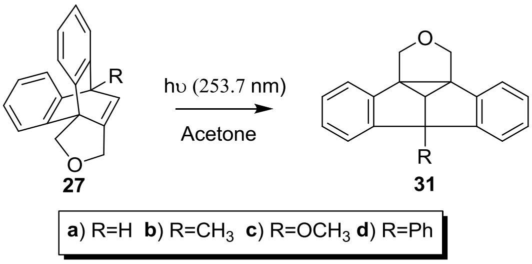
On the basis of thorough investigations of the direct irradiation of similar benzo- and naphthobarrelene systems, it has been proposed that formation of dibenzocycloocatetraene is mediated by the singlet excited states of dibenzobarrelenes involving initial intramolecular [2+2] cycloaddtion.[24,25] Thus direct irradiation of **27a** is assumed to proceed through an initially formed [2+2] adduct **29** which rearranges to **30** and finally to the corresponding tethered cyclooctatetraene **28** (Scheme 3.7).



Scheme 3.7

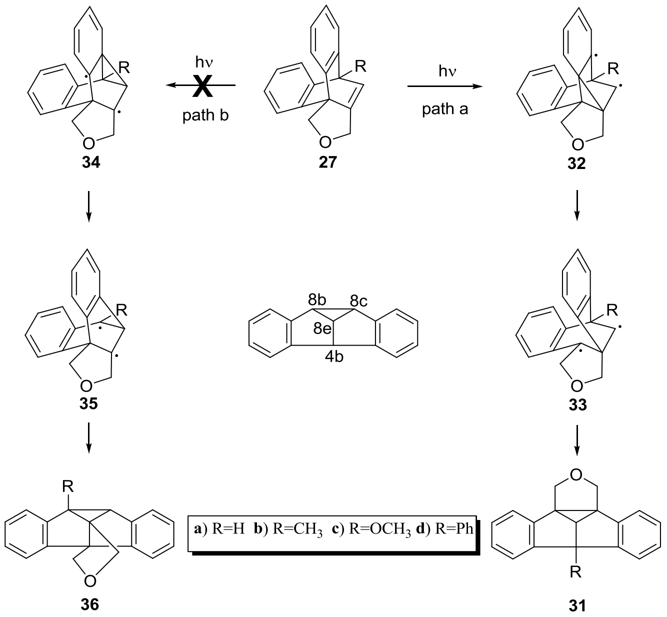
3.3.2. Sensitised Irradiation

When tethered barrelenes **27** were irradiated in dry acetone at 253.7 nm under argon atmosphere, it led to the exclusive formation of 4b-substituted tethered semibullvalenes **31** (Scheme 3.8).



Scheme 3.8

According to earlier reported mechanism for the barrelene rearrangement,[26] in the photoisomerization of compounds **27,** two semibullvalenes **31** and **36** can be expected. Formation of these could be rationalized in terms of the pathways shown in Scheme 3.9. A benzo-vinyl bridging can lead to the diradical intermediates **32** and **34**, which can then get transformed into the products **31** and **36**, respectively. There are reports[15,18] predicting exclusive formation of 8b-regioisomers with barrelenes having a phenyl bridgehead substituent. In contrast to this in our irradiation studies, only the other regioisomer **31d** was formed. This is probably due to the relief of steric strain induced by H···H interactions in intermediate **32**. In contrast, such relief is not materializing with intermediate **34**.



Scheme 3.9

The structures of tethered semibullvalenes **31** have been established on the basis of analytical results and spectral data. The ^{1}H NMR spectrum of **31a** (Figure 3.2), for example showed two doublets at δ 4.58 and δ 4.31, assigned to methylene protons and two doublets at δ 4.53 (1H) and δ 3.61 (1H) which have been assigned to H^{4b} and H^{8e} protons respectively. The eight aromatic protons appeared as a multiplet from δ 7.05 to δ 7.21. The ^{1}H NMR spectrum of **31b** and **31c** showed a singlet due to three protons at δ 1.81 and δ 3.46, assigned to methyl and methoxy protons respectively.

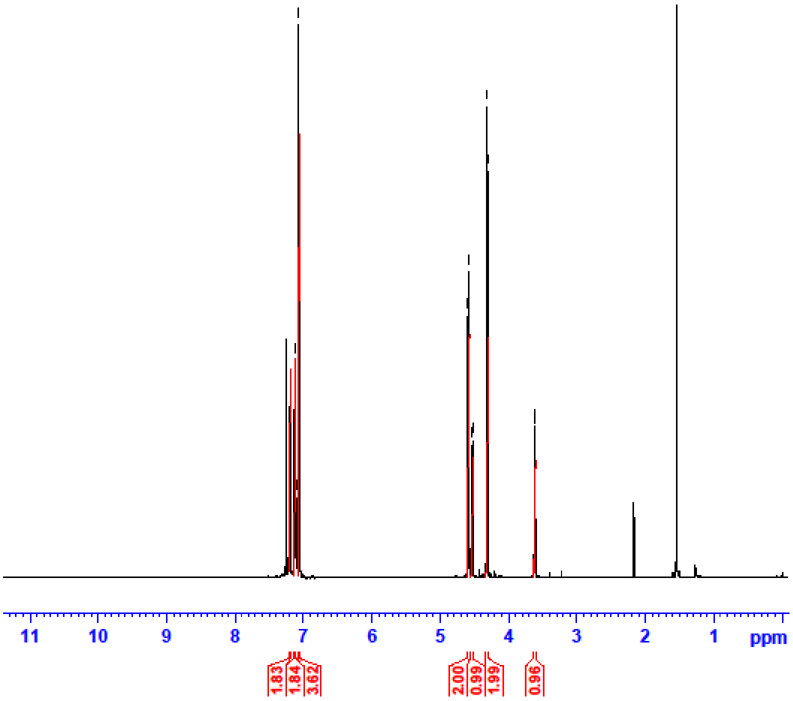


Figure 3.2 ^{1}H NMR spectrum of 31a

The ^{13}C NMR spectrum of **31a** (Figure 3.3) showed several signals at δ 148.89, 136.23, 126.66, 126.53, 122.68, 122.11, 68.30, 56.47, 54.42 and 53.15. Of these, the signals from δ 122.11 to 148.89 were assigned to aromatic carbons whereas the aliphatic carbons appeared from δ 53.15-68.30. The ^{13}C NMR spectrum of **31b** and **31c** showed signals at δ 18.70 and δ 54.71, assigned to methyl and methoxy carbons respectively.

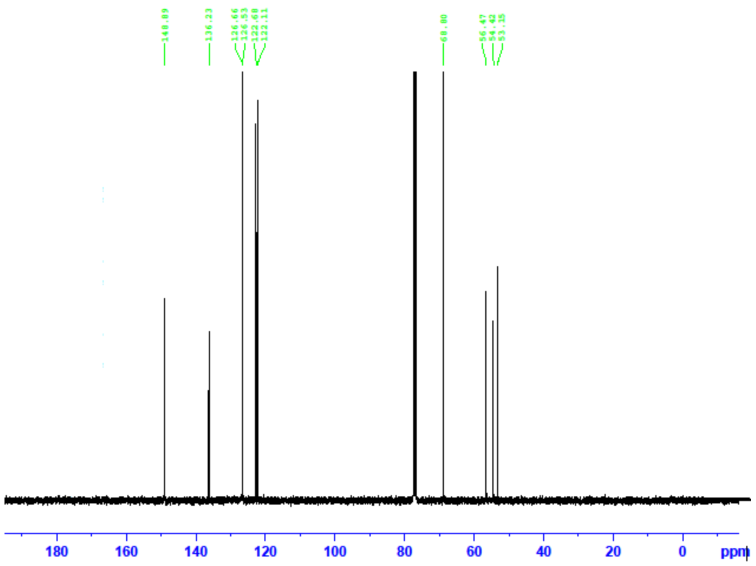


Figure 3.3 ^{13}**C NMR spectrum of 31a**

3.3.3 Conclusion

Eventhough earlier reports indicated the exclusive formation of 8b-regioisomer in the irradiation of barrelenes having a phenyl bridgehead substituent, the corresponding ether-tethered barrelenes in our studies of sensitized irradiation showed exclusive formation of 4b-regioisomer. Regioselectivity is shown by tethered ethers with various substituents like methyl, methoxy and a hydrogen at the bridge head position. Observed regioselectivity is determined by the relief of steric crowding in the case of tethered ethers.

3.4. Experimental Section

3.4.1. General Techniques

All reactions were carried out in oven dried glasswares. Except otherwise specified, all the solvents were used directly without any further purification. When further purification was needed, known methods and procedures were followed in each case. All the reagents were purchased from either *Sigma-Aldrich* or *Spectrochem Chemicals* and were used without further purification. Progress of the reaction and chromatographic separations were monitored by dried silica gel TLC plates (Aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was achieved by exposure to UV lamp or iodine vapours. Separation and purification of compounds were done by column chromatography using silica gel (*Spectrochem Chemicals*, 60-120 mesh). The products were further purified by recrystallization from suitable solvent systems. Solvent eluted from the column chromatography was concentrated using *Heidolph, IKA or Buchi* rotary evaporators. Melting points were determined on a *Neolab* melting point apparatus and are uncorrected. Infra-red spectra were recorded on *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ^{1}H and ^{13}C NMR spectra were recorded by 400 MHz *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario EL III)*.

Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*).

3.4.2. Direct irradiation

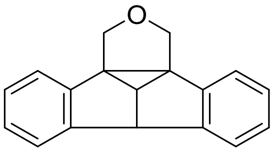
Acetonitrile was purified and distilled before use by a known procedure[27] and oxygen was purged by passing a steady flow of argon through the solution for 30 minutes prior to irradiation. The degassed solution of **20a** (50 mg) in dry acetonitrile (150 mL) was irradiated at (253.7 nm) under argon atmosphere for 8h using Rayonet photochemical reactor to give **21.** Structure of **21** was identified on the basis of ^{1}H NMR spectrum and literature precedence (mp 150 ^{o}C[23]).

3.4.3. General procedure for sensitized irradiation

Distilled and purified[27] acetone was purged with argon (30 minutes) prior to irradiation. Degassed solution of **20** (50-70 mg) in dry acetone (150-170 mL) was irradiated (253.7 nm) under argon or nitrogen using Rayonet photochemical reactor (25-35 min). Progress of the reaction was monitored by TLC. After the reaction, solvent was removed under reduced pressure. Preliminary examination of the ^{1}H NMR spectra of the residue indicated quantitative formation of single product and spectral and analytical data of the products in all the cases could be recorded without further purification.

3.4.4. Spectral and analytical data of novel compounds

3.4.4. 1 Compound 31a



mp: 108-110 °C.

IR ν_{max} (KBr): 2858 (-C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.21-7.05 (m, 8H), 4.58 (d, 2H, *J* = 8.8 Hz), 4.53 (d, 1H, *J* = 6 Hz), 4.31 (d, 2H, *J* = 8.8 Hz), 3.61 (d, 1H, *J* = 6 Hz).

^{13}C NMR ($CDCl_3$): δ 148.89, 136.23, 126.66, 126.53, 122.68, 122.11, 68.30, 56.47, 54.42, 53.15.

MS: *m/z* 246.

Elemental analysis calculated for $C_{18}H_{14}O$: C: 87.78, H: 5.73.

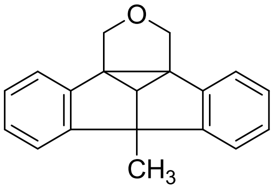
Found: C: 87.76, H: 5.72.

3.4.4. 2 Compound 31b

mp: 88-90 °C.

IR ν_{max} (KBr): 2834 (-C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.16-7.06 (m, 8H),



4.59 (d, 2H, *J* = 9.2 Hz), 4.32 (d, 2H, *J* = 8.8 Hz), 3.35(s, 1H), 1.81(s, 3H).

^{13}C NMR (CDCl$_3$): δ 151.79, 136.09, 126.59, 126.54, 122.33, 120.35, 68.88, 62.29, 57.60, 53.86, 18.70.

MS: *m/z* 260.

Elemental analysis calculated for $C_{19}H_{16}O$: C: 87.66, H: 6.19.

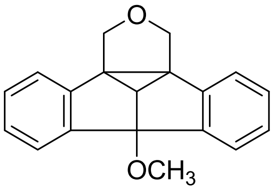
Found: C: 87.65, H: 6.17.

3.4.4. 3 Compound 31c

mp: 86-89 °C.

IR ν_{max} (KBr): 2852 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR (CDCl$_3$): δ 7.32-7.13 (m, 8H), 4.59 (d, 2H, *J* = 8.8 Hz) 4.35 (d, 2H, *J* = 8.8 Hz) 3.76 (s, 1H), 3.46 (s, 3H).



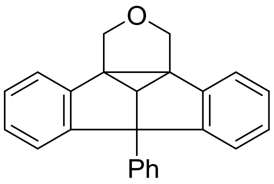
^{13}C NMR (CDCl$_3$): δ 147.26, 133.96, 127.74, 126.86, 122.52, 120.77, 96.19, 68.60, 58.98, 54.71, 53.39.

MS: *m/z* 276.

Elemental analysis calculated for $C_{19}H_{16}O_2$: C: 82.58, H: 5.84.

Found: C: 82.56, H: 5.82.

3.4.4. 4 Compound 31d



mp: 114-117 °C.

IR ν_{max} (KBr): 2832 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.42-7.09 (m, 13H), 4.63 (d, 2H, *J* = 8.8 Hz), 4.37 (d, 2H, *J* = 8.8 Hz), 3.42 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 150.13, 141.86, 136.51, 128.59, 128.54, 127.04, 126.87, 126.65, 123.18, 122.51, 68.74, 67.72, 64.87, 54.42.

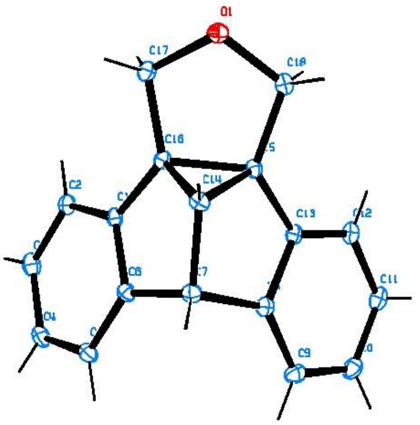
MS: *m/z* 322

Elemental analysis calculated for $C_{24}H_{18}O$: C: 89.41, H: 5.63.

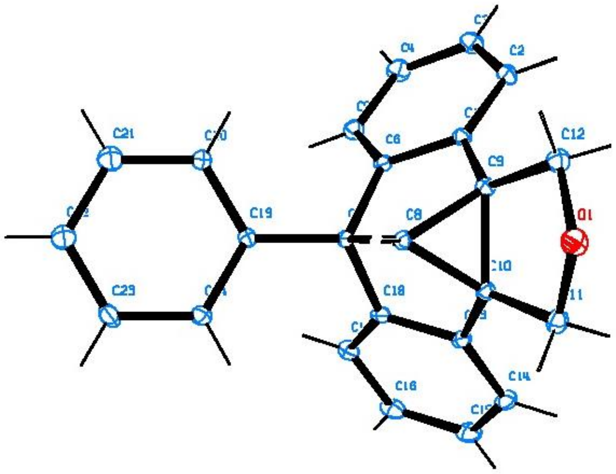
Found: C: 89.39, H: 5.61.

3.4.5. *ORTEP* diagrams of representative photoproducts

3.4.5.1 Compound 31a



3.4.5.2 Compound 31d



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CHAPTER 4

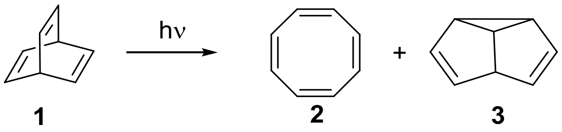
PHOTOCHEMICAL TRANSFORMATIONS OF TETHERED ESTERS

4.1. Abstract

Photochemical transformations of a few bridgehead-substituted tethered esters have been investigated. Irradiation of tethered dibenzobarrelenes in dry acetonitrile led to the formation of tethered dibenzocyclooctatetraenes and irradiation in dry acetone gave tethered dibenzosemibullvalenes. The regioselectivity in the formation of 4b- vs 8b-regioisomeric products was studied in the sensitized irradiation of phenyl bridge-head substituted tethered ester. Further, we have proposed a thermal mechanism for the hydrolysis of a tethered dibenzo-semibullvalene consisting of a methoxycyclopropane system.

4.2. Introduction

Zimmerman and Grunewald first reported the isomerization of barrelene in 1966.[1] Irradiation of 1-2% solutions of barrelene (**1**) with 3-8% acetone as the photosensitizer gave 25-40% of semibullvalene (**3**) and 1-2% of cyclooctatetraene (**2**) as shown in Scheme 4.1.

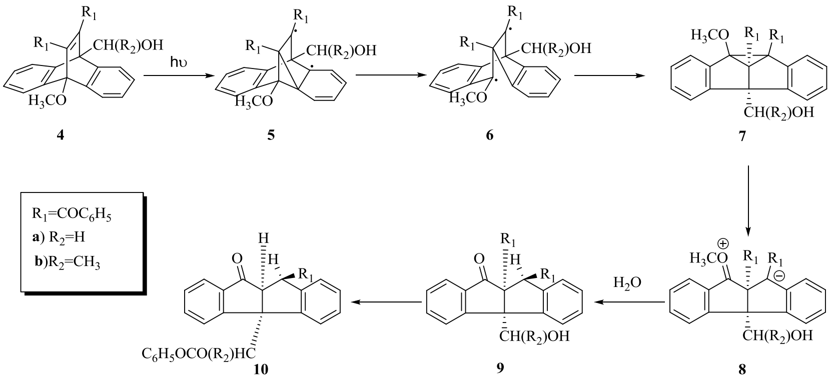


Scheme 4.1

There are various factors that govern the regioselectivity of di-π-methane rearrangement of dibenzobarrelenes to give the corresponding dibenzosemibullvalenes. According to Scheffer, steric crowding and electronic factors play an important role and the regioselectivity is mainly controlled by the relief of steric crowding in sterically crowded molecules like 9,10-ethenoanthracene derivatives that has been discussed in the previous chapter.

Various reports[2-4] suggest that primary photoproducts can be conveniently transformed into a variety of secondary photoproducts in a one pot reaction. For example, it has been reported that irradiation of 11,12-dibenzoyl-9,10-dihydro-9-(hydroxymethyl)-10-methoxy-9,10-ethenoanthracene (**4a**) and 11,12-dibenzoyl-9,10-dihydro-9-(1-hydroxy-ethyl)-10-methoxy-9,10-ethenoanthracene (**4b**) in methanol, acetone or benzene gives interesting dibenzopentalenones.

Irradiation of **4a** in methanol, acetone or benzene gives **10a** in 69-72% yields and irradiation of **4b** in benzene gives a mixture of products consisting of 41% of **10b** (Scheme 4.2). Bridgehead-unsymmetrically disubstituted barrelenes **4a**,**b** undergo di-π-methane rearrangement involving benzo-vinyl bridging leading to the diradical intermediates **5a**,**b**, which can subsequently get transformed to the regioisomeric semibullvalenes **7a**,**b** respectively. The ionic opening of the cyclopropyl ketone functionality in **7a**,**b** gives the zwitterionic intermediate **8a**,**b** which could then lead to the demethylated dibenzopentalene ketone **9a**,**b** through hydrolysis. Hydrolysis of **8a**,**b** is explained by the presence of adventitious water in the solvents used for irradiation. Since the hydroxymethyl and benzoyl groups in **9a** or **9b** are very close to each other, rearranged product **10a** or **10b** is formed by an aldol intermediate (Scheme 4.2).

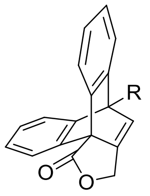


Scheme 4.2

From the above discussion it emerges that phototransformation of the compounds with restricted rotational freedom of the bridgehead methylene group like those we are dealing with is an exciting area of investigation. We have successfully introduced different substituents like methyl, methoxy and phenyl at the bridgehead position and studied the photorearrangements of these compounds.

4.3. Results and Discussion

A few tethered barrelenes **11** with different substituents at one of the bridgehead positions (Figure 4.1) were synthesized with a view to investigate the photochemical transformations of these compounds. Direct irradiation of **11** led to the formation of tethered cyclooctatetraene and sensitized irradiation led to the formation of tethered dibenzosemibullvalenes. With rigid cyclic systems, sensitized irradiation is the more efficient pathway and direct irradiation pathway is inefficient[5] for di-π-methane rearrangement. Through sensitized irradiation, we can investigate the effects of bridgehead-substituents in controlling the regioselectivity of photochemical transformations of tethered dibenzobarrelenes. Our motivation behind exploring the photochemistry of tethered barrelenes has already been discussed in previous chapters.



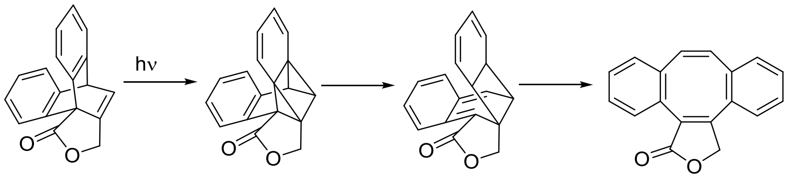
11

a) R=H **b**) R=CH_3 **c**) R=OCH_3 **d**) R=Ph

Figure 4.1

4.3.1. Direct irradiation of the tethered ester 11a

Irradiation of tethered barrelene **11a** in dry acetonitrile (253.7 nm) under argon atmosphere gave corresponding tethered cyclooctatetraene **14** (Scheme 4.3). Structure of **14** was identified on the basis of ^{1}H NMR spectra and literature precedence.[6]



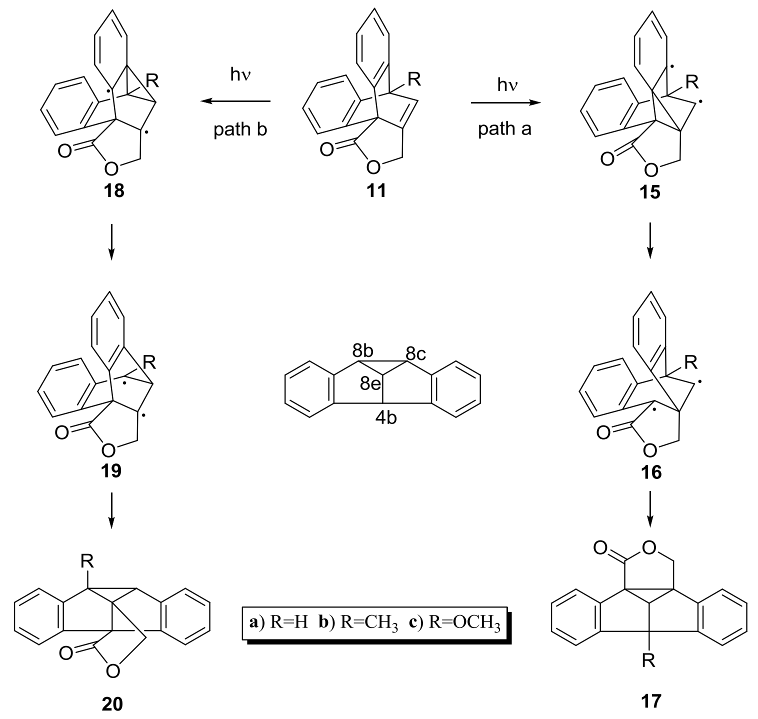
11a **12** **13** **14**

Scheme 4.3

On the basis of a comprehensive investigation of the direct irradiation of similar benzo and naphthobarrelene systems, it has been proposed that formation of dibenzocyclooctatetraene involves singlet excited states of dibenzobarrelenes and initial intramolecular [2+2] cycloaddtion. Thus direct irradiation of **11a** is assumed to proceed through initially formed [2+2] adduct **12** which is rearranged to **13** and finally to the tethered cyclooctatetraene **14** (Scheme 4.3).[7,8]

4.3.2. Sensitized irradiation of the tethered esters 11a-c

When tethered barrelenes **11a-c** in dry acetone were irradiated (253.7 nm) under argon atmosphere, mixtures of 4b- and 8b-substituted tethered semibullvalenes **17a-c** and **20a-c** were formed in near-quantitative yields (Scheme 4.4).



Scheme 4.4

Analysis of ^{1}H NMR spectra of the mixtures indicated the presence of both 4b- and 8b-regioisomers **17a-c** and **20a-c** in different ratios (Table 4.1).

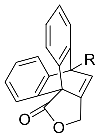
Irradiation of tethered ester	R	Percentage of 4b regioisomer	Percentage of 8b regioisomer
	H	50	50
	CH$_3$	40	60
	OCH$_3$	75	25

Table 4.1

Formation of semibullvalenes **17** and **20** in the photo-isomerization of compounds **11** could be rationalized by the pathway shown in Scheme 4.4, which is in agreement with the earlier reported mechanism for the barrelene rearrangement.[9] A benzo-vinyl bridging might lead to the diradical intermediates **15** and **18**, which were then transformed into the products **17** and **20** respectively.

The two regioisomers **17** and **20** were separated by column chromatography on silica gel. The structures of tethered semibullvalenes **17** have been established on the basis of analytical results and spectral data. The ^{1}H NMR spectrum of **17a** (Figure 4.2), for example showed two doublets at δ 4.96 and δ 4.63 due to geminal protons of the methylene group and two doublets at δ 4.58 (1H) and δ 3.88 (1H) which have been assigned to H^{4b} and H^{8e} protons respectively. The eight aromatic protons appeared as a multiplet from δ 7.04 to δ 7.44. The ^{1}H NMR spectrum of **17b** and **17c** showed a singlet due to three protons at δ 1.86 and δ 3.49, assigned to methyl and methoxy protons respectively.

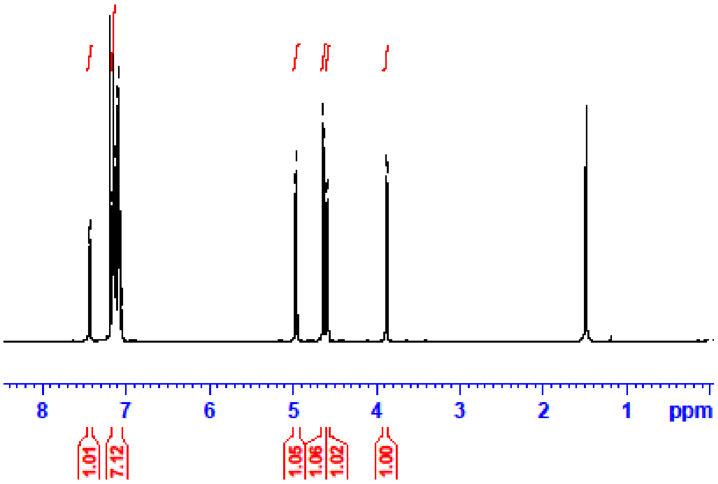


Figure 4.2 ^{1}**H NMR spectrum of 17a**

The ^{13}C NMR spectrum of **17a** (Figure 4.3) showed several signals at δ 170.72, 147.72, 146.47, 132.47, 130.94, 127.34, 126.72, 126.41, 126.10, 124.37, 121.88, 121.50, 120.82, 65.54, 58.26, 55.00, 52.79 and 50.11. Of these, the signal at δ 170.72 has been assigned to C=O group of the ester, whereas the signals from δ 120.82 to 147.72 were assigned to aromatic carbons. The aliphatic carbons appeared from δ 50.11-65.54. The ^{13}C NMR spectrum of **17b** and **17c** showed signals at δ 18.35 and around δ 53, assigned to methyl and methoxy carbons respectively.

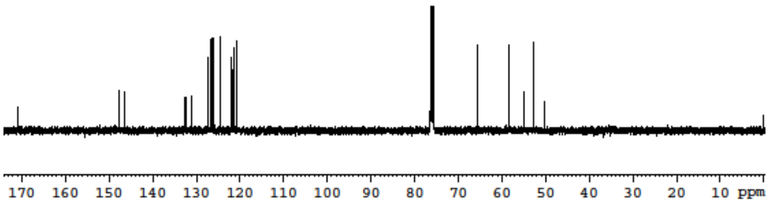


Figure 4.3 ^{13}C NMR spectrum of 17a

Structure of tethered semibullvalenes **20** has also been established on the basis of analytical results and spectral data. The ^{1}H NMR spectrum of **20a** (Figure 4.4), for example showed a singlet at δ 4.63 due to protons of the methylene group and a singlet at δ 3.36 which have been assigned to H^{8b} and H^{8c} protons. The eight aromatic protons appeared as a multiplet from δ 7.12 to δ 7.51. The ^{1}H NMR spectrum of **20b** showed a singlet due to three protons at δ 1.77, assigned to methyl protons.

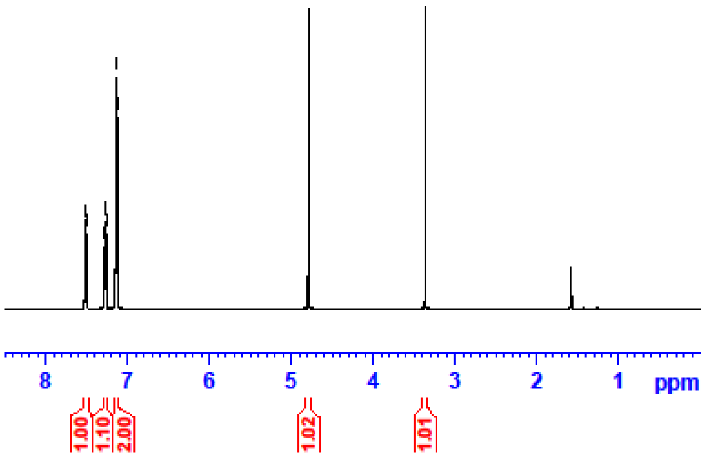


Figure 4.4 ^{1}H NMR spectrum of 20a

The ^{13}C NMR spectrum of **20a** (Figure 4.5) showed several signals at δ 173.79, 147.06, 136.63, 128.07, 127.20, 125.41, 120.87, 68.61, 67.5, 59.72. Of these, the signal at δ 173.79 has been assigned to C=O group of the ester, whereas the signals from δ 120.87 to 147.06 were assigned to aromatic carbons. The aliphatic carbons appeared in the range δ 59.72-68.61. The ^{13}C NMR spectrum of **20b** showed a signal at δ 14.92, assigned to methyl carbon.

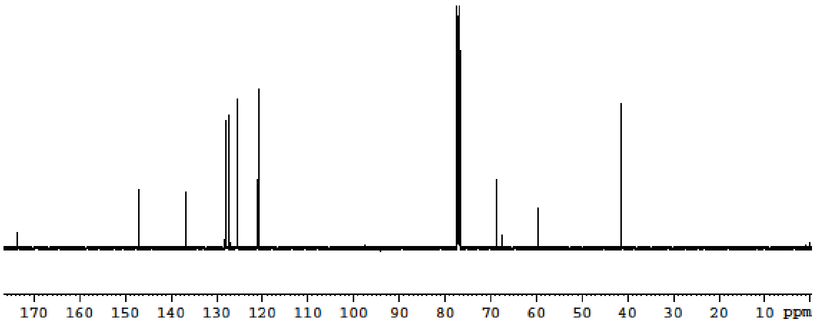


Figure 4.5 ^{13}C NMR spectrum of 20a

The carbonyl absorption of saturated δ-lactones[10] (six membered ring) occurs in the same region as straight-chain, unconjugated esters while saturated γ-lactones (five membered ring) absorb at high frequency. The C=O stretching vibration of **17a**, **17b**, **17c** and **17d** thus occurred at 1755 cm^{-1}, 1764 cm^{-1}, 1761 cm^{-1} and 1768 cm^{-1} respectively and the C=O stretching vibration of **20a** and **20b** occurred at 1756 cm^{-1} and 1771 cm^{-1} respectively.

4.3.3 Hydrolysis of 20c

We could isolate **17a-c** and **20a-b**, after column chromatography but we could not isolate **20c**. By comparing ^1H NMR signals of mixture of **17c** and **20c** (Figure 4.6) and ^1H NMR spectrum of pure **17c** which has been separated by column chromatography, we identified signals corresponding to **20c**. The ^1H NMR spectrum of **20c** showed two doublets at δ 4.87 (d, 1H, $J = 10$ Hz) and δ 4.77 (d, 1H, $J = 10$ Hz) due to geminal protons of the methylene protons and a singlet at δ 3.36 which has been assigned to H^{8c} proton. It also showed a singlet due to three protons at δ 3.69, assigned to methoxy protons.

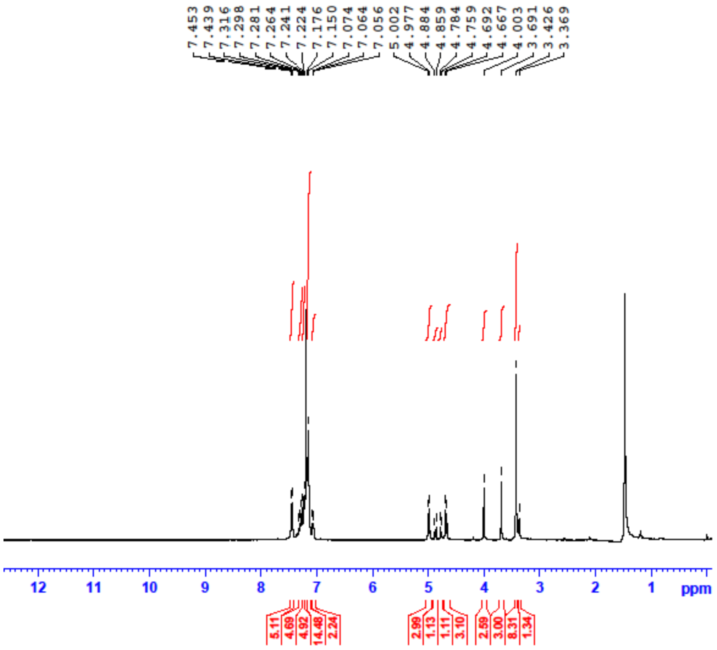
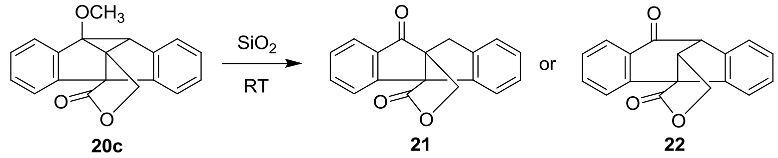


Figure 4.6 ^{1}H NMR spectrum of mixture of 17c and 20c

Earlier reports on analogous compounds[2-4] (as reported in Scheme 4.2) suggested that primary photoproduct formed by di-π-methane rearrangement underwent facile hydrolysis under photolytic conditions and hence it was nort possible to identify the primary photoproducts. In our studies we could identify the primary photoproduct formed by di-π-methane rearrangement after irradiation by comparing ^{1}H NMR spectrum of mixture. We also noted that **20c** underwent hydrolysis[11] during our attempts to separate the mixture of regioisomers by column chromatography on silica gel. Obviously, there are two possibilities in which **20c** could undergo hydrolysis (Scheme 4.5).



Scheme 4.5

The ^{1}H NMR spectrum of hydrolysis product (Figure 4.7) showed two doublets at δ 4.85 (d, 1H, J =10.4 Hz) and δ 4.46 (d, 1H, J =10.4 Hz) due to geminal protons and a multiplet of two protons from 3.42-3.49 (m, 2H). The eight aromatic protons appeared as a multiplet from δ 7.21 to δ 8.05. In the IR spectrum the C=O stretching vibration occurred at 1761 cm^{-1}.

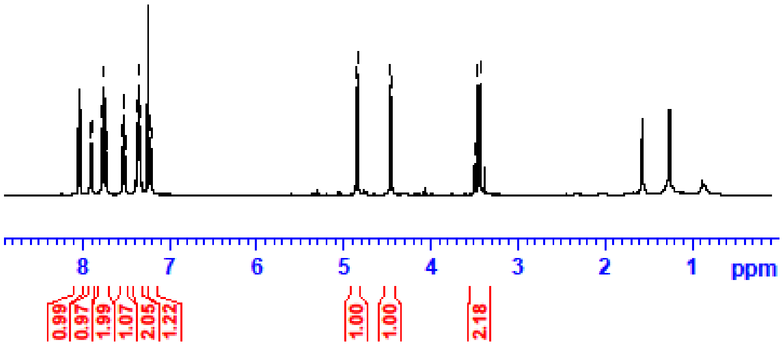


Figure 4.7 ^{1}H NMR spectrum of 21

The ^{13}C NMR spectrum of hydrolysis product (Figure 4.8) showed several signals at δ 204.55, 174.27, 151.40, 140.81, 138.29, 136.73, 134.51, 129.89, 129.70, 128.47, 125.50, 125.30, 125.02, 124.35, 73.76, 69.90, 63.13 and 40.00. Of these, the signal at δ 174.27 has been assigned to C=O group of the ester and the signal at δ 204.55 has been assigned to carbonyl carbon whereas the signals from δ 124.35 to 151.40

were assigned to aromatic carbons. The aliphatic carbons appeared from δ 73.76-40.00.

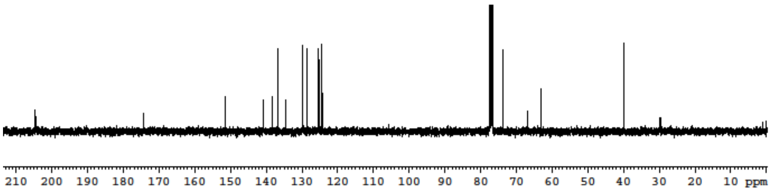


Figure 4.8 ^{13}C NMR spectrum of 21

From the ^{1}H NMR and ^{13}C NMR spectra, we could not distinguish between the hydrolysis products **21** and **22**. But DEPT 135 spectrum showed two downward peaks indicating two CH_2 groups in the compound which confirmed compound **21** as the hydrolysis product (Figure 4.9).

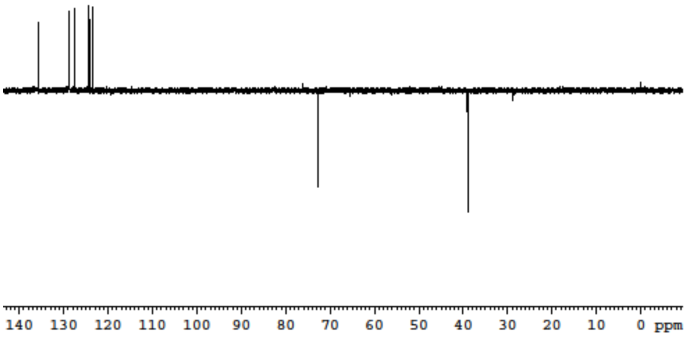
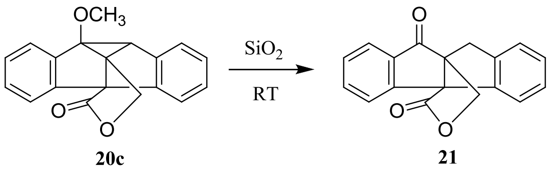


Figure 4.9 DEPT135 spectrum of 21

The acid hydrolysis of **20c** to **21** on the surface of the silica gel is depicted in the Scheme 4.6.



20c **21**

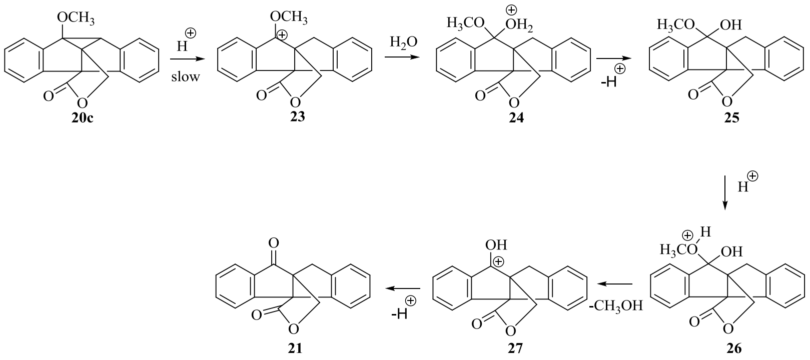
Scheme 4.6

4.3.4 Proposed mechanism for the hydrolysis

The methoxy group is not a good leaving group, and therefore such compounds must be converted to the conjugate acids before they are hydrolysed. Although 100% sulphuric acid and other concentrated strong acids are required for the ready cleavage of simple ethers, dilute acids are enough for the cleavage of acetals, enol ethers and similar compounds.[12]

Reactions in which leaving group does not come off until it has been protonated are called S_N1cA where cA stands for conjugate acid. Generally S_N1 reactions, that do not require powerful nucleophiles but do require good leaving groups take place under acidic conditions while S_N2 reactions, which require powerful nucleophiles (which are generally strong bases), take place under basic or neutral conditions. Therefore we propose S_N1cA mechanism for the hydrolysis of **20c.**

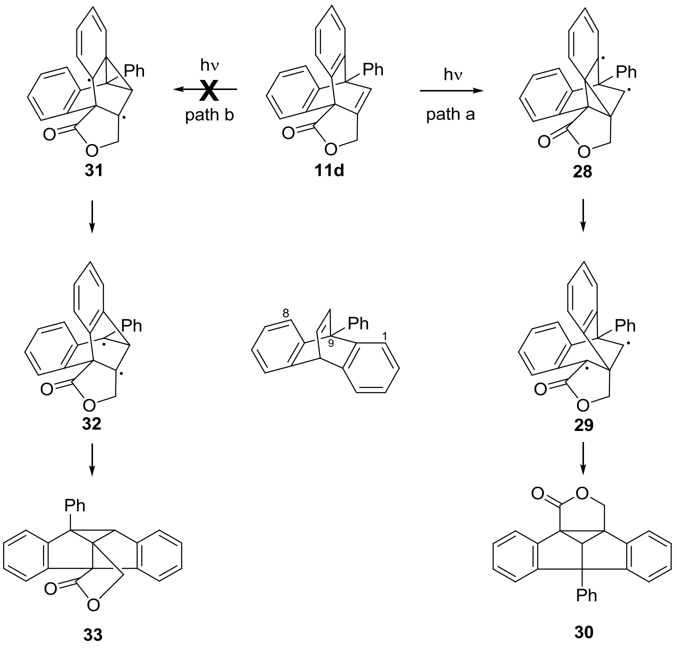
The compound **20c** underwent ready acid hydrolysis on the surface of the silica gel.[13-20] However, protonation does not take place at the oxygen but at the β-carbon,[21-27] giving rise to a stable carbocation[28] **23**, cleaving the cyclopropane ring. Rest of the mechanism is S_N1cA (Scheme 4.7) in which the leaving group OCH_3 has been protonated to give **26** before it comes out as methanol to give **27** followed by deprotonation to give the final hydrolysis product **21**.



Scheme 4.7

4.3.5 Sensitized irradiation of the tethered ester 11d

When tethered barrelene **11d** in dry acetone was irradiated (253.7 nm) under argon atmosphere, 4b-substituted tethered semibullvalenes **30** was formed as the only product (Scheme 4.8). Surprisingly, the 8b-substituted product **33** was not formed in this reaction. It may be recalled that barrelenes having a 9-aryl substituent and benzoyl or carbomethoxy substituents at the 11,12-positions have a strong tendency to yield the corresponding 8b-subtituted semibullvalens in their photo-rearrangement.[29,30] It is also worth mentioning in this context that barrelenes having strongly electron withdrawing groups such as cyano group as bridgehead substituents also yield the corresponding 8b-subtituted semibullvalene products.[31] Based on available data alone, we cannot unequivocally identify the variables controlling regioselectivity in the photrearrangement of tethered esters. However, we propose that the absence of a bulky substituent close to the phenyl group on the etheno bridge assumes a definite role in controlling the observed regioselectivity. The aryl group can now orient itself in a plane bisecting the dibenzobarrlene residue. This will minimize van der Waals interaction between ortho hydrogens of the 9-aryl substituent and hydrogens at 1 and 8 positions of the dibenzobarrelene residue. Under these circumstances, electronic factors assume prominence and hence the electronegative carbonyl group of the lactone residue will direct regioselectivity towards the generation of lactone **30**. In contrast, presence of methyl and methoxyl substituents at the bridgehead position will create adverse van der Waals interaction with the hydrogens at the 1- or 8-positions of the dibenzobarrelene residue. On the other hand, the planar carbonyl group will not exert analogous steric crowding with these hydrogens. Hence, steric factors as well as electronic factors have decisive roles to play in controlling regioselectivity in barrelenes such as **11b,c**. We have collected single crystal XRD data in support of these arguments.



Scheme 4.8

4.3.6. Conclusion

Regioselectivity observed in the phototransformations of ester thjethed barrelenes is expected on the basis of electronic and steric factors. Unusual regioselectivity exhibited by bridge-head aryl substituted tethered ester could be expalined in terms of the unique geometry of the molcule and orientation of the bridge-head aryl substituent.

Further, we have proposed a mechanism involving a stable carbocation followed by S_N1cA mechanism for the hydrolysis of **20c**.

4.4. Experimental Section

4.4.1. General Techniques

All reactions were carried out utilizing oven dried glasswares. Except otherwise specified, all the solvents were used directly without any further purification. When further purification was needed, known methods and procedures were followed in each case. All the reagents were purchased from either *Sigma-Aldrich* or *Spectrochem Chemicals* and were used without further purification. Progress of the reaction and chromatographic separations were monitored by dried silica gel TLC plates (Aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was achieved by exposure to UV lamp or iodine vapours. Separation and purification of compounds were done by column chromatography using silica gel (*Spectrochem Chemicals*, 60-120 mesh). The products were further purified by recrystallization from suitable solvent systems. Solvent eluted from the column chromatography was concentrated using *Heidolph, IKA or Buchi* rotary evaporators. Melting points were determined on a *Neolab* melting point apparatus and are uncorrected. Infra-red spectra were recorded by means of *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ^{1}H and ^{13}C NMR spectra were recorded using 400 MHz *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario*

EL III). Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A*, *Mass-5975C*).

4.4.2. Direct irradiation

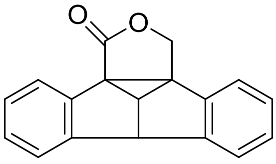
Acetonitrile was purified and distilled before use[32] and oxygen was purged by passing a steady flow of argon through the solution for 30 min prior to the irradiation. The degassed solution of **19a** (50 mg) was dissolved in dry acetonitrile (150 ml) and irradiated with 253.7 nm lamp under argon atmosphere for 8 h using Rayonet photochemical reactor to give **20**. Structure was identified on the basis of ^{1}H NMR spectra and literature precedence.[6]

4.4.3. General procedure for sensitized irradiation

Acetone was purified and distilled[32] and oxygen was purged by passing a steady flow of argon through the solution for 30 min prior to the irradiation. The degassed solution of **19** (50-70 mg) were dissolved in dry acetone (150-170 mL) and irradiated with 253.7 nm lamp under argon or nitrogen atmospheres (25-35 min) using Rayonet photochemical reactor. In this reaction acetone works as a sensitizer. Progress of the reaction was monitored by TLC. After the reaction, the solvent was removed under vacuum. The ^{1}H NMR spectra of the residue were recorded to get an approximate idea about the product composition. The residual solid was chromatographed on silica gel and eluted with dichloromethane and hexane to separate the products, which were finally purified by recrystallization from suitable solvents.

4.4.4. Spectral and analytical data of novel compounds

4.4.4. 1 Compound 17a



mp: 214-217 °C.

IR ν_{max} (KBr): 1755 (C=O stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.44-7.04 (m, 8H), 4.96 (d, 1H, *J* = 10 Hz), 4.63 (d, 1H, *J* = 10 Hz), 4.58 (d, 1H, *J* = 6 Hz), 3.88 (d, 1H, *J* = 5.6 Hz).

^{13}C NMR ($CDCl_3$): δ 170.72, 147.72, 146.47, 132.47, 130.94, 127.34, 126.72, 126.41, 126.10, 124.37, 121.88, 121.50, 120.82, 65.54, 58.26, 55.00, 52.79, 50.11.

MS: *m/z* 260.

Elemental analysis calculated for $C_{18}H_{12}O_2$: C: 83.06, H: 4.65.

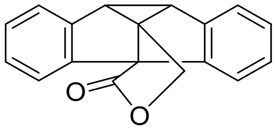
Found: C: 83.05, H: 4.63.

4.4.4. 2 Compound 20a

mp: 250-253 °C.

IR ν_{max} (KBr): 1756 (C=O stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.51-7.12 (m,



8H), 4.78 (s, 2H), 3.36 (s, 2H).

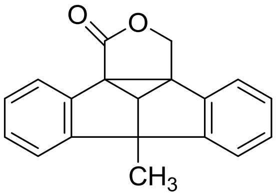
^{13}C NMR (CDCl$_3$): δ 173.79, 147.06, 136.63, 128.07, 127.20, 125.41, 120.87, 68.61, 67.50, 59.72.

MS: *m/z* 260.

Elemental analysis calculated for $C_{18}H_{12}O_2$: C: 83.06, H: 4.65.

Found: C: 83.04, H: 4.64.

4.4.4. 3 Compound 17b



mp: 217-220 °C.

IR ν_{max} (KBr): 1764 (C=O stretch), 2866 (-C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR (CDCl$_3$): δ 7.49-7.14 (m, 8H), 5.05 (d, 1H, *J* =10 Hz), 4.71 (d, 1H, *J* =10 Hz), 3.68 (s, 1H), 1.86(s, 3H).

^{13}C NMR (CDCl$_3$): δ 171.75, 151.66, 150.59, 133.25, 131.63, 128.31, 127.69, 127.49, 127.14, 125.05, 122.61, 120.80, 120.10, 66.60, 64.64, 58.83, 55.35, 50.70, 18.35.

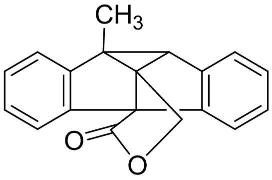
MS: *m/z* 274

Elemental analysis calculated for

$C_{19}H_{14}O_2$: C: 83.19, H: 5.14.

Found: C: 83.17, H: 5.12.

4.4.4. 4 Compound 20b



mp: 201-204 °C.

IR ν_{max} (KBr): 1771 (C=O stretch), 2964 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.53-7.11 (m, 8H), 4.73 (s, 2H), 3.09 (s, 1H), 1.77 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 172.93, 145.88, 145.53, 138.77, 136.76, 127.06, 126.85, 126.26, 125.95, 124.39, 123.32, 119.87, 119.75, 66.25, 65.48, 62.58, 45.80, 45.12, 14.92.

MS: *m/z* 274

Elemental analysis calculated for

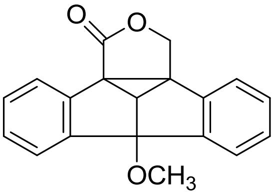
$C_{19}H_{14}O_2$: C: 83.19, H: 5.14.

Found: C: 83.17, H: 5.12.

4.4.4. 5 Compound 17c

mp: 178-181 °C.

IR ν_{max} (KBr): 1761 (C=O stretch), 2925



(C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.52-7.21 (m, 8H), 5.06 (d, 1H, *J* =10.4 Hz), 4.75 (d, 1H, *J* =10.4 Hz) 4.07 (s, 1H), 3.49 (s, 3H).

^{13}C NMR ($CDCl_3$):- δ 170.71, 146.78, 146.35, 131.24, 129.65, 128.71, 128.54, 128.38, 127.92, 125.21, 122.73, 121.22, 120.61, 96.92, 66.43, 61.68, 55.04, 53.76, 50.69.

MS: *m/z* 290.

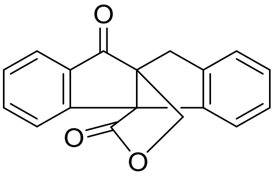
Elemental analysis calculated for $C_{19}H_{14}O_3$: C: 78.61, H: 4.86.

Found: C: 78.59, H: 4.84.

4.4.4. 6 Compound 21

mp: 148-151 °C.

IR ν_{max} (KBr): 1761(C=O stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).



^{1}H NMR ($CDCl_3$): δ 8.05-7.21 (m, 8H), 4.85 (d, 1H, *J* =10.4 Hz), 4.46 (d, 1H, *J* =10.4 Hz), 3.42-3.49 (m, 2H).

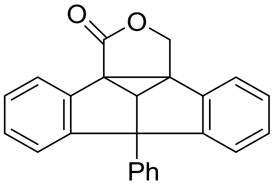
^{13}C NMR ($CDCl_3$): δ 204.55, 174.27, 151.40, 140.81, 138.29, 136.73, 134.51, 129.89, 129.70, 128.47, 125.50, 125.30, 125.02, 124.35, 73.76, 66.90, 63.13, 40.00.

MS: *m/z*. 276

Elemental analysis calculated for $C_{18}H_{12}O_3$: C: 78.25, H: 4.38.

Found: C: 78.23, H: 4.36.

4. 4.4. 7 Compound 30



mp: 138-141 °C.

IR ν_{max} (KBr): 1768 (C=O stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.58-6.79 (m, 13H), 4.74 (d, 1H, *J* =10 Hz), 4.62 (d, 1H, *J* =10 Hz), 3.80 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 173.93, 147.94, 146.70, 140.63, 137.10, 130.34, 129.04, 128.27, 128.08, 128.00, 127.53, 127.40, 126.09, 125.77, 121.06, 120.71, 66.77, 64.68, 55.71, 44.43, 31.26.

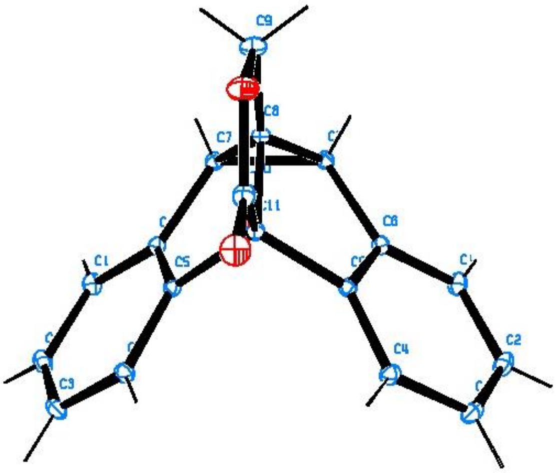
MS: *m/z* 336.

Elemental analysis calculated for $C_{24}H_{16}O_2$: C: 85.69, H: 4.79.

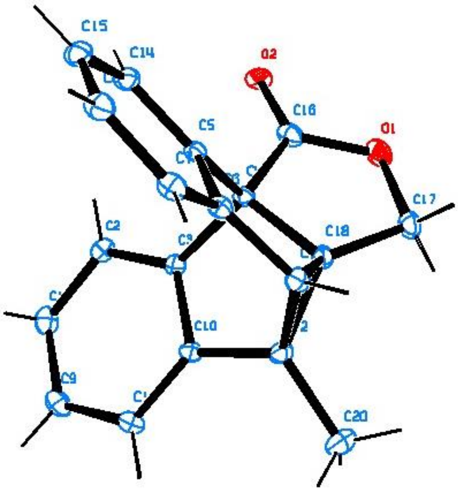
Found: C: 85.67, H: 4.77.

4.4.5. *ORTEP* diagrams of novel compounds

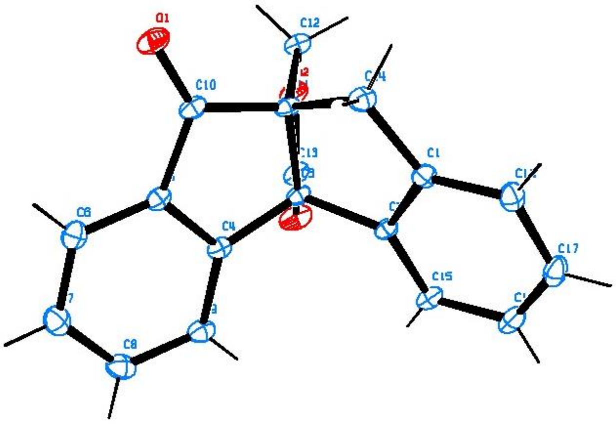
4.4.5.1 Compound 20a



4.4.5.2 Compound 20b



4.4.5.3 Compound 21



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CHAPTER 5

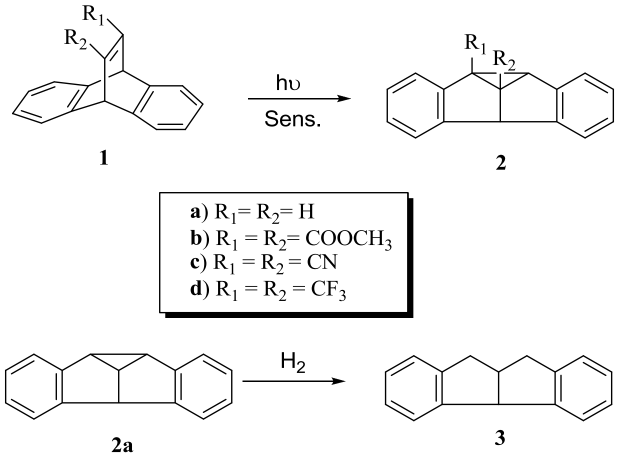
Di-π-METHANE REARRANGEMENT OF A FEW TETHERED SULFIDES AND A TETHERED SULFONE

5.1. Abstract

In this chapter, we describe our findings on the triplet-mediated phototransformations of a few bridgehead-substituted tethered sulfides and one sulfone. Irradiation of tethered sulfides in dry acetone gave a mixture of 4b- and 8b-substituted tethered dibenzosemibullvalenes while irradiation of tethered sulfone analogue gave exclusively the corresponding 8b-substituted tethered dibenzosemibullvalene.

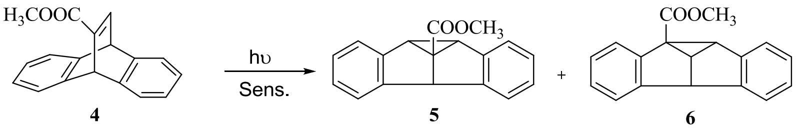
5.2. Introduction

Di-π-methane rearrangement[1] of bridgehead-substituted dibenzobarrelenes was first reported by Ciganek[2] in 1966. He observed that irradiation of dibenzobicyclo[2.2.2]octatriene (**1a)** in acetone gave dibenzotricyclo[3.3.0.0]octadiene (**2a)** in 85% yield (Scheme 5.1). Structure of **2a** was confirmed by converting it to the known dibenzobicyclo[3.3.0]octadiene (**3)** by catalytic hydrogenation.



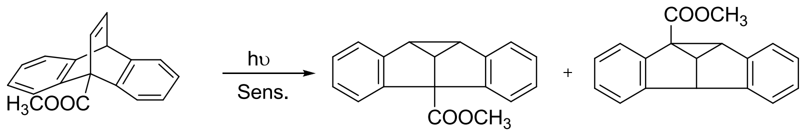
Scheme 5.1

Unsensitized photolysis of **1a** in benzene also gave **2a** in a very slow rate owing to inefficient intersystem crossing efficiency. On the other hand, the derivatives **1b-d** rearranged fairly rapidly in benzene or cyclohexane to give **2b-d**. However, acetone sensitisation proved to be more convenient for preparative purposes. Inspection of the NMR spectrum of the crude products showed the presence only single isomers **2b-d** with substituents R_1 and R_2 appearing on adjacent carbons. These dibenzobarrelenes **1a-d** are symmetrical, but different vinylic substituents would make them unsymmetrical. Ciganek showed that irradiation of unsymmetric dibenzobicyclo[2.2.2]octatriene **4** resulted in the formation of two regioisomers in 75% yield (Scheme 5.2).



Scheme 5.2

Presence of different groups at the bridgehead positions also could make the dibenzobarrelene unsymmetrical and their photorearrangement can lead to regiosmeric semibullvalenes. Indeed, irradiation of 1-methoxycarbonyl-dibenzobicyclo[2.2.2]octatriene (**7**) gave a mixture of the regioisomers **8** and **9** (ratio 2:1) in 91% yield (Scheme 5.3).

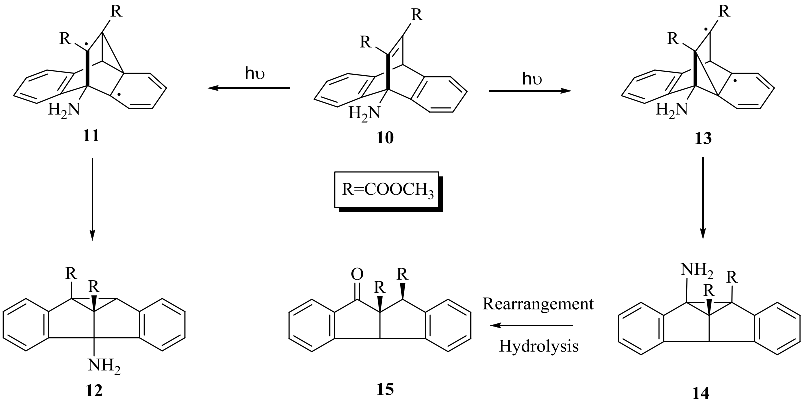


7 **8** **9**

Scheme 5.3

Later it was found that these types of rearrangements could be described by di-π-methane rearrangements and extensive studies have been carried out on different aspects of the rearrangements. Soon it was realized that initially generated semibullvalens can undergo further transformations to give other products either as secondary photoproducts or due to subsequent dark reactions. In some cases, origin of such secondary products remained unclear.

Anna D. Gudmundsdottir,[3] for example, reinvestigated the photolysis of the diester dimethyl-9-amino-9,10-dihydro-9,10-ethenoanthracene-11,12-di-carboxylate (**10**) which was earlier reported by Paddick *et al.*[4] to undergo conversion to the keto-diester **15** along with dibenzosemibullvalene **12** on irradiation in acetone. Paddick suggested that as a result of di-π-methane rearrangement semibullvalene **14** was formed which on rearrangement, presumably through γ-hydrogen abstraction in the excited state followed by ring opening and hydrolysis to give **15**. Careful reinvestigation of the irradiation of **10**, however, gave a different picture. GC analysis of the photolysate showed that semibullvalenes **14** and **12** were formed in a 7:3 ratio and no rearranged product **15** was detected. It was further confirmed that compounds **14** and **12** are sufficiently stable to be isolated. Independent irradiation of **14** resulted in no noticeable change ruling out a photochemical route for the transformation of **14** to**15**. When silica gel column chromatography was attempted, compound **12** could be isolated but compound **14** was converted into the keto-diester **15**. Solid-state irradiation of crystals of **11** also resulted in the formation of **14** and **12** in the ratio 86:14 and no rearranged product **15** could be detected. Based on these results, it was confirmed that transformation of **14** to **15** is through a dark reaction sequence.

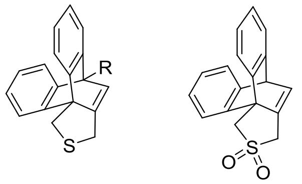


Scheme 5.4

From the above discussions, it is clear that photochemical transformations of unsymmetrical dibenzobarrelenes may lead to the formation of a mixture of regioisomers through di-π-methane rearrangement. As discussed in Chapters 3 and 4, several attempts have been made to identify the factors controlling regioselectivity in the photoransformations of unsymmetrically substituted semibullvalnes. In this context, we examined triplet-mediated transformations of a few unsymmetrical tethered sulfides and a sulfone and our findings are discussed in this chapter. We undertook this investigation to address three questions: a) what kind of regioslectivity is observed with tethered sulfides and sulfone, b) can we establish a structure-activity relationship (as far as control of regioselectivity is concerned) for these tethered barrelenes, and c) what role does the electronic environment around sulphur play in controlling the regioselectivity?

5.3. Results and Discussion

Di-π-methane rearrangement of a few bridgehead-substituted tethered barrelenes **16a-d** and **17** (Figure 5.1) was studied. In the case of **16**, a sulfide linkage acts as the tether while in **17**, sulfone linkage is the tether. Sensitized irradiation of both **16** and **17** led to the formation of the corresponding tethered dibenzosemibullvalenes. It may be mentioned here that di-π-methane rearrangement is possible through both singlet and triplet excited manifolds. As we are dealing with rigid cyclic systems, triplet-mediated pathway is significant[5] in the case of di-π-methane rearrangement.



16 **17**

a) R=H **b**) R=CH_3 **c**) R=OCH_3 **d**) R=Ph

Figure 5.1

5.3.1. Sensitized irradiation of tethered sulfides 16a-c

When tethered barrelenes **16a-c** in dry acetone were irradiated (254 nm) under argon atmosphere, mixtures of 4b-substituted tethered semibullvalenes **18a-c** and 8b-substituted tethered semibullvalenes **19a-c** were formed in high yield (Scheme 5.5).

The ^1H NMR chemical shifts of the mixtures indicated the presence of both 4b- and 8b-regioisomers **18a-c** and **19a-c** in nearly equal amounts (Table 5.1). Owing to the non-volatile nature of products, GC-MS analysis data of product mixture was deemed unreliable.

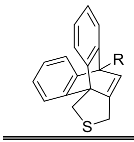
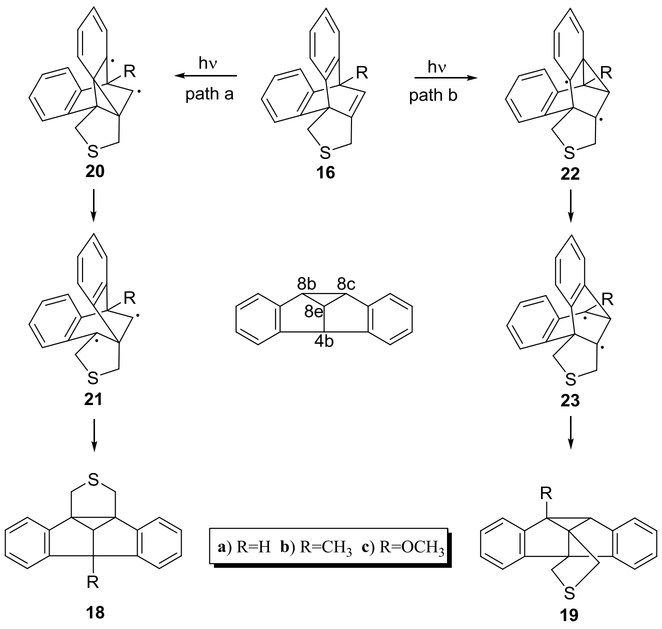
Irradiation of tethered sulfide	R	Percentage of 4b regioisomer	Percentage of 8b regioisomer
 R S	H	55	45
	CH_3	50	50
	OCH_3	45	55

Table 5.1

Formation of semibullvalenes **18** and **19** in the photoisomerization of **16** could be rationalized by the pathway shown in Scheme 5.5, which is in agreement with the earlier reported mechanism for the barrelene-semibullvalene rearrangement.[6]



Scheme 5.5

A benzo-vinyl bridging might lead to the diradical intermediates **20** and **22**, which were then transformed into the products **18** and **19** respectively. Inset shows numbering scheme adopted for dibenzosemibullvalenes.

The two regioisomers **18** and **19** were separated by column chromatography (silica gel). The structures of tethered semibullvalenes **18** have been established on the basis of analytical results and spectral data. ^{1}H NMR spectrum of **18a** (Figure 5.2), for example showed two doublets at δ 3.85 and δ 3.19, assigned to methylene protons and two doublets at δ 4.45 (1H) and δ 3.85 (1H) which have been assigned to H^{4b} and H^{8e} protons respectively. The eight aromatic protons appeared as a multiplet from δ 6.96 to δ 7.12. In addition, ^{1}H NMR spectrum of **18b** and **18c** showed a singlet due to three protons at δ 1.74 and δ 3.44, assigned to methyl and methoxy protons respectively.

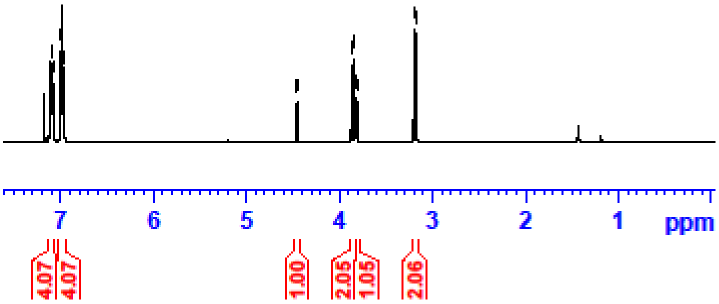


Figure 5.2 ^{1}H NMR spectrum of 18a

The ^{13}C NMR spectrum of **18a** (Figure 5.3) showed several signals at δ 148.81, 137.24, 125.71, 125.40, 122.00, 120.77, 54.82, 54.24, 51.94, 31.81. Of these, the signals from δ 120.77 to 148.81 were assigned to aromatic carbons whereas the aliphatic carbons appeared from δ 31.81-54.82. ^{13}C NMR spectrum of **18b** and **18c** showed a signal at δ 17.61 and δ 95.70 respecively, assigned to methyl and methoxy carbons present in them.

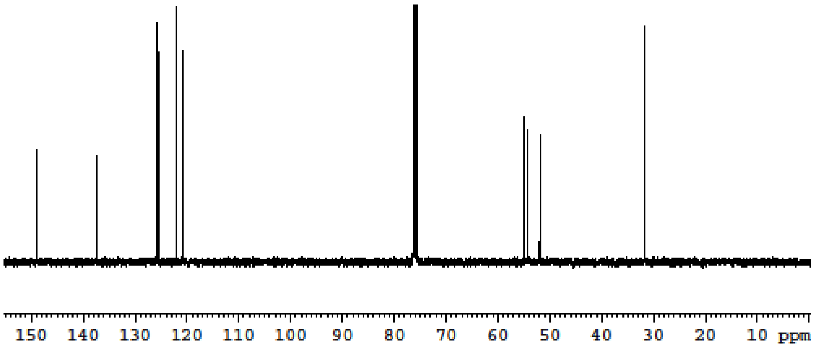


Figure 5.3 ^{13}**C NMR spectrum of 18a**

The structures of tethered semibullvalenes **19** have been established on the basis of analytical results and spectral data. ^{1}H NMR spectrum of **19a** (Figure 5.4) for example, showed singlets at δ 3.51, 3.19 and δ 3.15 due to protons of the methylene groups, H^{8b} and H^{8c} protons. The eight aromatic protons appeared as a multiplet from δ 6.88 to δ 7.23. ^{1}H NMR spectrum of **19b** showed a singlet due to three protons at δ 1.66, assigned to methyl protons.

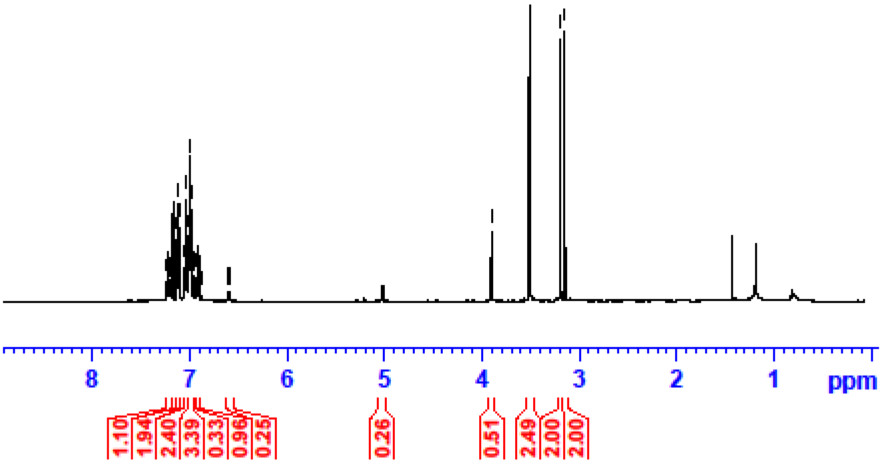


Figure 5.4 ^{1}**H NMR spectrum of 19a**

^{13}C NMR spectrum of **19a** (Figure 5.5) showed several signals at δ 149.38, 137.61, 125.99, 125.62, 123.77, 118.85, 74.91, 71.27, 50.63, 40.88, 36.45 and 33.49. Of these, the signals from δ 118.85 to 149.38 were assigned to aromatic carbons, whereas the aliphatic carbons appeared from δ 33.49-71.27. In the ^{13}C NMR spectrum of **19b**, the methyl carbon appeared at δ 15.59.

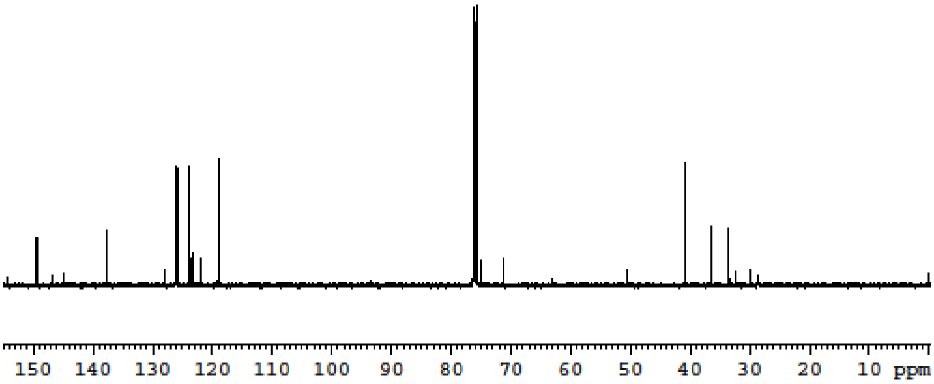


Figure 5.5 ^{13}C NMR spectrum of 19a

5.3.2 Hydrolysis of 19c

After column chromatography, though we could isolate **18a-c** and **19a-b,** we could not isolate **19c**. By comparing ^{1}H NMR spectrum of mixture of **18c** and **19c** (Figure 5.6) and ^{1}H NMR spectrum of pure **18c** (inset of Figure 5.6) isolated by column chromatography, we could identify the NMR signals corresponding to **19c**. ^{1}H NMR spectrum of **19c** showed peaks at δ 3.38 and δ 3.57 to δ 3.66, assigned to methylene protons and a peak at δ 3.32 which has been assigned to H^{8c} proton. It also showed a peak due to three protons at δ 3.69, assigned to methoxy protons.

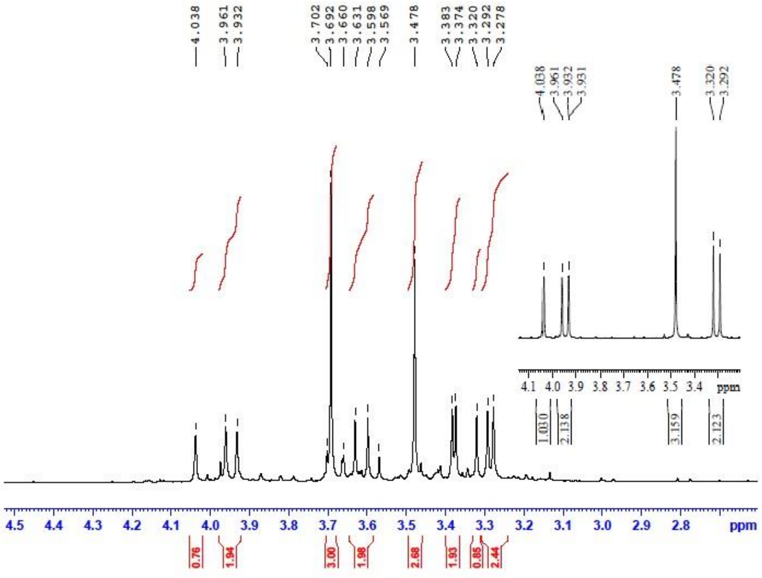
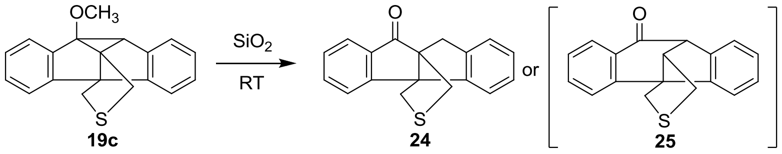


Figure 5.6 ^{1}H NMR spectrum of mixture of 18c and 19c

Earlier reports[4,7,8] of similar compounds suggested that primary photoproduct formed by di-π-methane rearrangement undergoes hydrolysis under photolytic conditions and the primary photoproduct could not be isolated. We could identify the primary photoproduct formed by di-π-methane rearrangement after irradiation by carefully studying ^{1}H NMR spectrum of mixture. However, when column chromatography on silica gel was attempted for separation of the regioisomers, **19c** underwent hydrolysis[9] (See Scheme 5.4). This type of hydrolysis in the case of a molecule like **19c** could be accompanied by the cleavage of either of the C—C bonds of the cycloprapane ring leading to two different products (Scheme 5.6).



Scheme 5.6

The ^1H NMR spectrum of hydrolysis product obtained (Figure 5.7) showed doublets at δ 3.50 (d, 1H, *J* = 12Hz) and δ 2.99 (d, 1H, *J* = 12Hz) due to geminal protons and multiplets of two protons from 3.39-3.45 (m, 2H) and 3.15-3.27 (m, 2H). The eight aromatic protons appeared as a multiplet from δ 7.09 to δ 7.77. In the IR spectrum the C=O stretching vibration occurred at 1694 cm^{-1}.

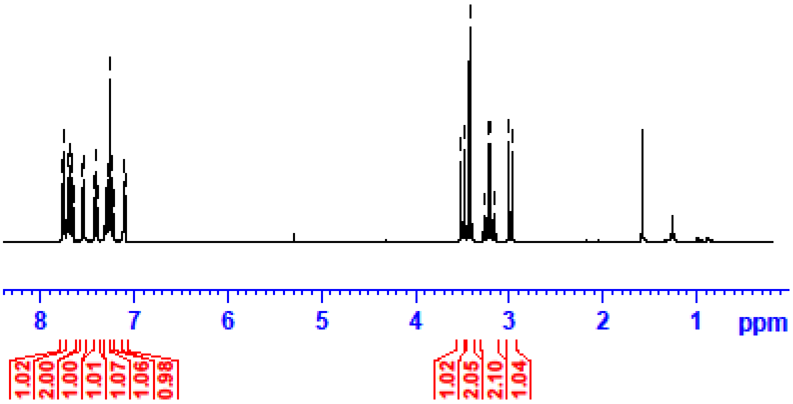


Figure 5.7 ^1H NMR spectrum of 24

The ^{13}C NMR spectrum of hydrolysis product (Figure 5.8) showed several signals at δ 206.64, 156.39, 143.68, 140.24, 135.13, 127.43, 126.91, 124.45, 123.07, 122.94, 122.72, 71.85, 71.76, 44.16, 40.51 and 38.57. Of these, the signal at δ 206.64 has been assigned to carbonyl carbon whereas the signals from δ 122.72 to 156.39 were assigned to aromatic carbons. The aliphatic carbons appeared from δ 38.57-71.85.

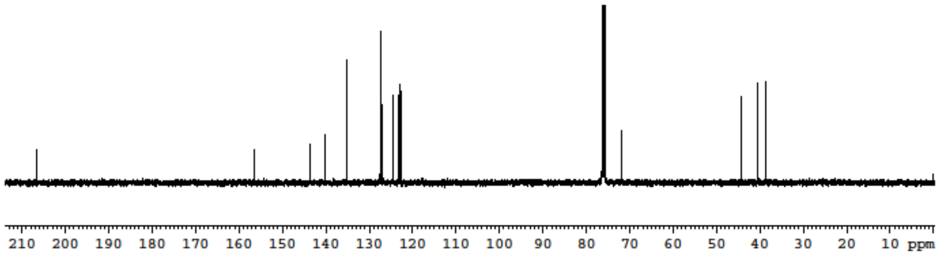


Figure 5.8 ^{13}C NMR spectrum of 24

From the ^{1}H NMR and ^{13}C NMR spectra alone, we could not distinguish between **24** and **25**. DEPT-135 analysis showed negative peaks indicating the presence of three CH_2 groups in the compound which confirmed that **24** is the hydrolysis product (Figure 5.9).

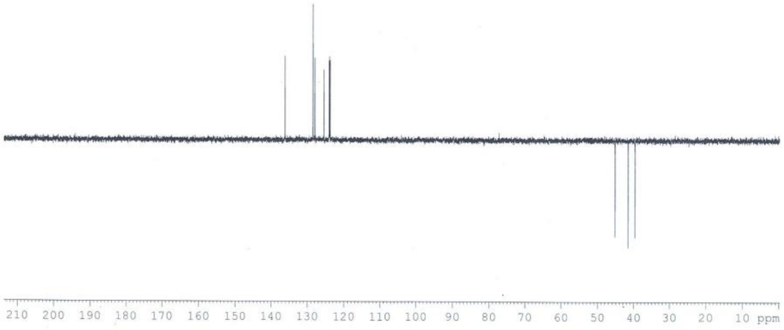


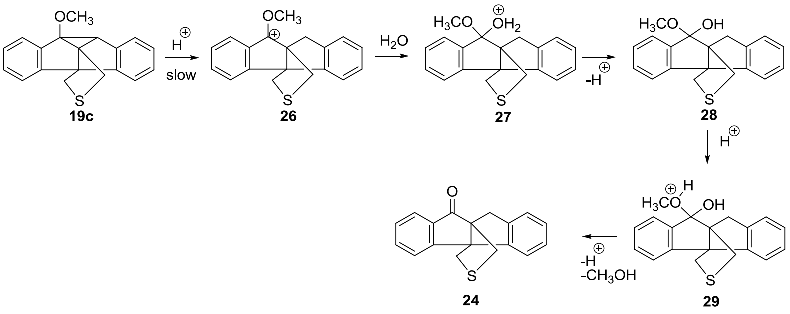
Figure 5.9 DEPT-135 specrum of 24

5.3.3 Proposed mechanism for the hydrolysis

Hydrolysis of **19c** to give **24** can be explained by S_N1cA mechanism (Scheme 5.7), similar to that discussed in Chapter 4 of this thesis.

As S_N1 reactions which involve good leaving groups take place under acidic conditions and S_N2 reactions, which require powerful nucleophiles take place under basic or neutral conditions, we suggest S_N1cA mechanism for the hydrolysis of **19c**.[10]

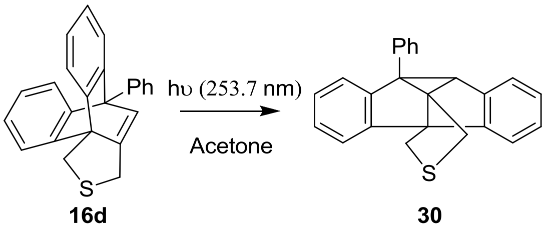
Compound **19c** underwent ready acid hydrolysis on the surface of the silica gel,[11-18] the rate determining step is the protonation of the substrate. Nevertheless, protonation did not take place at the oxygen but at the *β*-carbon,[19-25] because that gave rise to a stable carbocation[26] **26**, cleaving the cyclopropane ring. After that the mechanism was S_N1cA (scheme 5.7) in which the leaving group OCH_3 has been protonated to give **29.** Then it came off as methanol to obtain **30** which on deprotonation resulted in the hydrolysis product **24**.



Scheme 5.7

5.3.4. Sensitized irradiation of the tethered sulfide 16d

When tethered barrelene **16d** was irradiated in dry acetone (254 nm) under argon atmosphere, 8b-substituted tethered semibullvalenes **30** was generated as the only product (Scheme 5.8). Generation of **30** is explained in terms of path b shown in Scheme 5.5. Earlier reports[27,28] predict exclusive formation of 8b-regioisomer **30** with phenyl bridgehead substituent and we also observed the same outcome. The structure of tethered semibullvalenes **30** has been established on the basis of analytical results and spectral data.



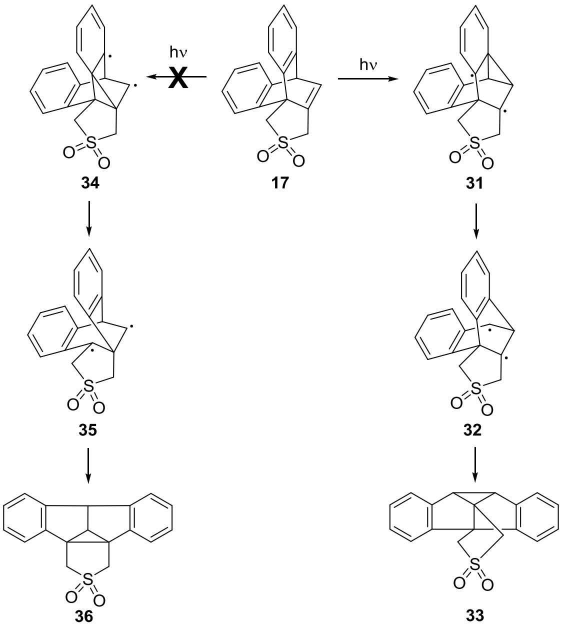
Scheme 5.8

Based on our findings on the irradiation of **16**, it appears that the tetrahydrothiophene tether exerts some control over the initial cyclopropyl diradial generation in di-π-methane rearrangement. It is well known that bridgehead methyl and methoxy substituents direct initial bridging to facilitate the generation of 4b-substituted semibullvalene. Consequently, irradiation of 1**6a**,**b** is expected to generate **18a**,**b** preferentially over **19a**,**b**. But the opposite trend is observed here. Intriguingly, with **16d,** exclusive generation of **18d** is in line with literature precedence. Based on these conflicting trends, we conclude that justifying regioslectivity in barrelene to semibullvalene rearrangement in terms of electronic and steric factors as given in literature is not fully palatable. Identifying the controlling factors here needs deeper scrutiny. As a first step, we collected the molecular structure of **16** by single crystal X-ray diffraction analysis. Though we tried to correlate structure with observed selectivity in the same lines reported by Scheffer etal, we could not arrive at an acceptable conclusion. Detailed theoretical calculations may shed some light on the factors controlling regioselectivity in these rearrangements. We suggest close examination of all possible intermediates involved in the generation of 4b- and 8b-substituted semibullvalenes by theoretical means to arrive at a more acceptable conclusion.

We anticipated possible electron transfer from sulphur atom to the barrelene excited state as a possible excited state pathway for barrelenes containing thioether tether. Efficient photorerrangement of **16** to give semibullvalenes **18**/**19** in near quantitative amounts rules out electron transfer possibility. This observation, in turn, suggests electron rich nature of the excited state of **16**.

5.3.5. Sensitized irradiation of the tethered sulfone

When tethered sulfone **17** was irradiated in dry acetone (254 nm) under argon, it led to the exclusive formation of 8b-substituted tethered semibullvalene **33** (Scheme 5.9).



Scheme 5.9

The formation of semibullvalenes **36** and **33** in the photoisomerization of compounds **17** could be rationalized by the pathway shown in Scheme 5.9, which is in agreement with the earlier reported mechanism for the barrelene rearrangement. A benzo-vinyl bridging might lead to the diradical intermediates **34** and **31**, which were then transformed into the products **36** and **33**, respectively. The structure of tethered semibullvalenes **33** has been established on the basis of analytical results and spectral data.

It is interesting to note that the sulfone tether exerts definite control in deciding the regioselectivity in barrelen-semibullvalne phootrearrangement. It is clear that sulfone tether directs the initital bonding to generate the 8b-substituted product exclusively. This is in agreement to the slight preference from the generation of 8b-substituted products in the case of thioether tethered barrelne **16** discussed earlier. Here also, a more detailed and comprehensive analysis is necessary to dilineate the real factors controlling regioselctivity.

5.3.6 Conclusion

Sensitized irradiation of phenyl bridgehead substituented tethered thioether led to exclusive formation of 8b-regioisomer as reported earlier in literatures.[27,28] Iradiation of tethered sulfone resulted in the exclusive formation of the 8b-regioisomer while the corresponding tethered sulfide gave a mixture of regioisomers on irradiation. Orientation of different groups at the bridgehead position of these tethered systems may have a role to play in controlling regioselectivity. We have proposed a mechanism involving a stable carbocation by S_N1cA mechanism for the hydrolysis of **19c**.

5.4. Experimental Section

5.4.1. General Techniques

All reactions were carried out using oven dried glasswares. Unless otherwise specified, all solvents were used directly without any further purification. When further purification was needed, known methods and procedures were followed in each case. All the reagents were purchased from either *Sigma-Aldrich* or *Spectrochem Chemicals* and were used without further purification. Progress of the reaction and chromatographic separations were monitored TLC analysis (aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was achieved by exposure to UV lamp and iodine vapour. Separation and purification of compounds were done by column chromatography using silica gel (*Spectrochem Chemicals*, 60-120 mesh). All products were further purified by recrystallization from suitable solvent systems. Solvent eluted from the column chromatography was removed on *Heidolph, IKA or Buchi* rotary evaporators under reduced pressure. Melting points were determined on a *Neolab* melting point apparatus and are uncorrected. Infra-red spectra were recorded by means of *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario EL III)*. Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*).

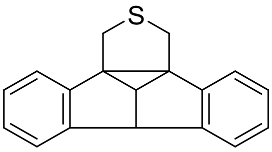
5.4.2. General procedure for sensitized irradiation

Acetone was purified and distilled before use by a known procedure[29] and was deoxygenated by passing a steady flow of argon through the solution for 30 min prior to irradiation. Degassed solution of **16** and **17** in dry acetone (50-70 mg in 150-170 mL) was irradiated (254 nm) under argon or nitrogen atmospheres (25-35 min) using Rayonet photochemical reactor. Progress of the reaction was monitored by TLC.

After the reaction, the solvent was removed under vacuum. ^{1}H NMR spectra of the residue were recorded to get an approximate idea about product composition. The residual solid was chromatographed over silica gel and eluted with different mixtures of dichloromethane and hexane to separate the products which were finally purified by recrystallization from suitable solvents.

5.4.3. Spectral and analytical data of novel compounds

5.4.3.1. Compound 18a



mp: 162-165 °C.

IR ν_{max} (KBr): 2919 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

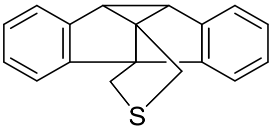
^{1}H NMR (CDCl$_3$): δ 7.12-6.96 (m, 8H), 4.45 (d, 1H, *J* = 6 Hz), 3.85 (d, 2H, *J* = 11.2 Hz), 3.81 (d, 1H, *J* = 6 Hz), 3.19 (d, 2H, *J* = 11.2 Hz).

^{13}C NMR (CDCl$_3$): δ 148.81, 137.24, 125.71, 125.40, 122.00, 120.77, 54.82, 54.24, 51.94, 31.81.

MS: *m/z* 262.

Elemental analysis calculated for $C_{18}H_{14}S$: C: 82.40, H: 5.38, S: 12.22. Found: C: 82.38, H: 5.40, S: 12.22.

5.4.3.2. Compound 19a



mp: 122-125 °C.

IR ν_{max} (KBr): 2918 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR (CDCl$_3$): δ 7.23-6.88 (m, 8H), 3.51 (s, 2H), 3.19 (s, 2H), 3.15 (s, 2H).

^{13}C NMR (CDCl$_3$): δ 149.38, 137.61, 125.99, 125.62, 123.77, 118.85, 74.91, 71.27, 50.63, 40.88, 36.45, 33.49.

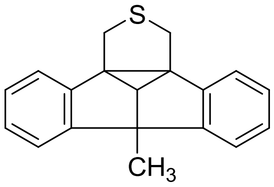
MS: *m/z* 262.

Elemental analysis calculated for $C_{18}H_{14}S$: C: 82.40, H: 5.38, S: 12.22. Found: C: 82.38, H: 5.38, S: 12.24.

5.4.3.3. Compound 18b

mp: 158-161 °C.

IR ν_{max} (KBr): 2916 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane



bending).

^{1}H NMR (CDCl$_3$): δ 7.09-6.96 (m, 8H), 3.87 (d, 2H, *J*=11.6 Hz), 3.56 (s, 1H), 3.21 (d, 2H, *J*=11.2 Hz), 1.74 (s, 3H).

^{13}C NMR (CDCl$_3$): δ 151.62, 137.10, 125.66, 125.43, 121.69, 119.04, 60.14, 56.31, 54.20, 31.88, 17.61.

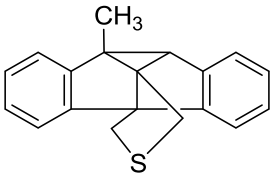
MS: *m/z* 276.

Elemental analysis calculated for $C_{19}H_{16}S$: C: 82.56, H: 5.83, S: 11.61. Found: C: 82.54, H: 5.83, S: 11.63.

5.4.3.4. Compound 19b

mp: 108-110 °C.

IR ν_{max} (KBr): 2912 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).



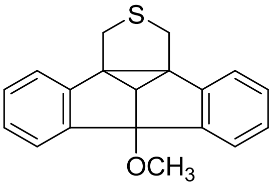
^{1}H NMR (CDCl$_3$): δ 7.09-6.93 (m, 8H), 3.52 (s, 2H), 3.13 (s, 2H), 2.86 (s, 1H), 1.66 (s, 3H).

^{13}C NMR (CDCl$_3$): δ 149.13, 148.97, 140.57, 138.68, 126.01, 125.80, 125.69, 125.42, 123.75, 122.75, 118.96, 118.62, 75.77, 74.73, 45.90, 45.18, 36.65, 30.46, 15.59.

MS: *m/z* 276.

Elemental analysis calculated for $C_{19}H_{16}S$: C: 82.56, H: 5.83, S: 11.61. Found: C: 82.54, H: 5.85, S: 11.61.

5.4.3.5. Compound 18c



mp: 148-151 °C.

IR ν_{max} (KBr): 2919 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

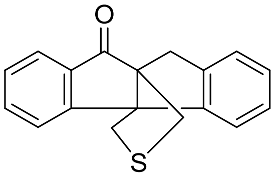
^{1}H NMR ($CDCl_3$): δ 7.23-7.11 (m, 8H), 4.04 (s, 1H), 3.95 (d, 2H, *J*=11.6 Hz), 3.48 (s, 3H) 3.31 (d, 2H, *J*=11.2 Hz).

^{13}C NMR ($CDCl_3$): δ 148.07, 135.94, 127.64, 126.95, 122.83, 120.48, 95.70, 57.82, 55.52, 53.44, 32.68.

MS: *m/z* 292.

Elemental analysis calculated for $C_{19}H_{16}OS$: C: 78.05, H: 5.52, S: 10.97. Found: C: 78.03, H: 5.53, S: 10.95.

5.4.3.6. Compound 24



mp: 112-115 °C.

IR ν_{max} (KBr): 1694 (C=O stretch), 2917 (-C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$): δ 7.77-7.09 (m, 8H), 3.50 (d, 1H, *J*=12 Hz), 3.42-3.41 (m, 2H), 3.27-3.15 (m, 2H), 2.99 (d, 1H, *J*=12 Hz).

^{13}C NMR ($CDCl_3$): δ 206.64, 156.39, 143.68, 140.24, 135.13, 127.43, 126.91, 124.45, 123.07, 122.94, 122.72, 71.85, 71.76, 44.16, 40.51, 38.57.

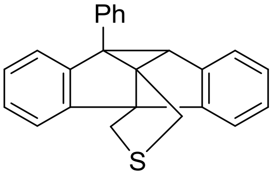
MS: *m/z* 278.

Elemental analysis calculated for $C_{18}H_{14}OS$: C: 77.66, H: 5.07, S: 11.50. Found: C: 77.64, H: 5.09, S: 11.48.

5.4.3.7. Compound 30

mp: 96-99 °C.

IR ν_{max} (KBr): 2918 (C-H stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).



^{1}H NMR (CDCl$_3$): δ 7.48-6.69 (m, 13H), 3.71 (s, 1H), 3.66-3.63 (m, 2H), 3.08 (d, 2H, *J*=2.8 Hz).

^{13}C NMR (CDCl$_3$): δ 150.82, 150.08, 142.48, 139.16, 139.11, 130.60, 128.76, 127.38, 127.17, 126.99, 126.93, 126.87, 125.52, 125.23, 120.20, 119.54, 76.70, 76.16, 55.80, 44.33, 37.76, 32.16.

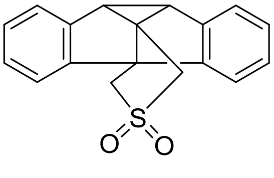
MS: *m/z* 338.

Elemental analysis calculated for $C_{24}H_{18}S$: C: 85.17, H: 5.36, S: 9.47. Found: C: 85.15, H: 5.36, S: 9.49.

5.4.3.8. Compound 33

mp: 129-132 °C.

IR ν_{max} (KBr): 1310 (asymmetric SO_2 stretch), 1350-1000 (C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).



^{1}H NMR (CDCl$_3$): δ 7.25-7.05 (m, 8H), 3.85 (s, 2H), 3.60 (s, 2H), 3.37 (s, 2H).

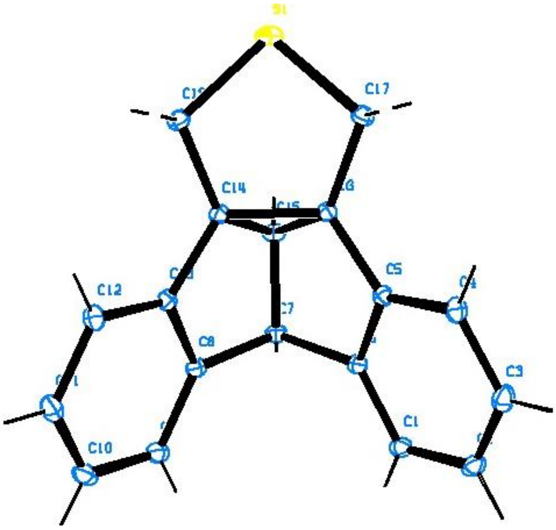
^{13}C NMR (CDCl$_3$): δ 148.90, 135.61, 126.81, 126.46, 126.33, 125.75, 124.34, 123.28, 118.94, 63.06, 60.17, 54.05, 52.33, 41.03.

MS: *m/z* 294.

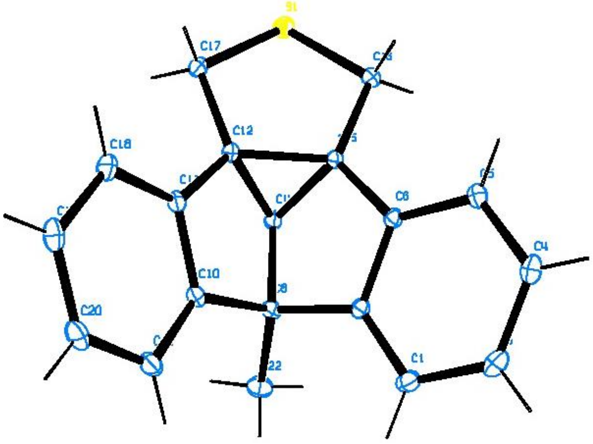
Elemental analysis calculated for $C_{18}H_{14}O_2S$: C: 73.44, H: 4.79, S: 10.89. Found: C: 73.42, H: 4.77, S: 10.87.

5.4.4. *ORTEP* diagrams of novel compounds

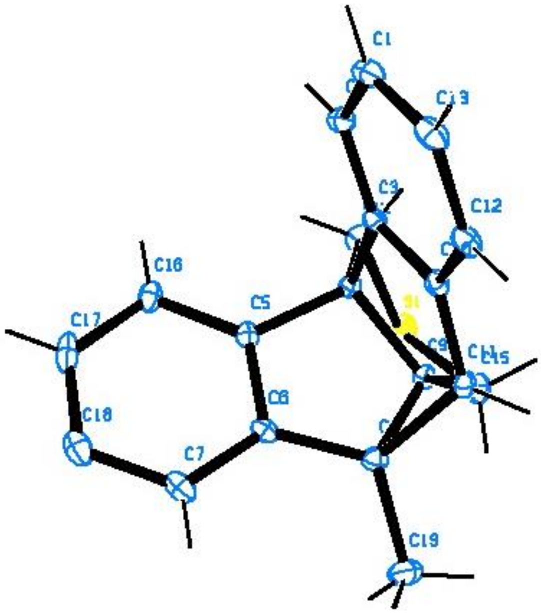
5.4.4.1 Compound 18a



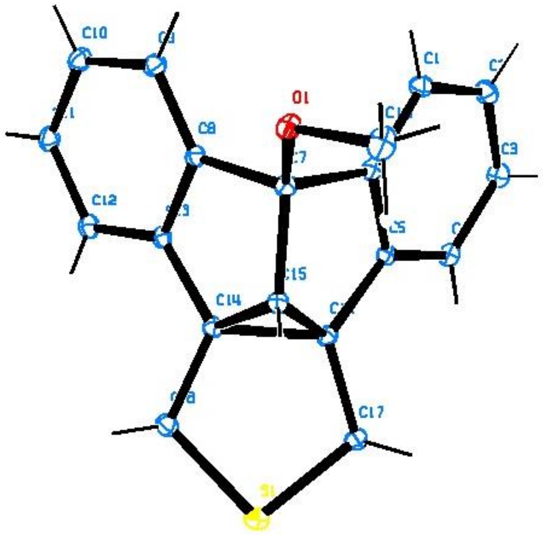
5.4.4.2 Compound 18b



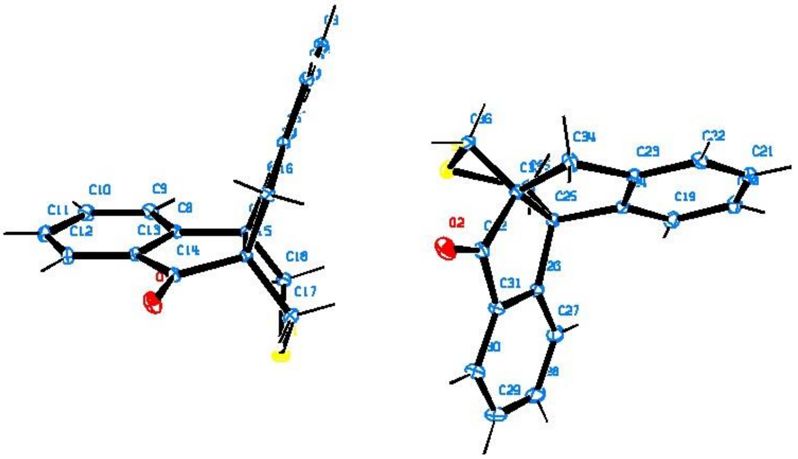
5.4.4.3 Compound 19b



5.4.4.4 Compound 18c



5.4.4.5 Compound 24



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Outcome

REGIOSELECTIVITY IN THE PHOTOTRANSFORMATIONS OF DIBENZOBARRELENES

Sensitized irradiation of tethered dibenzobarrelene derivatives yielded the corresponding 4b- and/or 8b-substituted tethered dibenzosemibullvalenes in near-quantitative yields. We explained regioselectivity observed in these transformations on the basis of structural features of tethered barrelenes revealed by single crystal X-ray structures and energy minimized structures (using ChemBio3D 11.0 Ultra).

In the introductory chapter, we have described regioselectivity of di-π-methane rearrangement exhibited by several acyclic, cyclic and bicyclic 1,4-dienes. Regioselectivity observed with such compounds was explained on the basis of accepted mechanism for di-π-methane rearrangement. The mechanism involves diradical intermediates and the stability of the initially formed diradical intermediate determines the regioselectivity in these systems. When there are electron donors and/or acceptors on one of both of the π-moieties, there is a strong tendency for electron donors to be found on the residual π-bond of the photoproduct and for electron withdrawing groups to appear on cyclopropane ring residue of the semibullvalene photoproduct. Closer look on literature reports, however, revealed conflicting reports on the effects of electronic and steric factors on the regioselectivity observed with barrelene-semibullvalene photorearrangement. In this context, we present our arguments to account for the observed regioselectivity. Our observations on sensitized irradiation of tethered barrelenes leading to corresponding semibullvalenes are given in Table 1.

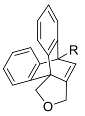
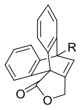
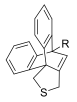
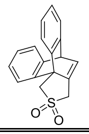
Irradiation of tethered barrelene	R	***Percentage of 4b regioisomer***	***Percentage of 8b regioisomer***
	H	100	0
	CH_3	100	0
	OCH_3	100	0
	Ph	100	0
	H	50	50
	CH_3	40	60
	OCH_3	75	25
	Ph	100	0
	H	55	45
	CH_3	50	50
	OCH_3	45	55
	Ph	0	100
		0	100

Table 1

One of the most surprising results here occurred with tethered barrelenes having bridgehead aryl substituents. Previous reports indicated exclusive formation of 8b-regioisomer in the photorerrangement of bridgehead aryl substituted dibenzobarrelenes. With ether and ester tethered barrelenes, we observed exclusive photorearrangement to yield the corresponding 4b-substituted semibullvalenes. On the other hand, thioether tethered barrelene gave the corresponding 8b-substituted semibullvalene as the only photoproduct. Such conflicting results are perplexing and deserve closer scruitiny. We surmised that a closer look at the structure of tethered barrelenes may reveal features that control regioslectivity. In this context, we adopted two different methods to examine the structure of tethered barrelene substrates: energy minimization studies and single crystal X-ray diffraction analysis. Firstly, we applied energy minimization studies to such systems. For example, the phenyl bridgehead substituent in the energy minimized structures of 11,12-dibenzoyl-9,10-dihydro-9-phenyl-9,10-ethenoanthracene and dimethyl 9,10-dihydro-9-phenyl-9,10-ethenoanthracene-11,12-dicarboxylate is aligned approximately parallel to the plane of the aromatic rings of the barrelene systems (Figure1). Such an orientation of bridgehead phenyl leads to adverse van der Waals interaction between the ortho hydrogens of bridgehead aryl substituent and hydrogens at the 1 and 8 positions of dibenzobarrelene unit. On the otherhand, vertical alignment of bridgehead phenyl group with the plane of aryl residues of dibenzobarrelenes ensues adverse steric crowding with 11,12-substituents that is even more damaging. Thus, bridgehead aryl substituted dibenzobarrelenes will have the 9-aryl substituent aligned parrelel to the plane of the aromatic rings of the barrelenes. When these dibenzobarrelenes undergo di-π-methane rearrangement, the initial vinyl-vinyl bridging will be in the manner in which such steric interactions are repelled. In this scenario, bridgehead aryl substituent will end up at the 8b-position of the semibullvalene photoproduct. We employed this hypothesis to justify regioselectivity of such systems by applying energy minimization of dibenzobarrelenes and observing the orientation of the phenyl bridgehead substituent.

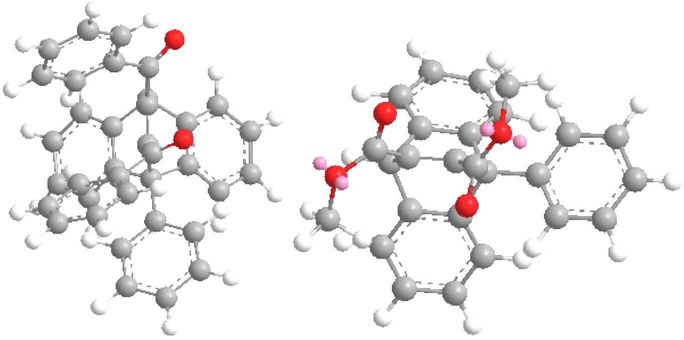


Figure 1

In the energy minimized structures of bridgehead phenyl substituted tethered ether, tethered ester and tethered sulfide (tethered dibenzobarrelenes), the phenyl group is aligned vertical to the plane of the aromatic rings of the barrelene systems as shown in Figure 2. We reason that the absence of substituents at the 11,12-positions permit such an alignment. We have already reported the single crystal X-ray structures of these tethered barrelenes in the Chapter 2 of this thesis that is in complete agreement with the energy minimized structures. We propose that if the bridgehead phenyl group is oriented in the above mentioned manner after energy minimization, the regioselectivity is then determined by the nature of the tethered ring (electronic and steric factors). The following factors neeed reckoning: 1) electron donating/witdrawing effects of the tethering group, 2) steric factors attributable to the tether and 3) strain created due to tethering. Needless to mention, gravity of these effects varies from tether to tether and hence each type of tethered barrelenes deserves individual scrutiny.

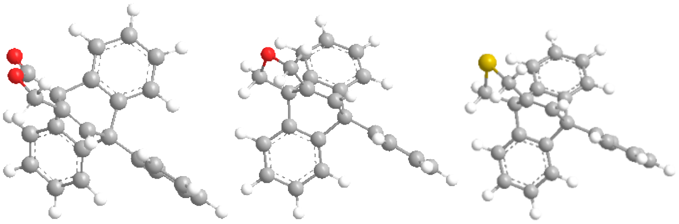


Figure 2

Based on our findings reported in Chapter 3 of this thesis, it is clear that ether tethered barrelenes exhibited remarkable regioselectivity in their photorearrangement. These results are explained on the basis of relief of minor small angle strain experienced with these systems. Energy minimaization and X-ray analysis of the structure of ether tethred barrelenes are in agreement with this justification outlined in Chapter 3.

Our findings on the photochemistry of ester tethered barrelenes reported in Chapter 4 are also explained in terms of electronic and steric factors. It may be noted that the sp^2carbon of the tether attached to the bridgehead position removes adverse steric interaction with hydrogens on the aromatic residue of dibenzobarrelenes. However, the lactone carbonyl is electron withdrawing in nature. It has already been established that bridgehead substituetns that are electron withdrawing in nature drives regioselectivity towards itself ending up on the cyclopropane ring. Other synergies also work in tandem. Prevoius reports indicate that both methyl and methoxy substituents at the bridgehead poision end up at the 4b-position. Bridgehead aryl substituents in tethered lactones are also expected to align itself in a plain bisecting the dibenzobarrelene structure ensuring regioselectivity tuned towarding ending itself as the cyclopropyl substituent. Relief of angle strain appears to be relatively insignificant in driving regioselectivity.

Thioether tethered barrelenes exhibited regioselectivity that is dramatically different from that exhibited by ether tethered barrelens. We propose that incorporation of sulfur into the tether withers angle strain and hence steric effects pertaining to the bridgehead substituent assumes the pole position in controlling regioselctivity. On the first look, regioselectivity exhibited by the bridgehead aryl substituent in tethered thioethers that is aligned in a plane bisecting the dibenzobarrelenes appears different from that observed with tethered ethers. We reason that in the absence of other dominating effects, phenyl substituent should end up at the cyclopropane ring ensuriung extended conjugation.

Our conclusion on the observed regioselectivity of di-π-methane rearrangement of tethered dibenzobarrelenes is supported by theoretical calculations and structural analysis. We have demonstrated that angle strain at the vinyl position, electronegativity and orientation of bridgehead substituent and van der Waals interaction between bridgehead substituent and aromatic hydrogens of dibenzobarrelenes contribute towards deciding the observed regioselectivity. Which among these factors is most important in controlling regioselctivity is still an open question. Additional experimental evidence is required to answer this question.

Furthermore we have proposed a mechanism involving a stable carbocation intermediate followed by S_N1cA mechanism for the hydrolysis of suitable primary photoproducts. Earlier reports suggested that such primary photoproducts formed by di-π-methane rearrangement underwent secondary photoreactions to give the final isolated products. But we demonstrrated that the secondary products are generated in a dark reaction; the hydrolysis leading to these occurred only when silica gel column chromatography was attempted for separation of the regioisomers generated as primary photoproducts.

It is worth mentioning here that photoinduced rearrangement of tethered barrelenes is a very clean reaction. In most cases, rearranged products were obtained in near-quantitative amounts. In reactions where only a single regioisomer was formed, pure product in analytically pure form was isolated by removal of solvents and no further purification of the material was necessary in these cases.

List of Publications

1. 8-Phenyl-16-thiapentacyclo[6.6.5.0^{1,18}.0^{2,7}.0^{9,14}]nonadeca-2,4,6,9,11,13,18-heptaene, **E. M. Mathew**, M. Sithambaresan, P. A. Unnikrishnan and M. R. P. Kurup, *Acta Cryst*.(2013).E**69**, o1165.
2. 3,5-Dihydro-1*H*-5,9b-*o*-benzonaphtho [1,2-*c*] furan-1-one, **E. M. Mathew**, M. Sithambaresan, P. A. Unnikrishnan and M. R. P. Kurup, *Acta Cryst.*, Section **E** (communicated).
3. Mechanistic investigation for the hydrolysis of dibenzosemibullvalenes, **Eason M. Mathew**, P. A. Unnikrishnan and S. Prathapan, *Tetrahedron Lett*. (under preparation).
4. Factors affecting regioselectivity of di-π-methane rearrangement of dibenzobarrelenes, **Eason M. Mathew**, P. A. Unnikrishnan and S. Prathapan, *Tetrahedron Lett*. (under preparation).

Posters in Conferences

1. Synthesis and characterization of a few tethered barrelenes, **Eason M. Mathew**, P. A. Unnikrishnan, S. Prathapan, *International Conference on Materials for the new Millennium, MatCon 2010*.
2. Synthesis of a few barrelene systems through intramolecular Diels-Alder reaction, **Eason M. Mathew**, P. A. Unnikrishnan, S. Prathapan, *Current Trends in Chemistry, CTriC 2011*.
3. Photochemical transformation of a tethered barrelene, **Eason M. Mathew**, *Current Trends in Chemistry, CTriC 2013*.