STUDIES ON THE SYNTHESIS AND TRANSFORMATIONS OF A FEW BICYCLIC AND DISPIRO COMPOUNDS

THESIS SUBMITTED TO THE
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

IN THE FACULTY OF SCIENCE

BY

JEAN JOHN VADAKKAN

DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI-682 022

September 2002

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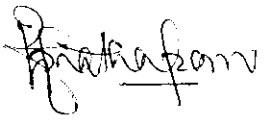
CERTIFICATE

This is to certify that the thesis herewith is an authentic record of research work carried out by the author 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 any other degree.



Kochi-22
September 27, 2002.

Dr. S. Prathapan
(Supervising Teacher)
Lecturer in Organic Chemistry
Department of Applied Chemistry
Cochin University of Science and Technology
Kochi-22.

DECLARATION

I hereby declare that the work presented in this thesis entitled: "**Studies on the Synthesis and Transformations of a few Bicyclic and Dispiro Compounds**" is original and was carried out by me independently under the supervision of Dr. S. Prathapan, Lecturer in Organic Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-22, India, and has not been included in any other thesis submitted previously for the award of any degree.

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September 27, 2002.

Jean John Vadakkan

ACKNOWLEDGEMENTS

To Dr. S. Prathapan, Lecturer in Organic Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, I express my sincere gratitude and obligation, sans him this thesis would have been a far-fetched dream. I am indebted to him for the fruitful discussions, boundless support and incredible patience he has shown through out my research tenure under his guidance. I consider it as a privilege that I could work under a teacher who inspires, criticizes, encourages and brings forth the best in you.

I am thankful to Prof. S. Sugunan, Head, and Department of Applied Chemistry for providing the facilities to carry out the work. My heartfelt gratitude to Prof. K. K. Mohammed Yusuff, Professor in Catalysis and Former Head, Department of Applied Chemistry for his kindheartedness and encouragement. I acknowledge the support extended by the faculty members of Department of Applied Chemistry.

I would like to place on record my wholehearted acknowledgement to Dr. P. A. Unnikrishnan, Dr. A. G. Ramachandran Nair, Dr. S. Mayadevi, Dr. Rani Abraham, Dr. K. O. Xavier, Dr. Biju P. Mangatt, Dr. Suresh Kumar, M. K., Miss. M. S. Sulatha, and Mr. Sunny Abraham for their help.

To Dr. Binoy Jose, I am obliged, for steering me carefully through the unpredictable maze of chemical methodologies. He answered my numerous questions, gave a reliable back up throughout my research career. I am grateful to Dr. Sreekumar Kurungot for his incessant smiles, solid support and for the knowledge he has shared with me. I am thankful to Miss. Vidya Raman, for her never ending doubts, which made me look at the blockages in the research work in different perspectives, for making the figures in my thesis aesthetically appealing. I owe Miss. Noeline B. Fernandez, special thanks for bearing with my dispositions. Miss. Ambily Mary Jacob and Miss. Rekha Mallia have given me encouragement whenever I needed it most. I am grateful to Mr. Vishnuunni M. V. for the discussions we have had on the various aspects of chemistry. I owe a lot to the "late-night research group" of our Department, Miss. Preetha G. Prasad, Miss. Suja Haridas, Miss, Chandini R. Nayar, Miss. Sreeja P. B., Miss. Suni V., and Miss. Daly Davis. I am in debt of Mrs. Jyothi Mariam John, Mr. Rohith P. John and Mr. Anas Khalid for their timely help and assistance. I would like to thank Miss. Pyroja S. and her lab-mates at Department of Bio-technology for allowing me to avail the facilities in their department. The endless affection and inspiration from my friends, Miss. Finu Cherian, Miss. Indu .J., Miss. Karthika Varma, Miss. Baghirathi Naidu, Miss. Mili Rani Jose, Mr. Manoj Kumar C., Mr. Prem Prabhakar, Mr. Sukesh T. V., Mr. Anurup Joseph and Mr. Mohan Kuruvilla are remembered with deep sense of gratitude. To Mr. Jean S. Babu, for his belief in my abilities and for his unconditional love and to Mr. Amey Karandikar, for being there, I am grateful. Many thanks to Mr. Harikrishna R., for the help he has extended to me in the initial stages of my work and for reminding me there is a world beyond chemistry. I am grateful to Mr. Biburaj T. P. for his help in designing the photochemical reactor. I would like to thank Miss. Sanuja A. and her class-mates, Miss. Rekha G., Miss. Sreerekha, Miss. Vineetha C. P. Miss. Suja N. R. and Miss. Ashley P. C. for their support and love.

I would like to thank Dr. Jayaprakash Narayanan Nair, North Carolina State University, Dr. Lakshmi Varma, RRL, Trivandrum, Mr Shivakumar P. and Miss. Anu Joy,

Sophisticated Instrumentation Centre, IISc, Bangalore for providing necessary spectral data. I acknowledge CDRI, Lucknow for elemental Analysis. Acknowledgements are due to Mr. Kasmir and Mr. Jose of Department of Instrumentation for their assistance in manufacturing the photochemical reactor.

I am grateful to all the non-teaching staff of this Department for their support and encouragement during my stint here. The financial support from Cochin University of Science and Technology and CSIR, Delhi is gratefully acknowledged.

To my parents, to my brothers and to my uncle, I owe immeasurably and vastly for whatever I am and for everything they have given me.

Jean John Vadakkan

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ABSTRACT

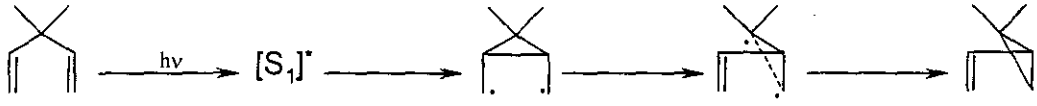
The thesis entitled "**Studies on the Synthesis and Transformations of a Few Bicyclic and Dispiro Compounds**" is divided into nine chapters. **Chapter 1** gives a general survey of Diels-Alder reactions and di-π-methane rearrangement. Additionally, this chapter includes a brief overview of the dibenzoylalkene rearrangement. **Chapter 2** deals with our endeavours on the synthesis of alkenylanthracenes. **Chapter 3** discusses our attempts to synthesise a few 9-ethynylanthracenes. **Chapter 4** presents syntheses of a few dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylates having alkenyl or alkynyl substituents at the bridgehead via Diels-Alder reaction. **Chapter 5** deals with our experiments to optimise conditions for intermolecular Diels-Alder and intramolecular Diels-Alder reactions of suitably 9-substituted anthracenes. **Chapter 6** mainly deals with the preliminary photochemical investigations on controlling the selectivity of di-π-methane rearrangement through intramolecular quenching of excited triplet states of dibenzobarrelenes. **Chapter 7** describes the preparation of a few 9-(*N,N*-dialkylamino)methylanthracenes and our attempts to synthesise the corresponding dibenzobarrelenes. **Chapter 8** describes the synthesis of a few ethenylfurans and their Diels-Alder reaction. **Chapter 9** describes the reaction of acenaphthenequinone with suitable acetophenones in methanol.

Chapter 1: Diels-Alder Reaction and Di-π-Methane Rearrangement- an abridgment

Diels-Alder reaction is one of the major synthetic strategies employed to generate bicyclic compounds. Bicyclic compounds have gained much importance in the recent past as they are commonly used as potential therapeutic agent against HIV and metastasis, anticancer drugs, anti-thrombotic compounds, therapeutic agents for diseases of the central nervous system, and so on.

The di-π-methane rearrangement is a very general and well-studied photorearrangement. The very broad spectrum of types of organic molecules obtainable by the di-π-methane rearrangement is remarkable and makes it particularly synthetically useful. Zimmerman discovered the di-π-methane rearrangement in 1967 when the photolysis of reactants having two vinyl moieties bonded to an sp^3-hybridised carbon led to the formation of vinylcyclopropane. This process, along with the mechanism suggested by Zimmerman, is depicted in Scheme A.1 for the di-π-methane reactant, 3,3-dimethyl-1,4-pentadiene (**34**).

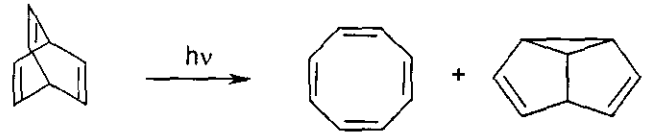
Scheme A.1



34 **35** **36** **37**

Zimmerman and Grunewald[131] studied the photochemical isomerisation of barrelene (**38**) to afford cyclooctatetraene (**39**) and semibullvalene (**40**). The photochemical conversion of barrelene to semibullvalene as given in Scheme 1.16 was instrumental in assessing the generality of the di-π-methane rearrangement.

Scheme A.2

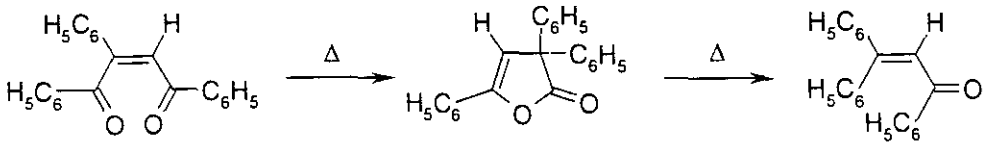


38 **39** **40**

Dibenzoylalkenes can undergo bond reorganisation process thermally and photochemically. The first reported dibenzoylalkene rearrangement is the pyrolysis of *cis*-dibenzoylstilbene to tetraphenylcrotonolactone by Zinin in 1872. Subsequently, several other reports on the synthesis and transformations of a variety of dibenzoylalkenes have appeared in the literature.

Dibenzoylalkenes on pyrolysis undergo ring closure and ring opening as well as ring enlargement and ring contraction. *cis*-Dibenzoylstyrene (**95**) on pyrolysis undergoes ring closure to form triphenylcrotonolactone (**96**) The lactone on further heating lost carbon monoxide to give β-phenylbenzalacetophenone (**97**) (Scheme A.3).

Scheme A.3



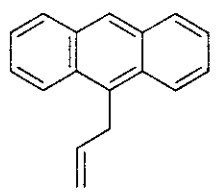
95 **96** **97**

Chapter 2: Synthesis of Alkenylanthracenes

To introduce the idea of selective quenching of excited triplet states of barrelenes and to understand the effect of an olefin unit on the photochemistry of barrelenes, we proposed to synthesise several dimethyl 9-alkenyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylates. As the first step in the synthesis of these dibenzobarrelenes, we proposed to synthesise the corresponding alkenylanthracenes, which included vinyl, allyl and homoallyl systems, and systems with a remote double bond. The methods we adopted were the Wittig reaction of 9-anthraldehyde (**1**) with suitable ylides, Claisen-Schmidt condensation of **1** with suitable methyl ketones **3**, Grignard reaction between anthrone (**4**) and suitable alkenylmagnesium bromides,

Williamson's ether type synthesis and esterification reactions. A few of the 9-alkenylanthracenes synthesised by us is presented in Chart A1.

Chart A.1



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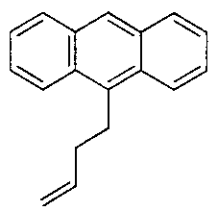

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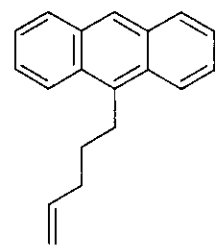

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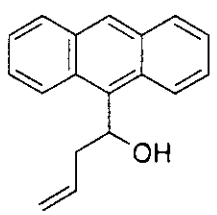

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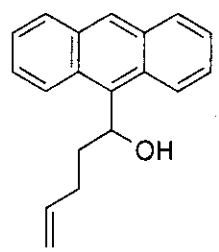

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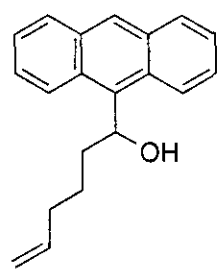

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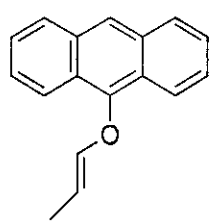

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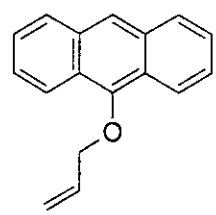

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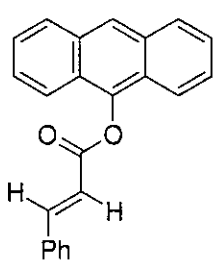

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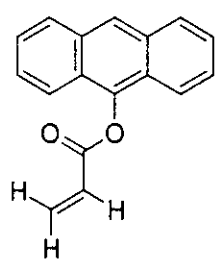

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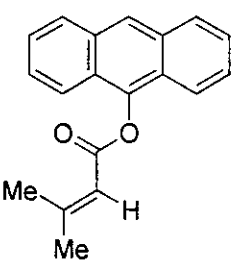

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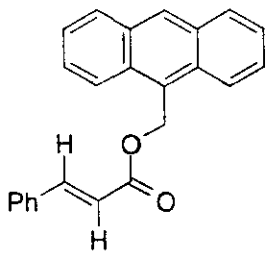

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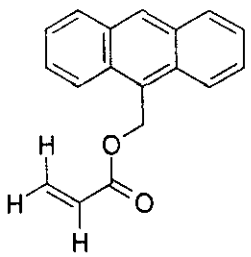

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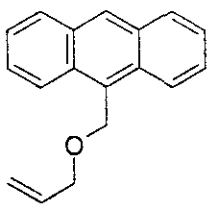

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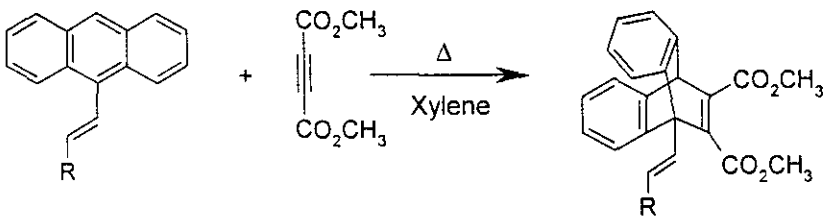
Chapter 3: Synthesis of Alkynylanthracenes

In continuation with our studies on the effects of an ethylenic substituent at the bridgehead position on the photochemistry of dibenzobarrelenes, we proposed to investigate the effect of acetylenic substituents at the bridgehead on the photochemistry of dibenzobarrelenes. Depending on the structure of the target molecule under consideration, we short-listed palladium-catalysed Heck's coupling reaction, Williamson's ether type synthesis and esterification reactions as possible methods for the synthesis of 9-alkynylanthracenes of our choice. Phase transfer catalysts were employed, where applicable, to improve the efficiency of ester and ether-forming reactions.

Chapter 4: Intermolecular Diels-Alder Reactions

We proposed to synthesise of a few dibenzobarrelenes with appended olefin units. We treated the alkenylanthracenes **1a-e** with dimethyl acetylenedicarboxylate (**2**, DMAD) to yield the corresponding Diels-Alder adducts **3a-e** under suitable conditions. Dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylates **3a,b,d,e** were obtained in good yields through the Diels-Alder reaction between alkenylanthracenes **1a,b,d,e** and **2** (Scheme A.4).

Scheme A.4



1a,b,d,e **2**

3a R = H
b R = C_6H_5
d R = COC_6H_5
e R = $COC_6H_4C_6H_5(p)$

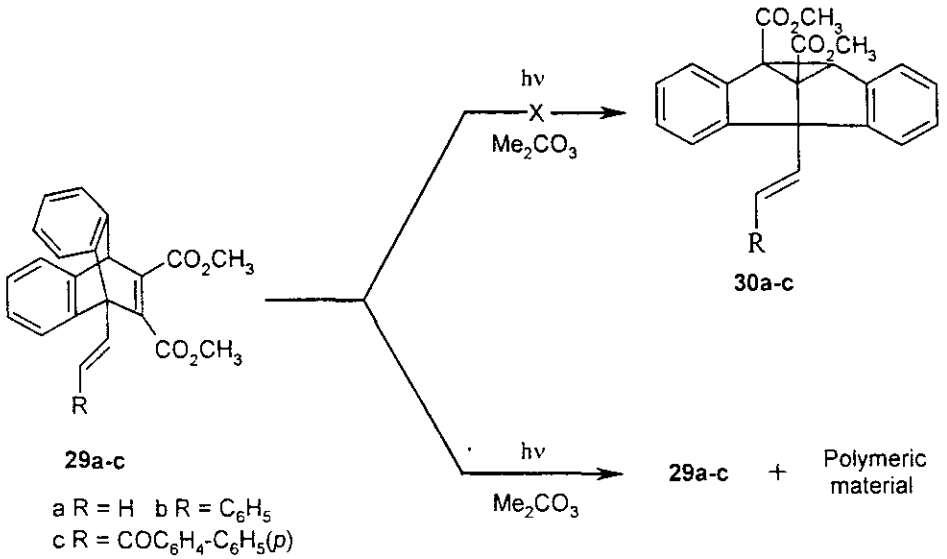
Chapter 5: Intramolecular Diels-Alder Reactions

We were interested in the synthesis of several 9-ethenyl and 9-ethynyl substituted ethenoanthracenes to test our hypothesis on intramolecular quenching of triplet excited states. We selected Diels-Alder reaction of suitable 9-substituted anthracenes with acetylenic dienophiles for the synthesis of the required substrates. While selecting this methodology, we were aware that IMDA reactions may be a serious side reaction in some cases. Hence, it was important for us to determine the optimal reaction conditions for the anthracenes synthesised by us to undergo intermolecular Diels–Alder reaction leading to the corresponding 9-substituted ethenoanthracenes. Our results are tabulated in Table 5.1.

Chapter 6: Preliminary Photochemical Studies

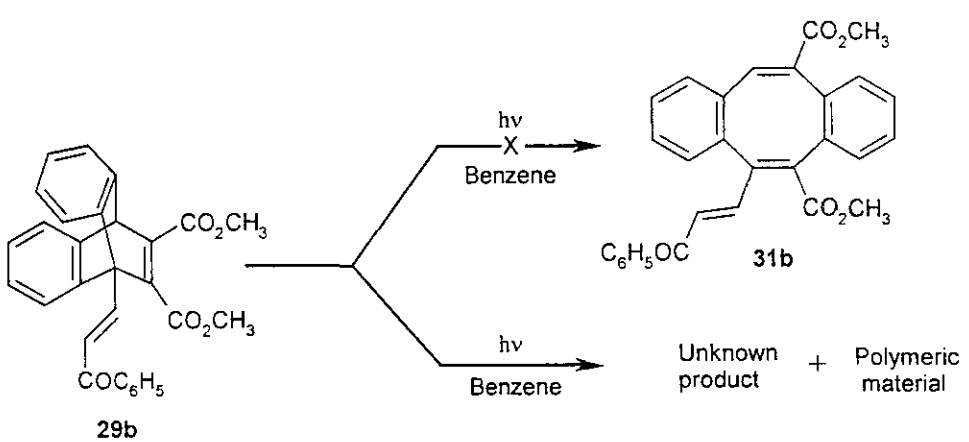
We proposed to carry out the direct as well as sensitised irradiation of a few dibenzobarrelenes we have synthesized to assess the effect of the fourth π-moiety on the photochemical reactions of dibenzobarrelenes. The photolysis of **29a-c** in acetone under nitrogen atmosphere, gave polymeric material along with varying amounts of unchanged reactant. As expected, the corresponding semibullvalenes were not formed through di-π-methane rearrangement (Scheme A.5).

Scheme A.5



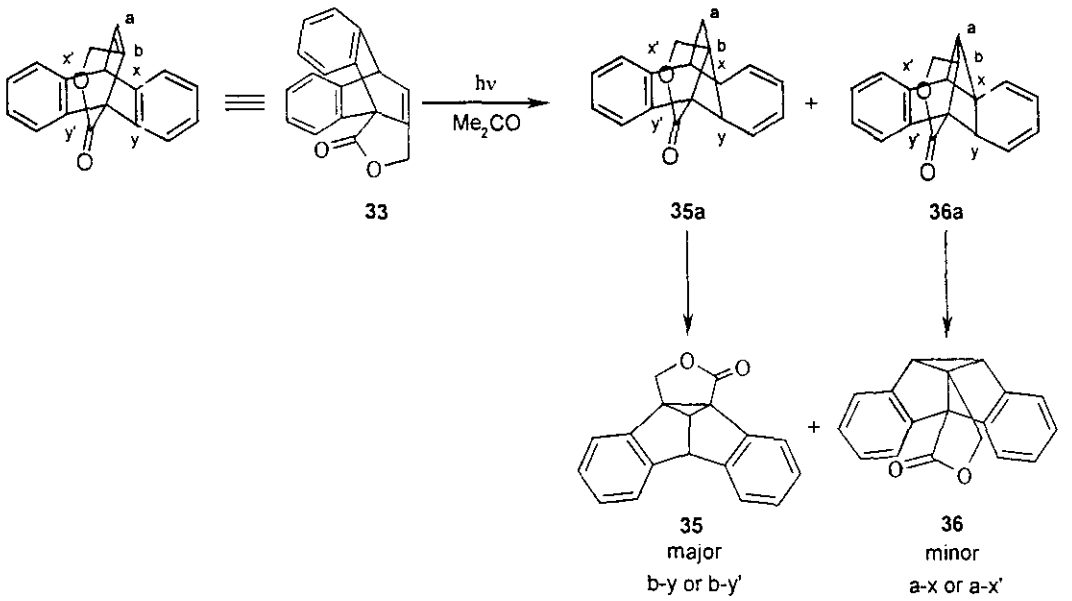
In continuation, we carried out the direct irradiation of a representative substrate such as **29b** to examine whether it will undergo singlet-mediated transformation leading to the formation of dibenzocyclooctatetraene **31c**. Direct irradiation of **29b** in benzene did not lead to the formation of **31c**, instead an unidentified compound was formed in trace amounts along with polymeric material (Scheme A.6).

Scheme A.6



Additionally, in the present study we carried out sensitized irradiation of **33** in acetone to give a 70:30 mixture of the regiomers **35** and **36.** The photochemical reaction of **33** substantiates the hypothesis that electronic factors control the regioselectivity in the di-π-methane rearrangement of 9,10-ethenoanthracene derivatives in sterically unbiased compounds of this genus (Scheme A.7).

Scheme A.7



Chapter 7: Synthesis and Diels–Alder Reactions of 9-(*N,N*-dialkylamino)methyl-9,10-dihydro-9,10-Ethenoanthracenes

We proposed to synthesise a few aminoanthracene precursors as well as the corresponding amine-appended dibenzobarrelenes to examine whether these substrates undergo intramolecular electron transfer. We were successful in synthesising the amine precursors **5a,b**. However, our attempts to synthesise the desired dibenzobarrelenes such as dimethyl 9-(*N*, *N*-dimethylamino)methyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**9a**) and dimethyl 9-(1-methylmorpholino)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**9b**) have not been successful. The intramolecular quenching of singlet excited states of barrelenes thus remains a distinct but yet to be demonstrated possibility.

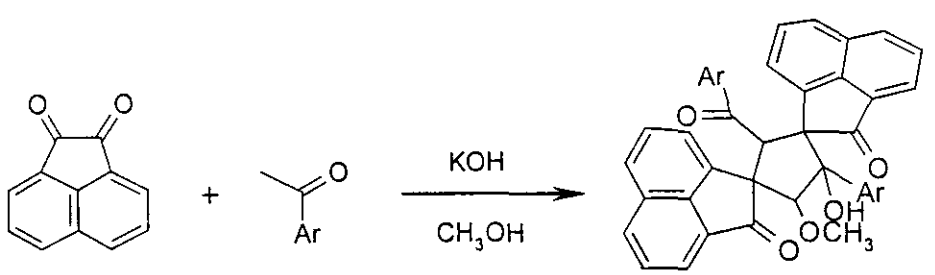
Chapter 8: Synthesis and Diels-Alder Reactions of Ethenylfurans

In an effort to investigate the scope of Diels-Alder reactions, we proposed to synthesise a few 7-oxabicyclo[2.2.1]heptadienes. Our long term goal, however, was to introduce an ethenyl group at the bridgehead position of 7-oxabicyclo[2.2.1]hepta-2,5-dienes to assess the role of the newly introduced π-moiety on the photo-chemistry of these bicyclic systems. We synthesised a few ethenylfurans **2a-d**. We attempted to synthesise the Diels-Alder adducts of these ethenylfurans with dimethyl acetylenedicarboxylate (DMAD, **3**). Attempted Diels-Alder reaction of **2a-d** with DMAD resulted in polymerisation of the staring materials at high as well as low temperatures.

Chapter 9: Synthesis and Transformations of Dispirocompounds

We have described our findings on the synthesis of a few dispirocompounds. These systems were encountered as unexpected products in the attempted synthesis of novel dibenzoylalkene-type systems. The reaction of acenaphthenequinone (**12**) with slight excess of acetophenone (**7a**) in methanol in the presence of KOH gave the dispiroderivative **13a**. Similarly, dispiroderivatives **13b,c** were synthesized by the reaction of acenaphthenequinone (**12**) with 4-methylacetophenone (**7b**) and 4-chloroacetophenone (**7c**) respectively (Scheme A.8).

Scheme A.8



12

7a Ar = C $_6$H$_5$
b Ar = C $_6$H$_4$-CH$_3$(*p*)
c Ar = C $_6$H$_4$-Cl(*p*)

13a Ar = C $_6$H$_5$
b Ar = C $_6$H$_4$-CH$_3$(*p*)
c Ar = C $_6$H$_4$-Cl(*p*)

In conclusion, a number of new compounds having fairly complex structural features were synthesised and characterised using spectral and analytical data. We have established that IMDA reactions predominate when the geometry of the parent molecule permits cycloaddition between the diene and dienophile components to yield five or six-membered rings. Additionally, high temperature is one of the ideal conditions for IMDA reactions provided the molecule has an excellent dienophile component. The incorporation of olefin units on to barrelenes resulted in polymerisation on direct as well as sensitised irradiation. Such barrelenes failed to give semibullvalenes through triplet excited state on photolysis. It appears that intramolecular energy transfer from a barrelene chromophore to an appended styrene moiety is a distinct possibility since dimethyl 9-(1-anthryl-2-phenylethylene)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**29d**) underwent facile $E \rightarrow Z$ isomerisation. Selective quenching of barrelene singlet state through intramolecular quenching remains a distinct possibility. For 9,10-ethenoanthracenes, where steric factors are not important, electronic factors govern the regioselectivity of di-π-methane rearrangement. Alkenylfurans do not undergo Diels-Alder reactions at low and high temperatures. Acenaphthenequinone with suitable methylketones gives novel dispiro compounds in good yields by domino Michael-aldol reactions.

Note: The numbers given to various compounds herein correspond to those given in respective chapters. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

CHAPTER 1

DIELS-ALDER REACTION AND DI-π-METHANE REARRANGEMENT- an abridgment

1.1. Abstract

Herein, we present a précis of Diels-Alder reactions and di-π-methane rearrangement since these two reactions form the basis of our proposed investigations. Additionally, this chapter includes a brief overview of the dibenzoylalkene rearrangement as an overture to the synthesis of dispirocompounds we encountered serendipitously.

1.2. Introduction

Scientific development is often the result of human effort either to mimic Nature or to "create the unnatural." This is particularly true in the case of chemistry where along with the synthesis of new compounds, enormous effort is devoted to the total synthesis of naturally occurring compounds as well. The total synthesis of complex natural products is very demanding, but the synthesis of simpler molecules or molecular fragments, natural or artificial, can also pose great challenges. Examination of many synthetic endeavours, large and small, reveals that each and every reaction requires the most strategic planning. Most of the chemical reactions in a synthesis, however, usually involve manipulation of functional groups in a systematic fashion.

In this thesis, we report our endeavours in the synthesis of a few polycyclic compounds. We were interested in the synthesis of a few bicyclic compounds designed to undergo interesting photochemical transformations including triplet-

mediated di-π-methane rearrangement and/or competing singlet-mediated electrocyclic reactions. Our target molecules have "inbuilt" structural features which will potentially alter the photochemistry of the substrate under consideration. The present investigation was undertaken to test our hypothesis on selective intramolecular quenching of singlet or triplet excited states of molecules. We adopted Diels-Alder reaction for the synthesis of several of the bicyclic compounds we were interested in. Some of the precursor dienes synthesised by us are capable of undergoing intramolecular cycloaddition reactions as well. So, it was important to delineate the conditions and structural features that will enable a particular molecule to undergo intermolecular and intramolecular Diels-Alder reaction when treated with a suitable dienophile. In this chapter, we present a comprehensive review of Diels-Alder reactions and di-π-methane rearrangement since these two reactions combined constitute the keystone of our proposed investigations.

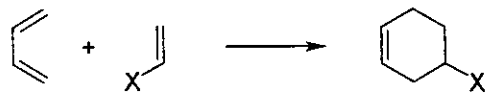
Though, the main focus of this thesis is on the synthesis of bicyclic and tricyclic systems capable of undergoing di-π-methane rearrangement, in the last chapter of this thesis, we describe our findings on the synthesis of a few dispirocompounds. These systems were encountered as unexpected products in the attempted synthesis of novel dibenzoylalkene-type systems. Consequently, a brief survey on the synthesis and transformations of dibenzoylalkenes is also included as an integral part of this thesis.

1.3. Diels–Alder Reaction

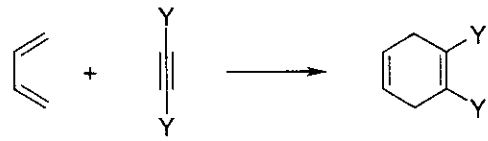
Diels-Alder reaction[1] is one of the major synthetic strategies employed to generate bicyclic compounds. Bicyclic compounds[2] have gained much importance in the recent past since they constitute the basic structural frame work of several compounds which are used as potential therapeutic agent against HIV and metastasis[3], anticancer drugs[4], anti-thrombotic compounds[5], therapeutic agents for diseases of the central nervous system[6], and so on.

In Diels-Alder reaction, a 1,3-diene reacts with an olefinic (Equation 1.1a) or acetylenic (Equation 1.1b) dienophile to form six-membered rings containing

one or two double bonds. Since its formulation in 1928[7], the utility of Diels-Alder reaction has remained inestimable for the synthesis of monocyclic as well as polycyclic compounds. It provides an unparalleled strategy for the regioselective and stereospecific introduction of multiple centers of configuration.



(1.1a)

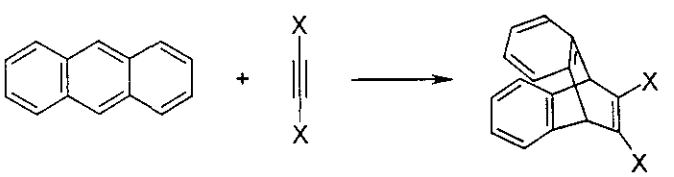


(1.1b)

The versatility of Diels-Alder reaction was recognised primarily through the pioneering efforts of Diels and Alder.[7] Isolated instances of the reaction, were discovered, however, as early as 1893 by Zincke[8-11], who subsequently formulated the reactions as additions, which conform to the general scheme of the diene synthesis. In 1906, Albrecht[12] described the addition products of *p*-benzoquinone with one and two molecules of cyclopentadiene. Euler and Josephson[13] reported that isoprene could be made to react with 1,4-benzoquinone. A series of cycloaddition reactions between azodicarboxylic ester and cyclopentadiene done by Diels, Blom, and Koll[14] paved the way for generalising Diels-Alder reactions. Yet, the true power and effectiveness of Diels-Alder reaction began to be realised and tapped only in the 1950s and 1960s with the elegant applications of this remarkable reaction to the total synthesis of many complex natural products.[15] Subsequent reports have consolidated the fact that Diels-Alder reaction serves as an efficient tool to generate synthons for the solution of many synthetic tasks. Diels-Alder reaction has both enabled and shaped the art and science of total synthesis over the last few decades to an extent which, arguably, has yet to be eclipsed by any other transformation in the current synthetic repertoire. With myriad applications, often as a crucial element in elegant and programmed cascade sequences facilitating the construction of complex molecules, the Diels-Alder cycloaddition has afforded numerous and unparalleled solutions to a diverse

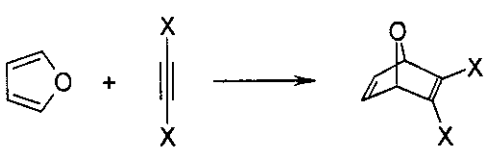
range of synthetic puzzles provided by nature in the form of natural products. Ever since its discovery, development continued with no let up in pace. Many different versions of the Diels-Alder reaction were elaborated, including intramolecular [4+2] cycloadditions[16-24], hetero Diels-Alder reactions[15,25-32], pressure-accelerated Diels-Alder reactions[33-44], Lewis acid accelerated Diels-Alder reactions[45-51] and Diels-Alder reactions in aqueous medium.[52-64] If one chemical reaction had to be selected from all those in the gamut of synthetic organic chemists as the most useful and powerful synthetic construction methodology, it was clear by 1970's that Diels-Alder reaction would be the logical choice. Its application not only leads to a strong increase in molecular complexity (molecular size, topology, stereochemistry, functionality, and appendages), but also can result in structures that lend themselves to additional amplification of complexity by the use of other powerful synthetic reactions.

A number of polycyclic aromatic hydrocarbons react with dienophiles by 1,4-addition, but the reaction is particularly characteristic of anthracenes (Equation 1.2) and the higher linear acenes.[65]



(1.2)

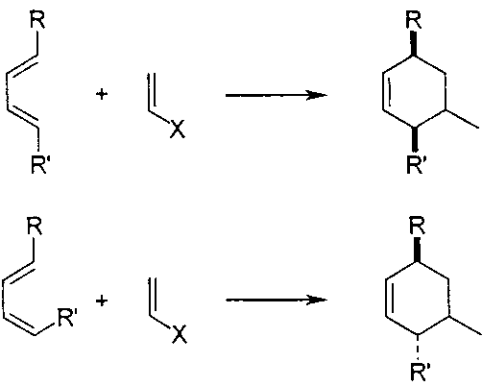
Many furan derivatives[66] react with ethylenic and acetylenic dienophiles with extraordinary facility to yield bicyclic compounds with an oxygen bridge (Equation 1.3).



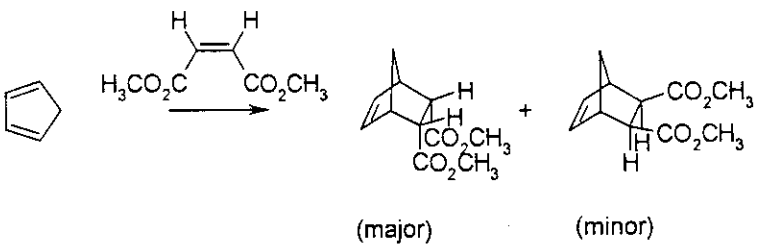
(1.3)

The great synthetic utility of Diels-Alder reaction depends on its remarkable stereo as well as regioselectivity. The structure and stereochemistry of the adducts formed can be predicted on the basis of two empirical rules, *The Cis Principle* (Equation 1.4a) and *The Endo Addition Rule*, (Equation 1.4b)

empirically formulated by Alder and Stein in 1937.[67] and explained later on the basis of frontier molecular orbital (FMO) theory.[68] According to the *Cis Principle* the relative stereochemistry of the substituents in both the dienophile and diene is retained in the adduct.[69] According to the *Endo Addition Rule*, in a diene addition reaction the diene and the dienophile arrange themselves in parallel planes, and the most stable transition state arises from the orientation in which there is maximum accumulation of double bonds. Thus in most cases, *endo* adduct predominates over the *exo* adduct.[69]



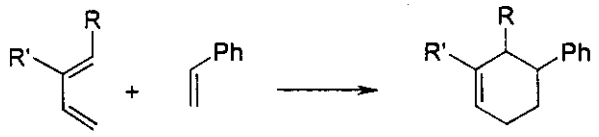
(1.4a)



(major) (minor)

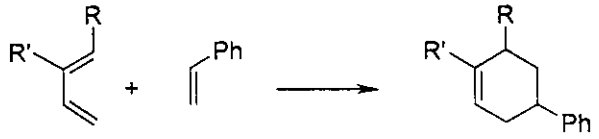
(1.4b)

Intermolecular Diels Alder reaction between unsymmetrically substituted dienes and dienophiles usually show regioselectivity. Recently, FMO theory has been applied with considerable success to the problem of regioselectivity in pericyclic reactions including the Diels-Alder reaction.[68] Given below are a few examples in which the observed regioselectivity is in accord with FMO theory (Equation 1.5a-o).



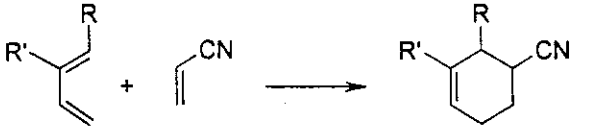
a R = Ph, R' = H; **b** R = CN, R' = H; **c** R = CH_3, R' = H

(1.5a)



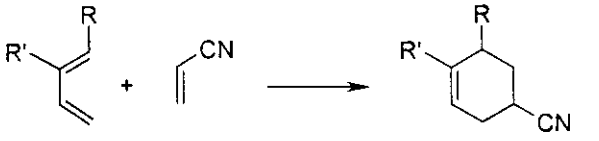
a R = H, R' = Ph; **b** R = H, R' = CN; **c** R = H, R' = CH_3

(1.5b)



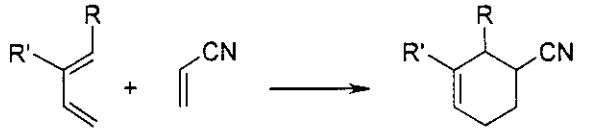
a R = Ph, R' = H; **b** R = CN, R' = H; **c** R = CH_3, R' = H

(1.5c)



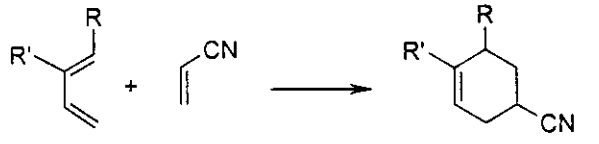
a R = H, R' = Ph; **b** R = H, R' = CN; **c** R = H, R' = CH_3

(1.5d)



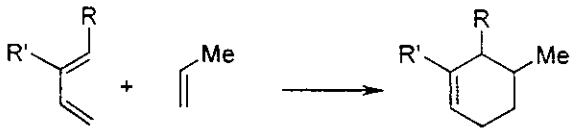
a R = Ph, R' = H; **b** R = CN, R' = H; **c** R = CH_3, R' = H

(1.5e)



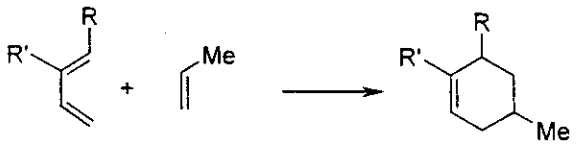
a R = H, R' = Ph; **b** R = H, R' = CN; **c** R = H, R' = CH_3

(1.5f)



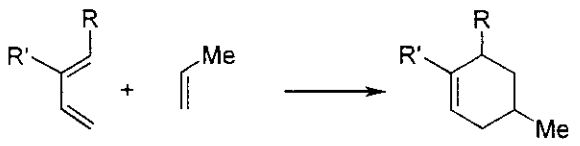
a R = Ph, R' = H; **b** R = CN, R' = H

(1.5g)



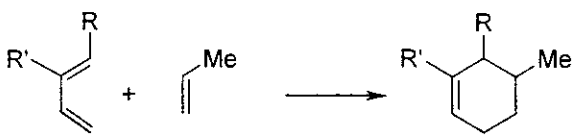
c R = CH_3, R' = H

(1.5h)



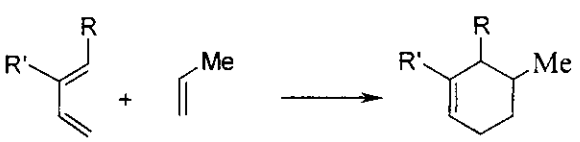
a R = H, R' = Ph; **b** R = H, R' = CN

(1.5i)



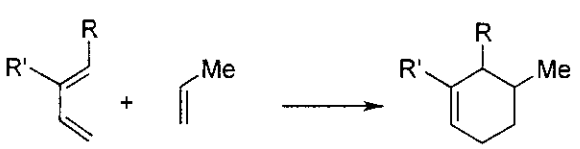
R = H, R' = CH_3

(1.5j)



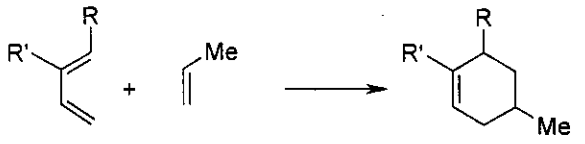
a R = Ph, R' = H; **b** R = CN, R' = H

(1.5k)



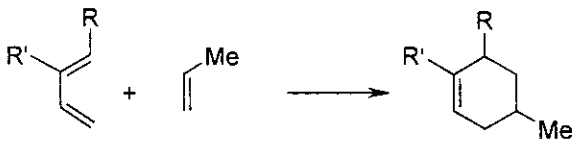
a R = Ph, R' = H; **b** R = CN, R' = H

(1.5l)



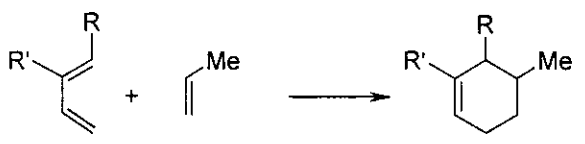
c R = CH_3, R' = H

(1.5m)



a R = H, R' = Ph; **b** R = H, R' = CN

(1.5n)



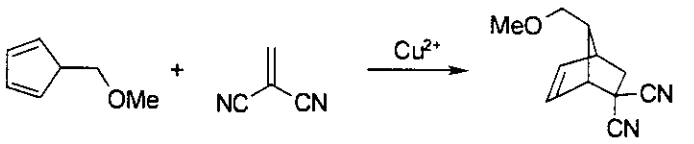
R = H, R' = CH_3

(1.5o)

1.3.1. Lewis Acid Catalysed Diels-Alder Reactions

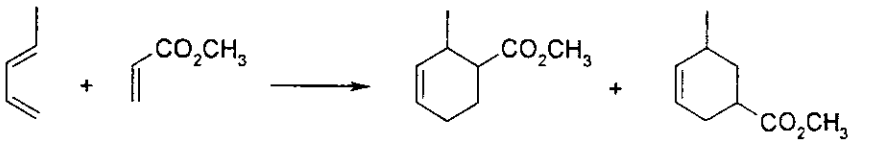
The rate of Diels-Alder reaction is little influenced by a change in polarity of the medium. Yet Lewis acids exert a strong catalysing effect. It has been found that certain Diels-Alder reactions are accelerated remarkably by $AlCl_3$ and other Lewis acids such as BF_3 and $SnCl_4$. Lewis acid catalysed Diels-Alder reactions are not only faster but also more stereo and regioselective than the uncatalysed reactions and hence, of great synthetic importance. Thus, cupric ion has been used to catalyse the Diels-Alder reaction of the 5-substituted cyclopentadiene **34** (Scheme 1.1a).[70] This is an example in which advantage is taken of the increase in rate of the catalysed reaction. Piperylene (**20c**) and methyl acrylate (**37**) give mainly the ortho product (**38**), but this preference is increased with Lewis acid catalysis (Scheme 1.6b).[71] To cite an example of enhanced stereoselectivity, the proportion of endo adduct (99%) in the $AlCl_3$ catalysed reaction of cyclopentadiene (**11**) and **37** (Scheme 1.6c) is substantially higher when compared to uncatalysed reaction (88%).[72]

Scheme 1.1a



1 2 3

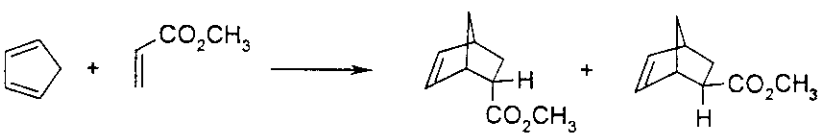
Scheme 1.1b



4 5 6 7

Without $AlCl_3$	90%	10%
With $AlCl_3$	98%	2%

Scheme 1.1c



8 5 10 11

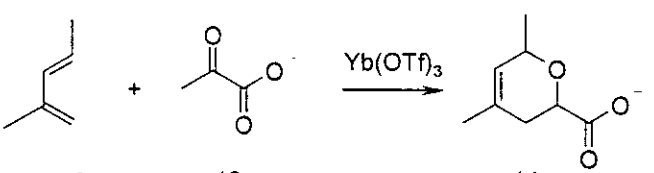
Without $AlCl_3$ at 0 °C	88%	12%
With $AlCl_3$ at O °C	96%	4%
With $AlCl_3$ at -80 °C	99%	1%

1.3.2. Diels-Alder Reactions is Aqueous Media

As stated earlier, Diels-Alder reaction is rather insensitive to the polarity of the solvent. An exception is, however, the case of water. It was found that in many Diels-Alder reactions, water had an unexpected accelerating effect. For example, the reaction of cyclopentadiene with butanone in water proceeds 740 times faster than in non-polar octane. The ratio of endo-exo adducts is also affected by water, which favours the endo stereoisomer. It is believed that in the Diels-Alder reaction the hydrophobic effect forces the diene and dienophile to come into close proximity and thus speeding up the reaction.[73] The aqueous Diels-Alder reactions of a series of dienylammonium chlorides derived from (*E*)-

2,4-pentadienylamine, (*E*)-3,5-hexadienylamine and (*E*)-4,6-heptadienylamine with a variety of dienophiles have been examined by Grieco *et al.*[55] A similar Diels-Alder study employing the sodium salt of *N*-(*E*)-4,6-heptadienyl succinamic acid in water was also undertaken. The preparation of a new chiral, water-soluble *E*-diene, which could be considered as the simplest diene obtainable from the simplest sugar, is described by Andre *et al.*, along with its use in cycloaddition with acrylaldehyde.[65] Water, as the solvent, enhanced the rate of the Diels-Alder reaction, promoted complete regio- and endo-selectivity, and improved α like (anti) facial selectivity, compared with the results obtained with organic solvents. Lewis-acid catalysis in aqueous medium[74-76] suffers from the intrinsic disadvantage that the majority of Diels-Alder reactants have a negligible tendency to interact with a Lewis-acid catalyst in water. Yet many reports show that the affinity of a Diels-Alder reactant for Lewis-acids can increase dramatically if the possibility of forming a chelate exists and thus Lewis-acid catalysis of a Diels-Alder reaction in water is feasible (Scheme 1.2).[77]

Scheme 1.2



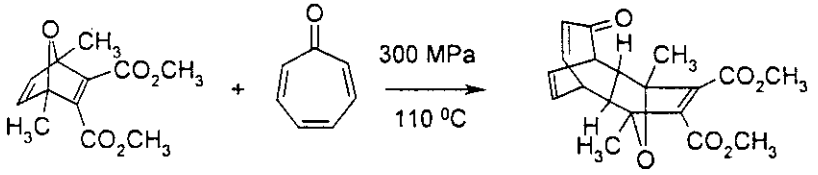
12 13 14

1.3.3. Pressure Assisted Diels-Alder Reactions

Since Diels-Alder reaction exhibits a negative volume of activation, an increase in pressure should accelerate the reaction rate. Pressure-assisted Diels-Alder reactions have attained significance in recent years.[34-45] Thus the Diels-Alder reaction of tropone (**16**) with 7-oxabicyclo[2.2.1]hepta-2,5-diene (**15**) under 300 MPa gave a 1:1-adduct **17** (Scheme 1.3).[35] Hetero Diels-Alder reaction of enaminoketones and ethyl vinyl ether to give the dihydropyrans in dichloromethane and in heptane/isodurene under high pressure up to 7 kbar at temperatures between 0.5°C and 130°C shows that a significant and synthetically useful increase of diastereoselectivity in chemical reactions is possible by

applying high pressure.[78] The cycloaddition shows a remarkable pressure-dependent increase of diastereoselectivity in favour of the cis adducts.

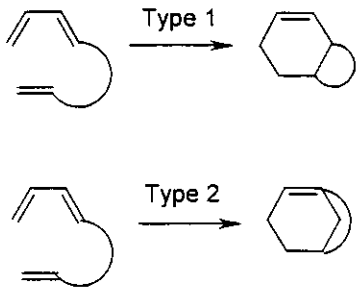
Scheme 1.3



15 **16** **17**

1.3.4. Intramolecular Diels-Alder Reactions

In recent years, the intramolecular Diels-Alder (IMDA)[16-25] reaction, in which both diene and dienophile components are part of the same molecule, has emerged as one of the most efficient mode to synthesise a variety of interesting bridged polycyclic compounds. In properly designed systems, these reactions accrue advantages in terms of ease of reaction, regioselectivity, stereoselectivity and introduction of multiple centres of configuration. IMDA reaction provides a simple and direct approach to polycyclic skeletons of special interest in the synthesis of natural products. Two rings (often obtained as fused bicyclic adducts) are formed in a single step, and the cyclisation often proceeds under remarkably mild conditions. The other variant of the intramolecular [4+2] cycloaddition reaction based on the connectivity available is the type 2 IMDA[79] reaction which results in bridged bicyclic ring system. The type 2 IMDA reaction provides a one-step entry into anti-Bredt alkenes, which were for many years regarded as chemical curiosities. When diene and dienophile are joined at position 1 of the diene (Type 1), cycloaddition usually gives rise to a fused bicyclic adduct (Equation 1.6a). The second variant involves union of diene and dienophile at position 2 of the diene (Type 2). Cycloaddition in this case results in the formation of a bridged bicyclic ring system (Equation 1.6b).

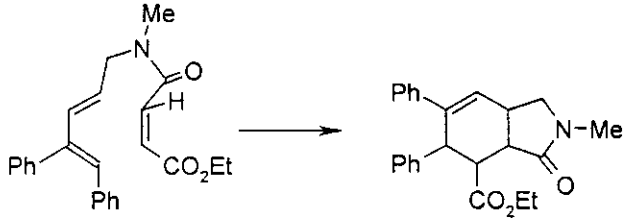


(1.6a)

(1.6b)

The first example of an intramolecular Diels-Alder reaction appears to be the unpublished result quoted by Alder on the conversion of 1,4-pentadiene and dimethyl acetylenedicarboxylate, via an unisolated ene adduct, to a bicyclo[4.1.0]heptene derivative.[80] Subsequent isolated reports[81-84] appear to be more incidental in nature until 1963, when two reports appeared on the deliberate application of IMDA reaction to natural product synthesis.[85,86] General contributions to the reaction mechanism were made in 1965.[87] Subsequently, several other reports on the synthetic utility of IMDA reactions (Scheme 1.4) have appeared in literature.[16,17,79]

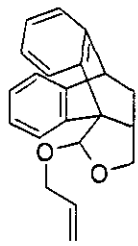
Scheme 1.4



18 **19**

IMDA cyclisation of a 9-substituted anthracene derivative was reported by Meek and Dann who obtained the cyclic acetal (**20**) in 2% yield on attempted preparation of 9-anthraldehyde diallyl acetal.[88,89] Cyclisation of the intermediate allyl 9-anthroate was considered as one of the possible mechanisms for the formation of the lactone (**21**) from 9-anthramide and allyl alcohol (Figure 1.1).

Figure 1.1



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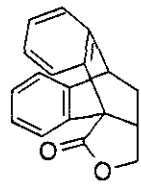
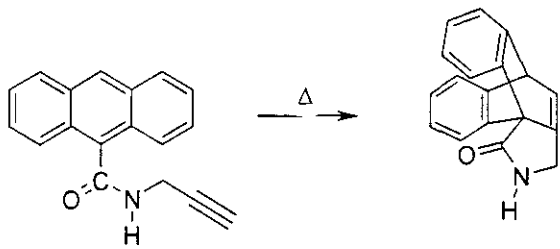


21

A wide assortment of 9,12-bridged ethano and ethenoanthracenes were prepared by the IMDA reaction of suitable 9-substiuted anthracenes by Ciganek.[6] The 9-substituted anthracenes include amide, imine, amine, ether, thioether, acetal and carbinol derivatives (Scheme 1.5).

Scheme 1.5



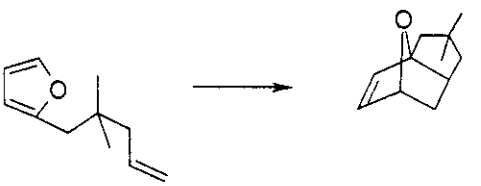
22 **23**

An area, which is gaining prominence in Diels-Alder chemistry involves the use of heteroaromtic compounds as either the diene or dienophile component.[90] By far the most extensively studied five-membered heteroaromatic system for Diels-Alder cycloaddition is furan and its derivatives.[91-93] The resultant 7-oxabicyclo[2.2.1]heptanes are valuable synthetic intermediates which have been further elaborated to substituted arenes, carbohydrate derivatives, and various natural products.[94-103] A crucial synthetic transformation employing these intermediates involves cleavage of the oxygen bridge to produce functionalised cyclohexene derivatives.[104-109] In many cases, however, the Diels-Alder strategy is not feasible because of the low reactivity of furan toward relatively unreactive dienophiles.[90] Additionally, furan and many of its derivatives are stable only at

low temperature. So, the successful Diels-Alder reactions involving furans are carried out under sub-ambient levels using activated dienophiles.

Intramolecular Diels-Alder reaction of furans, often designated as IMDAF, helps to overcome the sluggishness of this heteroaromatic ring system toward [4+2] cycloaddition (Scheme 1.6).

Scheme 1.6

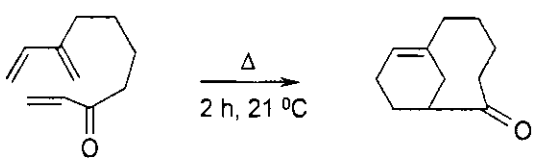


24 **25**

IMDAF reactions allow the preparation of complex oxygenated polycyclic compounds, and they often proceed at lower temperature than their intermolecular counter parts.[110] Even more significantly, unactivated π-bonds are often suitable dienophiles for the internal cycloaddition.[111]

As with intermolecular Diels-Alder reactions, the IMDA reactions are also catalysed by Lewis acids. Shea and Gilman[112] have reported a mild method for the synthesis of bicyclco[n.3.1] bridgehead alkenes by Lewis acid catalysed IMDA cycloadditions. Intramolecular cycloaddition of **26** in methylene chloride containing diethylaluminium chloride at 21 ^{0}C for 2h gave bicycloundecenone **27** (Scheme 1.7).

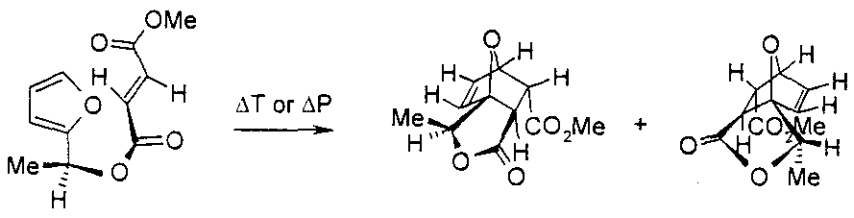
Scheme 1.7



26 **27**

The rate of IMDA reactions are also enhanced by applying pressure. Thus, the intramolecular Diels-Alder reactions of furans possessing a 2-alkyl substituent with a terminal α, β-unsaturated ketone have been reported by Laurence and co-workers.[113] The influence of high pressure on the IMDA reactions of optically active furfuryl fumarate (**28**) (Scheme 1.8) has been reported by Butz and Sauer.[114]

Scheme 1.8

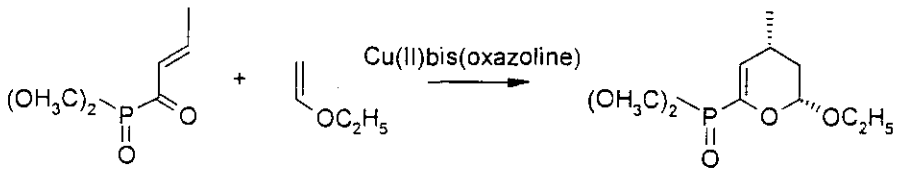


28 **29** 55% **30** 45%

1.3.5. Hetero Diels-Alder Reactions

Hetero Diels-Alder Reactions (HDA) was used as a new strategy for multichiral array synthesis in carbohydrate chemistry.[26] Thus hetero Diels-Alder reactions of α,β-unsaturated ketones and enol ethers led to the formation of fused dihydropyrans with complete stereospecificity and creation of chiral centres on the newly formed template.[26] Hetero-Diels-Alder reactions between α,β-unsaturated carbonyl compounds with functional substituents at α- and β-positions and enol ethers, ene-diol ethers, and ketene acetals, respectively, gave 3,4-dihydro-2H-pyrans, having functional substituents partially in all ring positions.[27] A method for the construction of substituted pyranoses by means of the hetero-Diels-Alder reaction of ethyl vinyl ether with 1-oxabuta-1,3-dienes bearing a thiazolyl ring at C-2. The asymmetric version of this synthetic sequence started from the HDA cycloaddition of the same alkene with the chiral oxabutadiene bearing the D-galacto-pentopyranosid-5-yl moiety at C-3.[29] Synthesis of azasugars via lanthanide-promoted aza Diels-Alder Reactions in aqueous medium was reported by Libing and his co-workers.[30] α, β-Unsaturated acylphosphonates (**31**) undergo enantioselective hetero Diels-Alder reactions with enol ethers (**32**) catalysed by chiral Cu(II) complexes to afford cyclic enol phosphonates (**33**), which are chemical entities that are shown to be useful building blocks for asymmetric synthesis (Scheme 1.9).[115]

Scheme 1.9

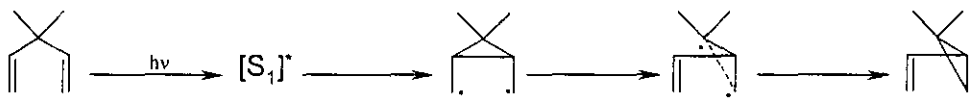


31 **32** **33**

1.4. Di-π-methane Rearrangement

Di-π-methane rearrangement[116-125] is a very general and well-studied photorearrangement. The very broad spectrum of types of organic molecules obtainable by the di-π-methane rearrangement is remarkable and makes it particularly synthetically useful. Zimmerman discovered the di-π-methane rearrangement in 1967 when the photolysis of reactants having two vinyl moieties bonded to an sp^3-hybridised carbon led to the formation of vinylcyclopropane.[126] This process, along with the mechanism suggested by Zimmerman[127,128], is depicted in Scheme 1.10 for the di-π-methane reactant, 3,3-dimethyl-1,4-pentadiene (**34**).

Scheme 1.10



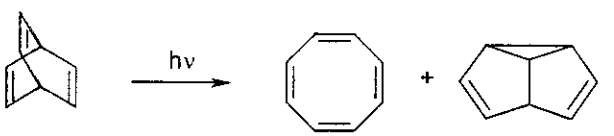
34 **35** **36** **37**

The same mechanism is applicable to those di-π-methane rearrangements, which proceed by way of singlet excited states and those proceeding via triplet counterparts.[124] Acyclic di-π-methane reactants rearrange effectively from their singlet excited states, whereas bicyclic di-π-methane systems prefer to rearrange via their triplet excited states.[127] A variation of this mechanism, proposed by Paquette[129,130], involves direct formation of diradical **36** from the reactant excited state. Both aliphatic and aromatic π-systems are capable of participating in the reaction. In addition to the basic di-π-methane rearrangement, there are variations

in which a carbon atom has been replaced by some other atom. The most common is the oxa-di-π-methane[120] rearrangement in which one of the two π-moieties is a carbonyl group. Similarly, the aza-di-π-methane[122] rearrangement has a C=N as one of the π-components.

Zimmerman and Grunewald[131] studied the photochemical isomerisation of barrelene (**38**) to afford cyclooctatetraene (**39**) and semibullvalene (**40**). Photolysis of **38** in isopentane containing 3-8% acetone as photosensitiser afforded 25-40% yields of semibullvalene and 1-2% of cyclooctatetraene. The photochemical conversion of barrelene to semibullvalene as given in Scheme 1.11 was instrumental in assessing the generality of di-π-methane rearrangement.

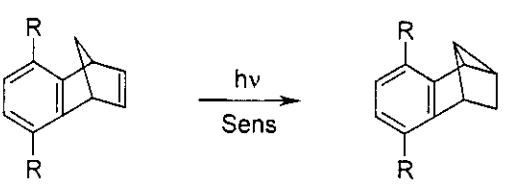
Scheme 1.11



38 **39** **40**

Edman[132] has reported the rearrangement of two benzonorbornadienes **41a,b** to the corresponding tetracyclo[5.4.0.0]undeca-1(7),8, 10-trienes **42a,b** on acetophenone photosensitisation. (Scheme 1.12) Direct irradiation of **41a** gave **42a** very slowly while **41b** afforded no **42b**.

Scheme 1.12



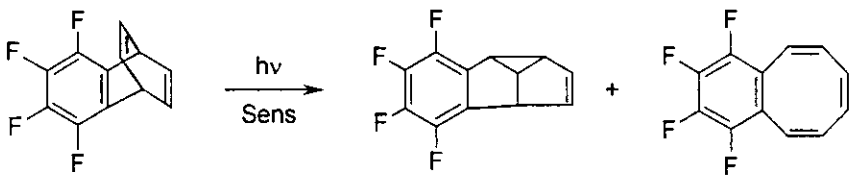
41 **42**

a R=H
b R=OAc

Rearrangement of 5,6,7,8-tetrafluoro-1, 4-dihydro-1, 4-ethenonaphthalene **43** on acetone sensitisation has been shown to give mainly

tetrafluorobenzosemibullvalene **44** plus a trace of tetrafluorobenzocyclooctatetraene **45** as shown in Scheme 1.13. However, on direct irradiation **45** was the major product.[133]

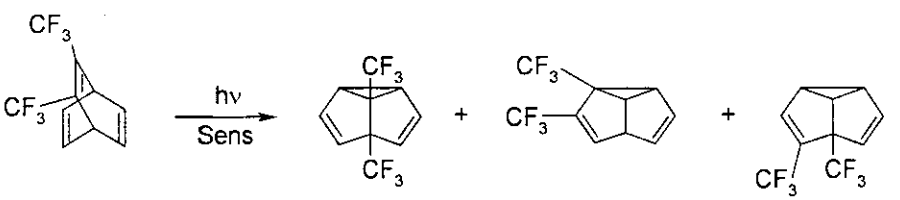
Scheme 1.13



43 **44** **45**

Sensitised irradiation of 2,3-bis(perfluoromethyl)bicyclo[2.2.2]octa-2,5,8-triene **46** led to three bis(perfluoromethyl)tricyclo[3.3.0.0]octa-3,6-dienes **47-49** alluding chemoselectivity as well as regioselectivity in barrelene-semibullvalene rearrangement[134] (Scheme 1.14).

Scheme 1.14



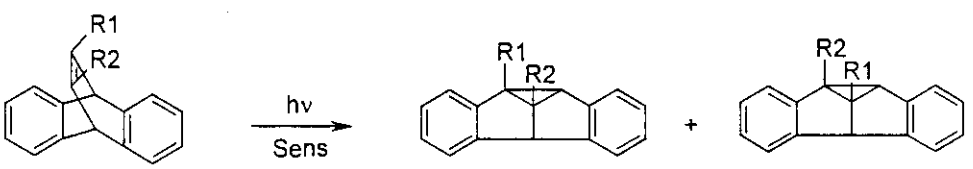
46 **47** **48** **49**

Zimmerman and coworkers observed the preference for vinyl-vinyl over benzo-vinyl bridging in benzobarrelene to benzosemibullvalene transformation.[135] Sensitised irradiation of 1,2-naphtobarrelene afforded solely the *syn*- and *anti*-1,2-naphthosemibullvalenes via the α-naphto-vinyl bridging.[136] Irradiation of benzo-2,3-naphthobarrelene gave benzo-2,3-naphthosemibullvalene.[137] Studies by Zimmerman and Bender[137] demonstrated that vinyl-vinyl bridging is preferred in the transformation of 2,3-naphthobarrelenes. The most striking result was the equal preference for the benzo-vinyl and β-naphtho-vinyl bridging reaction pathways. Thus, operationally there is a discernable pattern of reactivity in the bridging process: α–naphtho-vinyl > vinyl-vinyl > β-naphtho-vinyl ~benzo-vinyl. It was concluded by Zimmerman *et al.*[137] that the minimization of energy of the

reacting triplet along the reaction coordinate at the stage of transannular bridging is the controlling factor. The rearrangement of 2,3-anthrabarrlene to 2,3-anthrasemibullvalene proceeded via vinyl-vinyl bridging rather than anthraceno-vinyl bridging.[138]

Ciganek[139] has reported the rearrangement of a variety of dibenzobarrelenes such as **50a-e**. Irradiation of an acetone solution of dibenzobarrelene **50a-d** gave dibenzosemibullvalene **51a-d**. Dibenzosemibullvalene was also obtained, albeit in very low yields in the unsensitised photolysis of **50a** in benzene solution. Besides, the unsymmetrical dibenzobarrelene **50e** afforded **51e** in greater yields than other regioisomeric semibullvalene **52e** (Scheme 1.15).

Scheme 1.15

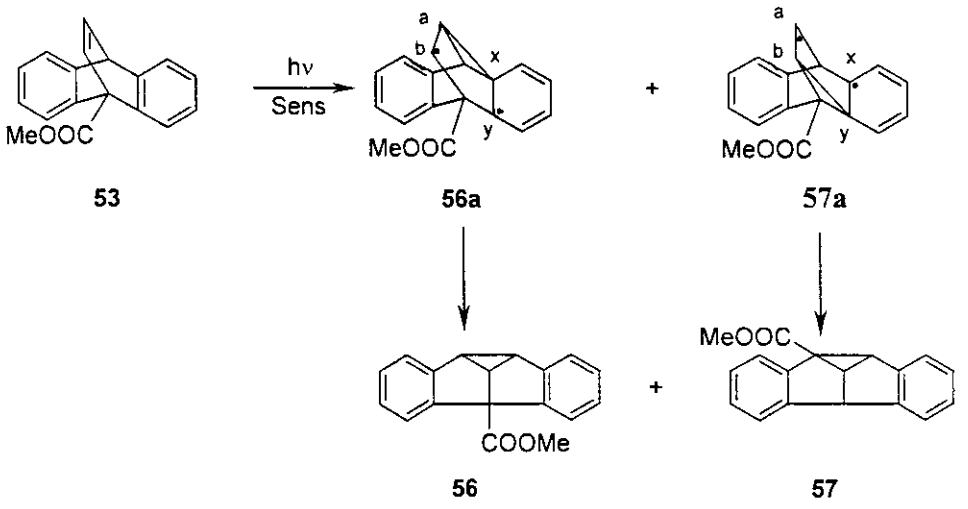


50 **51** **52**

a R1=R2=H b R1=R2=$COOCH_3$
c R1=R2=CN d R1=R2=CF_3
e R1=H; R2=$COOCH_3$

Ciganek showed that the isomerisation of **53** [139] lead to the formation of a mixture of **56** and **57** in a 2:1 ratio (Scheme 1.16). This clearly points out the fact that electronic effects are important in controlling regioselectivity by determining the course of initial bonding in di-π-methane rearrangement.

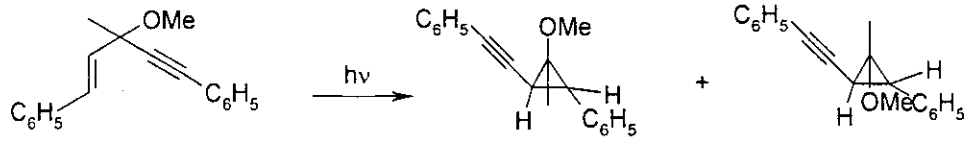
Scheme 1.16



53 **56a** **57a** **56** **57**

Griffin and coworkers[140] have studied several di-π-methane systems having moeities other than phenyl and vinyl. Thus *trans*- 1,5-diphenyl-3-methoxy-3-methylpent-1-en-4-yne (**58**) undergoes rearrangement upon direct irradiation to the corresponding acetylenic cyclopropanes (**59** and **60**) (Scheme 1.17).

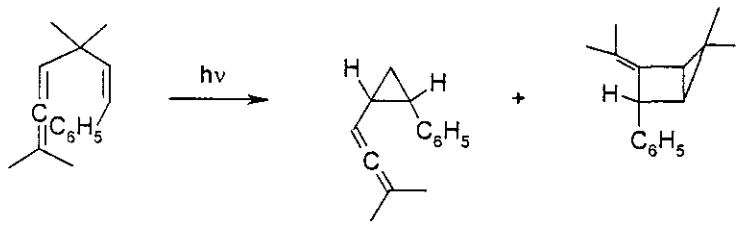
Scheme 1.17



58 **59** **60**

Di-π-methane rearrangement of allenylvinylmethanes (**61**) produce minor amounts of allenylcyclopropanes (**62**) (Scheme 1.18).[140]

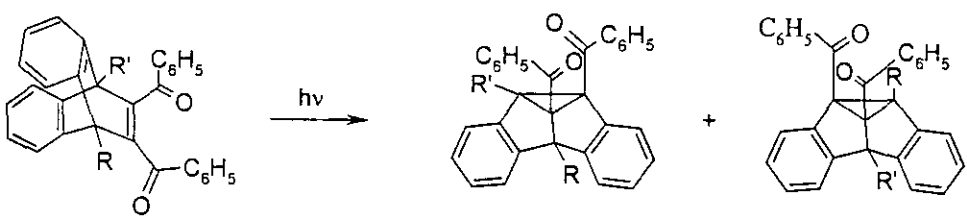
Scheme 1.18



61 **62** **63**

The steady-state and laser flash photolysis studies of dibenzobarrelenes containing 1,2-dibenzoylalkene (**64**) moieties have been carried out by George *et al* (Scheme 1.19).[141-146] These barrelenes undergo di-π-methane rearrangement and electrocyclic reactions characteristic of barrelene chromophore in preference to dibenzoylalkene rearrangement. Furthermore, it was established that the bridgehead substituent can control the regioselectivity of barrelene to semibullvalene transformation by a combination of steric and electronic factors.

Scheme 1.19



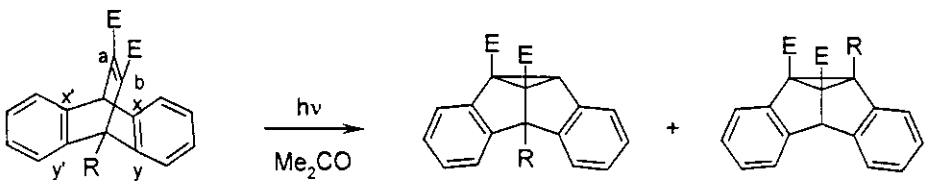
64 **65** **66**

The photorearrangement of a few 9,10-disubstituted naphthobarrelenes to corresponding naphthosemibullvalenes and their thermal transformations to the corresponding naphthopentalenofurans has also been studied.[147]

Scheffer[148-161] and his group have carried out extensive investigation on the solid state as well as solution phase photochemistry of dibenzobarrelenes (Scheme 1.20). Their investigations have proved that the regioselectivity of di-π-methane rearrangement is a function of reaction medium. In the solid state regioselectivity might be due to the steric inteaction between the reacting

molecule and its lattice neighbours.[148] In the solution phase rearrangement, regioselectivity is controlled by steric as well as electronic factors.[154]

Scheme 1.20



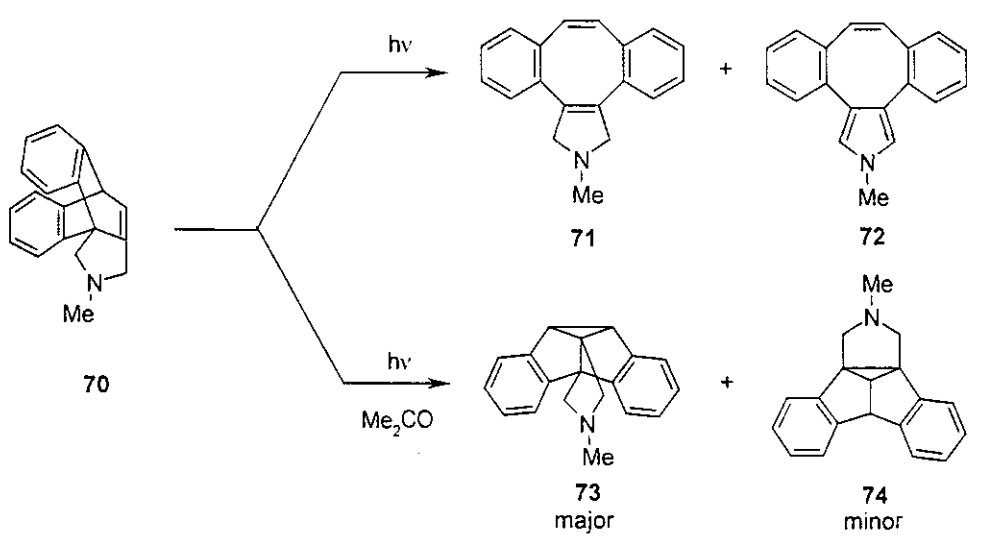
67
R = CH_2OAc
E = CO_2Me

68
a-x or a-x'
major

69
b-y or b-y'
minor

Synthesis and photochemical transformations of several 9,10-etheno as well as 9,10-ethanoanthracenes have been reported by Ciganek.[162] Upon direct irradiation, 2-methyl-1,2,3,5-tetrahydro-5,9b-*o*-benzenobenz[e]isoindole (**70**) gave a mixture of 2-methyl-1,3-dihydro-2H-dibenzo[3,4:7,8]cycloocta[c]pyrrole (**71**) and 2-methyl-2H-dibenzo[3,4:7,8]cycloocta[c]pyrrole (**72**). On the other hand, acetone-sensitised irradiation of **70** gave a 80:20 mixture of 10-methyl-4a,8d-(methaniminomethano)dibenzo[a,f]cyclopropa[cd]pentalene (**73**) and 2-methyl-1,2-dihydro-3a,8,12b-methenodibenzo[3,4:6,7]cyclo-hepta[1,2-c]pyrrole (**74**) (Scheme 1.21).

Scheme 1.21



Based on the structural variety of substrates enumerated above, it may be concluded that di-π-methane rearrangement is quite general and occurs in a

variety of substrates having the required di-π-methane component. The presence of other photophores does not affect the efficacy of the process as illustrated with dibenzobarrelenes containing a dibenzoylalkene component. Thus, it appears that di-π-methane rearrangement holds considerable synthetic potential. The synthetic potential of this remarkable rearrangement can further be realised by containing the competing singlet-mediated cycloaddition pathway. In this context, development of suitable singlet quenchers holds a lot of promise.

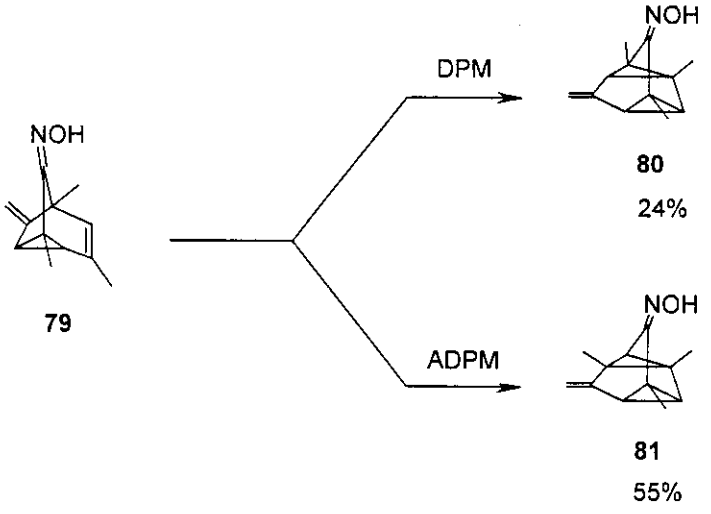
A di- π-methane like mechanism in the case of β,γ-unsaturated ketones was first suggested by Swenton[163] while a relationship to the ordinary di-π-methane rearrangement was first noted by Givens[164] and the process was termed oxa-di- π-methane rearrangement by Dauben.[165] The first example of an oxa-di-π-methane rearrangement in a β,γ-unsaturated aldehyde was reported by Schaffner et al.[166] One of the earliest examples of this photochemical rearrangement was reported by Tenney, et al., in 1966.[167] Thus, irradiation of 1,2,4,4-tetraphenyl-3-butenone gave a 7% yield of 2,2,3-triphenyl-1-benzoylcyclopropane. Following the observations of Tenney were reports by Williams and Ziffer[168] describing the rearrangement of unsaturated ketones to corresponding cyclopropyl ketones. The oxa-di- π-methane, in contrast to di- π-methane rearrangement, occurs exclusively from the triplet excited state (Scheme 1.22).

Scheme 1.22

75 **76** **77** **78**

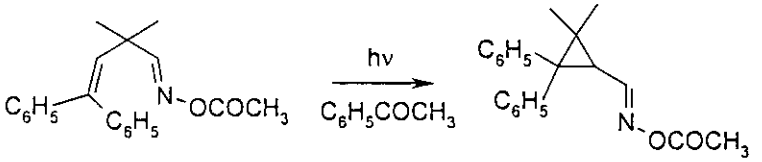
Illustration of di-π-methane rearrangement involving β,γ–unsaturated C-N double bond in imines and oxime acetates ensued the aza-di-π-methane rearrangement. The first example of an aza-di-π-methane rearrangement was reported by Nitta et al. in the irradiation of tricyclic oxime **79** (Scheme 1.23).[169]

Scheme 1.23



Quenching and sensitisation experiments by Armesto et al.[170-173] showed that the reaction proceeds via the triplet excited state. Acetophenone-sensitised irradiation of oxime acetate (**82**) gave the aza-di-π-methane product (**83**) (Scheme 1.24).

Scheme 1.24



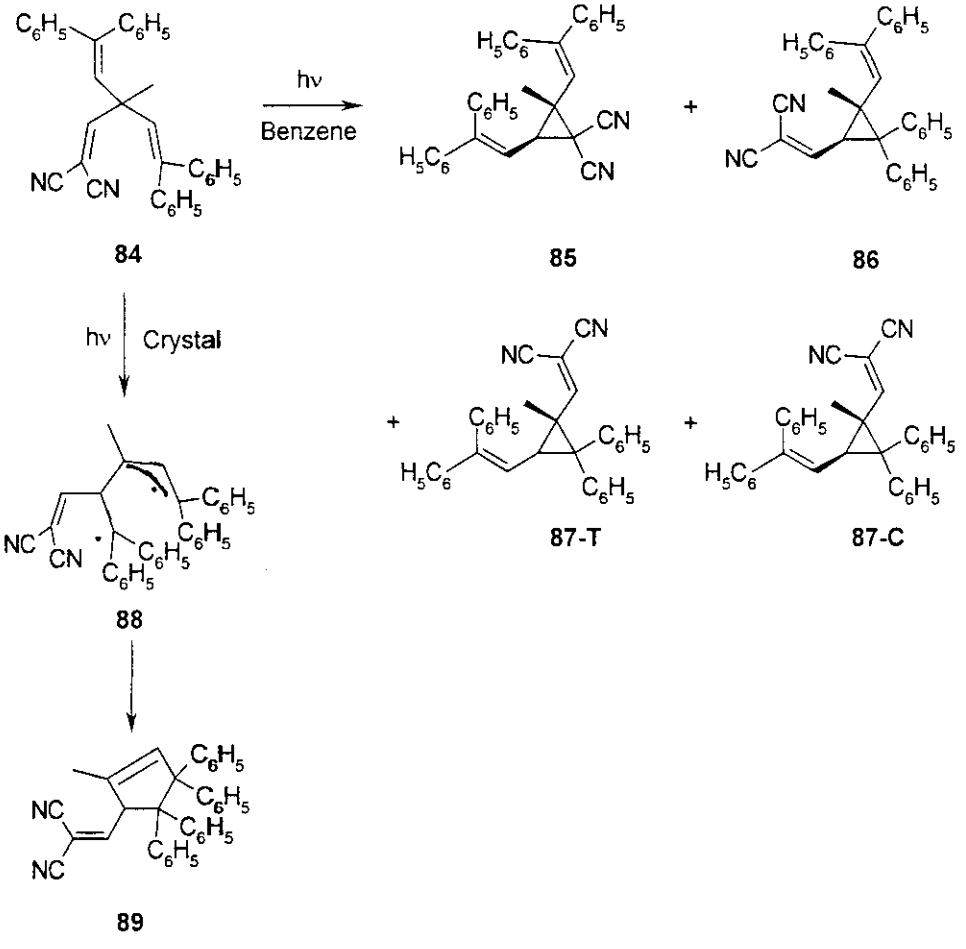
82 **83**

The aza-di- π-methane reactivity of C-N double bond is not limited to stable derivatives of β,γ-unsaturated aldehydes such as oxime acetates. A study has shown that other oxime esters such as oxime benzoate[174] and oxime trifluoroacetate[175], and hydrazine derivatives such as semicarbazone[174], acetyl hydrazone[175], benzoyl hydrazone[174], and tosyl hydrazone[176], undergo the rearrangement. The competition between di- π-methane and the aza-di- π-methane rearrangements has been studied and it appears that aza-di- π-methane rearrangement is more efficient than its all-carbon analogue.[177,178] The efficiency of aza-di- π-methane reactivity of oxime acetates has opened a new synthetic

route to the carboxylic acids present in pyrethroids of known insecticidal activity.[179]

Zimmerman *et al.*[180,181] have shown that a tri-π-methane system such as **84** gave cyclopropane derivatives (**85, 86, 87-T, 87-C**), on photolysis in solution through di-π-methane rearrangement while in solid state it gave a cyclopentene derivative (**89**) arising through tri-π-methane rearrangement. The mechanism as suggested by Zimmerman[181] for the formation of cyclopentene derivative is given in Scheme 1.25.

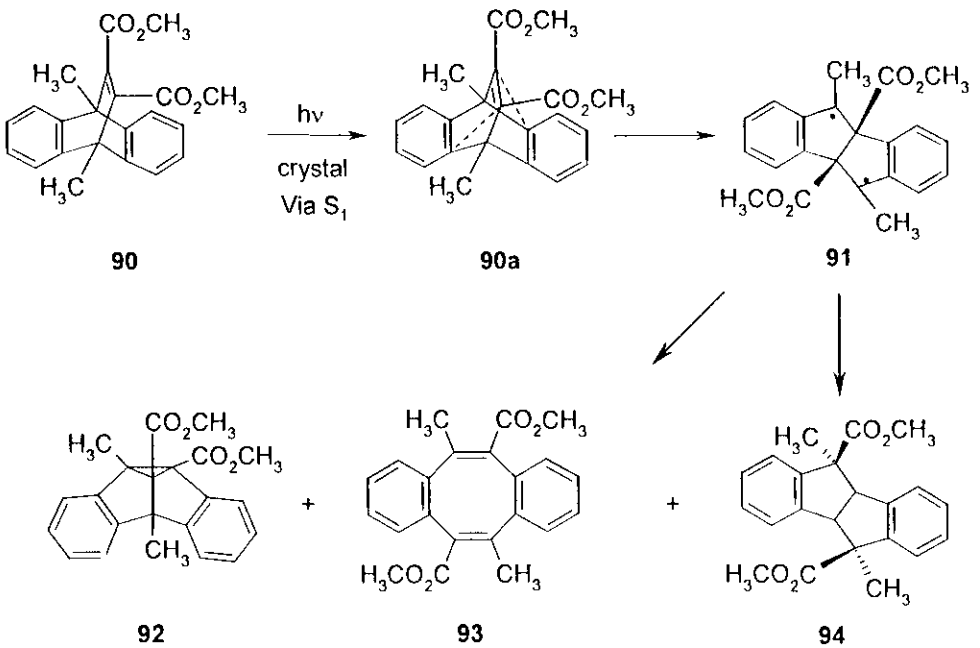
Scheme 1.25



Scheffer *et al.*[161] have reported that photolysis of crystals of dimethyl 9,10-dimethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**90**) afforded mainly a novel diester (**94**), along with small amounts of cyclooctatetraene

formation of biradical **91** is singlet mediated and involves, at least formally, a type of tri-π-methane interaction of both aromatic rings with the vinyl component present in the molecule. It seems likely that the mechanism by which diester **94** was formed involves sequential carbomethoxy group migration in the bis-benzylic biradical **91**.[161]

Scheme 1.26



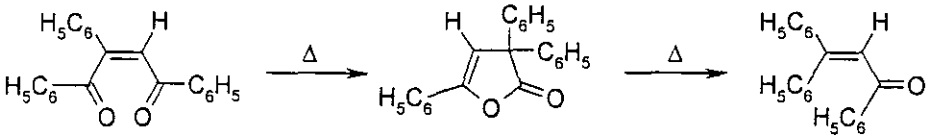
1.5. Dibenzoylalkene Rearrangement

Dibenzoylalkenes can undergo bond reorganisation process thermally and photochemically. The first reported dibenzoylalkene rearrangement is the pyrolysis of *cis*-dibenzoylstilbene to tetraphenylcrotonolactone by Zinin in 1872.[182] Subsequently, several other reports on the synthesis and transformations of a variety of dibenzoylalkenes have appeared in literature.

Dibenzoylalkenes on pyrolysis undergo ring closure and ring opening as well as ring enlargement and ring contraction. *cis*-Dibenzoylstyrene (**95**) on

pyrolysis undergoes ring closure to form triphenylcrotonolactone (**96**).[183-185] The lactone on further heating lost carbon monoxide to give β-phenylbenzalacetophenone (**97**) (Scheme 1.27).[186]

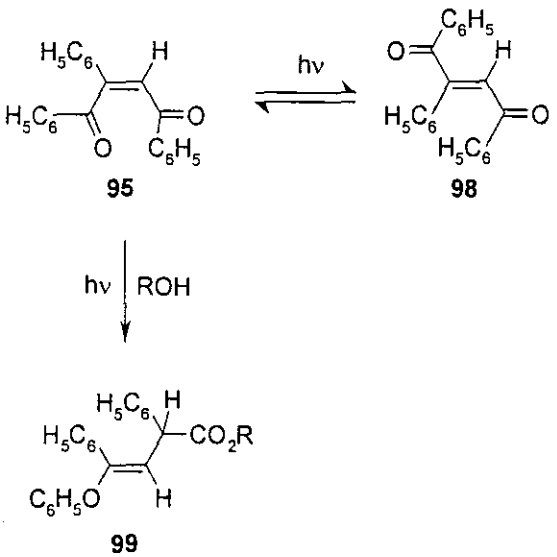
Scheme 1.27



95 **96** **97**

cis-Dibenzoylstyrene (**95**) on photolysis undergoes isomerisation to give *trans*-dibenzoylstyrene (**98**).[187] In alcohols as solvents, on photolysis, it undergoes intramolecular rearrangement through 1,5-phenyl migration to oxygen to give corresponding esters of 3-butenoic acid (**99**) (Scheme 1.28).[188-190]

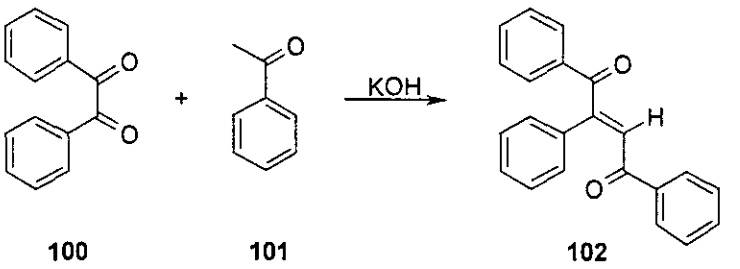
Scheme 1.28



95 **98** **99**

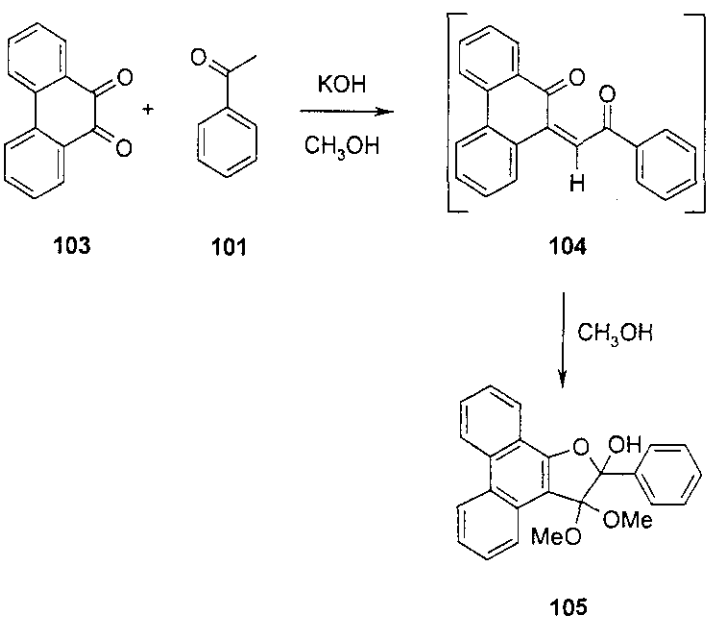
Base-catalysed aldol condensation of acetophenone (**101**) with 1,2-diketones such as benzil (**100**) yields the corresponding α,β-unsaturated ketone[191,192] (**102**) as a stable end product (Scheme 1.29).

Scheme 1.29



Based on this observation, we surmised that other 1,2-diones such as phenanthrenequinone (**103**) and acenapthenequinone also should react with acetophenone (**101**) to give the corresponding dibenzoylalkene-type systems. Earlier investigation carried out in our laboratory have revealed that phenanthrenequinone (**103**), indeed reacts with acetophenone (**101**) to yield phenanthrenone-9-ylidene ketone (**104**) which undergoes further transformation under the reaction conditions to yield the phenanthrofunaol **105** (Scheme 1.30).[193]

Scheme 1.30



As a logical extension to our studies, we propose to examine the base-catalysed reaction of acenaphthenequinone with suitable acetophenones in methanol to prepare a few dibenzoylalkene-type systems for further investigations.

1.6. Outline of the Research Problem and its Importance

Bicyclo[2.2.2]octa-2,5,7-triene (barrelene) undergoes photochemical transformations in high yields and exhibit remarkable selectivity based on the nature of excited states involved. It has been established that direct irradiation of barrelenes leads to the formation of the corresponding cyclooctatetraenes arising through a singlet-mediated pathway whereas triplet-sensitised irradiation leads to the formation of semibullvalenes. However, in most cases a mixture of both cyclooctatetraene and semibullvalene is formed. In principle, it should be possible to use a suitable singlet quencher to suppress the formation of cyclooctatetraene and a triplet quencher to suppress the formation of semibullvalene.

Our aim was to explore and illustrate the possibility of controlling competing pathways in the photochemical transformation of dibenzobarrelenes. We proposed to introduce the idea of selective intramolecular quenching of excited states by incorporating "inbuilt" quenchers onto the barrelene chromophore. It is known that appropriate olefins can quench triplet-excited states through energy transfer. We premise that the triplet excited state of a barrelene with an appended olefin unit might be quenched intramolecularly. In order to exploit the true potential of this possibility, it is important to fine-tune the triplet energy of the olefin unit. This entails the synthesis of several alkenylbarrelenes having olefin units possessing a range of triplet energies for identifying the ideal structural features for efficient intramolecular quenching. It is also possible that the appended olefin unit will introduce novel photochemical pathways unavailable to simple dibenzobarrelenes. We presume that the location of the additional π-system relative to the barrelene chromophore is of crucial importance in this context. Introduction of a vinyl substituent at the bridgehead position of dibenzobarrelenes, for example, will provide a tetra-π-methane system capable of exhibiting hitherto unexplored modes of photochemical transformations. It is also interesting to investigate the role of allyl, homoallyl and more remote alkenyl substituents in controlling the photochemistry of dibenzobarrelenes. Since we propose to employ suitably-substituted anthracenes

as logical precursors to the target dibenzobarrelenes, a major side reaction here may be intramolecular Diels-Alder reaction. So, it is important to identify the right structural features of alkenylanthracenes and the optimal reaction conditions that will enable them to undergo intermolecular or intramolecular Diels-Alder reactions.

In this context, we were interested in examining the photochemistry of two types of 9-alkenylbarrelenes. These include dibenzobarrelenes where the fourth π-moiety is directly attached to the barrelene chromophore and other barrelenes where the fourth π-moiety is present as a remote auxiliary. We intent to incorporate the auxiliaries in such a way that there is only minimal ground-state interaction between the two components (dibenzobarrelenes as precursor molecules and olefin component as auxiliary). We expect these components to absorb independently. So, it should be possible to excite the components independently by selecting the excitation wavelengths judiciously. However, excited interaction is possible leading to considerable alteration of physical properties (including preferential quenching of either singlet or triplet excited states) of dibenzobarrelene chromophore. We propose to gain access to these dibenzobarrelenes through the corresponding alkenylanthracenes. In continuation with our studies on the effects of an ethylenic substituent at the bridgehead position on the photochemistry of dibenzobarrelenes, we propose to investigate the effect of acetylenic substituents at the bridgehead on the photochemistry of dibenzobarrelenes. Such substituents can selectively stabilise the diradical intermediates involved in the barrelene to semibullvalene transformation and hence control the observed regioselectivity in this transformation.

As an extension to our studies on assessing the effect of vinyl moieties at the bridgehead of dibenzobarrelenes on its photochemical reactions, we proposed to synthesise a few dibenzobarrelenes possessing acetylenic substituents at the bridgehead position. Such barrelenes can readily be accessed through inter or intramolecular Diels-Alder reaction.

The reactions of amines with aromatic hydrocarbons in the excited state have attracted considerable attention in recent years, mainly in connection with electron-transfer reactions and/or exciplex formation. Our interest in this area has risen from the pursuits in controlling the selectivity of photochemical transformations in barrelenes by incorporating "inbuilt" quenchers and thereby facilitating intramolecular quenching by electron and or energy transfer. We reasoned that an intramolecular process should be much more efficient than the corresponding intermolecular process. Thus, amines could quench the short-lived singlet excited states by intramolecular electron transfer. This strategy has the advantage that back electron transfer from the radical cation of the amine to the radical anion of the selected chromophores is also intramolecular in nature resulting in highly efficient quenching. Based on these assumptions, we decided to explore the possibility of selective quenching of singlet excited states of a few representative substrates. These "inbuilt" quenchers should be remote to and hence possessing no ground-state interaction with the chromophore under consideration.

The objectives of the present work are:

1. Investigation of inter and intramolecular Diels-Alder reactions of anthracenes and furans
   a) To recognise the ideal structural features suitable for IMDA.
   b) To understand the effect of reaction conditions and concentration of reagents on the competition between IMDA and intermolecular Diels-Alder reactions.

2. Effect of an olefin unit on the photochemistry of barrelenes:- Will the fourth π-moiety act as an internal quencher?
   a) Synthesis and photochemical investigation of a few tetra-π-methane systems, which have the potential to undergo di-π-methane/tri-π-methane rearrangement.

b) Examine the effect of electron donating and / or electron accepting groups on the fourth vinylic group in the course of the rearrangement.

c) Investigate the effect of 9-allyl, 9-homoallyl (or, more remote) substituent in the photochemistry of barrelenes.

d) Probe the possibility of intramolecular quenching of excited singlet state of barrelenes.

3. Preliminary photochemical investigations to prove that electronic factors govern regioselectivity in the di-π-methane rearrangement of 9,10-ethenoanthracenes.

4. To synthesise a few 2-ethenylfurans and corresponding Diels-Alder adducts and to examine their photochemistry.

5. To synthesise a few dibenzoylalkene-type systems having rigid structural features. Our objective is to illustrate the generality of dibenzoylalkene rearrangement by examining substrates that are radically different from those investigated so far.

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CHAPTER 2

SYNTHESIS OF ALKENYLANTHRACENES

2.1. Abstract

Dibenzobarrelenes undergo interesting photochemical rearrangements. We proposed to introduce alkenyl groups at the bridgehead position of dibenzobarrelenes to assess the role of the fourth π-moiety on their photochemistry. Such barrelenes are readily accessible through the Diels-Alder reaction between 9-alkenylanthracenes and suitable dienophiles. This chapter deals with our endeavours on the synthesis of alkenylanthracenes that would serve as potential substrates for carrying out Diels-Alder reaction with suitable dienophiles to give dibenzobarrelenes containing alkenyl moiety at the bridgehead position.

2.2. Introduction

The purpose of our investigation is to introduce an alkenyl group at the bridgehead position of dibenzobarrelenes to assess the impact of the fourth π-moiety if di-π-methane and / or tri-π-methane rearrangement were to take place. In this context, we were interested in examining the photochemistry of two types of 9-alkenylbarrelenes. These include dibenzobarrelenes where the fourth π-moiety is directly attached to the barrelene chromophore and other substrates where the fourth π-moiety is present as a remote auxiliary. We proposed to gain access to these dibenzobarrelenes through the corresponding alkenylanthracenes. We employed Wittig reaction, Grignard reaction, Claisen-Schmidt condensation, Williamson's ether type synthesis, Esterification etc. for the preparation of alkenylanthracenes. Phase Transfer Catalysis was employed where applicable to improve the yield of desired

products. A brief overview of these methods is presented in the following paragraphs.

Wittig reaction[1-3] has been widely exploited in laboratory as well as industrial processes for the syntheses of steroids and carotenoids. The reaction involves a sequence starting from the quaternisation of triphenylphosphine with an alkyl halide to give a quaternary phosphonium halide, which under the influence of a strong base eliminates hydrogen halide to give an alkylidenephosphorane commonly referred to as a phosphorous ylide. The ylide reacts with an aldehyde or ketone to give a betaine intermediate, which then under the reaction conditions eliminates triphenylphosphine oxide to form an alkene. Consequently, the reaction between 9-anthraldehyde and its higher homologues with suitable ylides should yield a variety of alkenylanthracenes.

The addition of Grignard reagents to aldehydes and ketones is known as the Grignard reaction.[4,5] The reaction is of very broad scope and hundreds of alcohols have been prepared by this method. In some cases, the alcohols formed can easily be dehydrated during the work up of the reaction mixture under acidic conditions. Thus, it is known that the Grignard reaction between anthrone and methylmagnesium bromide results in the formation of 9-methylanthracene in high yields. Based on this, we surmised that the reaction of alkenylmagnesium halides with anthrone should lead to the corresponding 9-alkenylanthracenes.

α, β-Unsaturated ketones, are conveniently prepared by Claisen-Schmidt condensation.[6-12] It is the aldol condensation and subsequent elimination of elements of water in the presence of a basic catalyst. The aldol condensation, usually carried out in protic solvents, is one of the most versatile methods in organic synthesis. Aromatic aldehydes lacking alpha hydrogen atom undergo Claisen-Schmidt condensation with methyl ketones. The reaction involves the nucleophilic addition of the enolate ion of the methyl ketone onto the carbonyl group of the aldehyde giving rise to the corresponding aldol which undergoes dehydration to yield the desired α,β-unsaturated carbonyl compound.

The Williamson reaction [13-17], discovered in 1850, is still the best general method for the preparation of unsymmetrical ethers or, for that matter, symmetrical ones. The normal method involves treatment of an alkyl halide with alkoxide or aroxide ion prepared from alcohol or phenol, but it is also possible to mix the halide and alcohol or phenol directly with solid KOH in DMSO or with HgO and HBF_4 in dichloromethane.

Esters[18,19] are conveniently prepared from carboxylic acids and alcohols. Usually, the acid is first converted to corresponding acid chloride or acid anhydride and treated with the corresponding alcohol to give the desired ester. Alternatively, transesterification[20] and condensation between acids and alcohols under the influence of a suitable reagent such as DCC[21] are also widely employed for the synthesis of a variety of esters.

Phase transfer catalysis[22-25] is mainly employed when the reactants do not mix (or dissolve in a common solvent) when carrying out nucleophilic substitution reactions. In this method, a catalyst is used to transport the nucleophile from the aqueous into the organic phase. There are two principal types of phase transfer catalysts, quaternary ammonium or phosphonium salts and crown ethers and cryptands. Certain cross-linked polystyrene resins as well as alumina and silica, have been used as insoluble phase transfer catalysts. These triphasic catalysts have the advantage of simplified product work-up and easy and quantitative catalyst recovery.

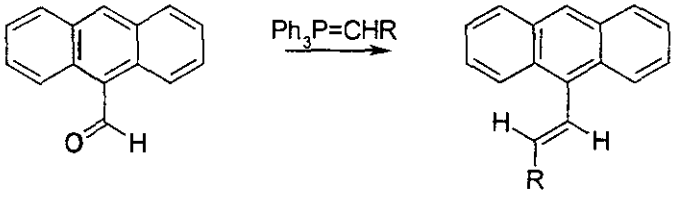
2.3. Results and Discussion

2.3.1. Preparation of Alkenylanthracenes

We employed Wittig reaction of 9-anthraldehyde for the preparation of a few of the desired ethenylanthracenes. Attempted preparation of **2a** by Wittig reaction of 9-anthraldehyde (**1**) with methyltriphenylphosphonium iodide[26] in dichloromethane in the presence of 50% aqueous solution of NaOH resulted in low yields.[27] On the other

hand, **2b** could be prepared from **1** and benzyltriphenylphosphonium chloride[26] in dichloromethane in the presence of 50% aqueous solution of NaOH in good yields[28] (Scheme 2.1).

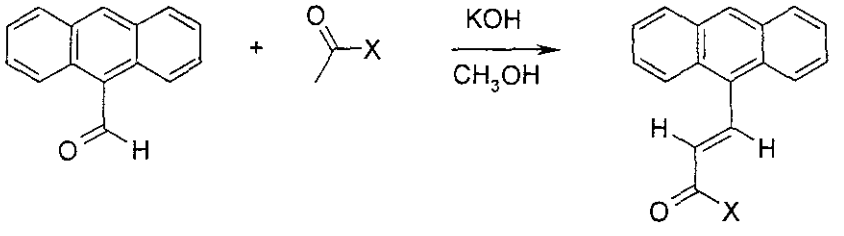
Scheme 2.1



1 **2a** R = H
b R = C_6H_5

Claisen-Schmidt condensation between aromatic aldehydes and methyl ketones result in unsaturated carbonyl compounds. Hence, we reasoned that the reaction of **1** with suitable methyl ketones **3a-c** should yield α,β-unsaturated ketones **2c-e**, which would serve as suitable alkenylanthracenes for our investigation. Thus, alkenylanthracenes **2c-e** were prepared by Claisen-Schmidt condensation of **1** with suitable methyl ketones **3a-c** in methanol in presence of potassium hydroxide (Scheme 2.2). Methyl ketones of our choice were acetone, (**3a**) acetophenone (**3b**) and 4-phenylacetophenone (**3c**). Our selection of these ketones was based on the large variation in the triplet energy of the incipient enone components derived from these ketones. We employed a previously reported procedure for the preparation of **3c**.[29]

Scheme 2.2



1 **3a** X = CH_3
b X = C_6H_5
c X = C_6H_4-C_6H_5(*p*)

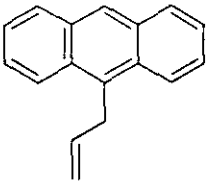
2c X = CH_3
d X = C_6H_5
e X = C_6H_4-C_6H_5(*p*)

The structures of alkenylanthracenes **2a-e** were established on the basis of analytical results and spectral data. The physical and spectral data of **2a,b** were identical to those reported in literature.[28,30] Compound **2d**, which was obtained in 65% yield showed a strong absorption at 1653 cm^{-1} indicating the presence of an α,β-unsaturated carbonyl group in the compound. UV absorptions at 323 nm and 234 nm are attributable to the anthracene component in the compound. In the ^1H NMR spectrum, the vinylic and aromatic protons were observed as a multiplet in the aromatic region δ 7.49-8.84. The ^{13}C NMR spectrum showed the carbonyl carbon at δ 189.67. The molecular ion of this compound was observed at *m/z* 308 confirming its identity. The structure was further confirmed by elemental analysis, which gave acceptable data.

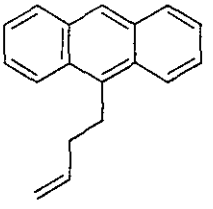
Compounds **2c** and **2e** showed very similar spectral behaviour with that of **2d.** These compounds also showed the IR absorption at ~1653 cm^{-1} due to the carbonyl group. The UV spectra of all these compounds were similar and were dominated by the absorption of anthracene component. ^1H NMR spectra of all these were comparable and they exhibited acceptable elemental analysis and mass spectral data. Based on these, the compounds were confirmed as alkenylanthracenes containing α,β-unsaturated carbonyl group.

We were interested in probing whether the chain length at the bridgehead and thus the position of unsaturation has any effect on the reactions of dibenzobarrelenes. Thus, we attempted the synthesis of alkenylanthracenes **2f-s** (Chart 2.1).

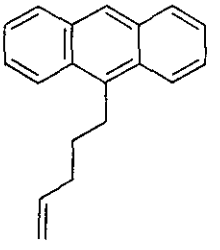
Chart 2.1



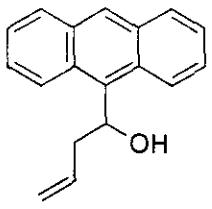
2f



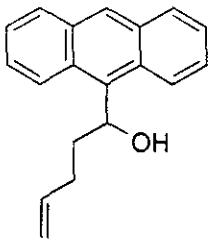
2g



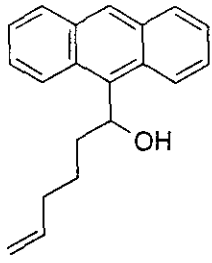
2h



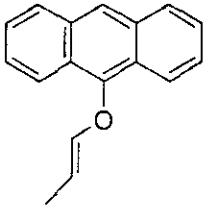
2i



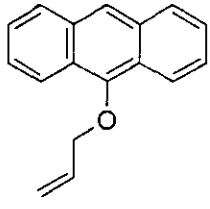
2j



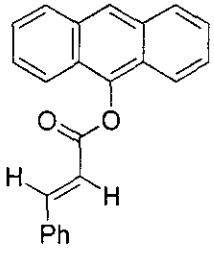
2k



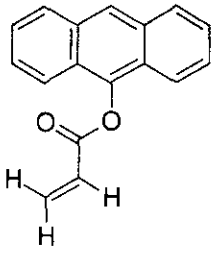
2l



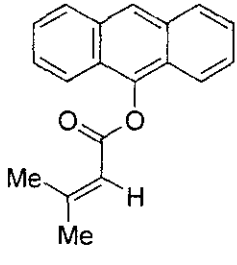
2m



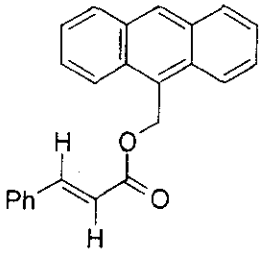
2n



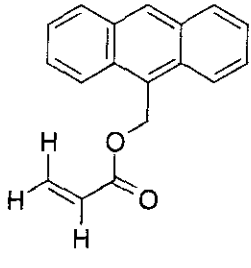
2o



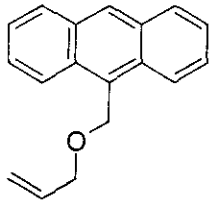
2p



2q



2r

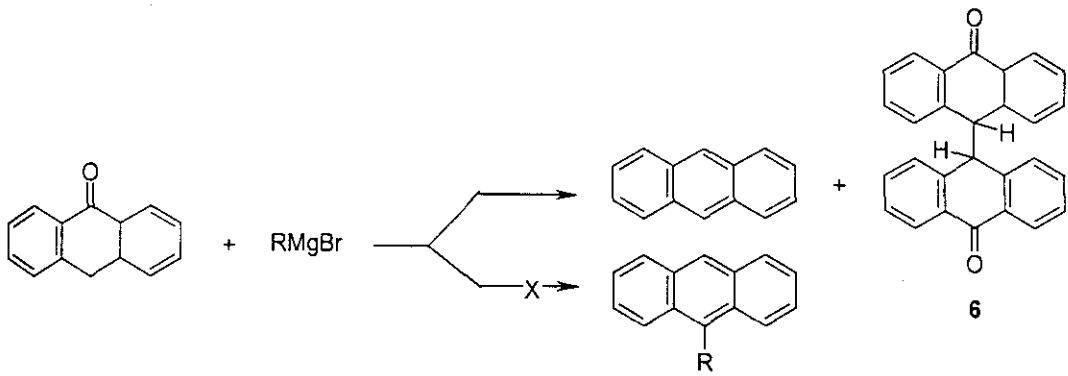


2s

We employed Grignard reaction of anthrone (**4**) with the corresponding alkenylmagnesium bromides **5a-c** to synthesise **2f-h** (Scheme 2.3). 2-Propenylmagnesium bromide (**5a**) and 4-pentenylmagnesium bromide (**5c**) were prepared by known procedures.[31,32] 3-Butenylmagnesium bromide (**5b**) was purchased from Sigma-Aldrich and used as such. However, Grignard reaction between **4** and **5a-c** under different conditions employed by us did not lead to the

formation of the desired alkenylanthracenes **2f-h**. In all three cases, TLC analysis of the product mixture indicated the presence of two products along with unchanged anthrone. The product mixture was subjected to column chromatography over silica. The first fraction obtained was identified as anthracene using UV absorption and ^{1}H NMR spectral data. The second fraction was identified as bianthron-9-yl[33] on the basis of spectral and analytical data. In the IR spectrum of **6**, strong absorptions were observed at 1661 cm^{-1} indicating the presence of carbonyl group. The ^{1}H NMR spectrum of **6** exhibits a singlet at δ 4.8 (2H) due to the aliphatic protons and multiplets at δ 6.8-6.9 (4H), δ 7.4-7.5 (8H) and δ 7.8-8.4 (4H) due to aromatic protons. In the ^{13}C NMR spectrum, peaks were observed at δ 54.3 (C-10), δ 182.9 (C=O), and δ 126.6-139.9 (aromatic carbons).

Scheme 2.3

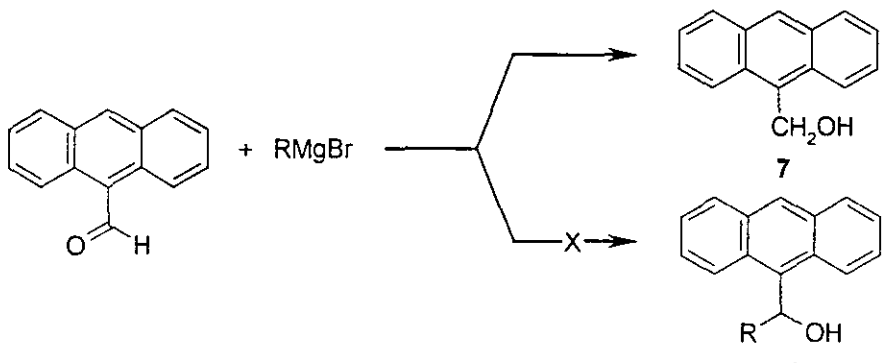


4 **5a** R = CH_2=CH-CH_2 **2f-h**
b R = CH_2=CH-$(CH_2)_2$
c R = CH_2=CH-$(CH_2)_3$

Having failed to introduce the 1-propenyl, 1-butenyl and 1-pentenyl chains on to the anthracene nucleus, we attempted to synthesise the corresponding unsaturated alcohols **2i-k** from **1** by Grignard reaction with suitable Grignard reagents **5a-c**. (Scheme 2.4) Under the conditions employed by us, 9-anthracenemethanol (**7**) arising through the reduction of **1** was obtained as the major product. The structure of **7** was arrived at by comparing its ^{1}H NMR spectrum with that of an authentic sample. The presence of β hydrogen in the Grignard reagents used by us might have facilitated the reduction reaction. The reduction of carbonyl compounds by Grignard

reagent, having β hydrogen has literature precedence.[34] The other side reactions are condensation between enolate anion and excess ketone and Wurtz-type coupling.[34]

Scheme 2.4



1 **5a** R = CH_2=CH-CH_2
b R = CH_2=CH-$(CH_2)_2$
c R = CH_2=CH-$(CH_2)_3$

In continuation, we attempted the synthesis of anthracene derivatives containing heteroatoms as well as unsaturation at selected positions of the 9-substituent. The viable synthetic targets were unsaturated ethers and esters **2l-s** containing anthracene nucleus. The isomerisation of the allylic ether to vinylic ether has literature precedence.[35] We employed Williamson's type ether synthesis and acid catalysed etherification reaction for the preparation of ethers and esterification reaction for the synthesis of esters. In order to enhance the efficiency of these reactions, we employed phase transfer catalysis in a few selected cases.

Our strategy was to synthesise the allyl ether **2m** initially and to convert it to the vinyl ether **2l.** The strategies employed by us for the synthesis of **2m** include Scheme 2.5):

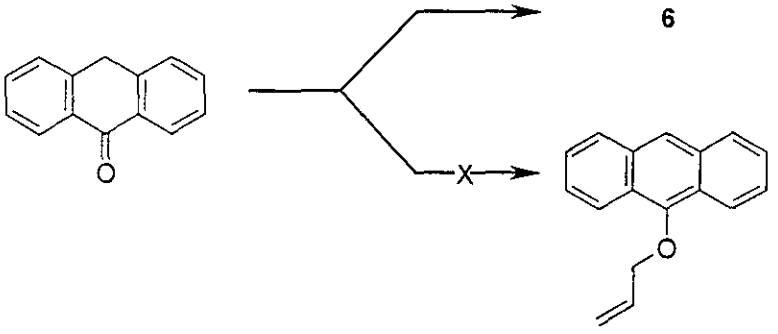
1. Williamson's type ether synthesis: anthrone **(4)** in *iso*-propanol was treated with allyl bromide in the presence of metallic sodium.[36] No new products were formed under these conditions. When we repeated the reaction in dimethyl sulphoxide, unchanged anthrone along with a polymeric material was obtained. The attempted synthesis of ether **2m** by Williamson's ether

type synthesis resulted in the formation of bianthron-9-yl along with unchanged anthrone.

2. Phase Transfer Catalysis: A solution of **4** in dichloromethane was treated with a mixture of allyl bromide and aqueous sodium hydroxide; the phase transfer catalyst used was triethylbenzylammonium chloride. It should be noted that similar reactions conducted in the absence of phase transfer catalysts resulted in the formation of product mixtures arising through competing *C*- and *O*-alkylations.[37] The attempted synthesis of ether **2m** in the presence of a phase transfer catalyst resulted in the formation of bianthron-9-yl along with unchanged anthrone.

3. Acid-catalyzed Etherification: A solution of **4** in toluene was treated with allyl alcohol in presence of catalytic amounts of sulphuric acid.[38] In the case of acid catalysed etherification, a resinous mass along with unchanged anthrone was obtained.

Scheme 2.5

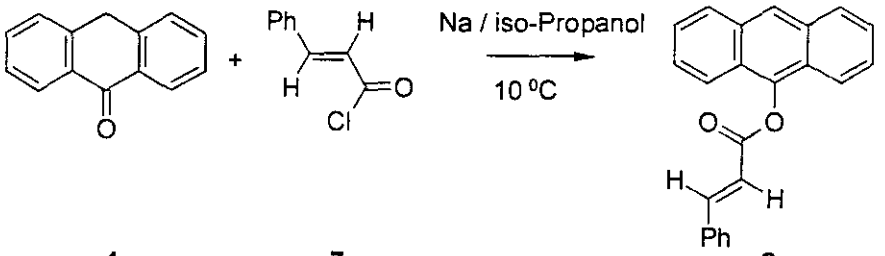


4 **2m**

1. Allyl Bromide / Na in iso-Propanol / 10 °C
2. Allyl Bromide / $(C_2H_5)_3C_6H_5CH_2NCl$ / CH_2Cl_2 / Room Temperatur
3. Allyl Alcohol / Dilute H_2SO_4 / Benzene / 80 °C

The ester **2n** was prepared by treating **4** with freshly prepared cinnamoyl loride in the presence of metallic sodium in *iso*-propanol[36] (Scheme 2.6). innamoyl chloride (**8**) was freshly prepared by a known procedure.[39]

Scheme 2.6

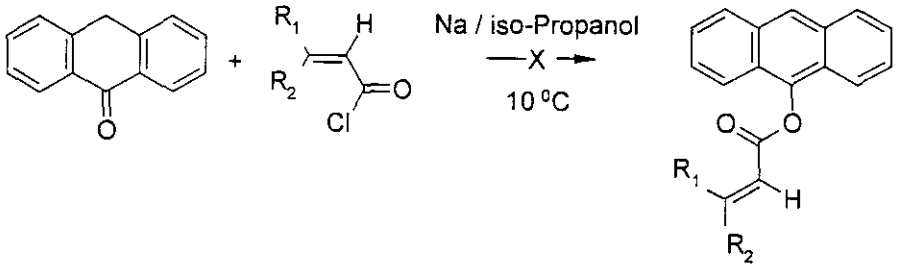


4 **7** **2n** (42%)

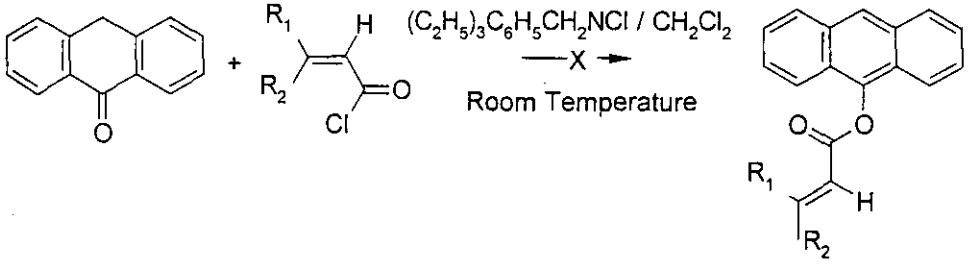
Compound **2n** showed IR absorption at 1726 cm^{-1} indicating the presence of a carbonyl group. The ^1H NMR spectrum showed two doublets at δ 6.9 (1H) and δ 8.1 (1H) with J_{AX} = 16Hz and a multiplet corresponding to fourteen hydrogen around δ 7.4-8.1 due to the aromatic hydrogens. The J_{AX} value is indicative of *E*-geometry. The ^{13}C NMR spectrum of **2n** showed a peak at δ 165.4 corresponding to the carbonyl group of α, β-unsaturated ester. The mass spectrum showed the molecular ion peak at *m/z* 324. The analytical data confirmed the structure of the compound.

We extended this strategy to the preparation of acrylic and dimethylacrylic analogues, **2o** and **2p** respectively. We attempted phase transfer catalysis for the preparation of the esters **2o** and **2p** as indicated in Scheme 2.7. However, esters **2o** and **2p** were not formed under various conditions attempted by us. We attribute the sluggish nature of the carbonyl group in anthrone coupled with the unstable nature of the acid chlorides **9a,b** for the failure of this reaction. Instead, bianthron-9-yl (**6**) was obtained in good yields in both the cases under the reaction conditions we employed. Spectral and analytical data confirmed the structure of the product obtained as **6.** When we repeated the reaction in dimethyl sulphoxide under analogous conditions, unchanged anthrone along with a polymeric material was obtained. When the reaction was repeated in the presence of potassium iodide under identical reaction conditions, bianthron-9-yl (**6**) was obtained as the major product.

Scheme 2.7



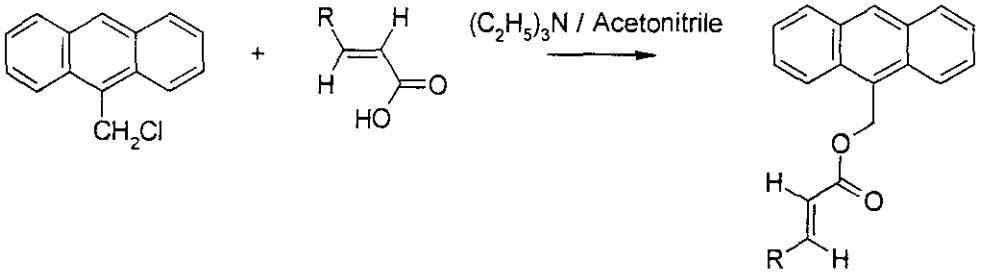
4 **9a** $R_1 = R_2 = H$; **b** $R_1 = R_2 = CH_3$ **2o** $R_1 = R_2 = H$; **p** $R_1 = R_2 = CH_3$



4 **9a** $R_1 = R_2 = H$; **b** $R_1 = R_2 = CH_3$ **2o** $R_1 = R_2 = H$; **p** $R_1 = R_2 = CH_3$

Esters **2q** and **2r** were synthesised by treating 9-chloromethylanthracene (**10**) with corresponding acids **11a-b** in the presence of triethylamine in acetonitrile[40] (Scheme 2.8). Compounds **2q** and **2r** showed IR absorption peaks at 1723 cm^{-1} and 1695 cm^{-1} respectively, indicating the presence of the ester linkage.

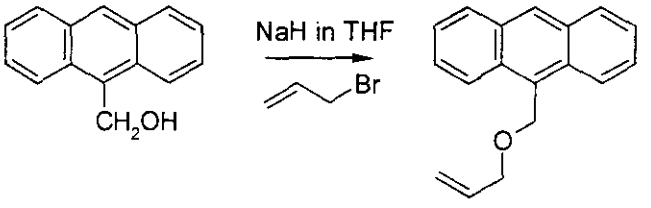
Scheme 2.8



10 **11a** R = Ph; **b** R = H **2q** R = Ph; **r** R = H

The ether **2s** was synthesised by adapting Williamson's ether type synthesis as shown in Scheme 2.9. We treated 9-anthracenemethanol (7) with allyl bromide in the presence of sodium hydride to yield **2s** in good yields.[32]

Scheme 2.9



7 **2s**

(62%)

Compound **2s** showed sharp IR absorptions at 1049 cm^{-1}, which indicates the presence of an ether linkage. The ^{1}H-NMR spectrum showed a two-proton singlet at δ 4.2, multiplets due to allylic protons around δ 5.3-5.5 and δ 6.0-6.1 and another multiplet around δ 7.5-8.5 due to aromatic protons. The ^{13}C-NMR spectrum further confirmed the presence of the allylic linkage in this compound. The molecular ion peak of this compound was observed at *m/z* 248 confirming its identity. The structure was further confirmed by elemental analysis, which gave acceptable data.

Thus, we were able to synthesise a few alkenylanthracenes, which are potential substrates for carrying out Diels-Alder reaction with suitable acetylenic dienophiles to yield dibenzobarrelenes with a π-moiety at the bridgehead. Besides, the alkenylanthracenes, **2q**, **2r**, **2s** are suitable compounds for studying intramolecular Diels-Alder reaction of anthracene derivatives.

2.4. Experimental

2.4.1. General Procedures. All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations

were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica or aluminium sheets coated with silica (MERCK) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapour or UV radiation. Column chromatography was carried out with slurry packed silica (Qualigens 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using Shimadzu-DR-8001 series FTIR spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 300, 400 and 500 MHz on a Bruker FT-NMR spectrometer or GE NMR OMEGA spectrometer with tetramethylsilane as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane (TMS). Elemental analysis was performed at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

2.4.2. Starting materials. Anthracene and anthrone were purchased from S. D. Fine Chem. Ltd. and were used as obtained. 3-Butenylmagnesium bromide and 4-bromo-1-pentene were purchased from Sigma-Aldrich and were used as received.

2.4.2.1. *N*-Methylformanilide: *N*-Methylformanilide was prepared by a known procedure[42] (97%, bp 243-244 ^{0}C).

2.4.2.2. 9-Anthraldehyde: 9-Anthraldehyde was prepared using a known procedure[41] (54%, mp 104-106 ^{0}C).

2.4.2.3. 4-Phenylacetophenone: 4-Phenylacetophenone was prepared using a known procedure[29] (76%, mp 120 ^{0}C).

2.4.2.4. Benzyltriphenylphosphonium chloride: Benzyltriphenylphosphonium chloride was prepared by a known procedure[26] (100%).

2.4.2.5. Methytriphenylphosphonium iodide: Methytriphenylphosphonium iodide was prepared by a known procedure[26] (100%).

2.4.2.6. Allylmagnesium bromide: Allylmagnesium bromide was prepared by a known procedure[31] (89%).

2.4.2.7. Triethylbenzylammonium chloride: Triethylbenzylammonium chloride was prepared by a known procedure[8] (100%).

2.4.2.8. 4-Pentenylmagnesium bromide: 4-Pentenylmagnesium bromide was prepared using a known method[32] (78%).

2.4.2.9. 9-Anthracenmethanol: 9-Anthracenemethanol was prepared using a known procedure[32] (60%, mp 158-162 ^{0}C).

2.4.2.10. 9-Chloromethylanthracene: 9-Chloromethylanthracene was prepared by a known method[32] (84%, mp 136-138 ^{0}C).

2.4.2.11. Cinnamoyl Chloride: Cinnamoyl chloride was prepared by a known procedure[39] (95%, mp 34-37 ^{0}C).

2.4.2.12. Acryloyl Chloride: Acryloyl Chloride was prepared by a known method[39] (78%, bp 70-72 ^{0}C)

2.4.2.13. 3,3-Dimethylacryloyl Chloride: Dimethylacryloyl chloride was prepared by a known method[39](66%, 142-145 ^{0}C).

2.4.3. Preparation of Ethenylanthracenes

2.4.3.1. Preparation of Ethenylanthracene 2a[10]**.** To a stirred mixture of dry THF (120 mL) and methyltriphenylphosphonium iodide (24.24g, 0.06 mol) under nitrogen

atmosphere, a solution of 9-anthraldehyde (4.12 g, 0.02 mol) in dry THF (80 mL) was added. The reaction mixture was stirred at room temperature for 7 h and aqueous solution of NaOH (50%) was added to the mixture. The reaction mixture was stirred for another 30 minutes, poured into water and extracted with diethyl ether. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the product formed was separated by column chromatography and purified by recrystallisation from *iso*-propanol.

Compound 2a: (0.48 g, 12%, mixture mp 69 ^{0}C); ^{1}H NMR ($CDCl_3$) δ 5.3 (1H, dd, vinylic), 5.8 (1H, dd, vinylic), 7.1-8.3 (10H, m, aromatic and vinylic); MS, *m/z* 204 (M^+), and other peaks.

2.4.3.2. Preparation of Ethenylanthracene 2b[11]. A mixture of 9-anthraldehyde (4.12 g, 0.02 mol), benzyltriphenylphosphonium chloride (8.00 g, 0.02 mol) in dichloromethane (24 mL) was stirred vigorously and 50% aqueous solution of NaOH was added to the mixture. The reaction mixture was stirred for another 30 minutes, poured into water and extracted with dichloromethane. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the residue obtained was chromatographed over silica. Elution with a mixture (1:4) of dichloromethane and hexane yielded unchanged 9-anthraldehyde (0.50 g, 10%). Further elution with a mixture (1:1) of dichloromethane and hexane gave **2b**.

Compound 2b: (4.14 g, 73%, mixture mp 131-133 ^{0}C); ^{1}H NMR ($CDCl_3$) δ 6.8 (1H, d, J_{AX} = 17 Hz, vinylic), 7.3-8.5 (15H, m, aromatic and vinylic).

2.4.3.3. Preparation of Ethenylanthracene 2c. A mixture of 9-anthraldehyde (4.12 g, 0.02 mol), acetone (3.48 g, 0.06 mol) and powdered potassium hydroxide (1.80 g, 0.03 mol) in methanol (30 mL) was stirred at 60 ^{0}C for 48 h and later kept in refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (1:2) of hexane and dichloromethane to give **2c**.

Compound 2c: (4.06 g, 78%); mp 167-169 ^{0}C; IR ν_{max} (KBr) 1668 (C=O) cm^{-1}; UV λ_{max} (Acetonitrile) 231 (ε 21 800), 242 (ε 23 300), 340 nm (ε 17 000); ^{1}H NMR ($CDCl_3$) δ 1.56 (3H, s, CH_3), 7.2 (1H, d, J_{AX} = 16Hz, vinylic), 7.4-8.5 (9H, m, aromatic), 8.8 (1H, d, J_{AX} = 16 Hz, vinylic); MS, *m/z* 246 (M^+), and other peaks. Anal. Calcd for $C_{18}H_{14}O$: C, 87.80; H, 5.69. Found: C, 87.57; H, 5.14.

2.4.3.4. Preparation of Ethenylanthracene 2d. A mixture of 9-anthraldehyde (4.12 g, 0.02 mol), acetophenone (2.44 g, 0.02 mol) and powdered potassium hydroxide (1.80 g, 0.03 mol) in methanol (30 mL) was stirred at 60 ^{0}C for 48 h and later kept in refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (1:2) of hexane and dichloromethane to give **2d**.

Compound 2d: (4.01 g, 65%); mp 120-124 ^{0}C; IR ν_{max} (KBr) 1653 (C=O) cm^{-1}; UV λ_{max} (Acetonitrile) 234 (ε 23 000), 251 (ε 7700), 323 nm (ε 16700); ^{1}H NMR ($CDCl_3$) δ 7.5-8.5 (15H, m, aromatic and vinylic), 8.8 (1H, d, J_{AX} = 15 Hz, vinylic); ^{13}C NMR ($CDCl_3$) δ 125.6, 125.4, 126.41, 128.4, 128.7, 128.9, 129.6, 130.2, 131.1, 131.31, 133.1, 137.9, 141.9, 189.7; MS, *m/z* 308 (M^+), and other peaks. Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 90.10; H, 5.42.

2.4.3.5. Preparation of Ethenylanthracene 2e. A mixture of 9-anthraldehyde (4.12 g, 0.02 mol), 4-phenylacetophenone (3.95 g, 0.02 mol) and powdered potassium hydroxide (1.8 g, 0.03 mol) in methanol (30 mL) was stirred around 60 ^{0}C for 48 h and later kept in refrigerator for 48 h. The solid product that separated out was

filtered and purified by recrystallisation from a mixture of hexane and dichloromethane (1:2) to give **2e**.

Compound 2e: (5.91 g, 77%); mp 145 ^{0}C; IR ν_{max} (KBr) 1662 (C=O) cm^{-1}; UV λ_{max} (Acetonitrile) 259 (ε 27 950), 284 (ε 26 000), 300 nm (ε 15 100); ^{1}H NMR ($CDCl_3$) δ 7.4-8.5 (19H, m, aromatic and vinylic), 8.8 (1H, d, J_{AX} = 16 Hz, vinylic); ^{13}C NMR ($CDCl_3$) δ 120.1, 120.2, 121.2, 123.7, 124.1, 124.5, 125.0, 125.9, 126.2, 131.4, 134.7, 136.6, 140.6, 183.7; Anal. Calcd for $C_{29}H_{20}O$: C, 90.60; H, 5.24. Found: C, 90.58; H, 5.22.

2.4.3.6. Attempted Preparation of Ethenylanthracene 2f. A solution of anthrone (3.88 g, 0.02 mol) in warm benzene (20 mL) was added drop-wise to a stirred solution of allylmagnesium bromide (8.71 g, 0.06 mol) in dry ether (60 mL). The mixture was refluxed for 4 h after the addition was complete. The reaction mixture was poured into saturated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.86 g, 31%, mixture mp 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained.

Compound 6: [33] (1.50 g, 58%); mp 215 ^{0}C (completely decomposed); IR ν_{max} (KBr) 1661 (C=O) cm^{-1}; UV λ_{max} (Acetonitrile) 259 (ε 15 100), 284 (ε 12 700), 341 nm (ε 7300); ^{1}H NMR ($CDCl_3$) δ 4. 8 (2H, s, methine), δ 6.9-8.4 (16H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 54.3, 126.1, 127.2, 127.9, 128.4, 132.1, 139.8, 182.9; Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.03; H, 4.69. Found: C, 86.89; H, 4.31.

In a repeat run, anthrone (3.88 g, 0.02 mol), dissolved in minimum quantity of THF was added drop-wise to a stirred solution of allylmagnesium bromide (8.71 g, 0.06 mol) in dry ether (60 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred at 40 ^{0}C for 30 minutes, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.74 g, 24%, mixture mp 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {1.92 g, 62%, mp 215 ^{0}C (complete decomposition)}.

In another repeat run, anthrone (3.88 g, 0.02 mol) in THF (10 mL) was added drop-wise to a stirred solution of allylmagnesium bromide (8.71 g, 0.06 mol) in dry ether (60 mL) keeping the temperature below 15 ^{0}C. The mixture was stirred at room temperature for 30 minutes and then refluxed for 48 h, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.75 g, 28%, mixture mp 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {1.74 g, 65%, mp 215 ^{0}C (complete decomposition)}.

In another repeat run, anthrone (3.88 g, 0.02 mol) in ether-benzene mixture (1:3) was added drop-wise to a stirred solution of allylmagnesium bromide (8.71 g, 0.06 mol) in dry ether (60 mL). The mixture was then refluxed for 48 h, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.88 g, 28%, mixture mp 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {1.66 g, 53%, mp 215 ^{0}C (complete decomposition)}.

In yet another run, anthrone (3.88 g, 0.02 mol) in THF (10 mL) was added drop-wise to a stirred solution of allylmagnesium bromide (8.71 g, 0.06 mol) in dry THF (25 mL). The mixture was then refluxed for 48 h, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.64 g, 20%, mixture mp. 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {2.26 g, 70%, mp 215 ^{0}C (complete decomposition)}.

2.4.3.7. Attempted Preparation of Ethenylanthracene 2g. A solution of anthrone (3.88 g, 0.02 mol) in warm benzene (20 mL) was added drop-wise to a stirred solution of 3-butenylmagnesium bromide (9.55 g, 0.06 mol) in THF. The mixture was refluxed for 4 h after the addition was complete. The reaction mixture was poured into saturated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.89 g, 35%, mixture mp. 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {1.07 g, 42%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, a solution of anthrone (3.88 g, 0.02 mol) in minimum quantity of dry THF was added drop-wise to a stirred solution of 3-butenylmagnesium bromide in THF (9.55 g, 0.06 mol) keeping the temperature below 15 ^{0}C. The mixture was then stirred at 40 ^{0}C for 30 minutes, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.83 g, 28%, mixture mp 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {1.91 g, 64%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, a solution of anthrone (3.88 g, 0.02 mol) in THF (10 mL) was added drop-wise to a stirred solution of 3-butenylmagnesium bromide in THF (9.55 g, 0.06 mol) keeping the temperature below 15 ^{0}C. The mixture was then stirred at room temperature for 30 minutes and refluxed for 48 h, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.67 g, 22%, mixture mp. 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {2.09 g, 68%, mp 215 ^{0}C (complete decomposition)}.

In another repeat run, anthrone (3.88 g, 0.02 mol) in ether-benzene mixture (1:3) was added drop-wise to a stirred solution of 3-butenylmagnesium bromide in THF (9.55 g, 0.06 mol). The mixture was then refluxed for 48 h, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.71 g, 26%, mixture mp. 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {2.61 g, 46%, mp 215 ^{0}C (complete decomposition)}.

2.4.3.8. Attempted Preparation of Ethenylanthracene 2h. Anthrone (3.88 g, 0.02 mol) in warm benzene (20 mL) was added drop-wise to a stirred solution of 4-pentenylmagnesium bromide (10.40 g, 0.06 mol) in THF (30 mL). The mixture was refluxed for 4 h after the addition was complete. The reaction mixture was poured into saturated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.61 g, 27%, mixture mp. 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {0.81 g, 36%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, anthrone (3.88 g, 0.02 mol) in THF (10 mL) was added drop-wise to a stirred solution of 4-pentenylmagnesium bromide (10.40 g, 0.06 mol) in THF (30 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred at 40 ^{0}C for 30 minutes, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.89 g, 31%, mixture mp. 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {1.67 g, 58%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, anthrone (3.88 g, 0.02 mol) in dry THF (10 mL) was added drop-wise to a stirred solution of 4-pentenylmagnesium bromide (10.40 g, 0.06 mol) in dry THF (30 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred at room temperature for 30 minutes and refluxed for 48 h, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.80 g, 25%, mixture mp. 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {1.97 g, 62%, mp 215 ^{0}C (complete decomposition)}.

In another repeat run, anthrone (3.88 g, 0.02 mol) in ether-benzene mixture (1:3) was added drop-wise to a stirred solution of 4-pentenylmagnesium bromide (10.40 g, 0.06 mol) in THF (30 mL). The mixture was then refluxed for 48 h, cooled and treated with concentrated NH_4Cl solution. The organic layer was collected and was washed sequentially with water, saturated $NaHCO_3$ solution and water, dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:1) of dichloromethane and hexane, anthracene was obtained in trace amounts (mixture mp 214-218 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave unchanged anthrone (0.98 g, 38%, mixture mp. 151 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {0.91 g, 35%, mp 215 ^{0}C (complete decomposition)}.

2.4.3.9. Attempted Preparation of Ethenylanthracene 2i. A solution of 9-anthraldehyde (4.12 g, 0.02 mol) in dry THF (10 mL) was added to freshly prepared allylmagnesium bromide (8.71 g, 0.06 mol) in dry ether (120 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred at 40 ^{0}C for 30 minutes, cooled and treated with concentrated NH_4Cl solution. The product was extracted with dichloromethane, washed several times with water, saturated $NaHCO_3$ solution, then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. Elution with a mixture (1:4) of dichloromethane and hexane gave unchanged 9-anthraldehyde (0.63 g, 15%, mixture mp 99-102 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane, gave 9-anthracenemethanol (2.40 g, 72%, mixture mp 166-167 ^{0}C).

In a repeat run, to freshly prepared allylmagnesium bromide (8.71 g, 0.06 mol) in dry ether (120 mL) was added a solution of 9-anthraldehyde (4.12 g, 0.02 mol) in dry THF (10 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred for 6 h keeping the temperature below 15 ^{0}C and poured into crushed ice-hydrochloric acid. The product was extracted with dichloromethane, washed several times with water, saturated $NaHCO_3$ solution, then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent gave unchanged 9-anthraldehyde (3.50 g, 85%, mixture mp 99-102 ^{0}C).

In a repeat run, to freshly prepared allylmagnesium bromide (8.71 g, 0.06 mol) in dry ether (120 mL) was added a solution of 9-anthraldehyde (4.12 g, 0.02 mol) in THF (10 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred at 40 ^{0}C for 1 h and refluxed for 48 h, cooled and poured into crushed ice-hydrochloric acid. The product was extracted with dichloromethane, washed with water several times, saturated $NaHCO_3$ solution, then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was

chromatographed on silica. Elution with a mixture (1:4) of dichloromethane and hexane gave unchanged 9-anthraldehyde (0.78 g, 22%, mixture mp 99-102 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane, gave 9-anthracenemethanol (2.87 g, 69%, mixture mp 166-167 ^{0}C).

2.4.3.10. Attempted Preparation of Ethenylanthracene 2j. To 3-butenylmagnesium bromide in THF (9.55 g, 0.06 mol) was added a solution of 9-anthraldehyde (4.12 g, 0.02 mol) in THF (10 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred at 40 ^{0}C for 30 minutes, cooled and treated with concentrated NH_4Cl solution. The product was extracted with dichloromethane, washed several times with water, saturated $NaHCO_3$ solution, then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. Elution with a mixture (1:4) of dichloromethane and hexane gave unchanged 9-anthraldehyde (0.61 g, 20%, mixture mp 99-102 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane, gave 9-anthracenemethanol (1.98 g, 65%, mixture mp 166-167 ^{0}C).

In a repeat run, to 3-butenylmagnesium bromide in THF (9.55 g, 0.06 mol) was added a solution of 9-anthraldehyde (4.12 g, 0.02 mol) in THF (10 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred for 6 h keeping the temperature below 15 ^{0}C and poured into crushed ice-hydrochloric acid. The mixture was extracted with dichloromethane, washed several times with water, saturated $NaHCO_3$ solution, then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. Elution with a mixture (1:4) of dichloromethane and hexane gave unchanged 9-anthraldehyde (3.63 g, 88%, mixture mp 99-102 ^{0}C).

In a repeat run, to 3-butenylmagnesium bromide in THF (9.55 g, 0.06 mol) was added a solution of 9-anthraldehyde (4.12 g, 0.02 mol) in THF (10 mL) keeping

the temperature below 15 ^{0}C. The mixture was then stirred at 40 ^{0}C for 1 h and refluxed for 48 h, cooled and poured into crushed ice-hydrochloric acid. The mixture was extracted with dichloromethane, washed several times with water, saturated $NaHCO_3$ solution, then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. Elution with a mixture (1:4) of dichloromethane and hexane gave unchanged 9-anthraldehyde (0.86 g, 25%, mixture mp 99-102 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane, gave 9-anthracenemethanol (2.34 g, 68%, mixture mp 166-167 ^{0}C).

2.4.3.11. Attempted Preparation of Ethenylanthracene 2k. To freshly prepared 4-pentenylmagnesium bromide (10.40 g, 0.06 mol) in dry ether (120 mL) was added a solution of 9-anthraldehyde (4.12 g, 0.02 mol) in dry THF (10 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred at 40 ^{0}C for 30 minutes, cooled and treated with concentrated NH_4Cl solution. The mixture was extracted with dichloromethane, washed several times with water, saturated $NaHCO_3$ solution, then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. Elution with a mixture (1:4) of dichloromethane and hexane gave unchanged 9-anthraldehyde (1.08 g, 32%, mixture mp 99-102 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane, gave 9-anthracenemethanol (1.76 g, 52%, mixture mp 166-167 ^{0}C).

In a repeat run, to freshly prepared 4-pentenylmagnesium bromide (10.40 g, 0.06 mol) in dry ether (120 mL) was added a solution of 9-anthraldehyde (4.12 g, 0.02 mol) in THF (10 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred for 6 h keeping the temperature below 15 ^{0}C and poured into crushed ice-hydrochloric acid. The product was extracted with dichloromethane, washed several times with water, saturated $NaHCO_3$ solution, then with water, and dried over

anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. Elution with a mixture (1:4) of dichloromethane and hexane gave unchanged 9-anthraldehyde (3.58 g, 90%, mixture mp 99-102 ^{0}C).

In a repeat run, to freshly prepared 4-pentenylmagnesium bromide (10.40 g, 0.06 mol) in ether (120 mL) was added a solution of 9-anthraldehyde (4.12 g, 0.02 mol) in THF (10 mL) keeping the temperature below 15 ^{0}C. The mixture was then stirred at 40 ^{0}C for 1 h and refluxed for 48 h, cooled and poured into crushed ice-hydrochloric acid. The mixture was extracted with dichloromethane, washed several times with water, saturated $NaHCO_3$ solution, then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. Elution with a mixture (1:4) of dichloromethane and hexane gave unchanged 9-anthraldehyde (0.75 g, 20%, mixture mp 99-102 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane, gave 9-anthracenemethanol (2.18 g, 55%, mixture mp 162-165 ^{0}C).

2.4.3.12. Attempted Preparation of Ethenylanthracene 2m. A solution of anthrone (3.88 g, 0.02 mol) and allyl bromide (7.56 g, 0.06 mol) in dichloromethane (100 mL) was added to a solution of sodium hydroxide (0.03 g, 0.8 mmol) and triethylbenzylammonium chloride (1.00g, 4.4 mmol) in water (100 mL) and the mixture was stirred at room temperature for 6 h. The mixture was then diluted with water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.78 g, 25%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained {2.12 g, 68%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) and anthrone (3.88 g, 0.02 mol) was added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Allyl bromide (2.62 g, 0.02 mol) was added with stirring over a period of 2 h. The reaction mixture was then cooled, kept in a refrigerator for 48 h. The mixture was then poured into water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water, and dried with anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.57 g, 25%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {1.88 g, 56%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) and anthrone (3.88 g, 0.02 mol) was added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Allyl bromide (2.62 g, 0.02 mol) was added with stirring over a period of 2 h. The reaction mixture was heated on a water bath for 1.5 h and then refluxed for 15 h. The mixture was cooled and then diluted with water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.58 g, 20%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {1.60 g, 55%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL). Potassium iodide (0.32 g, 1.9 mmol) and anthrone (3.88 g, 0.02 mol) were added to the solution, which was warmed to dissolve the ketone. The

mixture was cooled below 10 ^{0}C. Allyl bromide (2.62 g, 0.02 mol) was added with stirring over a period of 2 h. The reaction mixture was heated on a water bath for 1.5 h and then refluxed for 15 h. The mixture was cooled and then diluted with water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water, and dried with anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.69 g, 22%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained {1.85 g, 59%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, anthrone (3.88 g, 0.02 mol) was dissolved in minimum quantity of dimethyl sulphoxide with slight warming and metallic sodium (0.06 g, 2.6 mmol) was added to the solution with vigorous stirring. The mixture was cooled below 10 ^{0}C. Allyl bromide (2.62 g, 0.02 mol)) was added with stirring over a period of 2 h. The reaction mixture was then cooled, kept in a refrigerator for 48 h. The mixture was diluted with water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (2.33 g, 60%, mixture mp 150-153 ^{0}C).

On further elution with dichloromethane a polymeric material was obtained.

In another repeat run, a stirred mixture of anthrone (3.88 g, 0.02 mol), allyl alcohol (11.62 g, 0.2 mol) and sulphuric acid (1 mL) in benzene (80 mL) was refluxed for 48 h. The reaction mixture was cooled to room temperature, poured into saturated $NaHCO_3$ solution and extracted with ether. The organic extracts were washed with water, brine and water, and dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with

a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (1.61 g, 70%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane a resinous mass was obtained (0.51 g, 22%).

2.4.3.13. Preparation of Ethenylanthracene 2n. Sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) and anthrone (3.88 g, 0.02 mol) was added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Freshly prepared cinnamoyl chloride (3.44 g, 0.02 mol) was added with stirring over a period of 2 h. The mixture was then cooled, kept in a refrigerator for 48 h, poured into water, and extracted with dichloromethane. The organic layer was separated, washed with water, followed by saturated $NaHCO_3$ solution and then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (1:4) of dichloromethane and hexane, **2n** was obtained in good yield.

Compound 2n: (3.89 g, 62%); mp 188-190 ^{0}C; IR ν_{max} (KBr) 1726 cm^{-1} (C=O); UV λ_{max} (Acetonitrile) 223 (18 800), 242 (25 000), 254 nm (11 200), 392 (7000); ^{1}H NMR ($CDCl_3$) δ 7.0 (1H, d, J_{AX} = 16 Hz, vinylic), 7.4-8.1 (14 H, m, aromatic), 8.2 (1 H, d, J_{AX} = 16 Hz, vinylic); ^{13}C NMR ($CDCl_3$) δ 116.3, 121.9, 123.7, 125.5, 126.3, 126.8, 128.5, 128.7, 128.9, 129.1, 131.0, 131.1, 133.2, 134.2, 147.9, 165.4; MS, *m/z* 324 (M^+), and other peaks. Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 85.31; H, 5.02.

On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.61 g, 12%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained {0.77 g, 15%, mp 215 ^{0}C (complete decomposition)}.

2.4.3.14. Attempted Preparation of Ethenylanthracene 2o. Sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) and anthrone (3.88 g, 0.02 mol) was added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Freshly prepared acryloyl chloride (1.81 g, 0.02 mol) was added with stirring over a period of 2 h. The mixture was then cooled, kept in a refrigerator for 48 h, poured into water, and extracted with dichloromethane. The organic layer was separated, washed with water, followed by saturated $NaHCO_3$ solution and then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica.

On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (1.10 g, 30%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained {1.89 g, 53%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) and anthrone (3.88 g, 0.02 mol) was added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Freshly prepared acryloyl chloride (1.81 g, 0.02 mol) was added with stirring over a period of 2 h. The reaction mixture was then heated on a water bath for 1.5 h and then refluxed for 15 h. The mixture was cooled, poured into water, and extracted with dichloromethane. The organic layer was separated, washed with water followed by saturated $NaHCO_3$ solution and then with water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.81 g, 25%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained {1.88 g, 58%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) and potassium iodide (0.32 g, 1.92 mmol) and anthrone (3.88 g, 0.02 mol) were added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Freshly prepared acryloyl chloride (1.81 g, 0.02 mol) was added with stirring over a period of 2 h. The mixture was then cooled, kept in a refrigerator for 48 h, poured into water, and extracted with dichloromethane. The organic layer was separated, washed with water, followed by saturated $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.98 g, 34%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained {1.64 g, 57%, mixture mp 215 ^{0}C (complete decomposition)}.

In a repeat run, sodium metal (0.06 g, 2.60 mmol) was dissolved in *iso*-propanol (80 mL) and potassium iodide (0.32 g, 1.92 mmol) and anthrone (3.88 g, 0.02 mol) were added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Freshly prepared acryloyl chloride (1.81 g, 0.02 mol) was added with stirring over a period of 2 h, the reaction mixture was heated on a water bath for 1.5 h and then refluxed for 15 h. The mixture was cooled and then poured into water, and extracted with dichloromethane. The organic layer was separated, washed with water, followed by saturated $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.69 g, 28%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained {1.53 g, 62%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, a solution of anthrone (3.88 g, 0.02 mol) and freshly prepared acryloyl chloride (5.70 g, 0.063 mol) in dichloromethane (100 mL) was added to a solution of sodium hydroxide (0.032 g, 0.8 mmol) and triethylbenzylammonium chloride (1.00 g, 4.4 mmol) in water (100 mL) and the mixture was stirred at room temperature for 6 h. The mixture was then diluted with water and extracted with dichloromethane. The organic extract was washed with 10% HCl, 5% $NaHCO_3$ solution and water, and dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.73 g, 22%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained (2.31 g, 70%, mp 215 ^{0}C (complete decomposition).

2.4.3.15. Attempted Preparation of Ethenylanthracene 2p. Sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) and anthrone (3.88 g, 0.02 mol) was added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0} C. Freshly prepared dimethylacryloyl chloride (2.40 g, 0.02 mol) was added with stirring stirring over a period of 2 h. The reaction mixture was cooled and kept in a refrigerator for 48 h. The mixture was then poured into water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica.

On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (1.18 g, 35%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained (1.85 g, 55%, mp 215 ^{0}C (complete decomposition).

In a repeat run, sodium metal (0.06 g, 2.3 mmol) was dissolved in *iso*-propanol (80 mL) and anthrone (3.88 g, 0.02 mol) was added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Freshly prepared dimethylacryloyl chloride (2.40 g, 0.02 mol) was added with stirring over a period of 2 h. The reaction mixture was heated on a water bath for 1.5 h and then refluxed for 15 h. The mixture was cooled and then poured into water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.90 g, 28%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained (1.84 g, 57%, mixture mp 215 ^{0}C (complete decomposition).

In a repeat run, sodium metal (0.06 g, 2.3 mmol) was dissolved in *iso*-propanol (80 mL) potassium iodide (0.32 g, 1.93 mmol) and anthrone (3.88 g, 0.02 mol) were added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Freshly prepared dimethylacryloyl chloride (2.40 g, 0.02 mol) was added with stirring over a period of 2 h. The reaction mixture was heated on a water bath for 1.5 h and then refluxed for 15 h. The mixture cooled and then poured into water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.68 g, 22%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained (1.79 g, 58%), mp 215 ^{0}C (complete decomposition)}.

In a repeat run, a solution of anthrone (3.88 g, 0.02 mol) and freshly prepared dimethylacryloyl chloride (7.50 g, 0.063 mol) in dichloromethane (100 mL) was added to a solution of sodium hydroxide (0.032 g, 0.8 mmol) and triethylbenzylammonium chloride in water (100 mL) and the mixture was stirred at room temperature for 6 h. The mixture was then diluted with water and extracted with dichloromethane. The organic extract was washed with 10% HCl, 5% $NaHCO_3$ solution and water, and dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.67 g, 20%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (**6**) was obtained (2.53 g, 76%, mp 215 ^{0}C (complete decomposition).

2.4.3.16. Preparation of Ethenylanthracene 2q. A mixture of 9-chloromethylanthracene (4.52 g, 0.02 mol) and cinnamic acid (5.00 g, 0.02 mol) in acetonitrile (40 mL) was refluxed in the presence of triethylamine (7 mL) for 6 h. The reaction mixture was diluted with water, treated with saturated $NaHCO_3$ solution and filtered. The residue obtained was washed with water, dried and purified by recrystallisation from ethanol.

Compound 2q: (1.90 g, 42%); mp 102-104 ^{0}C; IR ν_{max} (KBr) 1695 cm^{-1}; UV λ_{max} (Methanol) 240 (ε 25 700), 284 (ε 22 000), 356 (ε 11 400), ^{1}H NMR ($CDCl_3$) δ 4.1 (2H, s), 6.4 (1H, d, J_{AX}= 15 Hz) 7.3-8.7 (15H, m, aromatic and vinylic).

2.4.3.17. Preparation of Ethenylanthracene 2r. A mixture of 9-chloromethylanthracene (4.52 g, 0.02 mol) and acrylic acid (1.5 g, 0.02 mol) in acetonitrile (40 mL) was refluxed in the presence of triethylamine (7 mL) for 6 h. The reaction mixture was diluted with water, treated with saturated $NaHCO_3$ solution and filtered. The residue obtained was washed with water, dried and purified by recrystallisation from ethanol.

Compound 2r. (2.23 g, 49%); mp 114 ^{0}C; IR ν_{max} (KBr) 1723 cm^{-1}; UV λ_{max} (Methanol) 242 (ε 23 600), 259 (ε 19 300), 395 nm (ε 15 100); ^{1}H NMR ($CDCl_3$) δ 4.1 (2H, s), 5.9 (1H, d) 6.1-6.2 (1H, m,), 6.4 (1H, d), 7.0-8.4 (9H, m, aromatic).

2.4.3.18. Preparation of Ethenylanthracene 2s. A mixture of sodium hydride (0.62 g) and 9-antracenemethanol (4.16 g, 0.02 mol) in dry THF (50 mL) was stirred at room temperature for 1 h and then heated under reflux for 1 h. The mixture was cooled and a solution of allyl bromide (3.2 g, 0.03 mol) in THF (5 mL) was added slowly. After heating under reflux for 2 h, the mixture was cooled, treated with water, and the product was extracted with ether. The residue obtained on evaporating the solvent was chromatographed on silica. Elution with a mixture (3:7) of dichloromethane and hexane gave **2s**.

Compound 2s: (3.32 g, 67%); mp 50-55 ^{0}C; IR ν_{max} (KBr) 1049 cm^{-1}, 1123 cm^{-1}; UV λ_{max} (Acetonitrile) 259 (ε 19 600), 341 (ε 14 500), 380 nm (ε 2500); ^{1}H NMR ($CDCl_3$) δ 4.2 (2H, d), 5.3-5.5 (4H, m) 6.0-6.1 (1H, m,), 7.3-8.5 (9H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 29.3, 46.9, 64.8, 66.7, 118.3, 125.1, 125.6, 126.9, 129.1, 129.7, 131.8, 135.7; MS, *m/z* 248 (M^+), and other peaks. Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 87.40; H, 6.42.

Further elution with a mixture (1:1) of dichloromethane and hexane, gave unchanged 9-anthracenemethanol (0.66 g, 20%, mixture mp 162-164 ^{0}C).

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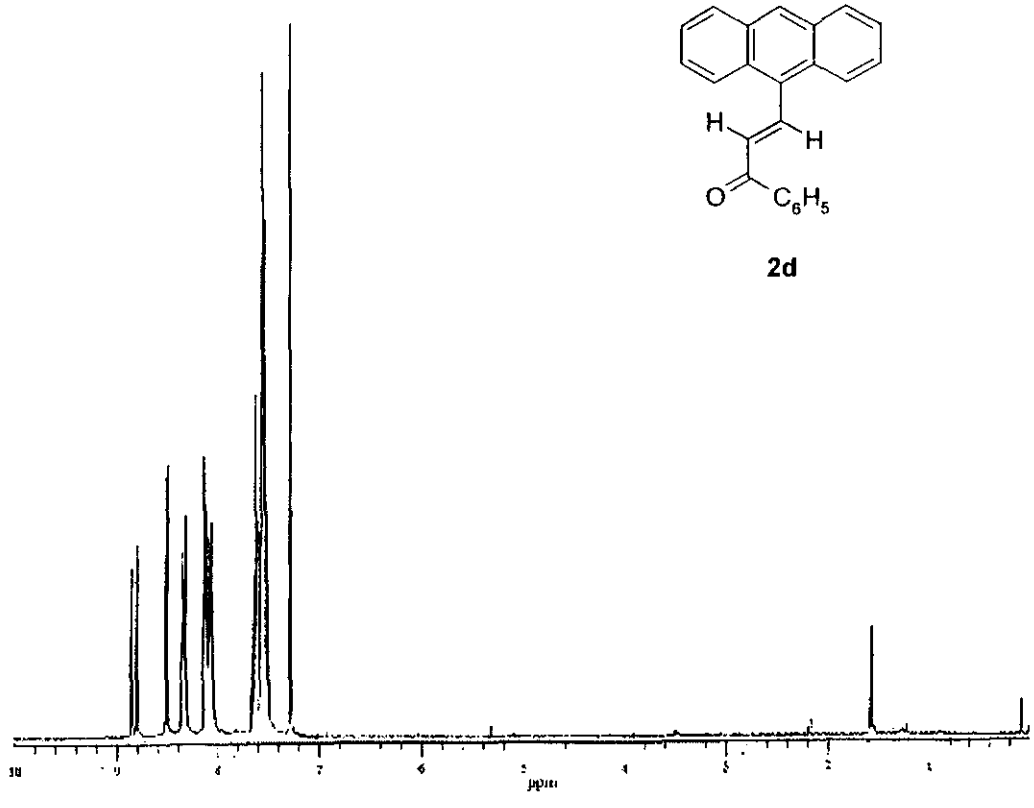
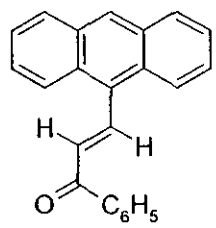


Figure 2.1. ^{1}H NMR spectrum of compound 2d



2d

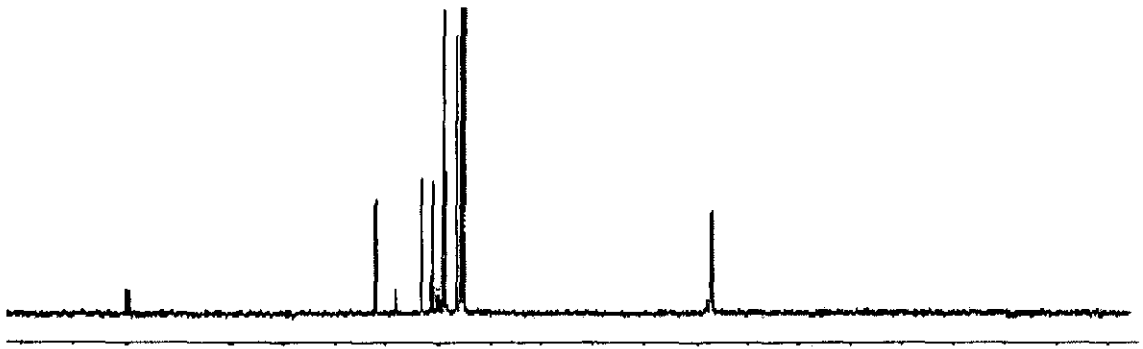


Figure 2.2. ^{13}C NMR spectrum of compound 2d

SYNTHESIS OF ALKYNYLANTHRACENES

3.1. Abstract

In order to assess the role of ethyne functionality in controlling the photochemistry of dibenzobarrelenes, we proposed to synthesize a few substrates having the desired structural features. We identified 9-ethynylanthracenes as potential precursors of the desired targets. In this chapter, we discuss our attempts to synthesise a few of these precursors.

3.2. Introduction

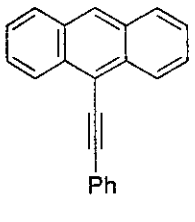
In continuation with our studies on the effects of an ethylenic substituent at the bridgehead position on the photochemistry of dibenzobarrelenes, we proposed to investigate the effect of acetylenic substituents at this position on the photochemistry of dibenzobarrelenes. Such substituents can selectively stabilise the diradical intermediates involved in the barrelene to semibullvalene transformation and hence control the observed regioselectiviy in this transformation.[1] We were interested in understanding the effect of an ethyne substituent either directly attached to, and hence possessing ground state interaction with, or more remotely attached to, and hence possessing no ground state but possible excited state interaction with the barrelene chromophore. We were also interested in altering the nature of the ethyne substituent. Such alterations are likely to facilitate the fine-tuning of the photophysical and photochemical properties of the substituent. As in the case of 9-alkenyldibenzobarrelenes the desired 9-alkynyldibenzobarelenes should be accessible through the Diels-Alder reaction between the corresponding 9-alkynylanthracenes

and suitable acetylenic dienophiles. A major side reaction in this case also is intramolecular Diels-Alder reaction involving the 9-alkynyl substituents leading to tricyclic systems. So, it is important to unravel the ideal structural features of alkynylanthracenes suitable for intermolecular and intramolecular Diels-Alder reactions. This information is vital in designing viable synthetic procedures for preparing the desired barrelene substrates in multi-gram quantities. Depending on the structure of the target molecule under consideration, we short-listed palladium-catalysed Heck coupling reaction[2], Williamson's ether type synthesis[3-7] and esterification reactions[8,9] as possible methods for the synthesis of 9-alkynylanthracenes of our choice. Phase transfer catalysts[10-13] were employed, where applicable, to improve the efficiency of ester and ether-forming reactions.

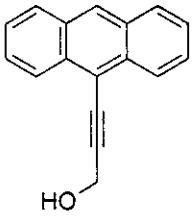
The palladium-catalyzed vinylation of organic halides[14-15] provides a very convenient method for forming carbon-carbon bonds at the vinylic position. A serious limitation to this procedure is that halides with an easily eliminated β-hydrogen cannot be used. Viable organic halides are limited to aryl, heteroaryl, benzyl or vinyl types with bromides and iodides employed most often. The base needed may be a secondary or tertiary amine, sodium or potassium acetate, carbonate or bicarbonate. The catalyst is commonly palladium acetate, although palladium chloride or preformed triphenylphosphine palladium complexes, as well as palladium on charcoal, have been used. Solvents such as acetonitrile, dimethylformamide, hexamethylphosphoramide, *N*-methylpyrrolidinone, and methanol have been used. The palladium-catalysed vinylic substitution reaction has received much attention in recent years owing to its broad scope and simplicity for the synthesis of a variety of olefinic compounds.[16]

In the present study, we attempted to synthesise the alkynylanthracenes **3a,b** (Chart 3.1) through Heck coupling reaction between 9-bromoanthracene and suitable acetylenic compounds. We propose to synthesise **3c** from anthrone by Williamson's ether type synthesis as well as by phase transfer catalysis, **3d** by Williamson's ether type synthesis, and **3e** by the esterification of 9-anthroic acid.

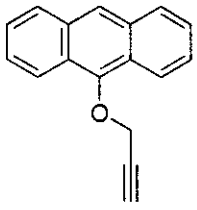
Chart 3.1



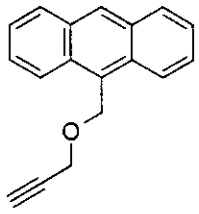
3a



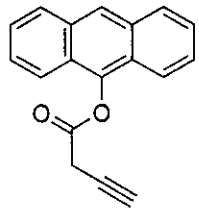
3b



3c



3d



3e

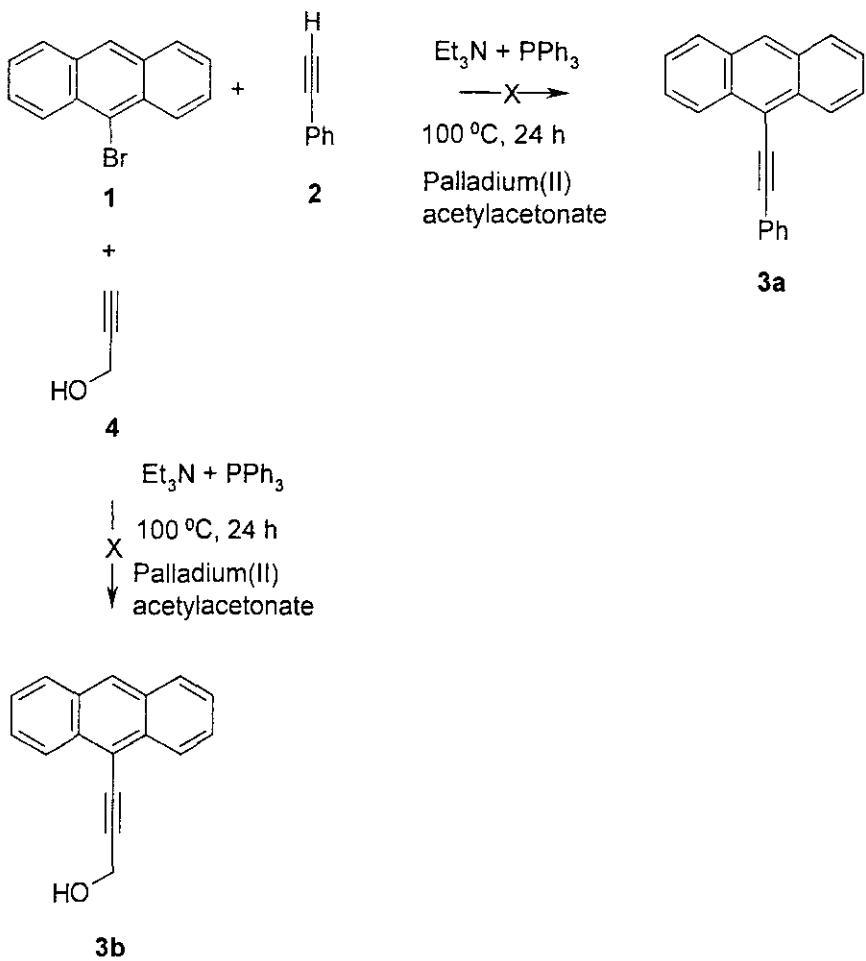
3.3. Results and Discussion

3.3.1. Preparation of Alkynylanthracenes

Heck[17], Cassar[18] and Sonogashira[19] have independently reported the Pd-catalysed cross-coupling reactions between aryl and vinyl halides and terminal acetylenes in 1975. These methods have been developed as an extension of the Heck reaction involving acetylenic CH-bond. These coupling reactions have been used extensively as a reliable method for the synthesis of eneyne-based acetylenic materials. The Pd–Cu catalysed cross-coupling reaction of terminal acetylenes with aryl and vinyl halides provides a useful method for synthesising conjugated acetylenic compounds, an important class of molecules that have found application in diverse areas ranging from natural products and pharmaceuticals to molecular organic materials for application as nanomaterials. Until recently, there remained three problems warranting improvement of Pd-catalysed cross coupling of aryl and vinyl halides with terminal acetylenes. These are (i) suppression of possible side reactions for terminal acetylenes at higher temperature, (ii) development of a catalyst for the coupling with cheaper but unreactive aryl chlorides and (iii) improvement of turn over numbers (TON) for the catalyst. Consequently, there was great interest in the development of suitable substrates and coupling agents that are both more economical and synthetically more easily accessible, and reactive even at lower reaction temperatures.[20] In the last decade, there have been tremendous development in Pd-catalysed coupling agents for Heck type reactions and the three problems cited above have been partially solved by adapting and discovering new methodologies.

We reasoned that a few alkynylanthracenes could be synthesized, from 9-bromoanthracene (**1**) through palladium-catalysed reactions. 9-Bromoanthracene (**1**) was prepared by a known procedure.[21] We attempted the synthesis of alkynylanthracene **3a** by treating **1** with phenylacetylene[22] (**2**) in the presence of triethylamine and palladium(II) acetylacetonate (Scheme 3.1). The reaction was unsuccessful and unchanged 9-bromoanthracene was obtained. Similarly, Heck coupling reaction between **1** and propargyl alcohol (**4**) did not yield **3b** (Scheme 3.1). Increasing the mole percent of the catalyst did not have any effect on the reaction. Palladium(II) acetylacetonate may not be a good catalyst as compared to palladium chloride or palladium acetate since it is less readily reduced to Pd(0). Hence, the formation of organopalladium complex, which is crucial for the progress of Heck coupling reaction, is less likely with palladium(II) acetylacetonate.

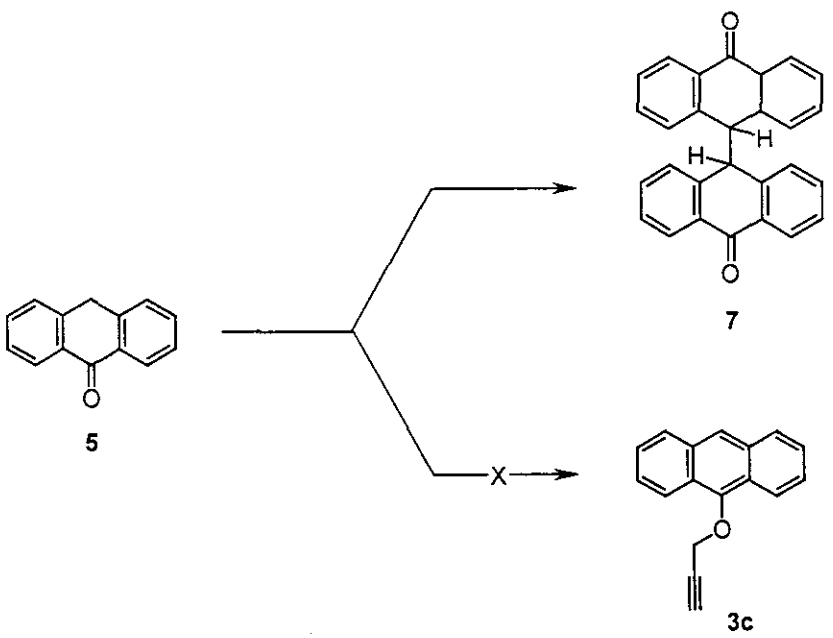
Scheme 3.1



Next, we focused our attention on the synthesis of anthracene derivatives containing heteroatoms as well as acetylenic moieties at the designated positions. The suitable synthetic targets were unsaturated ethers and esters **3c-e** containing anthracene nucleus. We employed Williamson's type ether synthesis, phase transfer catalysis, and acid catalysed etherification reaction for the preparation of ethers and esterification reaction for the synthesis of esters. The conditions employed by us did not facilitate the desired reactions except in the case of compound **3e**.

The procedures we employed for the synthesis of **3c** included: a) Williamson's type ether synthesis - anthrone (**5**) in *iso*-propanol was treated with propargyl chloride (**6**) in the presence of metallic sodium[23], b) Phase transfer catalysis - **5** in dichloromethane was treated with **6** and aqueous sodium hydroxide,[24] the phase transfer catalyst used was triethylbenzylammonium chloride, and c) Etherification - **5** in toluene was treated with **4** in presence of catalytic amount of sulphuric acid[25] (Scheme 3.2).

Scheme 3.2



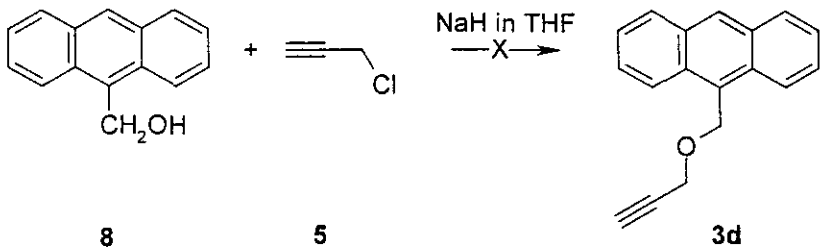
1. Propargyl chloride / Na in*iso*-Propanol / 10^{0}C
2. Propargyl chloride / $(C_2H_5)_3C_6H_5CH_2NCl$ / CH_2Cl_2 / Room Temperature
3. Propargyl alcohol / Dilute H_2SO_4 / Benzene / 80 ^{0}C

Under the conditions employed by us, TLC analysis of the product mixture indicated the presence of a new product along with unchanged anthrone. The reaction mixture was subjected to column chromatography on silica. The new product formed was identified as bianthron-9-yl[26] on the basis of spectral and analytical data. In the IR spectrum of **7**, strong absorptions were observed at 1661 cm^{-1} indicating the presence of carbonyl group. The ^{1}HNMR spectrum of **7** exhibited a singlet at δ 4.8 (2H) due to the aliphatic protons and multiplets at δ 6.8-6.9 (4H), δ 7.4-7.5 (8H) and δ 7.8-8.4 (4H) due to aromatic protons. In the ^{13}C NMR spectrum, peaks were observed at δ 54.3 (C-10), δ 182.9 (C=O), and δ 126.6-139.9 (aromatic carbons).

The attempted synthesis of ether **3c** by Williamson's ether type synthesis and in the presence of a phase transfer catalyst also resulted in the formation of **7**. In the case of acid catalysed etherification, a resinous mass along with unchanged anthrone was obtained.

We applied Williamson's ether type synthesis for the preparation of ether **3d** (Scheme 3.3). Thus, we treated 9-anthracenemethanol (**8**) with propargyl chloride (**5**) in the presence of sodium hydride. TLC analysis of the product mixture indicated the formation of two compounds **A** and **B** along with unreacted 9-anthracenemethanol. The ^{1}H NMR spectrum of compound **A** showed a multiplet at δ 7.7-8.3, singlets at δ 3.1 and δ 2.6, and a multiplet at δ 1.2-1.3. The ratio of protons is 3:4:1:2 respectively. The ^{1}H NMR spectrum of compound **B** showed a multiplet at δ 7.7-8.3, and a triplet at δ 1.2-1.3. The ratio of protons is 1:1 respectively. The structure of compounds **A** and **B** remain unidentified. It should be mentioned here that **3d** was prepared in good yields by the reaction between **8** and propargyl bromide in the presence of sodium hydride.[27] It appears that propargyl chloride is much less reactive than propargyl bromide and hence the expected product was not formed in the reaction of **8** with **5**

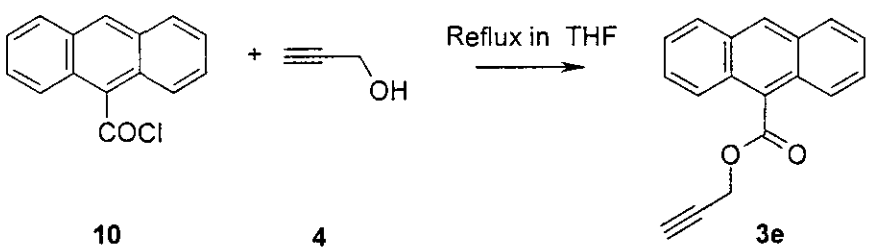
Scheme 3.3



8 **5** **3d**

The ester **3e** was synthesized by a known method from anthroic acid. Thus, we treated anthroyl chloride (**10**)[27] with **4** in THF to yield **3e** in good yields (Scheme 3.4). The IR spectrum of **3e** showed strong absorption at 1710 cm^{-1} due to the carbonyl group. In the ^1H NMR spectrum, the triplet at δ 2.7 is due to the acetylenic proton, the doublet at δ 5.3 is due to the $-OCH_2$ protons and the multiplet at δ 7.4-8.7 is due to the nine aromatic protons.

Scheme 3.4



10 **4** **3e**

Thus, our attempts to synthesise alkynylanthracenes achieved only limited success. We could synthesise an alkynylanthracene such as **3e** that can undergo Diels-Alder as well as Intramolecular Diels-Alder (IMDA) reactions.

3.4. Experimental

3.4.1. General Procedures. All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried

and activated silica or aluminium sheets coated with silica (MERCK) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry packed silica (Qualigens 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using Shimadzu-DR-8001 series FTIR spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 300, 400 and 500 MHz on a Bruker FT-NMR spectrometer or GE NMR OMEGA spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. We have reported only the relevant data for the characterisation of compounds synthesised by us.

3.4.2. Starting Materials. Anthracene and anthrone were purchased from S. D. Fine Chem. Ltd. and were used as obtained. Anthroic acid and propargyl alcohol were purchased from Sigma-Aldrich and were used as obtained.

3.4.2.1. 9-Bromoanthracene: 9-Bromoanthracene was prepared using a known procedure[21] (mixture mp 99 ^{0}C).

3.4.2.2. Phenylacetylene: Phenyl acetylene was prepared using a known procedure[22] (45%, bp 142-144 ^{0}C).

3.4.2.3. 9-Anthracenmethanol: 9-Anthracenemethanol was prepared using a known procedure[27] (60%, mixture mp 162-164 ^{0}C)

3.4.2.4. 9-Anthroyl chloride: 9-Anthroyl chloride was prepared by a known procedure[27] (99%).

3.4.3. Synthesis of Ethynylanthracenes

3.4.3.1. Attempted Synthesis of Ethynylanthracene 3a. A mixture of 9-bromoanthracene (5.14 g, 0.02 mol), phenylacetylene (2.55 g, 0.025 mol), triethylamine (6.07 g, 0.06 mol), palladium(II) acetylacetonate (0.06 g, 0.2 mmol) and triphenylphosphine (0.21 g, 0.8 mmol) was heated at 100 ^{0}C for 24 h. The reaction mixture was cooled, diluted with dichloromethane, and washed with water, 5% HCl, followed by water, saturated $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. Solvent was removed and the residue was worked up to yield unchanged 9-bromoanthracene (2.25 g, 44%, mixture mp 99 ^{0}C) as the only isolable material.

In a repeat run, a mixture of 9-bromoanthracene (5.14 g, 0.02 mol), phenylacetylene (2.55 g, 0.025 mol), triethylamine (6.07 g, 0.06 mol), palladium(II) acetylacetonate (0.06 g, 0.2 mmol) and triphenylphosphine (0.21 g, 0.8 mmol) was heated at 100 ^{0}C for 24 h. The cooled reaction mixture was dissolved in dichloromethane and washed with water, 5% HCl, followed by water, saturated $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. Solvent was removed and the residue was worked up to yield unchanged 9-bromoanthracene (2.25 g, 44%, mixture mp 99 ^{0}C) as the only isolable material.

3.4.3.2. Attempted Synthesis of Ethynylanthracene 3b. A mixture of 9-bromoanthracene (5.14 g, 0.02 mol), propargyl alcohol (1.40 g, 0.025 mol triethylamine (6.07 g, 0.06 mol), palladium(II) acetylacetonate (0.12 g, 0.4 mmol) and triphenylphosphine (0.42 g, 1.6 mmol) was heated at 100 ^{0}C for 24 h. The cooled reaction mixture was dissolved in dichloromethane and washed with water, 5% HCl, followed by water, saturated $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. Solvent was removed and the residue was worked up to yield unchanged 9-bromoanthracene (2.25 g, 44%, mixture mp 99 ^{0}C) as the only isolable material.

In a repeat run, a mixture of 9-bromoanthracene (5.14 g, 0.02 mol), propargyl alcohol (1.40 g, 0.025 mol) triethylamine (6.07 g, 0.06 mol), palladium(II)

acetylacetonate (0.12 g, 0.4 mmol) and triphenylphosphine (0.42 g, 1.6 mmol) was heated at 100 ^{0}C for 24 h. The cooled reaction mixture was dissolved in dichloromethane and washed with water, 5% HCl, followed by water, saturated $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. Solvent was removed and the residue was worked up to yield unchanged 9-bromoanthracene (2.25 g, 44%, mixture mp 99 ^{0}C) as the only isolable material.

3.4.3.3. Attempted Synthesis of Ethynylanthracene 3c. A solution of anthrone (3.88 g, 0.02 mol) and propargyl chloride (4.70 g, 0.063 mol) in dichloromethane (100 mL) was added to a solution of sodium hydroxide (0.032 g, 0.8 mmol) and triethylbenzylammonium chloride (1.00g, 4.4 mmol) in water (100 mL) and the mixture was stirred at room temperature for 6 h. The mixture was then diluted with water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture of dichloromethane and hexane (3:7), unchanged anthrone was obtained (0.56 g, 18%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane, bianthron-9-yl (7) was obtained.

Compound 7:[26] {(2.11 g, 68%); mp 215 ^{0}C (completely decomposed)}; IR ν_{max} (KBr) 1661 (C=O) cm^{-1}; UV λ_{max} (Acetonitrile) 259 (ε 15 100), 284 (ε 12 700), 341 nm (ε 7300); ^{1}H NMR ($CDCl_3$) δ 4. 8 (2H, s, bridgehead), δ 6.9-8.4 (16H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 54.3, 126.1, 127.2, 127.9, 128.4, 132.1, 139.8, 182.9; Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.03; H, 4.69. Found: C, 86.89; H, 4.31.

In a repeat run, sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) and anthrone (3.88 g, 0.02 mol) was added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. propargyl chloride (1.49 g, 0.02 mol) was added with stirring over a period of 2 h. The reaction

mixture was then cooled, kept in a refrigerator for 48 h. The mixture was then poured into water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water dried with anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.81 g, 25%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (7) was obtained in good yield {1.68 g, 52%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) and anthrone (3.88 g, 0.02 mol) was added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Propargyl chloride (1.49 g, 0.02 mol) was added with stirring over a period of 2 h. The reaction mixture was heated on a water bath for 1.5 h and then refluxed for 15 h. The mixture was cooled and then diluted with water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water, and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.61 g, 22%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (7) was obtained in good yield {1.51 g, 54%, mp 215 ^{0}C (complete decomposition)}.

In a repeat run, and sodium metal (0.06 g, 2.6 mmol) was dissolved in *iso*-propanol (80 mL) potassium iodide (0.32 g, 1.93 mmol) and anthrone (3.88 g, 0.02 mol) were added to the solution, which was warmed to dissolve the ketone. The mixture was cooled below 10 ^{0}C. Propargyl chloride (1.49 g, 0.02 mol) was added with stirring over a period of 2 h. The reaction mixture was heated on a water bath

for 1.5 h and then refluxed for 15 h. The mixture was cooled and then diluted with water and extracted with dichloromethane. The organic extract was washed with 10% HCl, water, 5% $NaHCO_3$ solution and water and dried over anhydrous $CaCl_2$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (0.86 g, 27%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane bianthron-9-yl (**6**) was obtained in good yield {1.86 g, 58%, mp 215 ^{0}C (complete decomposition)}.

In another repeat run, a stirred solution of anthrone (3.88 g, 0.02 mol), propargyl alcohol (11.21 g, 0.2 mol) and sulfuric acid (1 mL) in benzene (80 mL) was heated to reflux for 48 h. The reaction was cooled to room temperature, poured into saturated $NaHCO_3$ solution and extracted with ether. The organic extracts were washed with water, brine and water and dried over anhydrous $MgSO_4$. The residue obtained on evaporating the solvent was chromatographed on silica. On elution with a mixture (3:7) of dichloromethane and hexane, unchanged anthrone was obtained (1.86 g, 72%, mixture mp 150-153 ^{0}C).

On further elution with a mixture (1:1) of dichloromethane and hexane a resinous mass was obtained in trace amounts.

3.4.3.4. Attempted Synthesis of Ethynylanthracene 3d. A mixture of 1.25 g of 50% sodium hydride in oil (previously washed with hexane) and 9-anthracenemethanol (4.16 g, 0.02 mol) in dry THF (50 mL) was stirred at room temperature for 1 h and then heated under reflux for 1 h. The mixture was cooled and a solution of propargyl chloride (2.24 g, 0.03 mol) in THF (5 mL) was added slowly. After being heated under reflux for 2 h, the cooled mixture was treated with water, and the product was extracted with ether. The residue obtained on evaporating the

solvent was chromatographed on silica. On elution with a mixture (1:9) of dichloromethane and hexane, compound **A** was obtained.

Compound A: (20 mg); mp 65 ^{0}C (decomposed); ^{1}H NMR ($CDCl_3$) δ 1.2-1.3 (2H, m), 2.6 (1H, s), 3.1 (4H, s), 7.7-8.3 (3H, m, aromatic)

Further elution with a mixture (3:7) of dichloromethane and hexane gave compound **B**.

Compound B: (30 mg); mp 112 ^{0}C (decomposed); ^{1}H NMR ($CDCl_3$) δ 1.2-1.3 (H, m), 7.7-8.3 (H, m, aromatic)

Further elution with a mixture (1:1) of dichloromethane and hexane gave unchanged 9-anthracenemethanol (1.60 g, 45%, mixture mp 162-164 ^{0}C).

In a repeat run, a mixture of 1.25 g of 50% sodium hydride in oil (previously washed with hexane), 9-antracenemethanol (4.16 g, 0.02 mol) in dry THF (50 mL) was stirred at room temperature for 1 h and then heated under reflux for 1 h. The mixture was cooled and a solution of propargyl chloride (2.24 g, 0.03 mol) in THF (5 mL) was added slowly. After being heated under reflux for 2 h, the cooled mixture was treated with water, and the product was extracted with ether. The residue obtained on evaporating the solvent was chromatographed on silica. Elution with a mixture (1:1) of dichloromethane and hexane gave unchanged 9-anthracenemethanol (1.69 g, 48%, mixture mp 162-163 ^{0}C).

3.4.3.5. Synthesis of Ethynylanthracene 3e. To a solution of 9-anthroyl chloride (4.81 g, 0.02 mol) in THF (10 mL), propargyl alcohol (3.92 g, 0.07 mol) was added with stirring, keeping the temperature below 30 ^{0}C. The mixture was kept intact for 6 h and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane and the solution was washed with 5% $NaHCO_3$ solution and then

with water, and dried over anhydrous Na_2SO_4. The crude product was recrystallised from *iso*-propyl alcohol.

Compound 3e: (4.11 g, 79%); mp 90 ^{0}C; IR ν_{max} (KBr) 1653 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.8 (1H, t), 5.5 (2H, d) 7.4-8.7 (9H, m, aromatic).

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INTERMOLECULAR DIELS-ALDER REACTIONS

4.1. Abstract

9,10-Ethenoanthracenes or dibenzobarrelenes exhibit interesting photochemistry. This chapter presents the syntheses of a few dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylates having alkenyl or alkynyl substituents at the bridgehead. These bicyclic systems were synthesised through the Diels-Alder reaction between suitable anthracenes and dimethyl acetylenedicarboxylate.

4.2. Introduction

Diels-Alder reaction has remained remarkably useful in the armamentum of the synthetic organic chemist, ever since its formulation in 1928.[1-21] Diels-Alder reaction has both enabled and shaped the art and science of total synthesis over the last few decades to an extent which, arguably, has yet to be eclipsed by any other transformation in the current synthetic repertoire. With myriad applications, often as a crucial element in elegant and programmed cascade sequences facilitating the construction of complex molecules, Diels-Alder cycloaddition reaction has afforded numerous and unparalleled solutions to a diverse range of synthetic puzzles provided by nature in the form of natural products. Yet, the true power and effectiveness of the Diels-Alder reaction only began to be realized in the 1950s and 1960s with the elegant applications of the process to the total synthesis of many complex natural products.[22] The development continued with no let up in pace. Many different versions of Diels-Alder reaction were elaborated, including intramolecular [4+2] cycloadditions[23], hetero Diels-Alder reactions[24], pressure-accelerated Diels-Alder reactions[25], Lewis

acid accelerated Diels-Alder reactions[26] and Diels-Alder reactions in aqueous media.[27-32] If one chemical reaction had to be selected from all those in the gamut of synthetic organic chemists as the most useful and powerful synthetic construction, it was clear by 1970's that the Diels-Alder reaction would be the logical choice. Its application not only leads to a strong increase in molecular complexity (molecular size, topology, stereochemistry, functionality, and appendages), but also can result in structures that lend themselves to additional amplification of complexity by the use of other powerful synthetic reactions.

Our aim was to explore the possibility of controlling competing pathways in the photochemical transformation of dibenzobarrelenes. We proposed to introduce the idea of selective quenching of excited states intramolecularly by incorporating "inbuilt" quenchers onto the barrelene chromophore. It is known that appropriate olefins can quench triplet-excited states through energy transfer. We premise that the triplet excited state of a barrelene with an appended olefin unit might be quenched intramolecularly. In order to exploit the true potential of this possibility, it is important to fine-tune the triplet energy of the olefin unit. So, it is mandatory to synthesise several alkenylbarrelenes having olefin units possessing a range of triplet energies for identifying the ideal structural features for efficient intramolecular quenching. It is also possible that the appended olefin unit will introduce novel photochemical pathways unavailable to simple dibenzobarrelenes. We presume that the location of the additional π-system relative to the barrelene chromophore is of crucial importance in this context. Introduction of a vinyl substituent at the bridgehead position of dibenzobarrelenes, for example, will provide a tetra-π-methane system capable of exhibiting hitherto undemonstrated modes of photochemical transformations. It is also interesting to investigate the role of allyl, homoallyl and more remote alkenyl substituents in controlling the photochemistry of dibenzobarrelenes. Since we proposed to employ suitably-substituted anthracenes as logical precursors to the target dibenzobarrelenes, a major side reaction in the synthesis of dibenzobarrelenes may be intramolecular Diels-Alder reaction. So, it is important to identify the right structural features of alkenylanthracenes and the optimal reaction conditions that will enable them to undergo intermolecular or intramolecular Diels-Alder

reactions. Thus, we proposed to examine the reaction of several 9-alkenylanthrcenes with suitable dienophiles such as dimethyl acetylenedicarboxylate (DMAD) to synthesise the required olefin-appended dibenzobarrelenes. We also proposed to identify the structural features and reaction conditions that will enable intermolecular or intramolecular Diels-Alder reaction to proceed selectively. The novel dibenzobarrelenes synthesised by us through intermolecular Diels-Alder reaction include dimethyl 9-(1-anthrylethylene)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**3a**), dimethyl 9-(1-anthryl-2-phenylethylene)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**3b**), dimethyl 9-(1-anthryl-2-benzoylethylene)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**3d**), dimethyl 9-(1-anthryl-2-carboxybiphenylethylene)-9,10-dihydro-9,10-etheno-anthracene-11,12-dicarboxylate (**3e**), dimethyl-9-(3-anthrylmethoxy-propene)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**3g**), and dimethyl-9-(3-anthroic acid propynylester)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**3h**). The novel dibenzobarrelenes synthesised by us through IMDA reaction include 1,2,3a,4-tetrahydro-5*H*-5,9b-*o*-benzenaphtho-[1,2-c]furan (**5g**).

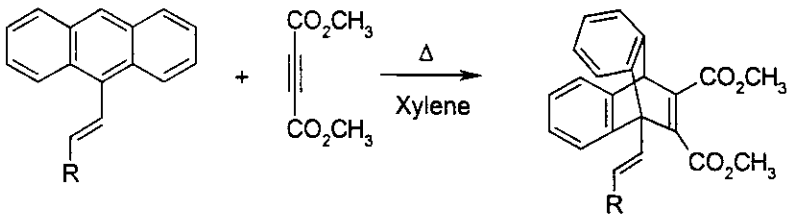
4.3. Results and Discussion

4.3.1. Intermolecular Diels-Alder Reactions of 9-Substituted Anthracenes

We employed Diels-Alder reaction for the synthesis of bicyclic compounds of our choice. These bicyclic systems are carefully designed to have a suitable chromophore and a built-in triplet quencher component, which might selectively and efficiently quench the triplet excited state of these molecules in an intramolecular fashion. In the present investigation, we explored the reaction of several 9-alkenylanthracenes with a suitable dienophile such as DMAD to synthesise the required olefin-appended barrelenes. We also proposed to identify the structural features and reaction conditions that will enable Diels-Alder or IMDA reaction to proceed selectively. Thus we treated the alkenylanthracenes **1a-e** with dimethyl acetylenedicarboxylate (**2**, DMAD) to yield the corresponding Diels-Alder adducts **3a-e** under suitable conditions. Dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylates **3a,b,d,e** were obtained in good yields

through the Diels-Alder reaction between alkenylanthracenes **1a,b,d,e** and **2** (Scheme 4.1).

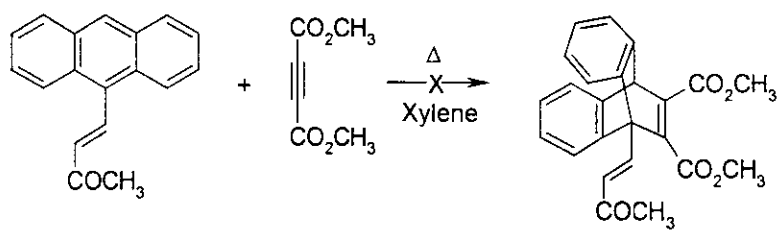
Scheme 4.1



1a,b,d,e **2** **3a** R = H
b R = Ph
d R = COC_6H_5
e R = $COC_6H_4C_6H_5(p)$

However, **1c** failed to yield the corresponding adduct **3c** under the reaction conditions employed by us (Scheme 4.2). Instead, **1c** underwent polymerisation under the conditions as indicated by the ^{1}H NMR.

Scheme 4.2



1c **2** **3c**

The structures of the Diels-Alder adducts **3a,b,d,e** were established on the basis of literature precedence, analytical results and spectral data. Compound **3a**, which was obtained in 75% yield showed prominent peaks at 1714 and 1732 cm^{-1} in the IR spectra indicating the presence of two carbonyl groups in the compound. In the ^{1}H NMR spectrum, two singlets were observed at δ 3.7 and 3.8 indicating the presence of two methoxy groups in the compound. The peaks at δ 5.6, δ 6.1 and δ 6.5-6.7 are due to the vinylic protons and the singlet at δ 5.7 is due to the bridgehead proton. The remaining vinylic and aromatic protons were observed as a multiplet in the aromatic region δ 7.0-7.5. The ^{13}C NMR spectrum showed

peaks at δ 158.5 and 162.3 due to ester carbonyl carbons. The molecular ion of this compound was observed at *m/z* 346 confirming its identity. The structure was further confirmed by elemental analysis, which gave acceptable data.

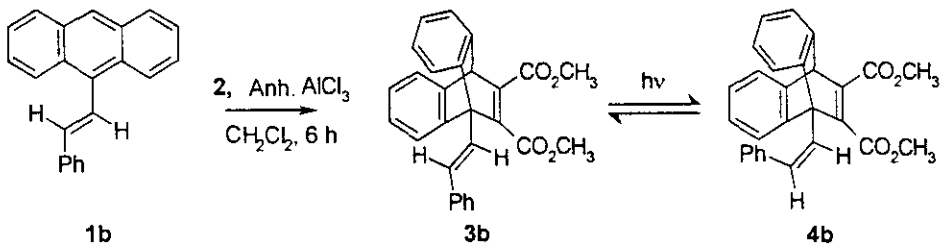
Similarly, compound **3d** showed the IR absorptions at 1674, 1724 and 1736 cm^{-1} due to the carbonyl groups. In the ^{1}H NMR spectrum, two singlets were observed at δ 3.7 and 3.8 indicating the presence of two methoxy groups in the compound. The one proton singlet at δ 5.7 is due to the bridgehead proton. The vinylic and aromatic protons were observed as a multiplet in the aromatic region δ 7.0-8.1. The ^{13}C NMR spectrum showed peaks at δ 163.5, 167.2, and 189.4 due to carbonyl carbons. The molecular ion of this compound was observed at *m/z* 450 confirming its identity. The structure was further confirmed by elemental analysis, which gave acceptable data.

Compound **3e** showed very similar spectral behaviour with that of **3d.** For **3e,** IR absorptions were observed at 1668, 1717 and 1730 cm^{-1} due to the carbonyl groups. ^{1}H NMR and ^{13}C NMR spectra of **3e** were comparable with those of **3d** and it gave acceptable analytical and mass spectral data.

Compound **1b** underwent efficient Lewis acid-catalysed Diels-Alder reaction at room temperature with DMAD to give the styrene-appended dibenzobarrelene **3b**. Even on brief exposure to diffuse light, **3b** underwent facile photoisomerisation to give the *Z*-isomer **4b** (Scheme 4.3). Though we were able to isolate and store **3b** as a solid in the pure form (as evidenced by TLC analysis), it underwent fast isomerisation under the conditions employed for collecting NMR spectral data. Based on this, it may be inferred that intramolecular energy transfer from a barrelene chromophore to an appended styrene moiety is a comprehensible possibility. In the IR spectrum of **3b**, strong absorptions were observed at 1714 cm^{-1} and 1734 cm^{-1} due to the ester carbonyl groups. The ^{1}H NMR spectrum showed two singlets around δ 5.8 due to the bridgehead proton in a 1:1 ratio indicating the presence of an equimolar mixture of isomers **3b** and **4b**. The ^{13}C NMR spectrum confirmed the presence of two isomers. In the ^{13}C NMR spectrum, peaks were observed at δ 45.3, 47.2, 47.9, 52.8, 115.9, 116.3, 116.7,

117.6, 118.8, 119.1, 119.8, 120.3, 121.3, 121.9, 122.6, 123.2, 123.4, 123.6, 125.7, 131.2, 131.6, 134.2, 136.4, 139.7, 139.9, 151.3, 158.5, 162.2.

Scheme 4.3

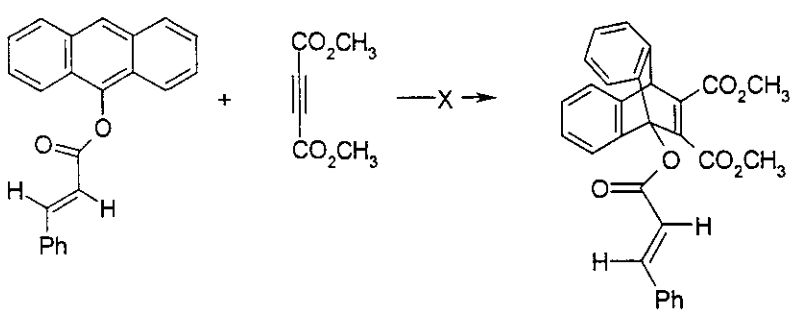


1b **3b** **4b**

Compound **1c** did not give the expected Diels-Alder adduct with DMAD. The ^{1}H NMR spectrum of the product obtained in the reaction between **1c** and DMAD showed peaks at δ 1.2 (s), 1.3 (s), 1.4 (s), 7.1-8.1 (m, aromatic), 8.7 (s), 9.0 (d, vinylic), and 11.6 (s). The integration factor for each peak suggests the formation of a polymer. Based on geometrical constraints, the possibility of intramolecular Diels-Alder reaction was ruled out in this case.

Next, we explored the Diels-Alder reaction of homoallylanthracene **1f** with DMAD under various conditions (Scheme 4.4). On refluxing **1f** with DMAD in benzene, toluene, xylene and in *o*-dichlorobenzene, we obtained unchanged **1f** in near-quantitative amounts. On neat heating with DMAD at 200 ^{0}C, unchanged **1f** was obtained in 55% yield. When the reaction temperature was increased to 250 ^{0}C, complete decomposition of **1f** occurred. Based on geometrical constraints, the possibility of intramolecular Diels-Alder reaction was ruled out in this case as well.

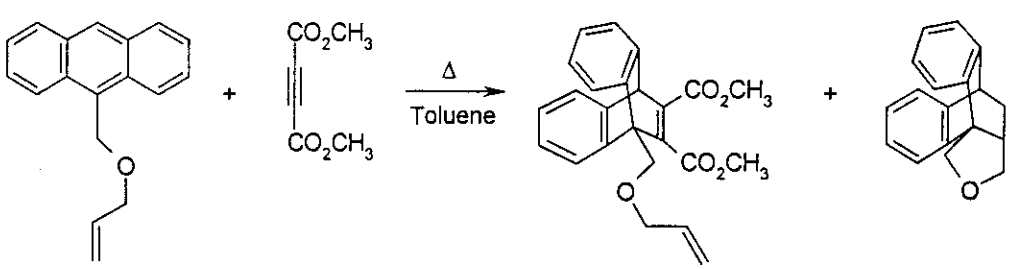
Scheme 4.4



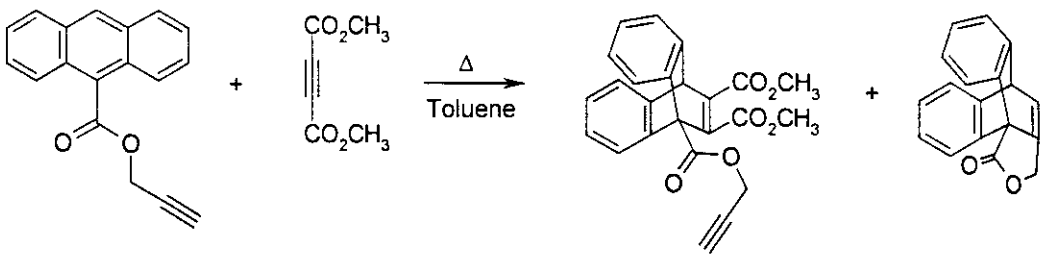
1f **2** **3f**

The system with remote double bond **1g** and the system with a remote triple bond **1h** underwent intermolecular Diels-Alder as well as intramolecular Diels-Alder, with the latter predominating at higher temperatures. In the case of compound **1g** the Diels-Alder adduct **3g** was formed in 30% yield when refluxed in toluene at 110-120 ^{0}C, while in the case of compound **1h**, the Diels-Alder adduct **3h** was formed only in trace amounts under analogous conditions (Scheme 4.5). Close examination of the product distribution in the case of **1g,h** reveals that **1h** is more reluctant to undergo intermolecular Diels-Alder reaction. For this molecule, IMDA reaction appears to be the preferred pathway. This is attributable to the nature of the dienophile components in **1g** and **1h** with the more active acetylenic unit in **1h** facilitating IMDA reaction. The Diels-Alder adduct **3g** and IMDA adduct **5g** were characterised by spectroscopic methods including COSY and HSQC spectroscopy. The COSY trace of **5g** showed coupling between the protons at δ 2.8, 2.3 and 4.1. HSQC of **5g** indicated that the protons appearing at δ 2.8 and 4.1 are attached to the carbon at δ 72.1. The proton at δ 2.3 is attached to carbon at δ 46.0. The proton at δ 2.3 is also coupled to protons at δ 2.0 and 1.4 and the protons at δ 2.0 and 1.4 are attached to the carbon at δ 29.2. The protons at δ 4.5 and 5.0 are attached to the same carbon atom at δ 66.5. On the basis of HSQC and COSY data, we confirmed the structure of IMDA adduct **5g** (Table 4.1). The ^{1}H NMR spectrum of intermolecular Diels-Alder adducts **3g** and **3h** showed the peaks at δ 3.7 and 3.8 indicating the presence of two methoxy groups in the adducts. The ^{1}H NMR spectrum of IMDA adduct **5h**, on the other hand, showed doublets at δ 5.1 and 5.2 and a multiplet in the aromatic region.

Scheme 4.5



1g **2** **3g** 30% **5g** 50%



1h **2** **3h** **5h**

Trace Amounts 65%

Thus we were successful in synthesising a few dibenzobarrelenes containing appended olefin units, which might serve as potential substrates for exploring the feasibility of selective quenching of triplet excited states of dibenzobarrelenes. However, it appears that there are limitations to our strategy to synthesise dibenzobarrelenes with "inbuilt" quenchers from the corresponding anthracenes. Depending on the nature of the 9-substituent, intramolecular Diels-Alder reaction can be a major side reaction. Additionally, there are instances where the anthracene precursors are reluctant to undergo Diels-Alder reaction. The reason for this unexpected behaviour is not fully understood.

4.4. Experimental

4.4.1. General Procedures: All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica or aluminium sheets coated with silica (MERCK) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry packed silica (Qualigens 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using Shimadzu-DR-8001 series FTIR spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 400 and 500 MHz on a Bruker FT-NMR spectrometer or GE NMR OMEGA spectrometer with tetramethylsilane s internal standard. Chemical shifts are reported as parts per million (ppm) downfield of tetramethylsilane (TMS). Elemental analysis was performed at Regional Sophisticated Instrumentation

Center, Central Drug Research Institute, Lucknow. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

4.4.2. Starting Materials: Dimethyl acetylenedicarboxylate (DMAD) was purchased from Sigma-Aldrich and was used as received.

4.4.3. Preparation of Alkenyldibenzobarrelenes

4.4.3.1. Synthesis of 3a. A sample of **1a** (1.02 g, 5mmol) was dissolved in minimum quantity of dry xylene and DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent under reduced pressure gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1a** (0.45 g, 25%, mixture mp 69 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **3a**. The solid product was purified by recrystallisation from a mixture (1:2) of dichloromethane and hexane.

Compound 3a: (1.30 g, 75%); mp 180-182 ^{0}C; IR ν_{max} (KBr) 1714, 1732 (C=O, ester) cm^{-1}; UV λ_{max} (Acetonitrile) 223 (ε 40 000), 230 (ε 20 000), 340 nm (ε 17 000); ^{1}H NMR ($CDCl_3$) δ 3.7 (3H, s, OCH_3), 3.8 (3H, s, OCH_3), 5.6 (1H, dd, vinylic), 5.7 (1H, s, methine) 6.1 (1H, dd, vinylic), 6.5-6.7 (1H, m, vinylic), 7.0-7.5 (8H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 45.2, 46.9, 47.2, 53.1, 117.5, 118.5, 118.9, 119.7, 120.2, 124.8, 136.5, 139.3, 139.94, 151.1, 158.5, 162.3; MS, *m/z* 346 (M^+), and other peaks. Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.46; H, 5.28.

4.4.3.2. Synthesis of 3b. **3b** was prepared by Lewis acid catalyzed Diels-Alder reaction. To a mixture of **1b** (1.4 g, 5 mmol) and anhydrous $AlCl_3$ (0.67 g, 5 mmol) in dry dichloromethane (10 mL), DMAD (1.06 g, 7.5 mmol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred for 6 h and poured over crushed ice, acidified with 50 mL hydrochloric acid and extracted with dichloromethane. The organic layer was separated, washed sequentially with

water, saturated $NaHCO_3$ solution, water, and dried over anhydrous $CaCl_2$. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1b** (0.35 g, 28%, mixture mp 131-133 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane gave **3b.** The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane. *Note*: The whole reaction and work up procedures were carried out in the dark. The NMR spectral data presented here is for a mixture of **3b** and **4b**. We could not collect NMR spectral data of pure components since the *E-Z* isomerisation of these compounds is quite fast in solution.

Compound 3b: (0.72 g, 57%); mp 128 ^{0}C; IR ν_{max} (KBr) 1714, 1734 (C=O, ester) cm^{-1}; UV λ_{max} (Acetonitrile) 227 (ε 40 000), 251 (ε 20 000), 371 nm (ε 17 000); MS, *m/z* 422 (M^+), and other peaks. Anal. Calcd for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 79.63; H, 5.74.

NMR Spectra of a 1:1 mixture of 3b and 4b: ^{1}H NMR ($CDCl_3$) δ 3.8 (OCH_3), 3.9 (OCH_3), 5.8 (methine), 6.7-7.5 (aromatic and vinylic); ^{13}C NMR ($CDCl_3$) δ 45.3, 47.2, 47.9, 52.8, 115.9, 116.3, 116.7, 117.6, 118.8, 119.1, 119.8, 120.3, 121.3, 121.9, 122.6, 123.2, 123.4, 123.6, 125.7, 131.2, 131.6, 134.2, 136.4, 139.7, 139.9, 151.3, 158.5, 162.2. (*Note:* TLC of a freshly purified sample of **3b** showed a single spot. But it underwent facile *E-Z* isomerisation in solution under the influence of diffuse laboratory light while recording the spectra.)

4.4.3.3. Attempted Synthesis of 3c: DMAD (1.06 g, 7.5 mmol) was added to a solution of **1c** (1.23 g, 5 mmol) in dry xylene, and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1c** (0.55 g, 50%, mixture mp 167-169 ^{0}C). Further elution with a mixture (1:1) of dichloromethane and hexane gave an unidentified polymeric material {0.39 g, 35% (w/w), mp 42-45 ^{0}C} exhibiting the following spectral data:

^{1}H NMR ($CDCl_3$) δ 1.2 (s), 1.3 (s), 1.4 (s), 7.1-8.1 (m, aromatic), 8.7 (s), 9.0 (d), 11.6 (s).

In a repeat run, **1c** (1.23 g, 5 mmol) was dissolved in minimum quantity of dry benzene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1c** (0.89 g, 72%, mixture mp 167-169 ^{0}C) as the only isolable material.

In a repeat run, **1c** (1.23 g, 5 mmol) was dissolved in minimum quantity of dry toluene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1c** (0.80 g, 65%, mixture mp 167-169 ^{0}C) as the only isolable material.

In yet another run, to a mixture of **1c** (1.84 g, 5 mmol) and anhydrous $AlCl_3$ (0.67 g, 5 mmol) in 10 mL dry dichloromethane DMAD (1.06 g, 7.5 mmol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred for 6 h and poured over crushed ice, acidified with 50 mL hydrochloric acid and extracted with dichloromethane. Unchanged **1c** was obtained in 80% yield (mixture mp 167-169 ^{0}C).

4.4.3.4. Synthesis of 3d. To a solution of **1d** (1.54 g, 5 mmol) in minimum quantity of dry xylene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1d** (0.56 g, 31%, mixture mp 120-124 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **3d**. The solid product was purified by recrystallisation from a mixture of dichloromethane and hexane (2:1).

Compound 3d: (1.15 g, 64%); mp 166-168 ^{0}C; IR ν_{max} (KBr) 1674 (C=O, ketone), 1724, 1736 (C=O, ester) cm^{-1}; UV λ_{max} (Acetonitrile) 234 (ε 48 000), 281 (ε 20000), 323 nm (ε 16700); ^{1}H NMR ($CDCl_3$) δ 3.8, (3H, s, OMe), 3.9 (3H, s, OMe), 5.7 (1H, s, methine), 7.0-8.1 (15H, m, aromatic and vinylic); ^{13}C NMR ($CDCl_3$) δ 50.5, 52.4, 52.5, 58.0, 122.4, 124.2, 125.2, 125.8, 128.8, 128.8, 132.5, 133.4, 137.4, 138.8, 142.1, 143.8, 144.8, 155.2, 163.5, 167.2, 189.4; MS, *m/z* 450 (M^+), and other peaks. Anal. Calcd for $C_{29}H_{22}O_5$: C, 77.32; H, 4.92. Found: C, 77.22; H, 5.11.

4.4.3.5. Preparation of 3e: Compound **1e** (1.84 g, 5 mmol) was dissolved in minimum quantity of dry xylene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1e** (0.63 g, 30%, mixture mp 145 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **3e**. The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

Compound 3e: (1.37 g, 52%); mp 94 ^{0}C (decomposed); IR ν_{max} (KBr) 1668 (C=O), 1717, 1730 (C=O, ester) cm^{-1}; UV λ_{max} (Acetonitrile) 259 (ε 55 700), 284 (ε 26 000), 341 nm (ε 2000); ^{1}H NMR ($CDCl_3$) δ 3.7 (3H, s, OMe), 3.8 (3H, s, OMe), 5.7 (1H, s, methine), 7.1-8.2 (19H, m, aromatic and vinylic); ^{13}C NMR ($CDCl_3$) δ 45.3 (), 47.3, 52.9, 58.0, 117.2, 119.0, 120.0, 120.6, 122.1, 122.3, 123.2, 123.8, 124.2, 127.3, 130.9, 133.5, 134.6, 136.9, 138.6, 139.6, 141.0, 149.9, 158.3, 162.0, 183.6; MS, *m/z* 526 (M^+), and other peaks. Anal. Calcd for $C_{35}H_{26}O_5$: C, 79.83; H, 4.98. Found: C, 79.65; H, 4.83.

4.4.3.6. Attempted Synthesis of 3f: To a solution of **1f** (1.10 g, 5 mmol) in dry xylene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1f** (1.29 g, 68%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, **1f** (1.62 g, 5 mmol) was dissolved in minimum quantity of dry benzene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1f** (1.22 g, 75%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, **1f** (1.62 g, 5 mmol) was dissolved in minimum quantity of dry toluene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1f** (1.10 g, 68%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, **1f** (1.62 g, 5 mmol) was dissolved in minimum quantity of dry *o*-dichlorobenzene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1f** (0.94 g, 58%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, to a mixture of **1f** (1.62 g, 5 mmol) and anhydrous $AlCl_3$ (0.67 g, 5 mmol) in 10 mL dry dichloromethane DMAD (1.06 g, 7.5 mmol) was added in small amounts at 0 ^{0}C. The reaction mixture was stirred for 6 h and poured over crushed ice, acidified with 50 mL hydrochloric acid and extracted with dichloromethane. Unchanged **1f** was obtained in 80% yield (mixture mp 188-190 ^{0}C) as the only isolable material.

In yet another run, a mixture of **1f** (100 mg, 0.3 mmol) and DMAD (0.07 g, 0.5 mmol) was heated in a sealed tube at 200 ^{0}C. The solid residue was extracted with dichloromethane and was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1f** (55 mg, 55%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, a sample of **1f** (100 mg, 0.3 mmol) and DMAD (0.07 g, 0.5 mmol) was heated in a sealed tube at 250 ^{0}C. The solid residue was extracted with dichloromethane. TLC showed complete decomposition of the starting material.

4.4.3.7. Reaction of 1g with DMAD: Compound **1g** (1.24 g, 5 mmol) was dissolved in minimum quantity of dry toluene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1g** in trace amounts (mixture mp 50-55 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave the adduct **3g**. The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

Compound 3g: (0.36 g, 30%, mp 72 ^{0}C); IR ν_{max} (KBr) 1714, 1730 (C=O, ester) cm^{-1}; UV λ_{max} (Acetonitrile) 259 (ε 55 700), 284 (ε 26 000), 341 nm (ε 2000); ^{1}H NMR ($CDCl_3$) δ 3.7 (3H, s, OMe), 3.8 (3H, s, OMe), δ 4.2 (2H, d), 5.3-5.4 (4H, m) 5.6 (1H, s, methine), 6.0-6.1 (1H, m), 7.0-7.4 (8H, m, aromatic).

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **5g**. The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

Compound 5g: (0.61 g, 50%, mp 94 ^{0}C); IR ν_{max} (KBr) cm^{-1}; UV λ_{max} (Acetonitrile) 259 (ε 55 700), 284 (ε 26 000), 341 nm (ε 2000); ^{1}H NMR ($CDCl_3$)

δ 1.3-1.4 (1H, m), 1.9-2.0 (1H, m), δ 2.3-2.4 (1H, m), 2.7-2.8 (2H, m) 4.4 (1H, s), 4.5 (1H, d), 5.0 (1H, d), 5.6 (1H, s, methine), 7.0-7.4 (8H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 29.0, 46.0, 50.5, 52.0, 66, 72.0, 119, 122.0, 122.5, 124.0, 125.0, 126.0, 126.5.

4.4.3.8. Reaction of 1h with DMAD: To a solution of **1h** (1.30 g, 5 mmol) in dry toluene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed on silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1h** in trace amounts (mixture mp 90 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave the adduct **3h**. The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

Compound 3h: (12 mg, ~1%); mp 122-124 ^{0}C (dec); ^{1}H NMR ($CDCl_3$) δ 2.8 (1H, t), 3.7 (3H, s, OMe), 3.8 (3H, s, OMe), 5.2 (2H, d) 5.6 (1H, s, methine), 7.0-7.7 (8H, m, aromatic).

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **5h**. The solid product was purified by recrystallisation from a mixture of dichloromethane and hexane (2:1).

Compound 5h[33]**:** (0.84 g, 65%); mp 258-262 ^{0}C; ^{1}H NMR ($CDCl_3$) δ 5.1 (2H, d), 5.2 (1H, d), 6.8-7.5 (9H, m, aromatic).

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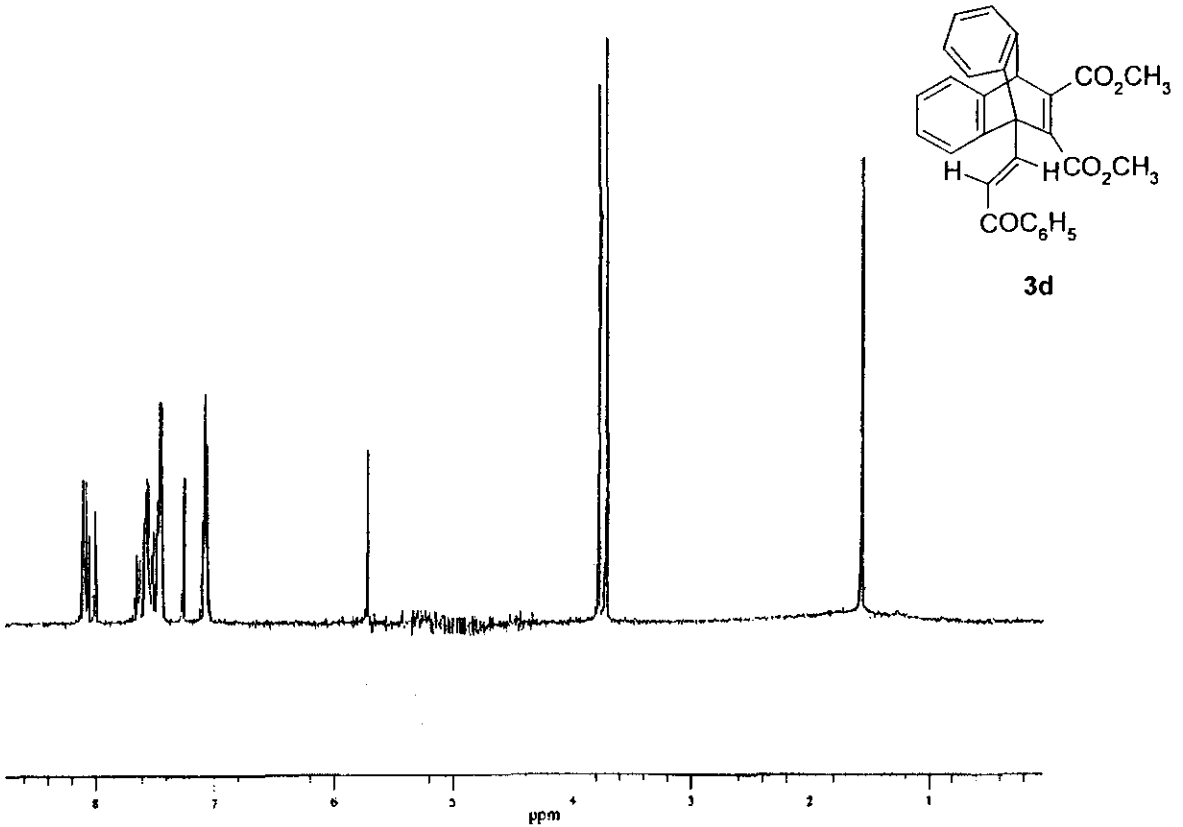
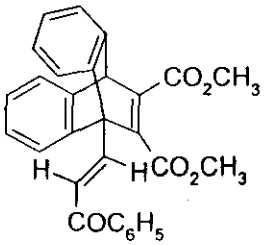


Figure 4.1. ^{1}H NMR spectrum of compound 3d



3d

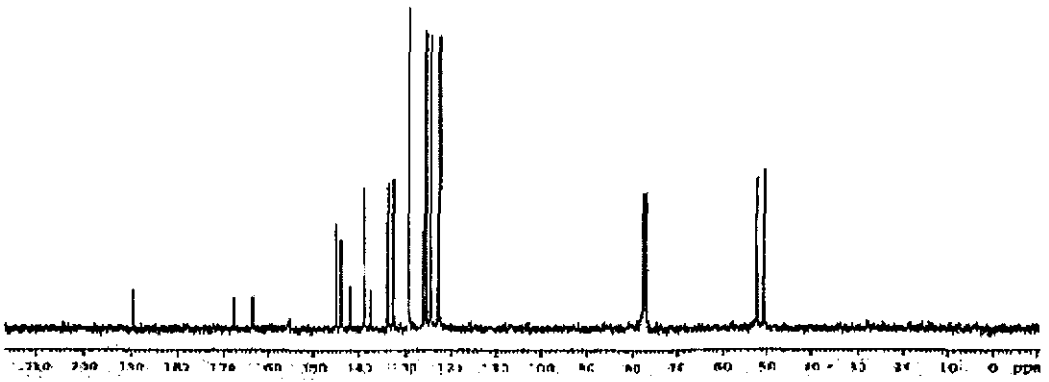
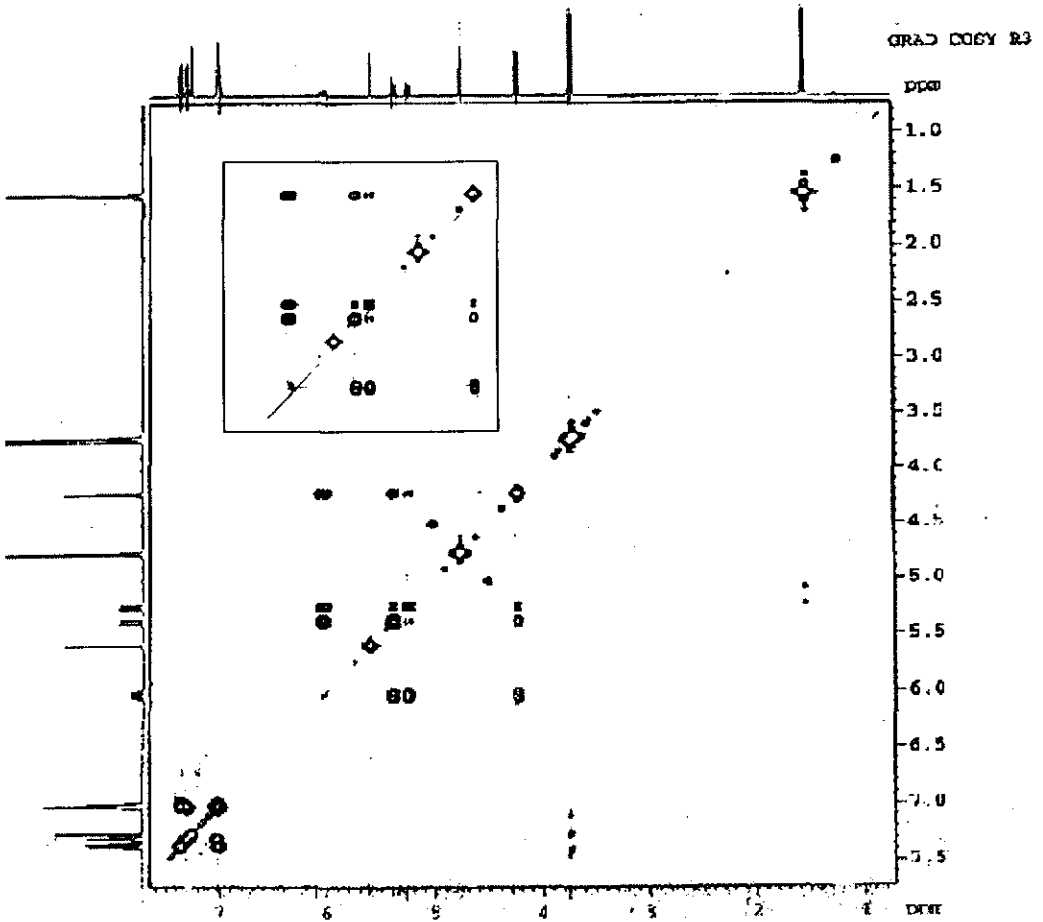
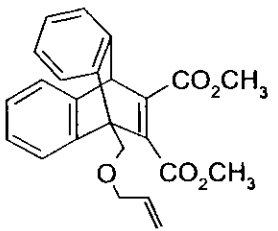


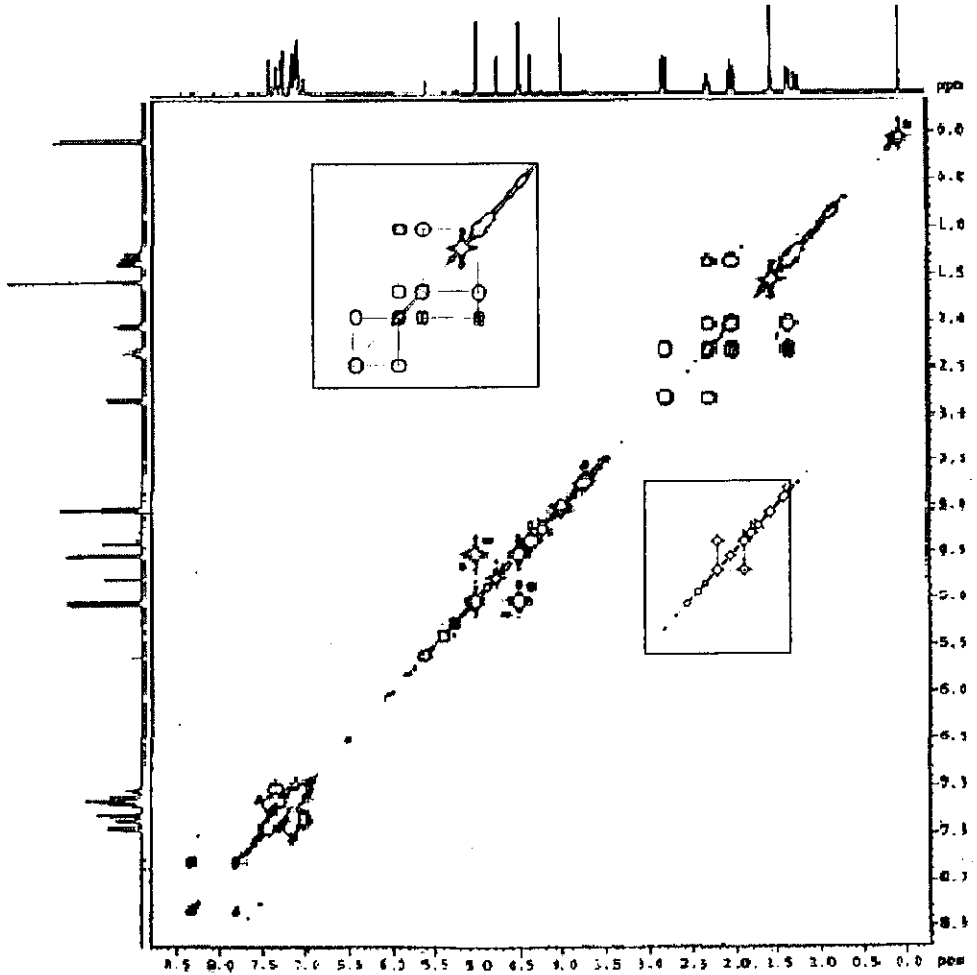
Figure 4.2. ^{13}C NMR spectrum of compound 3d

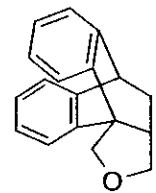




3g

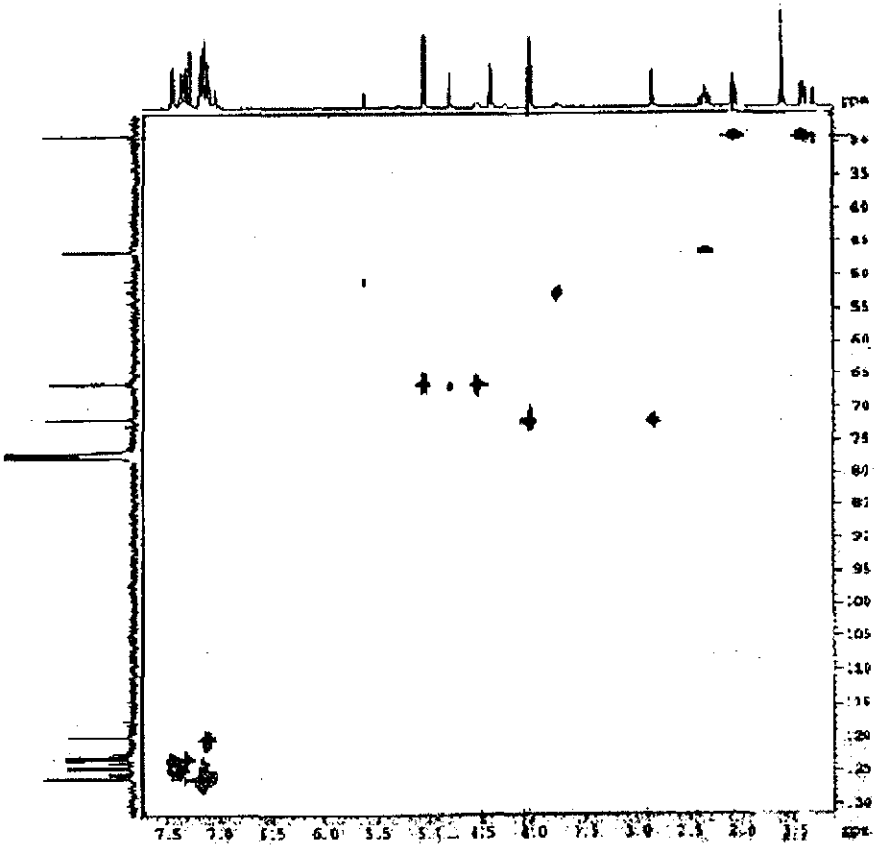
Figure 4.3. ^{1}H-^{1}H COSY of compound 3g

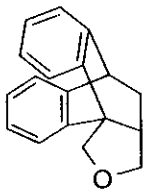




5g

Figure 4.4. ^{1}H-^{1}H COSY of compound 5g





5g

Figure 4.5. ^{1}H-^{13}C COSY of compound 5g

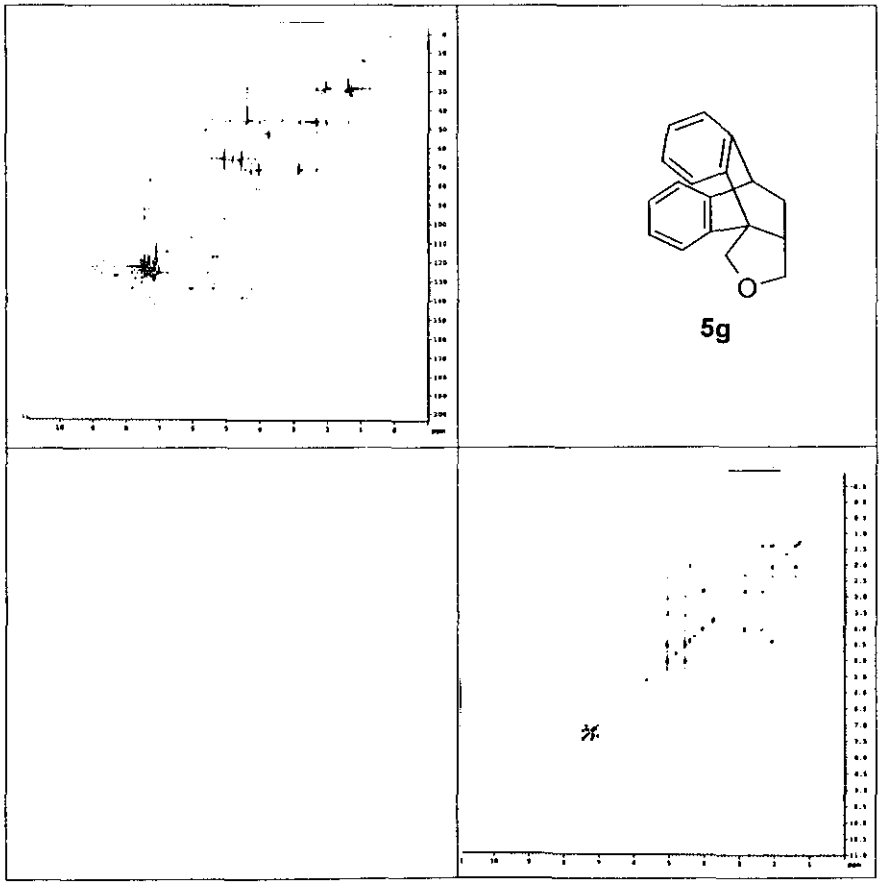


Figure 4.6. HSQC of compound 5g.

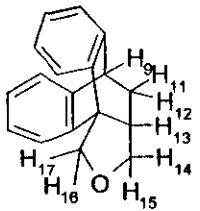
	H-H Coupling	C-H Connectivity
 **5g**	$J_{11,12}$ = 6.1 Hz $J_{11,13}$ = 1.8 Hz $J_{12,11}$ = 10.0 Hz $J_{12,13}$ = 3.4 Hz $J_{14,13}$ = 7.5 Hz $J_{14,15}$ = 11.3 Hz $J_{15,14}$ = 7.4 Hz $J_{16,17}$ = 8.7 Hz $J_{17,16}$ = 8.7 Hz	C_9-H_9 C_{11}-H_{11} C_{11}-H_{12} C_{12}-H_{13} C_{13}-H_{14} C_{13}-H_{15} C_{14}-H_{16} C_{14}-H_{17}

Table 4.1. ^{1}H / ^{1}H and ^{13}C / ^{1}H Connectivity of Compound 5g.

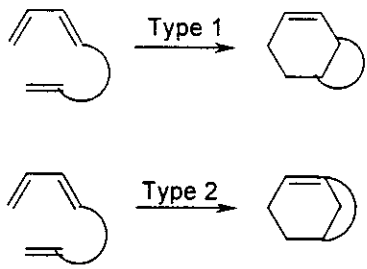
INTRAMOLECULAR DIELS-ALDER REACTIONS

5.1. Abstract

9,10-Ethano and ethenoanthracenes can be obtained by the Diels-Alder reaction of anthracenes with suitable dienophiles. This chapter presents our efforts to find out whether intermolecular Diels-Alder and Intramolecular Diels-Alder reactions compete with each other and thus to optimize the conditions for Diels-Alder and IMDA adducts of suitable 9-substituted anthracenes.

5.2. Introduction

Intramolecular Diels-Alder reaction (IMDA)[1-20] has assumed considerable importance in contemporary organic synthesis, and it has been applied to a number of synthetic objectives with notable success. IMDA reaction provides a simple and direct approach to polycyclic skeletons of special interest in the synthesis of natural products. Two rings (a fused bicyclic adduct) are formed in a single step, and the cyclisation often proceeds under remarkably mild conditions. The other variant of the intramolecular [4+2] cycloaddition reaction based on the connectivity available is the type 2 IMDA[21] reaction which results in bridged bicyclic ring system. The type 2 IMDA reaction provides a one-step entry into anti-Bredt alkenes, which were for many years regarded as chemical curiosities (Equation 5.1). When diene and dienophile are joined at position 1 of the diene (type 1), cycloaddition usually gives rise to a fused bicyclic adduct. The second variant involves union of diene and dienophile at position 2 of the diene (type 2). Cycloaddition in this case results in the formation of a bridged bicyclic ring system.

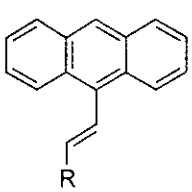


(5.1)

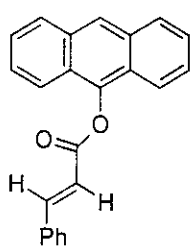
We were interested in exploring the potential of IMDA reaction for the preparation of 9,12-ethano as well as ethenoanthracenes. IMDA reaction of an anthracene derivative was reported by Meek and Dann.[22] Ciganek employed IMDA reaction for the preparation of 9,12-etheno and ethanoanthracenes having useful properties as therapeutic agents.[23]

In this chapter, we describe our investigations on intra as well as intermolecular Diels-Alder reaction of several 9-ethenyl and ethynylanthracenes. The substrates selected by us are presented in Chart 5.1.

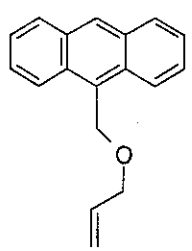
Chart 5.1



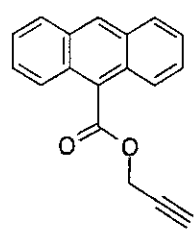
1a



1b



1c



1d

Close examination of the structural features of **1a,b** indicates that these are unlikely to undergo IMDA reaction due to steric constraints. However, **1c,d** are likely to undergo both IMDA reaction and normal Diels-Alder reaction with a suitable dienophile. Based on these, it may be concluded that **1a,b** are likely to undergo Diels-Alder reaction with DMAD to give 9-alkenylethenoanthracenes. It may further be inferred that **1c,d** are likely to undergo either Diels-Alder reaction

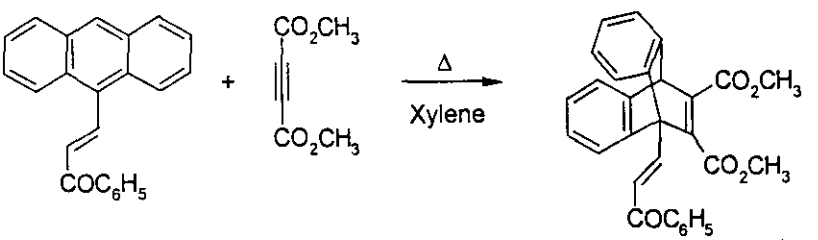
with DMAD to yield the corresponding 9,12-ethenoanthracenes or IMDA reaction to give the corresponding polycyclic adducts (*vide infra*). We were interested in the synthesis of several 9-ethenyl and 9-ethynyl substituted ethenoanthracenes to test our hypothesis on intramolecular quenching of triplet excited states. We selected Diels-Alder reaction of suitable 9-substituted anthracenes with acetylenic dienophiles for the synthesis of the required substrates. While selecting this methodology, we were aware that IMDA reactions may be a serious side reaction in some cases. Hence, it was important for us to determine the optimal reaction conditions for the synthesis of ethenoanthracenes of our choice.

5.3. Results and Discussion

5.3.1. Intermolecular v/s Intramolecular Diels-Alder Reactions of 9-Substituted Anthracenes

We examined the Diels Alder reaction between **1a** and DMAD under different conditions. Compound **1a** underwent Diels-Alder reaction with DMAD at temperatures above 100 ^{0}C. At room temperature and in refluxing benzene, neither Diels-Alder nor IMDA adducts were formed. Lewis-acid catalysed reaction at room temperature also did not give the adduct. At refluxing temperature of toluene, Diels-Alder adduct **3a** was formed in low yields. When refluxed in xylene, the Diels-Alder adduct **3a** was formed in good yields (65%) (Scheme 5.1). On refluxing **1a** in xylene, no product was formed.

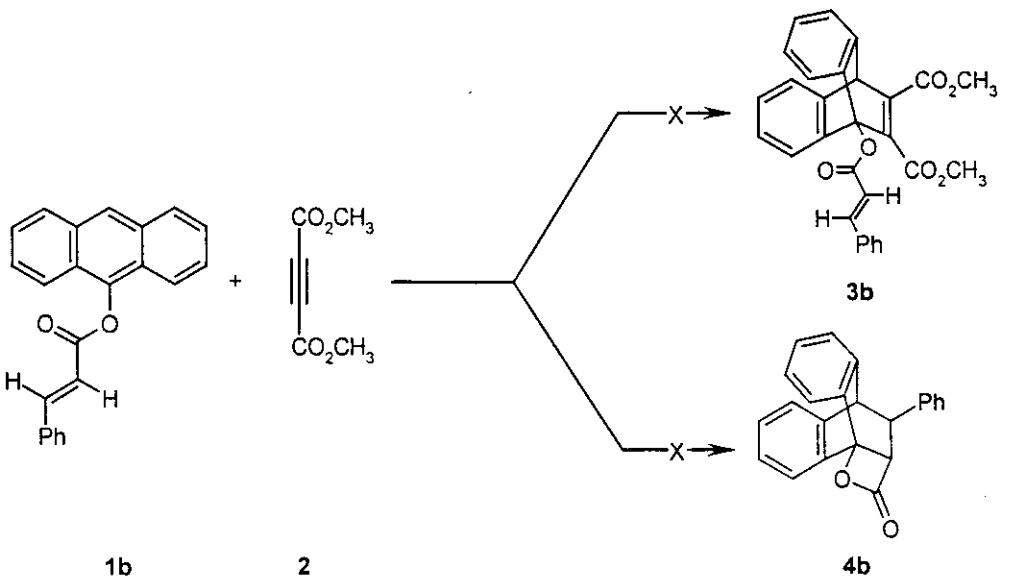
Scheme 5.1



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

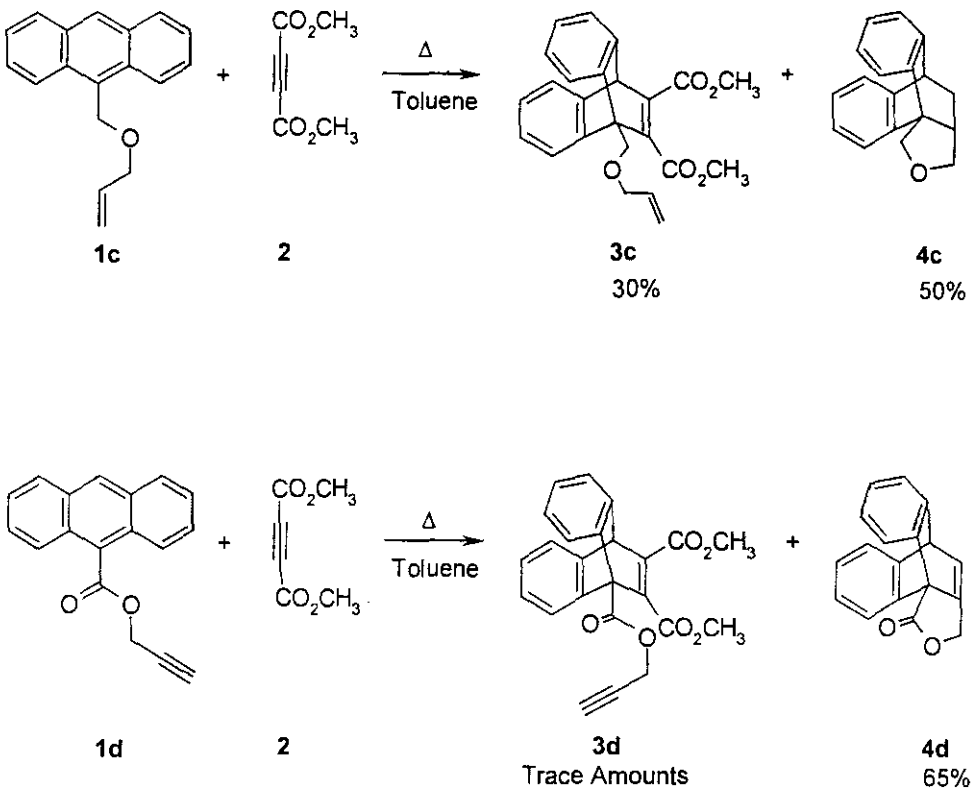
Compound **1b** did not give either Diels-Alder adduct **3b** or IMDA adduct **4b** (Scheme 5.2) under the various conditions employed by us. On neat thermolysis with DMAD, at 200 ^{0}C, the unchanged **1b** was obtained. The neat thermolysis either in the presence or absence of DMAD at 250 ^{0}C resulted in complete decomposition of the starting material.

Scheme 5.2



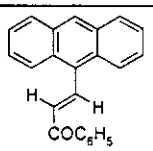
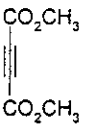
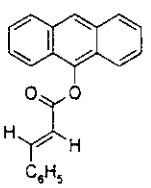
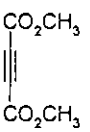
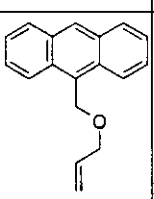
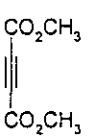
The system with remote double bond **1c** and the system with a remote triple bond **1d** underwent intermolecular Diels-Alder as well as IMDA reactions, with the latter predominating at higher temperatures. Interestingly, these IMDA adducts were formed in low yields along with the intermolecular Diels-Alder adducts when refluxed in toluene. On repeating these reactions in low temperatures, neither Diels-Alder adducts nor IMDA adducts were formed. At high temperatures, IMDA adduct formation was favoured. In the case of compound **1c** the Diels-Alder adduct **3c** was formed in 30% yield when refluxed in toluene, while in the case of compound **1d** the Diels-Alder adduct **3d** was formed in trace amounts (<1%) under analogous conditions (Scheme 5.3).

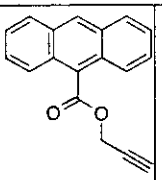
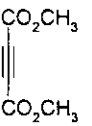
Scheme 5.3



Comparison of the reactions of **1c** and **1d** provides some interesting observations. While the Diels Alder adduct **3c** was formed in 30% yield, **3d** was formed in <1% yield. It appears that **1d** undergoes IMDA reaction much more efficiently than **1c**. This is not entirely surprising since the intramolecular acetylenic dienophile in the case of **1d** is more activated and thus facilitates IMDA reaction. When **1d** refluxed in xylene in the absence of DMAD, IMDA adduct was formed in 85% yields. We carried out the reaction in different conditions and the results obtained are tabulated in Table 5.1.

Table 5.1

Diene	Dienophile	Molar Ratio of Diene to Dienophile	Reaction Conditions	Yield	
				Diels-Alder Adduct	IMDA Adduct
 **1a**	 **2**	2:3	Benzene	No	No
		2:3	Toluene	15%	No
		2:3	Xylene	64%	No
		1:1	Xylene	60%	No
		1:0	Xylene	No	No
		2:3	Lewis Acid Catalysed	No	No
		2:3	Neat Thermolysis at		
			200 ^{0}C	45% With Partial Decompostion of **1a**	No
 **1b**	 **2**	2:3	Benzene	No	No
		2:3	Toluene	No	No
		2:3	Xylene	No	No
		2:3	*o*-Dichloro-benzene	No	No
		2:3	Lewis Acid Catalysed	No	No
			Neat Thermolysis at		
		2:3	200 ^{0}C	No	No
		2:3	250 ^{0}C	Complete Decomposition of **1b**	No
 **1c**	 **2**	2:3	Benzene	No	No
		2:3	Toluene	30%	50%
		2:3	Xylene	No	68%
			Neat Thermolysis at		
		2:3	200 ^{0}C	No	65%
		2:3	250 ^{0}C	Complete Decomposition of **1c**.	No

 1d	 2	2:3	Toluene	<1%	65%
		1:1	Toluene	<1%	63%
		2:3	Xylene	No	78%
		1:1	Xylene	No	74%
		1:0	Xylene	No	85%
			Neat Thermolysis at		
		2:3	200 °C	No	55%
		2:3	250 °C	Complete Decomposition of **1d**	No

The Diels-Alder adduct **3c** and IMDA adduct **4c** were characterised on the basis of spectral and analytical data including HMQC and COSY.[24]

From these experiments, we surmise that there is no IMDA reaction, if the π system is vinyl as in the case of **1a**. Neither Diels-Alder nor IMDA adducts were formed in the case of **1b**. But if the π-system is remote as in **1c,d**, the substrates preferentially undergo IMDA reaction over intermolecular Diels-Alder reaction. Even then, by controlling the reaction conditions the yield of the Diels-Alder adducts can be improved.

5.4. Experimental

5.4.1. General Procedures: All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica or aluminium sheets coated with silica (MERCK) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry packed silica (Qualigens 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using Shimadzu-DR-8001 series FTIR spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 400 and 500 MHz on a Brucker FT-NMR spectrometer or GE NMR OMEGA spectrometer with tetramethylsilane as internal standard. Elemental analysis was

performed at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow.

5.4.2. Starting materials: Dimethyl acetylenedicarboxylate (DMAD) was purchased from Sigma-Aldrich as used as received.

5.4.3. Optimization of Intramolecular and Intermolecular Diels-Alder reactions of 9-Substituted Anthracenes.

5.4.3.1. Reactions of Compound 1a

Compound **1a** (1.54 g, 5 mmol) was dissolved in minimum quantity of dry xylene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture of dichloromethane and hexane (1:4) gave unchanged **1a** (0.56 g, 31%, mixture mp 120-124 ^{0}C).

Further elution with a mixture of dichloromethane and hexane (1:1) gave the adduct **3a** (1.15 g, 64%, mixture mp 166-168 ^{0}C). The solid product was purified by recrystallisation from a mixture of dichloromethane and hexane (2:1).

In a repeat run, **1a** (1.54 g, 5 mmol) was dissolved in minimum quantity of dry benzene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1a** (1.22 g, 79%, 120-124 ^{0}C).

In a repeat run, **1a** (1.54 g, 5 mmol) was dissolved in minimum quantity of dry toluene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1a** (0.82 g, 62%, 120-124 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **3a** (0.25 g, 15%, mixture mp 166-168 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

In a repeat run, to a mixture of **1a** (1.54 g, 5 mmol) and anhydrous $AlCl_3$ (0.67 g, 5 mmol) in dry dichloromethane (10 mL) DMAD (1.06 g, 7.5 mmol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred for 6 h and poured over crushed ice, acidified with 50 mL hydrochloric acid and extracted with dichloromethane. Unchanged **1a** was obtained in 80% yield (mixture mp 120-124 ^{0}C).

Compound **1a** (0.31 g, 1 mmol) was dissolved in minimum quantity of dry xylene, DMAD (0.14 g, 1 mmol) was added and the mixture was refluxed for 6 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture of dichloromethane and hexane (1:4) gave unchanged **1a** (90 mg, 25%, mixture mp 120-124 ^{0}C).

Further elution with a mixture of dichloromethane and hexane (1:1) gave the adduct **3a** (0.21 g, 60%, mixture mp 166-168 ^{0}C). The solid product was purified by recrystallisation from a mixture of dichloromethane and hexane (2:1).

In yet another run, compound **1a** (100 mg, 0.3 mmol) was dissolved in minimum quantity of dry xylene and was refluxed for 12 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture of dichloromethane and hexane (1:4) gave unchanged **1a** (0.25 g, 25%, mixture mp 120-124 ^{0}C).

In a repeat run, a mixture of **1a** (100 mg, 0.3 mmol) and DMAD (70 mg, 0.5 mmol) was heated in a sealed tube at 200 ^{0}C. The solid residue was extracted with dichloromethane which was chromatographed over silica. TLC showed formation of **3a** along with partial decomposition of **1a**. Elution of the column with a mixture of dichloromethane and hexane (1:1) gave the adduct **3a** (22 mg, 45%, mixture mp 166-168 ^{0}C). The solid product was purified by recrystallisation from a mixture of dichloromethane and hexane (2:1).

5.4.3.2. Reactions of Compound 1b

Compound **1b** (1.62 g, 5 mmol) was dissolved in minimum quantity of dry xylene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1b** (1.04 g, 64%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, **1b** (1.62 g, 5 mmol) was dissolved in minimum quantity of dry benzene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1b** (1.22 g, 75%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, **1b** (1.62 g, 5 mmol) was dissolved in minimum quantity of dry toluene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1b** (1.10 g, 68%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, **1b** (1.62 g, 5 mmol) was dissolved in minimum quantity of dry *o*-dichlorobenzene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1b** (0.94 g, 58%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, to a mixture of **1b** (1.62 g, 5 mmol) and anhydrous $AlCl_3$ (0.67 g, 5 mmol) in dry dichloromethane (10 mL) was added DMAD (1.06 g, 7.5 mmol) in small portions at 0 ^{0}C. The reaction mixture was stirred for 6 h and poured over crushed ice, acidified with 50 mL hydrochloric acid and extracted

with dichloromethane. Unchanged **1b** was obtained in 80% yield (mixture mp 188-190 ^{0}C) as the only isolable material.

5.4.3.2.1. Neat Heating of 1b in the Presence of DMAD. A mixture of **1b** (100 mg, 0.3 mmol) and DMAD (70 mg, 0.5 mmol) was heated in a sealed tube at 200 ^{0}C. The solid residue was extracted with dichloromethane and was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1b** (55 mg, 55%, mixture mp 188-190 ^{0}C) as the only isolable material.

In a repeat run, a mixture of **1b** (100 mg, 0.3 mmol) and DMAD (70 mg, 0.5 mmol) was heated in a sealed tube at 250 ^{0}C. The solid residue was extracted with dichloromethane. TLC showed complete decomposition of the starting material.

5.4.3.3. Reactions of Compound 1c

A sample of **1c** (1.24 g, 5 mmol) was dissolved in minimum quantity of dry toluene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1c** in trace amounts (mixture mp 50-55 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave the adduct **3c** (0.36 g, 30%, mp 72 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **4c** (0.61 g, 50%, mp 94 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

In a repeat run, **1c** (1.24 g, 5 mmol) was dissolved in minimum quantity of dry benzene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed

for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1c** (1.06 g, 82%, 50-55 ^{0}C).

In a repeat run, **1c** (1.24 g, 5 mmol) was dissolved in minimum quantity of dry xylene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 12 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1c** (0.42 g, 21%, 50-55 ^{0}C).

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **4c** (1.37 g, 68%, mp 94 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

5.4.3.3.1. Neat Heating of 1c in the Presence of DMAD. A mixture of **1c** (100 mg, 0.4 mmol) and DMAD (90 mg, 0.6 mmol) was heated in a sealed tube at 200 ^{0}C. The solid residue was extracted with dichloromethane and was chromatographed over silica. Elution of the column with a mixture (1:1) of dichloromethane and hexane gave **4c** (65 mg, 65%, mixture mp 72 ^{0}C) as the only isolable material.

In a repeat run, a mixture of **1c** (100 mg, 0.4 mmol) and DMAD (90 mg, 0.6 mmol) was heated in a sealed tube at 250 ^{0}C. The solid residue was extracted with dichloromethane. TLC showed complete decomposition of the starting material.

5.4.3.4. Reactions of Compound 1d

A sample of **1d** (1.30 g, 5 mmol) was dissolved in minimum quantity of dry toluene, DMAD (1.06 g, 7.5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture of dichloromethane and hexane (1:4) gave unchanged **1d** in trace amounts (mixture mp 90 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave the adduct **3d** (12 mg, <1%, mp decomposed at 122-124 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **4d** (0.84 g, 65%, mp 258-262 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

In a repeat run, **1d** (1.30 g, 5 mmol) was dissolved in minimum quantity of dry toluene, DMAD (0.71 g, 5 mmol) was added and the mixture was refluxed for 10 h. Removal of the solvent gave a solid residue, which was chromatographed over silica. Elution of the column with a mixture (1:4) of dichloromethane and hexane gave unchanged **1d** (10 mg, 2%, 90 ^{0}C).

Further elution with a mixture (3:7) of dichloromethane and hexane gave the adduct **3d** (7 mg, <1%, mp decomposed at 122-124 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

Further elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **4d** (0.57 g, 63%, mp 258-262 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

In a repeat run, **1d** (100 mg, 0.4 mmol) was dissolved in minimum quantity of dry xylene, DMAD (90 mg, 0.6 mmol) was added and the mixture was refluxed for 48 h. Removal of the solvent gave a solid residue, which was chromatographed over silica.

Elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **4d** (0.11 g, 78%, mp 258-262 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane.

In a repeat run, **1d** (100 mg, 0.4 mmol) was dissolved in minimum quantity of dry xylene, DMAD (56 mg, 0.4 mmol) was added and was refluxed for 48 h. Removal of the solvent gave a solid residue, which was chromatographed over silica.

Elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **4d** (74 mg, 74%, mp 258-262 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane

In a repeat run, **1d** (100 mg, 0.4 mmol) was dissolved in minimum quantity of dry xylene and was refluxed for 48 h. Removal of the solvent gave a solid residue, which was chromatographed over silica.

Elution with a mixture (1:1) of dichloromethane and hexane gave the adduct **4d** (85 mg, 85%, mp 258-262 ^{0}C). The solid product was purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane

5.4.3.3.1. Neat Heating of 1d in the Presence of DMAD. A mixture of **1d** (100 mg, 0.4 mmol) and DMAD (90 mg, 0.6 mmol) was heated in a sealed tube at 200 ^{0}C. The solid residue was extracted with dichloromethane and was chromatographed over silica. Elution of the column with a mixture (1:1) of dichloromethane and hexane gave unchanged **3d** (55 mg, 55%, mixture mp decomposed at 122-124 ^{0}C) as the only isolable material.

In a repeat run, a mixture of **1d** (100 mg, 0.4 mmol) and DMAD (90 mg, 0.6 mmol) was heated in a sealed tube at 250 ^{0}C. The solid residue was extracted with dichloromethane. TLC showed complete decomposition of the starting material.

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24. For Spectral and Analytical data of **3a-d** and **4c-d**, see Chapter **4** of this thesis.

PRELIMINARY PHOTOCHEMICAL STUDIES

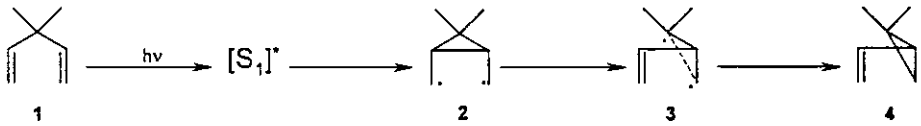
6.1. Abstract

This chapter deals with the preliminary photochemical investigations on controlling the selectivity of one of the synthetically useful photochemical reactions, viz., di-π-methane rearrangement through intramolecular quenching of excited triplet states of dibenzobarrelenes. Moreover, the photochemistry of compound 33 shows that electronic factors is one of the aspects that govern the regioselectivity of di-π-methane rearrangement of 9,10-ethenoanthracenes.

6.2. Introduction

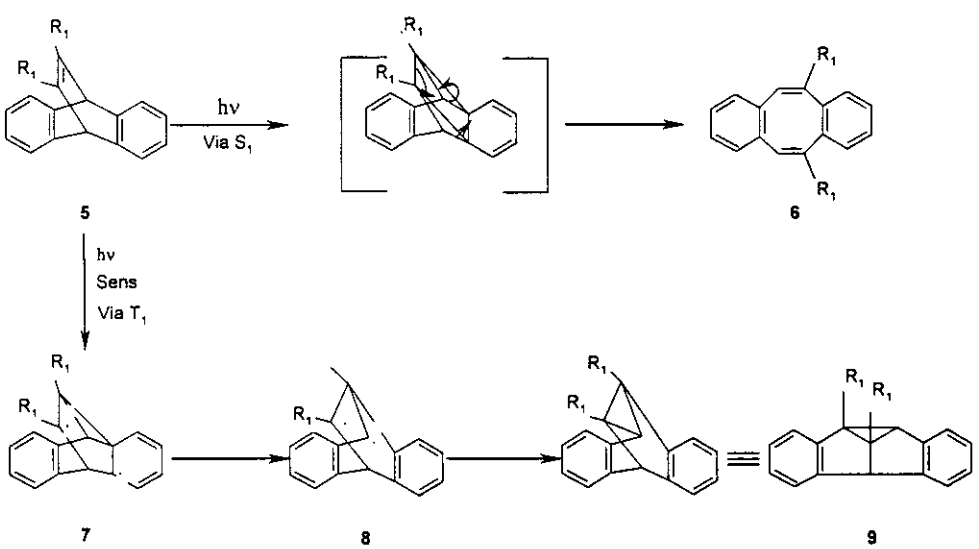
The search for general photochemical reactions and making them synthetically efficient and selective augments to the progress in organic photochemistry as more often than not, the photoproducts are not available by alternative routes. One of the major photochemical transformations that has been found synthetically useful is the di-π-methane rearrangement[1-8] for the synthesis of vinyl cyclopropanes and its heteroatom analogues such as oxa[9-14] and aza-di-π-methane[15-25] rearrangements. Di-π-methane rearrangement is a very general and well-studied photorearrangement. Zimmerman discovered di-π-methane rearrangement in 1967 when the photolysis of reactants having two vinyl moieties bonded to an sp^3-hybridised carbon led to the formation of vinylcyclopropanes.[26] This process, along with the mechanism suggested by Zimmerman, is depicted in Scheme 6.1 for the simplest di-π-methane reactant, 3,3-dimethyl-1, 4-pentadiene (**1**). A variation of this mechanism, proposed by Paquette[27,28], involves direct formation of biradical **3** from the reactant excited state.

Scheme 6.1



Barrelene and its derivative are known to undergo interesting photochemical transformations.[29] The major photochemical reaction pathway exhibited by dibenzobarrelenes (**5**) is presented in Scheme 6.2. On direct irradiation, dibenzobarrelene gives cyclooctatetraene derivative (**6**) by an electrocyclic [2π+2π] addition followed by a retrocycloaddition. On sensitized irradiation, **5** is excited to its triplet state, a 1, 5-biradical (**7**) is formed, which rearranges to give the 1,3-biradical (**8**), and finally the vinylcyclopropane analogue, viz., dibenzosemibullvalene (**9**). Based on extensive mechanistic investigations, Zimmermann established that for simple systems such as **1**, di-π-methane rearrangement is singlet mediated, whereas for cyclic systems such as **5**, the reaction is triplet mediated.[30]

Scheme 6.2



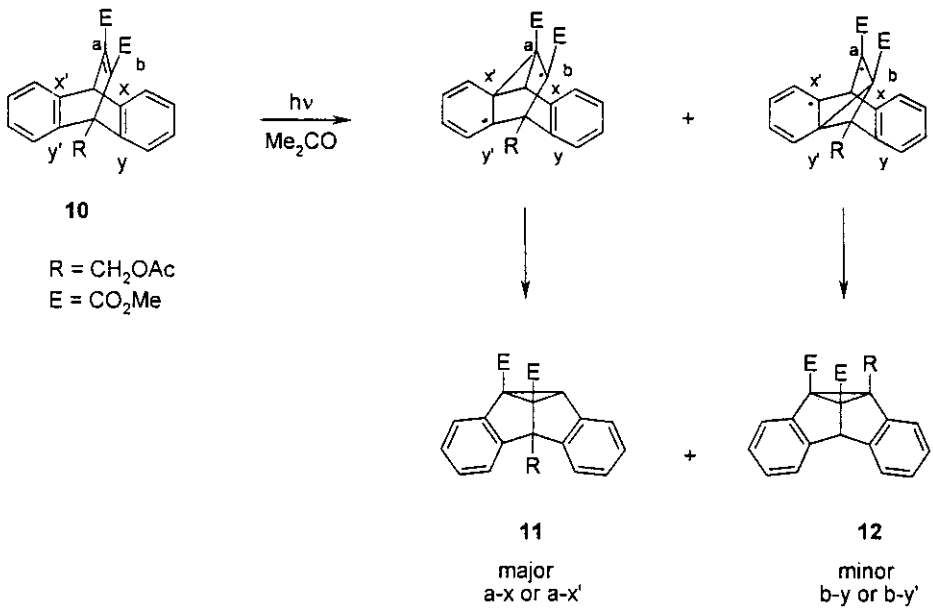
Thus, barrelenes in principle can give rise to different products depending on the irradiation mode, viz., direct or sensitised. However, in most cases, the

singlet and triplet mediated photoprocesses compete with each other giving rise to a mixture of products. We propose to improve the selectivity of photochemical reaction of barrelenes by controlling the competing pathways through intramolecular quenching. In principle, selective quenching of either the singlet or triplet excited state should lead to a single product and thereby improving the synthetic utility of the observed photochemical process. The natural question that arises in this context is: Is it possible to selectively and efficiently quench the excited states of barrelenes? While an appropriate external triplet quencher can quench the triplet excited state efficiently, the short-lived singlets are elusive and hence inefficiently quenched by a bimolecular process. We proposed to circumvent this problem by incorporating "inbuilt" quenchers whereby intramolecular quenching can be achieved. This is based on the premise that intramolecular quenching is more efficient than intermolecular quenching.

It is well known that olefins are efficient triplet quenchers. The auxiliary units are intended to quench triplet excited state by energy transfer. Intramolecular quenching of triplet excited state by a diene/diyne component is an attractive idea, but we recognised that introduction of such units is not synthetically facile, but feasible. However, suitable olefins possessing sufficiently low triplet energy can also act as efficient triplet quenchers. Based on these arguments, we selected olefin units as potential triplet excited state quenchers. We propose that a dibenzobarrelene having olefin unit of sufficiently low E_T is unlikely to undergo triplet-mediated transformation to yield the corresponding semibullvalene.

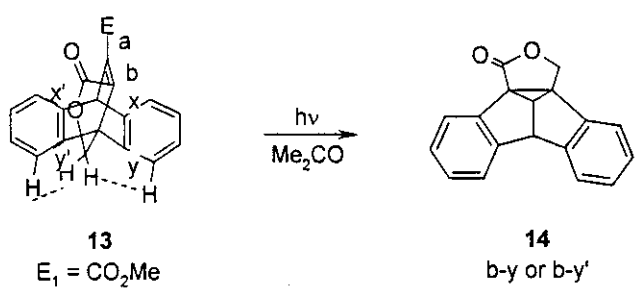
Additionally, di-π-methane rearrangement shows remarkable regioselectivity. As depicted in Scheme 6.3, di-π-methane rearrangement of 9-ethenylsubstituted 9,10-ethenoanthracenes can give two regioisomeric semibullvalenes. Thus in the case of 9,10-ethenoanthracene **10**, initial a-x or a-x' benzo-vinyl bridging will lead to regioisomer **11** whereas initial b-y or b-y' benzo-vinyl bridging affords **12**.[31] A few of the 9,10-ethenoanthracene systems selected by us offer the additional opportunity of investigating the regioselectivity of di-π-methane rearrangement as well.

Scheme 6.3



In compound **13,** the rotational freedom of the bridgehead methylene group is restricted, hence fixed non-bonding interaction between the methylene hydrogens and the aromatic hydrogen atoms is present. So the predominant reaction pathway should be the one that most effectively alleviates the unfavourable H...H interactions. Thus lactone **13** undergoes di-π-methane rearrangement to form the regioisomer **14**, arriving through initial b-y or b-y' benzo-vinyl bridging (Scheme 6.4). The regioselectivity, as expected, is governed by relief of the non-bonded repulsive interactions between the methylene hydrogen atoms of the lactone ring and the adjacent aromatic hydrogen atoms.[32]

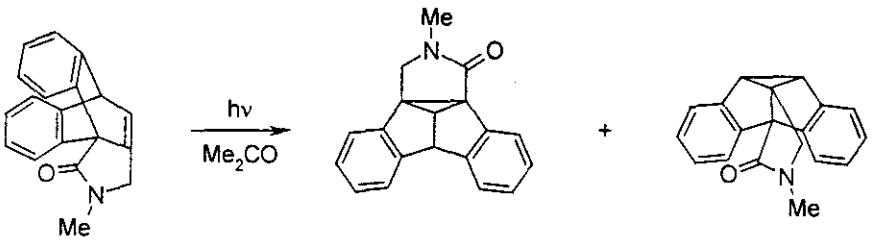
Scheme 6.4



2-Methyl-3,5-dihydro-5,9b-*o*-benzenobenz[e]isoindol-1-(*2H*)-one (**15**) on sensitized irradiation in acetone (Scheme 6.5) gave a 68:32 mixture of 2-methyl-

1*H*,8*H*-3a,8,12b-methenodibenzo[3,4:6,7]cyclo-hepta[1,2-c]pyrrol-1-one (**16**) and 10-methyl-4b,8d-(methaniminomethano)dibenzo[a,f]cyclopropa[cd]pentalen-11-one (**17**).[33]

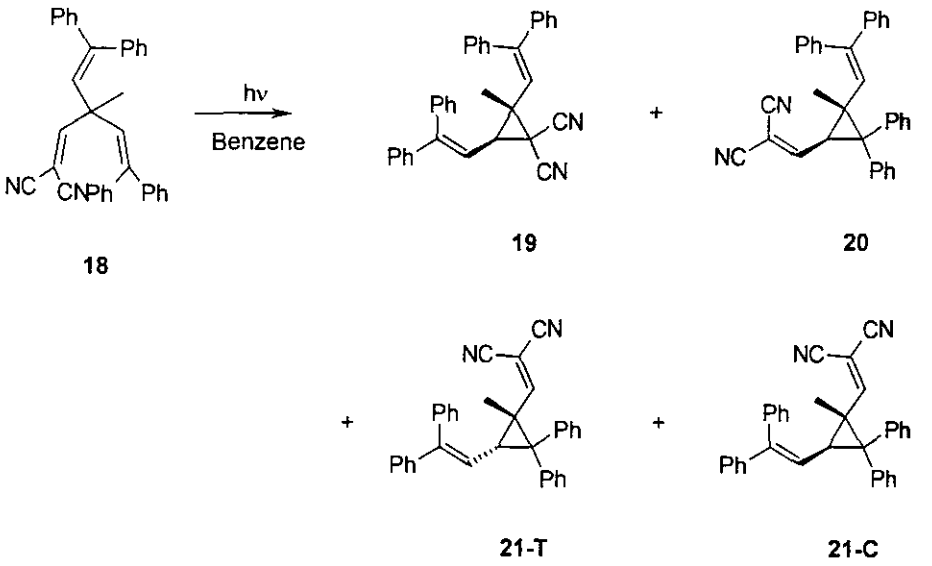
Scheme 6.5



15 **16** (major) **17** (minor)

As a logical extension of di-π-methane rearrangement, the possibility of tri-π-methane rearrangement was contemplated. Zimmerman *et al.*[34,35] showed that a tri-π-methane system such as**18** gave cyclopropane derivatives **19, 20, 21-T,** and **21-C**, on photolysis in solution through di-π-methane rearrangement

Scheme 6.6

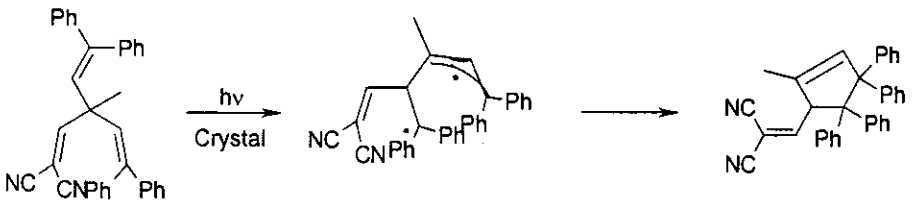


18 **19** **20** **21-T** **21-C**

However, upon irradiation in the solid state **18** gave the cyclopentene derivative **22**. The mechanism as suggested and christened as tri-π-methane

rearrangement by Zimmerman[34] for the formation of cyclopentene derivative **22** is given in Scheme 6.7.

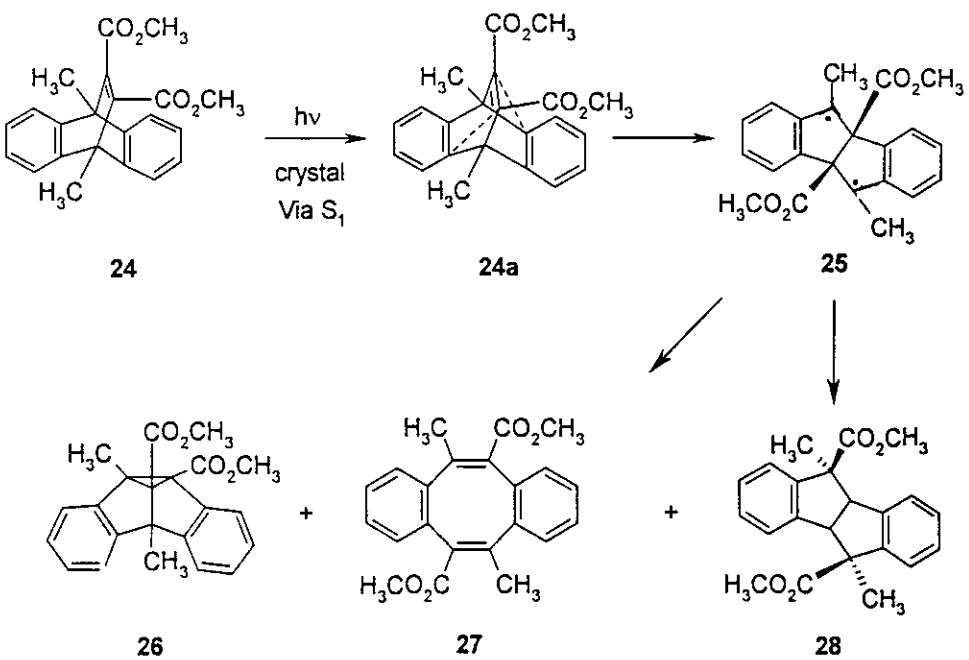
Scheme 6.7



18 **23** **22**

Scheffer *et al.*[36] have reported that photolysis of crystals of dimethyl-9,10-dimethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**24**) afforded the normal di-π-methane rearrangement product **26** along with two new products arising through a novel reaction pathway as indicated in Scheme 6.8. The origin of biradical **25** is most likely from the singlet excited state and its formation involves, at least formally, a type of tri-π-methane interaction of both aromatic rings with the etheno bridge. It appears that the mechanism by which diester **28** was formed involves sequential carbomethoxy group migration in the bis-benzylic biradical **25**.[36]

Scheme 6.8



24 **24a** **25**

26 **27** **28**

Scheffer[31,32] has shown that in 9,10-ethenoanthracene derivatives the steric crowding and radical stability work against one another and the regioselectivity of the di-π-methane rearrangement is mainly governed by the relief of steric crowding in sterically crowded compounds (Schemes 6.3 and 6.4). On the contrary, the photolysis of compound **15** (Scheme 6.5) as reported by Ciganek[33], showed regioselectivity which could be due to the electronic stabilisation of the radicals in the excited state. In this context, we have chosen a 9,10-ehtenoanthracene derivative (**33**) in which there are no induced steric factors and can show regioselectivity as in the case of a sterically unbiased molecule.

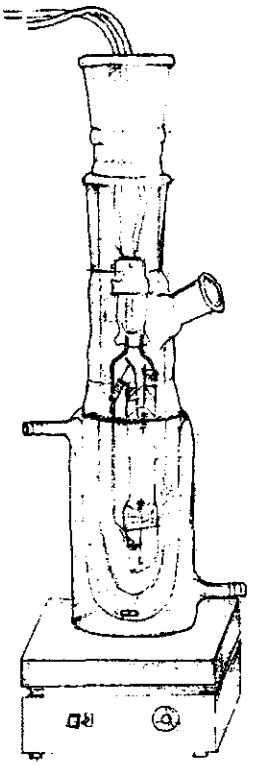
We propose to carry out the direct as well as sensitized irradiation of a few dibenzobarrelenes we have synthesized to assess the effect of the fourth π-moiety on the photochemical reactions of dibenzobarrlenes. The substrates we examined include dimethyl-9-(1-anthrylethylene)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **(29a)**, dimethyl-9-(1-anthryl-2-benzoylethylene)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **(29b)**, dimethyl-9-(1-anthryl-2-carboxybiphenylethylene)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **(29c)** and dimethyl-9-(1-anthryl-2-phenylethyl-ene)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **(29d)**.

Additionally, in the present study we propose to perform a few experiments that should corroborate the hypothesis that electronic factors control the regioselectivity in the di-π-methane rearrangement of 9,10-ethenoanthracene derivatives in sterically unbiased compounds of this genre. The substrate selected by us include 3,5-dihydro-59b-*o*-benzenaphtho-[1,2-c]furan-1-one (**33**).

Results and Discussion

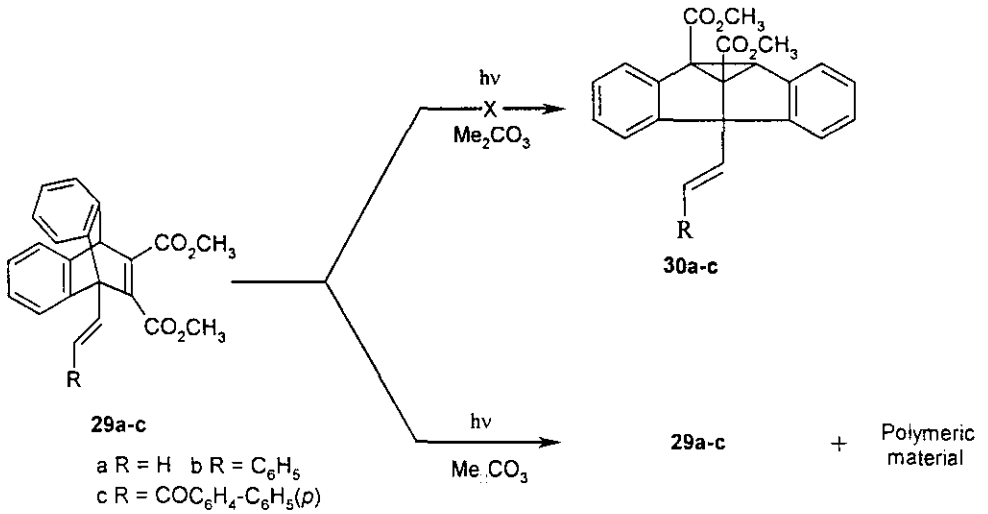
The photochemical reactions were carried out in a tailor-made photochemical reactor designed and fabricated by us (Figure 6.1).

Figure 6.1



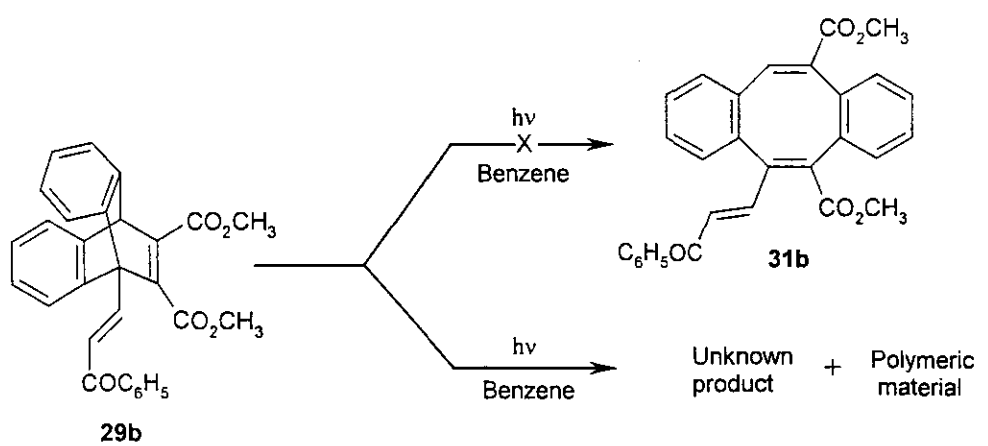
The photolysis of **29a-c** in acetone under nitrogen atmosphere, gave polymeric material along with varying amounts of unchanged reactant. As expected, the corresponding semibullvalenes were not formed through di-π-methane rearrangement. It is known that the bicyclic compounds containing alkene moieties undergo polymerisation on photolysis[14] (Scheme 6.8). It appears that the olefinic appendage might have functioned as an internal quencher, quenching the triplet state of dibenzobarrelenes, thus controlling the formation of expected semibullvalenes.

Scheme 6.9



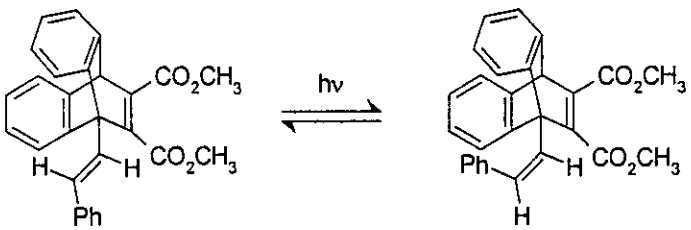
In continuation, we carried out the direct irradiation of a representative substrate such as **29b** to examine whether it will undergo singlet-mediated transformation leading to the formation of dibenzocyclooctatetraene **31b**. Direct irradiation of **29b** in benzene did not lead to the formation of **31b**, instead an unidentified compound was formed in trace amounts along with polymeric material. This result is not entirely surprising since the presence of a carbonyl component in **29b** is likely to facilitate efficient intersystem crossing of the initially formed singlet excited state to the triplet excited manifold. Thus, **29b** is unlikely to yield singlet-mediated photoproducts (Scheme 6.10).

Scheme 6.10



However, the styrene-appended dibenzobarelene (**29d**), underwent facile photoisomerisation even on brief exposure to diffuse light to give the *Z*-isomer **32d** (Scheme 6.11). Though we were able to isolate and store **29d** as a solid in the pure form (as evidenced by TLC analysis), it underwent fast isomerisation in solution. Based on this, it may be inferred that intramolecular energy transfer from a barrelene chromophore to an appended styrene moiety is a comprehensible possibility. The E_T values reported for similar dibenzobarrelenes and styrene suggests that such energy transfer, indeed, is feasible.

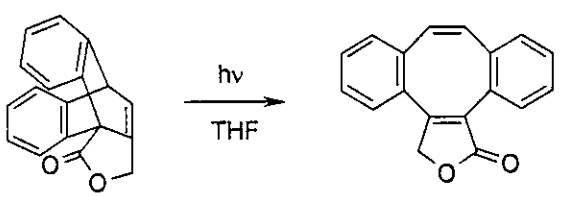
Scheme 6.11



29d **32d**

In continuation, we examined the photochemistry of a tricyclic system such as **33**. Direct irradiation of **33** leads to the formation of the corresponding cyclooctatetraene (**34**) (Scheme 6.12).[33]

Scheme 6.12

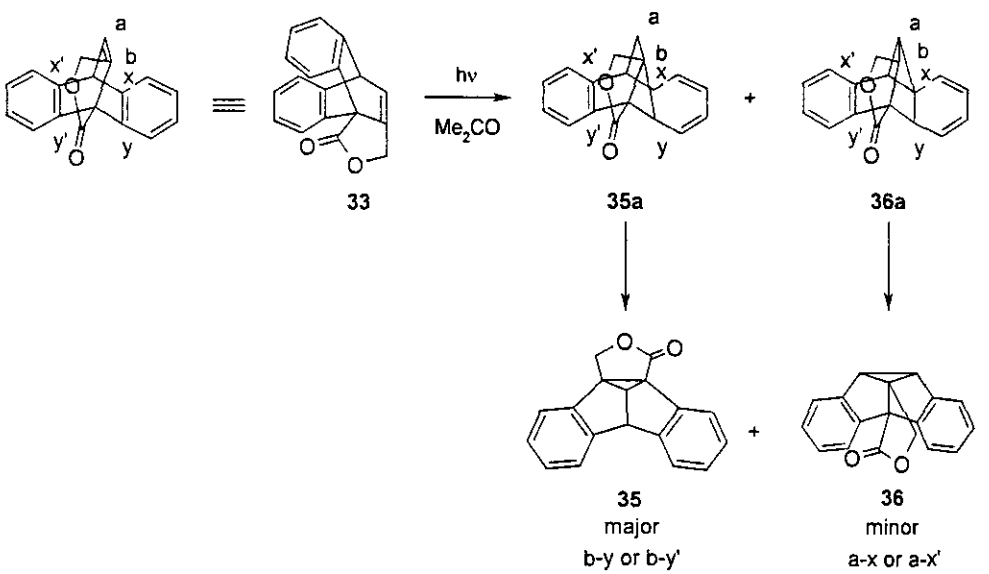


33 **34**

Sensitized irradiation of **33** in acetone gave a 70:30 mixture of the regioisomers **35** and **36** (Scheme 6.13). The observed regioselectivity in this case may be ascribed to electronic factors. There is general agreement that 1,3

diradicals such as **8** (Scheme 6.2) are key intermediates in the di-π-methane rearrangements of 9,10-ethenoanthracene derivatives.[1,38-41] These maybe visualized as being formed through the intermediacy of cyclopropyldicarbinyl diradicals such as **7** (Scheme 6.2), arising through either a benzo-vinyl bridging, [1,38] or by direct 1,2-migration of the aryl group to the vinyl carbon.[39] Depending on the nature of initial benzo-vinyl bridging, **33** can lead to the formation of two biradical intermediates **35a** and **36a**. Several factors must be considered while predicting the major reaction pathway followed by system like **33**. Scheffer has established that steric factors play an important role in deciding regioselectivity by controlling the initial benzo-vinyl bridging[31,32]. However, in the case of **33**, steric factors are less important and the observed regioselectivity is dictated by electronic factors. The lactone carbonyl group in **33** is fixed in an orientation that is favourable for resonance stabilisation of an adjacent radical.[31] This might favour an initial b-y or b-y' bridging as the resulting the 1,3-biradical might be electronically stabilised by the lactone carbonyl. A second factor to be considered concerns the electronic nature of the bridgehead substituent. Previous studies on the di-π-methane rearrangement of a series of 9-substituted-9,10-ethenoanthracene derivatives by Iwamura *et al.*[42], Paddick *et al.*[43] and George *et al.*[44,45] have established that there is a rough correlation between regioselectivity and electronegativity of the bridgehead substituent. In the present instance, compound **33** appears to conform to this reactivity profile.

Scheme 6.13



A deoxygenated solution of **33** in acetone under nitrogen atmosphere was irradiated for 10 h. TLC showed the formation of two products **35** and **36** along with unchanged **33**. The structures of two regioisomers were arrived at on the basis of spectral data and literature precedence.[33] Particularly, informative were the ^{1}H NMR spectra of the isomeric lactones. Thus the ^{1}H NMR spectrum of **35** showed doublets at δ 3.9, 4.6 and 4.7. The multiplet at δ 7.0-7.6 was due to the aromatic protons. The ^{1}H-NMR spectrum of **36** showed a two, two proton singlets at δ 3.2 and 3.4 and the aromatic protons in the region δ 7.0-7.6.

In conclusion, the preliminary photochemical investigation carried out by us on olefin-appended dibenzobarrelenes such as **29a-c** has indicated that selective quenching of triplet excited states of barrelenes might be possible. However, polymerisation of the starting material remains a major hurdle in realising the true potential of this remarkable observation. Further investigations employing an efficient photochemical reactor are required to delineate conditions under which the polymerisation process can be arrested. Besides, the photochemical reaction of **33** substantiates the hypothesis that electronic factors control the regioselectivity in the di-π-methane rearrangement of 9,10-ethenoanthracene derivatives in sterically unbiased compounds of this genus.

6.3. Experimental

6.3.1. General Procedures. All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica or aluminium sheets coated with silica (MERCK) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry packed silica (Qualigens 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using Shimadzu-DR-8001 series FTIR spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at

400 and 500 MHz on a Bruker FT-NMR spectrometer or GE NMR OMEGA spectrometer with tetramethylsilane s internal standard. Chemical shifts are reported as parts per million (ppm) downfield of tetramethylsilane (TMS). Elemental analysis was performed at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

6.3.2. Preliminary Photochemical Studies

6.3.2.1. Irradiation of 29a: A deoxygenated solution of **29a** (0.31 g, 0.9 mmol) in acetone (300 mL) was irradiated under nitrogen atmosphere using the output from a 125-W high-pressure mercury lamp for 6 h. The progress of the reaction was monitored by TLC. Acetone was removed under reduced pressure. The residue was chromatographed on silica. Elution with a mixture (1:1) of dichloromethane and hexane gave unchanged **29a** (20%, mp 166-168 ^{0}C). Further elution with a mixture (1:9) of methanol and hexane gave a polymeric material.

6.3.2.2. Irradiation of 29b: A deoxygenated solution of **29b** (0.41 g, 0.9 mmol) in acetone (300 mL) was irradiated under nitrogen atmosphere using the output from a 125-W high-pressure mercury lamp for 6 h. The progress of the reaction was monitored by TLC. Acetone was removed under reduced pressure. The residue was chromatographed on silica. Elution with a mixture (1:1) of dichloromethane and hexane gave unchaged **24b** (20%, mp 94 ^{0}C). Further elution with a mixture (1:9) of methanol and hexane gave a polymeric material.

6.3.2.3. Irradiation of 29c: A deoxygenated solution of **29c** (0.47 g, 0.9 mmol) in acetone (300 mL) was irradiated under nitrogen atmosphere using the output from a 125-W high-pressure mercury lamp for 6 h. The progress of the reaction was monitored by TLC. Acetone was removed under reduced pressure. The residue was chromatographed on silica. Elution with a mixture (1:1) of dichloromethane and hexane gave unchanged **29c** (20%, mp 180-182 ^{0}C). Further

elution with a mixture (9:1) of methanol and hexane (1:9) gave a polymeric material.

6.3.2.4. Irradiation of 29b: A deoxygenated solution of **29b** (0.41 g, 0.9 mmol) in benzene (300 mL) was irradiated under nitrogen atmosphere using the output from a 125-W high-pressure mercury lamp for 10 h. The progress of the reaction was monitored by TLC. Solvent was removed under reduced pressure. The residue was chromatographed on silica. Elution with dichloromethane-hexane (1:4) mixture gave an unidentified compound (**A**) in trace amounts.

Compound A: mp 162 ^{0}C; ^{1}H NMR ($CDCl_3$) δ 7.0-7.6 (m, aromatic).

Further elution with a mixture (1:1) of dichloromethane and hexane gave unchanged **29c** (10 mg, 20%, mp 166-168 ^{0}C). Further elution with a mixture (1:9) of methanol and hexane gave a polymeric material.

6.3.2.5. Isomerization of 29d.[46] Upon brief exposure to diffuse laboratory light, compound **29d** underwent isomerisation to give **32d**.

6.3.2.6. Direct Irradiation of 33.[33] A solution of of **33** (1.06 g, 4.3 mmol) in of THF (200 mL) was irradiated in a quartz vessel with a Hanovia 450-W medium pressure lamp for 3 h. Removal of the solvent and chromatography of the residue on silica using benzene as the elutant gave a fraction containing some unchanged starting material. Elution with dichloromethane and crystallization from *iso*-propanol gave 0.31 g, (29%) 0f **34**, mp 162 ^{0}C.[33]

6.3.2.7. Sensitised Irradiation of 33. A deoxygenated (74 mg, 0.3 mmol) solution of **33** in acetone (100 mL) under nitrogen atmosphere was irradiated using the output from a 125-W high-pressure mercury lamp for 4 h. The progress of the reaction was monitored by TLC. The TLC showed formation of two products along with unchanged reactant. The irradiation was continued for six more hours. Acetone was removed under reduced pressure. The residue was chromatographed on silica. Elution with a mixture (1:1) of dichloromethane and

hexane gave unchanged **33** (10 mg, 20%, mp 260 ^{0}C). Further elution with a mixture (2:3) of dichloromethane and hexane gave a 70:30 mixture of semibullvalenes. **35** and **36**. The two components were separated by repetitive preparative TLC to yield analytical quality material in very small amounts. The solvent system used was 1:1 mixture of dichloromethane-hexane.

Compound 35: ^{1}H NMR ($CDCl_3$) δ 3.9 (1H, d), 4.6 (2H, d), 4.7 (1H, d), 7.0-7.6 (8H, m, aromatic).

Compound 36: ^{1}H NMR ($CDCl_3$) δ 3.2 (2H, s), 3.4 (2H, s), 7.0-7.6 (8H, m, aromatic).

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46. For details on the isomerisation of **29d** to **32d**, see Chapter **4** of this thesis.

CHAPTER 7

SYNTHESIS AND DIELS–ALDER REACTIONS OF 9-(*N,N*-DIALKYLAMINO)METHYL-9,10-DIHYDRO-9,10-ETHENOANTHRACENES

7.1. Abstract

This chapter describes the preparation of a few 9-(N,N-dialkylamino)methylanthracenes which are potential precursors for 9,10-ethenoanthracenes containing appended amine functionalities intended to serve as potential intramolecular quenchers for the barrelene singlet excited states.

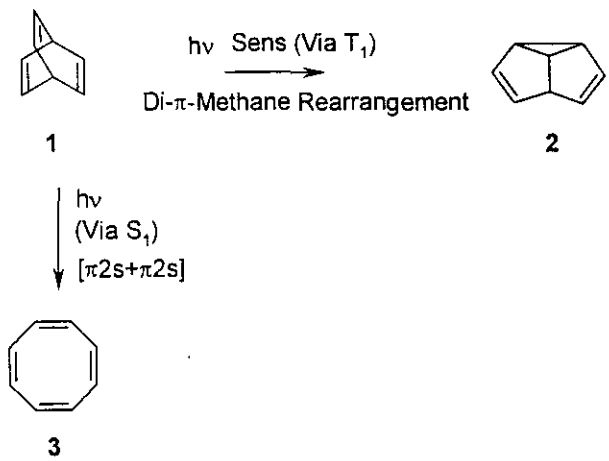
7.2. Introduction

The reactions of amines with aromatic hydrocarbons in the excited state have attracted considerable attention in recent years, mainly in connection with electron-transfer reactions and / or exciplex formation.[1-20] Our interest in this area has risen from our pursuit on controlling the selectivity of photochemical transformations of suitable substrates by incorporating "inbuilt" quenchers and thereby facilitating intramolecular quenching by electron and / or energy transfer. We reasoned that an intramolecular process should be much more efficient than the corresponding intermolecular process. Thus, amines should quench the short-lived singlet excited states by intramolecular electron transfer. This strategy has the advantage that back electron transfer from the incipient radical anion of the selected chromophores to the radical cation of the amine component is also intramolecular in nature resulting in highly efficient net quenching. Based on these assumptions, we decided to explore the possibility of selective quenching of singlet excited states of a few representative substrates. Ideally, these

"inbuilt" quenchers should be remote to and hence possessing no ground-state interaction with the chromophore under consideration.

Bicyclo[2.2.2]octatriene (barrelene) undergoes photochemical transformations in high yields and exhibit remarkable selectivity based on the nature of excited states involved. The major reaction pathways exhibited by bicyclo[2.2.2]octa-2,5,7-triene are summariSed in the following scheme (Scheme 7.1). It has been established that direct irradiation of barrelenes yields the corresponding cyclooctatetraene arising through a singlet-mediated pathway whereas triplet-sensitised irradiation leads to the formation of semibullvalenes.[21] However, in most cases a mixture of both cyclooctatetraene and semibullvalene is formed. In principle, it should be possible to use a suitable a singlet quencher to suppress the formation of cyclooctatetraene.

Scheme 7.1



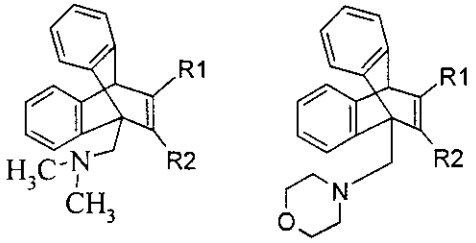
We proposed to incorporate "inbuilt" quenchers whereby intramolecular quenching can be achieved. We presume that dibenzobarrelene having remote tertiary amine functionality are not likely to undergo singlet-mediated transformation to yield the corresponding cyclooctatetraenes. Intramolecular quenching of singlet-excited states is more adept since singlets are short-lived than triplets and quenching singlet excited states by an intermolecular process may not be very efficient. Based on these arguments, we proposed to incorporate tertiary amine functionalities into various

molecules to achieve intramolecular quenching and accompanying selectivity in their photoreactions.

The redox potential and thus the accompanying ability of the barrelene chromophore to participate in electron transfer reactions can be fine-tuned by incorporating electron-withdrawing and donating groups. Fortunately, several such dibenzobarrelenes can be easily accessed by changing the nature of the acetylene dienophile employed in their preparation. Thus, the efficiency of electron transfer to the singlet excited states of barrelenes can be modulated.[20]

We proposed to synthesise the aminoanthracene precursors as well as the corresponding amine-appended dibenzobarrelenes to probe the effect of appended amine functionality on their photochemistry. The target molecules of our choice are given in Chart 7.1.

Chart 7.1



a **b**

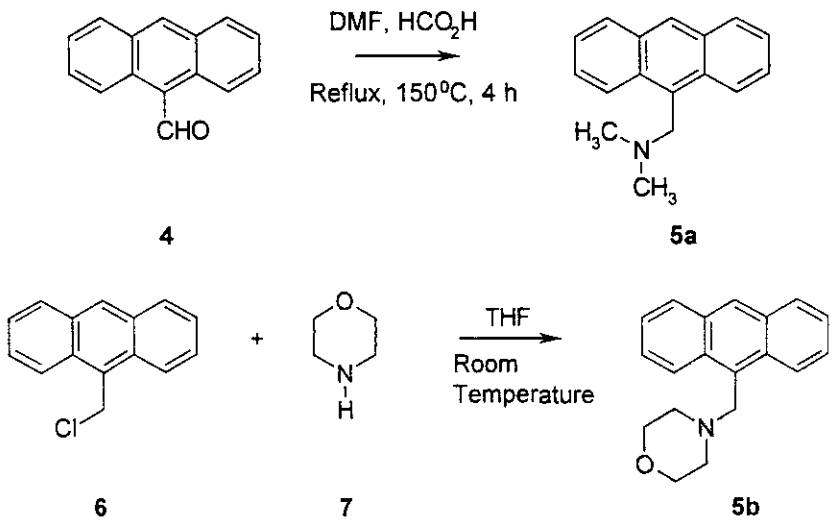
R1 = R2 = CO_2CH_3
R1 = R2 = C_6H_5
R1 = H, R2 = CO_2H

7.3. Results and Discussion

7.3.1. Synthesis of 9-(*N,N*-Dialkylamino)methylanthracenes

The amine precursor **5a** was prepared by a known procedure.[22] Compound **5b** was prepared by treating commercially available 9-chloromethylanthracene (**6**) with morpholine (**7**) in dry THF as given in Scheme 7.2.

Scheme 7.2

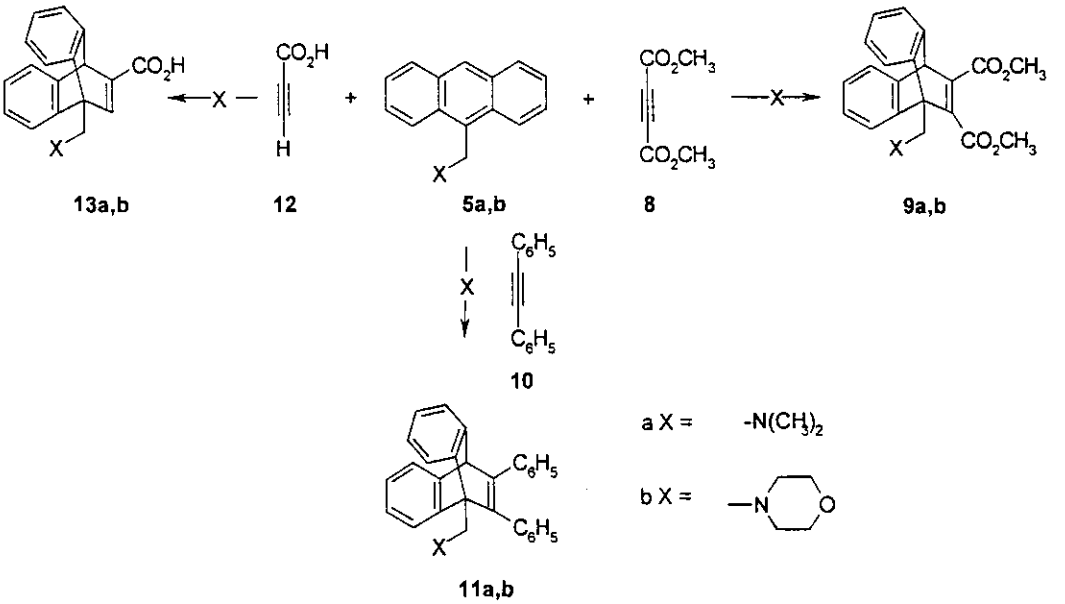


The ^{1}H NMR spectrum of compound **5b** showed two triplets at δ 2.6 (4H) and δ 3.6 (4H) and a singlet at δ 4.49 (2H). The multiplet at δ 7.3-8.5 (9H) corresponds to the aromatic protons. The ^{13}C NMR spectrum-of compound **5b** showed peaks at δ 53.7, 54.6, and 67.2 corresponding to N-CH_2 and O-CH_2 carbons. The peaks in the region δ 124.9-131.4 correspond to the aromatic carbons.

7.3.2. Attempted Synthesis of 9-(*N,N*-Dialkylamino)methyl-9,10-dihydro-9,10-ethenoanthracenes

In order to assess the effect of tertiary amine units as "inbuilt" singlet excited state quenchers, we proposed to synthesise a few amine-appended systems such as dimethyl 9-(*N,N*-dimethylamino)methyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**9a**) and dimethyl 9-(1-methylmorpholino)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**9b**), 9-(*N,N*-dimethylamino)methyl-9,10-dihydro-11,12-diphenyl-9,10-ethenoanthracene (**11a**), 9-(1-methylmorpholino)-9,10-dihydro-11,12-diphenyl-9,10-ethenoanthracene (**11b**), 9-(*N,N*-dimethylamino)methyl-12-carboxy-9,10-dihydro-9,10-ethenoanthracene (**13a**), 9-(1-methylmorpholino)-12-carboxy-9,10-dihydro-9,10-ethenoanthracene (**13b**) from the corresponding amine precursors **5a,b** (Scheme 7.3)

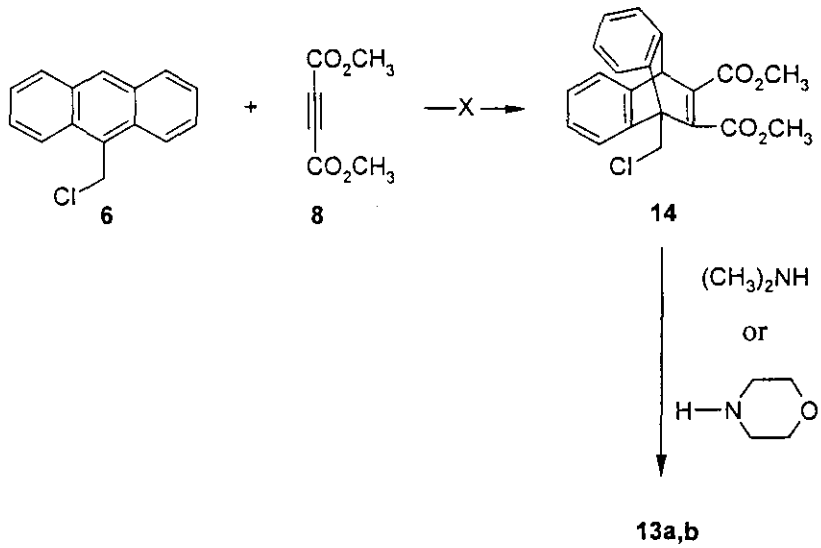
Scheme 7.3



We carried out the Diels-Alder reactions at refluxing temperatures of various solvents (ranging from 80 to 140 ^{0}C) and this resulted in extensive destruction of the aminoanthracene reactants as indicated by the ^{1}H NMR spectral analysis of the reaction mixture. On neat heating of the diene and dienophile components at 250 ^{0} C, complete decomposition of the starting materials occurred. Since decomposition of the material was observed at higher temperatures, we attempted the Diels-Alder reaction between **5a,b** and **8,10,12** in THF at room temperature. Under these conditions, in each case, **5a,b** were recovered unchanged in near-quantitative amounts.

The extensive decomposition of aminoanthracenes on exposure to acetylenic dienophiles is attributable to ground state electron transfer from the electron rich anthracenes to the dienophiles. So, we contemplated the alternate route to dibenzobarrelenes **13a,b** given in Scheme 7.5, which we abandoned after close scrutiny. Examination of the structural features of the intermediate dimethyl 9-chloromethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**14**) shows that it is a *neo*-pentyl-type system and hence reluctant to undergo substitution reactions[23] to give corresponding amine appended dibenzobarrelenes such as **13a,b**.

Scheme 7.4



In summary, we were successful in synthesising the amine precursors **5a,b**. However, our attempts to synthesise the desired dibenzobarrelenes such as dimethyl 9-(*N*, *N*-dimethylamino)methyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**9a**) and dimethyl 9-(1-methylmorpholino)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**9b**) have not been successful. The intramolecular quenching of singlet excited states of barrelenes thus remains a distinct but yet to be demonstrated possibility.

7.4. Experimental

7.4.1. General Procedures: All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica or aluminium sheets coated with silica (MERCK) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry packed silica (Qualigens 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using Shimadzu-DR-8001 series FTIR

spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 400 and 500 MHz on a Bruker FT-NMR spectrometer or GE NMR OMEGA spectrometer with tetramethylsilane as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane (TMS). Elemental analysis was performed at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. We have reported only the relevant data for the characterisation of compounds synthesised by us.

7.4.2. Starting materials: Dimethyl acetylenedicarboxylate (DMAD), 9-anthraldehyde, 9-chloromethylanthracene and propiolic acid were purchased from Sigma-Aldrich. Morpholine was purchased from S. D. Fine Chem. Ltd.

7.4.2.1. Diphenylacetylene: Diphenyl acetylene was prepared by a known procedure (86%, mp 59-60 ^{0}C).[24]

7.4.2.2. Preparation of 9-(*N,N*-Dialkylamino)methylanthracenes

7.4.2.2.1. Preparation of 5a[22]. A mixture of 9-anthraldehyde (4.12 g, 0.02 mol), DMF (11.01 g, 0.15 mol), and 90% formic acid (1 mL) was refluxed for 4 h at about 150 ^{0}C. After removal of excess of DMF and formic acid by distillation under reduced pressure, the residual oil was dissolved in diethyl ether, dried over anhydrous Na_2SO_4 and filtered. Introduction of gaseous hydrogen chloride into the ethereal solution precipitated *N,N*-dimethyl-1-anthracenemethylamine hydrochloride which was collected by filtration and purified by recrystallisation from 6N HCl. Compound **5a** (3.24 g, 69%, mp 90-92 ^{0}C) was regenerated from the neutral equivalent.

7.4.2.2.2. Preparation of 5b. A sample of 9-chloromethylanthracene (4.53 g, 0.02 mol) was dissolved in dry THF (10 mL) and morpholine (0.04mol) was added drop by drop with stirring over a period of 30 minutes. Stirring was continued at room temperature for 48 h. After removing the excess THF and morpholine by distillation under reduced pressure, the residual oil was washed with water, saturated $NaHCO_3$ solution, extracted into diethyl ether, dried over anhydrous Na_2SO_4 and filtered. The

residue obtained on evaporating the solvent was column chromatographed on silica. Elution with a mixture (2:3) of dichloromethane and hexane gave unchanged 9-chloromethylanthracene (0.79 g, 15%, mixture mp 136-138 ^{0}C). On further elution with a mixture (1:1) of dichloromethane and hexane, 9-anthracenemethanol was obtained (0.95 g, 18%, mixture mp 158-162 ^{0}C). Further elution with a mixture of ethyl acetate and hexane (1:24) gave compound **5b**.

Compound **5b** was purified by the following procedure: ntroduction of gaseous hydrogen chloride into the ethereal solution of **5b** precipitated *N, N*-dimethyl-1-anthracene-methylamine hydrochloride which was purified by recrystallisation from 6N HCl. Compound **5b** was regenerated from the neutral equivalent.

Compound 5b: (3.05 g, 58%); mp 120-124 ^{0}C; UV λ_{max} (Acetonitrile) 234 (17 136), 281 (20 318), 363 nm (3130); ^{1}H NMR ($CDCl_3$) δ 2.6 (4H, t), 3.6 (4H, t), 4.4 (2H, s), 7.3-8.5 (9H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.7, 54.6, 67.2, 124.9, 125.1, 125.6, 125.7, 127.6, 129.0, 131.4, 131.5 MS, *m/z* 277 (M^+). Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90. Found: C, 82.12.; H, 6.86.

7.4.3. Attempted Diels-Alder Reactions of 9-(1-Aminomethyl)anthracenes

7.4.3.1. Attempted Synthesis of 9a. Compound **5a** (0.47 g, 2mmol) was dissolved in of dry xylene (10 mL) and DMAD (0.43 g, 3 mmol) was added and the mixture was refluxed for 10 h. The progress of the reaction was monitored by TLC. Removal of the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material. The ^{1}H-NMR indicated that polymerisation of **5a** has occurred under the reaction conditions.

In a repeat run, **5a** (0.47 g, 2mmol) was dissolved in of dry toluene (20 mL) and DMAD (0.43 g, 3 mmol) was added and the mixture was refluxed for 10 h. The progress of the reaction was monitored by TLC. Removal of the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave a polymeric material.

In a repeat run, **5a** (0.47 g, 2mmol) was dissolved in dry benzene (20 mL) and DMAD (0.43 g, 3 mmol) was added and the mixture was refluxed for 6 h. Removal of the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, a mixture of **5a** (0.47 g, 2mmol) and DMAD (0.43 g, 3 mmol) was heated in a sealed tube around 150 ^{0} C for 1 h. The black residue was dissolved in dichloromethane and chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, a mixture of **5a** (0.47 g, 2mmol) and DMAD (0.43 g, 3 mmol) was heated around 250 ^{0} C for 30 minutes in a sealed tube. TLC analysis of the reaction mixture indicated complete decomposition of **5a**.

In a repeat run, a mixture of **5a** (0.47 g, 2mmol) and DMAD (0.43 g, 3 mmol) in dry THF was stirred at room temperature for 48 h. TLC showed the single spot corresponding to that of unchanged **5a**.

7.4.3.2. Attempted Synthesis of 9b. Compound **5b** (0.55 g, 2mmol) was dissolved in dry xylene (15 mL) and DMAD (0.43 g, 3 mmol) was added and the mixture was refluxed for 10 h. The progress of the reaction was monitored by TLC. Removal of the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave a polymeric material.

In a repeat run, **5b** (0.55 g, 2mmol) was dissolved in dry toluene (20 mL) and DMAD (0.43 g, 3 mmol) was added and the mixture was refluxed for 5 h. Removal of the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, **5b** (0.55 g, 2mmol) was dissolved in dry benzene (30 mL) and DMAD (0.43 g, 3 mmol) was added and the mixture was refluxed for 4 h. Removal of

the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, a mixture of **5b** (0.55 g, 2mmol) and DMAD (0.43 g, 3 mmol) was heated in a sealed tube around 150 ^{0}C for 1 h. The black residue was dissolved in dichloromethane and chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, a mixture of **5b** (0.55 g, 2mmol) and DMAD (0.43 g, 3 mmol) was heated in a sealed tube around 250 ^{0}C for 30 minutes. TLC showed complete decomposition of **5b**.

In a repeat run, a mixture of **5b** (0.55 g, 2mmol) and DMAD (0.43 g, 3 mmol) in dry THF was stirred at room temperature for 48 h. TLC showed the single spot corresponding to that of unchanged **5b**.

7.4.3.3. Attempted Synthesis of 11a. Compound **5a** (0.47 g, 2mmol) and diphenylacetylene (0.53 g, 3 mmol) was dissolved in dry xylene (20 mL) and the mixture was refluxed for 10 h. The progress of the reaction was monitored by TLC. Removal of the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, a mixture of **5a** (0.47 g, 2mmol) and diphenylacetylene (0.53 g, 3 mmol) was heated around 130 ^{0}C in a sealed tube for 1 h. The black residue was dissolved in dichloromethane and chromatographed on silica. Elution of the column with dichloromethane gave an amorphous mass. The ^{1}H NMR spectrum of the material indicated that polymerisation of **5a** had occurred under the reaction conditions.

In a repeat run, a mixture of **5a** (0.47 g, 2mmol) and diphenylacetylene (0.53 g, 3 mmol) was heated around 250 ^{0}C in a sealed tube for 30 minutes. TLC showed complete decomposition of **5a**.

In a repeat run, a mixture of **5a** (0.47 g, 2mmol) and diphenylacetylene (0.53 g, 3 mmol) in dry THF was stirred at room temperature for 48 h. TLC showed a single spot corresponding to that of unchanged **5a**.

7.4.3.4. Attempted Synthesis of 11b. Compound **5b** (0.55 g, 2mmol) and diphenylacetylene (0.53 g, 3 mmol) were dissolved in dry *o*-dichlorobenzene (15 mL) and the mixture was refluxed for 10 h. The progress of the reaction was monitored by TLC. Removal of the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, a mixture of **5b** (0.55 g, 2mmol) and diphenylacetylene (0.53 g, 3 mmol) was heated in a sealed tube around 100 ^{0}C for 1 h. The black residue was dissolved in dichloromethane and chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, a mixture of **5b** (0.55 g, 2mmol) and diphenylacetylene (0.53 g, 3 mmol) was heated in a sealed tube around 250 ^{0}C for 30 minutes. TLC showed complete decomposition of **5b**.

In a repeat run, **5b** (0.55 g, 2mmol) and diphenylacetylene (0.53 g, 3 mmol) in dry THF was stirred at room temperature for 48 h. TLC showed the single spot corresponding to that of unchanged **5b**.

7.4.3.5. Attempted Synthesis of 13a. Compound **5a** (0.47 g, 2mmol) was dissolved in dry xylene (15 mL) and propiolic acid (0.21 g, 3 mmol) was added and the mixture was refluxed for 10 h. The progress of the reaction was monitored by TLC. Removal of the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, a mixture of **5a** (0.47 g, 2mmol) and propiolic acid (0. g, 3 mmol) in dry THF was stirred at room temperature for 48 h. TLC showed the single spot corresponding to that of unchanged **5a**.

7.4.3.6. Attempted Synthesis of 13b. Compound **5b** (0.55 g, 2mmol) was dissolved in dry *o*-dichlorobenzene (10 mL) and propiolic acid (0.21 g, 3 mmol) was added and the mixture was refluxed for 10 h. The progress of the reaction was monitored by TLC. Removal of the solvent gave an amorphous residue, which was chromatographed on silica. Elution of the column with dichloromethane gave an amorphous polymeric material.

In a repeat run, a mixure of **5b** (0.55 g, 2mmol) and propiolic acid (0.21 g, 3 mmol) in dry THF was stirred at room temperature for 48 h. TLC showed the single spot corresponding to that of unchanged **5b**.

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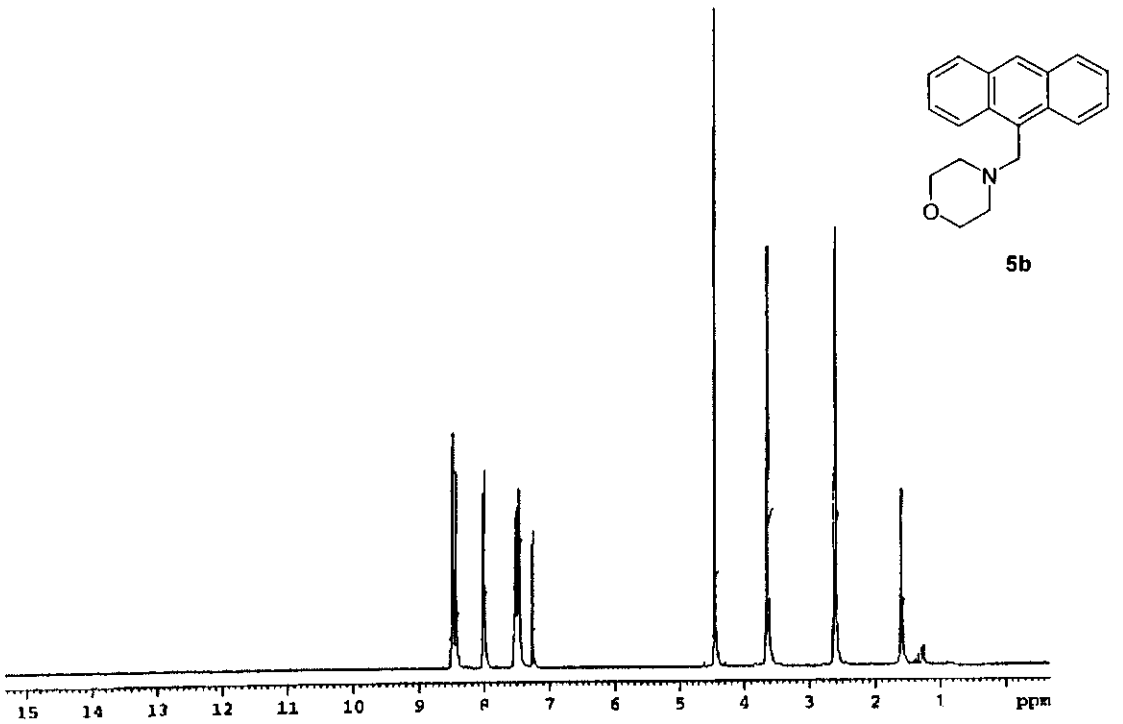


Figure 7.1. ^{1}H NMR spectrum of compound 5b

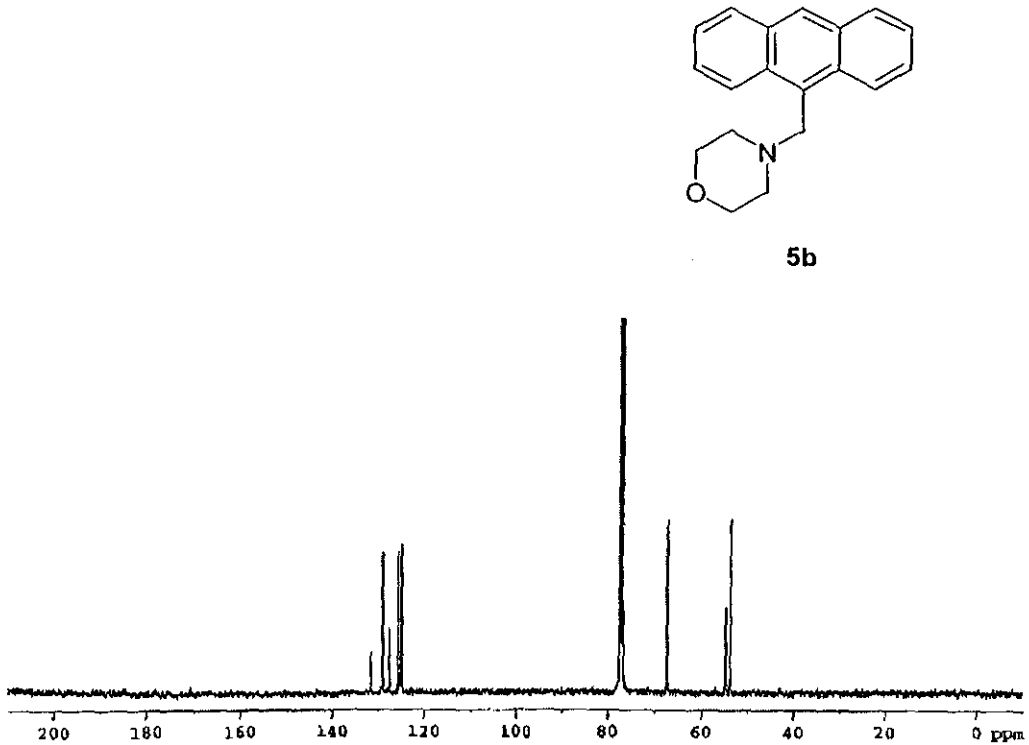


Figure 7.2. ^{13}C NMR spectrum of compound 5b

SYNTHESIS AND DIELS-ALDER REACTIONS OF ETHENYLFURANS

8.1. Abstract

This chapter describes the synthesis of a few ethenylfurans as part of our attempts to examine the scope of [4+2] cycloadditions of these systems with suitable acetylenic dienophiles leading to 7-oxanorbornadienes, which are potential substrates for studying di-π–methane rearrangement.

8.2. Introduction

The importance and versatility of the Diels-Alder reaction for the construction of six-membered rings containing one or two double bonds are well documented in literature.[1,2] An area, which is gaining prominence in Diels-Alder chemistry involves the use of heteroaromatic compounds as either the diene or dienophile component.[3-6] By far the most extensively studied five-membered heteroaromatic system for Diels-Alder cycloaddition is furan and its derivatives.[7-9] The resultant 7-oxabicyclo[2.2.1]heptenes are valuable synthetic intermediates which have been further elaborated to substituted arenes, carbohydrate derivatives, and various natural products.[10-19] A crucial synthetic transformation employing these intermediates involves cleavage of the oxygen bridge to produce functionalised cyclohexene derivatives.[20-25] In many cases, however, the Diels-Alder strategy is not feasible because of the low reactivity of furan toward monoactivated dienophiles.[6] Additionally, furan and many of its derivatives are stable only at low temperature. So, the successful Diels-Alder reactions involving furans are carried out under sub-ambient temperatures using activated dienophiles.

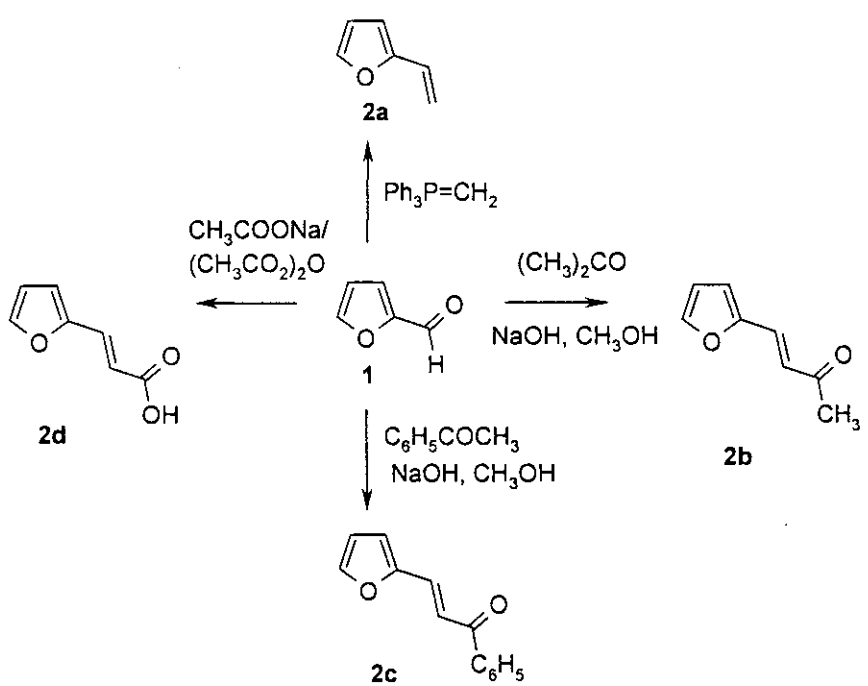
Intramolecular Diels-Alder reaction of furans, often designated as IMDAF, helps to overcome the sluggishness of this heteroaromatic ring system toward [4+2] cycloaddition. IMDAF reactions allow the preparation of complex oxygenated polycyclic compounds, and they often proceed at lower temperature than their intermolecular counter parts.[26] Even more significantly, unactivated π-bonds are often suitable dienophiles for intramolecular cycloaddition.[8]

8.3. Results and Discussion

8.3.1. Synthesis of a Few Ethenylfurans and Their Diels-Alder Reactions

In an effort to investigate the scope of Diels-Alder reactions, we proposed to synthesise a few 7-oxabicyclo[2.2.1]hepta-2,5-dienes. Our long term goal, however, was to introduce an ethenyl group at the bridgehead position of 7-oxabicyclo[2.2.1]hepta-2,5-dienes to assess the role of the newly introduced π-moiety on the photochemistry of these bicyclic systems. We proposed to gain access to these targets through the corresponding ethenylfurans. The ethenylfurans of our choice are given in Chart 8.1.

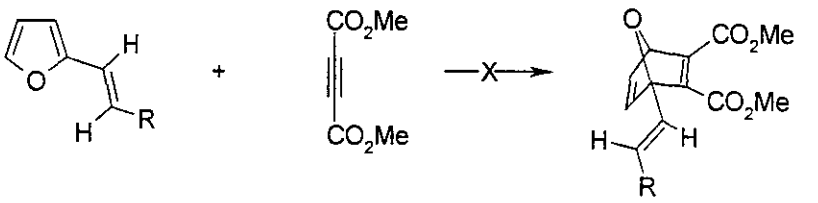
Chart 8.1



The ethenylfuran, **2a** was prepared by Wittig reaction between furfural (**1**) and the corresponding ylide.[27] Furans **2b,c** were prepared by Claisen-Schmidt condensation of **1** with suitable methyl ketones such as acetone and acetophenone respectively[28,29] and **2d** was prepared by Perkin reaction of **1**.[30] Ethenylfurans **2a-d** were identified by comparing physical, spectral and analytical data with those reported in literature.

We attempted to synthesise the Diels-Alder adducts of these ethenylfurans with dimethyl acetylenedicarboxylate (DMAD, **3**). Attempted Diels-Alder reaction of **2a-d** with DMAD resulted in polymerisation of the starting materials (Scheme 8.1), at high as well as low temperatures. It appears that furans **2a-d** are not reactive enough to undergo [4+2] cycloaddition with DMAD at low temperatures. This decrease in reactivity may be attributed to the vinyl substituents, which in turn can function as a net electron withdrawing substituent (-*M* effect). When the reaction was repeated at higher temperatures, the limited stability of these furans led to extensive decomposition. We attempted the Lewis acid catalysed reaction of representative examples such as **2a,b**. However, extensive decomposition of starting materials was observed under the conditions employed by us. Based on these, we concluded that ethenylfurans are reluctant to undergo Diels-Alder reaction at high as well as low temperatures.

Scheme 8.1



2a R = H
b R = $COCH_3$
c R = COC_6H_5
d R = COOH

3

4a R = H
b R = $COCH_3$
c R = COC_6H_5
d R = COOH

8.4. Experimental

8.4.1. General Procedures. All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica or aluminium sheets coated with silica (MERCK) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry packed silica (Qualigens 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using Shimadzu-DR-8001 series FTIR spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 400 and 500 MHz on a Bruker FT-NMR spectrometer or GE NMR OMEGA spectrometer with tetramethylsilane as internal standard. Elemental analysis was performed at Regional Sophisticated Instrumenttion Centre, Central Drug Research Institute, Lucknow. We have reported only the relevant data for the characterisation of compounds synthesised by us.

8.4.2. Starting materials: Furufural and acetic anhydride were purchased from S. D. Fine Chem. Ltd. and were purified by known methods.[31] Acetone and acetophenone purchased from S. D. Fine Chem. Ltd. were purified by distillation.

8.4.2.1. Methytriphenylphosphonium iodide: Methytriphenylphosphonium iodide was prepared by a known procedure[32].

8.4.3. Preparation of Ethenylfurans

8.4.3.1. Preparation of Ethenylfuran 2a[27]: To a stirred mixture of dry THF (180 mL) and methyltriphenylphosphonium iodide (36.36 g, 0.09 mol) under nitrogen atmosphere, a solution of freshly distilled furfural (2.88 g, 0.03 mol) in dry THF (80 mL) was added. The reaction mixture was stirred at room temperature for 7 h and

50% aqueous solution of NaOH (5mL) was added to the mixture. The reaction mixture was stirred for another 30 minutes and the organic layer was extracted repeatedly with ether. The combined organic extracts were washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give a yellow liquid.

Compound 2a: (1.18 g, 42%); IR ν_{max} (KBr) 3044 and 1641 cm^{-1}; MS, *m/z* 94 (M^+), and other peaks.

8.4.3.2. Preparation of Ethenylfuran 2b[28]: A mixture of freshly distilled furfural (2.88 g, 0.03 mol), acetone (3.86 g, 0.06 mol) and powdered sodium hydroxide (0.2 g, 5 mmol) in water (25 mL) was stirred at room temperature for 48 h and later stored overnight in a refrigerator. The mixture was washed with 10% sulphuric acid and then with water, and the organic layer was separated, dried with anhydrous $MgSO_4$ and distilled under reduced pressure. On cooling the product separated out as a brown solid.

Compound 2b: (2.34 g, 58%); mp 38-39 ^{0}C; IR ν_{max} (KBr) 1713 (C=O) cm^{-1}

8.4.3.3. Preparation of Ethenylfuran 2c[29]: To a solution of powdered sodium hydroxide (1.6 g, 0.04 mol) in water–ethanol mixture (2:1, 25 mL) was added acetophenone (3.72 g, 0.03 mol) and freshly distilled furfural (2.88 g, 0.03 mol) with stirring. The reaction mixture was stirred for 2 h and later kept in refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (2:1) of dichloromethane and hexane to give **2c**.

Compound 2c: (2.65 g, 12%, mixture mp 26 ^{0}C); IR ν_{max} (KBr) 1713 (C=O) cm^{-1}; MS, *m/z* 136 (M^+), and other peaks.

8.4.3.4. Preparation of Ethenylfuran 2d[30]. A mixture of freshly distilled furfural (2.88 g, 0.03 mol)), pure acetic anhydride (5.13 g, 0.05 mol) and dry, powdered, freshly fused sodium acetate (2.46 g, 0.03 mol) was heated at 150 ^{0}C for 12 h. The reaction mixture was cooled and poured into cold water with stirring. The mixture

was boiled with animal charcoal and filtered while hot. The hot filtrate was acidified with 50% hydrochloric acid and cooled to room temperature with stirring. The acidic product that crystallized out upon cooling was collected by filtration and recrystallised from benzene.

Compound 2d: (2.15g, 52%, mixture mp 138-139 ^{0}C); IR ν_{max} (KBr) 3300 (OH) and 1701 (C=O) cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 112.5, 115.3, 115.5, 133.1, 145,3; 151.1; 172.4; MS, *m/z* 138 (M^+), and other peaks.

8.4.3.5. Attempted Preparation of Diels-Alder Adduct 4a. To a mixture of (1.88 g, 0.02 mol) of **2a** in 10 mL dry dichloromethane was added DMAD (2.82 g, 0.03 mol) in small amounts at 0 ^{0}C. The reaction mixture was stirred for 6 h at room temperature. Removal of the solvent gave a tarry material which appears to be polymeric in nature.

In a repeat run, to a mixture of **2a** (100 mg, 1.1 mmol) in dry benzene (10 mL) DMAD (0.24 g, 1.7 mmol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred at room temperature for 6 h. TLC showed no product formation. The reaction mixture was then refluxed for 30 minutes and benzene was removed under reduced pressure to give a tarry substance.

In a repeat run, to a stirred mixture of **2a** (100 mg, 1.1 mmol) and anhydrous aluminium chloride (0.15 g. 1.1 mmol) in dry dichloromethane (10 mL) DMAD (0.23 g, 1.7 mmol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred for 30 minutes at room temperature. The starting material underwent extensive decomposition and no new products could be isolated.

8.4.3.6. Attempted Preparation of Diels-Alder Adduct 4b. To a mixture of **2b** (1.36 g, 0.01 mol) in dry dichloromethane (10 mL) DMAD (2.13 g, 0.015 mol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred for 6 h at room temperature. No product was formed. Removal of the solvent under reduced pressure gave an amorphous material which could not be characterised.

In a repeat run, to a mixture of **2b** (136 mg, 1.0 mmol) in dry benzene (10 mL) DMAD (0.21 g, 1.5 mmol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred for 6 h at room temperature. TLC showed no product formation. The reaction mixture was refluxed for 18 h. TLC analysis of the reaction mixture indicated total consumption of **2b**. Benzene was removed under reduced pressure and the residue was charged on to a column, which on elution with dichloromethane gave a polymeric material.

In a repeat run, to a stirred mixture of **2b** (136 mg, 1.0 mmol) and anhydrous aluminium chloride (0.13 g, 1.0 mmol) in 10 mL dry dichloromethane DMAD (0.21 g, 1.5 mmol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred for 30 minutes at room temperature. Even under these conditions, total decomposition of the starting material was observed.

8.4.3.7. Attempted Preparation of Diels-Alder Adduct 4c. To a mixture of **2c** (1.98 g, 0.01 mmol) in dry dichloromethane (10 mL) DMAD (2.13 g, 0.015 mol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred for 5 h at room temperature. Removal of the solvent under reduced pressure gave an amorphous material that could not be characterised.

In a repeat run, to a mixture of **2c** (200 mg, 1.0 mmol) in 10 mL dry benzene was added DMAD (0.21 g, 1.5 mmol) in small amounts at 0 ^{0}C. The reaction mixture was stirred for 6 h at room temperature. TLC showed no product formation. The reaction mixture was refluxed for 10 h. TLC showed product formation. Benzene was removed under reduced pressure and the residue was charged on to a column, which on elution with a mixture (1:9) of hexane and dichloromethane gave a polymeric material.

8.4.3.8. Attempted Preparation of Diels-Alder Adduct 4d. To a mixture of **2d** (1.38 g, 0.01 mol) in 10 mL dry dichloromethane was added DMAD (2.13 g, 0.015 mol) in small amounts at 0 ^{0}C. The reaction mixture was stirred for 8 h at room

temperature. The solvent was removed under reduced pressure and the residue was charged on to a silica column, which on elution with a mixture (1:1) of dichloromethane and hexane gave unchanged **2d** (100 mg, mixture mp 138 ^{0}C). Further elution with a mixture (1:99) of methanol and dichloromethane gave a polymeric material.

In a repeat run, to a mixture of **2d** (138 mg, 1 mmol) in dry benzene (10 mL) DMAD (0.21 g, 1.5 mmol) was added in small portions at 0 ^{0}C. The reaction mixture was stirred for 6 h at room temperature. TLC showed no product formation. The reaction mixture was refluxed for 12 h. TLC analysis indicated the formation of a new compound. Benzene was removed under reduced pressure and the residue was charged on to a silica column, which on elution with a mixture (1:99) of methanol and dichloromethane gave a polymeric material.

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SYNTHESIS AND TRANSFORMATIONS OF DISPIRO COMPOUNDS

9.1. Abstract

Reaction of acenaphthenequinone with acetophenone in methanol in the presence of KOH provides a highly substituted dispirocompound in good yields arising through a novel three-component Michael-aldol tandem reaction.

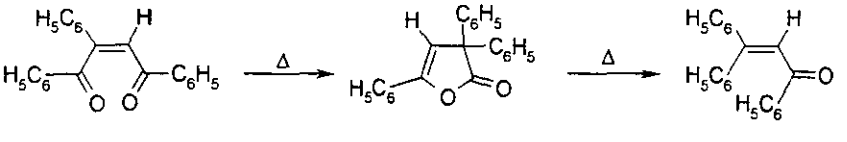
9.2. Introduction

The efficiency of organic reactions is recognized as an important problem and a tandem reaction sometimes provides a fascinating solution.[1,2] Combining more than one reaction in one flask usually provides better yield and a chance for reactive but not-easy-to-generate and isolate intermediates to be used in the synthetic sequence. Michael addition[3] and aldol condensations[4-7] are widely acknowledged as useful tools for constructing complex organic molecules, and combining these two reactions in one flask has been of interest in current organic synthesis. Here, in this chapter we discuss a novel domino reaction of acenaphthenequinone with acetophenones in methanol that involves aldol and Michael reactions leading to the formation of a highly-substituted dispirocompound that we encountered serendipitously during our investigation on the synthesis of dibenzoylalkene-type systems. This reaction caught our fancy since dispirocompounds are interesting synthetic targets due to their presence in many important natural products.[8-12]

Dibenzoylalkenes can undergo bond reorganisation process thermally and photochemically. The first reported dibenzoylalkene rearrangement is on the

pyrolysis of *cis*-dibenzoylstilbene to tetraphenylcrotonolactone by Zinin in 1872.[13] Subsequently, several other reports on the synthesis and transformations of a variety of dibenzoylalkenes have appeared in the literature. *cis*-Dibenzoylstyrene (**1**) on pyrolysis, for example, undergoes ring closure to form triphenylcrotonolactone (**2**).[14,15,16] The lactone on further heating undergoes decarbonylation to give β-phenylbenzalacetophenone (**3**).[17]

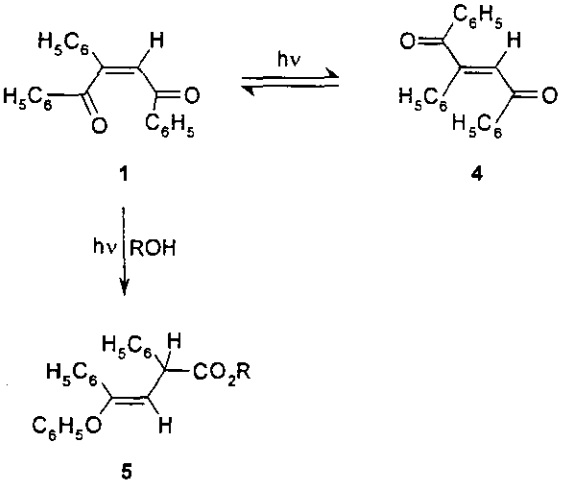
Scheme 9.1



1 **2** **3**

The photochemistry of dibenzoylalkenes is equally interesting. Earlier reports indicated that upon irradiation, dibenzoylalkenes undergo cis-trans isomerisation.[18] Later it was established that when the irradiation is carried out in alcohols as solvents, dibenzoylalkenes undergo intramolecular rearrangement involving 1,5-phenyl migration to oxygen to give the corresponding esters of substituted 3-butenoic acids (Scheme 9.2).[19-21]

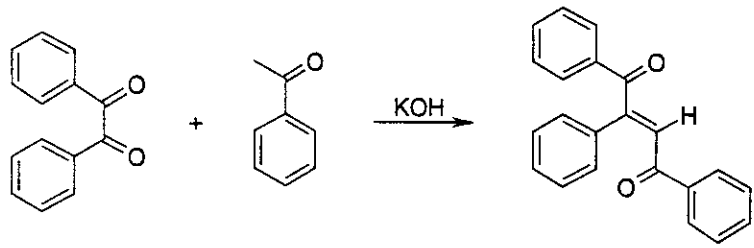
Scheme 9.2



1 **4** **5**

Dibenzoylstyrenes are conveniently prepared by the base-catalyzed aldol condensation of acetophenone with benzil (Scheme 9.3).

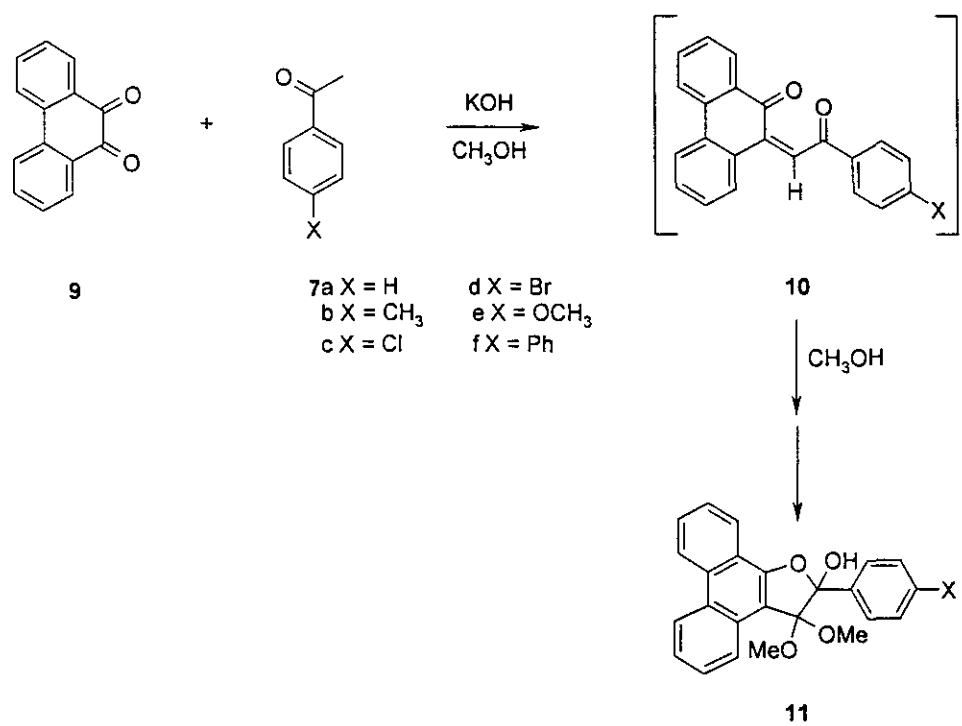
Scheme 9.3



6 **7** **8**

Based on this observation, we surmised that other 1,2-dones such as phenanthrenequinone and acenapthenequinione also should react with acetophenone to give the corresponding dibenzoylalkene-type systems. Earlier investigastions carried out in our laboratory have revealed that phenanthrenequinone, indeed reacts with acetophenone to yield phenanthrenone-9-ylidene ketones which undergo further transformation under the reaction conditions to yield phenanthrofunaols (Scheme 9.4).[24]

Scheme 9.4



9

7a X = H, **b** X = CH_3, **c** X = Cl, **d** X = Br, **e** X = OCH_3, **f** X = Ph

10

11

As a logical extension, we examined the base-catalysed reaction of acenaphthenequinone with acetophenone and encountered the novel doimno reaction mentioned above. Also, we discuss the reactions of the resultant dispirocompounds.

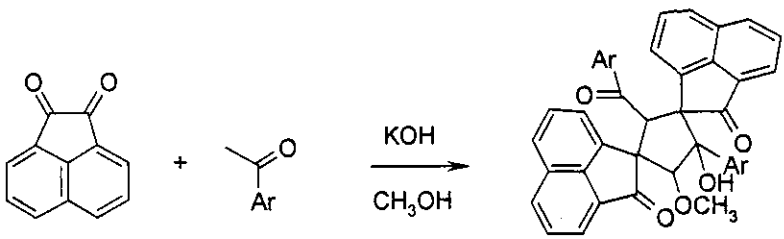
9.3. Results and Discussion

9.3.1. Synthesis

The reaction of acenaphthenequinone (**12**) with slight excess of acetophenone (**7a**) in methanol in the presence of KOH gave a colourless amorphous product. The product showed a broad band at 3345 cm^{-1} in the IR spectrum indicating the presence of a hydroxy group. In addition, two peaks were observed at 1711 and 1678 cm^{-1}. The peak at 1711 cm^{-1} is ascribed to indenone-type carbonyl. In the ^1H NMR spectrum, four singlets were observed at δ 2.8 (3H), 5.67 (1H), 6.11 (1H, D_2O-exchangeable), and 6.23 (1H) along with other signals attributable to aromatic protons. In the ^{13}C NMR spectrum, thirty five signals were observed in the region δ60-209. The signals observed at δ 197.9, 205.2, and 208.7 are attributed to carbonyl carbons. Signals due to aromatic carbons are observed in the region δ 120-143 (26 signals). Attached proton test indicated that three of the carbons appearing in the δ 60-92 region are attached to either zero or two hydrogens while the remaining three are attached to one or three hydrogens. Based on these data, the compound was identified as the dispirocompound **13a**. Mass spectral data and elemental analysis are in agreement with the proposed structure. Similarly, dispirocompounds **13b,c** were synthesized by the reaction of acenaphthenequinone (**12**) with 4-methylacetophenone (**7b**) and 4-chloroacetophenone (**7c**) respectively.

In order to broaden the scope of this novel domino rection, we attempted the base-catalysed reaction of acenapthenequinone with propiophenone in methhnol. However, acenaphtehenequinone did not react with propiophenone even after prolonged heating.

Scheme 9.5



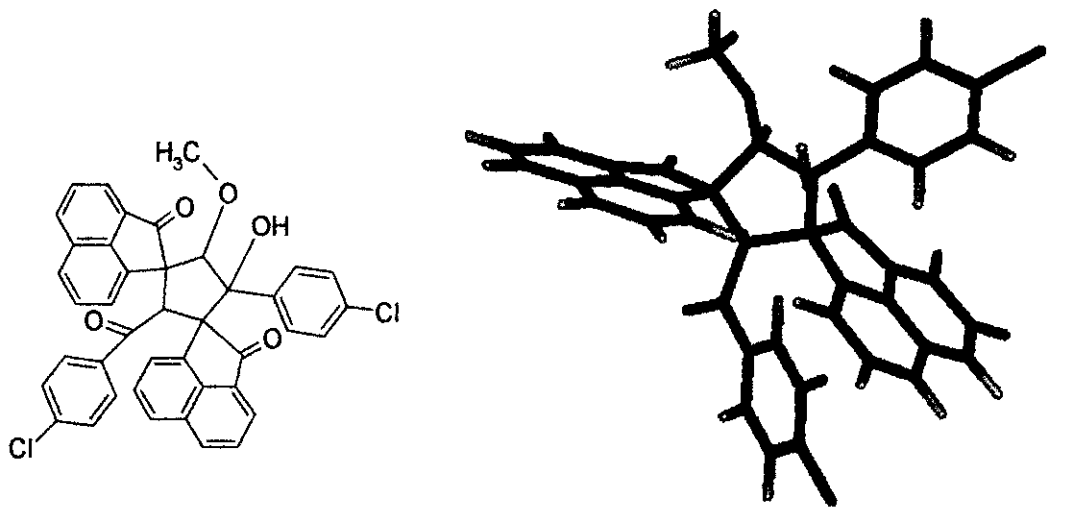
12 **7a** Ar = C_6H_5
b Ar = C_6H_4-CH_3(*p*)
c Ar = C_6H_4-Cl(*p*)

13a Ar = C_6H_5
b Ar = C_6H_4-CH_3(*p*)
c Ar = C_6H_4-Cl(*p*)

9.3.2. Energy Minimisation studies

It is interesting to note that **5** has five assymmetric carbons leading to the possibility of a maximum of 32 stereoisomers. However, the ^1H and ^{13}C NMR spectra of **13** indicate that the material obtained is homogenous. Since diffraction-quality crystals of **13a-c** could not be obtained, we carried out energy minimisation studies to determine their lowest energy configurations. The computer-generated 3D structure of **13c** is shown in Figure 9.1. We employed the molecular modeling program CERIUS2 (MSI, USA) using COMPASS force field calculation for energy minimisation. Among the various possible diastereomers, the isomer having *syn*-arrangement of two acenaphthenone units appears to be of lowest energy. Furthermore, the unusual upfield shift of the methoxy protons in **13a-c** to around δ 2.8 is attributable to the positioning of the methoxy group right above the acenaphthenone moiety as observed in the energy-minimised structure of **13c**.

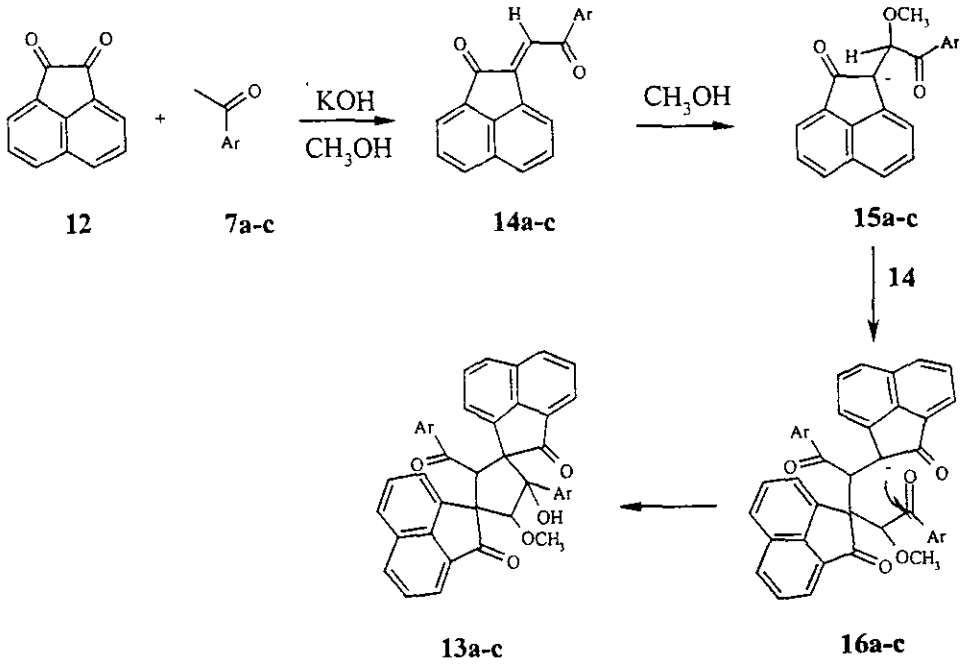
Figure 9.1



9.3.3. Mechanism

A possible mechanism for the formation of **13** involving a dibenzoylalkene-type intermediate **14**[24] is given in Scheme 9.6. The initial Claisen-Schmidt reaction between acenaphthenequinone (**12**) and acetophenone (**7**) gives the acenaphthenone-2-ylidene ketone **14**, which undergoes Michael addition with a molecule of methanol to give the intermediate **15**. Michael addition of **15** to another molecule of **14** followed by cyclization yields **13**. Though analogous Michael addition reaction of *trans*-dibenzoylalkenes with acetophenones resulting in the formation of highly substituted cyclohexanol derivatives is reported in the literature,[25,26] our findings represent the first observation of solvent-assisted dimerisation of a dibenzoylalkene-type system.

Scheme 9.6



9.3.4. Reactions of Dispirocompound

With a view to synthesise a crystalline derivative of **13**, we attempted the dehydration and acetylation reactions of **13**. Our attempts to subject the dispirocompound to dehydration was prompted by the observation that none of the disirocompounds exhibited M^+ peak, but all of them gave strong *M-18* peak in their mass spectra suggesting facile dehydration under suitable reaction conditions. However, our attempts at both dehydration and esterification were unsuccessful. We attribute the reluctance of these compounds to give the corresponding esters to steric factors.

Table 9.1

Reactions of **13a** with	
Acetic Anhydride in THF	No Reaction
Acetyl Chloride in CH_2Cl_2	No Reaction
TFA in CH_2Cl_2	No Reaction
Neat in TFA	Decomposition
Oxalic Acid On Silica	No Reaction
PTSA	No Reaction
P_2O_5	No Reaction

We also carried out the thermolysis and photolysis of dispirocompounds **13a-c**. Thermolysis in *o*-dichlorobenzene yielded unchanged starting material while on neat thermolysis at 270 ^{0} C, decomposition of the starting material occurred. Direct irradiation of a representative dispirocompound such as **13a** in benzene resulted in extensive decomposition of the material.

9.4. Experimental

9.4.1. General Procedures. All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica or aluminium sheets coated with silica (MERCK) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry packed silica (Qualigens 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using Shimadzu-DR-8001 series FTIR spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 400 and 500 MHz on a Bruker FT-NMR spectrometer or GE NMR OMEGA spectrometer with tetramethylsilane internal standard. Chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane (TMS). Elemental analysis was performed at Regional Sophisticated Instrumentation

Centre, Central Drug Research Institute, Lucknow. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

9.4.2. Starting Materials: Acenaphthenequinone was purchased from E. Merck and was used as obtained.

9.4.2.1. 4-Methylacetophenone: 4-Methylacetophenone was prepared using a known procedure.[27]

9.4.2.2. 4-Chloroacetophenone: 4-Chloroacetophenone was prepared using a known procedure.[27]

9.4.3. Preparation of Dispirocompounds

9.4.3.1. Preparation of Dispirocompound 5a. A mixture of acenaphthenequinone (4.60 g, 25 mmol), acetophenone (3.20 g, 27 mmol), and powdered potassium hydroxide (1.00 g) in methanol (30 mL) was stirred around 60 ^{0}C for 12 h and later kept in a refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **5a**

Compound 5a: (4.0 g, 47%); mp >250 ^{0}C; IR ν_{max} (KBr) 3345 (OH), 1711 and 1678 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 215 (ε 44,000), 248 (ε 15,000), 341 nm (ε 4,600); ^{1}H NMR ($CDCl_3$) δ 2.84 (s, 3H, OCH_3), 5.67 (s, 1H), 6.11 (s, D_2O-exchangeable, 1H), 6.23 (s, 1H), 6.6-8.5 (m, 22H, aromatic); ^{13}C NMR ($CDCl_3$) δ 60.3 (OCH_3), 63.6 (C), 65.2 (CH), 70.0 (C), 84.0 (C), 91.2 (CH), 120.8 (CH), 123.0 (CH), 123.9 (CH), 124.2 (CH), 125.1 (CH), 125.4 (CH), 127.2 (CH), 127.5 (CH), 127.6 (CH), 127.7 (CH), 128.1 (CH), 128.4 (CH), 128.8 (CH), 129.8 (CH), 130.6 (C), 131.2 (CH), 132.2 (CH), 133.0 (C), 133.1 (CH), 134.8 (C), 136.5 (C), 138.0 (C), 138.3 (C), 140.6 (C), 142.2 (C), 142.7 (C), 197.9 (C=O), 205.2 (C=O), 208.7 (C=O); MS, *m/z* 582 $(M-H_2O)^+$. Anal. Calcd for $C_{41}H_{28}O_5$: C, 81.98; H, 4.70. Found: 81.71; H, 4.77.

9.4.3.2. Preparation of Dispirocompound 5b. A mixture of acenaphthenequinone (4.60 g, 25 mmol), 4-methylacetophenone (3.60 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 12 h and later kept in a refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **5b**.

Compound 5b: (5.5 g, 60%); mp >250 ^{0}C; IR ν_{max} (KBr) 3348 (OH), 1711, and 1676 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 215 (ε 42,000), 251 (ε 16,000), 341 nm (ε 4,600); ^{1}H NMR ($CDCl_3$) δ 1.92 (s, 3H, CH_3) 2.05 (s, 3H, CH_3), 2.82 (s, 3H, OCH_3), 5.63 (s, 1H), 6.03 (s, D_2O-exchangeable, 1H), 6.21 (s, 1H), 6.4-8.5 (m, 20H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.02 (CH_3), 21.28 (CH_3), 60.15 (OCH_3), 63.63 (C), 64.92 (CH), 69.76 (C), 84.58 (C), 91.12 (CH), 120.80 (CH), 122.53 (CH), 123.35 (CH), 124.11 (CH), 124.59 (CH), 124.91 (CH), 126.77 (CH), 127.16 (CH), 122.77 (CH), 127.84 (CH), 128.01 (CH), 128.11 (CH), 128.43 (CH), 129.58 (CH), 130.21 (C), 130.30 (C), 130.85 (CH), 132.46 (CH), 132.89 (C), 133.74 (C), 134.60 (C), 134.83 (C), 136.82 (C), 137.96 (C), 140.52 (C), 142.06 (C), 142.45 (C), 142.68 (C), 197.19 (C=O), 205.38 (C=O), 208.34 (C=O). MS *m/z* 610 $(M-H_2O)^+$. Anal. Calcd for $C_{43}H_{32}O_5$: C, 82.15; H, 5.13. Found: 82.18; H, 5.19.

9.4.3.3. Preparation of Dispirocompound 5c. A mixture of acenaphthenequinone (4.60 g, 25 mmol), 4-chloroacetophenone (4.20 g, 27 mmol), and powdered potassium hydroxide (1.00 g) in methanol (30 mL) was stirred around 60 ^{0}C for 12 h and later kept in a refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **5c**.

Compound 5c: (3.6 g, 45%); mp >250 ^{0}C; IR ν_{max} (KBr) 3341(OH), 1707, and 1682 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 218 (ε 39,000), 251 (ε 14,000), 341 nm (ε 4,000); ^{1}H NMR ($CDCl_3$) δ 2.8 (s, 3H, OCH_3), 5.57 (s, 1H), 5.94 (s, D_2O-exchangeable, 1H), 6.13 (s, 1H), 6.5-8.1 (m, 20H, aromatic); ^{13}C NMR ($CDCl_3$) δ 60.25 (OCH_3), 63.41 (C), 64.97 (CH), 69.70 (C), 84.26 (C), 90.87 (CH), 121.17 (CH), 122.95 (CH), 123.46 (CH), 124.13 (CH), 125.02 (CH), 125.32 (CH), 127.55 (CH), 127.72 (CH), 128.08 (CH), 128.28 (CH), 128.39 (CH), 128.49 (CH), 129.61

(CH), 130.26 (C), 130.35 (CH), 131.32 (CH), 132.56 (C), 133.06 (CH), 133.43 (C), 134.21 (C), 134.53 (C), 136.37 (C), 137.14 (C), 138.34 (C), 140.00 (C), 141.99 (C), 142.41 (C), 196.38 (C=O), 205.17 (C=O), 207.95 (C=O). Anal. Calcd for $C_{41}H_{26}O_5Cl_2$: C, 73.55; H, 3.91. Found: 73.77; H, 4.04.

9.4.3.4. Attempted Reaction of Acenaphthenequinone with Propiophenone: A mixture of acenaphthenequinone (4.60 g, 25 mmol), propiophenone (3.60 g, 27 mmol), and powdered potassium hydroxide (1.00 g) in methanol (30 mL) was stirred around 60 ^{0}C for 12 h. The reaction was monitored by TLC. The reaction mixture was stirred further for 48 h. TLC showed no new product formation. Unchanged acenaphthenequinone was obtained in quantitative yield (mixture mp 249-252 ^{0}C)

9.4.4. Reactions of 5a

9.4.4.1. Dehydration

9.4.4.1.1. With Trifluoroacetic Acid: A solution of **5a** (20 mg, 2.8 mmol) was treated with trifluoroacetic acid (20 μL in 2 mL dichloromethane) and stirred for 24 h at room temperature. Unchanged **5a** was recovered in near-quantitative amounts (mixture mp >250 ^{0}C).

In a repeat run, a solution of **5a** (20 mg, 2.8 mmol) in trifluoroacetic acid (2 mL) was stirred for 2 h at room temperature. TLC showed complete decomposition of **5a** to a complex mixture of products.

9.4.4.1.2. With Oxalic Acid on Silica: A sample of **5a** (20 mg, 2.8 mmol) in dichloromethane (2 mL) was stirred with oxalic acid adsorbed on silica (20 mg wt/100 mg) for 24 h. Unchanged **5a** was recovered in near-quantitative amounts (mixture mp >250 ^{0}C).

9.4.4.1.3. With *p*-Toluenesulphonic Acid: A sample of **5a** (20 mg, 2.8 mmol) in dichloromethane (2 mL) was stirred with *p*-toluenesulphonic acid (20 mg) for 24 h. Unchanged **5a** was obtained in near-quantitative amounts (mixture mp >250 ^{0}C).

9.4.4.1.4. With P_2O_5: A sample of **5a** (20 mg, 2.8 mmol) in dichloromethane (2 mL) was stirred with P_2O_5 (20 mg,) for 24 h. Unchanged **5a** was obtained in near-quantitative amounts (mixture mp >250 ^{0}C).

9.4.4.1.5. Acetylation: To a solution of **5a** (20 mg, 2.8 mmol) in THF (2 mL), acetic anhydride (20 mL) was added and stirred at room temperature for 3 h and then refluxed for 1h. Unchanged starting material was obtained almost quantitatively (mixture mp >250 ^{0}C).

In a repeat run, a mixture of **5a** (20 mg, 2.8 mmol) acetylchloride (20 μL) and pyridine (50 mL) in dichloromethane (2 mL) was stirred at room temperature for 12 h. Unchanged **5a** was recovered in near-quantitative amounts (mixture mp >250 ^{0}C).

In a repeat run, a mixture of **5a** (20 mg, 2.8 mmol) in dichloromethane (2 mL) acetylchloride (20 μL) and triethylamine (50 mL) was stirred at room temperature for 12 h. Unchanged **5a** was recovered in near-quantitative amounts (mixture mp >250 ^{0}C).

9.4.4.2. Attempted Thermolysis of 5a

9.4.4.2.1. In *o*-Dichlorobenzene. A solution of **5a** (100 mg, 14 mmol) in *o*-dichlorobenzene (25 mL) was refluxed for 12 h and the solvent was removed under reduced pressure. The residue was washed with petroleum ether and recrystallised from methanol-dichloromethane mixture (2:1) to give 86 mg (86%) of unchanged **5a** (mixture mp >250 ^{0}C) as the only isolable material.

9.4.4.2.2. Neat Thermolysis: A sample of **5a** (100 mg, 14 mmol) was heated in a sealed tube around 270 ^{0} C for 6 h. The dark residue was extracted with dichloromethane. TLC showed complete decomposition of the starting material and no new products could be isolated.

9.4.4.3. Photolysis of 5a: A benzene solution of **5a** (200 mg, 28 mmol in 350 mL) was irradiated for 5 h using the output from a Hanovia 450-W medium pressure mercury lamp in a quartz-jacketed immersion well with a pyrex filter. Solvent was removed under reduced pressure and residue was extracted with dichloromethane. TLC showed complete decomposition of the starting material and no new products could be isolated.

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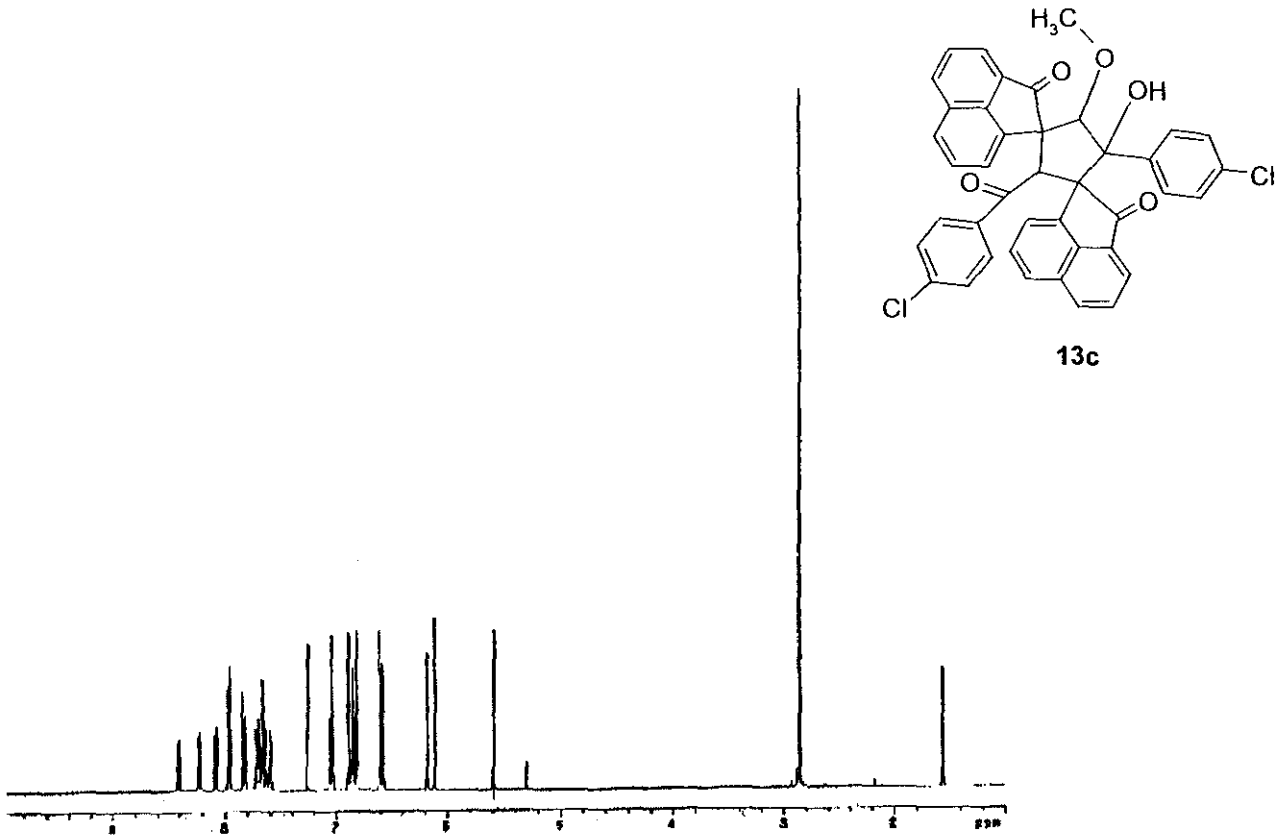
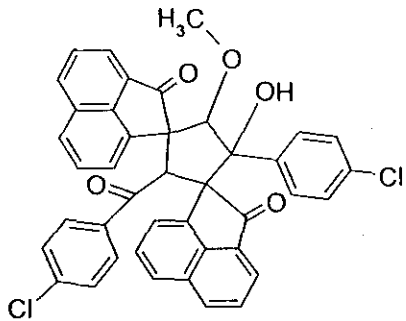


13c

Figure 9.2. ^{1}H NMR spectrum of compound 13c



13c

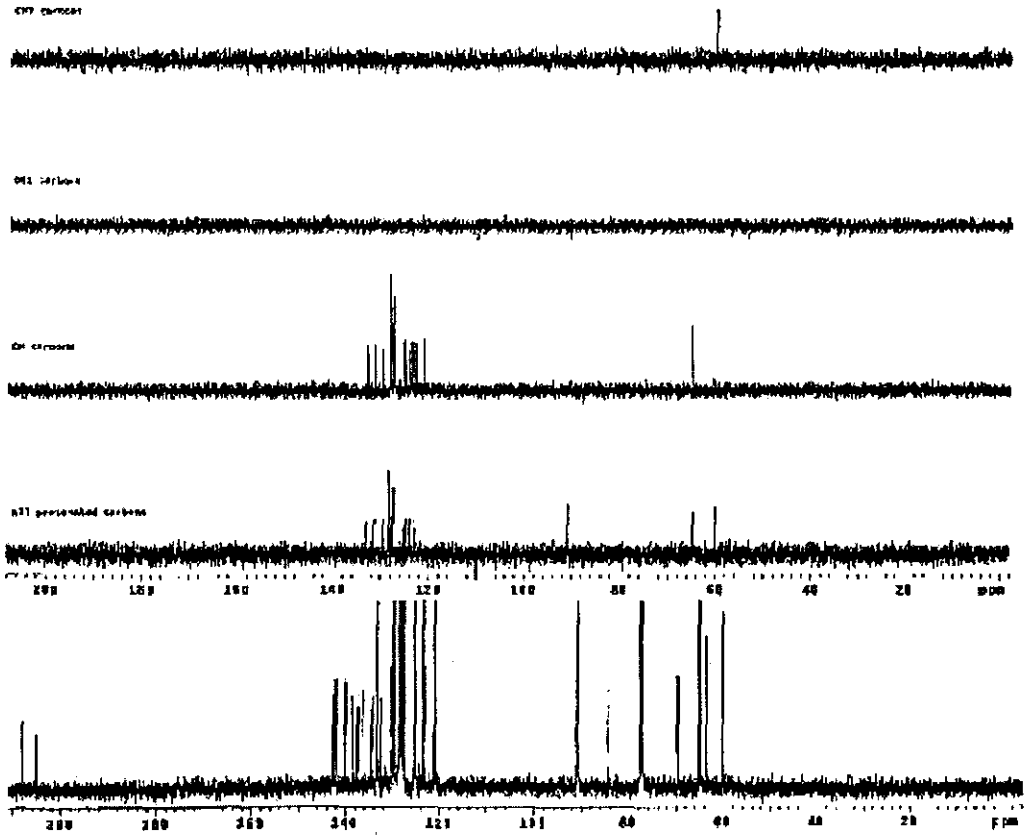


Figure 9.3. ^{13}C NMR spectrum of compound 13c

"Through doubting we come to questioning and through questioning we come to truth....."

Peter Abelard, Paris, 1122