STUDIES ON THE SYNTHESIS AND TRANSFORMATIONS OF A FEW DIBENZOYLALKENE-TYPE SYSTEMS

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IN THE FACULTY OF SCIENCE

BY

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March 2000

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
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CONTENTS

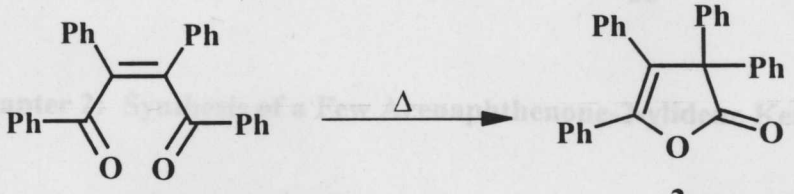
ABSTRACT

The thesis entitled "**Studies on the Synthesis and Transformations of a Few Dibenzoylalkene-type Systems**" has been divided into seven chapters. **Chapter 1** gives a general survey of dibenzoylalkene rearrangement and highlights the significance of the present investigation. **Chapter 2** deals with the reaction of acenaphthenequinone with acetophenones. **Chapter 3** describes the thermal and photochemical studies on a few acenaphthenone-2-ylidene ketones. **Chapter 4** deals with the reactions of phenanthrenequinone with acetophenones. **Chapter 5** describes the thermal rearrangement of phenanthro-2,3-dihydro-2-furanols to phenanthro-2(3H)-furanones. **Chapter 6** deals with the photochemical transformation of phenanthro-2(3H)-furanones. **Chapter 7** describes the cyclic voltammetric studies on some selected dibenzoylalkene-type systems.

Chapter 1: Dibenzoylalkene Rearrangement - An Overview

Dibenzoylalkenes undergo bond reorganisation process thermally and photochemically. The first reported dibenzoylalkene rearrangement was the pyrolysis of *cis*-dibenzoylstilbene (**1**) to tetraphenylcrotonolactone (**2**) by Zenin in 1872 (Scheme A.1). Subsequently, several other reports on the synthesis and transformations of a variety of dibenzoylalkenes have appeared in literature.

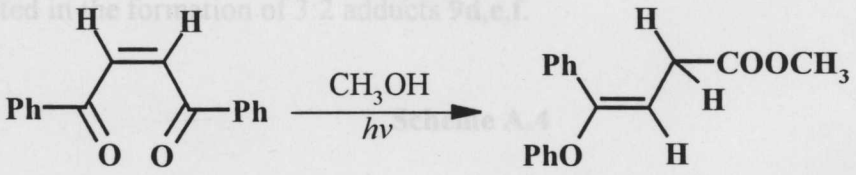
Scheme A.1



1 **2**

It was reported by Cauzzo *et al* that dibenzoylstyrene and dibenzoylethylene undergo cis-trans isomerisation upon irradiation. Later, Zimmermann and Griffin independently observed an interesting rearrangement of dibenzoylalkenes. Griffin observed the rearrangement of *cis*-dibenzoylethylene (**16**) to methyl 4-phenyl-4-phenoxy-3-butenoate (**19**) on irradiation in methanol (Scheme A.2).

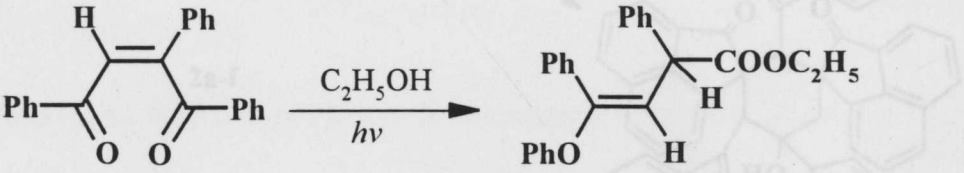
Scheme A.2



16 **19**

Zimmermann *et al* studied the photochemistry of *cis*-dibenzoylstyrene (**3**) in ethanol and they also observed the intramolecular rearrangement involving 1,5-phenyl migration to oxygen to give ethyl 2,4-diphenyl-4-phenoxy-3-butenoate (**20**) (Scheme A.3).

Scheme A.3



3 **20**

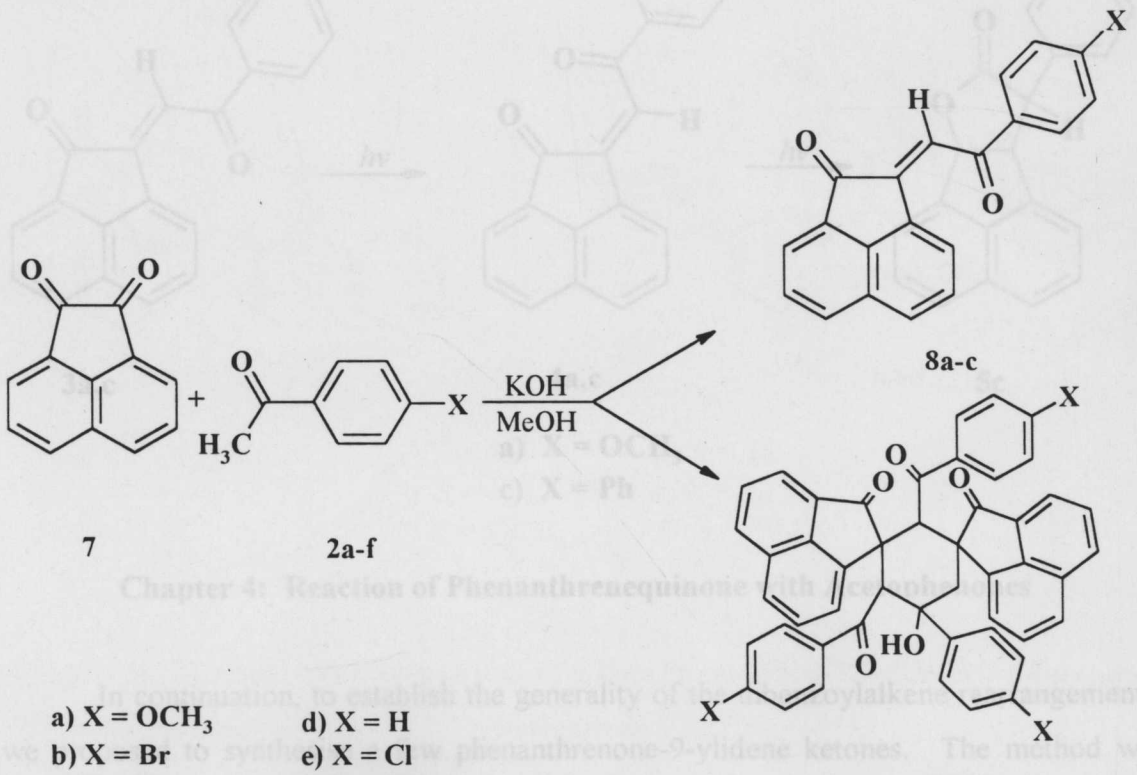
Chapter 2: Synthesis of a Few Acenaphthenone-2-ylidene Ketones

To establish the generality of the dibenzoylalkene rearrangement, we synthesised a few acenaphthenone-2-ylidene ketones containing dibenzoylalkene moiety. The method we adopted was the Claisen-Schimdt condensation of acenaphthenequinone (**7**)

with suitable methyl ketones (**2**). The ketones of our choice were 4-methoxyacetophenone (**2a**), 4-bromoacetophenone (**2b**), 4-phenylacetophenone (**2c**), acetophenone (**2d**), 4-chloroacetophenone (**2e**), and 4-methylacetophenone (**2f**).

We have observed that the reaction of acenaphthenequinone (**7**) with acetophenone and its derivatives gives rise to two types of products depending on the nature of the 4-substituents (Scheme A.4). While **2a**,**b**,**c** on reaction with **7** yielded the corresponding acenaphthenone-2-ylidene ketones **8a**,**b**,**c** in good yields, reaction of **2d**,**e**,**f** with **7** resulted in the formation of 3:2 adducts **9d**,**e**,**f**.

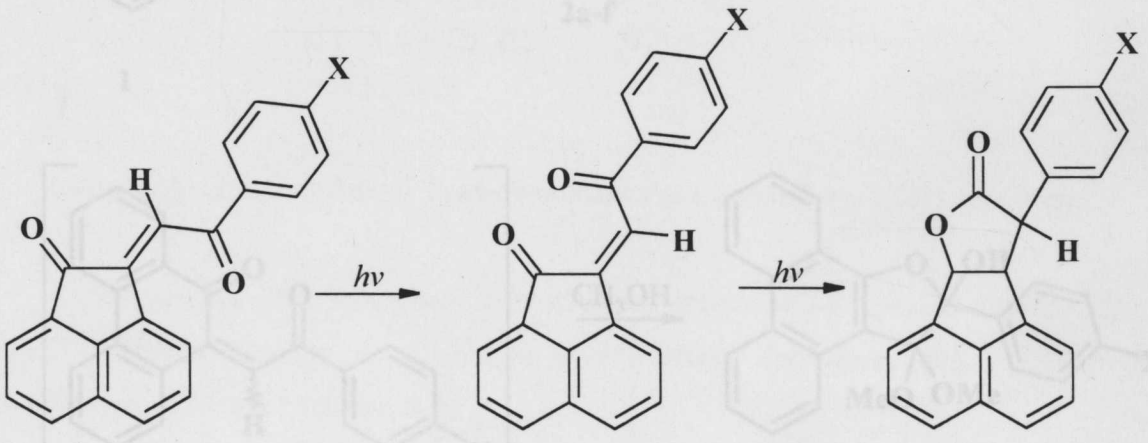
Scheme A.4



Chapter 3: Thermal and Photochemical Studies on a Few Acenaphthenone-2-ylidene Ketones

We studied the thermal and photochemical transformations of acenaphthenone-2-ylidene ketones **3a-c**. These acenaphthenone-2-ylidene ketones underwent extensive decomposition on heating. Upon irradiation, they underwent cis-trans isomerisation and lactonisation analogous to those reported for dibenzoylalkenes (Scheme A.5).

Scheme A.5



3a,c **4a,c** **5c**

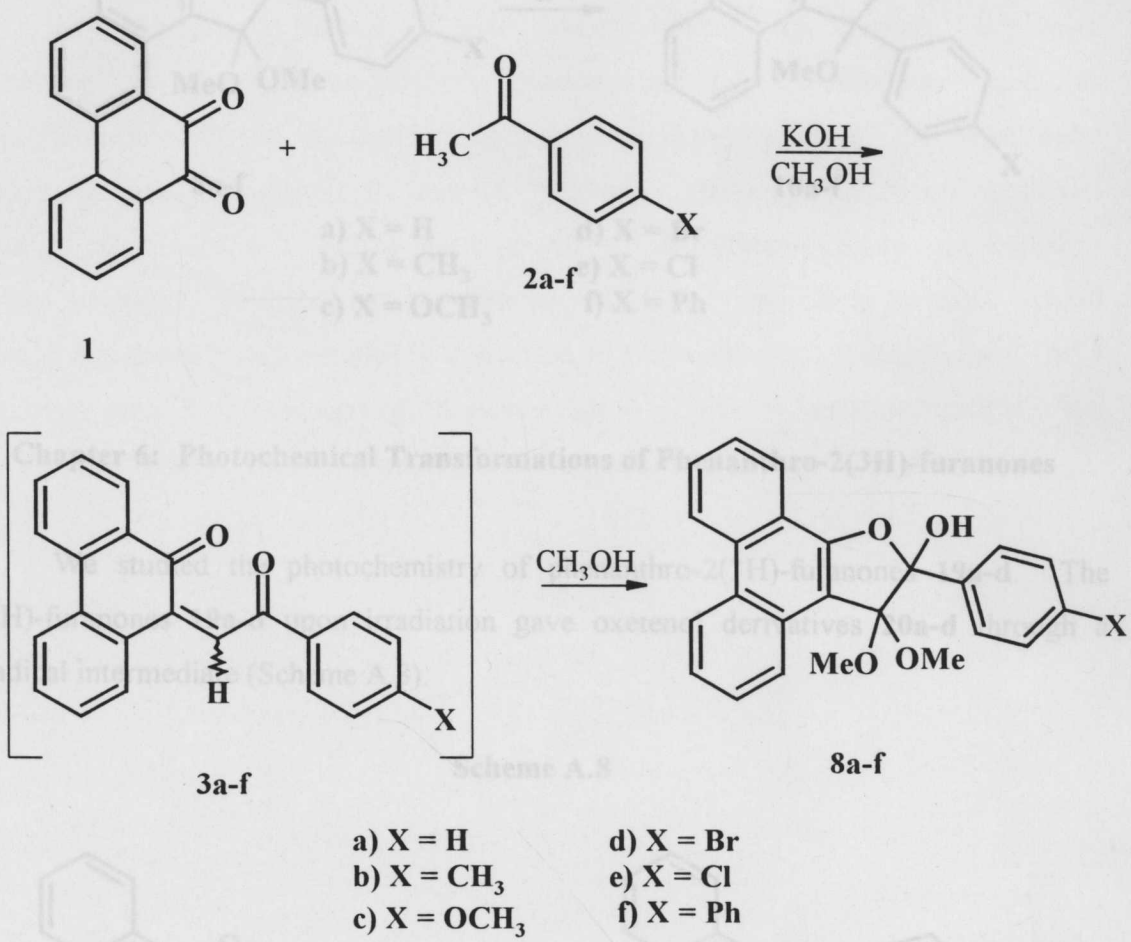
a) X = OCH_3
c) X = Ph

Chapter 4: Reaction of Phenanthrenequinone with Acetophenones

In continuation, to establish the generality of the dibenzoylalkene rearrangement, we proposed to synthesise a few phenanthrenone-9-ylidene ketones. The method we adopted was the Claisen-Schimdt condensation of phenanthrenequinone (**1**) with suitable methyl ketones **2a-f**. The ketones of our choice were acetophenone (**2a**), 4-methylacetophenone (**2b**), 4-methoxy-acetophenone (**2c**), 4-bromoacetophenone (**2d**), 4-chloroacetophenone (**2e**) and 4-phenylacetophenone (**2f**). Here, the initially formed

phenanthrenone-9-ylidene ketones underwent further transformation to give phenanthro-2,3-dihydrofuranols **8a-f** as given in Scheme A.6.

Scheme A.6

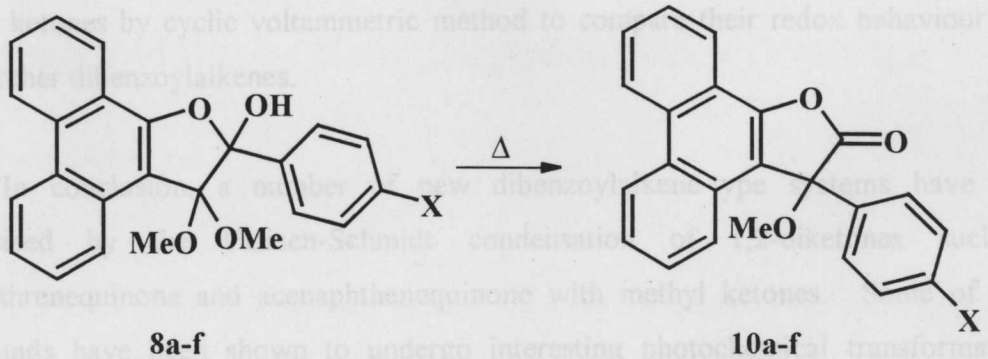


a) X = H **d) X = Br**
b) X = CH_3 **e) X = Cl**
c) X = OCH_3 **f) X = Ph**

Chapter 5: Thermal Transformations of a Few Phenanthro-2,3-dihydro-2-furanol Derivatives

The dihydrofuranols **8a-f** formed by the base-catalysed reaction of phenanthrenequinone and methyl ketones were unstable and underwent rearrangement on heating to give 2(3H)-furanones **10a-f** (Scheme A.7).

Scheme A.7



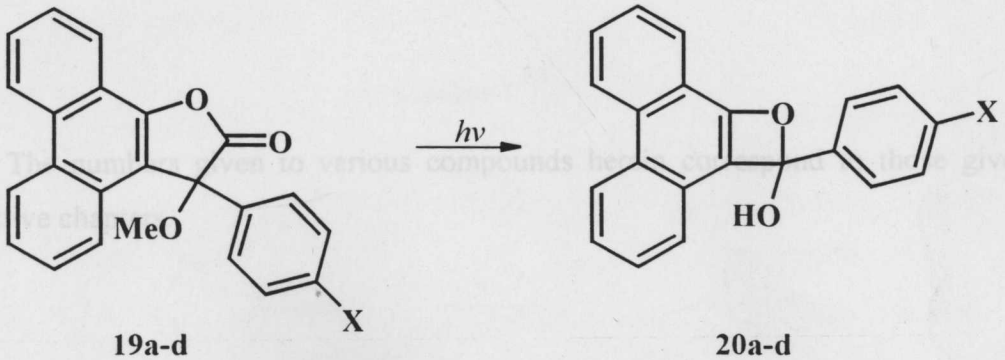
8a-f **10a-f**

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

Chapter 6: Photochemical Transformations of Phenanthro-2(3H)-furanones

We studied the photochemistry of phenanthro-2(3H)-furanones **19a-d**. The 2(3H)-furanones **19a-d** upon irradiation gave oxetenol derivatives **20a-d** through a diradical intermediate (Scheme A.8).

Scheme A.8



19a-d **20a-d**

a) X = H
b) X = OCH_3
c) X = CH_3
d) X = Ph

Chapter 7: Cyclic Voltammetric Studies on a Few Dibenzoylalkene Systems

We studied the redox behaviour of a few *E* and *Z* isomers of acenaphthenone-2-ylidene ketones by cyclic voltammetric method to compare their redox behaviour with that of other dibenzoylalkenes.

In conclusion, a number of new dibenzoylalkene-type systems have been synthesised by the Claisen-Schmidt condensation of 1,2-diketones such as phenanthrenequinone and acenaphthenequinone with methyl ketones. Some of these compounds have been shown to undergo interesting photochemical transformations. Based on our results we conclude that phenanthrenone-9-ylidene ketones are excellent Michael acceptors. Methanol adds to these to yield the corresponding furanols. These furanols are unstable and are slowly converted to phenanthro-2(3H)-furanones. Upon irradiation, these furanones undergo decarbonylation to give oxetenol derivatives. We have proposed plausible mechanisms for all the novel transformations observed by us.

Note: The numbers given to various compounds herein correspond to those given in respective chapters.

Chapter 1

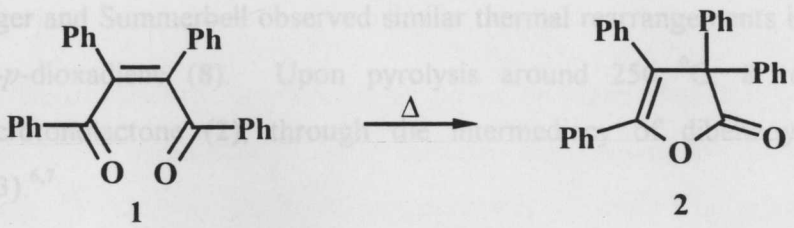
Dibenzoylalkene Rearrangement - An Overview

1.1. Introduction

A rearrangement is a chemical process involving the breaking and forming of σ and π bonds, in which an atom or group moves from one atom to another, resulting in structural reorganisation of the original molecule. Rearrangements have always fascinated organic chemists. They have provided rich and rewarding areas of study particularly in the field of biosynthesis, mechanistic studies and stereochemistry. Many reliable and useful synthetic methods have resulted from the study of rearrangements.

Dibenzoylalkenes can undergo bond reorganisation process thermally and photochemically. The simplest member in this family is 1,4-diphenyl-2-butene-1,4-dione (dibenzoylethylene). The first reported dibenzoylalkene rearrangement is the pyrolysis of *cis*-dibenzoylstilbene (**1**) to tetraphenylcrotonolactone (**2**) by Zenin in 1872 (Scheme 1.1).[1] Subsequently, several other reports on the synthesis and transformations of a variety of dibenzoylalkenes have appeared in literature.

Scheme 1.1



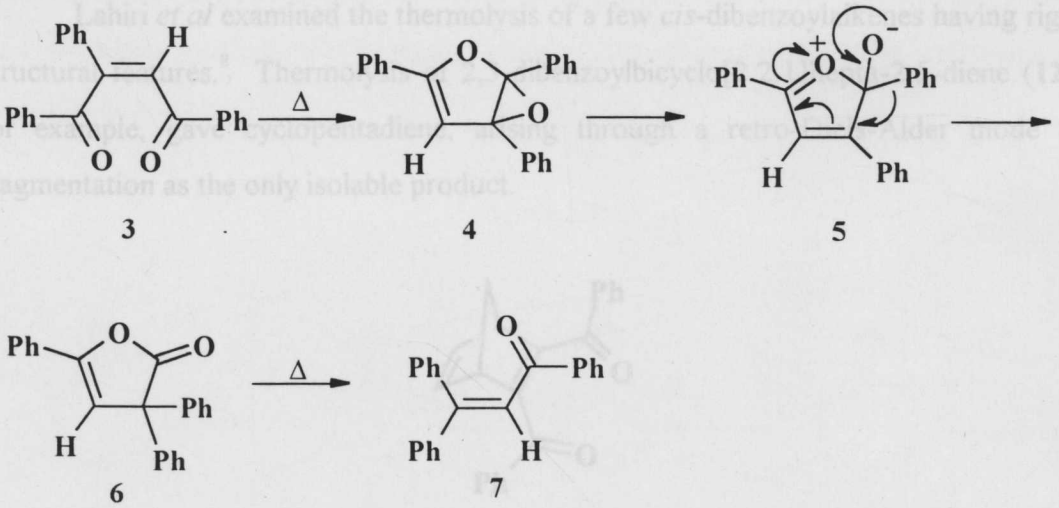
1 **2**

This review summarises the findings on the rearrangements of dibenzoylalkenes under thermal and photochemical conditions.

1.2. Thermal Rearrangement of Dibenzoylalkenes

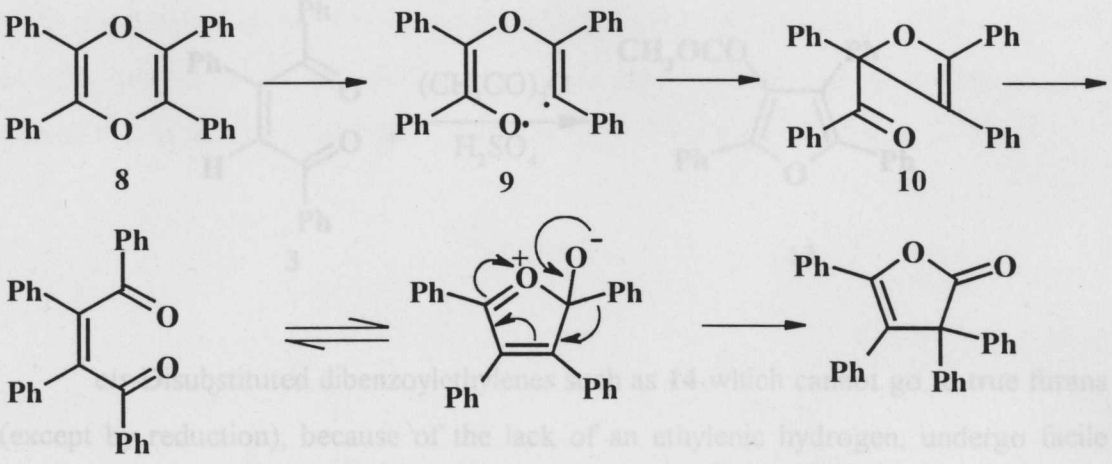
Dibenzoylalkenes undergo a variety of striking reactions on pyrolysis. These reactions include ring closure and ring opening as well as ring enlargement and contraction. *cis*-Dibenzoylstyrene (**3**) on pyrolysis undergoes ring closure to form triphenylcrotonolactone (**6**).[2,3,4] The lactone on further heating eliminates a molecule of carbon monoxide to give β-phenylbenzalacetophenone (**7**) (Scheme 1.2).[5]

Scheme 1.2

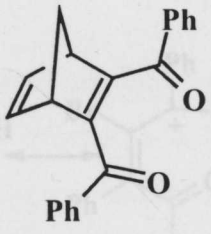


Berger and Summerbell observed similar thermal rearrangements in the case of tetraphenyl-*p*-dioxadiene (**8**). Upon pyrolysis around 250 ^{0}C, **8** rearranges to tetraphenylcrotonolactone (**2**), through the intermediacy of dibenzoylstilbene (**1**) (Scheme 1.3).[6,7]

Scheme 1.3



Lahiri *et al* examined the thermolysis of a few *cis*-dibenzoylalkenes having rigid structural features.[8] Thermolysis of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**12**), for example, gave cyclopentadiene, arising through a retro-Diels-Alder mode of fragmentation as the only isolable product.

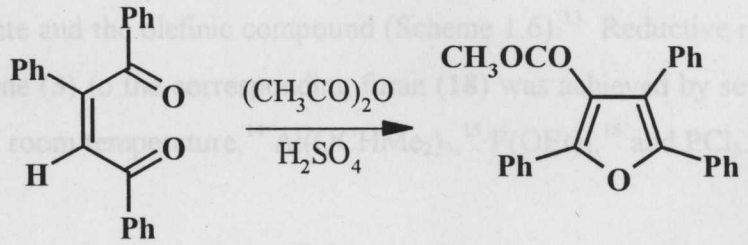


12

1.3. Acid-Catalysed Rearrangements

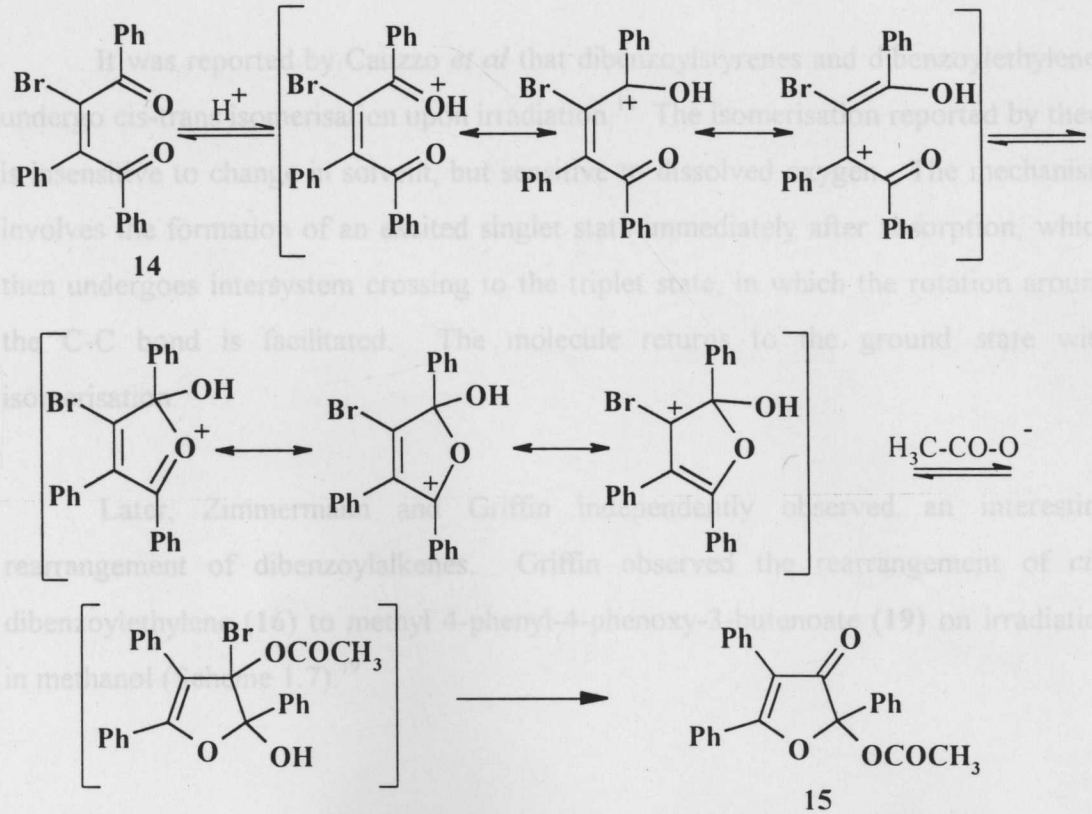
cis-Dibenzoylalkenes are known to be more stable than the corresponding *trans*-isomers.[9,10] Consequently, *trans* isomers are known to isomerise to the corresponding *cis* isomers. Such rearrangements are favoured by protic solvents[11]. However, certain *cis*-dibenzoylalkenes are more readily furanised by acidic reagents, than the corresponding more labile *trans* isomers. *cis*-Dibenzoylstyrene (**3**), for example, on treatment with acetic anhydride in the presence of trace amounts of H_2SO_4, gave 4-acetoxy 2,3,5-triphenylfuran (**13**) (Scheme 1.4).[12]

Scheme 1.4



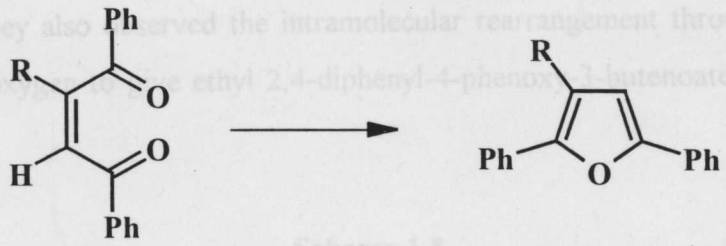
cis-Disubstituted dibenzoylethylenes such as **14** which cannot go to true furans (except by reduction), because of the lack of an ethylenic hydrogen, undergo facile acid-catalysed addition-cyclisation to the corresponding hydroxyfuranones. These observations are explained in terms of reversible protonation of the carbonyl oxygen of the α,β-unsaturated ketone system, and passage through successive ionic intermediates as shown in Scheme 1.5.

Scheme 1.5



Dibenzoylethylene (**16**) on treatment with $(EtO)_3P$, at 120 ^0C in a sealed tube gives 2,5-diphenylfuran (**17**) by the involvement of a covalently bonded cyclic adduct of the phosphate and the olefinic compound (Scheme 1.6).[13] Reductive ring closure of dibenzoylstyrene (**3**) to the corresponding furan (**18**) was achieved by several reagents such as P_2I_4 at room temperature,[14] $Al(OCHMe_2)_3$,[15] $P(OEt)_3$,[16] and PCl_3.[17]

Scheme 1.6



3 (R = Ph)
16 (R = H)

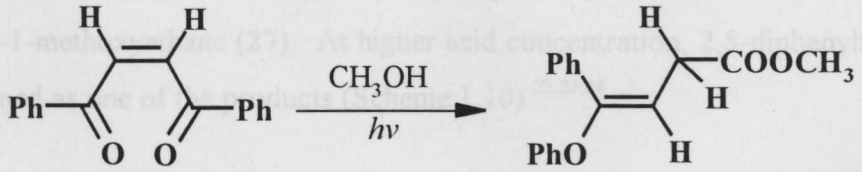
17 (R = H)
18 (R = Ph)

1.4. Photochemical Rearrangements

It was reported by Cauzzo *et al* that dibenzoylstyrenes and dibenzoylethylenes undergo cis-trans isomerisation upon irradiation.[18] The isomerisation reported by them is insensitive to change in solvent, but sensitive to dissolved oxygen. The mechanism involves the formation of an excited singlet state immediately after absorption, which then undergoes intersystem crossing to the triplet state, in which the rotation around the C-C bond is facilitated. The molecule returns to the ground state with isomerisation.

Later, Zimmermann and Griffin independently observed an interesting rearrangement of dibenzoylalkenes. Griffin observed the rearrangement of *cis*-dibenzoylethylene (**16**) to methyl 4-phenyl-4-phenoxy-3-butenoate (**19**) on irradiation in methanol (Scheme 1.7).[19]

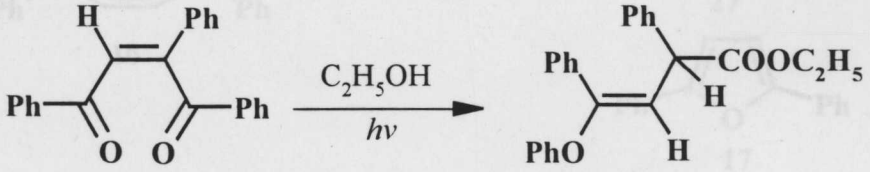
Scheme 1.7



16 **19**

Zimmermann *et al* studied the photochemistry of *cis*-dibenzoylstyrene (**3**) in ethanol and they also observed the intramolecular rearrangement through 1,5-phenyl migration to oxygen to give ethyl 2,4-diphenyl-4-phenoxy-3-butenoate (**20**) (Scheme 1.8).[20]

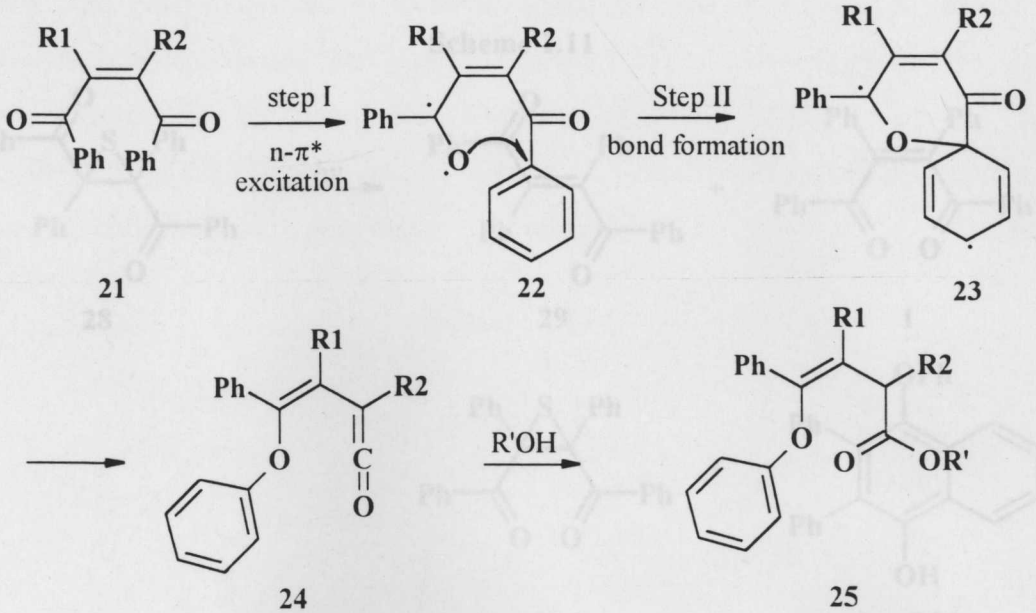
Scheme 1.8



3 **20**

The mechanism of this reaction proposed by Zimmermann is given below in Scheme 1.9.[21]

Scheme 1.9

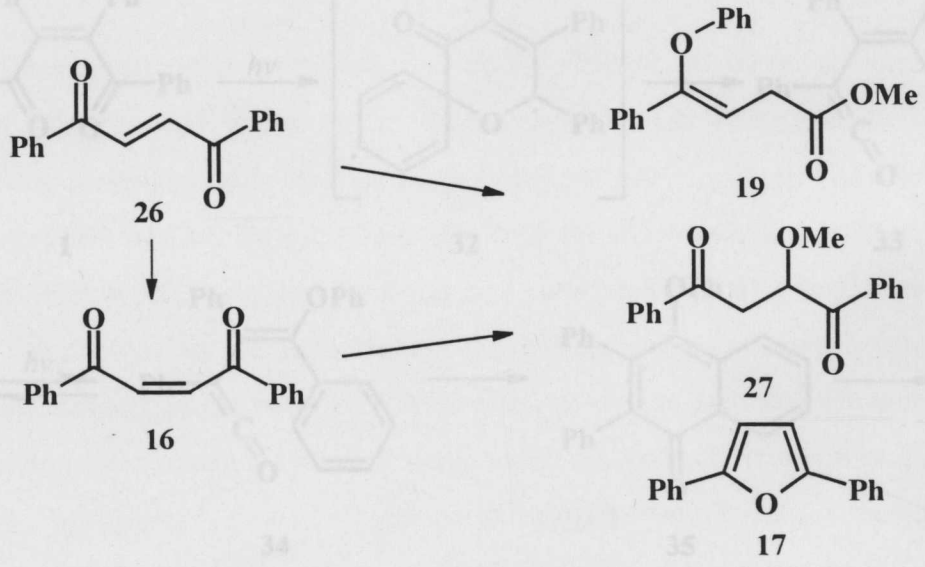


21 **22** **23**

24 **25**

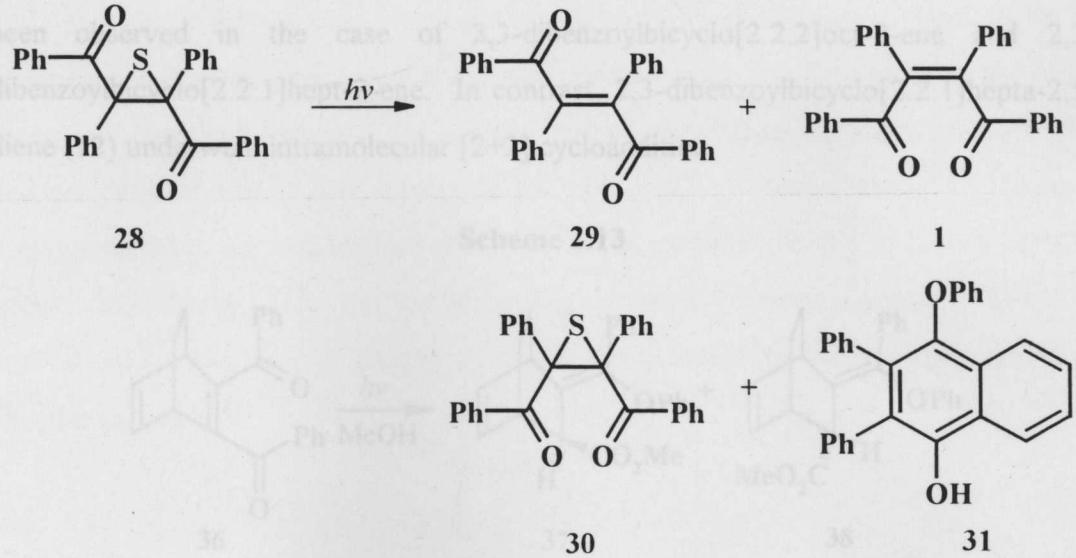
Sugiyama and Kashima have reported that irradiation of 1,2-dibenzoylethylene in acidic methanol gives methyl 4-phenyl-4-phenoxy-3-butenoate (**19**) and 1,2-dibenzoyl-1-methoxyethane (**27**). At higher acid concentration, 2,5-diphenylfuran was also obtained as one of the products (Scheme 1.10).[22,23,24]

Scheme 1.10



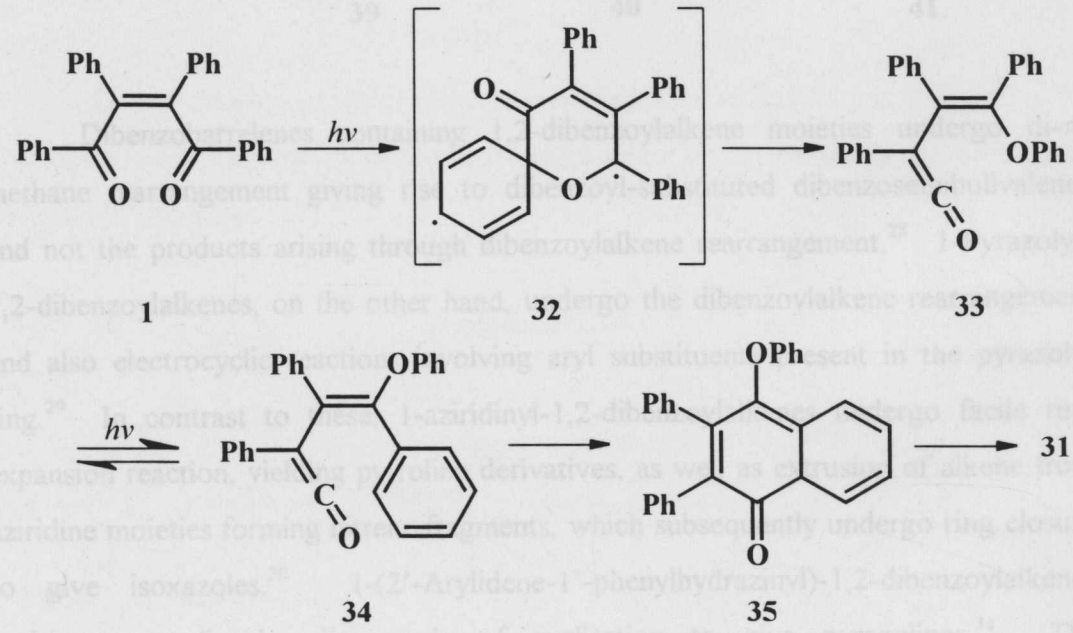
Photolysis of *trans*-dibenzoylstilbene episulphide (**28**) in benzene gives *trans*-dibenzoylstilbene (**29**), *cis*-dibenzoylstilbene episulphide (**30**), *cis*-dibenzoylstilbene (**1**) and 1-hydroxy-2,3-diphenyl-4-phenoxy naphthalene (**31**) (Scheme 1.11).[25]

Scheme 1.11



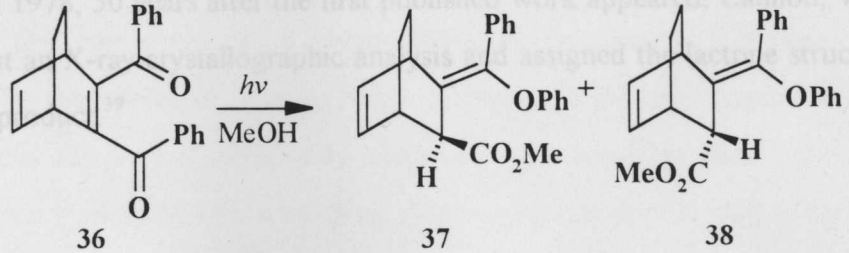
It has been postulated that **31** is a secondary photoproduct and is formed through the intermediacy of **1**. The rearrangement of **1** to **31** may be regarded as a variation of dibenzoylalkene rearrangement (Scheme 1.12).

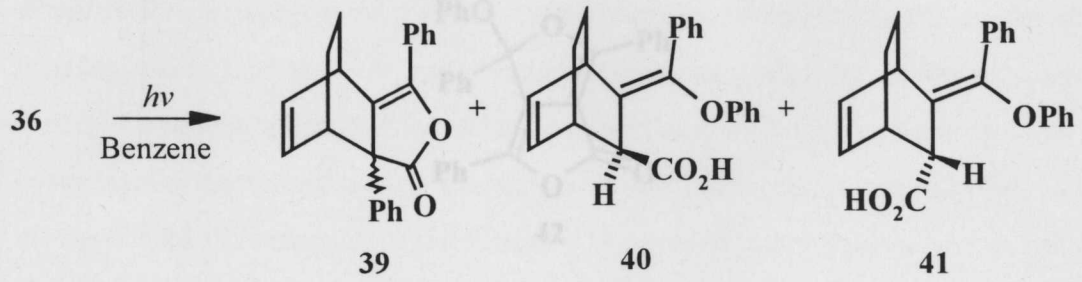
Scheme 1.12



Lahiri *et al* studied the photochemical transformation of a few *cis*-dibenzoylalkenes having rigid structural features wherein cis-trans isomerisation is prevented.[26,27] For e.g., 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**36**) on irradiation in methanol gave a mixture of isomeric esters, whereas in benzene a mixture of carboxylic acids and lactone was formed (Scheme 1.13). Similar rearrangements have been observed in the case of 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene and 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene. In contrast, 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**12**) underwent intramolecular [2+2] cycloaddition.

Scheme 1.13

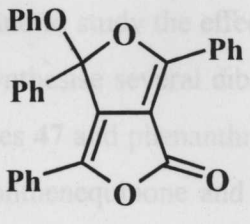




39 40 41

Dibenzobarrelenes containing 1,2-dibenzoylalkene moieties undergo di-π-methane rearrangement giving rise to dibenzoyl-substituted dibenzosemibullvalenes and not the products arising through dibenzoylalkene rearrangement.[28] 1-Pyrazolyl-1,2-dibenzoylalkenes, on the other hand, undergo the dibenzoylalkene rearrangement and also electrocyclic reactions involving aryl substituents present in the pyrazolyl ring.[29] In contrast to these, 1-aziridinyl-1,2-dibenzoylalkenes undergo facile ring expansion reaction, yielding pyrroline derivatives, as well as extrusion of alkene from aziridine moieties forming nitrene fragments, which subsequently undergo ring closure to give isoxazoles.[30] 1-(2'-Arylidene-1'-phenylhydrazinyl)-1,2-dibenzoylalkenes undergo pentadienyl anion mode of cyclisation to give pyrazolines.[31] The photochemistry of 1-imidazolyl-1,2-dibenzoylalkenes and 1-benzimidazolyl-1,2-dibenzoylalkenes have been investigated by George *et al.* These compounds were shown to undergo dibenzoylalkene rearrangement along with other transformations.[32]

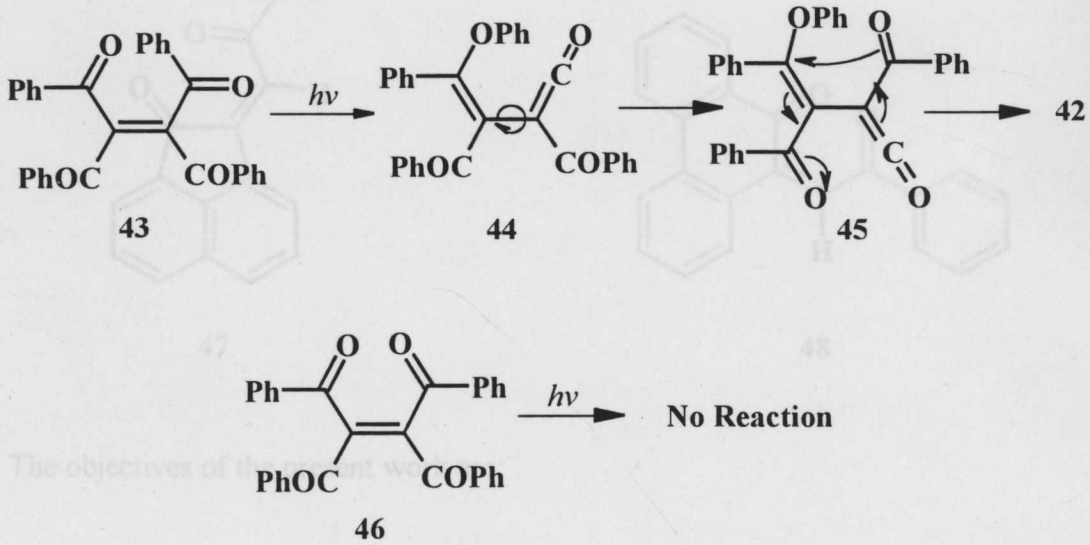
The photochemistry of tetrabenzoylethylene was investigated during the period 1901 to 1948, mainly by van Halben and coworkers.[33-38] Of the two isomeric forms of tetrabenzoylethylene, one crystal form produced **42** upon irradiation while the other was photochemically inert. The major difference between the two forms is the conformation of the benzoyl group; in the photoreactive form, but not in the inert form, a phenyl group was in close proximity of the carbonyl oxygen of the *cis*-benzoyl group. In 1978, 50 years after the first published work appeared, Cannon, White *et al* carried out an X-ray crystallographic analysis and assigned the lactone structure **42** to the photoproduct.[39]



42

The mechanism of photoisomerisation explained by Sander and Rubin involves the formation of a ketene and rotation around a single bond followed by intramolecular cyclisation (Scheme 1.14).[40]

Scheme 1.14



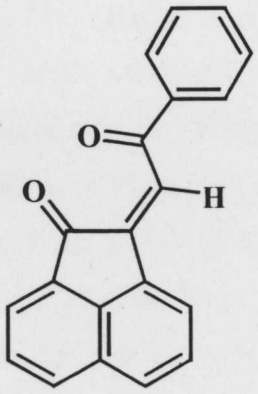
43 44 45 42

46

1.5. Outline of the Research Problem and its Importance

Photochemical and thermal rearrangements of dibenzoylalkenes, besides being mechanistically interesting, are useful methods for the synthesis of furanones. However, the mere presence of dibenzoylalkene component in a molecule does not ensure that the molecule will undergo dibenzoylalkene rearrangement. Though dibenzoylalkenes have received only scant attention, available data suggest that the photochemistry of molecules containing dibenzoylalkene components is influenced by

other chromophores present in them. So we propose to investigate the generality of dibenzoylalkene rearrangement and to study the effect of structure on the course of the rearrangement. Our aim is to synthesise several dibenzoylalkene-type systems such as acenaphthenone-2-ylidene ketones **47** and phenanthrenone-9-ylidene ketones **48** by the condensation reaction of acenaphthenequinone and phenanthrenequinone with methyl ketones. Close examination of the structural features of these systems reveals the 1,4-diarylbut-2-ene-1,4-dione (dibenzoylalkene) component in these systems. Alternatively, these systems can be categorised as quinonemethides which are valuable synthetic intermediates. These dibenzoylalkenes which can double as quinonemethides are expected to undergo a variety of thermal and photochemical rearrangements.



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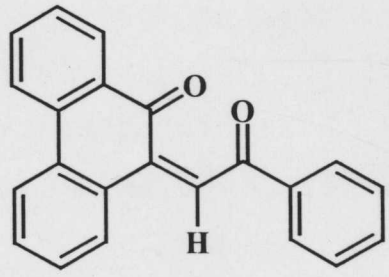

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The objectives of the present work are:

1. To synthesise acenaphthenone-2-ylidene ketones by the Claisen-Schmidt condensation of acenaphthenequinone and methyl ketones.
2. To synthesise phenanthrenone-9-ylidene ketones by the Claisen-Schmidt condensation of phenanthrenequinone and methyl ketones.
3. Thermal studies on acenaphthenone-2-ylidene ketones and phenanthrenone-9-ylidene ketones.
4. Photochemical studies on acenaphthenone-2-ylidene ketones and phenanthrenone-9-ylidene ketones to establish the generality of dibenzoylalkene rearrangement.

5. Cyclic voltammetric studies on these dibenzoylalkenes to compare their redox behaviour with that of the cis and trans isomers of dibenzoylethylene, dibenzoylstyrene, and dibenzoylstilbene. These results should provide some information about their reactivity.
6. To assess and exploit the potential of these systems as quinonemethides.

References

1. Zenin, N. *Ber.* **1872**, *5*, 1104.
2. Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1890**, *57*, 669.
3. Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1890**, *57*, 685.
4. Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1890**, *57*, 689.
5. Blatt, A. H. *J. Org. Chem.* **1950**, *15*, 869-872.
6. Berger, D. R.; Summerbell, R. K. *J. Org. Chem.* **1959**, *24*, 1881-1883.
7. Lahiri, S.; Dabral, V.; George, M. V. *Tetrahedron Lett.* **1976**, *26*, 2259-2262.
8. Lahiri, S.; Dabral, V.; Mahajan, M. P.; George, M. V. *Tetrahedron* **1977**, *33*, 3247-3260.
9. Lutz, R. E.; Bauer, C. R. *J. Am. Chem. Soc.* **1937**, *59*, 2314-2317.
10. Lutz, R. E.; McGinn, C. R. *J. Am. Chem. Soc.* **1942**, *64*, 2855-2859.
11. Bhattacharyya, K.; Prathapan, S.; Scaria, P. M.; Das, P. K.; George, M. V. *J. Photochem. Photobiol., A: Chem.* **1987**, *37*, 147-157.
12. Lutz, R. E.; Bauer, C. R. *J. Org. Chem.* **1954**, *19*, 324-327.
13. Kukhtin, A.; Orekhova, K. M. *Zhur. Obshcheikhim.* 1960, *30*, 1526-1529.(*Chem. Abstr. 55*: 1567)
14. Demirdji, S. H.; Haddadin, M. J.; Issidirides, C. H. *J. Heterocylic Chem.* **1985**, *22*, 495-496.
15. Yasa, I.; Yutake, I. *Nippon Kayaku Kaishi* **1985**, 134-137. (*Chem. Abstr. 102*: 203818v).
16. Haddadin, M. J.; Agha, B. J.; Tatin, R. F. *J. Org. Chem.* 1979, *44*, 494-497.
17. Kumar, A.; David, B. W. *Synth. Commun.* **1995**, *25*, 2071-2078.
18. Cauzzo, G.; Mazzucato, U.; Foffani, A. *Bull. Soc. Chim. Belges.* **1962**, *71*, 834-844. (*Chem. Abstr. 58*: 9784).
19. Griffin, G. W.; O'Connell, E. J. *J. Am. Chem. Soc.* **1962**, *84*, 4148-4149.
20. Zimmermann, H. E.; Durr, H. G.; Lewis, R. G.; Bram, S. *J. Am. Chem. Soc.* **1962**, *84*, 4149-4150.
21. Zimmermann, H. E.; Durr, H. G.; Givens, R. S.; Lewis, R. G. *J. Am. Chem. Soc.* **1962**, *89*, 1863-1874
22. Sugiyama, N.; Kashima, C. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1875-1877.

23. Sugiyama, N.; Kataoka, H.; Kashima, C. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1353-1359.

24. Kashima, C.; Kataoka, H.; Tanaka, K.; Sugiyama, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1473-79.

25. Padwa, A.; Crumrine, D.; Shebber, A. *J. Am. Chem. Soc.* **1966**, *88*, 3064-3069.

26. Lahiri, S.; Dabral, V.; Chauhan, S. M. S.; Chakachery, E.; Kumar, C. V.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* **1980**, *45*, 3782-3790.

27. Maji, D.; Singh, R.; Mostafa, G.; Ray, S.; Lahiri, S. *J. Org. Chem.* **1996**, *61*, 5165-5168.

28. Kumar, C. V.; Murty, B. A. R. C.; Lahiri, S.; Chakachery, E.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4923-4929.

29. Lohray, B. B.; Kumar, C. V.; Das, P. K.; George M. V. *J. Org. Chem.* **1984**, *49*, 4647-4656.

30. Barik, R.; Kumar, C. V.; Das P. K.; George M. V. *J. Org. Chem.* **1985**, *50*, 4309-4317.

31. Prathapan, S.; Scaria, P. M.; Bhattacharyya, K.; Das, P. K.; George, M. V. *J. Org. Chem.* **1986**, *51*, 1972-1976.

32. Barik, R.; Bhattacharyya, K.; Das P. K.; George M. V. *J. Org. Chem.* **1986**, *51*, 3420-3428.

33. Keller, H.; van Halben, H. *Helv. Chim. Acta* **1944**, *27*, 1253-1275.

34. Schimid, H.; Hochweber, M.; van Halben, H. *Helv. Chim. Acta* **1946**, *29*, 1466-1472.

35. Schimid, H.; Hochweber, M.; van Halben, H. *Helv. Chim. Acta* **1947**, *30*, 423-431.

36. Schimid, H.; Hochweber, M.; van Halben, H. *Helv. Chim. Acta* **1947**, *30*, 1135-1146.

37. Schimid, H.; Hochweber, M.; van Halben, H. *Helv. Chim. Acta* **1948**, *31*, 1899-1907.

38. Jack, R. C.; Vincent, A. P.; White, P. L.; Allan, H. *Aust. J. Chem.* **1978**, *31*, 1265-1283.

39. Cannon, J. R.; Patrick, V. A.; Raston, C. L.; White, A. H. *Aust. J. Chem.* 1978, 31, 1265-1270.

40. Rubin, M. B.; Sander, W. *Tetrahedron Lett.* **1987**, *28*, 5137-5140.

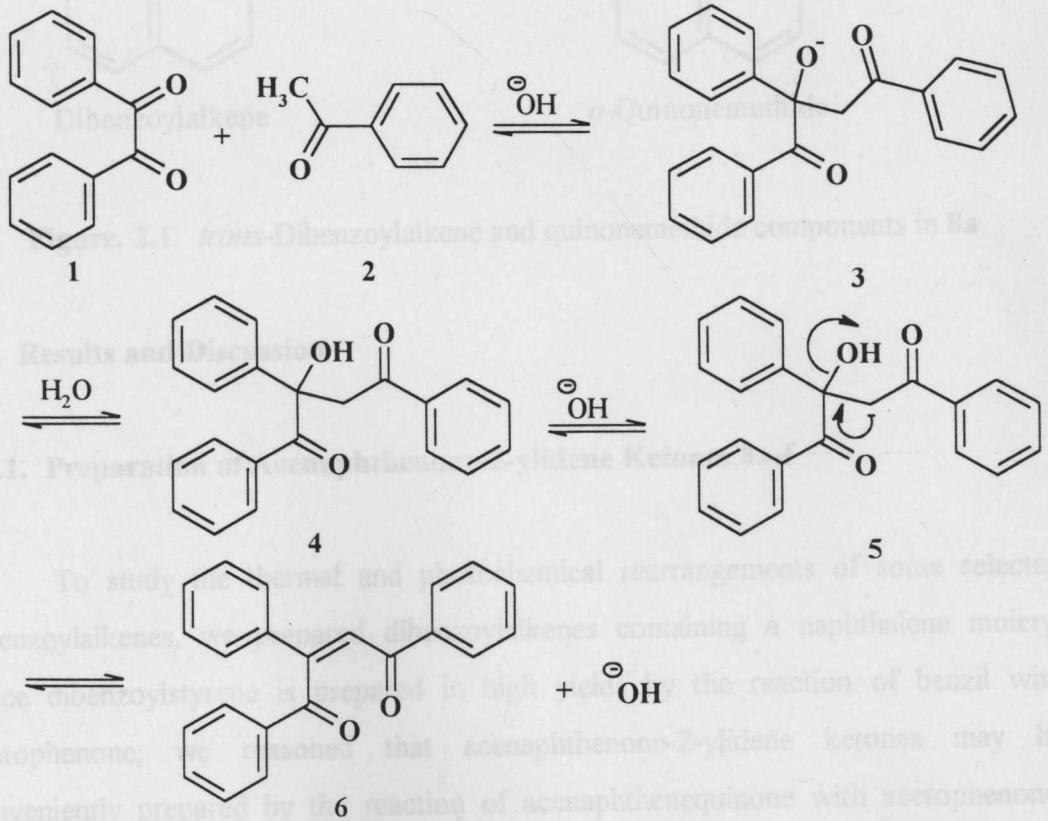
Chapter 2

Synthesis of a Few Acenaphthenone-2-ylidene Ketones

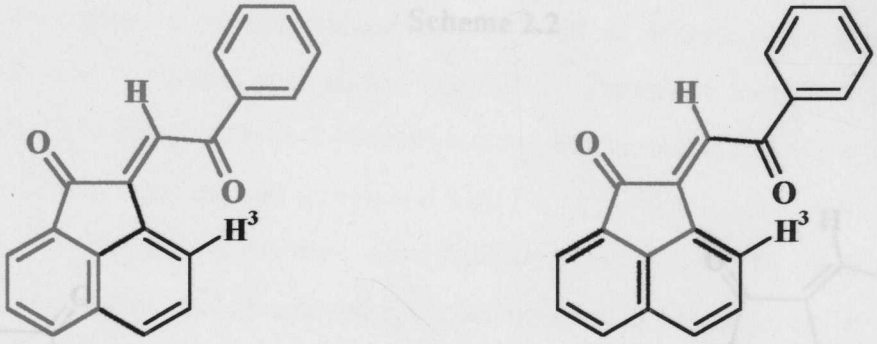
2.1. Introduction

α,β-Unsaturated ketones are conveniently prepared by Claisen-Schmidt condensation.[1,2] It is the Aldol condensation and subsequent elimination of a water molecule in presence of a basic catalyst. The Aldol reaction, usually carried out in protic solvents, is one of the most versatile methods in organic synthesis.[3,4] By application of this reaction, a great number of aldols and related compounds have been prepared from various carbonyl compounds. 1,2-Diketones like benzil (**1**), for example, undergo condensation with acetophenone (**2**) to yield dibenzoylstyrene (**6**). The probable mechanism for the formation of dibenzoylstyrene is given in Scheme 2.1. The reaction is simply the nucleophilic addition of an enolate ion onto the carbonyl group of another, unionised molecule. Dehydration of β-hydroxyketone formed in this reaction yields an α,β-unsaturated carbonyl compound.[5,6,7]

Scheme 2.1



In the present study, we propose to synthesise several acenaphthenone-2-ylidene ketones **8a-f** by the Claisen-Schmidt condensation of acenaphthenequinone with methyl ketones. Close examination of the structural features of acenaphthenone-2-ylidene ketones indicates their similarity with dibenzoylalkenes. Alternatively, they may be regarded as quinonemethides (Figure 2.1). So, these acenaphthenone-2-ylidene ketones, upon irradiation, are expected to undergo dibenzoylalkene rearrangement and/or cis-trans isomerisation. Also, dibenzoylalkenes are good Michael acceptors. They undergo Michael addition with active methylene compounds.[8-12] As quinonemethides, **8a-f** are expected to undergo a variety of transformations including Diels-Alder reactions. Our attempts to synthesise acenaphthenone-2-ylidene ketones by the reaction of acenaphthenequinone with acetophenone are discussed in this chapter.



Dibenzoylalkene *o*-Quinonemethide

Figure. 2.1. *trans*-Dibenzoylalkene and quinonemethide components in **8a**

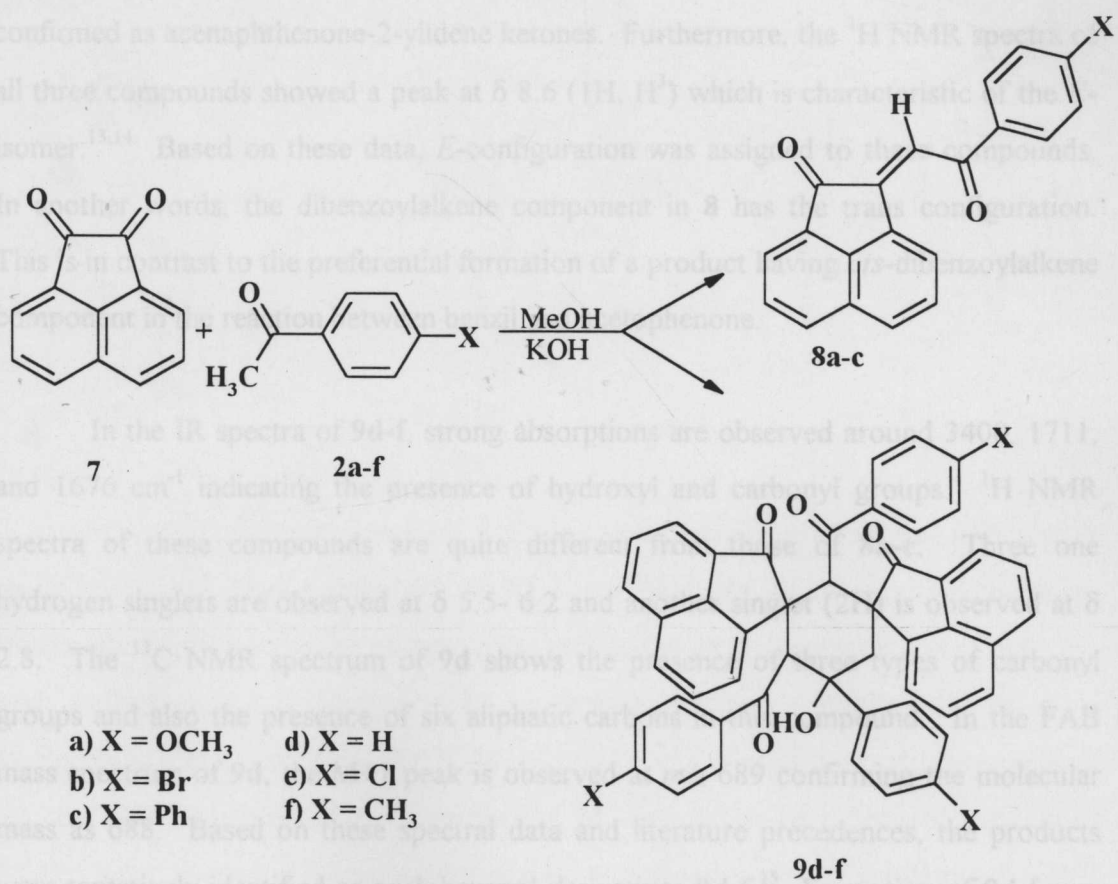
2.2. Results and Discussion

2.2.1. Preparation of Acenaphthenone-2-ylidene Ketones 8a-f

To study the thermal and photochemical rearrangements of some selected dibenzoylalkenes, we prepared dibenzoylalkenes containing a naphthalene moiety. Since dibenzoylstyrene is prepared in high yields by the reaction of benzil with acetophenone, we reasoned that acenaphthenone-2-ylidene ketones may be conveniently prepared by the reaction of acenaphthenequinone with acetophenone.

Thus, we treated acenaphthenequinone (7) with acetophenones **2a-f** in methanol in the presence of potassium hydroxide (Scheme 2.2). Methyl ketones of our choice were 4-methoxyacetophenone (**2a**), 4-bromoacetophenone (**2b**), 4-phenylacetophenone (**2c**), acetophenone (**2d**), 4-chloroacetophenone (**2e**), and 4-methylacetophenone (**2f**) which were synthesised using previously reported procedures. We observed that the reaction of acenaphthenequinone (7) with acetophenone and its derivatives gave two types of products depending on the nature of the 4-substituents (Scheme 2.2). While **2a**,**b**,**c** on reaction with 7 yielded the corresponding acenaphthenone-2-ylidene ketones **8a**,**b**,**c** in good yields, reaction of **2d**,**e**,**f** with 7 resulted in the formation of 3:2 adducts **9d**,**e**,**f**. The structures of the adducts **8a-c** were established on the basis of analytical results and spectral data and structures of the adducts **9d-f** were tentatively assigned on the basis of literature precedences, analytical results and spectral data.

Scheme 2.2



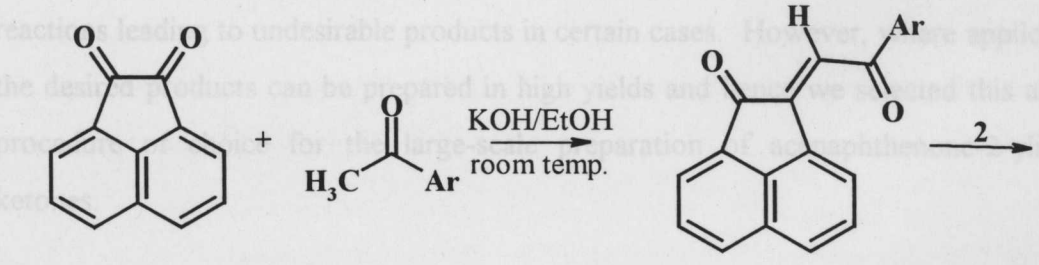
Compound **8a**, which was obtained in 50% yield, showed two strong absorption in the IR spectrum at 1714 and 1655 cm^{-1}. These are due to the presence of two carbonyl groups in the compound. The absorption at 1714 cm^{-1} is assigned to indenone-type carbonyl group present in these systems. UV absorptions at 340 and 280 nm are due to the presence of naphthalene residue in the compound. In the NMR spectrum, the vinylic and aromatic protons of the compound were observed as a multiplet in the aromatic region δ 7.5-9. The molecular ion peak of this compound was observed at *m/z* 284 confirming its identity. The structure was further confirmed by elemental analysis, which gave acceptable data.

Compounds **8b** and **8c** showed very similar spectral behavior with **8a**. These compounds also showed the IR absorptions at ~1714 and at ~1660 cm^{-1} due to two carbonyls. The UV spectra of all these compounds were similar and were dominated by the absorption of naphthalene residue. ^1H NMR of all these were comparable and these showed acceptable analysis and mass data. Therefore, these compounds were confirmed as acenaphthenone-2-ylidene ketones. Furthermore, the ^1H NMR spectra of all three compounds showed a peak at δ 8.6 (1H, H^3) which is characteristic of the *E*-isomer.[13,14] Based on these data, *E*-configuration was assigned to these compounds. In another words, the dibenzoylalkene component in **8** has the trans configuration. This is in contrast to the preferential formation of a product having *cis*-dibenzoylalkene component in the reaction between benzil and acetophenone.

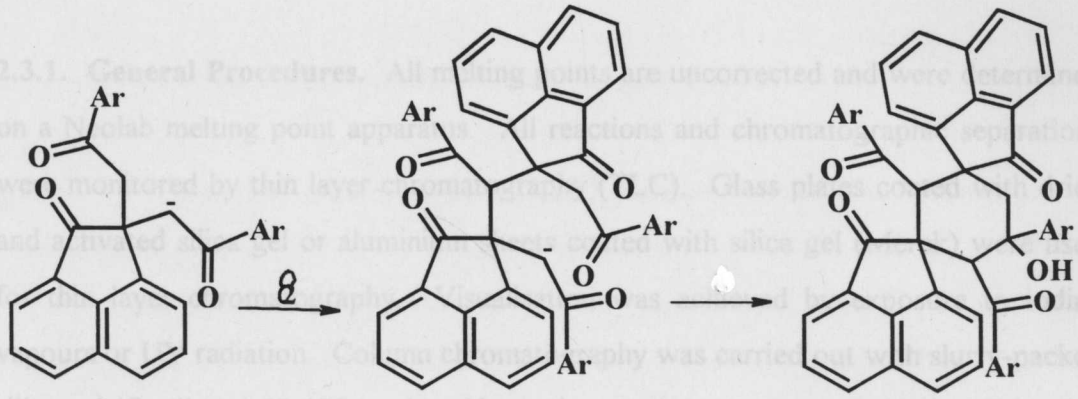
In the IR spectra of **9d-f**, strong absorptions are observed around 3400, 1711, and 1676 cm^{-1} indicating the presence of hydroxyl and carbonyl groups. ^1H NMR spectra of these compounds are quite different from those of **8a-c**. Three one hydrogen singlets are observed at δ 5.5- 6.2 and another singlet (2H) is observed at δ 2.8. The ^{13}C NMR spectrum of **9d** shows the presence of three types of carbonyl groups and also the presence of six aliphatic carbons in this compound. In the FAB mass spectrum of **9d**, the M+1 peak is observed at *m/z* 689 confirming the molecular mass as 688. Based on these spectral data and literature precedences, the products were tentatively identified as cyclohexanol derivatives **9d-f**.[15] Formation of **9d-f** may be understood in terms of the pathways shown in Scheme 2.3. The initially-formed *E*-

acenaphthenone-2-ylidene ketones underwent further Michael addition with acetophenones followed by intramolecular aldol condensation to give the cyclohexanol derivatives. The formation of highly substituted cyclohexanol derivatives by analogous reaction of *trans*-dibenzoylalkenes with acetophenones were studied by Al-Arab *et al.*[15,16]

Scheme 2.3



7 2 8



10 11 9

We subjected **9d** to chemical degradation for obtaining additional information on its structure. Thus thermolysis of **9d** was carried out under various conditions. Neat heating of **9d** above its melting point resulted in total decomposition of **9d**. No new products could be isolated. In another experiment, a solution of **9d** in *o*-dichlorobenzene was refluxed for 12 h. Work up of the reaction mixture resulted in the near-quantitative recovery of unchanged **9d**. Irradiation of a benzene solution of **9d** also led to extensive decomposition and no new products could be isolated.

Thus, the base-catalysed reaction between acetophenones and acenaphthenequinone appears to be a suitable method for the preparation of some acenaphthenone-2-ylidene ketones. Some of these derivatives have already been prepared by a Wittig reaction between acenaphthenequinone and the corresponding α-aroylmethylenetriphenylphosphorane. α-Haloacetophenones (prepared by the α-halogenation of acetophenones) are required for this process whereas the process developed by us employs acetophenones as such. Thus, though the novel method developed by us is simple and more convenient, it suffers from the possibility of side reactions leading to undesirable products in certain cases. However, where applicable, the desired products can be prepared in high yields and hence we selected this as the procedure of choice for the large-scale preparation of acenaphthenone-2-ylidene ketones.

2.3. Experimental

2.3.1. 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 gel or aluminium sheets coated with silica gel (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 gel (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 and 75 MHz respectively on a Brucker 300 FT-NMR spectrometer or a GE NMR OMEGA spectrometer with tetramethylsilane as 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.

2.3.2. Starting materials. Acenaphthenequinone was purchased from E. Merck and was used as obtained.

2.3.2.1. 4-Methoxyacetophenone (2a): 4-Methoxyacetophenone was prepared using a known procedure[17] (90%, bp 265 ^{0}C).

2.3.2.2. 4-Bromoacetophenone (2b): 4-Bromoacetophenone was prepared using a known procedure[17] (75%, bp 255 ^{0}C).

2.3.2.3. 4-Phenylacetophenone (2c): 4-Phenylacetophenone was prepared using a known procedure[17] (76%, mp 120 ^{0}C).

2.3.2.4. 4-Chloroacetophenone (2e): 4-Chloroacetophenone was prepared using a known procedure[17] (75%, bp 237 ^{0}C).

2.3.2.5. 4-Methylacetophenone (2f): 4-Methylacetophenone was prepared using a known procedure[17] (85%, bp 93-94 ^{0}C/7 mmHg).

2.3.3. Preparation of Acenaphthenone-2-ylidene Ketones

2.3.3.1. Preparation of Acenaphthenone-2-ylidene Ketone 8a. A mixture of acenaphthenequinone (4.6 g, 25 mmol), 4-methoxyacetophenone (4.1 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **8a**.

Compound 8a: (4.4 g, 56%); mp 160-162 ^{0}C; IR ν_{max} (KBr) 1714, and 1655 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 233 (ε 48,000), 281 (ε 20,000), 323 nm (ε 16,700); ^{1}H NMR ($CDCl_3$) δ 3.9 (3H, s, methoxy) 6.9-8.7 (11H, m, aromatic and vinylic); MS, *m/z* 314 (M^+), 286, 252, 105, 91 and other peaks. Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.25; H, 4.49. Found: C, 79.78; H, 4.58.

2.3.3.2. Preparation of Acenaphthenone-2-ylidene Ketone 8b. A mixture of acenaphthenequinone (4.6 g, 25 mmol), 4-bromoacetophenone (5.4 g, 27 mmol), and

powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **8b**.

Compound 8b: (4.27 g, 47%); mp 198-200 ^{0}C; IR ν_{max} (KBr) 1714, and 1659 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 230 (ε 55,700), 284 (ε 26,000), 341 nm (ε 22,000); ^{1}H NMR ($CDCl_3$) δ 7.2-8.8 (m, aromatic and vinylic); MS, *m/z* 364 {$(M+2)^+$}, 362 (M^+), 337, 335, 255, 153, 151, and other peaks. Anal. Calcd for $C_{20}H_{11}O_2Br$: C, 66.12; H, 3.05. Found: C, 66.30; H, 3.09.

2.3.3.3. Preparation of Acenaphthenone-2-ylidene Ketone 8c. A mixture of acenaphthenequinone (4.6 g , 25 mmol), 4-phenylacetophenone (5.3 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **8c**.

Compound 8c: (4 g, 45%); mp 187-189 ^{0}C; IR ν_{max} (KBr) 1716, and 1657 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 230 (ε 40,000), 287 (ε 20,000), 340 nm (ε 17,000); ^{1}H NMR ($CDCl_3$) δ 7.3-8.8 (m, aromatic and vinylic); MS, *m/z* 360 (M^+), 332, 256, 181, 152 and other peaks. Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.67; H, 4.47. Found: C, 86.12; H, 4.67.

2.3.4. Preparation of Cyclohexanols

2.3.4.1. Preparation of Cyclohexanol 9d. A mixture of acenaphthenequinone (4.6 g, 25 mmol), acetophenone (3.2 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **9d**.

Compound 9d: (4 g, 47%); mp 256-258 ^{0}C; IR ν_{max} (KBr) 3352 (OH), 1711, and 1676 (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 (DMSO-d_6) δ 2.8 (s, 2H, CH_2), 5.6 (s, 1H), 6.1 (s, 1H), 6.2 (s, 1H), 6.6-8.5 (m, 27H, aromatic); ^{13}C NMR ($CDCl_3$) δ 59, 63, 64, 69, 84, 90, 120, 122, 123, 123.5, 124, 124.5, 126, 126.5, 127, 127.2, 127.5, 127.7, 128, 129, 130, 131, 132, 137, 140, 197, 205, 207; FAB-MS, *m/z* 689 $(M+H)^+$.

In a repeat run, reaction of acenaphthenequinone (4.6 g, 25 mmol) with 2 equivalents of acetophenone (6.4 g, 54 mmol) under analogous conditions gave **9d** in 25% yield.

2.3.4.2. Preparation of Cyclohexanol 9e. A mixture of acenaphthenequinone (4.6 g, 25 mmol), 4-chloroacetophenone (4.2 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **9e**.

Compound 9e: (3.6 g, 45%); mp 216-219 ^{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, 2H, CH_2), 5.57 (s, 1H), 5.94 (s, 1H), 6.13 (s, 1H), 6.5-8.1 (m, 24H, aromatic).

2.3.4.3. Preparation of Cyclohexanol 9f. A mixture of acenaphthenequinone (4.6 g, 25 mmol), 4-methylacetophenone (3.6 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **9f**.

Compound 9f: (5.5 g, 60%); mp 216-218 ^{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 2.1 (s, 3H), 2.25 (s, 6H), 2.8 (s, 2H, CH_2), 5.63 (s, 1H), 5.88 (s, 1H), 6.16 (s, 1H), 6.4-8.4 (m, 24H, aromatic); ^{13}C NMR ($CDCl_3$) δ 29, 59, 63, 64, 69, 84, 90, 120, 126, 126.7, 127, 127.5, 132, 140, 142, 196, 204, 207.

2.3.5. Attempted Thermolysis of 9d

2.3.5.1. In *o*-Dichlorobenzene. A solution of **4d** (100 mg, 14 mmol) in *o*-dichlorobenzene 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 the unchanged starting material (**9d**). mp 256-258 ^{0}C (mixture melting point).

2.3.5.2. Neat Thermolysis. A sample of **9d** (100 mg, 14 mmol) was heated in a sealed tube around 270 ^{0}C for 6 h. The solid was extracted with dichloromethane. TLC showed complete decomposition of the starting material.

2.3.6. Photochemical Transformation of 9d. A benzene solution of **9d** (200 mg, 28 mmols in 350 mL) was irradiated for 5 h using the out put 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 the residue was extracted with dichloromethane. TLC showed complete decomposition of the starting material and no new products could be isolated.

References

1. Nielsen, A. T.; Houliban, W. J. *Organic Reactions* **1968**, *16*, 1-438.
2. Claisen, L.; Claparede, A. *Ber.* **1881**, *14*, 2460.
3. House, H.O. *Modern Synthetic Reactions*; 2nd ed.; Benjamin: Menlopark, CA, **1972**.
4. Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: Ithaca, New York; **1953**; pp 673-699.
5. House, H. O.; Ro, R. S. *J. Am. Chem. Soc.* **1958**, *80*, 2428-2433.
6. Payne, G. B.; Willaims, P. H. *J. Org. Chem.* **1961**, *26*, 651-659.
7. Buckles, R. E.; Mock, G. V.; Locatell, L. Jr. *Chem. Rev.* **1955**, *55*, 656-692.
8. Saito, K.; Kambe, S.; Nakano, Y.; Sakurai, A.; Midorikawa, H. *Synthesis* **1983**, 210-212.
9. Kambe, S.; Saito, K.; Sakurai, A.; Midorikawa, H. *Synthesis* **1980**, 366-368.
10. Al-Hajjar, F. H.; Jarrar, A. A. *J. Heterocycl. Chem.* **1980**, *17*, 1521-1525.
11. Joucla, M.; Hamelin, J. *Tetrahedron Lett.* **1978**, 2885-2888.
12. Rober, S. *Heterocycles* **1980**, *14*, 461-465.
13. Tsuge, O.; Tashiro, M.; Shinkai, I. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 185-190.
14. Faita, G.; Mella, M.; Righetti, P.; Tacconi, G. *Tetrahedron* **1994**, *50*, 10955-10962.
15. Al-Arab, M. M.; Atfah, M. A.; Al-Saleh, F. S. *Tetrahedron* **1997**, *53*, 1045-1052.
16. Atfah, M. A.; Al-Arab, M. M. *J. Heterocycl. Chem.* **1990**, *27*, 599-603.
17. Vogel, A. I. *A Text Book of Practical Organic Chemistry*; English Language Book Society and Longman Group Ltd.: London; **1996**; pp 1012-1013.

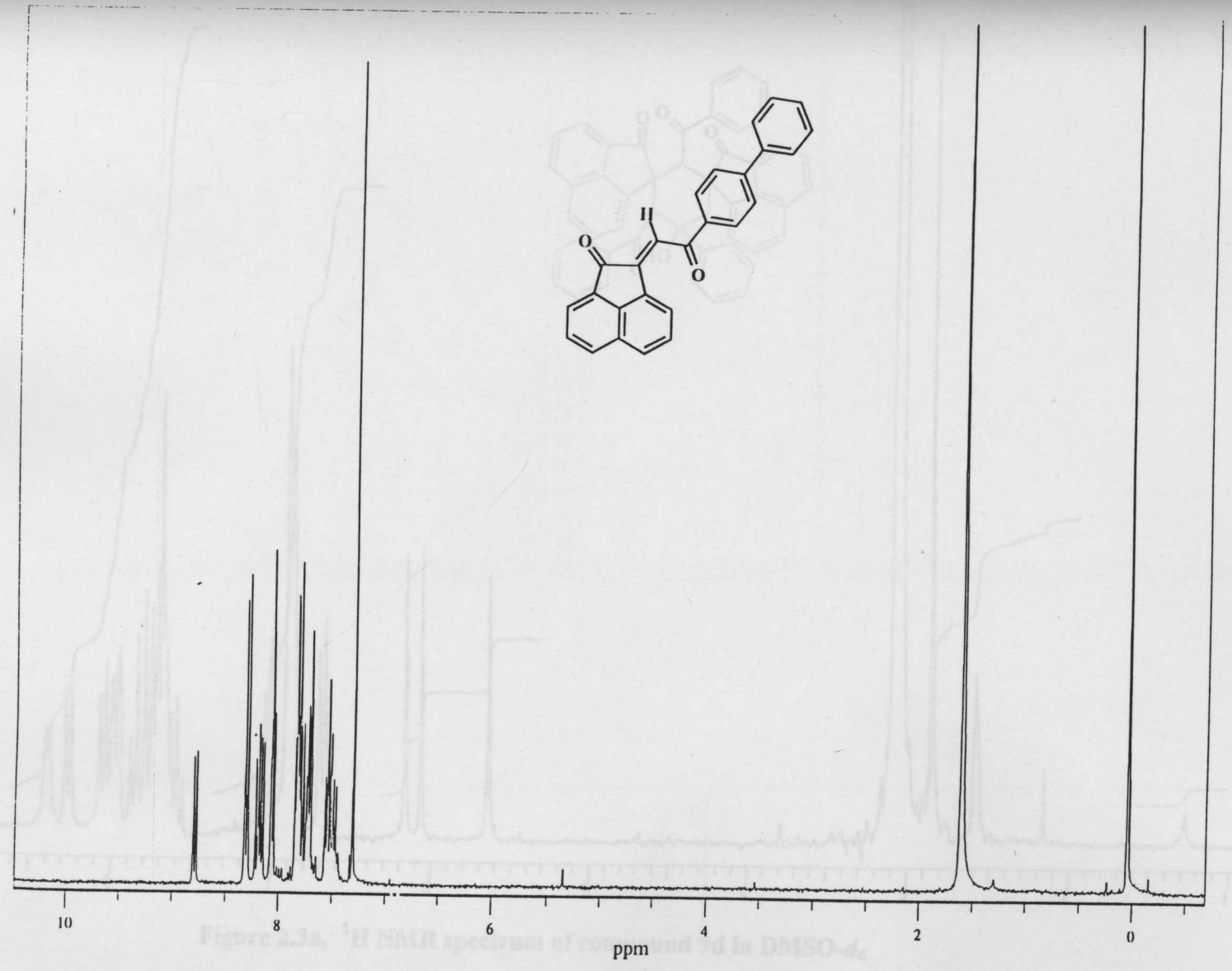


Figure 2.2. ^{1}H NMR spectrum of compound 8c.

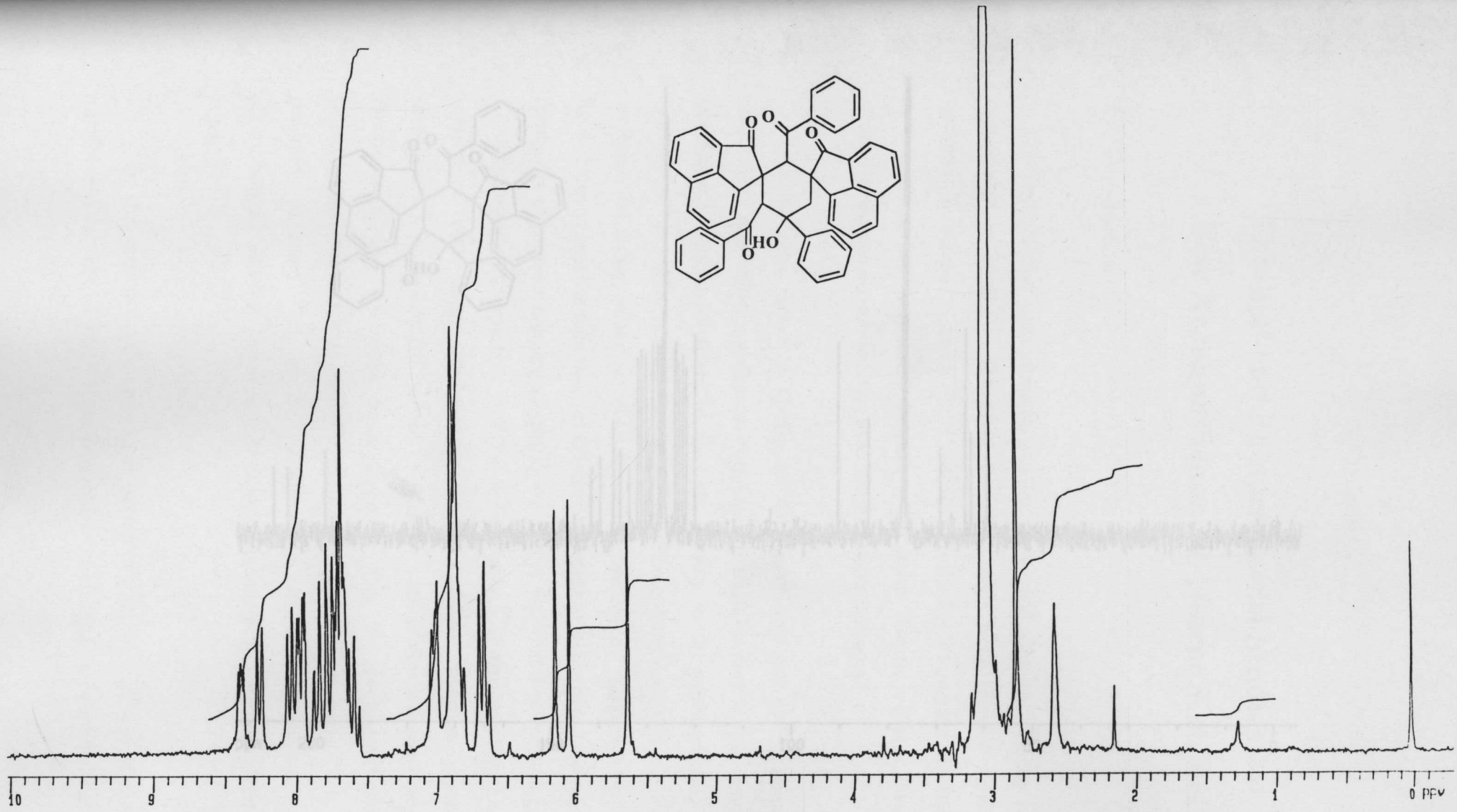


Figure 2.3a. ^{1}H NMR spectrum of compound 9d in DMSO-d_6

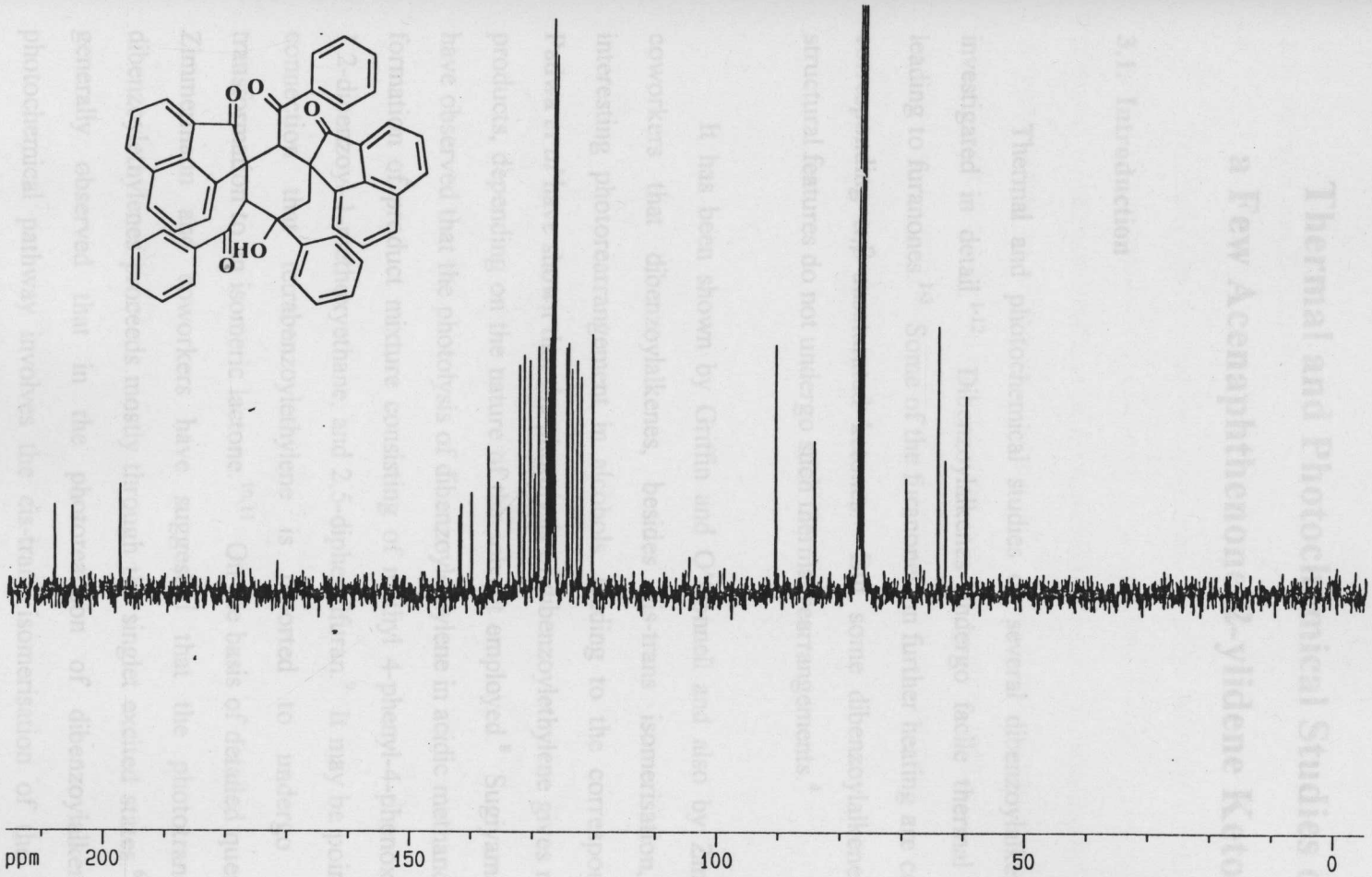


Figure 2.3b. ^{13}C NMR spectrum of compound 9d.

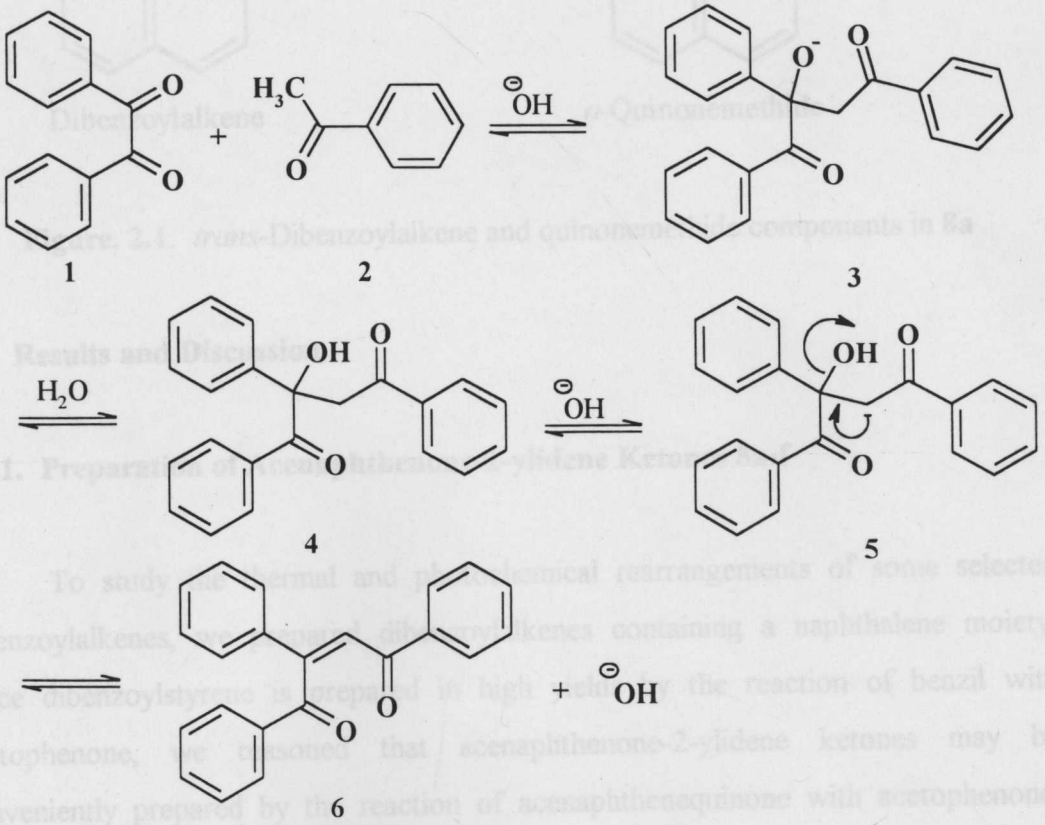
Chapter 2

Synthesis of a Few Acenaphthenone-2-ylidene Ketones

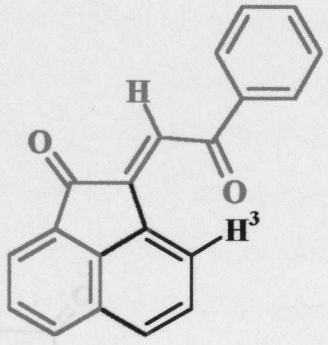
2.1. Introduction

α,β-Unsaturated ketones are conveniently prepared by Claisen-Schmidt condensation.[1,2] It is the Aldol condensation and subsequent elimination of a water molecule in presence of a basic catalyst. The Aldol reaction, usually carried out in protic solvents, is one of the most versatile methods in organic synthesis.[3,4] By application of this reaction, a great number of aldols and related compounds have been prepared from various carbonyl compounds. 1,2-Diketones like benzil (**1**), for example, undergo condensation with acetophenone (**2**) to yield dibenzoylstyrene (**6**). The probable mechanism for the formation of dibenzoylstyrene is given in Scheme 2.1. The reaction is simply the nucleophilic addition of an enolate ion onto the carbonyl group of another, unionised molecule. Dehydration of β-hydroxyketone formed in this reaction yields an α,β-unsaturated carbonyl compound.[5,6,7]

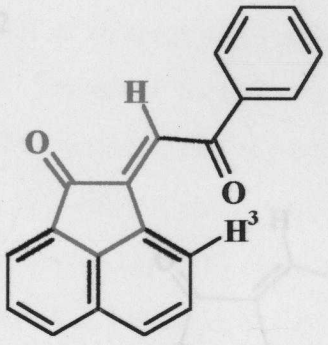
Scheme 2.1



In the present study, we propose to synthesise several acenaphthenone-2-ylidene ketones **8a-f** by the Claisen-Schmidt condensation of acenaphthenequinone with methyl ketones. Close examination of the structural features of acenaphthenone-2-ylidene ketones indicates their similarity with dibenzoylalkenes. Alternatively, they may be regarded as quinonemethides (Figure 2.1). So, these acenaphthenone-2-ylidene ketones, upon irradiation, are expected to undergo dibenzoylalkene rearrangement and/or cis-trans isomerisation. Also, dibenzoylalkenes are good Michael acceptors. They undergo Michael addition with active methylene compounds.[8-12] As quinonemethides, **8a-f** are expected to undergo a variety of transformations including Diels-Alder reactions. Our attempts to synthesise acenaphthenone-2-ylidene ketones by the reaction of acenaphthenequinone with acetophenone are discussed in this chapter.



Dibenzoylalkene



o-Quinonemethide

Figure. 2.1. *trans*-Dibenzoylalkene and quinonemethide components in **8a**

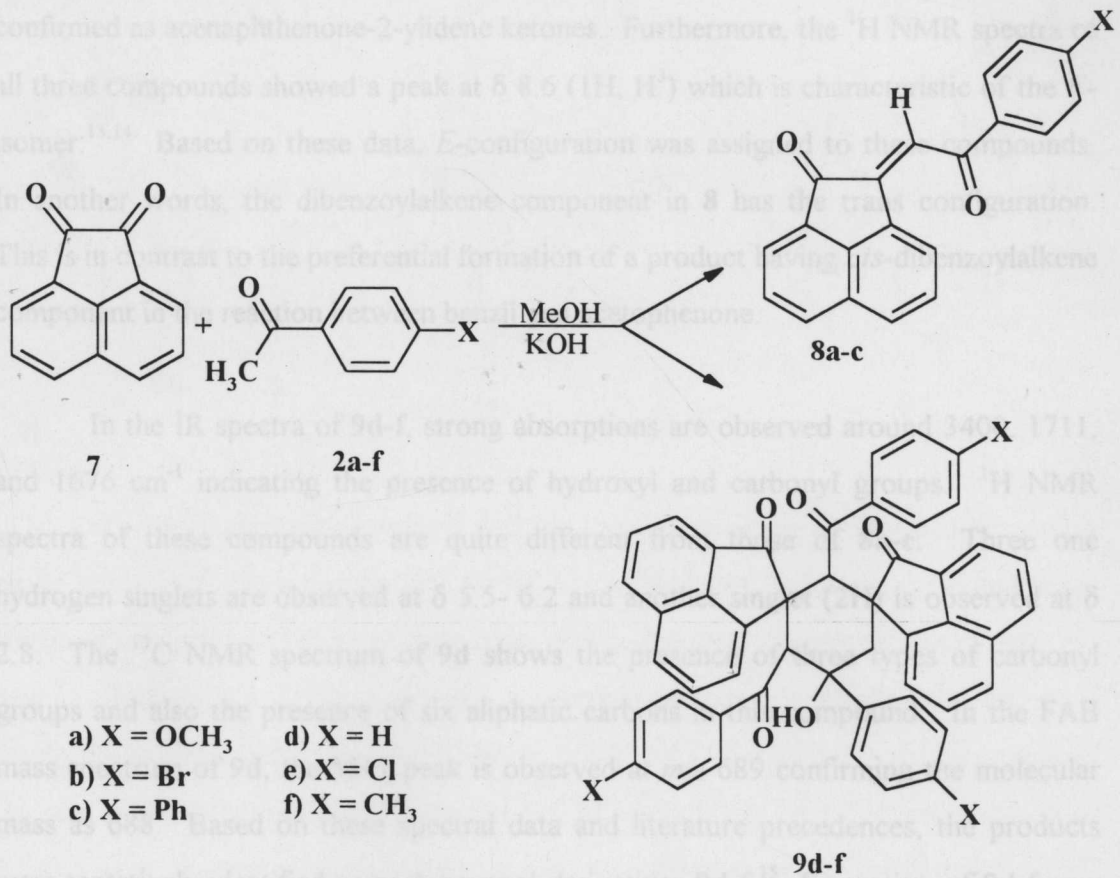
2.2. Results and Discussion

2.2.1. Preparation of Acenaphthenone-2-ylidene Ketones 8a-f

To study the thermal and photochemical rearrangements of some selected dibenzoylalkenes, we prepared dibenzoylalkenes containing a naphthalene moiety. Since dibenzoylstyrene is prepared in high yields by the reaction of benzil with acetophenone, we reasoned that acenaphthenone-2-ylidene ketones may be conveniently prepared by the reaction of acenaphthenequinone with acetophenone.

Thus, we treated acenaphthenequinone (7) with acetophenones **2a-f** in methanol in the presence of potassium hydroxide (Scheme 2.2). Methyl ketones of our choice were 4-methoxyacetophenone (**2a**), 4-bromoacetophenone (**2b**), 4-phenylacetophenone (**2c**), acetophenone (**2d**), 4-chloroacetophenone (**2e**), and 4-methylacetophenone (**2f**) which were synthesised using previously reported procedures. We observed that the reaction of acenaphthenequinone (7) with acetophenone and its derivatives gave two types of products depending on the nature of the 4-substituents (Scheme 2.2). While **2a**,**b**,**c** on reaction with 7 yielded the corresponding acenaphthenone-2-ylidene ketones **8a**,**b**,**c** in good yields, reaction of **2d**,**e**,**f** with 7 resulted in the formation of 3:2 adducts **9d**,**e**,**f**. The structures of the adducts **8a-c** were established on the basis of analytical results and spectral data and structures of the adducts **9d-f** were tentatively assigned on the basis of literature precedences, analytical results and spectral data.

Scheme 2.2



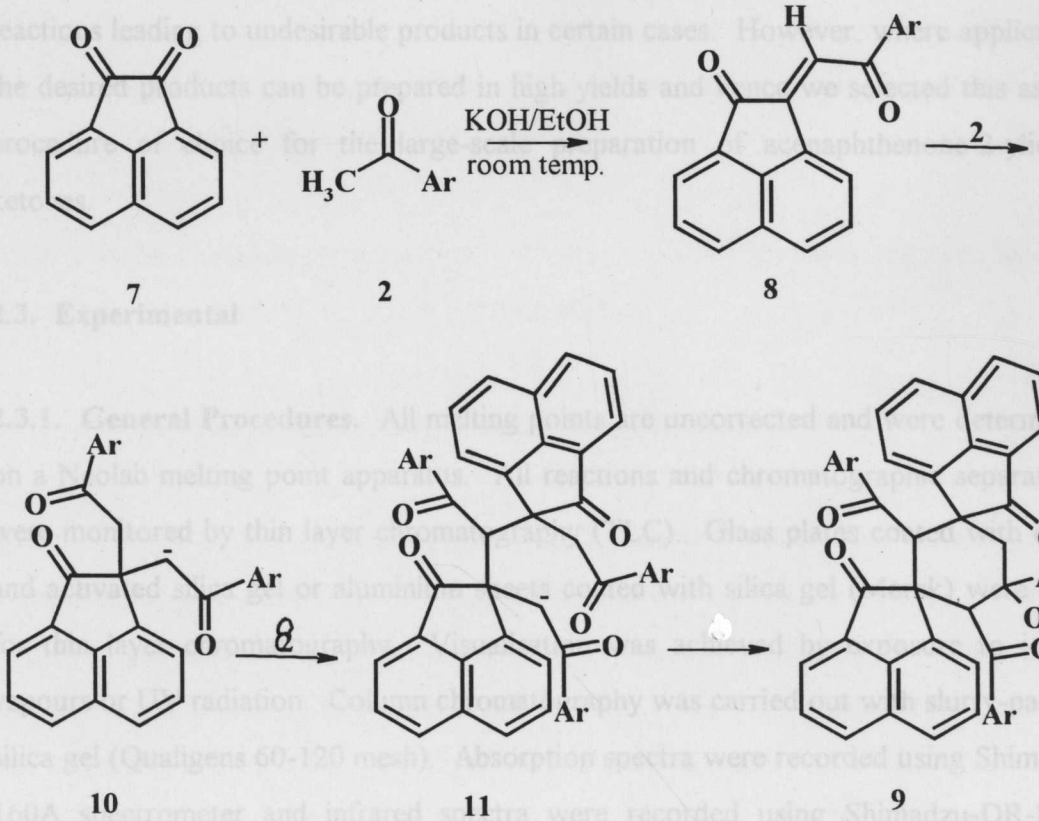
Compound **8a**, which was obtained in 50% yield, showed two strong absorption in the IR spectrum at 1714 and 1655 cm^{-1}. These are due to the presence of two carbonyl groups in the compound. The absorption at 1714 cm^{-1} is assigned to indenone-type carbonyl group present in these systems. UV absorptions at 340 and 280 nm are due to the presence of naphthalene residue in the compound. In the NMR spectrum, the vinylic and aromatic protons of the compound were observed as a multiplet in the aromatic region δ 7.5-9. The molecular ion peak of this compound was observed at *m/z* 284 confirming its identity. The structure was further confirmed by elemental analysis, which gave acceptable data.

Compounds **8b** and **8c** showed very similar spectral behavior with **8a**. These compounds also showed the IR absorptions at ~1714 and at ~1660 cm^{-1} due to two carbonyls. The UV spectra of all these compounds were similar and were dominated by the absorption of naphthalene residue. ^1H NMR of all these were comparable and these showed acceptable analysis and mass data. Therefore, these compounds were confirmed as acenaphthenone-2-ylidene ketones. Furthermore, the ^1H NMR spectra of all three compounds showed a peak at δ 8.6 (1H, H^3) which is characteristic of the *E*-isomer.[13,14] Based on these data, *E*-configuration was assigned to these compounds. In another words, the dibenzoylalkene component in **8** has the trans configuration. This is in contrast to the preferential formation of a product having *cis*-dibenzoylalkene component in the reaction between benzil and acetophenone.

In the IR spectra of **9d-f**, strong absorptions are observed around 3400, 1711, and 1676 cm^{-1} indicating the presence of hydroxyl and carbonyl groups. ^1H NMR spectra of these compounds are quite different from those of **8a-c**. Three one hydrogen singlets are observed at δ 5.5- 6.2 and another singlet (2H) is observed at δ 2.8. The ^{13}C NMR spectrum of **9d** shows the presence of three types of carbonyl groups and also the presence of six aliphatic carbons in this compound. In the FAB mass spectrum of **9d**, the M+1 peak is observed at *m/z* 689 confirming the molecular mass as 688. Based on these spectral data and literature precedences, the products were tentatively identified as cyclohexanol derivatives **9d-f**.[15] Formation of **9d-f** may be understood in terms of the pathways shown in Scheme 2.3. The initially-formed *E*-

acenaphthenone-2-ylidene ketones underwent further Michael addition with acetophenones followed by intramolecular aldol condensation to give the cyclohexanol derivatives. The formation of highly substituted cyclohexanol derivatives by analogous reaction of *trans*-dibenzoylalkenes with acetophenones were studied by Al-Arab *et al.*[15,16]

Scheme 2.3



We subjected **9d** to chemical degradation for obtaining additional information on its structure. Thus thermolysis of **9d** was carried out under various conditions. Neat heating of **9d** above its melting point resulted in total decomposition of **9d**. No new products could be isolated. In another experiment, a solution of **9d** in *o*-dichlorobenzene was refluxed for 12 h. Work up of the reaction mixture resulted in the near-quantitative recovery of unchanged **9d**. Irradiation of a benzene solution of **9d** also led to extensive decomposition and no new products could be isolated.

Thus, the base-catalysed reaction between acetophenones and acenaphthenequinone appears to be a suitable method for the preparation of some acenaphthenone-2-ylidene ketones. Some of these derivatives have already been prepared by a Wittig reaction between acenaphthenequinone and the corresponding α-aroylmethylenetriphenylphosphorane. α-Haloacetophenones (prepared by the α-halogenation of acetophenones) are required for this process whereas the process developed by us employs acetophenones as such. Thus, though the novel method developed by us is simple and more convenient, it suffers from the possibility of side reactions leading to undesirable products in certain cases. However, where applicable, the desired products can be prepared in high yields and hence we selected this as the procedure of choice for the large-scale preparation of acenaphthenone-2-ylidene ketones.

2.3. Experimental

2.3.1. 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 gel or aluminium sheets coated with silica gel (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 gel (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 and 75 MHz respectively on a Brucker 300 FT-NMR spectrometer or a GE NMR OMEGA spectrometer with tetramethylsilane as 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.

2.3.2. Starting materials. Acenaphthenequinone was purchased from E. Merck and was used as obtained.

2.3.2.1. 4-Methoxyacetophenone (2a): 4-Methoxyacetophenone was prepared using a known procedure[17] (90%, bp 265 ^{0}C).

2.3.2.2. 4-Bromoacetophenone (2b): 4-Bromoacetophenone was prepared using a known procedure[17] (75%, bp 255 ^{0}C).

2.3.2.3. 4-Phenylacetophenone (2c): 4-Phenylacetophenone was prepared using a known procedure[17] (76%, mp 120 ^{0}C).

2.3.2.4. 4-Chloroacetophenone (2e): 4-Chloroacetophenone was prepared using a known procedure[17] (75%, bp 237 ^{0}C).

2.3.2.5. 4-Methylacetophenone (2f): 4-Methylacetophenone was prepared using a known procedure[17] (85%, bp 93-94 ^{0}C/7 mmHg).

2.3.3. Preparation of Acenaphthenone-2-ylidene Ketones

2.3.3.1. Preparation of Acenaphthenone-2-ylidene Ketone 8a. A mixture of acenaphthenequinone (4.6 g, 25 mmol), 4-methoxyacetophenone (4.1 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **8a**.

Compound 8a: (4.4 g, 56%); mp 160-162 ^{0}C; IR ν_{max} (KBr) 1714, and 1655 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 233 (ε 48,000), 281 (ε 20,000), 323 nm (ε 16,700); ^{1}H NMR ($CDCl_3$) δ 3.9 (3H, s, methoxy) 6.9-8.7 (11H, m, aromatic and vinylic); MS, *m/z* 314 (M^+), 286, 252, 105, 91 and other peaks. Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.25; H, 4.49. Found: C, 79.78; H, 4.58.

2.3.3.2. Preparation of Acenaphthenone-2-ylidene Ketone 8b. A mixture of acenaphthenequinone (4.6 g, 25 mmol), 4-bromoacetophenone (5.4 g, 27 mmol), and

powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **8b**.

Compound 8b: (4.27 g, 47%); mp 198-200 ^{0}C; IR ν_{max} (KBr) 1714, and 1659 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 230 (ε 55,700), 284 (ε 26,000), 341 nm (ε 22,000); ^{1}H NMR ($CDCl_3$) δ 7.2-8.8 (m, aromatic and vinylic); MS, *m/z* 364 {$(M+2)^+$}, 362 (M^+), 337, 335, 255, 153, 151, and other peaks. Anal. Calcd for $C_{20}H_{11}O_2Br$: C, 66.12; H, 3.05. Found: C, 66.30; H, 3.09.

2.3.3.3. Preparation of Acenaphthenone-2-ylidene Ketone 8c. A mixture of acenaphthenequinone (4.6 g , 25 mmol), 4-phenylacetophenone (5.3 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **8c**.

Compound 8c: (4 g, 45%); mp 187-189 ^{0}C; IR ν_{max} (KBr) 1716, and 1657 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 230 (ε 40,000), 287 (ε 20,000), 340 nm (ε 17,000); ^{1}H NMR ($CDCl_3$) δ 7.3-8.8 (m, aromatic and vinylic); MS, *m/z* 360 (M^+), 332, 256, 181, 152 and other peaks. Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.67; H, 4.47. Found: C, 86.12; H, 4.67.

2.3.4. Preparation of Cyclohexanols

2.3.4.1. Preparation of Cyclohexanol 9d. A mixture of acenaphthenequinone (4.6 g, 25 mmol), acetophenone (3.2 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **9d**.

Compound 9d: (4 g, 47%); mp 256-258 ^{0}C; IR ν_{max} (KBr) 3352 (OH), 1711, and 1676 (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 (DMSO-d_6) δ 2.8 (s, 2H, CH_2), 5.6 (s, 1H), 6.1 (s, 1H), 6.2 (s, 1H), 6.6-8.5 (m, 27H, aromatic); ^{13}C NMR ($CDCl_3$) δ 59, 63, 64, 69, 84, 90, 120, 122, 123, 123.5, 124, 124.5, 126, 126.5, 127, 127.2, 127.5, 127.7, 128, 129, 130, 131, 132, 137, 140, 197, 205, 207; FAB-MS, *m/z* 689 $(M+H)^+$.

In a repeat run, reaction of acenaphthenequinone (4.6 g, 25 mmol) with 2 equivalents of acetophenone (6.4 g, 54 mmol) under analogous conditions gave **9d** in 25% yield.

2.3.4.2. Preparation of Cyclohexanol 9e. A mixture of acenaphthenequinone (4.6 g, 25 mmol), 4-chloroacetophenone (4.2 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **9e**.

Compound 9e: (3.6 g, 45%); mp 216-219 ^{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, 2H, CH_2), 5.57 (s, 1H), 5.94 (s, 1H), 6.13 (s, 1H), 6.5-8.1 (m, 24H, aromatic).

2.3.4.3. Preparation of Cyclohexanol 9f. A mixture of acenaphthenequinone (4.6 g, 25 mmol), 4-methylacetophenone (3.6 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 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 **9f**.

Compound 9f: (5.5 g, 60%); mp 216-218 ^{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 2.1 (s, 3H), 2.25 (s, 6H), 2.8 (s, 2H, CH_2), 5.63 (s, 1H), 5.88 (s, 1H), 6.16 (s, 1H), 6.4-8.4 (m, 24H, aromatic); ^{13}C NMR ($CDCl_3$) δ 29, 59, 63, 64, 69, 84, 90, 120, 126, 126.7, 127, 127.5, 132, 140, 142, 196, 204, 207.

2.3.5. Attempted Thermolysis of 9d

2.3.5.1. In *o*-Dichlorobenzene. A solution of **4d** (100 mg, 14 mmol) in *o*-dichlorobenzene 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 the unchanged starting material (**9d**). mp 256-258 ^{0}C (mixture melting point).

2.3.5.2. Neat Thermolysis. A sample of **9d** (100 mg, 14 mmol) was heated in a sealed tube around 270 ^{0}C for 6 h. The solid was extracted with dichloromethane. TLC showed complete decomposition of the starting material.

2.3.6. Photochemical Transformation of 9d. A benzene solution of **9d** (200 mg, 28 mmols in 350 mL) was irradiated for 5 h using the out put 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 the residue was extracted with dichloromethane. TLC showed complete decomposition of the starting material and no new products could be isolated.

References

1. Nielsen, A. T.; Houliban, W. J. *Organic Reactions* **1968**, *16*, 1-438.
2. Claisen, L.; Claparede, A. *Ber.* **1881**, *14*, 2460.
3. House, H.O. *Modern Synthetic Reactions*; 2nd ed.; Benjamin: Menlopark, CA, **1972**.
4. Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: Ithaca, New York; **1953**; pp 673-699.
5. House, H. O.; Ro, R. S. *J. Am. Chem. Soc.* **1958**, *80*, 2428-2433.
6. Payne, G. B.; Willaims, P. H. *J. Org. Chem.* **1961**, *26*, 651-659.
7. Buckles, R. E.; Mock, G. V.; Locatell, L. Jr. *Chem. Rev.* **1955**, *55*, 656-692.
8. Saito, K.; Kambe, S.; Nakano, Y.; Sakurai, A.; Midorikawa, H. *Synthesis* **1983**, 210-212.
9. Kambe, S.; Saito, K.; Sakurai, A.; Midorikawa, H. *Synthesis* **1980**, 366-368.
10. Al-Hajjar, F. H.; Jarrar, A. A. *J. Heterocycl. Chem.* **1980**, *17*, 1521-1525.
11. Joucla, M.; Hamelin, J. *Tetrahedron Lett.* **1978**, 2885-2888.
12. Rober, S. *Heterocycles* **1980**, *14*, 461-465.
13. Tsuge, O.; Tashiro, M.; Shinkai, I. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 185-190.
14. Faita, G.; Mella, M.; Righetti, P.; Tacconi, G. *Tetrahedron* **1994**, *50*, 10955-10962.
15. Al-Arab, M. M.; Atfah, M. A.; Al-Saleh, F. S. *Tetrahedron* **1997**, *53*, 1045-1052.
16. Atfah, M. A.; Al-Arab, M. M. *J. Heterocycl. Chem.* **1990**, *27*, 599-603.
17. Vogel, A. I. *A Text Book of Practical Organic Chemistry*; English Language Book Society and Longman Group Ltd.: London; **1996**; pp 1012-1013.

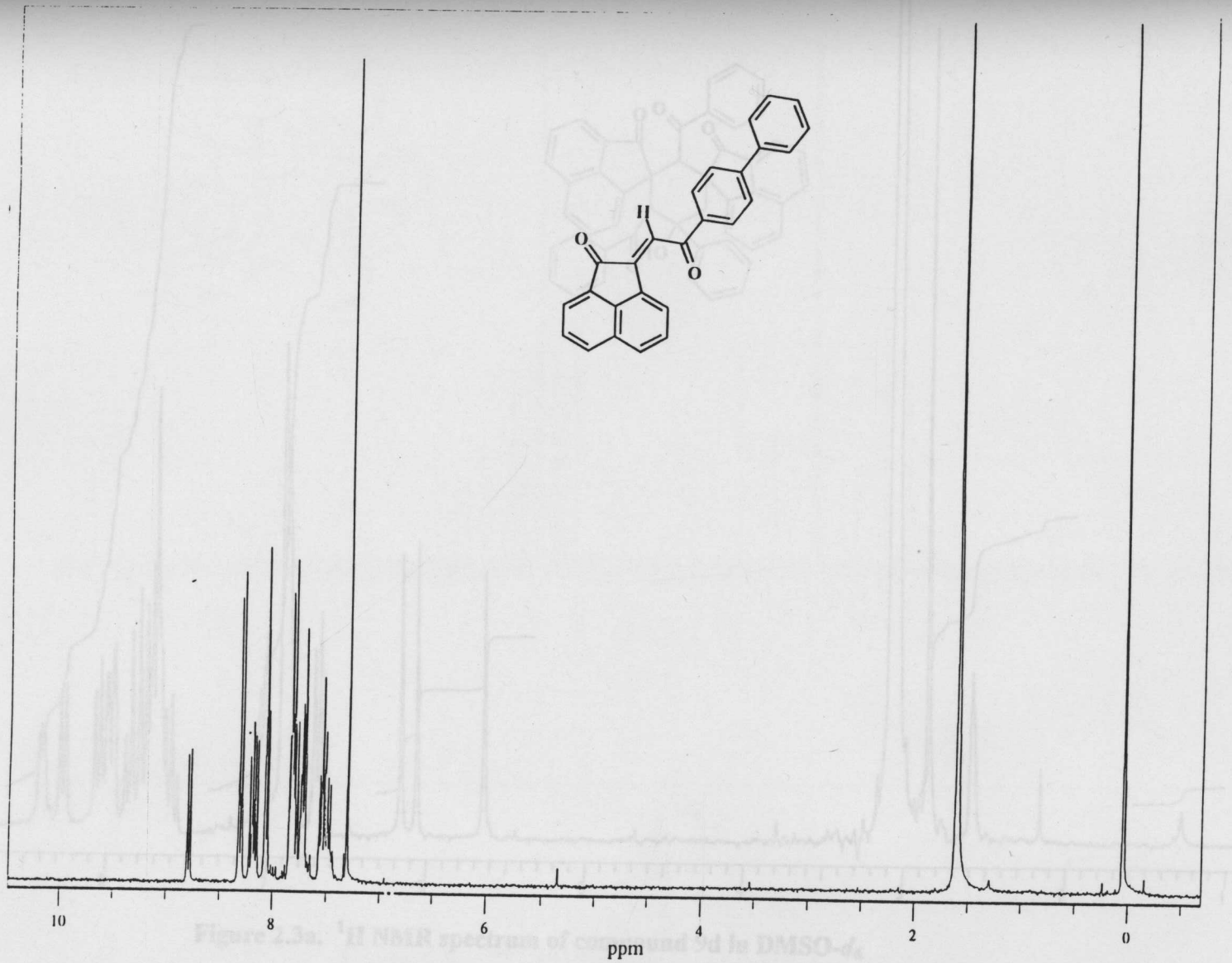


Figure 2.2. ^{1}H NMR spectrum of compound 8c.

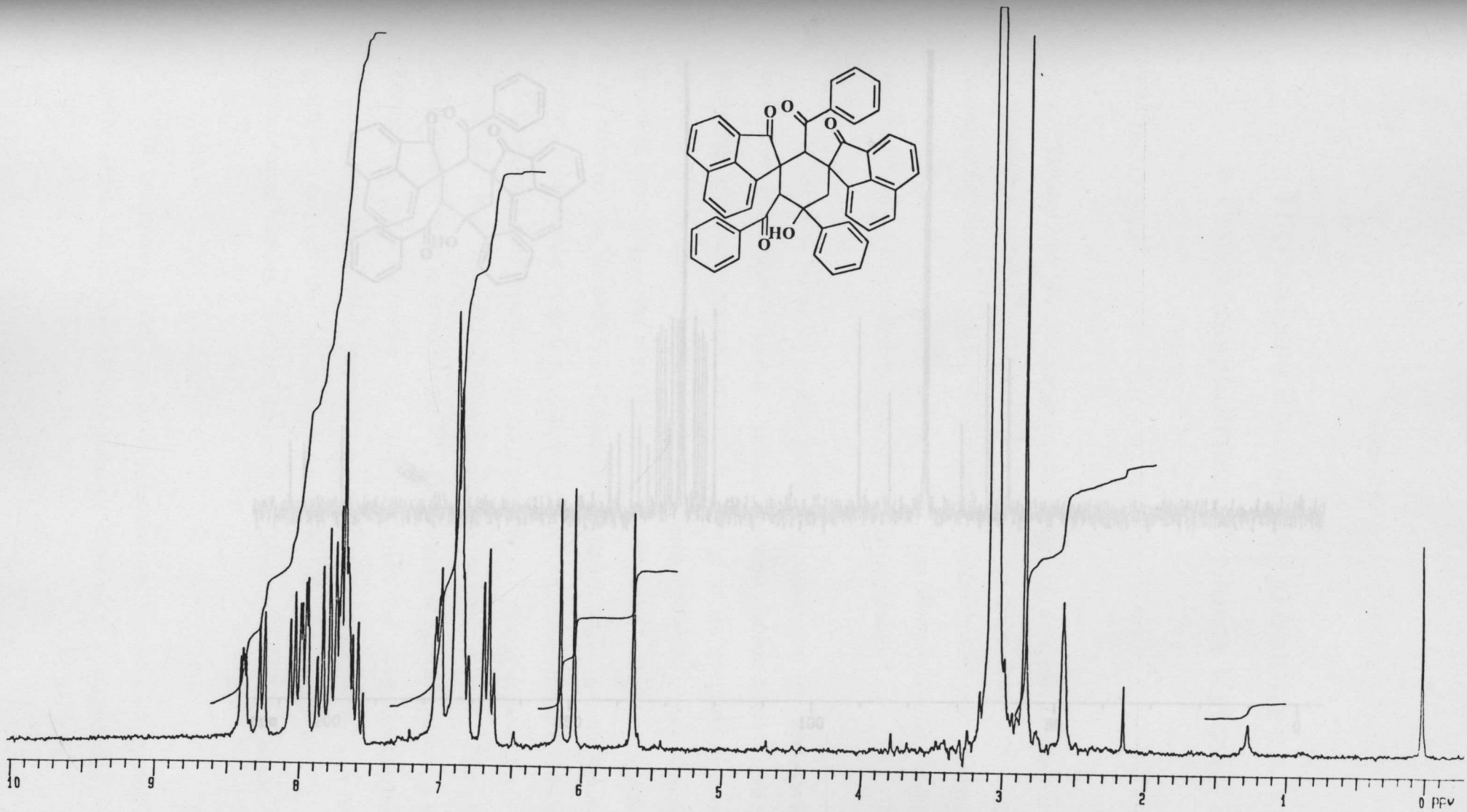


Figure 2.3a. ^{1}H NMR spectrum of compound 9d in DMSO-d_6

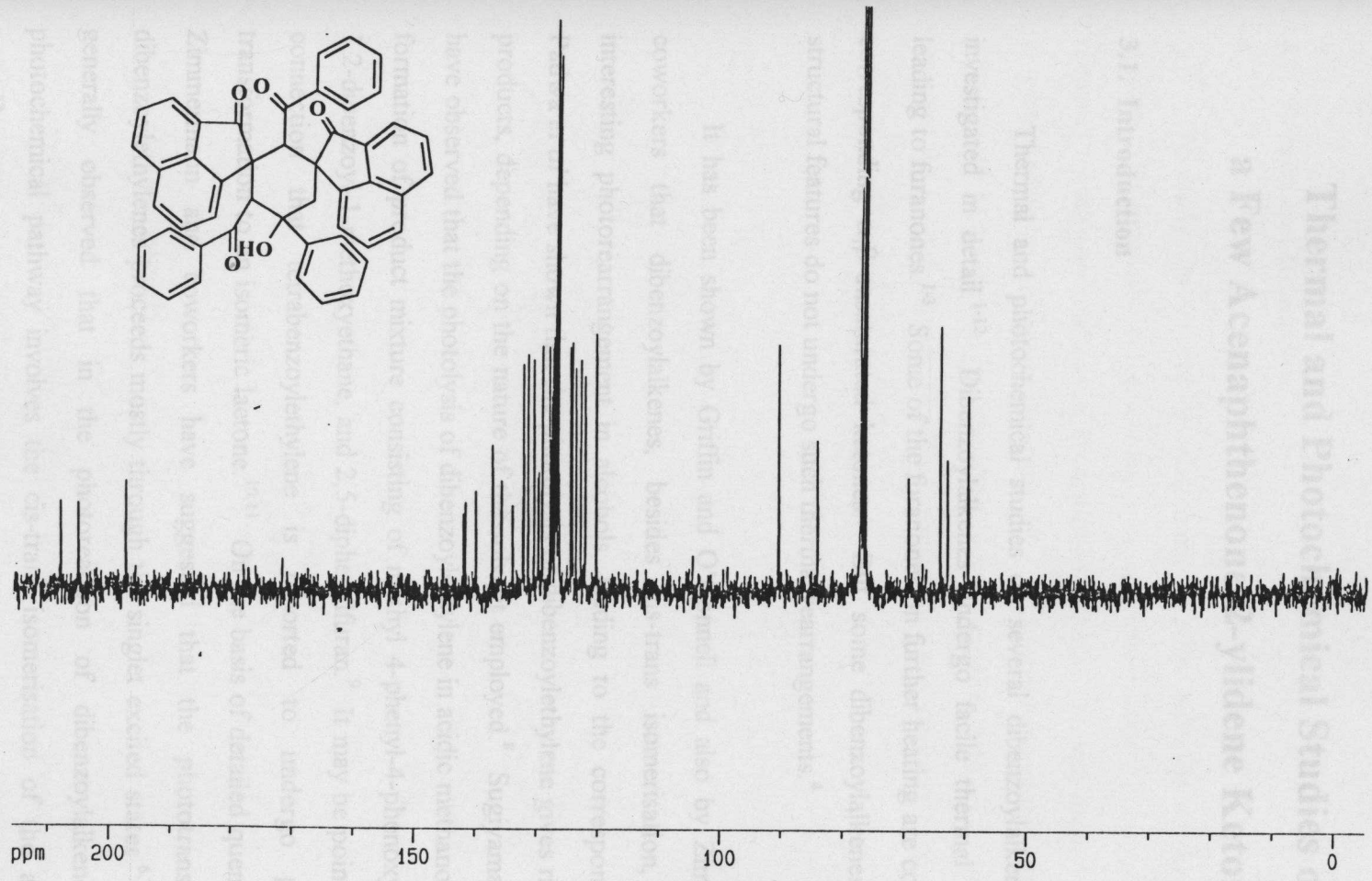


Figure 2.3b. ^{13}C NMR spectrum of compound 9d.

Chapter 3

Thermal and Photochemical Studies on a Few Acenaphthenone-2-ylidene Ketones

3.1. Introduction

Thermal and photochemical studies on several dibenzoylalkenes have been investigated in detail.[1-12] Dibenzoylalkenes undergo facile thermal rearrangement leading to furanones.[1-3] Some of the furanones on further heating are converted to the corresponding α,β-unsaturated ketones. But some dibenzoylalkenes having rigid structural features do not undergo such thermal rearrangements.[4]

It has been shown by Griffin and O'Connell and also by Zimmermann and coworkers that dibenzoylalkenes, besides cis-trans isomerisation, undergo an interesting photorearrangement in alcohols, leading to the corresponding esters.[5-7] Padwa *et al* have shown that the photolysis of dibenzoylethylene gives rise to different products, depending on the nature of the solvent employed.[8] Sugiyama and Kashima have observed that the photolysis of dibenzoylethylene in acidic methanol results in the formation of product mixture consisting of methyl 4-phenyl-4-phenoxy-3-butenoate, 1,2-dibenzoyl-1-methoxyethane, and 2,5-diphenylfuran.[9] It may be pointed out in this connection that tetrabenzoylethylene is reported to undergo photochemical transformation to an isomeric lactone.[10,11] On the basis of detailed quenching studies, Zimmermann and coworkers have suggested that the phototransformation of dibenzoylethylenes proceeds mostly through the singlet excited states.[6,7] It has been generally observed that in the photoreaction of dibenzoylalkenes, a major photochemical pathway involves the cis-trans isomerisation of the alkene double bond.[12]

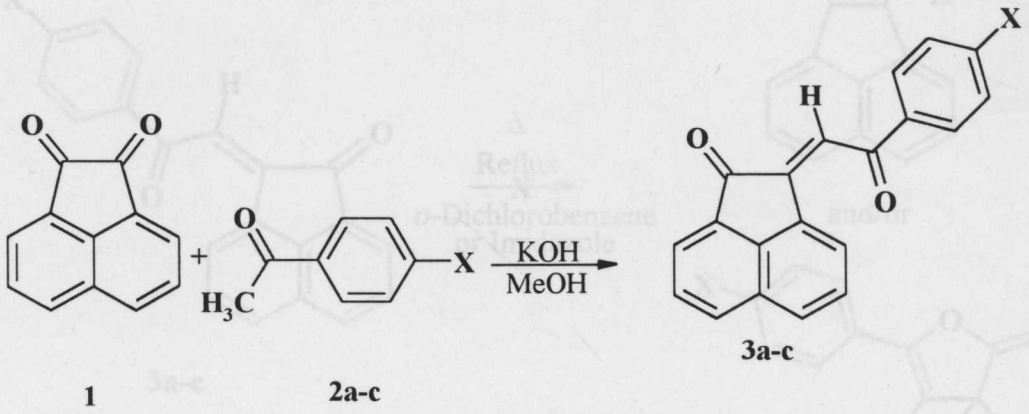
In the present study, we have examined the thermal and photochemical transformations of a few dibenzoylalkenes containing a naphthalene moiety.

Interestingly, these compounds do not undergo thermal rearrangement but they undergo photochemical rearrangement typical of dibenzoylalkenes.

3.2. Results and Discussion

To study the thermal rearrangement of some selected dibenzoylalkenes, we prepared dibenzoylalkenes containing a naphthalene moiety. The compounds were prepared by the condensation of acenaphthenequinone (**1**) with methyl ketones (**2a-c**) in good yields as shown in Scheme 3.1. The acenaphthenone-2-ylidene ketones formed were characterised by their spectral and analytical data. The compounds were assigned the *E*-configuration, based on spectral data and literature precedence.[13]

Scheme 3.1



1 **2a-c** **3a-c**

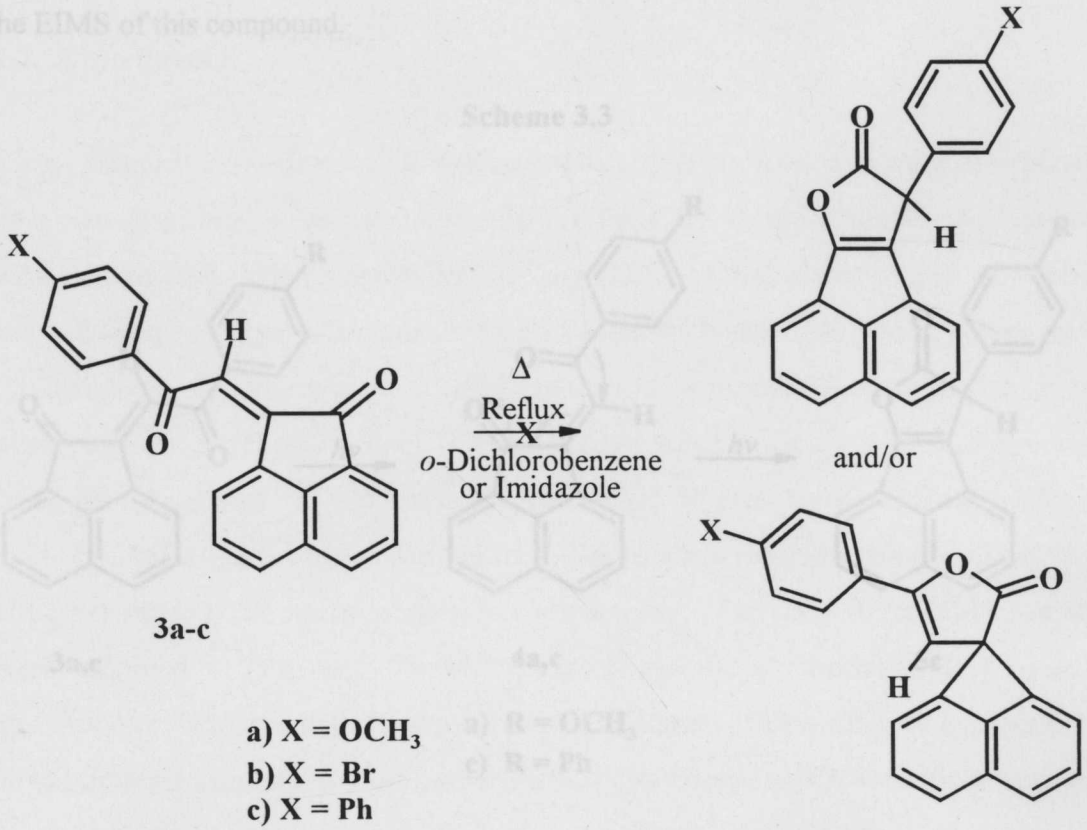
a) X = OCH_3
b) X = Br
c) X = Ph

3.2.1. Thermal Studies

According to previous reports, dibenzoylalkenes should undergo thermal rearrangement to 2(3H)-furanones. Therefore, we investigated the thermal rearrangement of these acenaphthenone-2-ylidene derivatives by taking **3a** as a representative example. The compound decomposed completely during neat thermolysis in a sealed tube above the melting point of the compound. Therefore, we changed the reaction condition. A solution of **3a** in *o*-dichlorobenzene was refluxed at

180 ^{0}C for several hours. But the reactant was recovered almost quantitatively even after prolonged refluxing. Then we studied the thermal behaviour using imidazole as a solvent at 257 ^{0}C. But in this case also we recovered unchanged **3a** in almost quantitative amounts. From these observations it was concluded that the thermal transformation of compounds **3a-c** to the corresponding furanone derivative was not possible (Scheme 3.2). Our results are consistent with the observation that *trans*-dibenzoylalkenes fail to undergo such thermal rearrangements.[14]

Scheme 3.2



3a-c

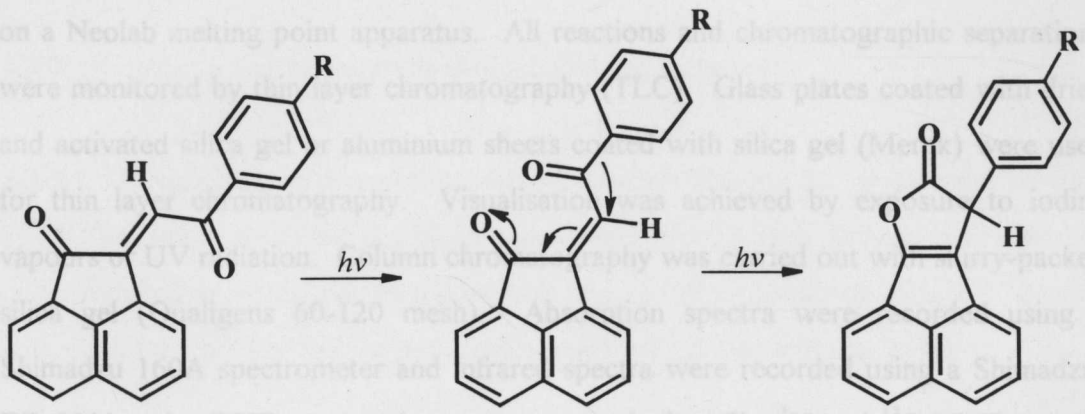
a) X = OCH_3
b) X = Br
c) X = Ph

3.2.2. Preparative Photochemistry and Product Identification

Dibenzoylalkenes undergo interesting photochemical rearrangements. The important reactions taking place under irradiation are cis-trans isomerisation, 1,5-phenyl migration etc. We studied the photochemical transformations of some representative systems. The compounds selected for the studies were **3a**, and **3c**.

Irradiation of **3a** in benzene gave the *Z*-isomer **4a**. However in the case of **3c**, a different product was isolated in low yields whose structure is tentatively assigned as the lactone **5c** (Scheme 3.3). The structure of *Z*-isomer **4a** was arrived at on the basis of spectral and analytical data. The IR spectrum of the compound is different from that of the *E*-isomer. The ^{1}H NMR spectrum of *E*-isomer is also different from that of the *Z*-isomer. The ^{1}H NMR spectra (partial) of the *E* and *Z*-isomers are given in Figure 3. 1. The structure of **5c** was assigned on the basis of spectral and analytical data. The IR spectrum of **5c** showed a strong absorption at 1776 cm^{-1} indicating the presence of lactone carbonyl. The ^{1}H NMR spectrum showed the presence of a proton at δ 4.8 and all other protons are at δ 6.8-7.6 (15H). The M^+ peak was not observed in the EIMS of this compound.

Scheme 3.3



3a,c **4a,c** **5c**

a) R = OCH_3
c) R = Ph

The difference in the observed photochemistry of **3a** and **3c** may be attributed to the alteration of excited state properties of **3c** and **4c** by the presence of the biphenyl moiety. It is known that the intersystem crossing efficiency and triplet life times (τ^T) of 3,3,5-triaryl-2(3H)-furanones are considerably enhanced by the presence of a biphenyl substituent at the 5-position.[15] The triplet life time of 5-(4'-methoxy)-3,3-diphenyl-2(3H)-furanone in benzene is 1.9 μs whereas that of 5-(4'-phenylphenyl)-3,3-diphenyl-2(3H)-furanone in benzene is 7.7 μs. Such changes in the excited state properties of

4c will enable it to undergo transformations which are less likely with **4a**. Further evidence for the involvement of **4c** as a probable intermediate in the transformation of **3c** to **5c** was obtained by isolating it under carefully-controlled conditions.

We have shown that the *Z*-isomer **4a**, on heating in a suitable solvent, undergoes facile isomerisation to the *E*-isomer **3a**. The *Z*-*E* isomerisation is faster in protic solvents. These results are also in contrast to the cis-trans isomerisation possiblity of simple dibenzoylalkenes where trans to cis isomerisation if facilitated under thermal conditions[16]. However, **4a** appears to be stable in the solid state.

3.3. Experimental

3.3.1. 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 gel or aluminium sheets coated with silica gel (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 gel (Qualigens 60-120 mesh). Absorption spectra were recorded using a Shimadzu 160A spectrometer and infrared spectra were recorded using a Shimadzu-DR-8001 series FTIR spectrophotometer respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively on a Brucker 300 FT-NMR spectrometer with tetramethylsilane as internal standard. Unless otherwise mentioned, all steady-state irradiations were carried out using a Hanovia 450-W medium pressure mercury lamp in a quartz-jacketed immersion well with a pyrex filter. Solvents for steady-state photolysis were purified and distilled before use.

3.3.2. Attempted Thermolysis of Acenaphthenone-2-ylidene Ketone 3a

3.3.2.1. In *o*-Dichlorobenzene. A solution of **3a** (100 mg, 0.32 mmol) in *o*-dichlorobenzene was refluxed for 12 h and the solvent was removed under reduced pressure. The residue was washed with petroleum ether and recrystallised from a

mixture (2:1) of methanol and dichloromethane to give 90 mg (90%) of unchanged **3a**. mp 160-162 ^{0}C (mixture melting point).

3.3.2.2. In Imidazole. A solution of **3a** (100 mg, 0.32 mmol) in imidazole (2.0 g) was refluxed for 12 h and the solvent was removed by washing with water. The residue obtained was washed with petroleum ether and recrystallised from a mixture (2:1) of methanol and dichloromethane to give 90 mg (90%) of the unchanged **3a**. mp 160-162 ^{0}C (mixture melting point).

3.3.2.3. Neat Thermolysis. A sample of **3a** (100 mg, 0.32 mmol) was heated in a sealed tube around 270 ^{0}C for 6 h. The solid was extracted with dichloromethane. TLC showed complete decomposition of the starting material. Workup of the reaction mixture did not lead to any isolable products.

3.3.3. Irradiation of Acenaphthenone-2-ylidene Ketones

3.3.3.1. Irradiation of Acenaphthenone-2-ylidene Ketone 3a. A benzene solution of **3a** (200 mg, 0.64 mmol in 350 mL) was irradiated for 5 h. Solvent was removed under reduced pressure and the residue was charged to a column of silica gel. Elution with a mixture (1:1) of hexane and dichloromethane gave **4a** (50 mg, 25%).

Compound 4a: mp 160-162 ^{0}C; IR ν_{max} (KBr) 1711, and 1647 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 233 (ε 48,000), 281 (ε 20,000), 323 nm (ε 16,700); ^{1}H NMR ($CDCl_3$) δ 3.93 (3H, s, methoxy) 6.9-8.7 (11H, m, aromatic and vinylic); MS, *m/z* 314 (M^+), 286, 151, 92, 77 and other peaks. Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.25; H, 4.49. Found: C, 79.78; H, 4.58.

Further elution of the column with dichloromethane gave unchanged **3a** (30 mg, 15%).

In a repeat run, a methanol solution of **3a** was irradiated for 5 h under analogous conditions and worked up to give **4a** (50 mg, 25%) along with unchanged **3a** (20 mg, 10%).

3.3.3.2. Irradiation of Acenaphthenone-2-ylidene Ketone 3c. A benzene solution of **3c** (200 mg, 0.53 mmol in 350 mL) was irradiated for 5 h. Solvent was removed and the residue was then charged to a column of silica gel. Elution with a mixture (1:1) of hexane and dichloromethane gave **5c** (25 mg, 13%).

Compound 5c: mp 187-189 ^{0}C; IR ν_{max} (KBr) 1776 cm^{-1}; UV λ_{max} (CH_3CN) 230 (ε 40,000), 287 (ε 20,000),340 nm (ε 17,000); ^{1}H NMR ($CDCl_3$) δ 4.8 (1H, s) 6.8-7.6 (17H, m, aromatic); MS, *m/z* 238 {$(M-C_{11}H_6)^+$ }, 222, 170 and other peaks.

Further elution of the column with dichloromethane gave unchanged **3c** (10 mg, 5%).

In a repeat run, a methanol solution of **3c** was irradiated for 5 h under analogues condition and worked up to give **5c** (30 mg, 15%).

In yet another run, a benzene solution of **3c** (20 mg, 0.053 mmol in 20 mL) was irradiated for 5 h using an output from a 250 W GE sunlamp. Solvent was removed and the residue was then charged to a column of silica gel. Elution with a mixture (1:1) of hexane and dichloromethane gave **4c** (8 mg, 40%).

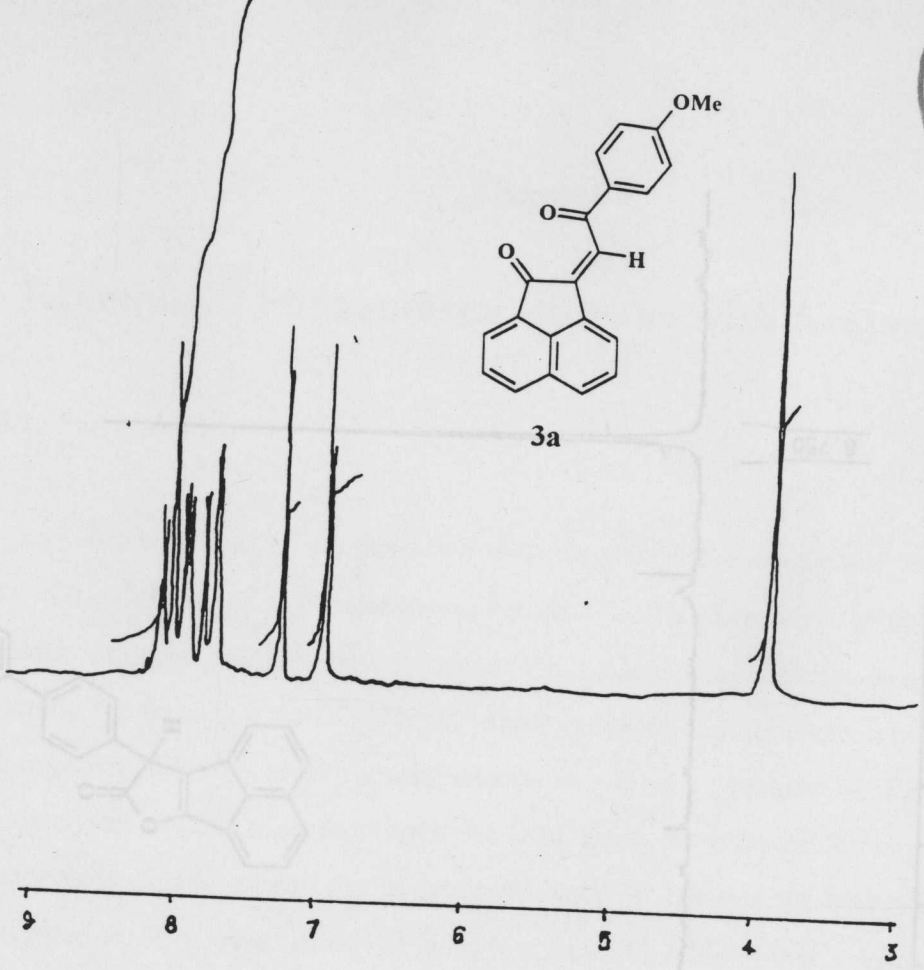
Compound 4c: mp 176-178 ^{0}C; IR ν_{max} (KBr) 1710, and 1648 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 230 (ε 52,000), 285 (ε 23,000), 327 nm (ε 18,600); ^{1}H NMR ($CDCl_3$) δ 6.7-8.8 (m, aromatic and vinylic); MS, *m/z* 360 (M^+), 256, 181, and other peaks. Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.67; H, 4.47. Found: C, 86.78; H, 4.59.

Further elution of the column with dichloromethane gave unchanged **3c** (4 mg, 20%).

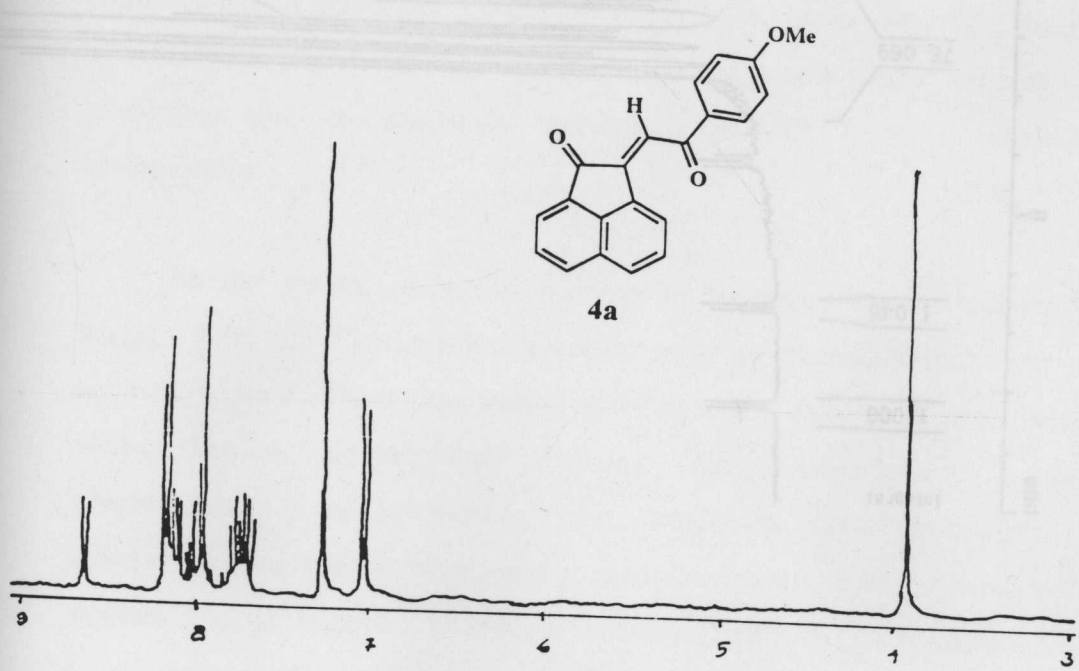
3.3.4. Thermal Isomerisation of Acenaphthenone-2-ylidene Ketone 4a. A methanol solution of **3a** (20 mg, 0.064 mmol in 20 mL) was refluxed for 12 h. The progress of the reaction was monitored by TLC. Solvent was removed under reduced pressure and the residue was charged to a column of silica gel. Elution with a mixture (1:1) of hexane and dichloromethane gave unchanged **4a** (8 mg, 40%). Further elution of the column with dichloromethane gave **3a** (5 mg, 25%).

References

1. Zenin, N.; *Ber.* **1872**, *5*, 1104.
2. Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1890**, *57*, 669, 685, 689.
3. Blatt, A. H. *J. Org. Chem.* **1950**, *15*,.869-872.
4. Lahiri, S.; Dabral, V.; Mahajan, M. P.; George, M. V. *Tetrahedron* **1977**, *33*, 3247-3260.
5. Griffin, G. W.; O'Connell, E. J. *J. Am. Chem. Soc.* **1962**, *84*, 4148-4149.
6. Zimmermann, H. E.; Durr, H. G.; Lewis, R. G.; Bram, S. *J. Am. Chem. Soc.* **1962**, *84*, 4149-4150.
7. Zimmermann, H. E.; Durr, H. G.; Givens, R. S.; Lewis, R. G. *J. Am. Chem. Soc.* **1962**, *89*, 1863-1874.
8. Sugiyama, N.; Kashima, C. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1875-1877.
9. Padwa, A.; Crumrine, D.; Shebber, A. *J. Am. Chem. Soc.* **1966**, *88*, 3064-3069.
10. Rubin, M. B.; Sander, W. *Tetrahedron Lett.* **1987**, *28*, 5137-5140.
11. Schimid, H.; Hochweber, M.; van Halben, H. *Helv. Chim. Acta* **1946**, *29*, 1466-1472.
12. Cauzzo, G.; Mazzucato, U.; Foffani, A. *Bull. Soc. Chim. Belges.* **1962**, *74*, 834-844.
13. Tsuge, O.; Tashiro, M.; Shinkai, I. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 185-190.
14. Lahiri, S.; Dabral, V.; Chauhan, S. M. S.; Chakachery, E.; Kumar, C. V.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* **1980**, *45*, 3782-3790.
15. Prathapan, S.; Ashok, K.; Cyr, D. R.; Das P. K.; George, M. V. *J. Org. Chem.* **1988**, *53*, 5826-5831.
16. Bhattacharyya, K.; Prathapan, S.; Scaria, P. M.; Das, P. K.; George, M. V. *J. Photochem. Photobiol., A: Chem.* **1987**, *37*, 147-157.



3a



4a

Figure 3.1. ^{1}H NMR spectrum (partial) of 3a and 4a.

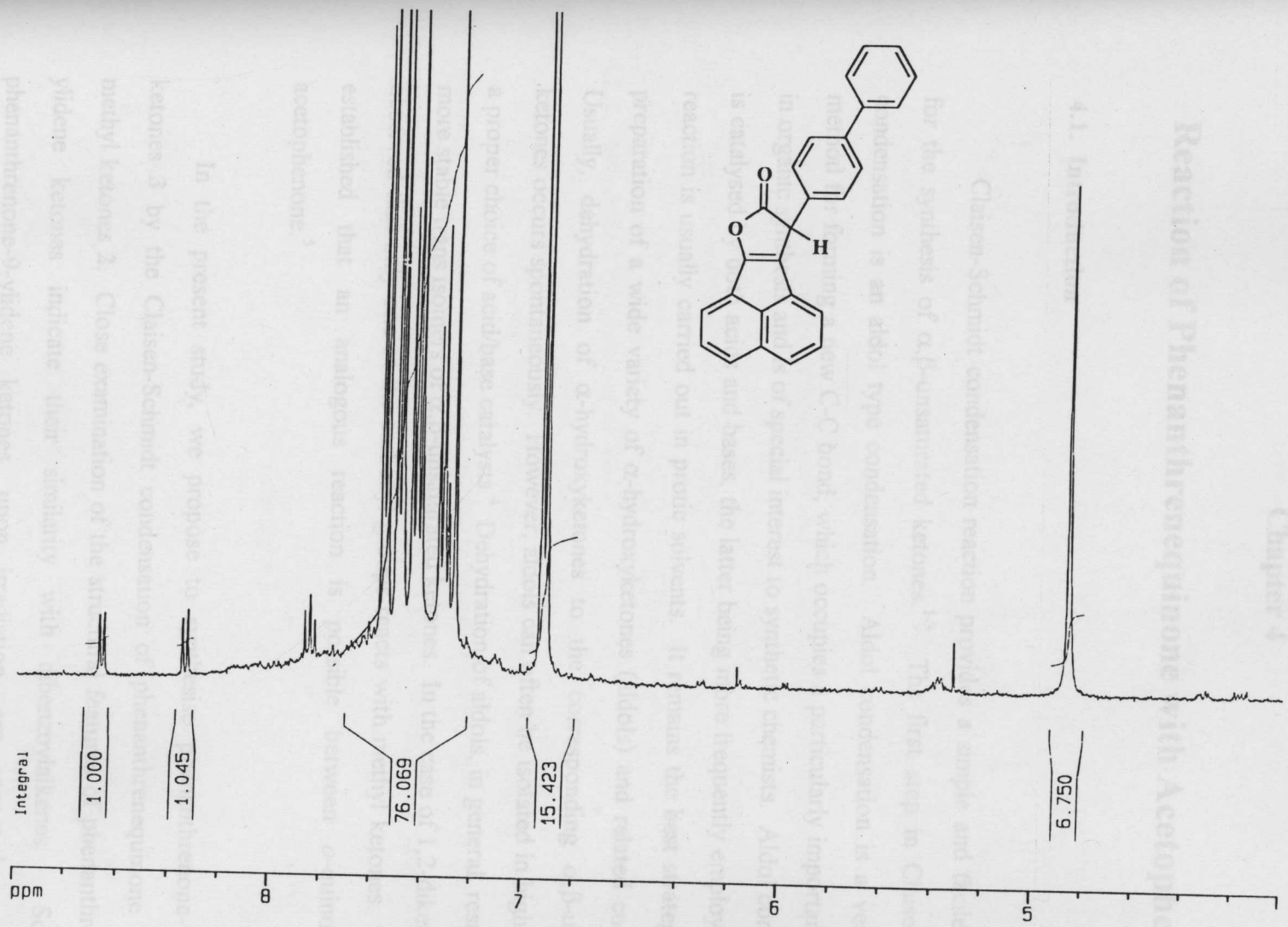


Figure 3.2. ^{1}H NMR spectrum (partial) of compound 5c.

Chapter 4

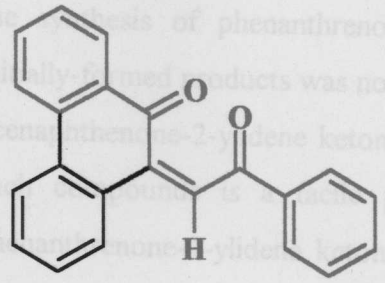
Reaction of Phenanthrenequinone with Acetophenones

4.1. Introduction

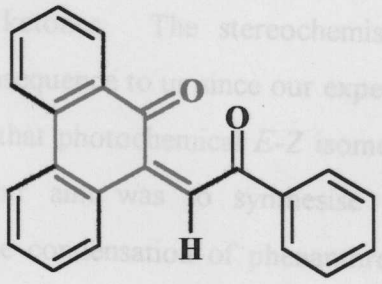
Claisen-Schmidt condensation reaction provides a simple and facile approach for the synthesis of α,β-unsaturated ketones.[1-3] The first step in Claisen-Schmidt condensation is an aldol type condensation. Aldol condensation is a very general method for forming a new C-C bond, which occupies a particularly important position in organic synthesis and is of special interest to synthetic chemists. Aldol condensation is catalysed by both acids and bases, the latter being more frequently employed.[4] This reaction is usually carried out in protic solvents. It remains the best strategy for the preparation of a wide variety of α-hydroxyketones (aldols) and related compounds. Usually, dehydration of α-hydroxyketones to the corresponding α,β-unsaurated ketones occurs spontaneously. However, aldols can often be isolated in high yields by a proper choice of acid/base catalysts.[4] Dehydration of aldols, in general, results in the more stable trans isomers of α,β-unsaturated ketones. In the case of 1,2-diketones it is observed that only one of the carbonyl groups reacts with methyl ketones. We have established that an analogous reaction is possible between *o*-quinones and acetophenone.[5]

In the present study, we propose to synthesise phenanthrenone-9-ylidene ketones **3** by the Claisen-Schmidt condensation of phenanthrenequinone (**1**) with methyl ketones **2**. Close examination of the structural features of phenanthrenone-9-ylidene ketones indicate their similarity with dibenzoylalkenes. So, these phenanthrenone-9-ylidene ketones, upon irradiation, are expected to undergo dibenzoyl alkene rearrangement and/or cis-trans isomerisation. Alternatively, these systems may be regarded as quinonemethides (Figure 4.1). Quinonemethides are known to undergo a variety of interesting reactions such as Diels-Alder reaction,

nucleophilic addition etc. The reaction of phenanthrenequinone with acetophenone is discussed in this chapter.



Dibenzoylalkene



o-Quinonemethide

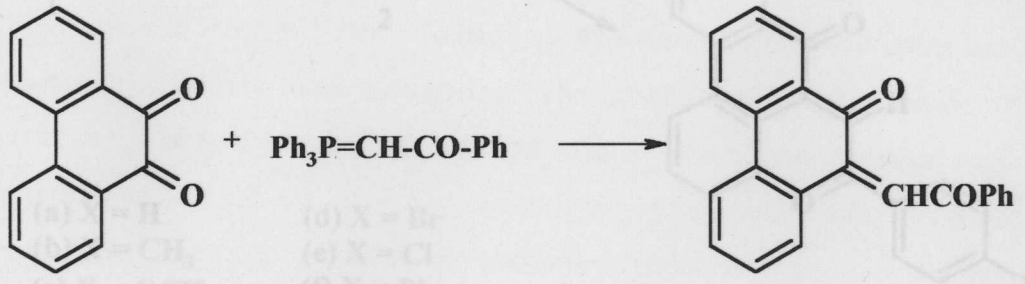
Figure. 4.1. *cis*-Dibenzoylalkene and quinonemethide components in **3a**

4.2. Results and Discussion

4.2.1. Attempted Preparation of 3a-3f

It was reported by Shechter *et al* that the Wittig reaction of phenanthrenequinone (**2**) with α-benzoylmethylenetriphenylphosphorane (**5**) gives the corresponding phenanthrenone-9-ylidene ketone[6] **3** or **4** of undefined stereochemistry (Scheme 4.1).

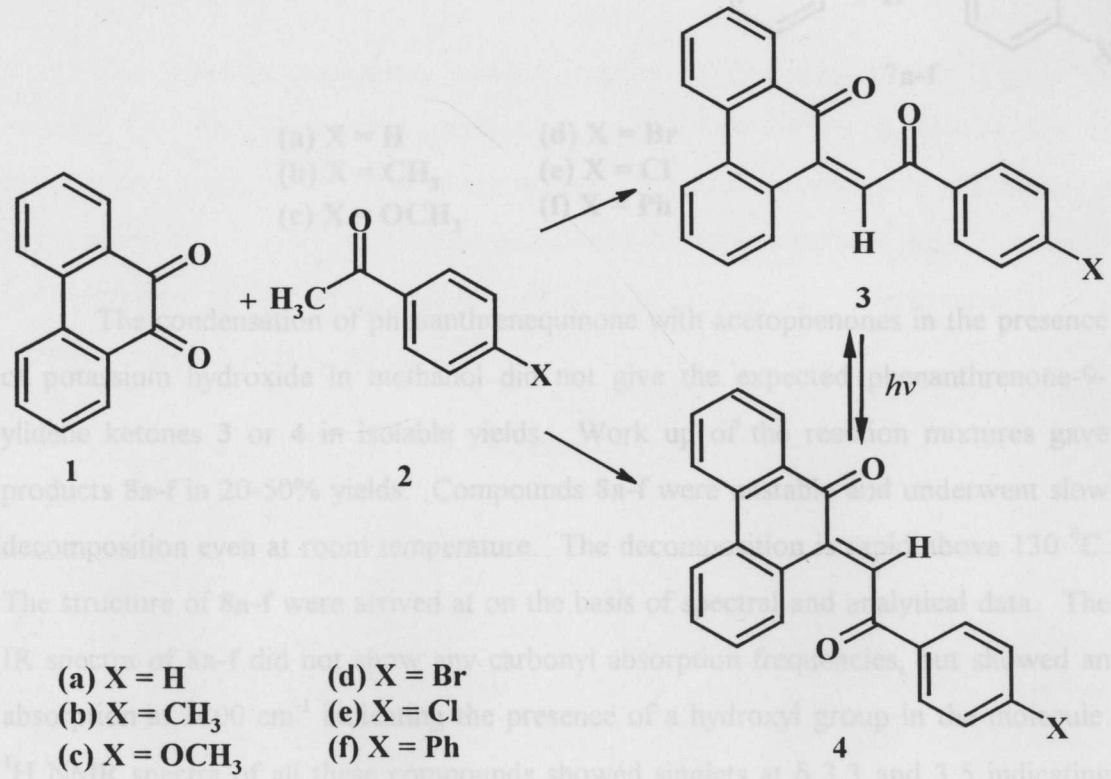
Scheme 4.1



1 **5** **3** or **4**

Based on the observation that benzil[7] and acenaphthenequinone[8] react with acetophenone to give the corresponding dibenzoylalkenes, we reasoned that the reaction of phenanthrenequinone with acetophenone should provide a simple route for the synthesis of phenanthrenone-9-ylidene ketones. The stereochemistry of the initially-formed products was not of much consequence to us since our experience with acenaphthenone-2-ylidene ketones taught us that photochemical *E-Z* isomerisation of such compounds is a facile process[5]. Our aim was to synthesise several *Z*-phenanthrenone-9-ylidene ketones **3a-f** by the condensation of phenanthrenequinone (**1**) with selected methyl ketones **2a-f** in methanol in the presence of potassium hydroxide as catalyst and, where necessary, by subsequent photochemical cis-trans isomerisation (Scheme 4.2). Methyl ketones of our choice were acetophenone (**2a**), 4-methylacetophenone (**2b**), 4-methoxyacetophenone (**2c**), 4-bromoacetophenone (**2d**), 4-chloroacetophenone (**2e**), and 4-phenylacetophenone (**2f**).

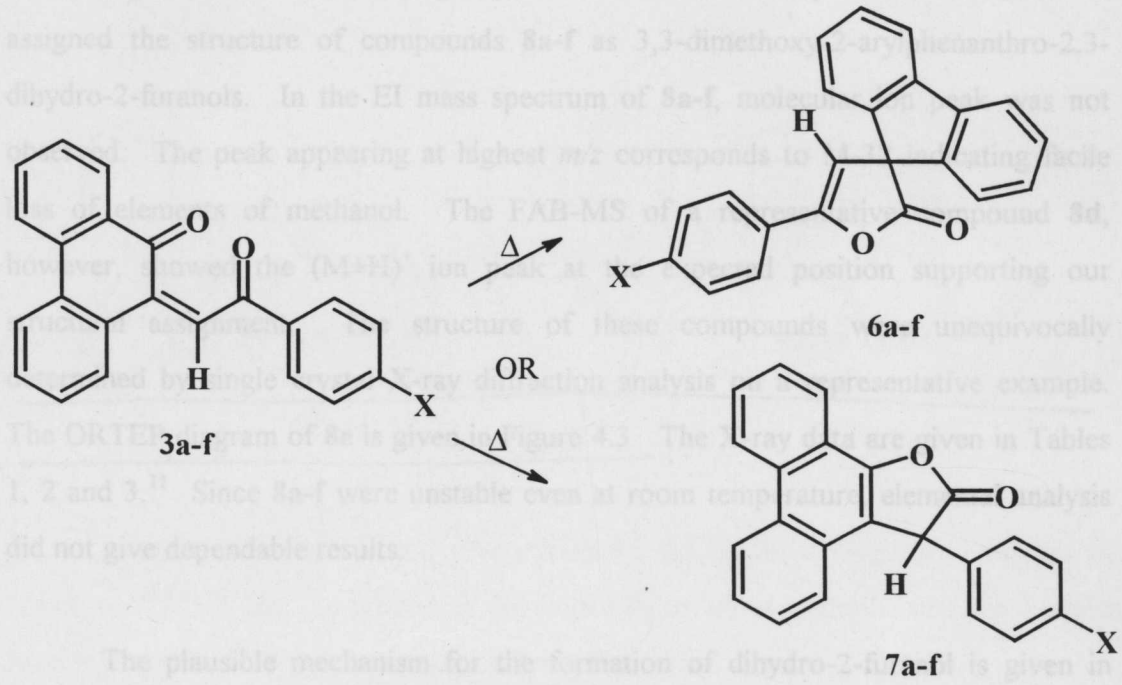
Scheme 4.2



(a) X = H **(d) X = Br**
(b) X = CH_3 **(e) X = Cl**
(c) X = OCH_3 **(f) X = Ph**

Z-phenanthrenone-9-ylidene ketones are expected to undergo facile thermal rearrangement to give furanones **6** and/or **7** (Scheme 4.3) based on the observation that *cis*-dibenzoylalkenes undergo thermal rearrangement to give furanones.[9,10]

Scheme 4.3



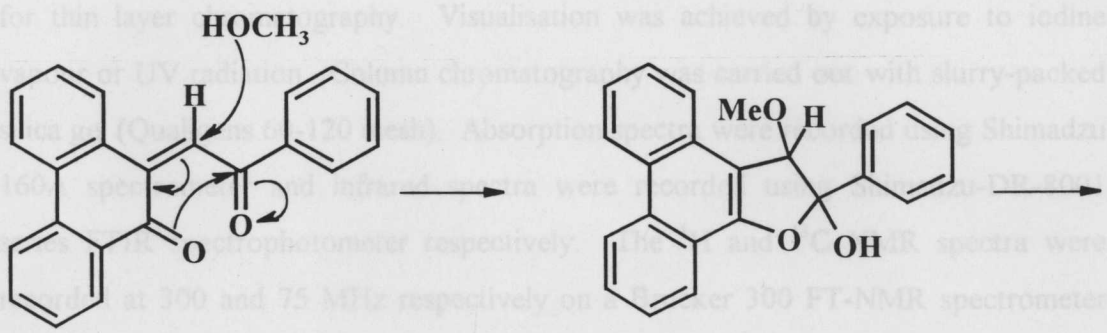
(a) X = H **(d) X = Br**
(b) X = CH_3 **(e) X = Cl**
(c) X = OCH_3 **(f) X = Ph**

The condensation of phenanthrenequinone with acetophenones in the presence of potassium hydroxide in methanol did not give the expected phenanthrenone-9-ylidene ketones **3** or **4** in isolable yields. Work up of the reaction mixtures gave products **8a-f** in 20-50% yields. Compounds **8a-f** were unstable and underwent slow decomposition even at room temperature. The decomposition is rapid above 130 ^{0}C. The structure of **8a-f** were arrived at on the basis of spectral and analytical data. The IR spectra of **8a-f** did not show any carbonyl absorption frequencies, but showed an absorption at 3400 cm^{-1} indicating the presence of a hydroxyl group in the molecule. ^{1}H NMR spectra of all these compounds showed singlets at δ 3.3 and 3.5 indicating the presence of two methoxy groups in the molecule. ^{13}C NMR spectra did not show the presence of carbonyl carbon in the molecule but showed the presence of two

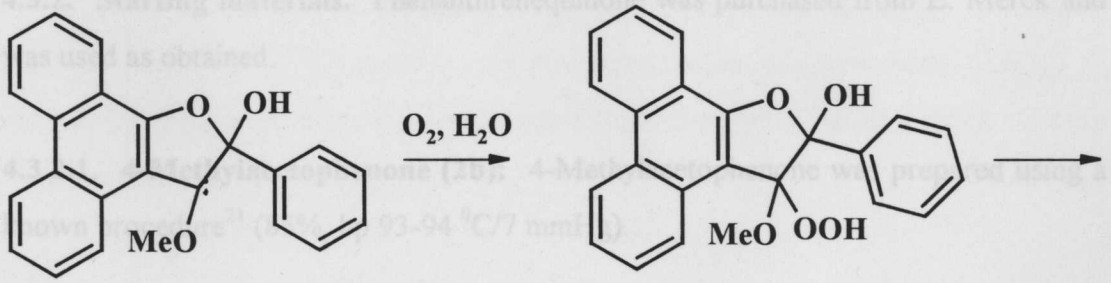
methoxy carbons at δ 51 and 52. The ^{13}C NMR signals at δ 108 and 110 suggest the presence of hemiacetal and acetal carbons. All other ^{13}C NMR signals correspond to aromatic carbons. IR, ^{1}H NMR, and ^{13}C NMR spectra of compound **8b** are given in Figure 4.2. The UV spectra of all these compounds were similar to that of phenanthrene. Therefore, compounds **8a-f** should contain a phenanthrene moiety, two methoxy groups and a hydroxyl group. Based on all these spectral information we assigned the structure of compounds **8a-f** as 3,3-dimethoxy-2-arylphenanthro-2,3-dihydro-2-furanols. In the EI mass spectrum of **8a-f**, molecular ion peak was not observed. The peak appearing at highest *m/z* corresponds to M-32 indicating facile loss of elements of methanol. The FAB-MS of a representative compound **8d**, however, showed the $(M+H)^+$ ion peak at the expected position supporting our structural assignment. The structure of these compounds were unequivocally determined by single crystal X-ray diffraction analysis on a representative example. The ORTEP diagram of **8e** is given in Figure 4.3. The X-ray data are given in Tables 1, 2 and 3.[11] Since **8a-f** were unstable even at room temperature, elemental analysis did not give dependable results.

The plausible mechanism for the formation of dihydro-2-furanol is given in Scheme 4.4. Initially formed phenanthrenone-9-ylidene ketone underwent further reaction with methanol in the presence of base to yield the more stable phenanthrene ring system **9**. Under the reaction conditions **9** underwent autoxidation to give hydroperoxide **11**[12,13] and **11** was converted to hemiacetal **12**. Hemiacetal **12** was subsequently converted to acetal **8**.[14,15,16]

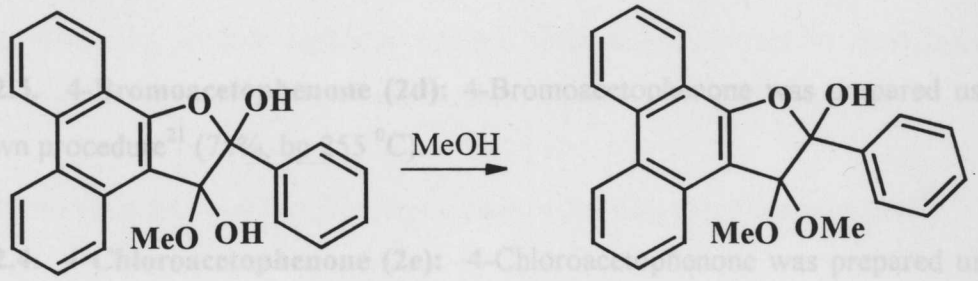
Scheme 4.4



3 **9**



10 11



12 8

Several methods for the preparation of 2,3-dihydrofurans are reported in literature.[17,18,19,20] But the procedure developed by us offers a simple, one pot method for the preparation of phenanthro-2,3-dihydrofuran derivatives.

4.3. Experimental

4.3.1. 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 gel or aluminium sheets coated with silica gel (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 gel (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 and 75 MHz respectively on a Brucker 300 FT-NMR spectrometer with tetramethylsilane as internal standard.

4.3.2. Starting materials. Phenanthrenequinone was purchased from E. Merck and was used as obtained.

4.3.2.1. 4-Methylacetophenone (2b): 4-Methylacetophenone was prepared using a known procedure[21] (85%, bp 93-94 ^{0}C/7 mmHg).

4.3.2.2. 4-Methoxyacetophenone (2c): 4-Methoxyacetophenone was prepared using a known procedure[21] (90%, bp 265 ^{0}C).

4.3.2.3. 4-Bromoacetophenone (2d): 4-Bromoacetophenone was prepared using a known procedure[21] (75%, bp 255 ^{0}C).

4.3.2.4. 4-Chloroacetophenone (2e): 4-Chloroacetophenone was prepared using a known procedure[21] (75%, bp 237 ^{0}C).

4.3.2.5. 4-Phenylacetophenone (2f): 4-Phenylacetophenone was prepared using a known procedure[21] (76%, mp 120 ^{0}C).

4.3.3. Preparation of 8a-f

4.3.3.1. Preparation of 8a. A mixture of phenanthrenequinone (5.2 g, 25 mmol), acetophenone (3.24 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 h and later kept in a refrigerator for 48 h. The solid product separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane.

3,3-Dimethoxy-2-phenylphenanthro-2,3-dihydro-2-furanol (8a): (30%); mp 116-118 ^{0}C (dec.); IR ν_{max} (KBr) 3408 cm^{-1} (OH); UV λ_{max} (CH_3CN) 224 (ε 20,000), 248 (ε 30,000), 302 (ε 5,100), 359 nm (ε 2,400); ^{1}H NMR ($CDCl_3$) δ 3.24 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 5.6 (s, 1H, OH), 7.2-8.5 (m, 13H, aromatic); MS, *m/z* 340 {(M-CH_3OH)$^+$}, 208, 180, 152, 135 and other peaks.

In a repeat run a mixture of phenanthrenequinone (5.2 g, 25 mmol), acetophenone (3.2 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred at room temperature overnight. No new products were formed under these conditions.

4.3.3.2. Preparation of 8b. A mixture of phenanthrenequinone (5.2 g, 25 mmol), 4-methylacetophenone (3.6 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 h and later kept in a refrigerator for 48 h. The solid product separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane.

3,3-Dimethoxy-2-(4'-methylphenyl)phenanthro-2,3-dihydro-2-furanol (8b): (20%); mp 116-118 ^{0}C (dec.); IR ν_{max} (KBr) 3406 (OH), and 2941, 1633, 1500 cm^{-1}; UV λ_{max} (CH_3CN) 215 (ε 14,000), 251 (ε 5,800), 341 nm (ε 1,500); ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 3H, CH_3); 3.2 (s, 3H, OCH_3), 3.5 (s, 3H, OCH_3), 5.6 (s,1H, OH), 7-8.6 (m, 12H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.1, 51.2, 52.2, 108.7, 110.5, 121.6, 122.8, 123, 123.1, 123.5, 123.9, 124.1, 125.7, 126.6, 126.9, 127.1, 128.3, 128.4, 129.3, 130.1, 132.7, 134.6, 138.6; MS, *m/z* 354 {$(M-CH_3OH)^+$}, 326, 221, 119, 91 and other peaks.

4.3.3.3. Preparation of 8c. A mixture of phenanthrenequinone (5.2 g, 25 mmol), 4-methoxyacetophenone (4.1 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 h and later kept in a refrigerator for 48 h. The solid product separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane.

3,3-Dimethoxy-2-(4'-methoxyphenyl)phenanthro-2,3-dihydro-2-furanol (8c): (50%); mp 136-138 ^{0}C (dec.); IR ν_{max} (KBr) 3408, 2992, and 1635 cm^{-1}; UV λ_{max} (CH_3CN) 248 (ε 42,000), 302 (ε 8,300), 359 nm (ε 2,600); ^{1}H NMR ($CDCl_3$) δ 3.22 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 5.6 (s, 1H, OH), 6.9-8.7 (m, 12H, aromatic); MS, *m/z* 370 {$(M-CH_3OH)^+$}, 342, 107 and other peaks.

4.3.3.4. Preparation of 8d. A mixture of phenanthrenequinone (5.2 g, 25 mmol), 4-bromoacetophenone (5.4 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 h and later kept in a refrigerator for 48 h. The solid product separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane.

3,3-Dimethoxy-2-(4'-bromophenyl)phenanthro-2,3-dihydro-2-furanol (8d): (25%); mp 140-143 ^{0}C (dec.); IR ν_{max} (KBr) 3400, 2943, 1614, 1589, and 1520 cm^{-1}; UV λ_{max} (CH_3CN) 224 (ε 32,200), 248 (ε 37,000), 308 (ε 7,100) 341 nm (ε 2,000); ^{1}H NMR ($CDCl_3$) δ 3.19 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 5.6 (s, 1H, OH), 7.2-8.8 (m, 12H, aromatic); ^{13}C NMR δ 51.3, 52.2, 108.7, 109.9, 111, 122.9, 124.1, 124.2, 126.8, 127.2, 128.9, 130.8, 132.8, 136.9, 154.2; EIMS, *m/z* 420 {$(M-CH_3OH)^+$}, 390, 221, 185; FAB-MS, *m/z* 453 {$(M+H)^+$}. Anal. Calcd for $C_{24}H_{19}O_4Br$: C, 63.87; H, 4.24. Found: C, 64.47; H, 4.21.

4.3.3.5. Preparation of 8e. A mixture of phenanthrenequinone (5.2 g, 25 mmol), 4-chloroacetophenone (4.2 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 h and later kept in a refrigerator for 48 h. The solid product separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane.

3,3-Dimethoxy-2-(4'-chlorophenyl)phenanthro-2,3-dihydro-2-furanol (8e): (20%); mp 142-143 ^{0}C (dec.); IR ν_{max} (KBr) 3419 (OH), 2949, 1637, 1603, 1506, 756 cm^{-1}; UV λ_{max} (CH_3CN) 209 (ε 55,000), 263 (ε 56,000), 320 (ε 8,200), 410 nm (ε 3,300); ^{1}H NMR ($CDCl_3$) δ 3.25 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 5.6 (s, 1H, OH), 6.5-8.5 (m, 13H, aromatic); MS, *m/z* 374 {$(M-CH_3OH)^+$}, 346, 315, 139, 111 and other peaks.

4.3.3.6. Preparation of 8f. A mixture of phenanthrenequinone (5.2 g, 25 mmol), 4-phenylacetophenone (5.3 g, 27 mmol), and powdered potassium hydroxide (1.0 g) in methanol (30 mL) was stirred around 60 ^{0}C for 1 h and later kept in a refrigerator for

48 h. The solid product separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane.

3,3-Dimethoxy-2-(4'-phenylphenyl)phenanthro-2,3-dihydro-2-furanol (8f): (30%); mp 136-138 ^{0}C (dec.); IR ν_{max} (KBr), 3404 (OH), 1635, 1610 and 1506 cm^{-1}; UV λ_{max} (CH_3CN) 203 (ε 60,000), 257 (ε 59,000), 308 (ε 9,200), 341 nm (ε 2,400); ^{1}H NMR ($CDCl_3$) δ 3.28 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 5.6 (s, 1H, OH), 7.4-8.8 (m, 17H, aromatic); MS, *m/z* 416 {$(M-CH_3OH)^+$}, 416, 388, 357, 181 and other peaks. Anal. Calcd for $C_{30}H_{24}O_4$: C, 80.34; H, 5.39. Found: C, 80.30; H, 5.14.

4.3.4. X-Ray Crystallographic Analysis of 8e

The crystal was grown in a mixture (3:2) of dichloromethane and hexane. A single crystal of suitable size (0.2 x 0.2 x 0.1 mm) was taken from it. X-ray diffraction experiments were performed at room temperature on a Enraf-Nonius CAD4 Diffractrometer with a graphite-monochromated Mo Kα radiation (l = 1.5 A^0). The intensity data were measured using ω–2θ scan technique. The structure was solved by SHELXS-97 and refined by SHELXL-97 with anisotropic temperature factors for the non-hydrogen atoms.

References

1. Nielsen, A. T.; Houliban, W. J. *Organic Reactions* **1968**, *16*, 1-438.
2. Claisen, L.; Claparede, A. *Ber.* **1881**, *14*, 2460.
3. House, H.O., *Modern Synthetic Reactions,* 2nd ed.; Benjamin: Menlopark, CA, **1972**.
4. Perkin, W. *Ber.* **1882**, *15*, 2802.
5. For the reaction between acenaphthenequinone and acetophenones, see Chapter 2 of this thesis.
6. Sullivan, W. W.; Ullman, D.; Shechter, H. *Tetrahedron Lett.* **1969**, *6*, 457-461.
7. Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1890**, *57*, 689.
8. Tsuge, O.; Tashiro, M.; Shinkai, I. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 185-190.
9. Zenin, N.; *Ber.* **1872**, *5*, 1104.
10. Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1890**, *57*, 669.
11. Govindasamy, L.; Velmurugan, D.; Jose, B.; Prathapan, S.; Suh, H. *Acta Crystallogr. Sect. C: Struct. Commun.* (communicated).
12. Barton, D. H. R.; Jones, D. W. *J. Chem. Soc.* **1965**, 3563-3571.
13. Russell, G. A.; Bemis, A. G. *J. Am. Chem. Soc.* **1966**, *88*, 5491-5495.
14. Grunwald, E. *J. Am. Chem. Soc.* **1985**, *107*, 4715-4720.
15. Soerensen, P. E.; Pedersen, K. J.; Pedersen, P. R.; Kanagasabapathi, V. M.; Mc Clelland, K. A. *J. Am. Chem. Soc.* **1988**, *110*, 5118-5123.
16. Leussing, P. L. *J. Org. Chem.* **1990**, *55*, 666-673.
17. Mawaziny, S.; Lakani, A. M. *Chim. Chron.* **1996**, *25*, 215-234 (*Chem. Abstr.* **1998**, *126*, 31704).
18. Cameron, B.; Serge, L.; Petpiboon, P.; Zhaoyin, W.; Pierre, H.; Yongxin, H.; Gregory, H. U.S. patent 9716, 435, 1998 (*Chem. Abstr.* **1998**, *127*, 34112).
19. Srogl, J. *Synthesis* **1975**, 717-724.
20. Parkanyi, C.; Lablache-Combier, A.; Marko, I.; Ofenberg, H. *J. Org. Chem.* **1976**, *41*, 151-153.
21. Vogel, A. I. *A Text Book of Practical Organic Chemistry*; English Language Book Society and Longman Group Ltd.: London; **1996**; pp 1012-1013.

Table 1. Crystal Data and Structure Refinement for 8e

Empirical formula	$C_{24}H_{19}O_4Cl$	
Formula weight	406.84	
Temperature	293(2) K	
Wavelength	1.54180 A	
Crystal system, space group	Monoclinic, $P2_{1/n}$	
Unit cell dimensions	a = 8.797(3) A	$\alpha = 90.00^0$
	b = 11.916(1) A	$\beta = 100.18(2)^0$
	c = 19.083(3) A	$\gamma = 90.00(7)^0$
Volume	1968.9(8) A^3	
Z, Calculated density	4, 1.372 Mg/m^3	
Absorption coefficient (μ)	0.223 mm^{-1}	
F(000)	848	
Crystal size	0.2 x 0.2 x 0.1 mm	
θ range for data collection	4.47 to 69.99^0	
Index ranges	-10<=h<=10, 0<=k<=14, 0<=l<=22	
Reflections collected / unique	3402 / 3172 [R(int) = 0.0280]	
Completeness to $2\theta = 69.99$	99.8%	
Absorption correction	Psi scan	
Max. and min. transmission	0.9504 and 0.8915	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3172 / 0 / 236	
Goodness-of-fit on F^2	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.1521	
R indices (all data)	R1 = 0.0561, wR2 = 0.1554	
Extinction coefficient	0.0123(16)	
Largest diff. peak and hole	0.316 and -0.225 $e.A^{-3}$	

Table 2. Bond Lengths [in angstroms] of 8e

C(11)-C(20)	1.744(3)
O(1)-C(16)	1.375(3)
O(1)-H(1)	0.8200
O(2)-C(15)	1.407(3)
O(2)-C(23)	1.433(3)
O(3)-C(15)	1.405(3)
O(3)-C(24)	1.423(3)
O(4)-C(1)	1.374(3)
O(4)-C(16)	1.456(3)
C(1)-C(14)	1.344(4)
C(1)-C(2)	1.427(4)
C(2)-C(7)	1.412(4)
C(2)-C(3)	1.404(4)
C(3)-C(4)	1.360(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.386(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.367(5)
C(5)-H(5)	0.9300
C(6)-C(7)	1.408(4)
C(6)-H(6)	0.93(3)
C(7)-C(8)	1.457(4)
C(8)-C(13)	1.426(4)
C(8)-C(9)	1.402(4)
C(9)-C(10)	1.362(5)
C(9)-H(9)	0.96(3)
C(10)-C(11)	1.389(5)
C(10)-H(10)	0.9300
C(11)-C(12)	1.371(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.407(4)

C(12)-H(12)	0.9300
C(13)-C(14)	1.438(4)
C(14)-C(15)	1.517(4)
C(15)-C(16)	1.586(4)
C(16)-C(17)	1.515(4)
C(17)-C(18)	1.387(4)
C(17)-C(22)	1.382(4)
C(18)-C(19)	1.389(4)
C(18)-H(18)	0.9300
C(19)-C(20)	1.364(5)
C(19)-H(19)	0.9300
C(20)-C(21)	1.371(5)
C(21)-C(22)	1.382(4)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600

Table 2. Bond Angles [in degrees] of 8e

C(16)-O(1)-H(1)	109.50
C(15)-O(2)-C(23)	116.1(2)
C(15)-O(3)-C(24)	116.9(2)
C(1)-O(4)-C(16)	106.11(19)
C(14)-C(1)-O(4)	115.3(2)
C(14)-C(1)-C(2)	124.9(2)
O(4)-C(1)-C(2)	119.8(2)
C(7)-C(2)-C(1)	116.5(3)
C(7)-C(2)-C(3)	121.0(2)
C(1)-C(2)-C(3)	122.5(3)
C(4)-C(3)-C(2)	120.5(3)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	119.2(3)
C(3)-C(4)-H(4)	120.4
C(5)-C(4)-H(4)	120.4
C(4)-C(5)-C(6)	121.6(3)
C(4)-C(5)-H(5)	119.2
C(6)-C(5)-H(5)	119.2
C(7)-C(6)-C(5)	121.2(3)
C(7)-C(6)-H(6)	118.0(19)
C(5)-C(6)-H(6)	120.7(18)
C(2)-C(7)-C(6)	116.6(3)
C(2)-C(7)-C(8)	120.2(2)
C(6)-C(7)-C(8)	123.2(3)
C(13)-C(8)-C(9)	117.8(3)
C(13)-C(8)-C(7)	120.2(2)
C(9)-C(8)-C(7)	121.9(3)
C(10)-C(9)-C(8)	122.2(3)
C(10)-C(9)-H(9)	123.1(18)
C(8)-C(9)-H(9)	114.7(18)
C(9)-C(10)-C(11)	120.0(3)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(12)-C(11)-C(10)	120.0(3)
C(12)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0
C(11)-C(12)-C(13)	121.2(3)
C(11)-C(12)-H(12)	119.4
C(13)-C(12)-H(12)	119.4
C(8)-C(13)-C(14)	117.8(3)
C(8)-C(13)-C(12)	118.7(3)
C(14)-C(13)-C(12)	123.4(3)
C(1)-C(14)-C(13)	120.2(2)
C(1)-C(14)-C(15)	107.1(2)

C(13)-C(14)-C(15)	132.7(2)
O(3)-C(15)-O(2)	112.0(2)
O(3)-C(15)-C(14)	115.2(2)
O(2)-C(15)-C(14)	109.5(2)
O(3)-C(15)-C(16)	105.6(2)
O(2)-C(15)-C(16)	113.3(2)
C(14)-C(15)-C(16)	100.7(2)
O(1)-C(16)-O(4)	109.1(2)
O(1)-C(16)-C(17)	109.0(2)
O(4)-C(16)-C(17)	106.6(2)
O(1)-C(16)-C(15)	110.9(2)
O(4)-C(16)-C(15)	103.17(19)
C(17)-C(16)-C(15)	117.7(2)
C(18)-C(17)-C(22)	119.2(3)
C(18)-C(17)-C(16)	120.8(3)
C(22)-C(17)-C(16)	120.0(3)
C(17)-C(18)-C(19)	120.5(3)
C(17)-C(18)-H(18)	119.7
C(19)-C(18)-H(18)	119.7
C(20)-C(19)-C(18)	118.9(3)
C(20)-C(19)-H(19)	120.5
C(18)-C(19)-H(19)	120.5
C(19)-C(20)-C(21)	121.6(3)
C(19)-C(20)-C(11)	118.9(3)
C(21)-C(20)-C(11)	119.6(3)
C(20)-C(21)-C(22)	119.5(3)
C(20)-C(21)-H(21)	120.2
C(22)-C(21)-H(21)	120.2
C(17)-C(22)-C(21)	120.2(3)
C(17)-C(22)-H(22)	119.9
C(21)-C(22)-H(22)	119.9

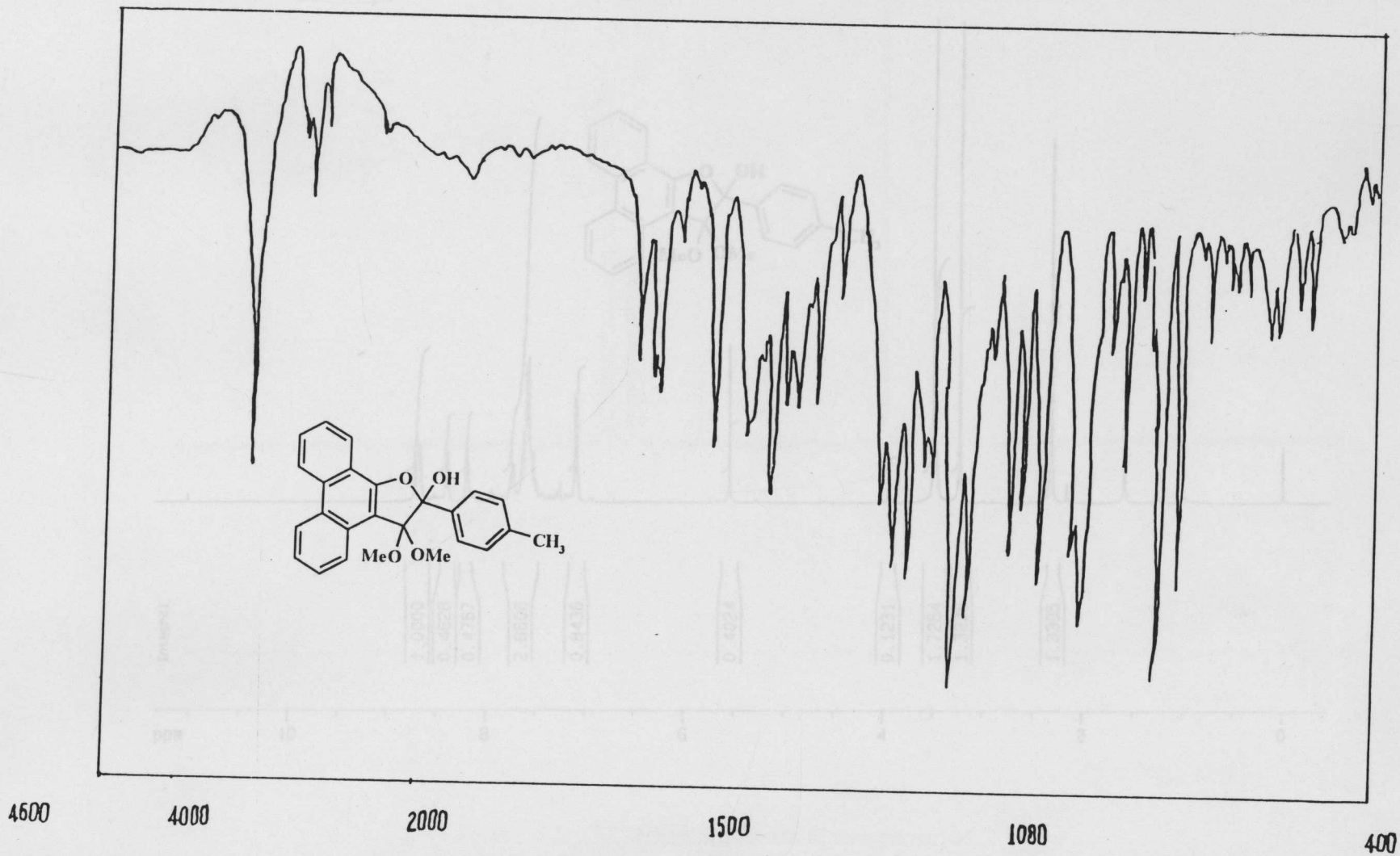


Figure 4.2a. FTIR spectrum of compound 8b.

Figure 4.2b. ^{1}H NMR spectrum of compound 8b.

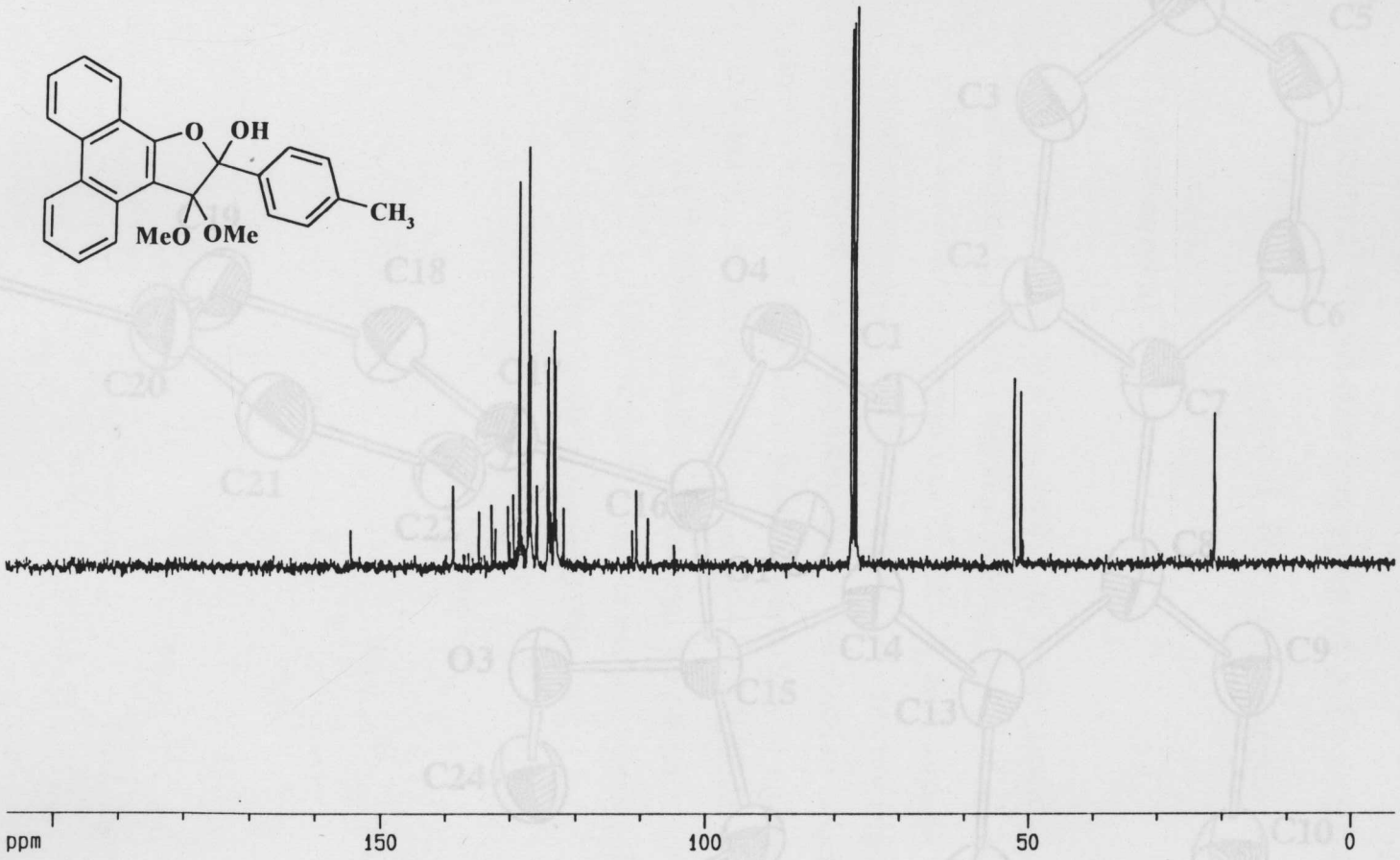


Figure 4.2c. ^{13}C NMR spectrum of compound 8b.

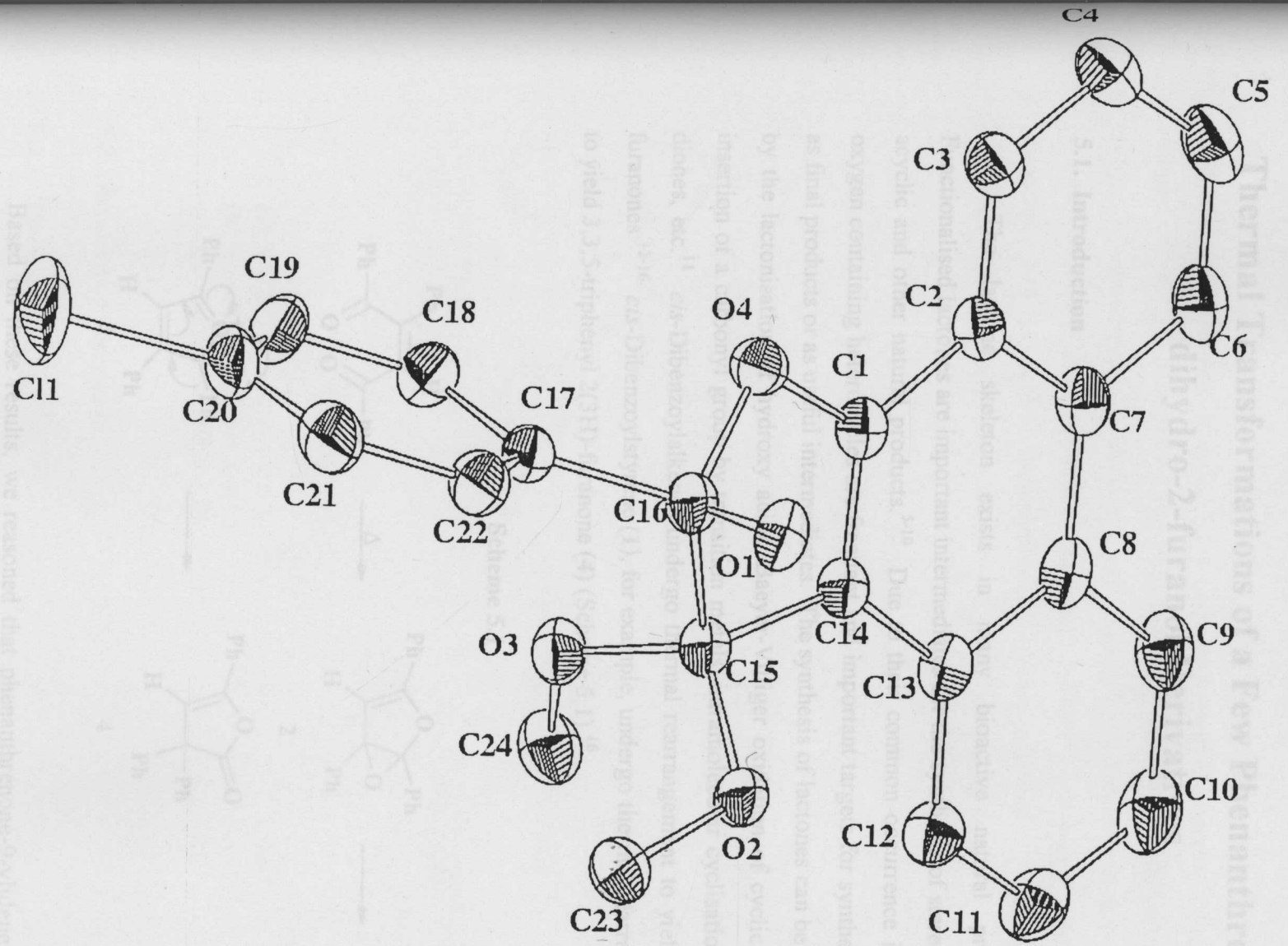


Figure 4.3. ORTEP diagram of molecular structure of 8e in the crystal. All the thermal ellipsoids are represented at the 50% probability density level.

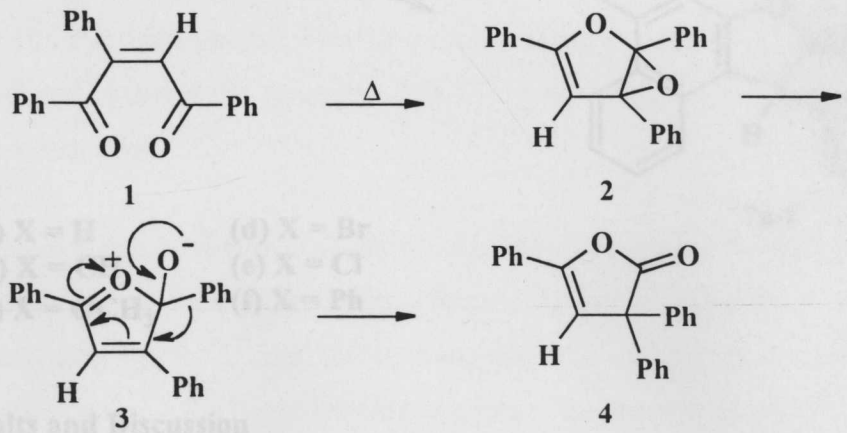
Chapter 5

Thermal Transformations of a Few Phenanthro-2,3-dihydro-2-furanol Derivatives

5.1. Introduction

The lactone skeleton exists in many bioactive natural products.[1-4] Functionalised lactones are important intermediates for the synthesis of stereo-defined acyclic and other natural products.[5-10] Due to their common occurrence in nature, oxygen containing heterocycles are frequent and important targets for synthesis either as final products or as useful intermediates. The synthesis of lactones can be achieved by the lactonisation of hydroxy acids, Baeyer-Villiger oxidation of cyclic ketones, insertion of a carbonyl group by transition metals, intramolecular cyclisation of 1,4-diones, etc.[11] *cis*-Dibenzoylalkenes undergo thermal rearrangement to yield 2(3H)-furanones.[12-16] *cis*-Dibenzoylstyrene (**1**), for example, undergo thermal rearrangement to yield 3,3,5-triphenyl 2(3H)-furanone (**4**) (Scheme 5.1).[16]

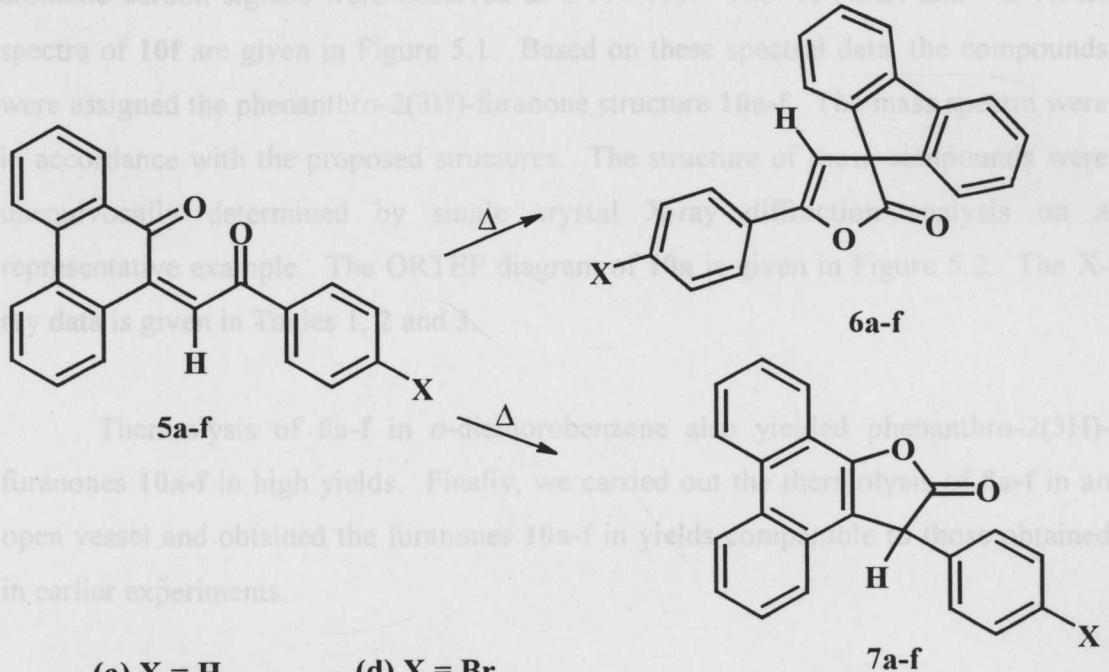
Scheme 5.1



Based on these results, we reasoned that phenanthrenone-9-ylidene ketones **5a-f** on heating should yield either spirofuranones **6a-f** or phenanthrofuranones **7a-f** (Scheme 5.2). However, our attempts to synthesise phenanthrenone-9-ylidene

ketones **5a-f** by the condensation of phenanthrenequinone with acetophenone were not successful. The only isolated product in these reactions were the corresponding furanols **8a-f** formed by the addition of methanol to **5a-f**. In this chapter, we discuss the thermal and chemical transformation of a few representative furanols. The furanols we examined include 3,3-dimethoxy-2-phenylphenanthro-2,3-dihydro-2-furanol (**8a**), 3,3-dimethoxy-2-(4'-methylphenyl)phenanthro-2,3-dihydro-2-furanol (**8b**), 3,3-dimethoxy-2-(4'-methoxyphenyl)phenanthro-2,3-dihydro-2-furanol (**8c**), 3,3-dimethoxy-2-(4'-bromophenyl)phenanthro-2,3-dihydro-2-furanol (**8d**), 3,3-dimethoxy-2-(4'-chlorophenyl)phenanthro-2,3-dihydro-2-furanol (**8e**), 3,3-dimethoxy-2-(4'-phenylphenyl)phenanthro-2,3-dihydro-2-furanol (**8f**).

Scheme 5.2



(a) X = H **(d) X = Br**
(b) X = CH_3 **(e) X = Cl**
(c) X = OCH_3 **(f) X = Ph**

5.2. Results and Discussion

5.2.1. Thermal Studies

The dihydrofuranol derivatives **8a-f** were unstable and underwent facile thermal rearrangement when heated upto their melting points. We have carried out

the thermolysis of **8a-f** under different conditions namely neat thermolysis in a sealed vessel, neat thermolysis in an open vessel, and thermolysis in a suitable solvent. The neat thermolysis of **8a-f** in sealed tubes gave **10a-f** in high yields (>80%). The structures of **10a-f** were arrived at on the basis of spectral and analytical data. All these thermolysis products showed strong IR absorptions at 1813 cm^{-1} indicating the presence of a γ-lactone residue in the molecule. UV absorption spectra of these compounds were dominated by absorption of the phenanthrene chromophore. ^1H NMR spectrum of **10a** showed a singlet (3H) at δ 3.4 due to the methoxy group and multiplet at δ 7.2-8.9 (13H) due to aromatic protons indicating the loss of a molecule of methanol from the parent compound **8a**. ^{13}C NMR spectrum of **10c** and **10f** were recorded. Compound **10f** showed the presence of a methoxy carbon at δ 54, lactone carbonyl at δ 175 and the carbon which is attached to methoxy group at δ 80. All the aromatic carbon signals were observed at δ 110-160. The ^1H NMR and ^{13}C NMR spectra of **10f** are given in Figure 5.1. Based on these spectral data, the compounds were assigned the phenanthro-2(3H)-furanone structure **10a-f**. The mass spectra were in accordance with the proposed structures. The structure of these compounds were unequivocally determined by single crystal X-ray diffraction analysis on a representative example. The ORTEP diagram of **10a** is given in Figure 5.2. The X-ray data is given in Tables 1, 2 and 3.

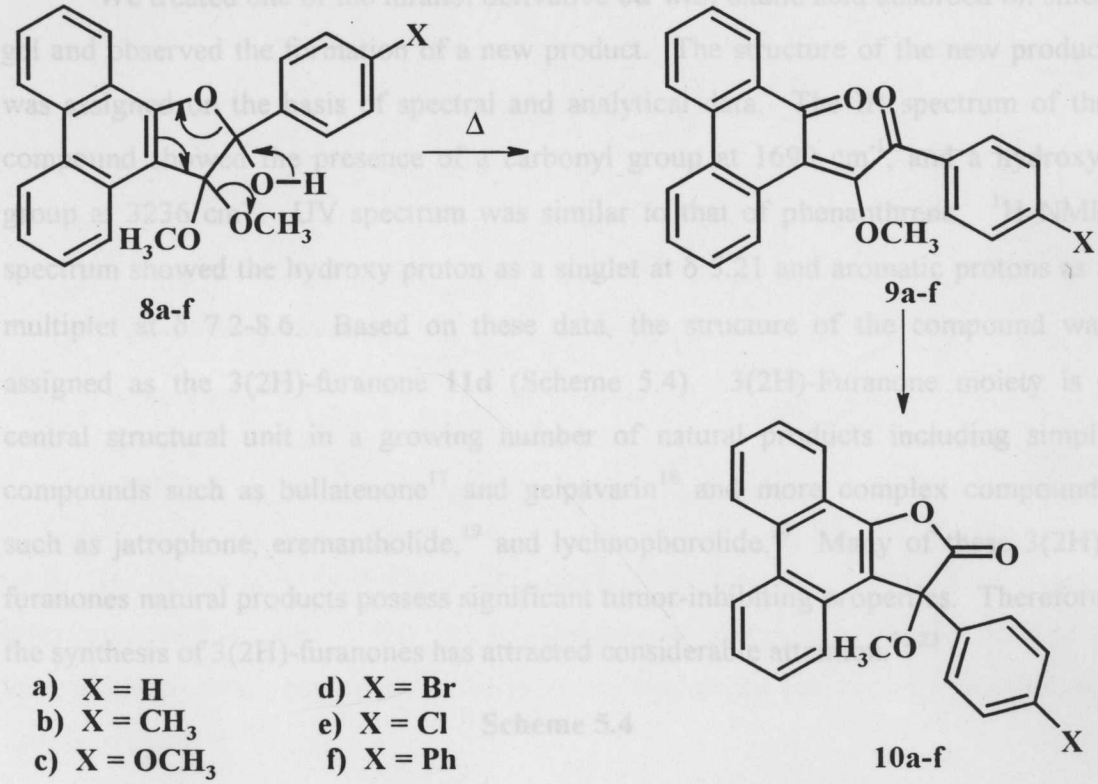
Thermolysis of **8a-f** in *o*-dichlorobenzene also yielded phenanthro-2(3H)-furanones **10a-f** in high yields. Finally, we carried out the thermolysis of **8a-f** in an open vessel and obtained the furanones **10a-f** in yields comparable to those obtained in earlier experiments.

We have also carried out the thermogravimetric studies (TG) on **8** to study the thermal behaviour of these compounds. According to the TG data, the compound starts rearranging at 90 ^0C and the rearrangement is completed at 140 ^0C under nitrogen atmosphere. This rearrangement appears to proceed through a three-step process. The TG and DTA traces of **8a** are given in Figure 5.3.

Based on these results, we propose the following mechanism for the thermal rearrangement of **8** to **10** (Scheme 5.3). The furanol **8** on heating eliminate a

molecule of methanol to give methoxydibenzoylalkene **9**. Subsequently, **9** undergoes thermal transformation analogous to that reported for other dibenzoylalkenes[12-16] to yield the corresponding 2(3H)-furanone **10**. It is interesting to notice that the rearrangement of **9** to **10** takes place below 140 ^{0}C whereas analogous rearrangement of dibenzoylstyrene takes place at temperatures well above 240 ^{0}C. The facile rearrangement in the case of **9** may be attributed to the formation of the stable phenanthrene ring system present in **10**.

Scheme 5.3



8a-f **9a-f** **10a-f**

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

In order to establish the intermediacy of methoxydibenzoylalkene **9** in the thermal rearrangement of **8** to **10**, we attempted to trap **9** using diphenylacetylene and cyclohexene. This was prompted by the observation that **9** may be regarded as a quinonemethide. Quinonemethides are known to undergo [4+2] additions with suitable dienophiles. When **8a** was thermolysed in the presence of diphenylacetylene, a new product was formed in low yields (<2%) along with the normal thermolysis

product **10a**. Even after repeated runs, this new product could not be isolated in sufficient amounts for characterisation. In another experiment, when **8a** was refluxed in cyclohexene (bp 83 ^{0}C) no cycloaddition was observed, the only product formed in this case was **10a**.

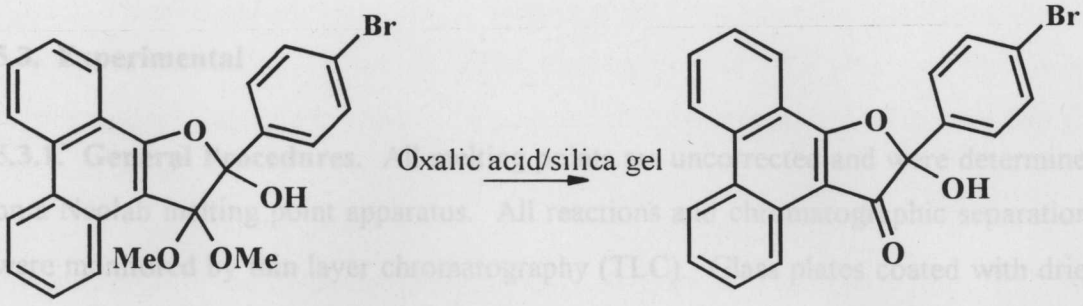
5.2.2. Reaction of 8a with Base

The furanol, **8a** was treated with ethanolic potassium hydroxide and was found to be stable under basic conditions. This observation is consistent with the fact that **8** is formed by the base-catalysed reaction between phenanthrenequinone and acetophenone in methanol.

5.2.3. Reaction of 8d with Acid

We treated one of the furanol derivative **8d** with oxalic acid adsorbed on silica gel and observed the formation of a new product. The structure of the new product was assigned on the basis of spectral and analytical data. The IR spectrum of the compound showed the presence of a carbonyl group at 1690 cm^{-1}, and a hydroxyl group at 3236 cm^{-1}. UV spectrum was similar to that of phenanthrene. ^{1}H NMR spectrum showed the hydroxy proton as a singlet at δ 5.21 and aromatic protons as a multiplet at δ 7.2-8.6. Based on these data, the structure of the compound was assigned as the 3(2H)-furanone **11d** (Scheme 5.4). 3(2H)-Furanone moiety is a central structural unit in a growing number of natural products including simple compounds such as bullatenone[17] and geipavarin[18] and more complex compounds such as jatrophone, eremantholide,[19] and lychnophorolide.[20] Many of these 3(2H)-furanones natural products possess significant tumor-inhibiting properties. Therefore, the synthesis of 3(2H)-furanones has attracted considerable attention.[21-23]

Scheme 5.4

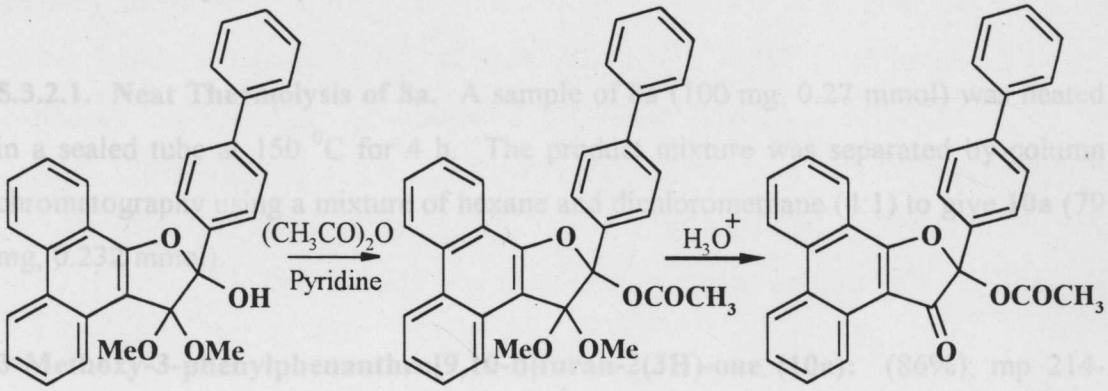


8d **11d**

5.2.4. Reaction of 8f with Acetic anhydride/Pyridine

We acetylated one of the furanol derivatives namely 3-methoxy-3-(4'-phenylphenyl)phenanthro-2,3-dihydro-2-furanol (**8f**) using acetic anhydride in pyridine. The product obtained showed the presence of two carbonyls at 1774 cm^{-1} and 1713 cm^{-1}. ^1H NMR showed the presence of acetyl protons at δ 2.29 and aromatic protons at δ 7.2-8.8. Based on spectral and analytical data, the compound was identified as 2-acetoxy-2-(4'-phenylphenyl)phenanthro[9,10-b]furan-3(2H)-one (**13f**). It seems likely that the initial acetylation product **12** undergoes hydrolysis during aqueous work up of the reaction mixture (Scheme 5.5).

Scheme 5.5



8f **12f** **13f**

In conclusion, we have illustrated that furanols undergo interesting transformations to give 2(3H) or 3(2H)-furanones depending on the conditions applied. Such furanones are attractive synthetic targets and our findings provide easy access to them.

5.3. Experimental

5.3.1. 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 gel or aluminium sheets coated with silica gel (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 gel (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 and 75 MHz respectively on a Brucker 300 FT-NMR spectrometer with tetramethylsilane as internal standard. Simultaneous TG-DTA analysis of the samples were performed on a automatic derivatograph (SETARAM TG-DTA 92). The thermograms of the sample were recorded under the following conditions: weight of the sample-3.7 mg, heating rate-10 ^{0}C/min, N_2 flow, α-alumina was used as the reference material.

5.3.2. Thermolysis Experiments

5.3.2.1. Neat Thermolysis of 8a. A sample of **8a** (100 mg, 0.27 mmol) was heated in a sealed tube at 150 ^{0}C for 4 h. The product mixture was separated by column chromatography using a mixture of hexane and dichloromethane (4:1) to give **10a** (79 mg, 0.232 mmol).

3-Methoxy-3-phenylphenanthro[9,10-b]furan-2(3H)-one (10a): (86%); mp 214-216 ^{0}C; IR ν_{max} (KBr) 1813 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 208 (ε 17,200), 222 (ε 13,000), 245 (ε 17,600), 257 (ε 14,100), 276 (ε 6,300), 308 (ε 3,000), 337 (ε 900), 355 nm (ε 800); ^{1}H NMR ($CDCl_3$) δ 3.4 (3H, s, methoxy), 7.2-8.9 (13H, m, aromatic); MS, *m/z* 340 (M^+), 312, 281, 239, 125 and other peaks. Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.22; H, 4.74.

5.3.2.2. Neat Thermolysis of 8b. A sample of **8b** (100 mg, 0.26 mmol) was heated in a sealed tube at 150 ^{0}C for 4h. The reaction product was separated by column chromatography using a mixture of hexane and dichloromethane (4:1) to give **10b** (75 mg, 0.21 mmol).

3-Methoxy-3-(4'-methylphenyl)phenanthro[9,10-b]furan-2(3H)-one (10b): (82%); mp 160-162 ^{0}C; IR ν_{max} (KBr) 1813 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 208 (ε

17,200), 222 (ε 13,000), 245 (ε 17,600), 257 (ε 14,100), 276 (ε 6,300), 308 (ε 3,000), 337 (ε 900), 355 nm (ε 800); ^{1}H NMR ($CDCl_3$) δ 2.3 (3H, s, methyl); δ 3.35 (3H, s, methoxy); 7-8.9 (12H, m, aromatic); MS, *m/z* 354 (M^+), 326, 91 and other peaks. Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.62; H, 5.34.

5.3.2.3. Neat Thermolysis of 8c. A sample of **8c** (100 mg, 0.25 mmol) was heated in a sealed tube at 150 ^{0}C for 4 h. The reaction product was separated by column chromatography using a mixture of hexane and dichloromethane (4:1) to give **10c** (80 mg, 0.22 mmol).

3-Methoxy-3-(4'-methoxyphenyl)phenanthro[9,10-b]furan-2(3H)-one (10c): (86%); mp 135-138 ^{0}C; IR ν_{max} (KBr) 1815 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 208 (ε 23,300), 225 (ε 20,000), 246 (ε 29,900), 257 (ε 22,000), 275 (ε 10,500), 304 (ε 5,000), 339 (ε 2,400), 355 nm (ε 2,000); ^{1}H NMR ($CDCl_3$) δ 3.3 (3H, s, methoxy), 3.8 (3H, s, methoxy), 6.8-8.9 (12H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 54.20, 55.26, 85.10, 114.09, 120.04, 122.55, 122.9, 123.38, 123.52, 123.74, 124.0, 124.19, 126.0, 127.49, 127.51, 127.69, 127.99, 128.32, 128.78, 128.91, 129.18, 132.54, 149.59, 175.28.; MS, *m/z* 371 (M^+), 341, 204, 135 and other peaks. Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.9. Found: C, 78.1; H, 4.94.

5.3.2.4. Neat Thermolysis of 8d. A sample of **8d** (100 mg, 0.22 mmol) was heated in a sealed tube at 150 ^{0}C for 4 h. The reaction product was separated by column chromatography using a mixture of hexane and dichloromethane (4:1) to give **10d** (75 mg, 0.18 mmol).

3-Methoxy-3-(4'-bromophenyl)phenanthro[9,10-b]furan-2(3H)-one (10d): (82%); mp 191-193 ^{0}C; IR ν_{max} (KBr) 1811 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 208 (ε 23,300), 225 (ε 20,000), 246 (ε 29,900), 257 (ε 22,000), 275 (ε 10,500), 304 (ε 5,000), 339 (ε 2,400), 355 nm (ε 2,000); ^{1}H NMR ($CDCl_3$) δ 3.3 (3H, s, methoxy), 7.2-8.9 (12H, m, aromatic); MS, *m/z* 420 (M^+), 394, 361, 155 and other peaks. Anal. Calcd for $C_{23}H_{15}O_3Br$: C, 65.9; H, 3.61. Found: C, 65.56; H, 3.76.

5.3.2.5. Neat Thermolysis of 8e. A sample of **8e** (100 mg, 0.25 mmol) was heated in a sealed tube at 150 ^{0}C for 4 h. The reaction was monitored by TLC. The reaction product was separated by column chromatography using a mixture of hexane and dichloromethane (4:1) to give **10e** (76 mg, 0.202 mmol).

3-Methoxy-3-(4'-chlorophenyl)phenanthro[9,10-b]furan-2(3H)-one (10e): (81%); mp 142-143 ^{0}C; IR ν_{max} (KBr) 1813 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 209 (ε 55,000), 263 (ε 56,000), 320 (ε 8,200), 410 nm (ε 3,300); ^{1}H NMR ($CDCl_3$) δ 3.34 (3H, s, methoxy), 7.2-8.8 (12H, m, aromatic); MS, *m/z* 374 (M^+), 346, 239, 163,111 and other peaks. Anal. Calcd for $C_{23}H_{15}O_3Cl$: C, 73.85; H, 4.03. Found: C, 74.02; H, 4.05.

5.3.2.6. Neat Thermolysis of 8f. A sample of **8f** (100 mg, 0.22 mmol) was heated in a sealed tube at 150 ^{0}C for 4h. The reaction was monitored by TLC. The reaction product was separated by column chromatography using a mixture of hexane and dichloromethane (4:1) to give **10f** (75 mg, 0.18 mmol).

3-Methoxy-3-(4'-phenylphenyl)phenanthro[9,10-b]furan-2(3H)-one (10f): (82%); mp 136-138 ^{0}C; IR ν_{max} (KBr), 1813 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 203 (ε 60,000), 257 (ε 59,000), 308 (ε 9,200), 341 nm (ε 2,400); ^{1}H NMR ($CDCl_3$) δ 3.35 (3H, s, methoxy), 7.3-8.8 (17H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 54.27, 85.42, 114.05, 120.09, 122.65, 123.48, 123.62, 124.21, 126.18, 126.72, 127.52, 127.58, 128.81, 128.93, 132.68, 136.17, 140.45, 141.96, 149.80, 175.06.; MS, *m/z* 416 (M^+), 388, 357, 281 and other peaks. Anal. Calcd for $C_{29}H_{20}O_3$: C, 83.64; H, 4.84. Found: C, 83.48; H, 4.86.

5.3.2.7. Thermolysis of 8a-f in an Open Vessel. The samples **8a-f** were thermolysed in an open vessel to give phenanthro-2(3H)-furanones. In a typical experiment, a sample of **8a** (100 mg, 0.27 mmol) was heated in a conical flask in an air oven maintained at 150 ^{0}C for 4h. The solid was extracted with dichloromethane. Column chromatography by using a mixture of hexane and dichloromethane (4:1) gave **10a** (75 mg, 0.22 mmol, 82%).

5.3.2.8. Thermolysis of 8a-f in *o*-Dichlorobenzene. Samples **8a-f** (~0.25 mmol each) were refluxed in *o*-dichlorobenzene to give the corresponding phenanthro-2(3H)-furanones. In a typical experiment, a sample of **8a** (100 mg, 0.27 mmol) was dissolved in *o*-dichlorobenzene (10 mL) and refluxed for 4 h. Solvent was removed under reduced pressure. The residue was extracted with dichloromethane. Column chromatography by using a mixture of hexane and dichloromethane (4:1) gave **10a** (71 mg, 0.21 mmol, 78%).

5.3.3. Reaction of 8a with Base. A sample of **8a** (100 mg, 0.27 mmol) was dissolved in dichloromethane (10 mL) and potassium hydroxide (0.5 g) in ethanol (2 mL) was added and stirred for 12 h. The reaction was monitored by TLC. No change was observed. The solution was then refluxed for 6 h and was monitored by TLC. The unreacted **8a** was recovered almost quantitatively (90 mg, 90%).

5.3.4. Reaction of 8d with Acid. A sample of **8d** (100 mg, 0.26 mmol) was dissolved in dichloromethane (10 mL) and oxalic acid adsorbed on silica gel was added. The mixture was stirred at room temperature for 12 h. The progress of the reaction was monitored by TLC. The product formed was separated by column chromatography and recrystallised from a mixture of dichloromethane and hexane (2:1) to give **11d** (71 mg, 0.17 mmol).

2-Hydroxy-2-(4'-bromophenyl)phenanthro[9,10-b]furan-3(2H)-one (11d): (67%); mp 195-197 ^{0}C; IR ν_{max} (KBr), 3236 (OH), 1690 (carbonyl), 1618 and 1506 cm^{-1}; UV λ_{max} (CH_3CN) 202 (ε 40,000), 254 (ε 28,000), 306 (ε 5,300), 338 nm (ε 1,700); ^{1}H NMR ($CDCl_3$) δ 7.2-8.6 (m, aromatic and hydroxy). Anal. Calcd for $C_{28}H_{18}O_3$: C, 83.57; H, 4.51. Found: C, 83.30; H, 4.6.

5.3.5. Reaction of 8f with Acetic Anhydride. A sample of **8f** (100 mg, 0.22 mmol) was dissolved in dichloromethane (20 mL) and pyridine (5 mL) was added. Acetic anhydride was added dropwise to the mixture over a period of 30 min and then refluxed for 2 h. The mixture was cooled and diluted with dichloromethane. It was then washed with dil. H_2SO_4, sodium bicarbonate, and with water. The organic layer

was separated, dried over anhydrous sodium sulphate, and solvent was removed to yield **13f**. It was then recrystallised from dichloromethane-hexane mixture (2:1).

2-Acetoxy-2-(4'-phenylphenyl)phenanthro[9,10-b]furan-3(2H)-one (13f): (62%); mp 182-185 ^{0}C; IR ν_{max} (KBr), 1774, 1713 (carbonyls), 1620, 1600 cm^{-1}; UV λ_{max} (CH_3CN) 202 (ε 45,000), 255 (ε 31,000), 306 (ε 8,200), 340 nm (ε 2,100); ^{1}H NMR ($CDCl_3$) δ 2.29 (3H, s, methyl), 7.2-8.8 (17H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.7, 102, 108, 109, 120.8, 122.9, 123.1, 123.7, 124, 126.1, 126.9, 127.1, 127.3, 127.5, 127.7, 128.8, 131.8, 132, 136, 140.3, 143, 168.3, 171.2, 194.2; MS, *m/z* 444 (M^+), 386, 263, 181 and other peaks. Anal. Calcd for $C_{30}H_{20}O_4$: C, 81.07; H, 4.54. Found: C, 81.30; H, 4.14.

5.3.6. Attempted Trapping Experiments

5.3.6.1. Neat Thermolysis of 8a in the Presence of Diphenylacetylene. A sample of **8a** (100 mg, 0.27 mmol) was mixed with diphenylacetylene (48 mg, 0.27 mmol) in a sealed tube and heated at 150 ^{0}C for 4 h. The progress of the reaction was monitored by TLC and was stopped when all of **8a** was consumed. The residue was extracted with dichloromethane. The product formed was separated by column chromatography using a mixture of hexane and dichloromethane (4:1) to give **10a** (69 mg, 0.202 mmol, 75%) as the only isolable product.

5.3.6.2. Reaction of 8a with Diphenylacetylene in Toluene. A mixture of **8a** (100 mg, 0.27 mmol) and diphenylacetylene (48 mg, 0.27 mmol) in toluene (20 mL) was refluxed for 4 h. The reaction was monitored by TLC. TLC showed the formation of a new product in very small yield along with **10a**. Solvent was removed and the residue was subjected to column chromatography over silica gel. Elution using a mixture (4:1) of hexane and dichloromethane gave **10a** (65 mg, 0.19 mmol, 71%) as the only isolable product.

5.3.6.3. Reaction of 8a in Cyclohexene. A sample of **8a** (100 mg, 0.27 mmol) was taken in cyclohexene (10 mL) and refluxed for 12 h. The reaction was monitored by TLC. Column chromatography using a mixture (4:1) of hexane and dichloromethane

gave **10a** (30 mg, 0.09 mmol, 33%). Further elution using a mixture (2:1) of hexane and dichloromethane gave unchanged **8a** (40 mg, 0.11 mmol, 40%).

5.3.7. X-ray Crystallographic analyses of 10a

The crystal was grown in a mixture (3:2) of dichloromethane and hexane. A single crystal of suitable size (0.2 x 0.2 x 0.1 mm) was taken from it. X-ray diffraction experiments were performed at room temperature on a CAD4 DIFFRACTOMETER with a graphite-monochromated Cu Kα radiation (l = 1.5418 A^0). The intensity data was measured using ω–2θ scan technique. The structure was solved by SHELXS-97 and refined by SHELXL-97 with anisotropic temperature factors for the non-hydrogen atoms.

References

1. Drioli, S.; Felluga, F.; Forzato, C.; Nitti, P.; Pitacco, G.; Valentin, E. *J. Org. Chem.* **1998**, *63*, 2385-2388.
2. Rossi, R.; Bellina, F.; Mannina, F. *Tetrahedron Lett.* **1998**, *39*, 3017-3020.
3. Jacobi, P. A.; Herradura, P. *Tetrahedron Lett.* **1996**, *37*, 8297-8300.
4. Rodriguez, C. M.; Martin, T.; Martin, V. S. *J. Org. Chem.* **1996**, *61*, 8448-8452.
5. Robin, S.; Huet, F.; Fuve, A.; Veschambre, H. *Tetrahedron Asymmetry* **1993**, *4*, 239-246.
6. Hanessian, S.; Murray, P. J.; Sahoo, S. P. *Tetrahedron Lett.* **1985**, *26*, 5623-5626.
7. Cossy, J.; Ranaivosata, J. L.; Bellosta, V. *Tetrahedron Lett.* **1994**, *35*, 1205-1208.
8. Rojo, J.; Oarcia, M.; Carretero, J. C. *Tetrahedron* **1993**, *49*, 9787-9800.
9. Koch, S. C.; Chamberlin, A. R. *J. Org. Chem.* **1993**, *58*, 2725-2737.
10. Brown, H. C.; Kulkstni, S. V.; Rscherla, U. S. *J. Org. Chem.* **1994**, *59*, 365-369.
11. Ogliaruso, M. A.; Wolfe, J. F. *Synthesis of Lactones and Lactams*; John Wiley & Sons: New York, 1993.
12. Zenin, N. *Ber.* **1872**, *5*,1104.
13. Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1890**, *57*, 669, 685, 689.
14. Blatt, A. H. *J. Org. Chem.* **1950**, *15*, 869-872.
15. Berger, D. R.; Summerbell, R. K. *J. Org. Chem.* **1959**, *24*, 1881-1883.
16. Lahiri, S.; Dabral, V.; George, M. V. *Tetrahedron Lett.* **1976**, *26*, 2259-2262.
17. Parker, W.; Raphael, R. A.; Wilkinson, D. I. *J. Chem. Soc.* **1958**, 3871-3879.
18. Dreyer, D. L.; Lee, A. *Phytochemistry* **1972**, *11*, 763-767.
19. Le Quesne, P.W.; Levery, S. B.; Menachery, M. D.; Brennan, T. F.; Onan, K. D.; Raffauf R. F. *J. Chem. Soc. Perkin Trans. I*, **1978**, 1572-1580.
20. Le Quesne, P.W.; Menachery, M. D.; Pastore, M. P.; Kelley, C. J.; Brennan, T. F.; Onan, K. D.; Raffauf, R. F. *J. Org. Chem.* **1982**, *47*, 1519-1521.
21. Smith, A. B. III.; Levenberg, P.A.; Jerris, P. J.; Scarborough, R. M. Jr.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 1501-1513.
22. Smith, A. B. III.; Jerris, P. J. *Tetrahedron Lett.* **1980**, *21*, 711-714.
23. Saimoto, H.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1981**, *103*, 4975-4977.

Table 1. Crystal Data and Structure Refinement for 10a

Empirical formula	$C_{11.50}\ H_8\ O_{1.50}$	
Formula weight	170.18	
Temperature	293(2) K	
Wavelength	1.54180 A	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 8.4695(7) A	$\alpha = 100.368(5)^0$
	b = 10.2384(9) A	$\beta = 110.282(4)^0$
	c = 10.9698(5) A	$\gamma = 102.529(7)^0$
Volume	836.51(11) A^3	
Z, Calculated density	4, 1.351 Mg/m^3	
Absorption coefficient (μ)	0.715 mm^{-1}	
F(000)	356	
Crystal size	0.2 x 0.2 x 0.1 mm	
θ range for data collection	4.47 to 69.99^0	
Index ranges	0<=h<=10, -12<=k<=12, -13<=l<=12	
Reflections collected / unique	3402 / 3172 [R(int) = 0.0280]	
Completeness to $2\theta = 69.99$	99.8%	
Absorption correction	Psi scan	
Max. and min. transmission	0.99 and 0.76	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3172 / 0 / 236	
Goodness-of-fit on F^2	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.1521	
R indices (all data)	R1 = 0.0561, wR2 = 0.1554	
Extinction coefficient	0.0123(16)	
Largest diff. peak and hole	0.316 and -0.225 $e.A^{-3}$	

Table 2. Bond Lengths [in angstroms] of 10a

O(1)-C(1)	1.1901(19)
O(3)-C(16)	1.4184(18)
O(3)-C(23)	1.420(2)
C(1)-O(2)	1.369(2)
C(1)-C(16)	1.557(2)
O(2)-C(2)	1.4047(19)
C(2)-C(15)	1.339(2)
C(2)-C(3)	1.418(2)
C(3)-C(4)	1.404(2)
C(3)-C(8)	1.415(3)
C(4)-C(5)	1.362(3)
C(5)-C(6)	1.392(4)
C(6)-C(7)	1.372(3)
C(7)-C(8)	1.413(2)
C(8)-C(9)	1.459(2)
C(9)-C(10)	1.411(2)
C(9)-C(14)	1.421(2)
C(10)-C(11)	1.364(3)
C(11)-C(12)	1.392(3)
C(12)-C(13)	1.369(2)
C(13)-C(14)	1.403(2)
C(14)-C(15)	1.431(2)
C(15)-C(16)	1.5032(19)
C(16)-C(17)	1.523(2)
C(17)-C(22)	1.381(2)
C(17)-C(18)	1.389(2)
C(18)-C(19)	1.383(2)
C(19)-C(20)	1.371(3)
C(20)-C(21)	1.374(3)
C(21)-C(22)	1.389(3)

Table 2. Bond Angles [in degrees] of 10a

C(16)-O(3)-C(23)	115.30(12)
O(1)-C(1)-O(2)	121.62(15)
O(1)-C(1)-C(16)	128.43(15)
O(2)-C(1)-C(16)	109.94(12)
C(1)-O(2)-C(2)	106.97(11)
C(15)-C(2)-O(2)	113.81(13)
C(15)-C(2)-C(3)	125.02(15)
O(2)-C(2)-C(3)	121.16(14)
C(4)-C(3)-C(8)	121.71(17)
C(4)-C(3)-C(2)	122.44(17)
C(8)-C(3)-C(2)	115.85(14)
C(5)-C(4)-C(3)	119.5(2)
C(4)-C(5)-C(6)	119.9(2)
C(7)-C(6)-C(5)	121.51(19)
C(6)-C(7)-C(8)	120.7(2)
C(7)-C(8)-C(3)	116.67(17)
C(7)-C(8)-C(9)	122.59(18)
C(3)-C(8)-C(9)	120.74(14)
C(10)-C(9)-C(14)	116.87(16)
C(10)-C(9)-C(8)	123.25(15)
C(14)-C(9)-C(8)	119.88(14)
C(11)-C(10)-C(9)	121.85(16)
C(10)-C(11)-C(12)	120.60(16)
C(13)-C(12)-C(11)	119.78(17)
C(12)-C(13)-C(14)	120.60(16)
C(13)-C(14)-C(9)	120.28(14)
C(13)-C(14)-C(15)	122.20(14)
C(9)-C(14)-C(15)	117.51(14)
C(2)-C(15)-C(14)	120.99(14)
C(2)-C(15)-C(16)	108.97(13)
C(14)-C(15)-C(16)	130.05(13)
O(3)-C(16)-C(15)	115.41(12)
O(3)-C(16)-C(17)	107.23(11)
C(15)-C(16)-C(17)	115.17(12)
O(3)-C(16)-C(1)	109.94(12)
C(15)-C(16)-C(1)	100.11(12)
C(17)-C(16)-C(1)	108.63(12)
C(22)-C(17)-C(18)	119.04(15)
C(22)-C(17)-C(16)	121.28(14)
C(18)-C(17)-C(16)	119.63(14)
C(19)-C(18)-C(17)	120.30(17)
C(20)-C(19)-C(18)	120.40(19)
C(19)-C(20)-C(21)	119.70(18)
C(20)-C(21)-C(22)	120.41(19)
C(17)-C(22)-C(21)	120.12(18)

Figure 5.1a. ^{1}H NMR spectrum of compound 10f.

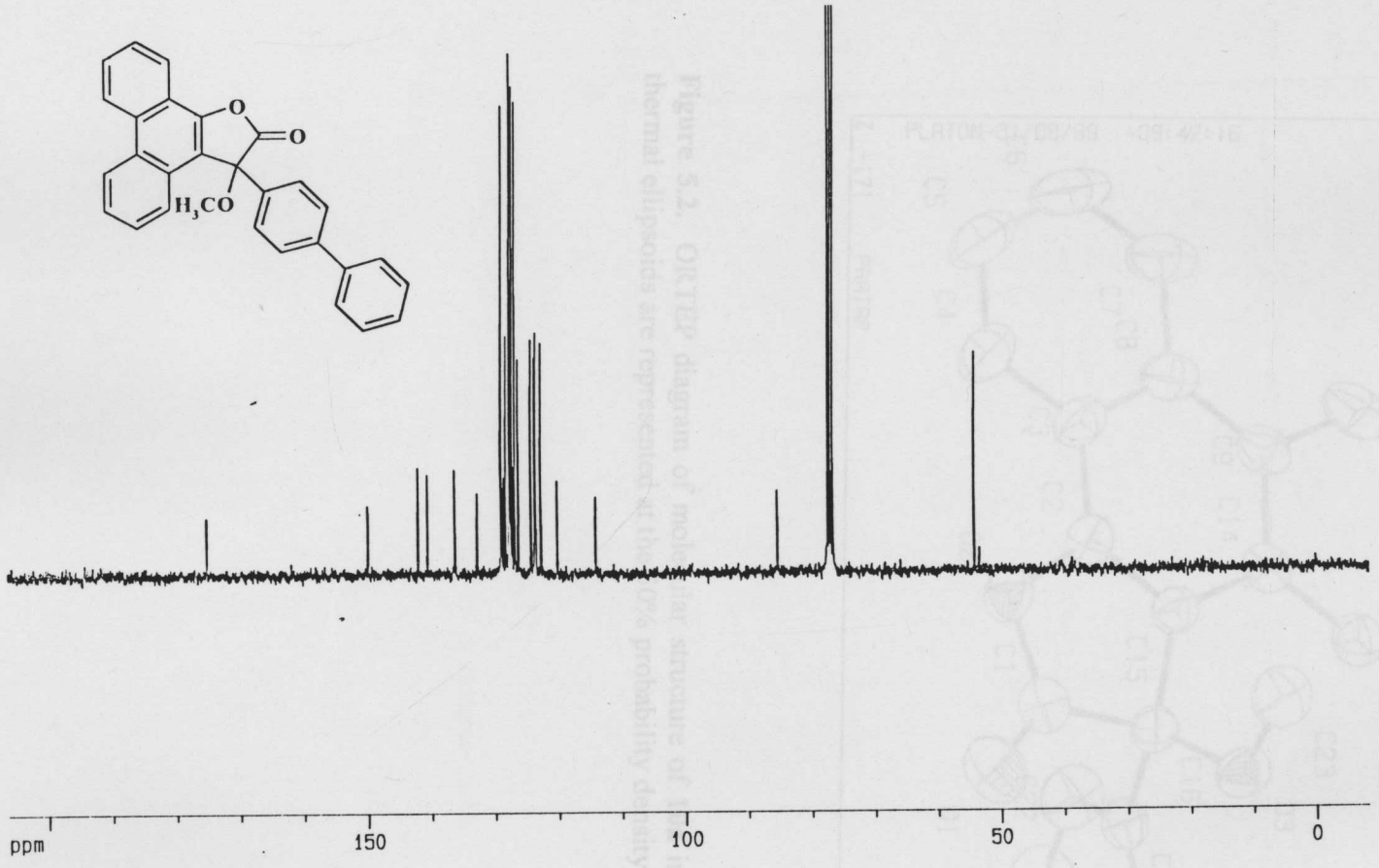


Figure 5.1b. ^{13}C NMR spectrum of compound 10f.

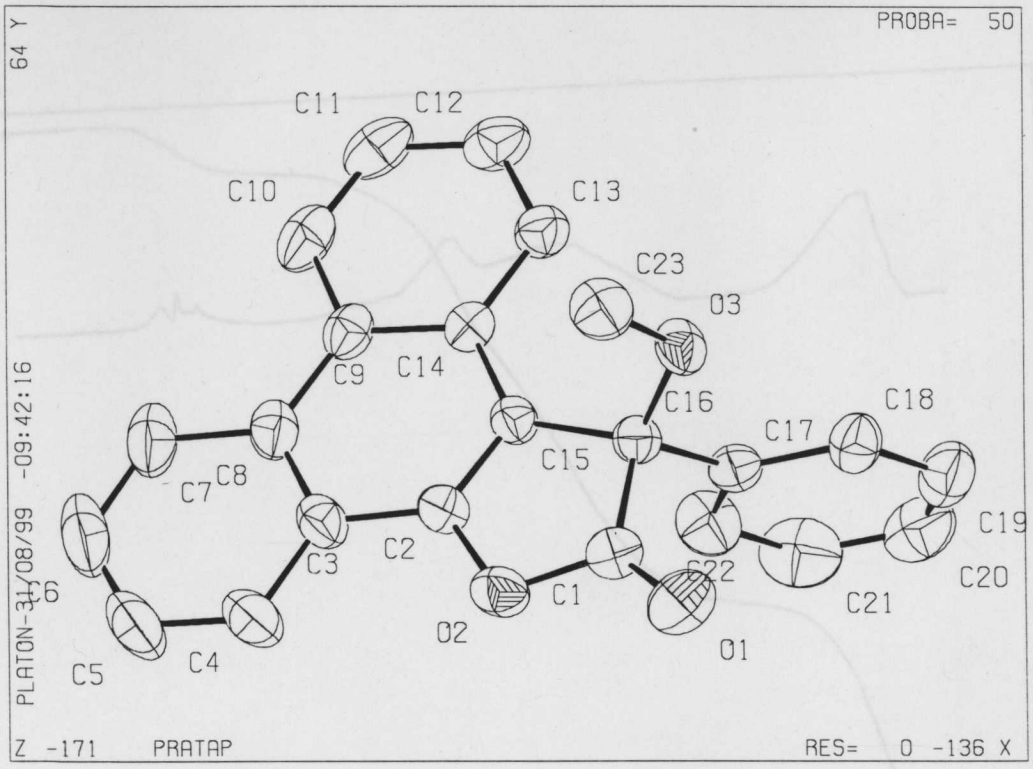


Figure 5.2. ORTEP diagram of molecular structure of **10a** in the crystal. All the thermal ellipsoids are represented at the 50% probability density level.

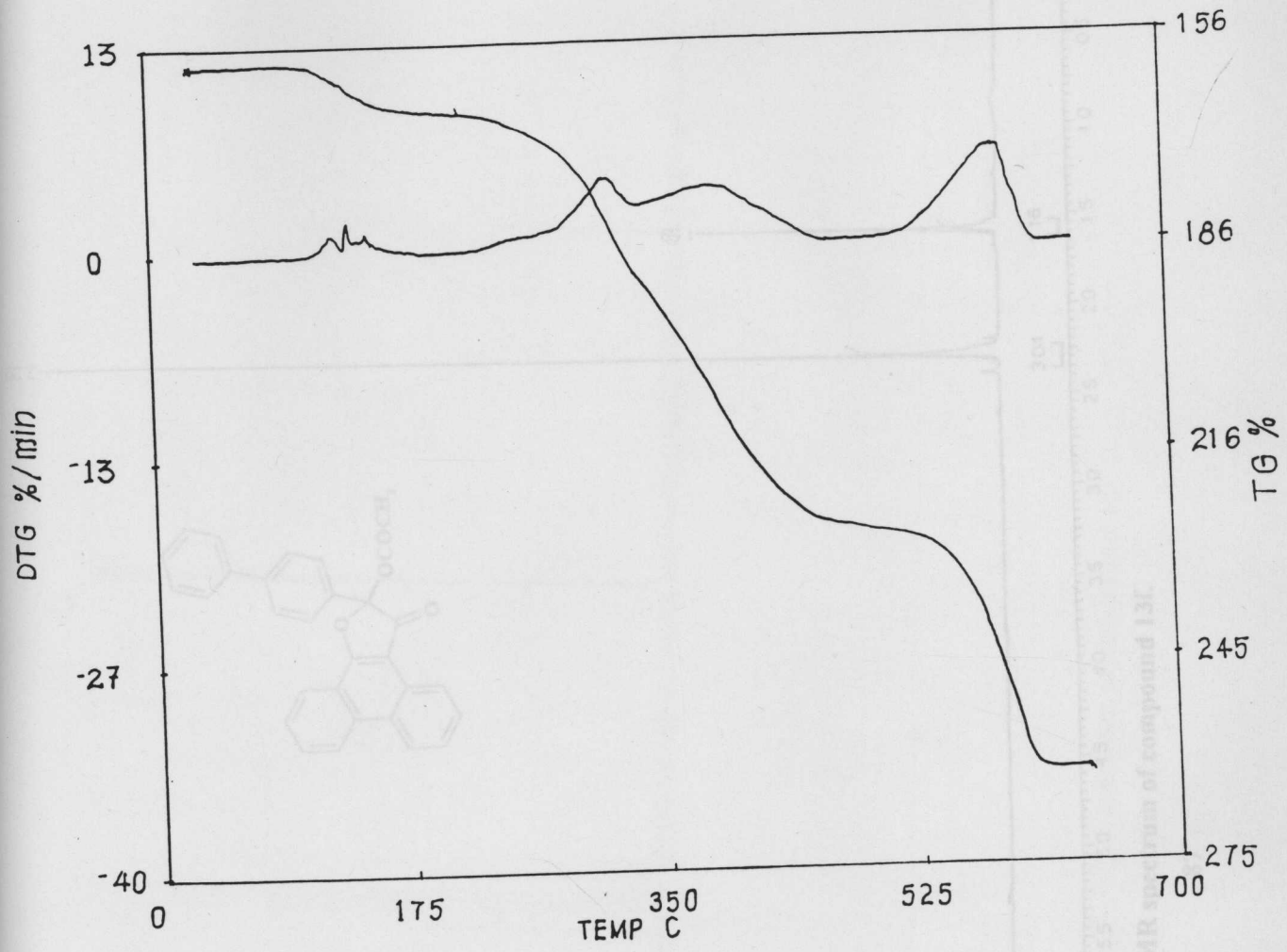


Figure 5.3. TG/DTA of compound 8a.

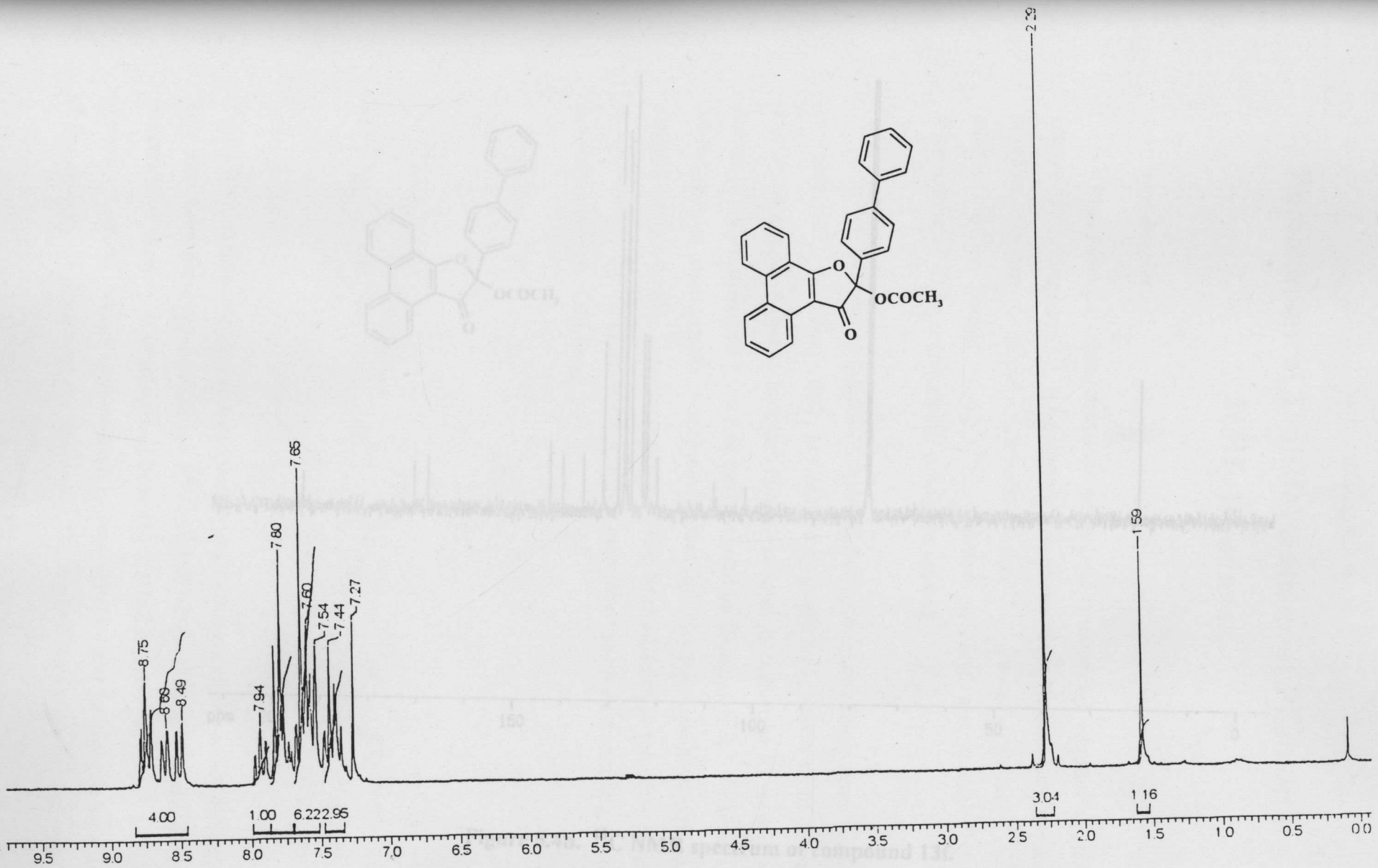


Figure 5.4a. ^{1}H NMR spectrum of compound 13f.

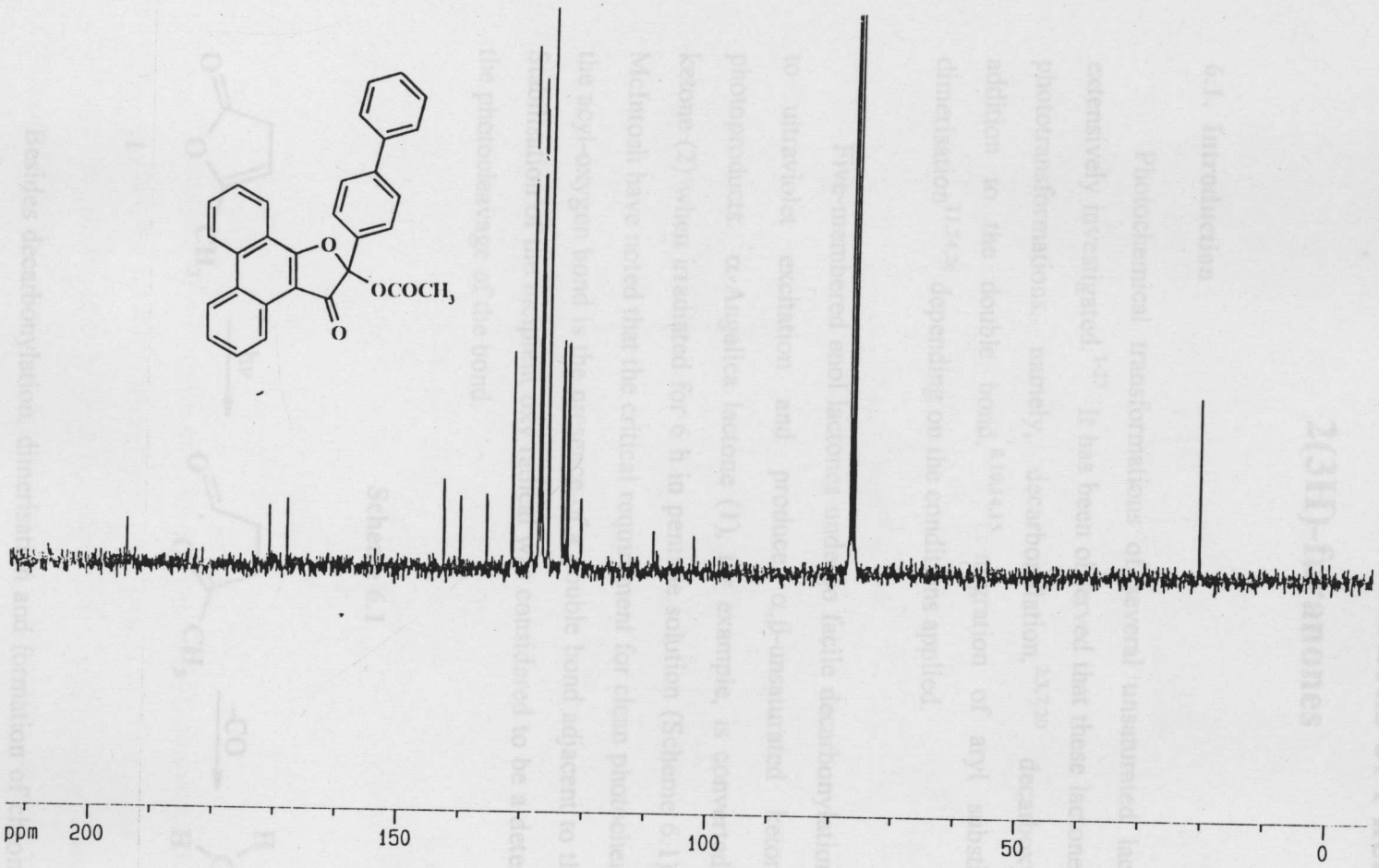


Figure 5.4b. ^{13}C NMR spectrum of compound 13f.

Chapter 6

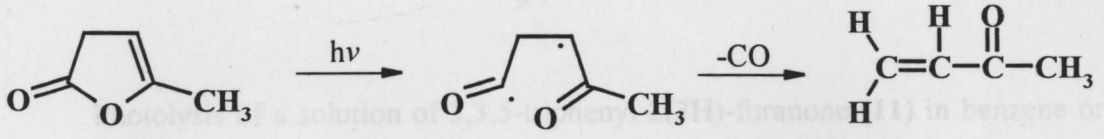
Photochemical Transformations of Phenanthro-2(3H)-furanones

6.1. Introduction

Photochemical transformations of several unsaturated lactones have been extensively investigated.[1-27] It has been observed that these lactones undergo several phototransformations, namely, decarbonylation,[2,3,7,20] decarboxylation,[4] solvent addition to the double bond,[8,10,14,15] migration of aryl substituents[15,21,24] and dimerisation[11,24,26] depending on the conditions applied.

Five-membered enol lactones undergo facile decarbonylation when subjected to ultraviolet excitation and produce α,β-unsaturated ketones as primary photoproducts. α-Angelica lactone (**1**), for example, is converted to methyl vinyl ketone (**2**) when irradiated for 6 h in pentane solution (Scheme 6.1).[2] Chapman and McIntosh have noted that the critical requirement for clean photochemical cleavage of the acyl-oxygen bond is the presence of a double bond adjacent to the ether oxygen.[7] Stabilisation of the incipient oxy radical was considered to be a determining factor in the photocleavage of the bond.

Scheme 6.1

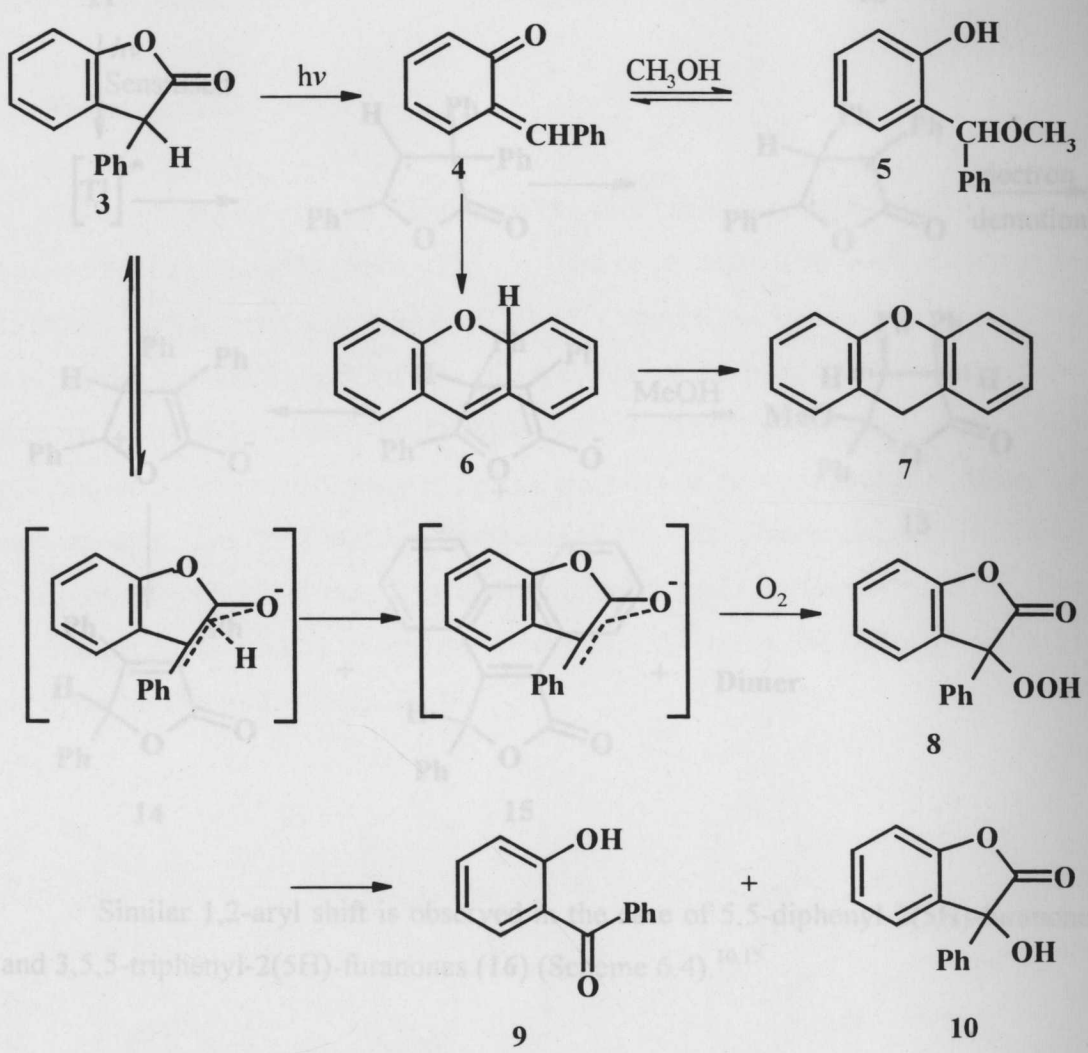


1 **2**

Besides decarbonylation, dimerisation and formation of chromone derivatives have also been observed in the case of several 2(3H)-furanones. Padwa and co-workers have shown that irradiation of benzo[b]-2(3H)-furanones (**3**) lead to a variety of products arising through quinonemethide intermediate **4** and through the excitation of the enolate ion present in the solution. The enolate ion in the excited state is

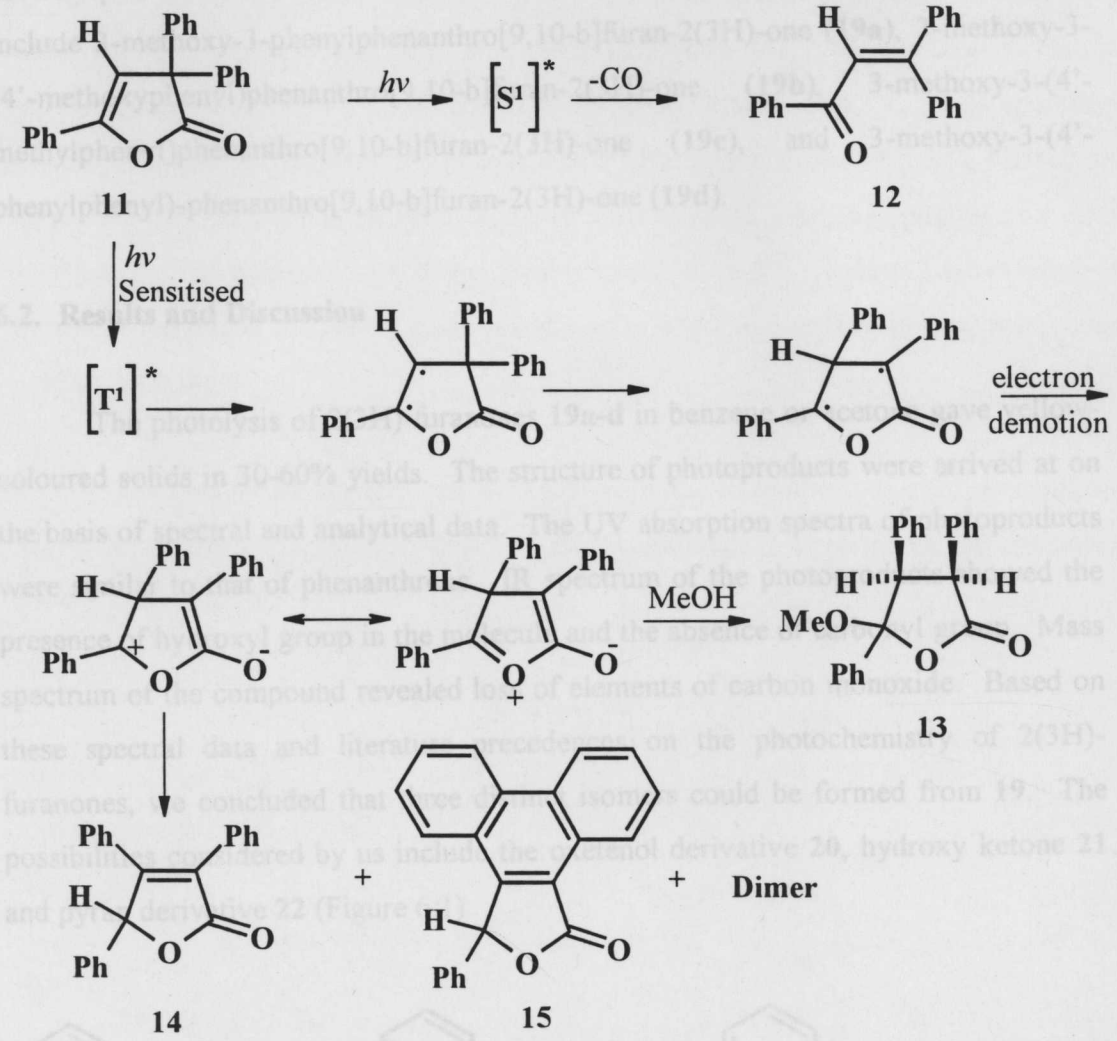
attacked by the ground state oxygen to give α-hydroperoxylactone (**8**). This transient intermediate is subsequently converted to compounds **9** and **10** (Scheme 6.2).[25]

Scheme 6.2



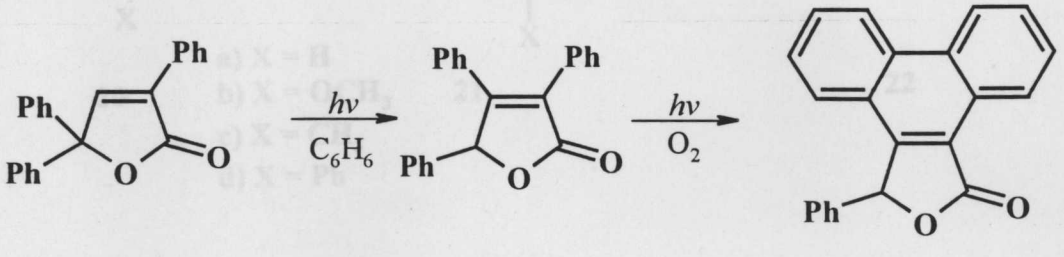
Photolysis of a solution of 3,3,5-triphenyl-2(3H)-furanone (**11**) in benzene or methanol gives 1,3,3-triphenylprop-2-en-1-one (**12**), i.e., the 2(3H)-furanones undergo singlet-mediated decarbonylation to yield α,β-unsaturated carbonyl compounds.[21] But sensitised irradiation of **11** in benzene results in triplet-mediated reaction leading to the formation of 3,4,5-triphenyl-2(5H)-furanone (**14**), 5-phenylphenanthro[9,10-c]furan-2(5H)-one (**15**) and a photodimer (Scheme 6.3).[24,27]

Scheme 6.3



Similar 1,2-aryl shift is observed in the case of 5,5-diphenyl-2(5H)-furanones and 3,5,5-triphenyl-2(5H)-furanones (**16**) (Scheme 6.4).[10,15]

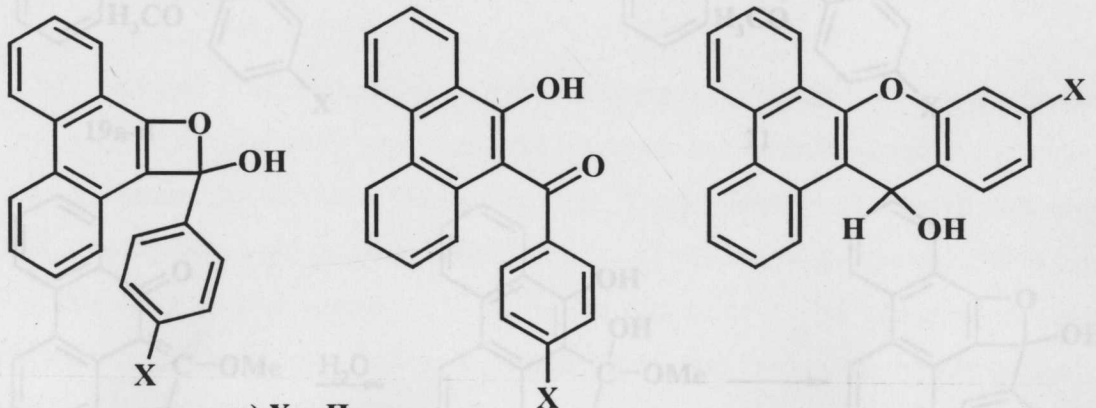
Scheme 6.4



In the present study, we have examined the direct and sensitised photolysis of several phenanthro-2(3H)-furanones. The 2(3H)-furanones we have examined include 3-methoxy-3-phenylphenanthro[9,10-b]furan-2(3H)-one (**19a**), 3-methoxy-3-(4'-methoxyphenyl)phenanthro[9,10-b]furan-2(3H)-one (**19b**), 3-methoxy-3-(4'-methylphenyl)phenanthro[9,10-b]furan-2(3H)-one (**19c**), and 3-methoxy-3-(4'-phenylphenyl)-phenanthro[9,10-b]furan-2(3H)-one (**19d**).

6.2. Results and Discussion

The photolysis of 2(3H)-furanones **19a-d** in benzene or acetone gave yellow-coloured solids in 30-60% yields. The structure of photoproducts were arrived at on the basis of spectral and analytical data. The UV absorption spectra of photoproducts were similar to that of phenanthrene. IR spectrum of the photoproducts showed the presence of hydroxyl group in the molecule and the absence of carbonyl group. Mass spectrum of the compound revealed loss of elements of carbon monoxide. Based on these spectral data and literature precedences on the photochemistry of 2(3H)-furanones, we concluded that three distinct isomers could be formed from **19**. The possibilities considered by us include the oxetenol derivative **20**, hydroxy ketone **21** and pyran derivative **22** (Figure 6.1).



20 **21** **22**

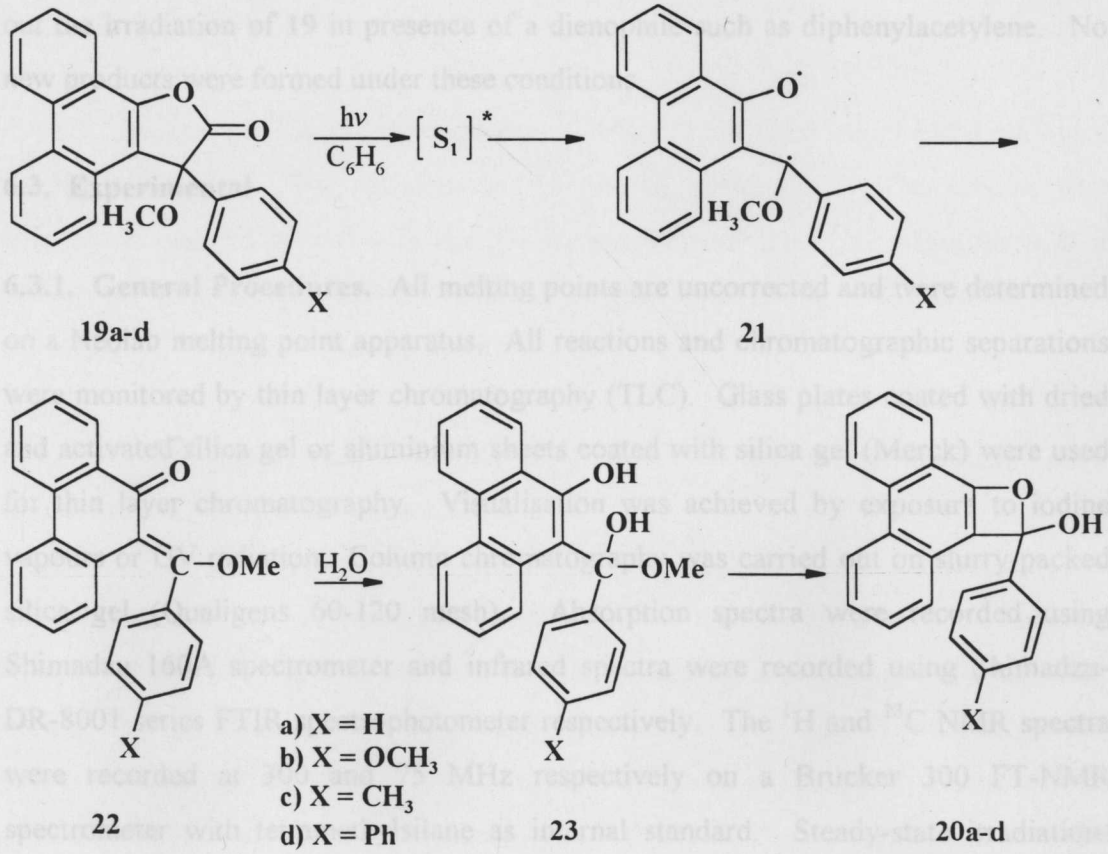
a) X = H
b) X = OCH_3
c) X = CH_3
d) X = Ph

Figure. 6.1. Possible photoproducts: oxetenol derivative **20**, hydroxy ketone **21** and pyran derivative **22**

We ruled out the possibility of hydroxy ketone **21** due to the absence of carbonyl peak in the IR and ^{13}C NMR spectra. The ^{1}H NMR and ^{13}C NMR spectra of a representative photoproduct **20b** are given in Figure 6.2. IR spectral evidence indicates the presence of a hydroxyl group in the molecule. The ^{13}C NMR spectrum of the photoproduct suggests the presence of a hemiacetal carbon at δ 104. Based on these, we ruled out the possibility of pyran derivative **22**. All the spectral data thus suggest that the photoproduct is the oxetenol derivative **20**. It should be mentioned here that oxetenols are rather elusive and so far, there are only very few references available on them.

The formation of oxetenol derivative **20** on irradiation of the phenanthro-2(3H)-furanones in benzene or acetone can be understood in terms of the pathways shown in Scheme 6.5.

Scheme 6.5



The initial excitation of the 2(3H)-furanones to the corresponding singlet excited states resulted in decarbonylation to the diradical intermediate which undergoes bond reorganisation to give the quinonemethide intermediate **22.** Water addition to **22** followed by ring closure with elimination of CH_3OH will lead to **20a-d**. It is interesting to note that irradiation of **19a-d** in acetone or in benzene in the presence of acetophenone or benzophenone also leads to the formation of **20a-d** in comparable yields. This is probably due to the preferential absorption by **19a-d** over these triplet sensitisers under the condition applied by us. Furthermore, the phototransformation of **19a** to **20a** is not quenched by ferrocene ($E_T \approx 40$ Kcal mol^{-1}) suggesting a singlet mediated pathway. Thus the photochemical transformation of **19a-d** involving acyl-oxygen bond cleavage appears to be analogous to that of other 2(3H)-furanones. The important difference here is the dark reaction leading to the formation of the oxetenol derivative **20a-d**.

Further evidence for the involvement of quinonemethide intermediate **22** in the phototransformation of **19** to **20** was sought by trapping experiments. We carried out the irradiation of **19** in presence of a dienophile such as diphenylacetylene. No new products were formed under these conditions.

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 gel or aluminium sheets coated with silica gel (Merck) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out on slurry-packed silica gel (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 ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively on a Brucker 300 FT-NMR spectrometer with tetramethylsilane as internal standard. Steady-state irradiations were carried out using a 250-W high pressure mercury lamp in pyrex vessels ($\lambda > 300$ nm). Solvents for steady-state irradiation were purified and distilled before use.

6.3.2. Irradiation of 19a

6.3.2.1. In Benzene. A benzene solution of **19a** (20 mg, 0.06 mmol in 20 mL) was irradiated for 6 h. The reaction was monitored by TLC. Solvent was removed and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **20a** (11 mg, 0.037 mmol).

Compound 20a: (61%); mp 128-130 ^{0}C; IR ν_{max} (KBr) 3428 cm^{-1} (OH), 1620 cm^{-1}, and 1600 cm^{-1}; UV λ_{max} (CH_3CN) 215 (ε 17,200), 252 (ε 13,000), 296 (ε 7,600), 379 nm (ε 800); ^{1}H NMR ($CDCl_3$) δ 7.1-8.7 (m, aromatic and hydroxy protons); ^{13}C NMR ($CDCl_3$) δ 111.05, 122.69, 122.73, 124.50, 125.16, 125.99, 126.24, 127.19, 127.76, 128.56, 129.54, 130.34, 130.71, 132.53, 134.1, 140.43, 160.75; MS, *m/z* 298 (M^+), 239, 220, 165, 105, 77 and other peaks. Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.54; H, 4.74. Found: C, 84.26; H, 4.81.

Further elution with a mixture (2:1) of hexane and dichloromethane gave unreacted **19a** (3 mg, 0.01 mmol, 15%).

6.3.2.2. In Acetone. An acetone solution of **19a** (20 mg, 0.06 mmol in 20 mL) was irradiated for 6 h. The reaction was monitored using TLC. The solvent was evaporated and the residue was charged to a column of silica gel. Elution with a mixture of hexane and dichloromethane (4:1) gave **20a** (10 mg, 0.032 mmol, 55%). mp 128-130 ^{0}C (mixture melting point).

Further elution with a mixture (2:1) of hexane and dichloromethane gave unreacted **19a** (4 mg, 0.015 mmol, 20%).

6.3.2.3. Acetophenone-Sensitised Irradiation of 19a in Benzene. A benzene solution of **19a** (20 mg, 0.06 mmol in 20 mL) containing acetophenone (14 mg, 0.12 mmol) was irradiated for 6h. The reaction was monitored using TLC. The solvent was evaporated and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **20a** (9 mg, 0.028 mmol, 50%). mp 128-130 ^{0}C (mixture melting point).

Further elution with a mixture (2:1) of hexane and dichloromethane gave unreacted **19a** (4 mg, 0.015 mmol, 20%).

6.3.2.4. Benzophenone-Sensitised Irradiation of 19a in Benzene. A benzene solution of **19a** (20 mg, 0.06 mmol in 20 mL) containing benzophenone (22 mg, 0.12 mmol) was irradiated for 6 h. The reaction was monitored by TLC. The solvent was removed and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **20a** (9 mg, 0.028 mmol, 50%). mp 128-130 ^{0}C (mixture melting point).

Further elution with a mixture (2:1) of hexane and dichloromethane gave unreacted **19a** (4 mg, 0.015 mmol, 20%).

6.3.2.5. Irradiation of 19a in Benzene in Presence of Ferrocene. A benzene solution of **19a** (20 mg, 0.06 mmol in 20 mL) containing ferrocene (10 mg, 0.06 mmol) was irradiated for 6 h. The reaction was monitored using TLC. Solvent was removed and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **20a** (6 mg, 0.028 mmol, 33%). mp 128-130 ^{0}C (mixture melting point).

Further elution with a mixture (2:1) of hexane and dichloromethane gave unreacted **19a** (3 mg, 0.01 mmol, 15%).

6.3.2.6. Irradiation of 19b in Benzene. A benzene solution of **19b** (20 mg, 0.06 mmol in 20 mL) was irradiated for 6 h. The reaction was monitored using TLC. Solvent was removed and the residue was charged to a column of silica gel. On elution using a mixture (4:1) of hexane and dichloromethane gave **20b** (11 mg, 0.037 mmol).

Compound 20b: (56%); mp 136-137 ^{0}C; IR ν_{max} (KBr) 3428cm^{-1} (OH), and 1600 cm^{-1}; UV λ_{max} (CH_3CN) 251 (ε 21,000), 293 (ε 9,500), 375 nm (ε 1,500); ^{1}H NMR ($CDCl_3$) δ 3.86 (3H, s, methoxy) 6.8-8.7 (13H, m, aromatic and hydroxy protons); ^{13}C NMR ($CDCl_3$) δ 55, 104, 114, 122.4, 122.9, 124.4, 125, 126.2, 127, 127.6, 130.3, 132,

159; MS, *m/z* 328 (M^+), 220, 77 and other peaks. Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.9. Found: C, 80.18; H, 4.94.

Further elution with a mixture (2:1) of hexane and dichloromethane gave unreacted **19b** (4 mg, 0.011 mmol, 20%).

6.3.2.7. Irradiation of 19c in Benzene. A benzene solution of **19c** (20 mg, 0.06 mmol in 20 mL) was irradiated for 6 h. The reaction was monitored using TLC. The solvent was evaporated and the residue was charged to a column of silica gel. On elution using a mixture (4:1) of hexane and dichloromethane gave **20c** (11 mg, 0.037 mmol).

Compound 20c: (30%); mp 136-138 ^{0}C; IR ν_{max} (KBr), 3428 (OH), 1600 cm^{-1}; UV λ_{max} (CH_3CN) 217 (ε 55,000), 255 (ε 52,000), 302 (ε 8,500), 376 nm (ε 2,100); ^{1}H NMR ($CDCl_3$) δ 1.8 (s, 3H, methyl), 6.8-8.7 (m, 15H, aromatic and hydroxy protons); MS, *m/z* 312 (M^+), 220, 163, 91 and other peaks. Anal. Calcd for $C_{27}H_{18}O_2$: C, 80.34; H, 5.39. Found: C, 80.30; H, 5.14.

Further elution with a mixture (2:1) of hexane and dichloromethane gave unreacted **19c** (3 mg, 0.01 mmol, 15%).

6.3.2.8. Irradiation of 19d in Benzene. A benzene solution of **19d** (20 mg, 0.06 mmol in 20 mL) was irradiated for 6 h. The reaction was monitored using TLC. Solvent was removed and the residue was charged to a column of silica gel. On elution using a mixture (4:1) of hexane and dichloromethane gave **20d** (11 mg, 0.037 mmol).

Compound 20d: (30%); mp 136-138 ^{0}C; IR ν_{max} (KBr), 3428 (OH), 1600 cm^{-1}; UV λ_{max} (CH_3CN) 217 (ε 55,000), 255 (ε 52,000), 302 (ε 8,500), 376 nm (ε 2,100); ^{1}H NMR ($CDCl_3$) δ 6.8-8.7 (m, aromatic and hydroxy protons); MS, *m/z* 374 (M^+), 220, 163, 77 and other peaks. Anal. Calcd for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.30; H, 5.14.

Further elution with a mixture (2:1) of hexane and dichloromethane gave unreacted **19d** (4 mg, 0.01 mmol, 20%).

6.3.2.9. Irradiation of 19a in the Prsence of Diphenylacetylene in Benzene. A mixture of **19a** (20 mg, 0.06 mmol) and diphenylacetylene (10 mg, 0.06 mmol) in benzene (20 mL) was irradiated for 6 h. The reaction was monitored by TLC. TLC showed the presence of a new product in very small yields other than **20a**. Solvent was removed and the residue on column chromatography using a mixture (4:1) of hexane and dichloromethane gave **20a** (8 mg, 0.232 mmol, 44%) as the only isolable product.

References

1. Rao, Y. S. *Chem. Rev.* **1976**, *76*, 625-694.
2. Yogev, A.; Mazur, Y. *J. Am. Chem. Soc.* **1965**, *87*, 3520-3521.
3. Gutsche, C. D.; Oude-Alink, B. A. M. *J. Am. Chem. Soc.* **1968**, *90*, 5855-5861.
4. Krull, I. S.; Arnold, D. R. *Tetrahedron Lett.* **1969**, 1247-1249.
5. Rio, G.; Hardy, J. C. *Bull. Soc. Chim. Fr.* **1970**, 3572-3578.
6. Rio, G.; Hardy, J. C. *Bull. Soc. Chim. Fr.* **1970**, 3578-3584.
7. Chapman, O. L.; McIntosh, C. L. *J. Chem. Soc., Chem. Commun.* **1971**, 383-384.
8. Ohga, K.; Matsuo, T. *J. Org. Chem.* **1974**, *39*, 106-108.
9. Skorianetz, W.; Ohloff, G. *Helv. Chim. Acta* **1975**, *58*, 1272-1275.
10. Padwa, A.; Dehm, D. *J. Am. Chem. Soc.* **1975**, *97*, 4779-4781.
11. Ogha, K.; Matsuo, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1590-1594.
12. Kosugi, K.; Sekiguchi, S.; Sekita, R.; Uda, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 520-528.
13. Padwa, A.; Ku, A.; Sato, E. *Tetrahedron Lett.* **1976**, 2409-2412.
14. Padwa, A.; Brookhart, T.; Dehm, D.; Wubbels, G. *J. Am. Chem. Soc.* **1977**, *99*, 2347-2348.
15. Padwa, A.; Brookhart, T.; Dehm, D.; Wubbels, G. *J. Am. Chem. Soc.* **1978**, *100*, 8247-8259.
16. Zimmer, H.; Downs, B. W. *J. Heterocycl. Chem.* **1978**, *15*, 703-704.
17. Utrilla, R. M.; Mirada, M. A. *Tetrahedron* **1981**, *37*, 2111-2114.
18. Wiberg, K. B.; Hutton, T. W. *J. Am. Chem. Soc.* **1954**, *76*, 5367-5371.
19. Oude-Alink, B. A. M.; Chan, A. W. K.; Gutsche, C. D. *J. Org. Chem.* **1973**, *38*, 1993-2001.
20. Tokumaru, K.; Sakuragi, H.; Takahashi, T. *Chem. Lett.* **1972**, 957-962.
21. Lohray, B. B.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Am. Chem. Soc.* **1984**, *106*, 7352-7359.
22. Bhattacharyya, K.; Das, P. K.; Fessenden, R. W.; George, M. V.; Gopidas, K. R.; Hug, G. L. *J. Phys. Chem.* **1985**, *89*, 4164-4166.
23. Davis, H. G.; Lohray, B. B.; Gopidas, K. R.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 3685-3692.
24. Gopidas, K. R.; Lohray, B. B.; Rajadurai, S.; Das, P. K.; George, M. V. *J. Org. Chem.* **1987**, *52*, 2831-2838.

25. Padwa, A.; Lee G. A. *J. Am. Chem. Soc.* **1973**, *95*, 6147-6149.

26. Prathapan, S.; Ashok, K.; Cyr, D. R.; Das, P. K.; George, M. V. *J. Org. Chem.* **1988**, *53*, 5826-5831.

27. Gopidas, K. R.; Cyr, D. R.; Das, P. K.; George, M. V. *J. Org. Chem.* **1987**, *52*, 5505-5511.

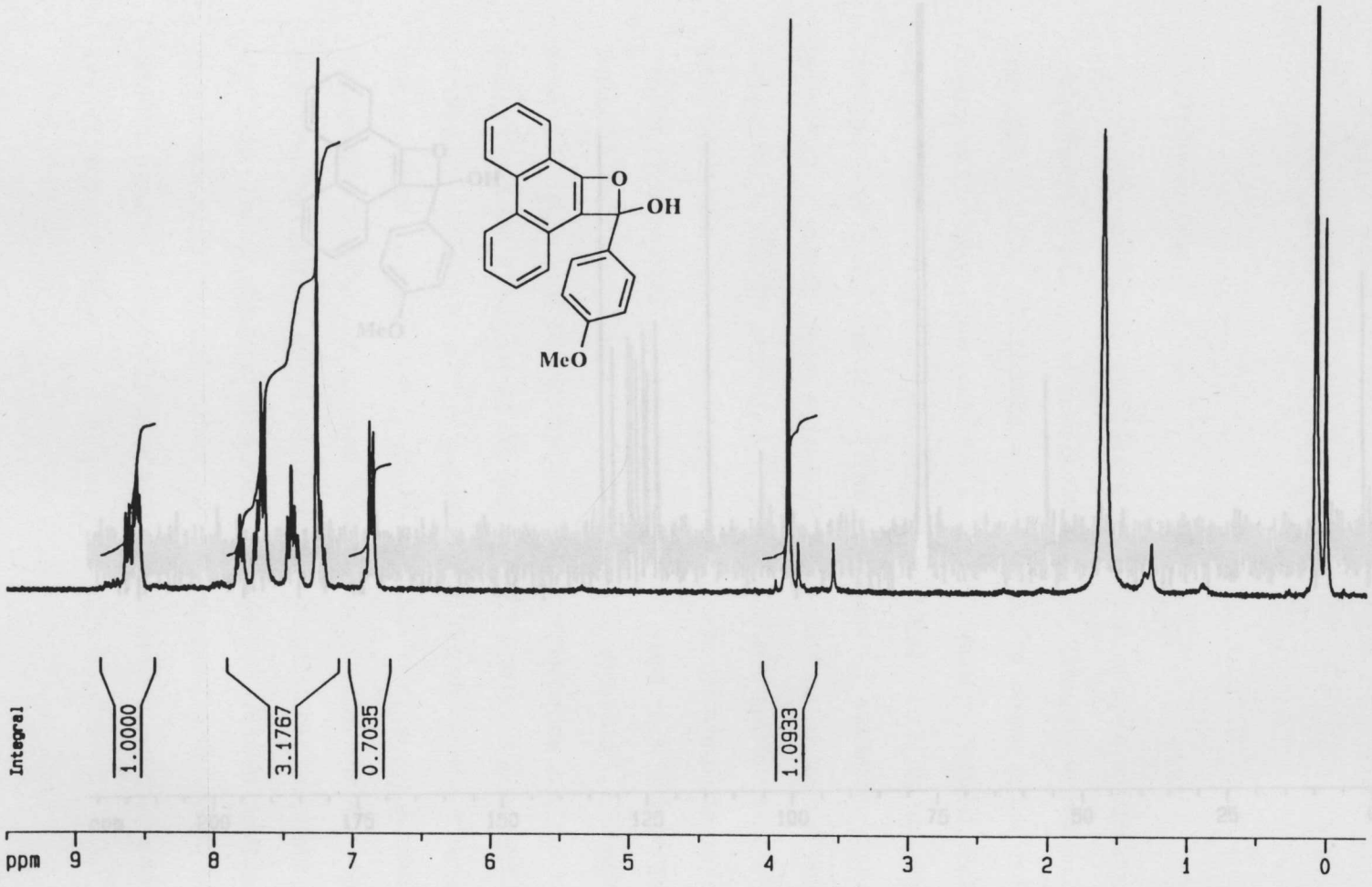


Figure 6.1a. ^{1}H NMR spectrum of compound 20b.

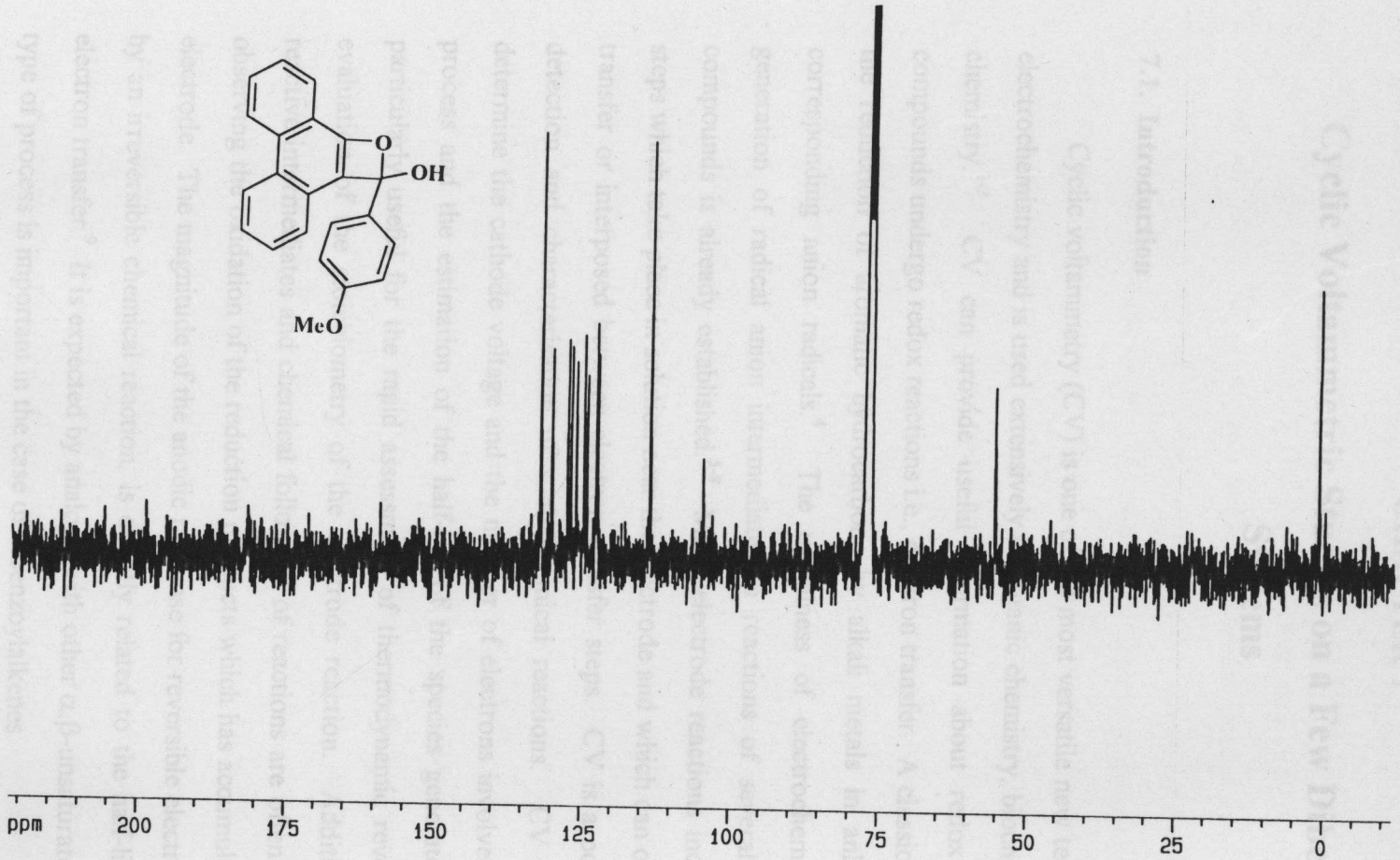


Figure 6.1b. ^{13}C NMR spectrum of compound 20b.

CHAPTER 7

Cyclic Voltammetric Studies on a Few Dibenzoylalkene Systems

7.1. Introduction

Cyclic voltammetry (CV) is one of the most versatile new techniques performed in electrochemistry and is used extensively in organic chemistry, biochemistry, and inorganic chemistry.[1-3] CV can provide useful information about redox reactions. Organic compounds undergo redox reactions i.e., electron transfer. A classical example is found in the reduction of aromatic hydrocarbons by alkali metals in anhydrous ether to the corresponding anion radicals.[4] The usefulness of electrochemical methods in the generation of radical anion intermediates in reactions of several unsaturated organic compounds is already established.[5-8] Many electrode reactions include purely chemical steps which take place in solution near the electrode and which can occur prior to electron transfer or interposed between electron transfer steps. CV is a powerful technique for detection and characterisation of such chemical reactions. CV also permits one to determine the cathode voltage and the number of electrons involved in each step of the process and the estimation of the half-life of the species generated there by. CV is particularly useful for the rapid assessment of thermodynamic reversibility and for the evaluation of the stoichiometry of the electrode reaction. Additional information on reactive intermediates and chemical follow-up of reactions are often obtained by CV and observing the oxidation of the reduction products which has accumulated at the stationary electrode. The magnitude of the anodic response for reversible electron transfer, followed by an irreversible chemical reaction, is directly related to the half-life of the product of electron transfer.[9] It is expected by analogy with other α,β-unsaturated ketones[10] that this type of process is important in the case of dibenzoylalkenes.

There have been only a limited number of investigations comparing the effect of geometry on ease of electrochemical reduction for stereoisomers. Cis and trans isomers of stilbene have been reduced electrochemically in DMF and CH_3CN; the $E_{p/2}$ values are -2.07 V (for cis) and -2.08 V (for trans) in DMF and -1.87 V (for cis) and -1.73 V (for trans) in CH_3CN.[11,12] It appears that in this system there is little difference in the ease of reduction of the isomers. A study of fumaric and maleic acid and their esters in pyridine showed that the trans isomers are reduced at slightly more positive potentials.[13] On the other hand, fumaronitrile is reduced at a more negative potential than maleonitrile, and *trans*-crotononitrile is reduced at a more negative potential than *cis*-crotononitrile in aqueous media.[14] The easier reduction of these cis isomers was attributed to adsorption on the electrode. The reduction of *cis* and *trans*-dibenzoylethylenes in aqueous media shows that the trans isomer is more readily reduced than the cis isomer, $E_{1/2}$(trans) -0.46 V and $E_{1/2}$(cis) -0.75 V.[15,16]

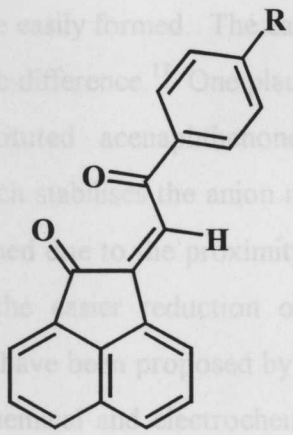
Winecoff *et al* have examined the electrochemical reduction of the geometric isomers of different 1,2-dibenzoylalkenes such as dibenzoylethylene, dibenzoylstyrene and dibenzoylstilbene through polarographic and cyclic voltammetric techniques.[17] They have shown that there is appreciable difference in the ease of reduction between the cis and trans isomers of dibenzoylethylene. Dibenzoylalkenes became more difficult to reduce upon successive addition of phenyl groups. The cyclic voltammograms of *cis* and *trans*-dibenzoylethylenes are given in Figure 7.1, and the reduction potential values of cis and trans isomers of dibenzoylethylene, dibenzoylstyrene and dibenzoylstilbene are given in Table 7.1. Winecoff *et al* have also reported that the inductive effect of the phenyl group do not play a predominate role in determining the $E_{p/2}$ values.[17] The decrease in the ease of reduction of dibenzoylstyrene and dibenzoylstilbene in comparison with dibenzoylethylene could be explained as follows: the stability of the presumed intermediate anion radical is decreased by the incorporation of a phenyl group to the system which leads to increased steric crowding resulting in a decrease in coplanarity and accompanying delocalisation of charge. Anodic sweep of cyclic voltammograms of each isomer of the geometric sets provides additional information concerning the stability of anion radicals

produced on reduction. It is evident from the cyclic volatammograms for the dibenzoylethylene pair given in Figure 7.1 that a relatively stable radical anion which can be reoxidised at expected potential is produced in the case of the trans isomer. On the other hand, for the cis isomer, the absence of reverse anodic wave suggests that the radical anion produced by reduction is unstable and does not survive to be reoxidised.[15,16] The cyclic voltammograms of dibenzoylstyrene show the absence of significant anodic waves for both isomers due to the short half-lives of the anion radicals. Ashok *et al* have examined the electrochemical behaviour of 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes and observed the reduction potentials of one electron and two electron processes leading to the generation of the corresponding radical anion and dianion intermediates.[18] The cyclic voltammogram of 11,12-dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethenoanthracene is given in Figure 7.2 and the reduction peaks are in the ranges -1.37 to -1.65 V and -1.91 to -2.1 V versus SSCE.

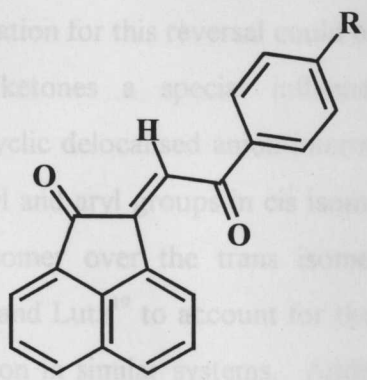
Table 7.1

$E_{1/2}$ (V) Values of Dibenzoylalkenes		
	trans	cis
Dibenzoylethylene	-0.89	-1.15
Dibenzoylstyrene	-1.19	-1.19
Dibenzoylstilbene	-1.22	-1.19

In the present study, the redox behaviour of a few acenaphthenone-2-ylidene ketones is investigated to compare their electrochemical behaviour with that of other dibenzoylalkenes such as dibenzoylethylene, dibenzoylstyrene, and dibenzoylstilbene. The compounds selected for the study are *cis* and *trans*-acenaphthenone-2-ylidene ketones **1a,b** and **2a,b**. Moreover, the isomeric pairs selected by us should provide an opportunity to compare the effect of geometry on ease of electrochemical reduction for stereoisomers.



1a,b



2a,b

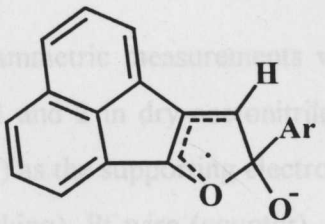
a) R = OCH_3
b) R = Ph

7.2. Results and Discussion

To study the redox behaviour of acenaphthenone-2-ylidene ketones, we synthesised a few acenaphthenone-2-ylidene ketones by the condensation of acenaphthenequinone with selected methyl ketones. The *trans*(*E*)-acenaphthenone-2-ylidene ketones obtained were converted to *cis*(*Z*)-acenaphthenone-2-ylidene ketones photochemically. Close examination of the structural features of these ketones reveals their similarity with dibenzoylstyrene.

Examination of $E_{p/2}$ values for the acenaphthenone-2-ylidene ketones reveals interesting trends. The reduction potential values of acenaphthenone-2-ylidene ketones are much lower than that of other dibenzoylalkenes. Therefore, it could be deduced that these systems undergo reduction easily. It was observed that the cis and trans isomer pair **1a** and **2a** undergo reduction at different potentials. The Δ value ($E_{p/2}$cis - $E_{p/2}$trans) is -0.03 V, indicating that the trans isomer **2a** is reduced slightly more easily than the cis isomer **1a**. The symmetrical peak observed at –0.92 V in the redution wave of **2a** is probably due to adsorption.[17] Thus the behaviour of **1a** and **2a** is similar to that of *cis*- and *trans*-dibenzoylstyrenes. But in the case of the isomer pair **1b** and **2b** the behaviour is analogous to that of *cis* and *trans*-dibenzoylstilbenes. Here the cis isomer **1b** has a lower $E_{p/2}$ value than trans isomer **2b** ($E_{p/2}$trans - $E_{p/2}$cis = -0.11 V), i.e., the anion radical of cis

isomer is more easily formed. The ease of reduction of the cis isomer **1b** can be attributed to the isomeric difference.[17] One plausible explanation for this reversal could be that in the biphenyl-substituted acenaphthenone-2-ylidene ketones a special influence may be operative which stabilises the anion radical. A cyclic delocalised anion intermediate such as **3** or **4** formed due to the proximity of carbonyl and aryl groups in cis isomer **1b** could account for the easier reduction of the cis isomer over the trans isomer. Similar intermediates have been proposed by Winecoff[17] and Lutz[19] to account for the "cis-group effects" on chemical and electrochemical reduction in similar systems. Additionally, we have observed that only **1b** undergoes lactonisation upon irradiation indicating that a cyclic delocalised anion radical such as **3** or **4** is more readily formed in this case.[20] The symmetrical peak observed at –0.89 V and –1.03 V in the reduction wave of **1b** and **2b** respectively are probably due to adsorption. Cyclic voltammograms of **1a,b** and **2a,b** are given in Figure 7.3. The reduction peak potentials of **1a,b** and **2a,b** are given in Table 7.2.



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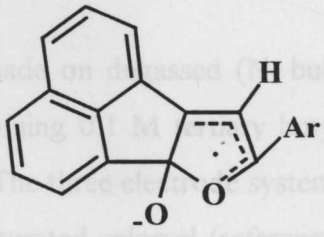

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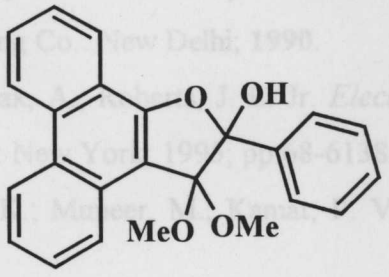
TABLE 7.2

Electrochemical Data of Acenaphthenone-2-ylidene Ketones 1a,b and 2a,b.

Compound	Reduction peak potential $E_{p/2}$ (V versus SCE)
1a	**-0.60**
2a	**-0.57, -0.92**
1b	**-0.54, -0.89**
2b	**-0.65, -1.03**

We have also examined the redox behaviour of 3,3-dimethoxy-2-phenylphenanthro-2,3-dihydro-2-furanol **5**. The two reduction peaks observed in the cyclic voltammogram of **5** are not prominent. The reduction peak potentials are at -0.7 and -0.9 V. No anodic waves are observed here. The cyclic voltammogram of **5** is given in Figure 7.4.



5

7.3. Experimental

Cyclic voltammetric measurements were made on degassed (N_2 bubbling for 15 min) solutions of **1** and **2** in dry acetonitrile containing 0.1 M tertiary butyl ammonium perchlorate (TBAP) as the supporting electrolyte. The three electrode system consisted of glassy carbon (working), Pt wire (counter), and saturated calomel (reference) electordes. Compound **1a** (63 mg, 2 mmol) was dissolved in acetonitrile and cyclic voltammetric measurements were done at scan rate 100 mVs^{-1}. Compound **2a** (63 mg, 2 mmol) was dissolved in acetonitrile and cyclic voltammetric measurements were carried out at 100 mVs^{-1}. Compound **1b** (72 mg, 2 mmol) was dissolved in acetonitrile and cyclic voltammetric measurements were done at scan rate 100 mVs^{-1}. Compound **2b** (72 mg, 2 mmol) was dissolved in acetonitrile and cyclic voltammetric measurements were carried out at 100 mVs^{-1}. Compound **5** (74 mg, 2 mmol) was dissolved in DMF and cyclic voltammetric measurements were carried out at scan rate 100 mVs^{-1}.

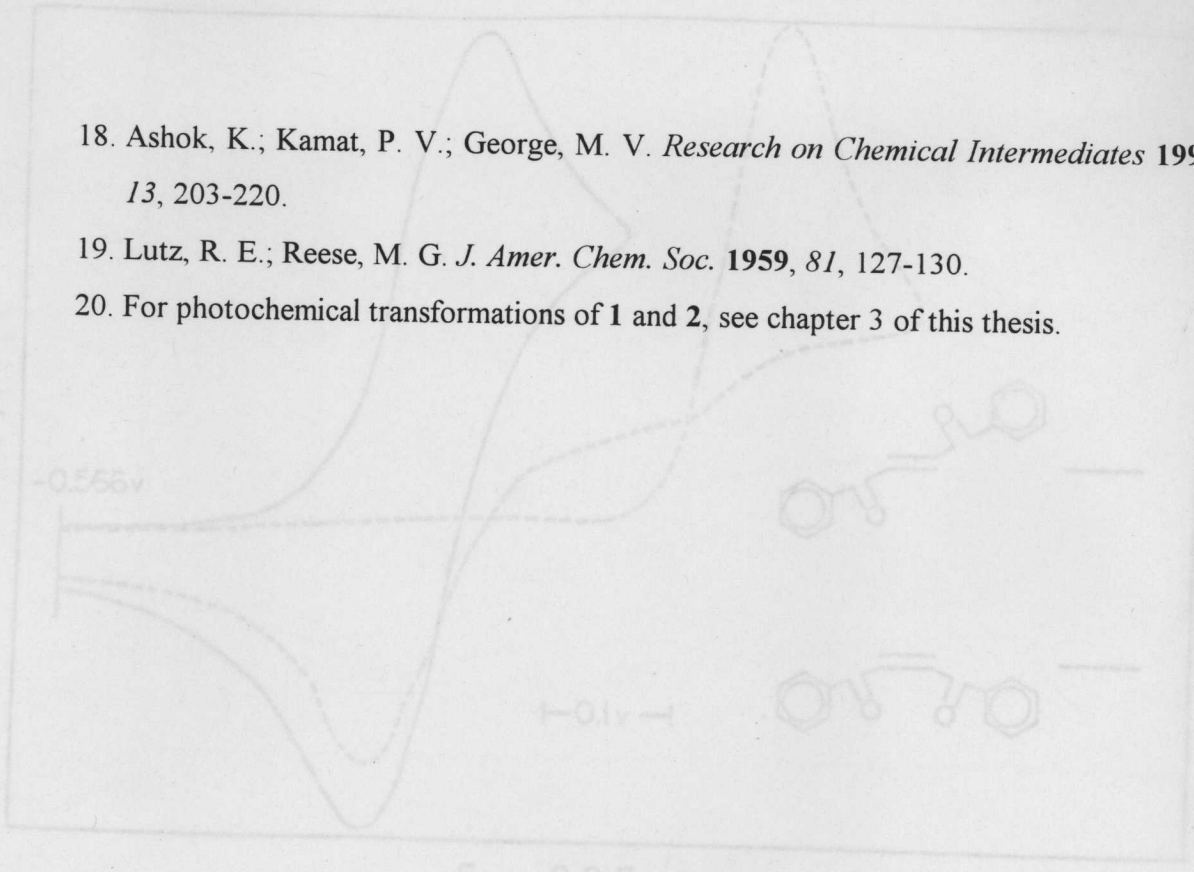
References

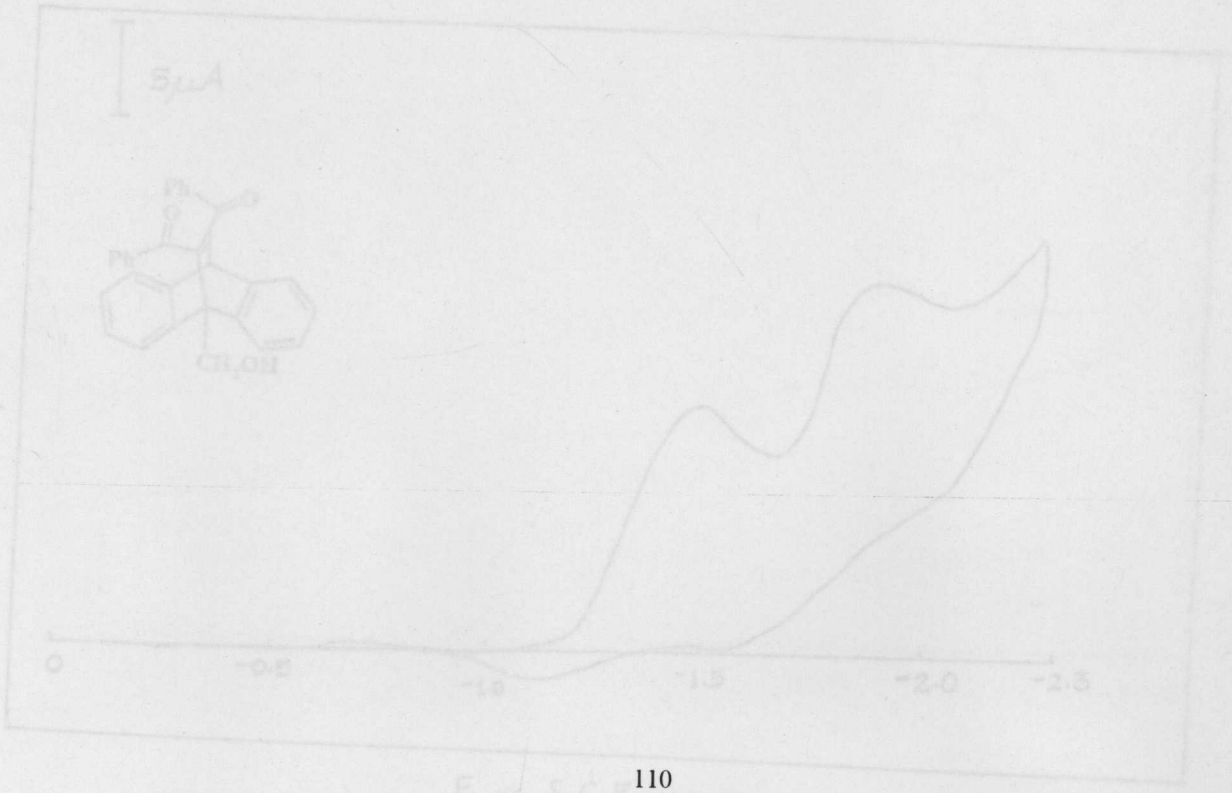
1. Kissinger, P. T.; Heineman, W. R. *J. Chem. Educ.* **1983**, *60*, 702-707.
2. Hammerich, O.; Svensmark, B.; Parker, V. D.; In *Organic Electrochemistry: An Introduction and a Guide;* Baizer, M. M.; Lund, H., Ed.; Marcel Dekker: New York; **1983**; pp 77-150.
3. Noel, M.; Vasu, K. I. *Cyclic Voltammetry and the Frontiers of Electrochemistry:* Oxford and IBH Publishing Co.: New Delhi; **1990**.
4. Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L. Jr. *Electrochemistry for Chemists*, 2nd ed.; John Wiley and sons: New York; 1995; pp 68-6138.
5. Pandey , B.; Tikare, R. K.; Muneer, M.; Kamat, P. V.; George, M. V. *Chem. Ber.* **1986**, *119*, 917-928.
6. Muneer, M.; Tikare, R. K.; Kamat, P. V.; George, M. V. *Can. J. Chem.* **1987**, *65*, 1624-1630.
7. Ashok, K.; Scaria, P. M.; Kamat, P. V.; George, M. V. *Can. J. Chem.* **1987**, *65*, 2039-2049.
8. Muneer, M.; Tikare, R. K.; Kamat, P. V.; George, M. V. *New. J. Chem.* **1989**, *13*, 215-219.
9. Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706-723.
10. Zimmer, J. P.; Richards, J. A.; Turner, J. C.; Evans, D. H.; *Anal. Chem.* **1971**, *43*, 1000-1006.
11. Wawzonek, S.; Blaha, E. W.; Berkey, R.; Runner, M. E. *J. Electrochem. Soc.* **1955**, *102*, 235-239.
12. Grodzka, P. G.; Elving, P. J. *J. Electrochem. Soc.* **1963**, *225*, 231-237.
13. Takahashi, R.; Elving, P. *Electrochem. Acta* **1967**, *12*, 213-217.
14. Smirov, S. K.; Sevastyanov, I. G.; Tomilov, A. P.; Federova, L. A.; Strukov, O. G. *Zh. Org. Khim.* **1969**, *5*, 1392-1396. (*Chem. Abstr.* **1969**, *71*, 108455d).
15. Keller, H.; Pasternak, R.; Halban, H. V. *Helv. Chim. Acta* **1946**, *29*, 512-520.
16. Pasternak, R. *Helv. Chim. Acta* **1948**, *31*, 753-776.
17. Winecoff W. F. III.; O'Brien, Boykin D. W. J. Jr. *J. Org. Chem.* **1974**, *38*, 1474-1479.

18. Ashok, K.; Kamat, P. V.; George, M. V. *Research on Chemical Intermediates* **1990**, *13*, 203-220.

19. Lutz, R. E.; Reese, M. G. *J. Amer. Chem. Soc.* **1959**, *81*, 127-130.

20. For photochemical transformations of **1** and **2**, see chapter 3 of this thesis.





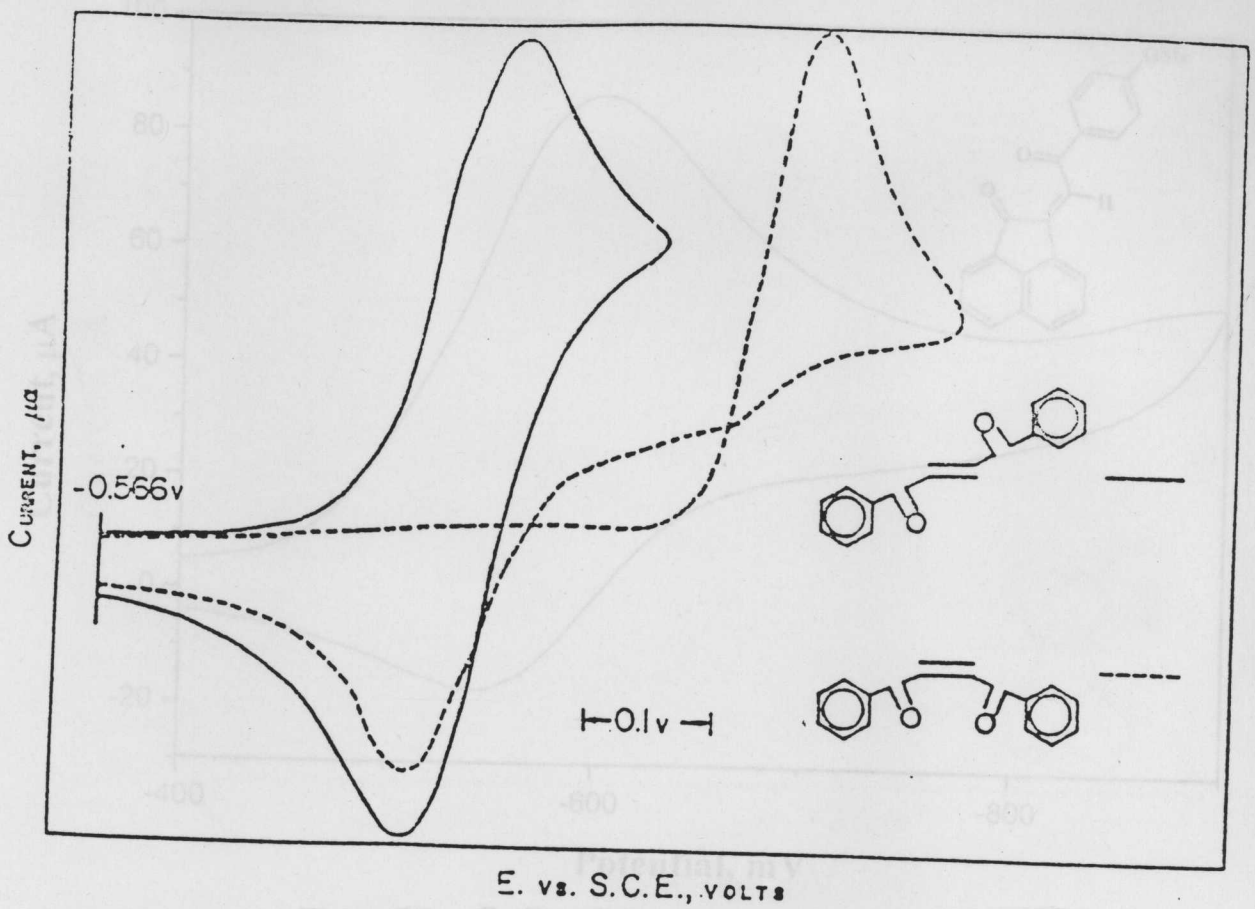


Figure 7.1. Cyclic voltammograms of *cis* and *trans*-dibenzoylethylene.

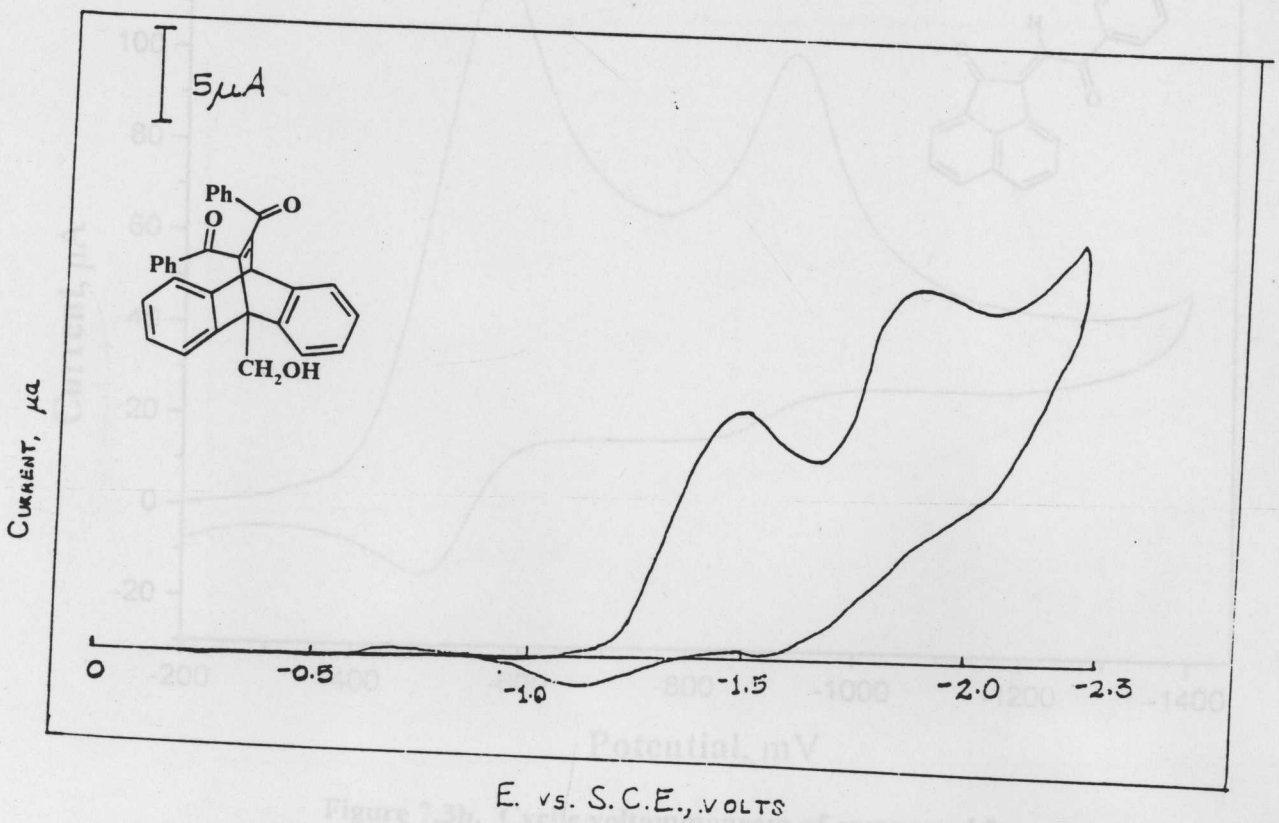


Figure 7.2. Cyclic voltammogram of 11,12-dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethenoanthracene.

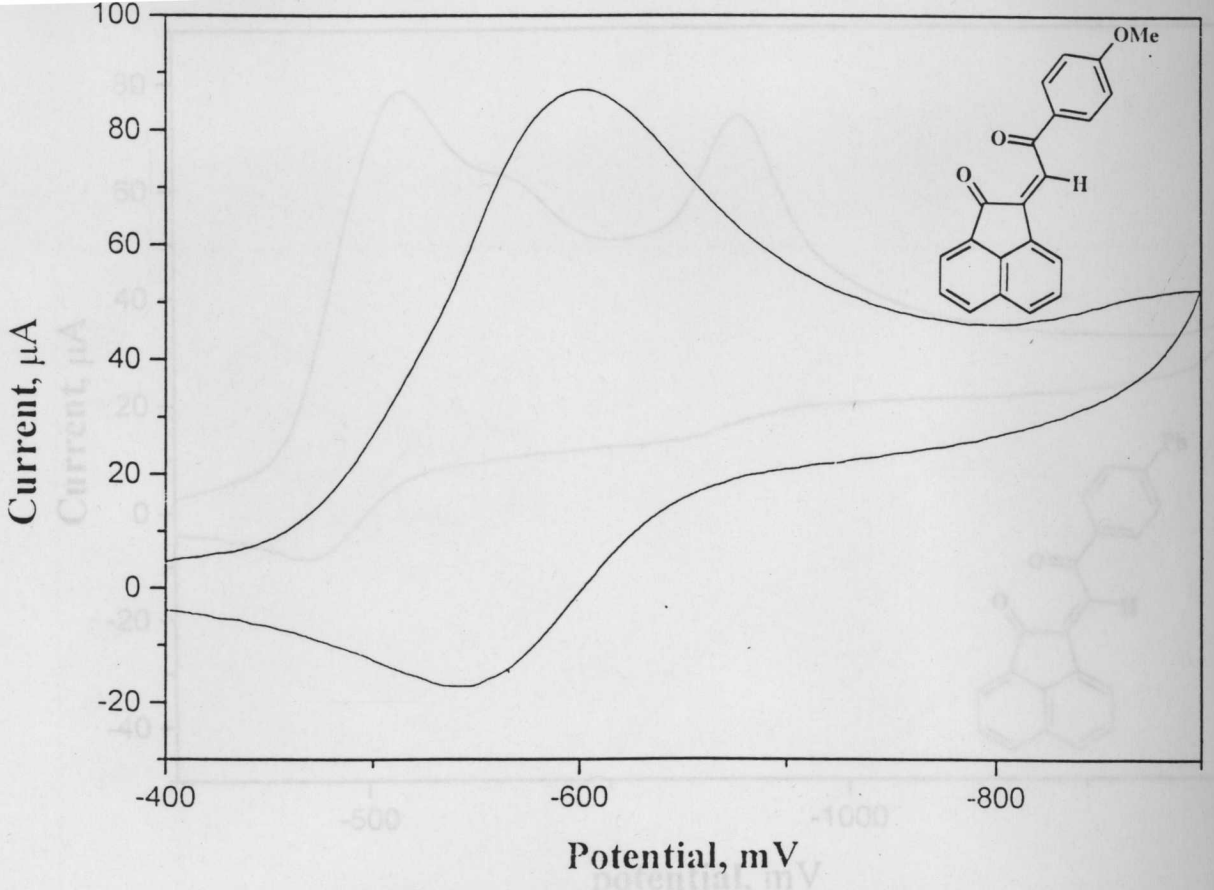


Figure 7.3a. Cyclic voltammogram of compound 1a.

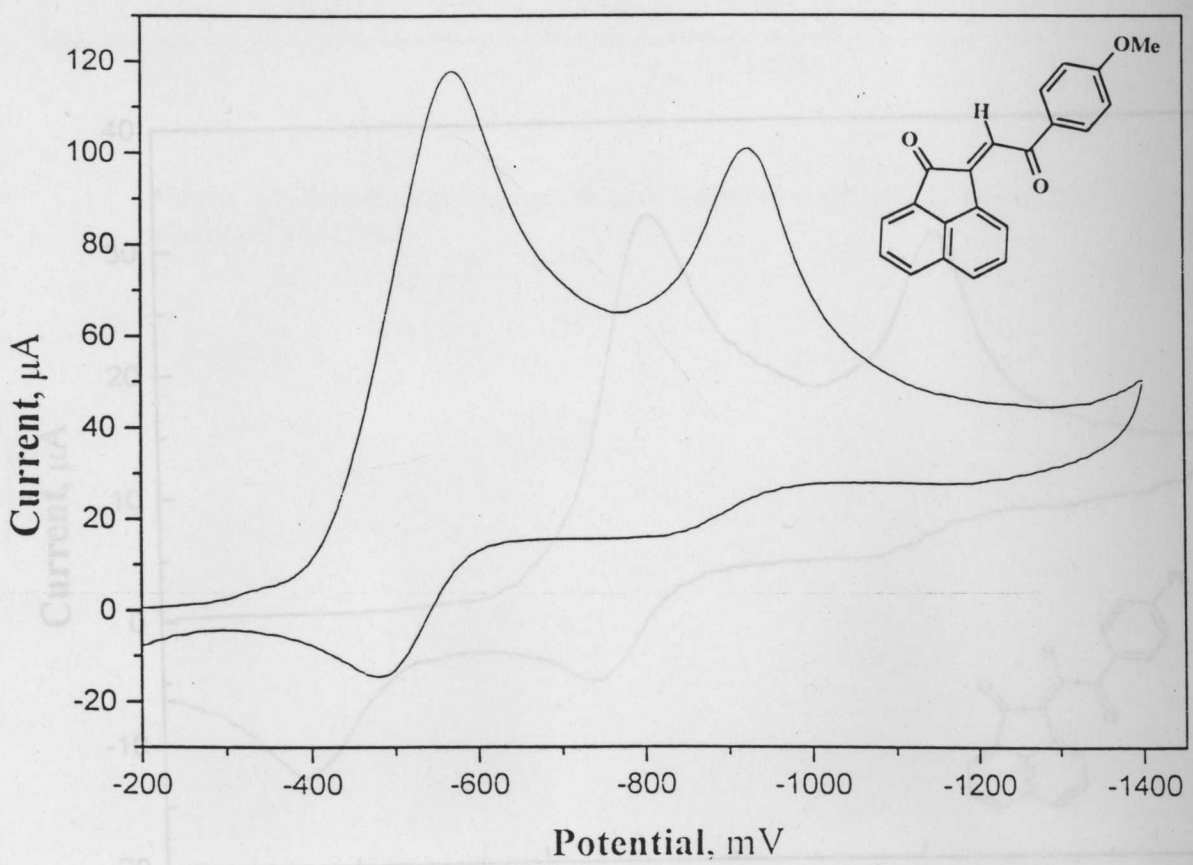


Figure 7.3b. Cyclic voltammogram of compound 2a.

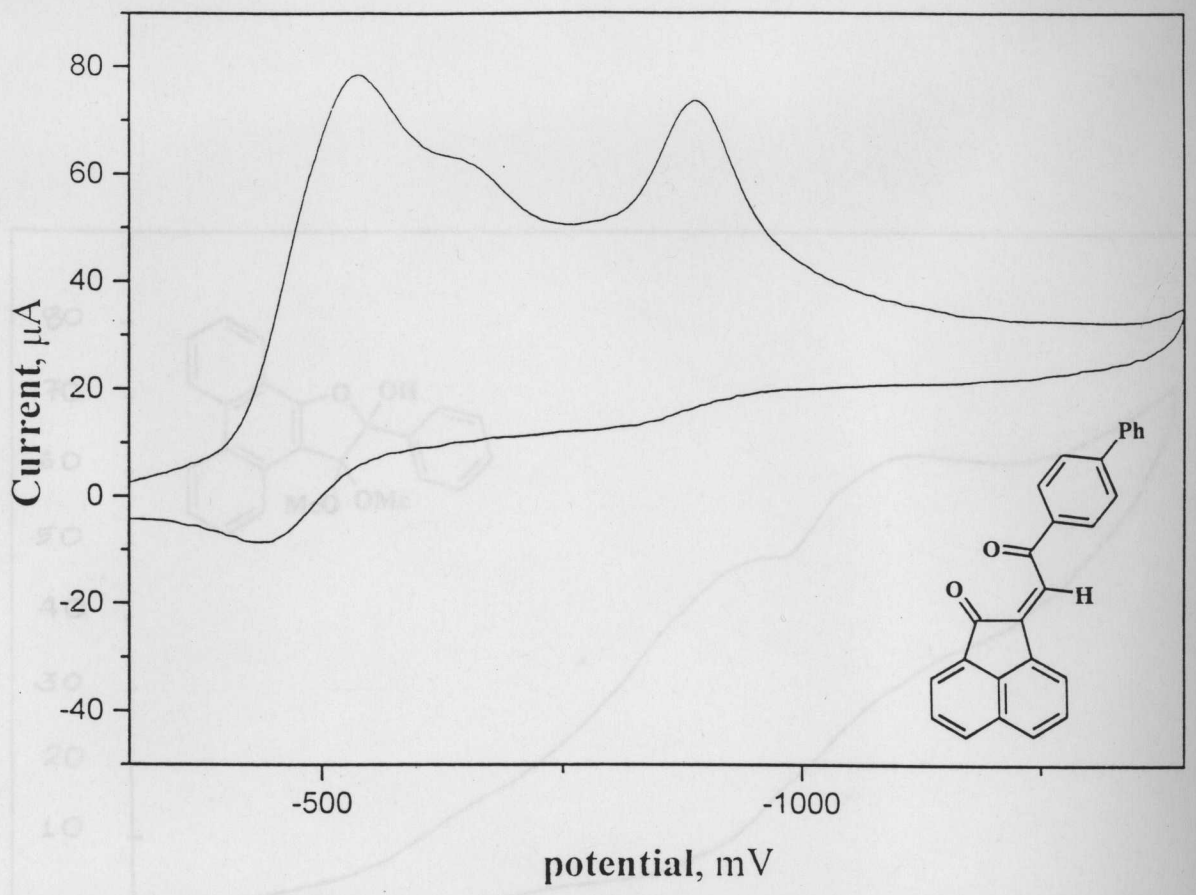


Figure 7.3c. Cyclic voltammogram of compound 1b.

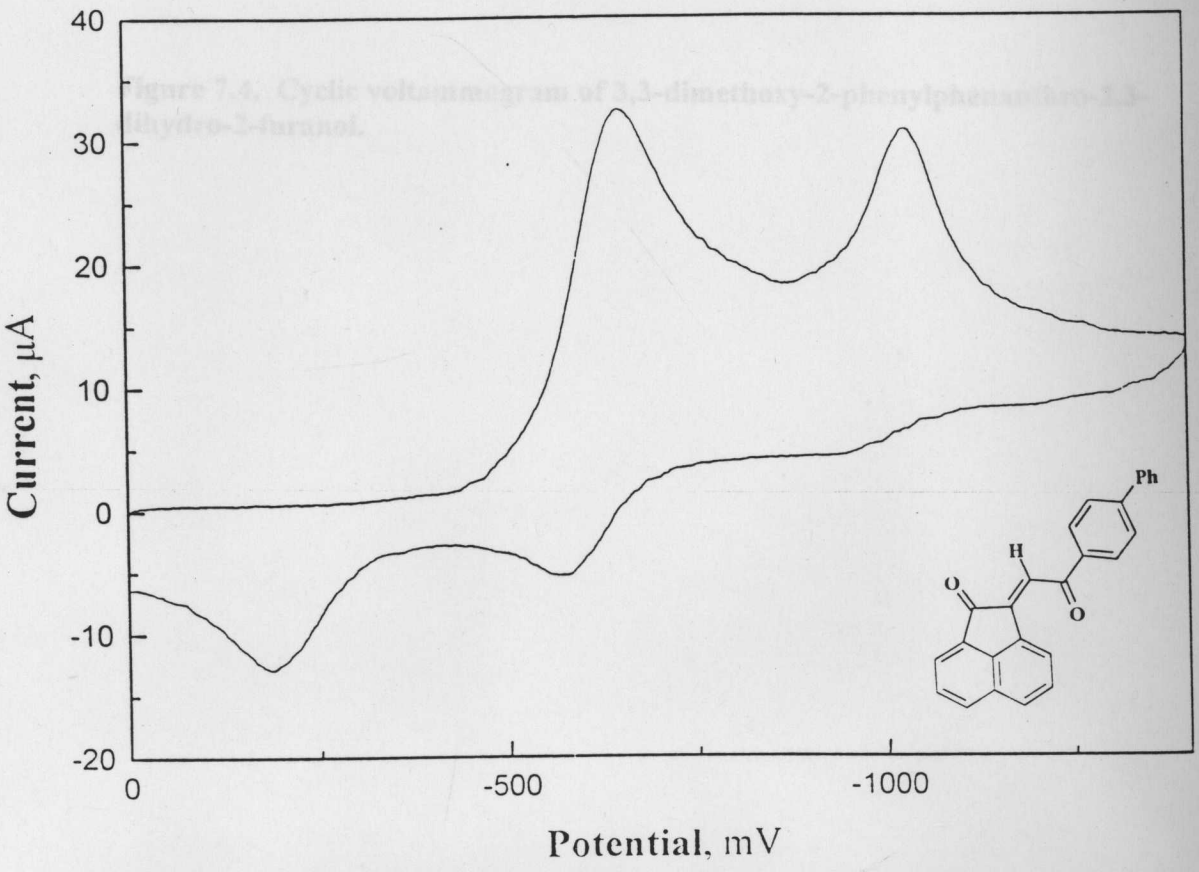


Figure 7.3d. Cyclic voltammogram of compound 2b.

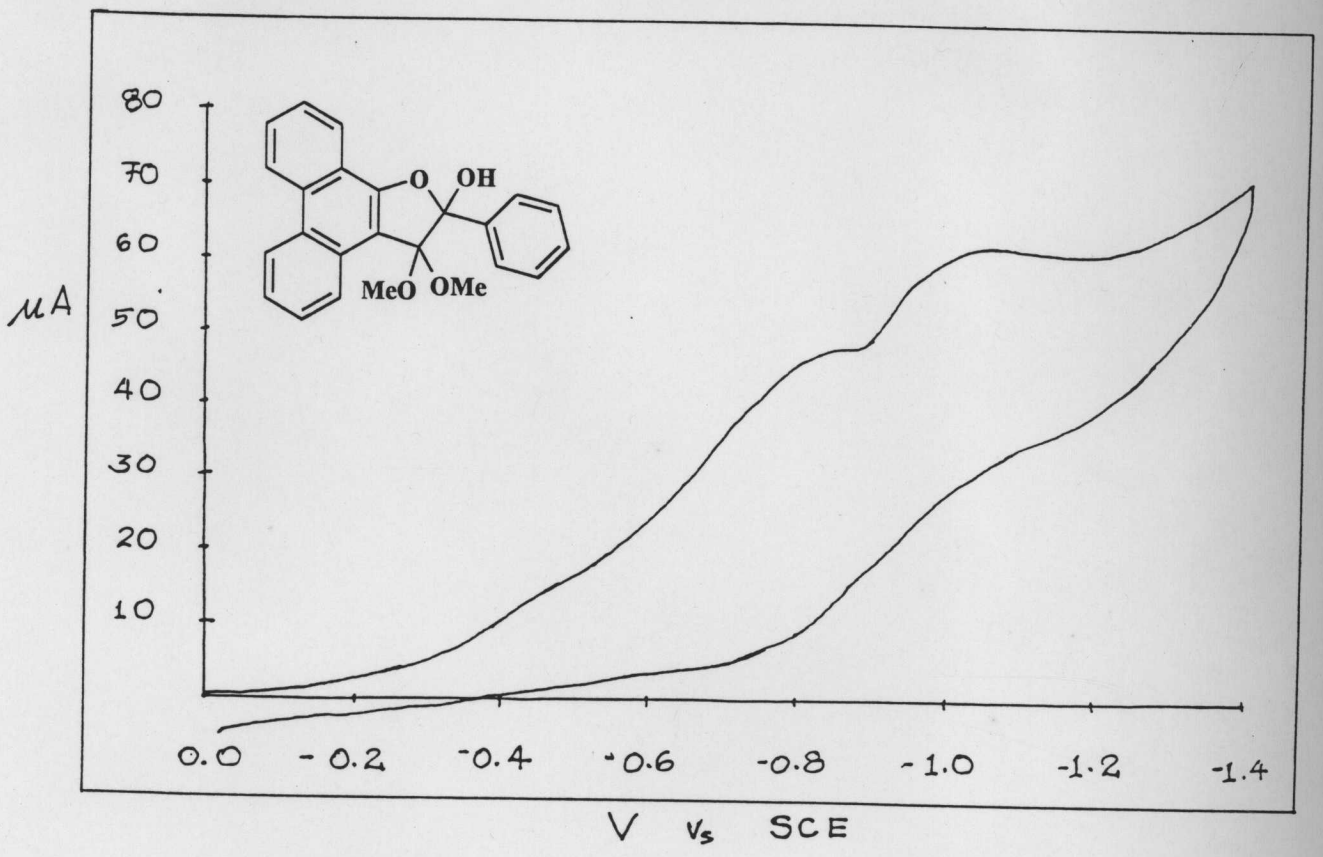


Figure 7.4. Cyclic voltammogram of 3,3-dimethoxy-2-phenylphenanthro-2,3-dihydro-2-furanol.