2(3*H*)-FURANONES AND RELATED SUBSTRATES: SYNTHETIC STRATEGIES AND SELECTIVITY PROFILE IN THEIR REACTIVITY

THESIS SUBMITTED TO THE
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DOCTOR OF PHILOSOPHY

IN

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IN THE FACULTY OF SCIENCE

BY

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November 2007

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
12th November, 2007

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DECLARATION

I hereby declare that the work presented in this thesis entitled: **"2(3H)-Furanones and related substrates: Synthetic strategies and selectivity profile in their reactivity"** is original and was carried out by me independently under the supervision of Dr. Prathapan S., Reader in Organic Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-682 022, India, and has not been included in any other thesis submitted previously for the award of any other degree.

Roshini K. Thumpakara

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12th November, 2007

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Roshini K. Thumpakara

CONTENTS

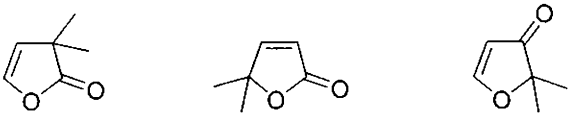
Abstract

The thesis entitled: **'2(3*H*)-Furanones and related substrates: Synthetic strategies and selectivity profile in their reactivity'** is divided into 5 chapters.

In **Chapter 1**, a brief overview of the synthesis and photochemistry of various furanones is presented. **Chapter 2** deals with our endeavours on the synthesis and photochemistry of 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-ones. **Chapter 3** presents synthesis of 3,3,5-triaryl-3*H*-furan-2-ones and their photochemistry. **Chapter 4** describes the synthesis and photochemical studies of a few 2-aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones. **Chapter 5** mainly deals with synthesis, photolysis and solvent assisted chemical transmogrification of acenaphthenone-2-ylidene ketones.

Chapter 1: A Preamble on Furanones: Synthesis and Photochemistry

Furanones represent an interesting class of heterocyclic compounds, which constitute the central ring system of many natural products. They are derivatives of furan and, depending on structure, are divided into three main types: 2(3*H*)-furanones (**I**), 2(5*H*)-furanones (**II**), and 3(2*H*)-furanones (**III**) (Figure 1).



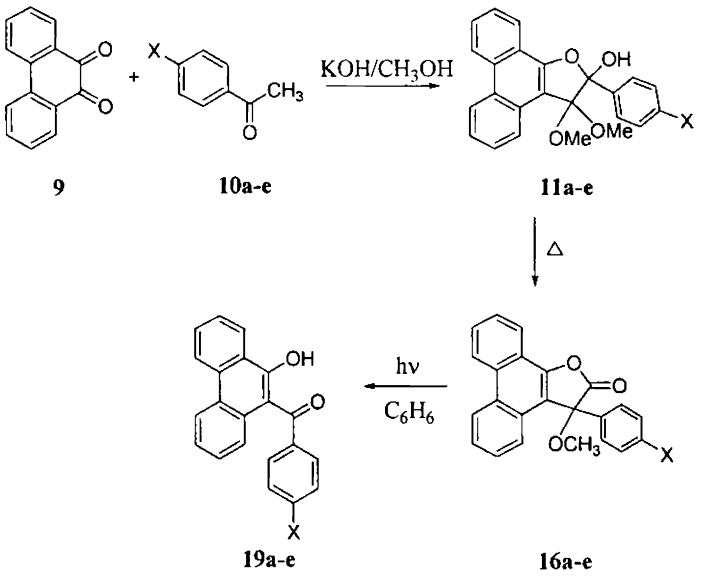
2(3*H*)-furanone **I** 2(5*H*)-furanone **II** 3(2*H*)-furanone **III**

Figure 1

The IUPAC-approved names for these heterocycles are: 2,3-dihydrofuran-2-ones, 2,5-dihydrofuran-2-ones and 3,2-dihydrofuran-3-ones respectively.

In light of enormous interest in the versatile utility of these classes of heterocyclic compounds, numerous synthetic efforts have been directed towards these substances. These compounds are also reported to undergo various interesting photochemical transformations depending on the nature of the furanone ring and the substituents present. A brief survey of the major synthetic routes and photochemical transformations of various furanones is provided in this chapter.

Chapter 2: 3-Methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-ones: Synthesis and Photochemistry



9 **10a-e** **11a-e** **19a-e** **16a-e**

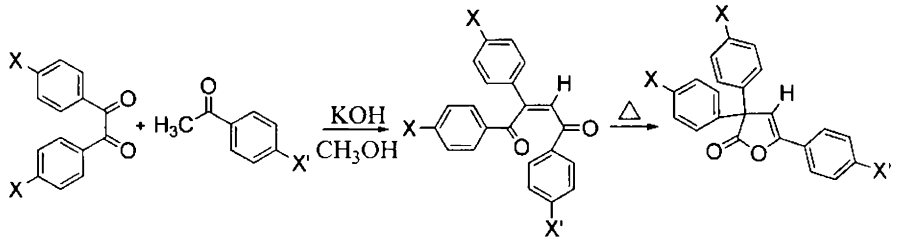
a) X = H b) X = CH_3 c) X = OCH_3 d) X = Cl e) X = Ph

Scheme A 1

To study the effect of a radical stabilising group at 3-position of furanone ring on its photochemistry, we synthesised a few 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenathren-2-ones from 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol precursors, that were in turn, prepared by the Claisen-Schmidt condensation reaction between phenanthrenequinone and 4-substituted acetophenones. By synthesising and irradiating the suitable substrates, we have successfully demonstrated that the methoxy group in the lactone ring has a profound effect on the acyl-oxygen bond cleavage leading to decarbonylation reaction. Our attempts to trap the proposed intermediates by using DMAD and 2-propanol were unsuccessful presumably due to their reactive nature.

Chapter 3: Synthesis and Photochemical Transformations of a Few 3,3,5-Triaryl-3*H*-furan-2-ones

In order to explore the triplet-mediated transformations of 2(3*H*)-furanones in polar and nonpolar solvents, we proposed to synthesise various 3,3-bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones and 3,3-di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones. The method we adopted involved the base catalysed

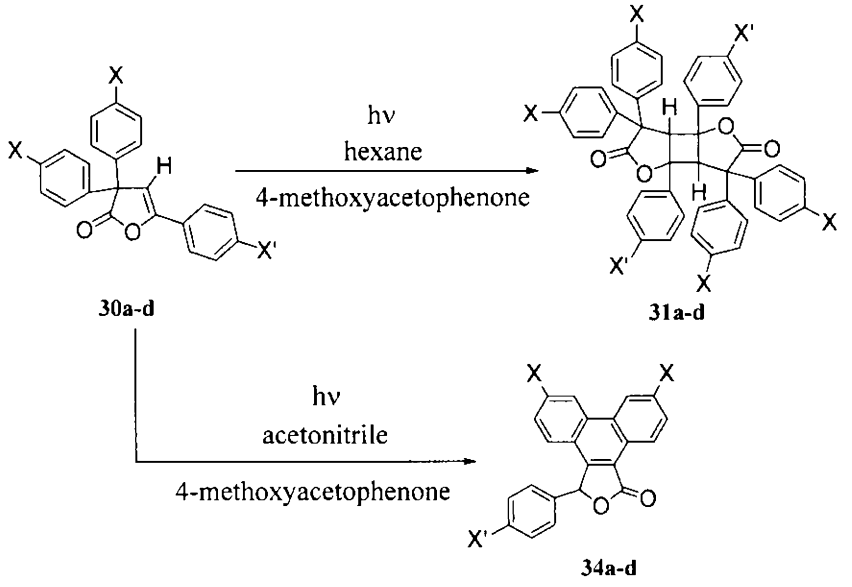


26a,c,e **27a,b** **28a-f** **30a-f**

a) X = Cl X' = H c) X = Me X' = H e) X = OMe X' = H
b) X = Cl X' = Cl d) X = Me X' = Cl f) X = OMe X' =Cl

Scheme A 2

condensation of 4,4'-disubstituted benzils with suitably-substituted acetophenones to give diaroylstyrenes which upon thermolysis yield the corresponding 2(3*H*)-furanones (Scheme A2). Our observations clearly indicated that with 4-methoxyacetophenone as sensitizer, irradiation in acetonitrile, lead to the formation of 2(5*H*)-furanones which undergo further transformation to yield the corresponding phenanthrofuranones. But in nonpolar solvents like hexane, sensitized irradiation resulted in head-to-tail dimerisation of starting 2(3*H*)-furanone. In this chapter, we describe our endeavours on the synthesis and characterisation of several 3,3,5-triaryl-3*H*-furan-2-ones and their photochemistry.

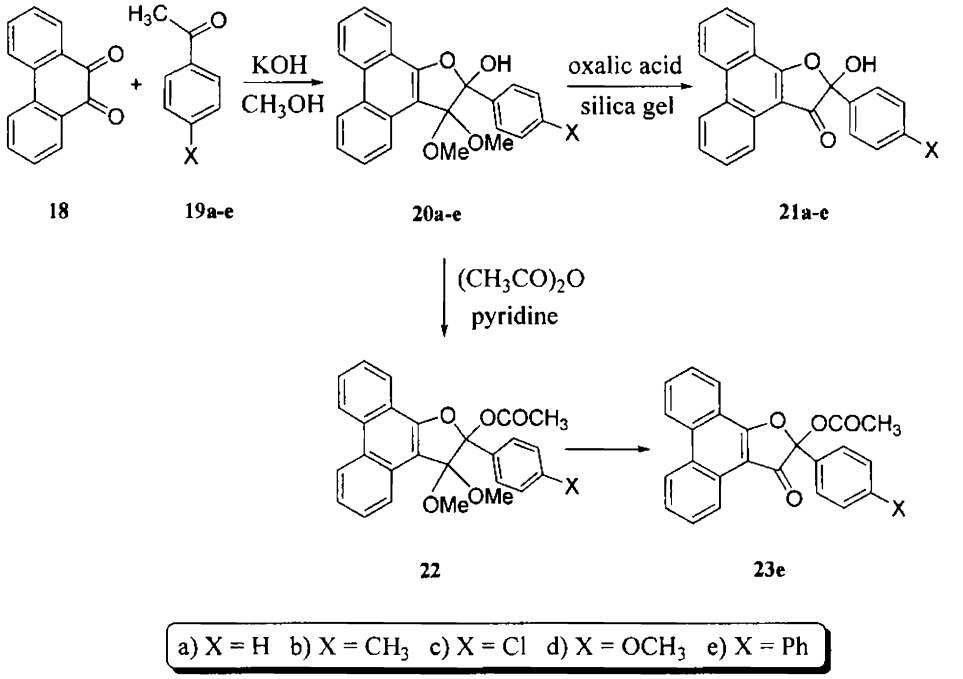


a) X = Cl X' = H c) X = Me X' = H
b) X = Cl X' = Cl d) X = Me X' = Cl

Scheme A 3

Chapter 4: Synthesis and Photochemical Studies of a Few 2-Aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones

3(2*H*)-Furanones are valuable synthetic intermediates and key structural subunits of a variety of natural products. This chapter presents our efforts on the development of a new and efficient method for the synthesis of a few 2-aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones. The protocol developed by us employs readily available phenanthrenequinone and various para substituted acetophenones as starting materials and provides easy access to the required 3(2*H*)-furanone targets. The photolysis of these compounds in presence of a tertiary amine resulted in extensive decomposition leading to intractable mixtures.

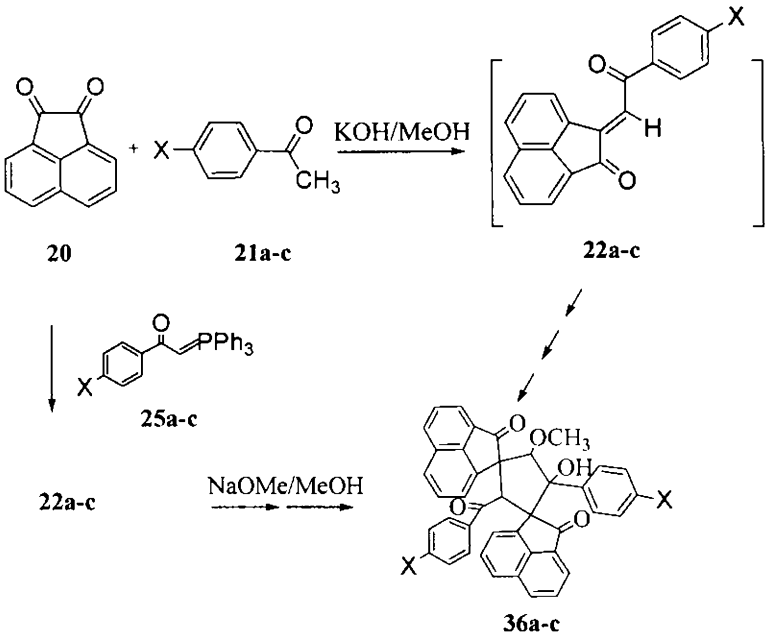


Scheme A 4

Chapter 5: Synthesis, Photolysis and Solvent Assisted Chemical Transmogrification of Acenaphthenone-2-ylidene ketones.

As a logical extension to our continued interest in the synthesis and chemistry of dibenzoylalkene derived furanones, we targeted the synthesis of a few acenaphthenone-2-ylidene ketones and phenanthrenone-9-ylidene ketones. Acenaphthenone-2-ylidene ketones were synthesised via Claisen-Schmidt condensation and Wittig reaction. The condensation of acenaphthenequinone with 4-methoxyacetophenone and 4-phenylacetophenone gave acenaphthenone-2-ylidene ketones whereas the reaction between acenaphthenequinone and acetophenone and 4-methylacetophenone resulted in domino reaction sequence involving a novel three-component Michael-aldol tandem reaction. With 4-chloroacetophenone, both acenaphthenone-2-ylidene ketone and dispirocompound were formed by controlling the reaction conditions. Isolation of the intermediate by Wittig reaction and further reaction on that clearly supported the proposed mechanism for the domino process. Our observations clearly indicated the role of substituents in the reactivity of acenaphthenone-2-ylidene ketones.

Our endeavours towards the synthesis of phenanthrenone-9-ylidene ketone resulted in pyran derivative. *E-Z* isomerisation was observed with acenaphthenone-2-ylidene ketones under photochemical and Lewis acid catalysed conditions. However, the *E*-isomers appear to be more stable than the corresponding *Z*-isomers. Both these isomers appear to be reluctant to undergo [4+2] cycloaddition reaction under the applied reaction conditions. Further our furanisation attempts using stannous chloride-acetic acid-hydrochloric acid mixture resulted in simple reduction of the 1,4-enedione component.



Scheme A 5

In conclusion a number of 2(3*H*)- and 3(2*H*)-furanones were synthesised from phenanthrofuranol precursors and were characterised on the basis of spectral, analytical and X-ray data. On direct irradiation, 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-ones underwent decarbonylation, illustrating the role of a radical stabilising group on acyl-oxygen bond cleavage. We have developed a new and efficient method for the synthesis of a few 2-aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones. These furanone derivatives have immense potential for further investigations. Our studies on these 3(2*H*)-furanones revealed that these compounds are found to be stable towards UV light on direct irradiation, while they undergo extensive decomposition to intractable mixtures in presence of a tertiary amine. Acenaphthenone-2-ylidene ketones were synthesised via Claisen-Schmidt

condensation and Wittig reaction. With a few acetophenones, the condensation reaction gave dispirocompounds by a domino Michael-aldol reaction. Isolation of the intermediate by Wittig reaction and further reaction on that clearly supports the proposed mechanism for the domino process. We also examined effect of substituents on the aryl group on the thermal, photochemical and Lewis acid catalysed transformations of acenaphthenone-2-ylidene ketones. In addition to these a few reactions were carried out to study their potential as *o*-quinonemethides.

Note: The numbers given to various compounds herein correspond to those given in respective chapters. All new compounds were fully characterised on the basis of spectral and analytical data. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

Chapter 1

A Preamble on Furanones: Synthesis and Photochemistry

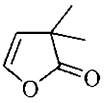
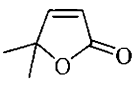
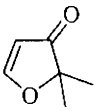
1.1. Introduction

Organic molecules, and the access to them provided by organic synthesis, have a tremendous impact on the way humans live and function. We are made of them and they have implications in almost every aspect of our everyday life. Small organic molecules can, if designed properly, provide us with an almost infinite array of properties, with applications ranging from fuels and material science to electronics, biology and medicine. To this day, the undisputed master of creating molecules with unique, selective and potent properties is Nature. Consequently, immense part of modern research has been directed at designing artificial ways to mimic Nature's solutions. This often presents formidable challenges to human ingenuity and skill.

The field of organic synthesis is generally recognized as having commenced with Wöhler's synthesis of urea and Hennell's synthesis of ethyl alcohol in 1828.[1] The synthesis of urea, while not very complex in itself, brought about a proof that an organic substance could be formed *in vitro* from inorganic precursors, cyanic acid and ammonia.[2] These discoveries influenced the chemical community and triggered a field that eventually resulted in landmark achievements. Thus the science of organic synthesis is constantly enriched by new inventions and discoveries pursued deliberately for their own sake or as subgoals within a program directed towards the synthesis of a target molecule.

The known organic compounds have an enormous diversity of structure. Heterocyclic compounds probably constitute the largest and most diverse family of organic compounds. Besides the vast distribution of heterocycles in natural compounds, they are also the major components of biological molecules such as DNA. DNA is without a doubt the most important macromolecule of life. Nucleotides, the building blocks of our genes are derivatives of pyrimidine and purine ring structures. Chlorophyll and heme, the oxygen carriers in plants and animals respectively are derivatives of cyclic tetrapyrroles. Three out of twenty natural amino acids have heterocyclic ring components, as do many essential vitamins i.e. vitamin B series and vitamin C. They are also predominant among all types of pharmaceuticals, agrochemicals and veterinary products.[3] After all, every carbocyclic compound, regardless of structure and functionality, may in principle be converted into a collection of heterocyclic analogs by replacing one or more of the ring carbon atoms with a different element. In organic synthesis, heterocycles make helpful intermediates,[4-6] since they are usually stable enough to survive several reaction steps unaltered. In the end, they may be cleaved or further modified. It is not surprising, therefore, that a great deal of current research work is concerned with methods of synthesis and examining the properties of heterocyclic compounds.

In this chapter a précis of the synthesis and photochemistry of furanones, an interesting class of heterocyclic compounds is presented. They are derivatives of furan and, depending on structure, are divided into three main types: 2(3*H*)-furanones (I), 2(5*H*)-furanones (II), and 3(2*H*)-furanones (III).[5] The IUPAC-approved names for these heterocycles are 2,3-dihydrofuran-2-ones, 2,5-dihydrofuran-2-ones[7] and 3,2-dihydrofuran-3-ones respectively (Figure1).

2(3*H*)-furanone **I** 2(5*H*)-furanone **II** 3(2*H*)-furanone **III**

Figure 1

Systems **I** and **II** are unsaturated γ-lactones known as 'butenolides'. Compounds of this type are also known as 'crotonolactones' based on the parent crotonic acid. On the other hand, **III** is a cyclic α,β-unsaturated ketone.

1.2. Synthesis of Furanones

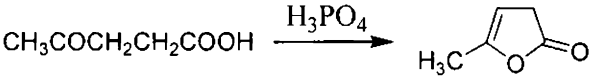
Furanones are of valuable synthetic and biological importance. They serve as useful synthetic building blocks for lactones and furans and comprise an important heterocyclic incorporated in natural products. The products of ring opening of these compounds with nucleophiles are the precursors of a wide variety of biologically important heterocyclic systems *viz.* pyrrolones,[8,9] pyridazinones,[10,11] pyrazoles,[12] and triazoles.[13] The longstanding interest in these heterocyclic compounds is testified by the wide variety of methods reported in literature for their preparation. A brief survey of the major synthetic routes to furanones is provided in the following section. Not all the methods discussed below qualify as general methods and may be useful only in specific cases.

1.2.1. Methods of 2(3*H*)-Furanone Synthesis

1.2.1.1.From γ–Keto Acids

A common method for the synthesis of 2(3*H*)-furanones involve intramolecular dehydration of the corresponding γ–ketoacids.[14-24] For

example, levulinic acid which can enolise readily, gives α-angelica lactone on slow distillation. Aliphatic acids may be cyclised by heating with orthophosphoric acid (Scheme1).



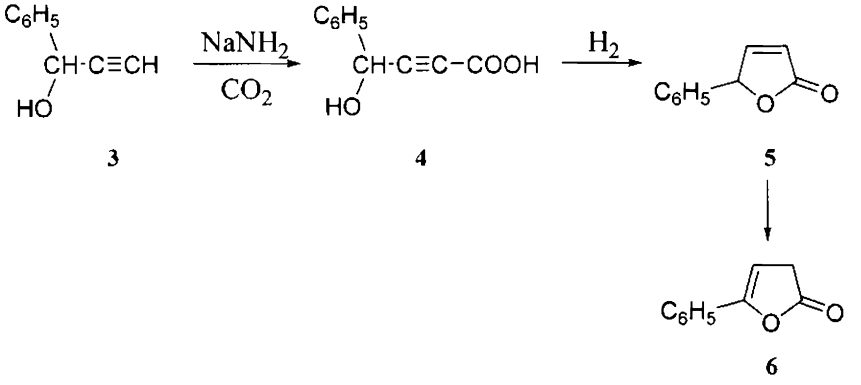
1 2

Scheme 1

The cyclisation can also be effected by heating with acetic anhydride, acetyl chloride or a mixture of acetic anhydride and sulphuric acid. However heating in acetic anhydride is sometimes too vigorous for other functional groups to survive and often brings about concomitant formation of isomeric 2(5*H*)-furanones.

1.2.1.2.From Acetylenic Acids

Nineham *et al.* have reported the synthesis of 2(3*H*)-furanones from acetylenic acids. Carboxylation of phenylethynylcarbinol **3** in presence of sodamide gives 4-hydroxy-4-phenylbut-2-ynoic acid **(4)**. Upon hydrogenation



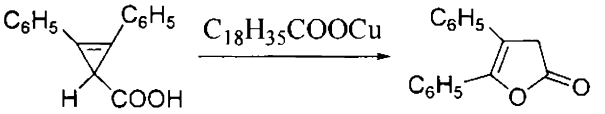
3 4 5 6

Scheme 2

4 gives the corresponding 2(5*H*)-furanone **5** which isomerises to 5-phenyl-2(3*H*)-furanone **(6)**.[25]

1.2.1.3.From Cyclopropane Derivatives

When 2,3-diphenyl-2-cyclopropene-1-carboxylic acid **(7)** is heated in benzene[26] in the presence of a catalytic amount of copper stearate, it rearranges to give corresponding β,γ–diphenyl-2(3*H*)-furanone **8** in good yields.

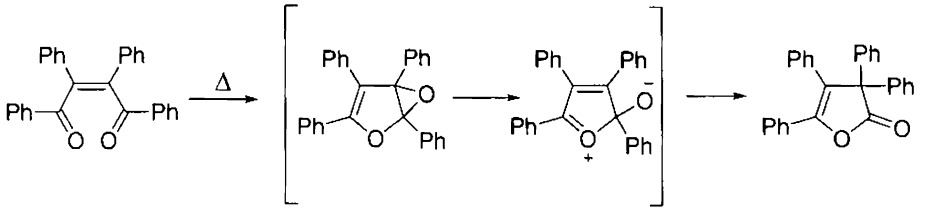


7 **8**

Scheme 3

1.2.1.4.Thermal Rearrangement

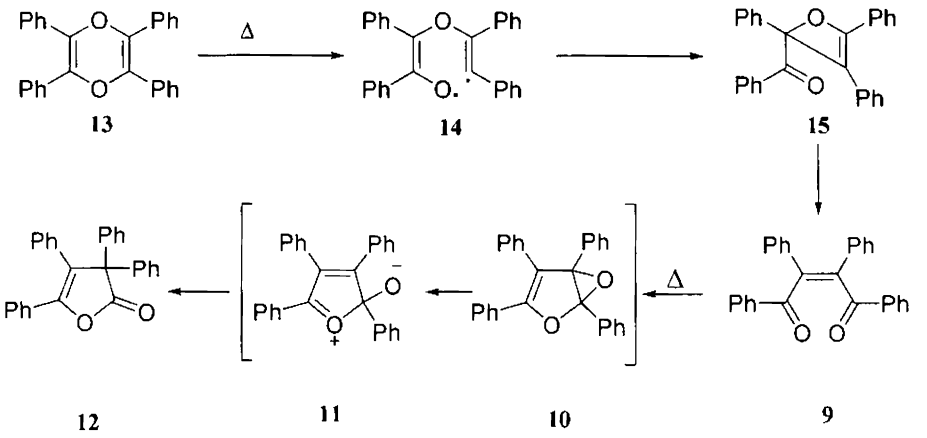
Zenin in 1872 reported the thermal rearrangement of *cis*-dibenzoyl-stilbene **(9)** to tetraphenylcrotonolactone **(12)** (Scheme 4).[27-29]



9 **10** **11** **12**

Scheme 4

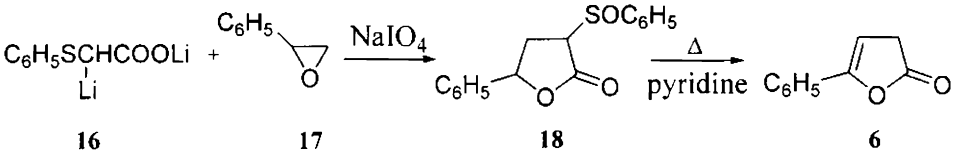
Later Berger and Summerbell observed similar thermal rearrangements with tetraphenyl-*p*-dioxadiene **(13)**. Upon pyrolysis around 250 ^{0}C, **13** rearranges to tetraphenylcrotonolactone **(12)** through the intermediacy of dibenzoyl-stilbene **(9)**.[30,31]



Scheme 5

1.2.1.5.From Epoxides and Dianions

When phenylthioacetic acid in dry THF is treated with lithium diisopropylamide, the dianion **16** is formed. Compound **16** at –60 ^{0}C gives with styrene oxide, a butyrolactone derivative, which on oxidation and pyrolysis in pyridine gives the corresponding 2(3*H*)-furanone **6** (Scheme 6).[32]



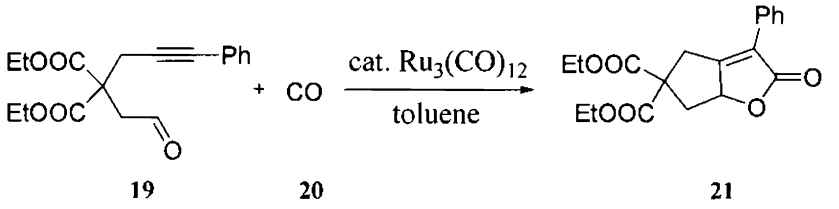
Scheme 6

1.2.2. Methods of 2(5*H*)-Furanone Synthesis

1.2.2.1.By Hetero-Pauson-Khand Reaction

Chatani *et al.* reported the first catalytic synthesis of bicyclic 2(5*H*)-furanones via a [2+2+1] cyclocoupling reaction, incorporating the aldehyde π-bond, the alkyne π-bond, and the carbon atom of CO into a five membered ring.[33,34] The reaction of phenyl substituted yne-aldehyde **19** with CO in

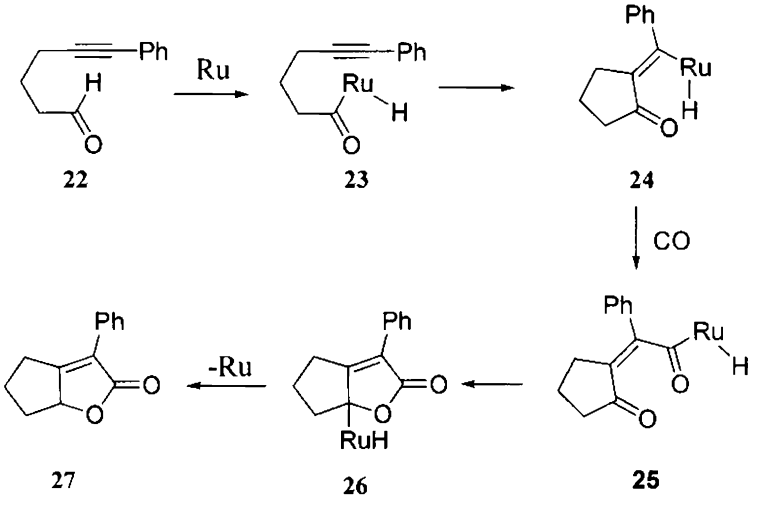
toluene in the presence of a catalytic amount of $Ru_3(CO)_{12}$ gave the corresponding bicyclic lactone **21** in high yields (Scheme 7).



19 **20** **21**

Scheme 7

The proposed mechanism for the above reaction that involves the oxidative addition of an aldehyde C-H bond to ruthenium is shown below:



22 **23** **24** **25** **26** **27**

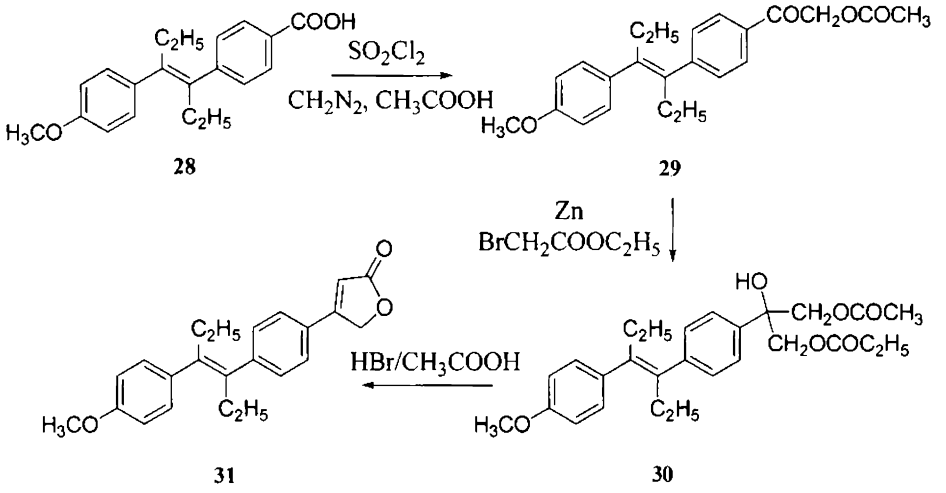
Scheme 8

Heterocycle fused 2(5*H*)-furanones were also obtained in high yields when yne-aldehydes containing heteroatoms, such as oxygen and nitrogen were employed.[33] The formation of these polyfunctional compounds in a single step is quite noteworthy, since they are amenable to further elaboration, and no

simple alternative methods are available to give these multifunctionalised compounds.

1.2.2.2.By Reformatsky-Elderfield Reaction

The reaction of α-acetoxy ketones with bromoacetic esters under Reformatsky condition is one of the most common methods for the synthesis of 2(5*H*)-furanones and steroidal lactones[35-46] (Scheme 9).

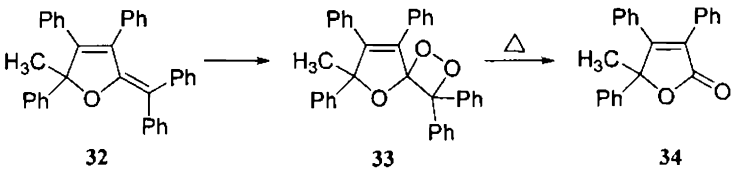


Scheme 9

A variation of the Reformatsky reaction has been employed by Epstein and Sonntag[47,48] Instead of α-acetoxy ketones, α-halo ketones were reacted with bromoacetic ester in the presence of zinc to give unstable Reformatsky adducts which were converted to 2(5*H*)-furanones either by pyrolysis or by conversion to unsaturated hydroxymethyl esters and photolysis of the latter.

1.2.2.3.From Furan Derivatives

When the furan derivative **32** is subjected to photosensitized oxidation, it gives oxygenated derivative **33**, which on heating gives the lactone **34**. By ozonolysis also above compound can be isolated.[49,50]

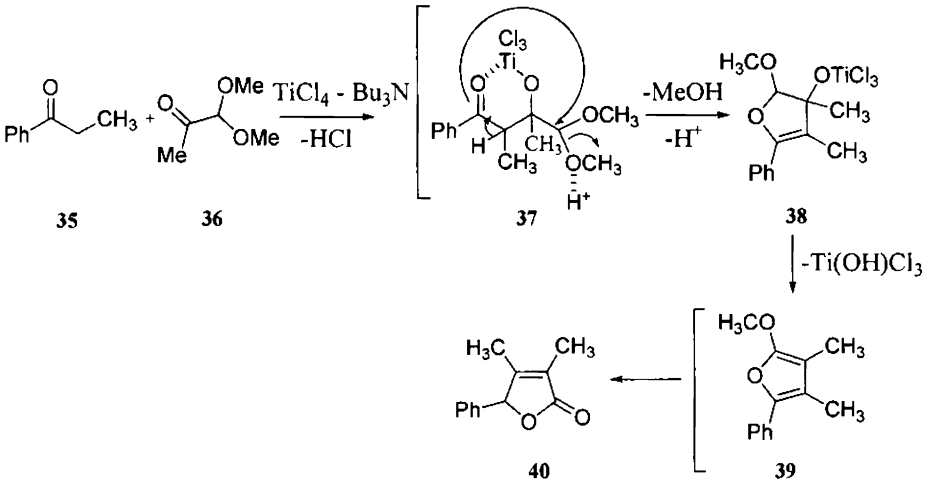


Scheme 10

Titanium silicate molecular sieves having MFI (TS-1) topology catalyses the oxidation of furans to corresponding furanones using dilute hydrogen peroxide as an oxidising agent.[51] Chiral Ni(II) complexes, which are readily prepared from chiral BINIM-2QN or its derivatives and $Ni(ClO_4)_2.6H_2O$, were found to be efficient Lewis acid catalysts in the synthesis of chiral γ-butenolides from 2-silyloxyfurans and 3-alkenoyl-2-oxazolidinones resulting in high anti and enantioselectivities.[52]

1.2.2.4.By Ti-Crossed Aldol Condensation

A general synthetic method for trialkylsubstituted 2(5*H*)-furanone utilizing direct Ti-aldol condensation was reported by Tanabe *et al.*[53]

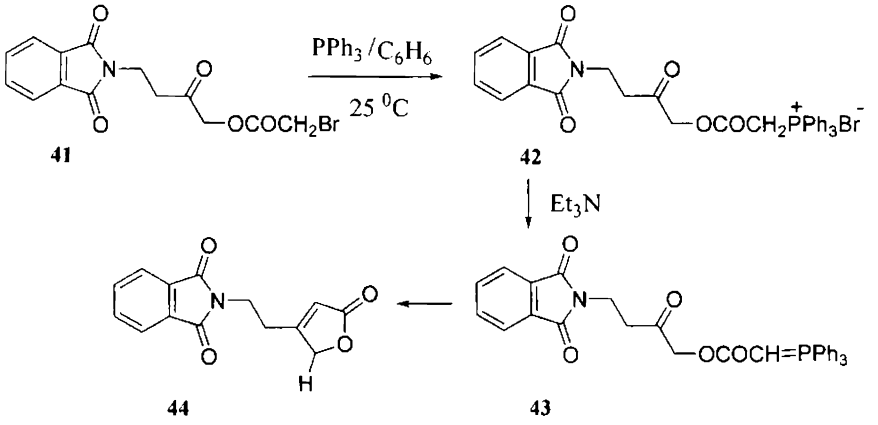


Scheme 11

$TiCl_4$-Bu_3N-mediated condensation of ketones with α,α'-dimethoxyketones afforded 2(5*H*)-furanones in a one pot manner, wherein aldol addition and furanone formation occurred sequentially. The proposed mechanism was illustrated (Scheme 11). Initial Ti mediated direct aldol addition gives aldol adduct **37**, subsequent formation of dihydrofuran **38**, followed by elimination of $Ti(OH)Cl_3$ gives 1-methoxyfuran **39**, and final isomerisation leads to 2(5*H*)-furanone

1.2.2.4.Wittig Method

Wittig reaction is extensively employed in the synthesis of steroids containing 2(5*H*)-furanone ring systems.[54-60] Krauser *et al.* employed this reaction as an efficient route to β-(2-phthalimidoethyl)-2(5*H*)-furanone **44** in connection with the synthesis of alkaloid, cocculolidine.[60]

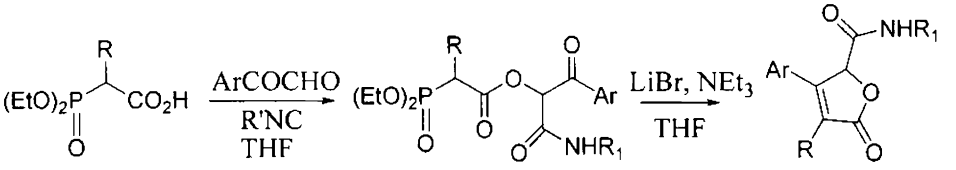


Scheme 12

1.2.2.5.*via* Olefination–cyclisation

An innovative new synthetic method to furanones, *via* a Passerini-like three-component condensation, was reported by Beck *et al.*[61] The first step in the reaction sequence involves combination of an arylglyoxal with an alkyl-

isonitrile and a 2-substituted 2-(diethoxyphosphoryl)acetic acid. The product of this reaction is a 2-[2-(phosphoryl)acetoxy]ketoamide **46**, which cyclises upon exposure to Rathke conditions by an intramolecular Wittig-type reaction to give 4-aryl-5-(carboxyamido)furanone **47** in generally good overall yields. A wide range of isonitriles and arylglyoxals undergo the reaction (Scheme 13).



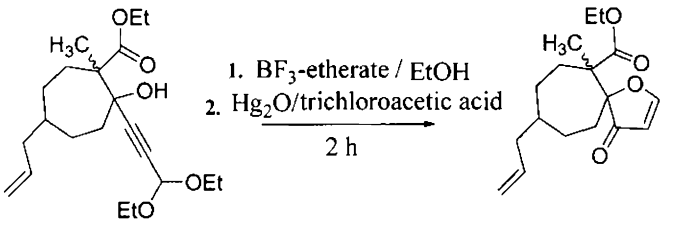
45 **46** **47**

Scheme 13

1.2.3. Methods of 3(2*H*)-Furanone Synthesis

1.2.3.1.From Acetylenic Compounds

Williams *et al.* reported a useful method, where acetylenic alcohols is used as efficient substrates for 3(2*H*)-furanone synthesis.[62]

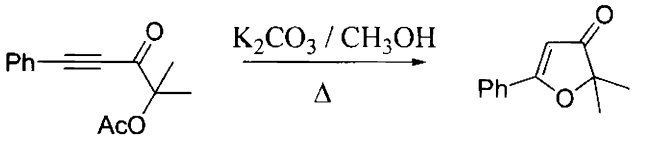


48 **49**

Scheme 14

Acetylenic alcohol on reaction with boron trifluoride-etherate in absolute ethanol in the presence of catalytic amounts of mercuric oxide and trichloroacetic acid yielded spiro 3(2*H*)-furanone **49** in good yield.

Jackson *et al.* reported the synthesis of 3(2*H*)-furanones by the hydrolysis of corresponding readily accessible acetylenic ketones.[63] Acetylenic ketone **50** on heating under reflux with potassium carbonate in methanol yielded bullatenone.

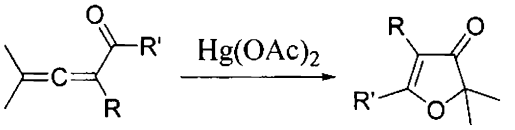


50 **51**

Scheme 15

1.2.3.2.By Mercuric Acetate Oxidation

Wolff *et al.* have synthesised 3(2*H*)-furnanones by mercuric acetate oxidation of allenic ketones.[64] These results provide a simple conversion of readily accessible allenic ketones to 3(2*H*)-furanones (Scheme 16).

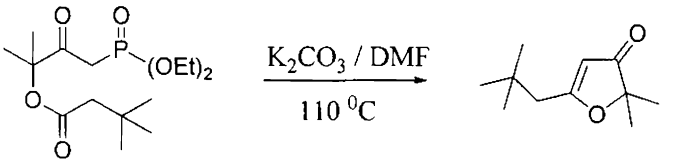


52 **53**

Scheme 16

1.2.3.3.By Wadsworth-Emmons Condensation of γ-(Acyloxy)-β-keto phosphonates.

Sampson and his group has provided a new route for the synthesis of 3(2*H*)-furanone ring system.[65] γ-(Acyloxy)-β-ketophosphonates **54** when treated with potassium carbonate undergo an intramolecular Wadsworth-Emmons type condensation to afford 3(2*H*)-furanones **55** (Scheme 17).

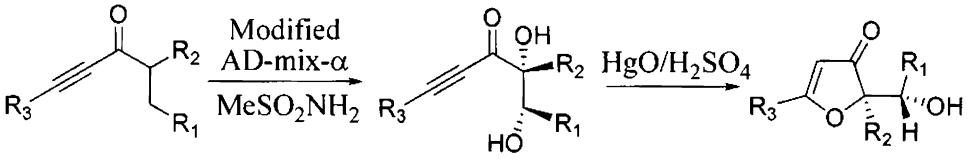


54 **55**

Scheme 17

1.2.3.4.From Enynones

Marson *et al.*[66] reported the synthesis of 3(2*H*)-furanones by a catalytic asymmetric protocol from enynones, which if electron rich, require only one reagent and involve two reactions in a single operation - a domino process. It is the first route to 3(2*H*)-furanones that is both catalytic and asymmetric.



56 **57** **58**

Scheme 18

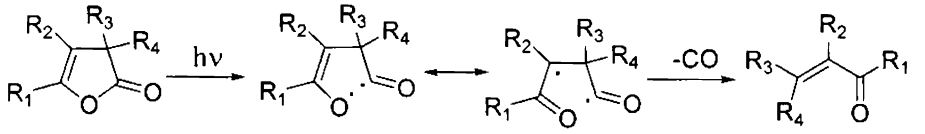
The required enynone precursors were obtained by addition of a terminal alkynyllithium to the appropriate 2-alkenal in THF to give the corresponding enynol which was oxidized to the requisite enynone **56** using MnO_2. The dihydroxy-ynones **57** were obtained from Sharpless asymmetric dihydroxylation using modified AD-mix-α containing $(DHQ)_2PHAL$ and potassium osmate. Treatment of **57** with catalytic mercuric oxide in aqueous sulphuric acid, afforded the corresponding 3(2*H*)-furanone **58**.

1.3. Photochemistry of 2(3*H*)-, 2(5*H*)- and 3(2*H*)-Furanones

The light induced transformations of furanone ring systems have been the subject of intensive study.[67-73] Depending on the nature of the furanone ring and the substituents present, these compounds undergo various interesting photochemical transformations. The most general photoreaction of 2(3*H*)-furanones is singlet mediated decarbonylation to vinyl ketones, although in some cases the formation of cyclobutane dimers and oxetanes has been observed. Product analysis based on steady-state irradiation and laser flash photolysis has been used to study the phototransformations of 2(3*H*)-furanones. On the other hand, 2(5*H*)-furanones preferentially undergo dimerisation, cycloaddition or hydrogen abstraction from their triplet states. For these compounds decarboxylation or nucleophilic solvent addition have also been reported. Other processes, observed only in the presence of the appropriate substituents, are stilbene-phenanthrene cyclisation or substituent migrations as well as chromone formation or fragmentation. With 3(2*H*)-furanones only a few significant reports are available regarding their photochemistry.[74-76] They were also reported to undergo dimerisation, intermolecular cyclisation, decarbonylation etc upon irradiation depending on the nature of substituents.

1.3.1. Decarbonylation

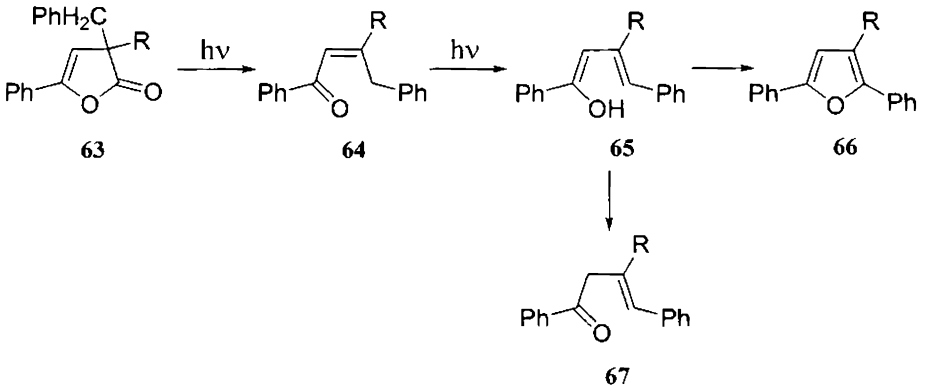
The photochemical decarbonylation of enol lactones has been reported to give the corresponding vinylketones.[77-83] It appears to occur from their lowest lying singlet states, through a primary cleavage of the carbonyl–oxygen bond. This leads to the formation of diradical intermediates which can be stabilised by the loss of carbon monoxide.[84-90]



59 **60** **61** **62**

Scheme 19

In the case of the 3-benzyl derivatives decarbonylation followed by double bond isomerisation and/or cyclisation to furan derivatives **66** was observed.[91]

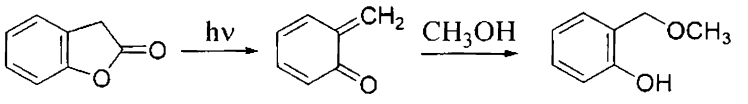


63 **64** **65** **66**

67

Scheme 20

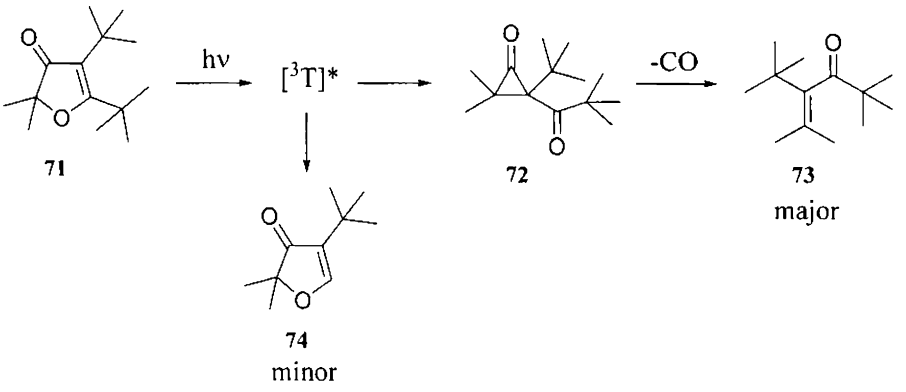
Chapman and McIntosh[92] have described a photodecarbonylation of benzofuran-2(3*H*)-one which upon irradiation in methanol affords *o*-hydroxybenzyl methyl ether **(70)** via the intermediacy of **69**. Analogous results are observed with substituted derivatives.[93-97]



68 **69** **70**

Scheme 21

Highly-crowded 2,2-dimethyl-4,5-di-*tert*-butyl-3(2*H*)-furanone (**71**) gave the decarbonylated product **73** as major and 2,2-dimethyl-4-*tert*-butyl-3(2*H*)-furanone (**74**) as minor product on irradiation in benzene[98] (Scheme 22).

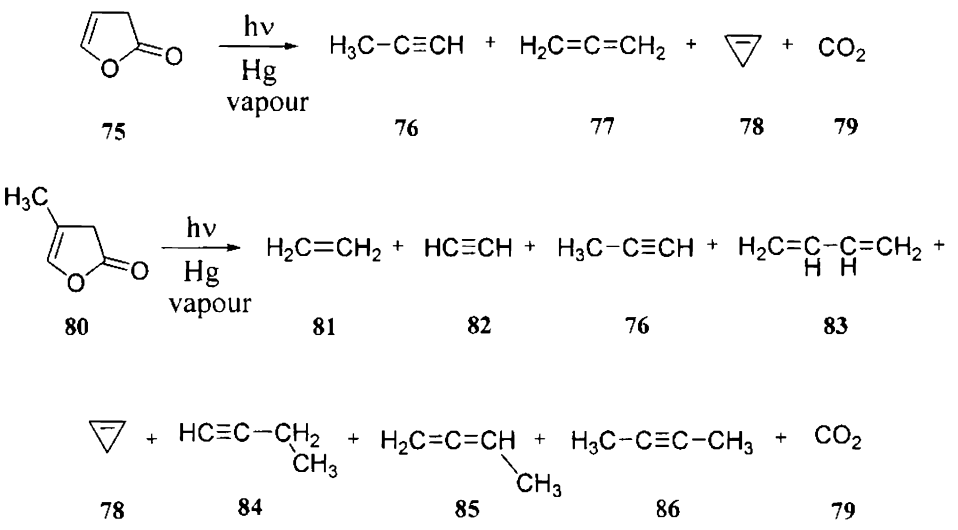


Scheme 22

The mechanism involves the rearrangement of the furanone to an acylcyclopropanone followed by decarbonylation to yield **73**. This unique observation is due to the nonbonded strain energy of **71**, which is released on conversion to **72** and its rotation about acyl-cyclopropyl bond. Mechanism leading to **74** is less obvious. Direct γ-cleavage and disproportionation to isobutylene and **74** could be the simplest rationalisation.

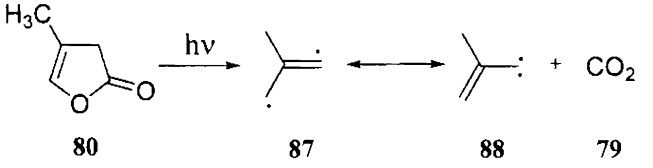
1.3.2. Decarboxylation

Kroll and Arnold[99] have studied the mercury sensitized vapour phase photochemistry of 2(5*H*)-furanone (**75**) and 4-methyl-2(5*H*)-furanone (**80**). The photolysis of **75** gives propyne (**76**), allene (**77**) and cyclopropene (**78**). However **80** leads to a complex mixture of primary and secondary photoproducts. 2(5*H*)-Furanones do not undergo cleavage of the carbonyl-oxygen bond, since the sp^3 hybridised C-5 does not allow resonance stabilisation of the intermediate.



Scheme 23

The formation of 1-butyne and 1,2-butadiene was first thought to be a secondary reaction of 1-methylcyclopropene, but this hypothesis was questioned after studying the chemical reactivity of the latter compound, which gave rise to propyne, acetylene and ethylene. However we cannot exclude the possibility that some 1-butyne and/or 1,2 butadiene is formed via a 1,2-methyl migration in the intermediate **87** previously postulated by Closs.[100]

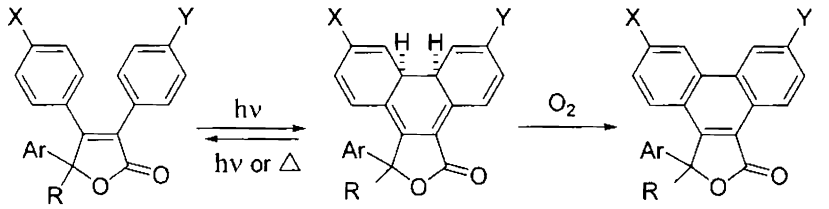


Scheme 24

1.3.3. Stilbene–phenanthrene like Cyclisation

The photocyclisation of *cis*-stilbene to phenanthrene is a well known reaction.[101,102] Rio[103] and Hardy, Lohrary *et al.*[80] and Gopidas *et al.*[81] have

studied the photochemistry of lactones **89** which possess a *cis*-stilbene moiety. Thus when the lactones **89** are irradiated in the presence of oxygen, in chloroform or benzene as solvent, a cyclisation to the corresponding phenanthrene derivatives **91** is observed to take place. In these experiments a wood glass filter ($310 < \lambda < 390$ nm) was used in order to irradiate selectively at the absorption bands of compounds **89**.

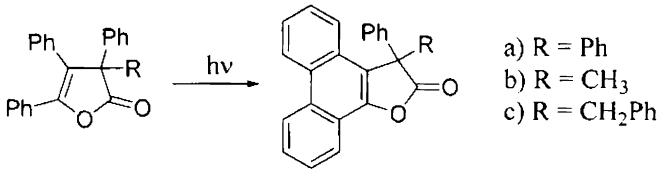


89 **90** **91**

Scheme 25

If oxygen is slowly bubbled through the solutions, a photochromism phenomenon is observed due to the intermediates **90**. The filter does not allow to irradiate these intermediates. However in the absence of the filter, the production of phenanthrenes is very slow due to the reverse reaction of the intermediates to the starting compounds.

Similar processes have been reported for 2(3*H*)-furanones. Lohray *et al.* found that the photolysis of 3,3,4,5-tetraphenyl-2(3*H*)-furanone **(92a)**, 3-methyl-3,4,5-triphenyl-2(3*H*)-furanone **(92b)**, 3-benzyl-3,4,5-triphenyl-2(3*H*)-furanone **(92c)** in the presence of oxygen, afford the corresponding phenanthrene derivatives.[80] Laser flash photolysis leads to spectral changes that suggest the involvement of excited singlet states in these cyclisations.

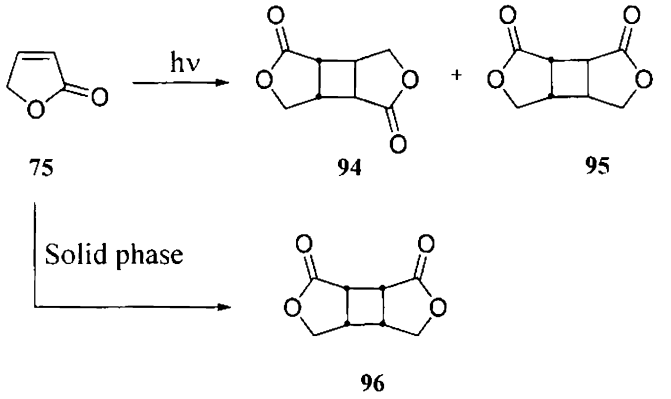


92 **93**

Scheme 26

1.3.4. Dimerisation

Irradiation of 2(5*H*)-furanone **75** in solution leads to the formation of anti photodimers **94** and **95**. Compound **94** is the result of a head-to-head dimerisation while **95** arises from a head to tail dimerisation. On the other hand, irradiation of 2(5*H*)-furanone **75** in solid phase at low temperature gives a head to head dimer **96**.[104]



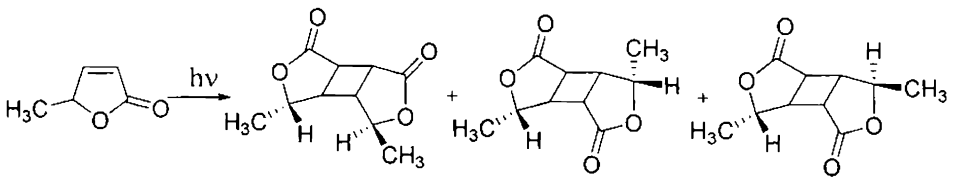
75 **94** **95**

96

Scheme 27

The photodimerisation of substituted 2(5*H*)-furanones has also been observed.[105] Thus, irradiation of 5-methyl-2(5*H*)-furanone **(97)** in acetonitrile with 254 nm light gave a mixture of compounds with the relative yield 3:0.9:3. The solvent effects on the yield of each isomer have been studied. In this way, it has been found that the ratio **(98)/(100)** decreases from 3:1 on going from acetonitrile to benzene, while the ratio **(99)/(100)** remains essentially

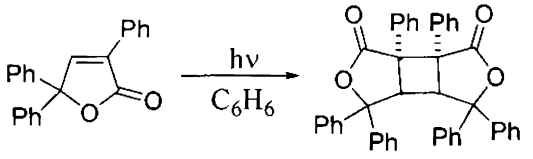
unchanged. This is in accordance with the expectations based on the higher dipole moments of the head-to-head dimers.



Scheme 28

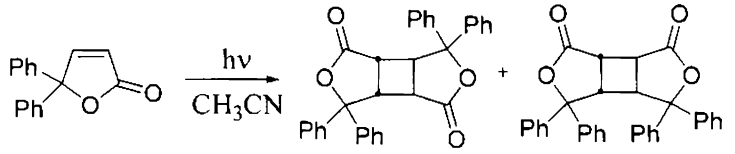
Furthermore the photodimerisation of **97** can be sensitized by the ketones with triplet energies higher than that of xanthone and quenched by 1,3-pentadiene, which suggest that the three photodimers are formed through an excited triplet state, whose estimated energy level is about 70 kcal/mol.

Padwa and co-workers[106] have studied the irradiation of 3,5,5-triphenyl-2(5*H*)-furanone **(101)** in concentrated benzene solution (Scheme 29). Under these conditions the formation of a dimer **(102)** tentatively assigned as syn-head-to-head has been observed.



Scheme 29

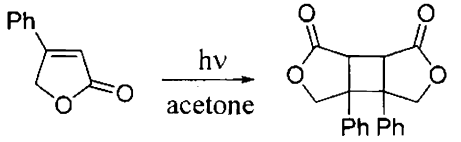
Likewise, irradiation of 5,5-diphenyl-2(5*H*)-furanone **(103)** in acetonitrile affords a mixture of the anti-head-to-tail and head to head dimers **104** and **105** as the only photoproducts.[106,107] In more dilute solutions, solvent addition products are also formed.



103 **104** **105**

Scheme 30

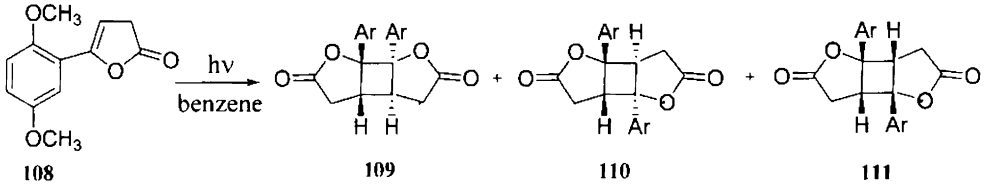
A cyclobutane dimer **107** has been also isolated upon irradiation of 4-phenyl-2(5*H*)-furanone **(106)** in acetone[108], although the syn/anti nature could not be determined.



106 **107**

Scheme 31

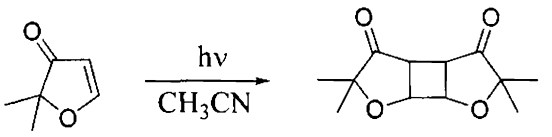
Martinez-Utrilla and Miranda[79] have reported a photodimerisation of enol lactone. Thus irradiation of 5-(2',5'-dimethoxyphenyl)-2(3*H*)-furanone **(108)** in benzene under nitrogen gives the anti-head-to-head dimer **109** and anti and syn head-to-tail isomers **110** and **111** respectively.



108 **109** **110** **111**

Scheme 32

3(2*H*)-Furanones undergo photodimerisation in acetonitrile in the absence of alkenes (Scheme 33).[109]

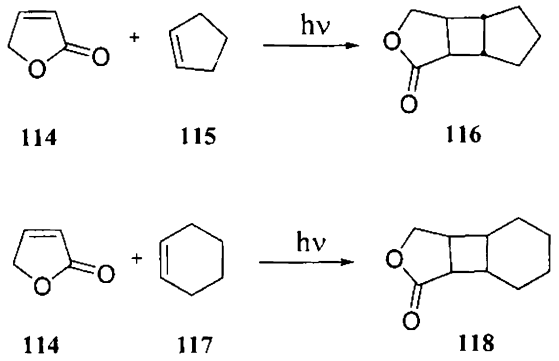


112 **113**

Scheme 33

1.3.5. Cycloadditions

The [2+2] photocycloaddition of alkenes to furanones is a well known approach to obtain cyclobutanic compounds. Tada and co-workers[110] have observed a photoaddition of cyclopentene and cyclohexene to 2(5*H*)-furanone **(114)** to give **116** and **118** respectively. According to them these reactions are sensitized by acetone, but not by acetophenone, and are quenched by 1,3-pentadiene and dimethoxyethene. These facts suggest that the above cycloadditions proceed via a triplet excited state, whose energy lies between 75 and 80 kcal/mol.



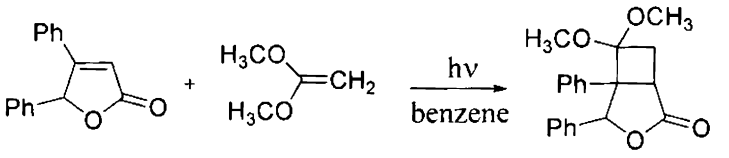
114 **115** **116**

114 **117** **118**

Scheme 34

However more recent work by Kosugi *et al.*[111] has proven that dimethoxyethene does not actually quench the reaction but it adds to 2(5*H*)-furanone to gave oxetane derivative. Acetone was not used as solvent because of the easy formation of the oxetane derivative with dimethoxyethene.

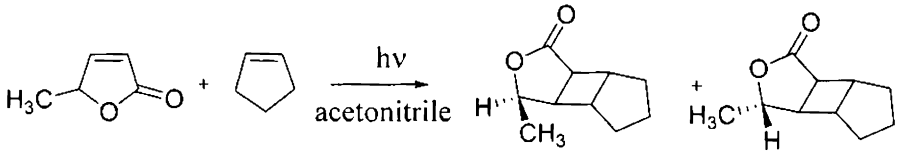
A similar photochemical reaction between dimethoxyethene and 3,5-diphenyl-2(5*H*)-furanone in benzene has been reported by Padwa and Dehm (Scheme 35).[112] Usual phenyl migration was not observed under this condition.



119 **120** **121**

Scheme 35

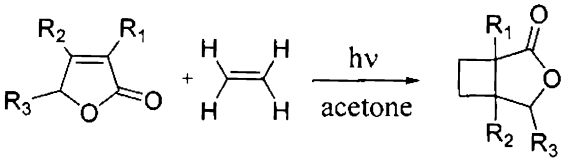
The photochemical addition of cyclopentene to 5-methyl-2(5*H*)-furanone has been studied by Ohga and Matsuo.[105] Using excess of cyclopentene, the irradiation of this lactone in acetonitrile under oxygen gives two isomeric cycloadducts (Scheme 36).



97 **115** **122** **123**

Scheme 36

Kosugi *et al.*[111] have studied the addition of ethylene and acetylene to a series of 2(5*H*)-furanones.

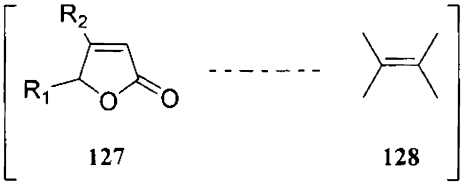


124 **125** **126**

Scheme 37

For example, the irradiation of **124** with ethene gives the cycloadduct **126** in high yields. Acetone is the best solvent and it seems to act as a sensitizer. It is worth mentioning that 3-methyl-2(5*H*)-furanone does not give the adduct, in contrast with the behaviour of analogous 3-phenyl substituted furanone. This fact suggests that the electronic effect of the conjugated phenyl group plays an important role in this reaction. Similar results were observed in the irradiation experiments with acetylene whereby the lack of reactivity of 3-methyl-2(5*H*)-furanone was confirmed.

Later Alibes *et al.*[113] demonstrated that the cycloaddition of furanones like **127** to electron rich olefins like TME is inefficient in acetone and efficient in ether, while the cycloaddition to electron poor olefins like ethylene or vinylene carbonate is efficient in acetone but not in ether. This dichotomous behaviour can be explained if we assume that a charge transfer from furanone to alkene is possible for electron rich alkenes (Scheme 38) like TME, but not possible for electron poor alkenes like ethylene or vinylene carbonate.



127 **128**

(Charge Transfer Complex)

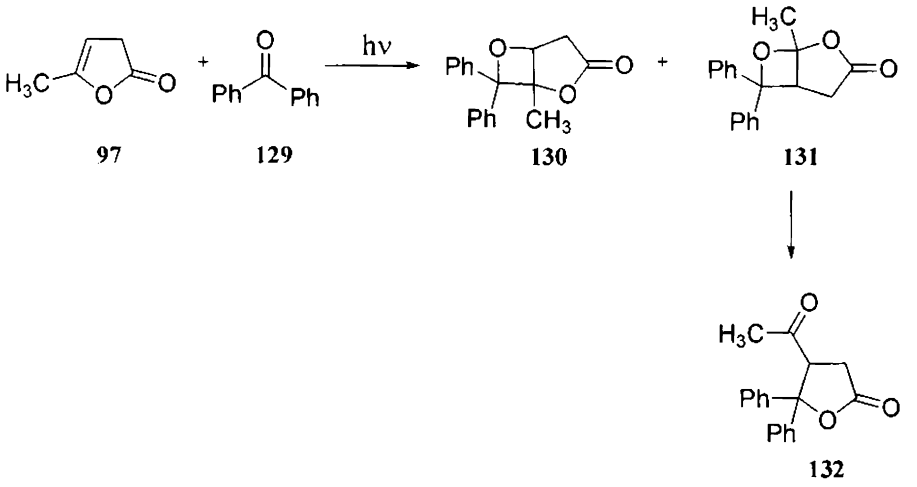
a) $R_1 = CH_2OOCC(CH_3)_3$ b) $R_2 = CH_3$, H

Scheme 38

As it is well known, cycloaddition between lactones like **127** and olefins are sensitized by acetone and proceed via a triplet excited state.[110,111] For an efficient triplet-triplet energy transfer acetone, has to collide with the furanone. This is not possible if the furanone has its two faces hindered, one

by the bulky R_1 group and the other by the olefin complex. That would be the situation for the TME: the acetone cannot sensitize the cycloaddition but the chemical reaction can progress under direct irradiation in ether; since the TME and excited furanone are close, they can react immediately to yield the diradical species and eventually the cycloadducts.[114] On the contrary, direct irradiation of mixtures of furanone and ethylene or vinylene carbonate in ether gives excited states of the furanone that deactivate quickly in processes others than cycloaddition; these processes lead to byproducts. If acetone is the solvent, the lactone can be excited to its long lived triplet by sensitization and will approach the olefin to form the diradical and the cycloadduct.

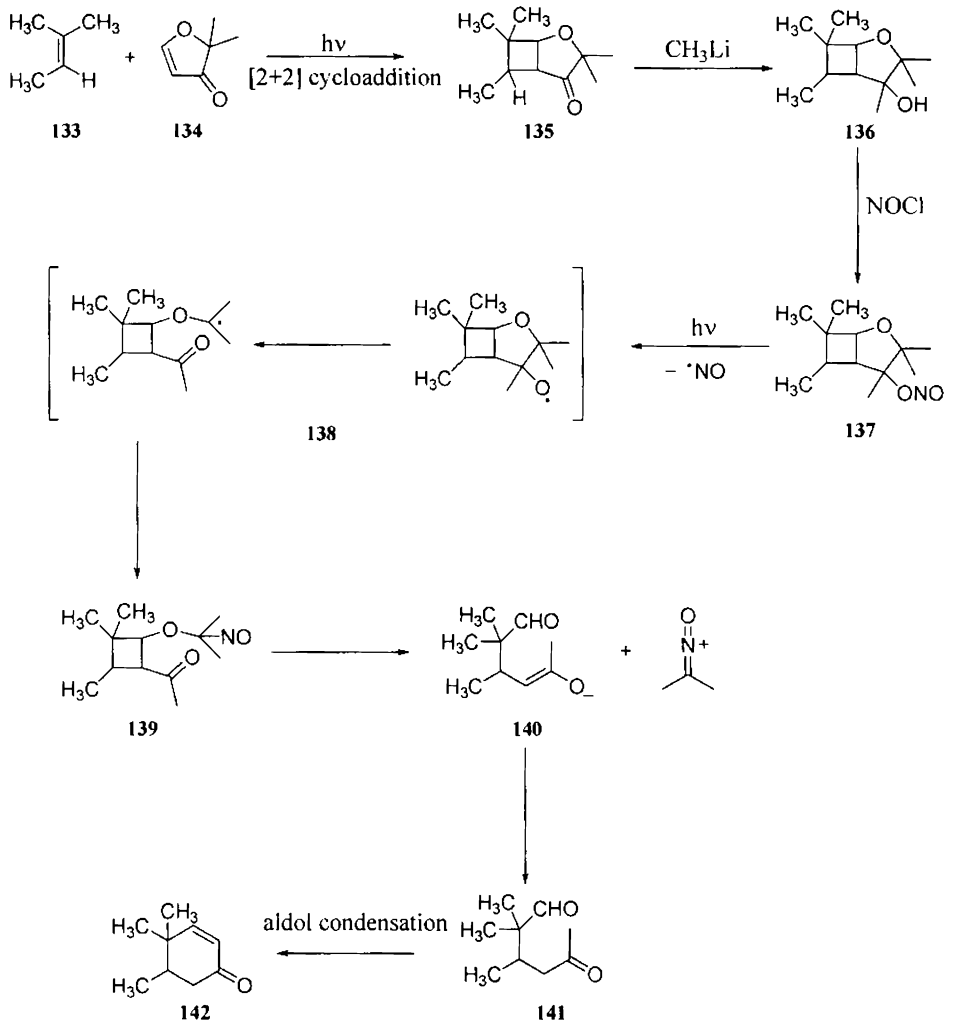
The photoreaction of 2(3*H*)-furanones that can be included in this section is the formation of oxetanes **130** and **131** through Paterno-Buchi addition of 5-methyl-2(3*H*)-furanone (**97**) and benzophenone (Scheme 39).[115] Compound **130** is thermally stable, but **131** react further to give the saturated lactone **132**.



97 **129** **130** **131** **132**

Scheme 39

Baldwin *et al.* have reported photoinduced intermolecular cycloaddition reaction of various 3(2*H*)-furnaones.[116-118]

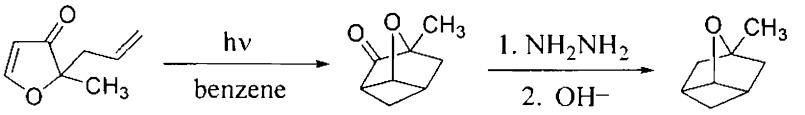


Scheme 40

The furanone/alkene cycloaddion reaction presents an interesting and novel pathway to cyclohexanones.[119] The high material yields and regiochemcial preferences of the photoaddition step when combined with the overall ease and efficiency of the fragmentation/cyclodehydration process render the

reaction sequences a general annelation technique. It involves the oxidative fragmentation of C_2-C_3 bond of **137** by virtue of the considerable stability of the radical **138**

Margaretha and coworkers[120] have reported the light-induced regioselective intramolecular [2+2] photocycloaddition reactions of 2-methyl-2-(alk-2-enyl)-3(2*H*)-furanone (**143**). Irradiation of **143** resulted in the cycloaddition to terminal alkene with a high degree of regioselectivity where always only one orientation of addition of the exocyclic double bond to the C=O bond was observed (Scheme 41).

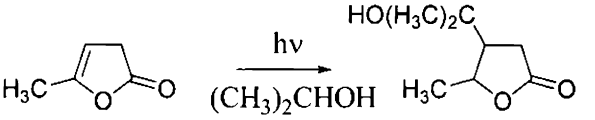


143 **144** **145**

Scheme 41

1.3.6. Hydrogen Abstraction

According to Ohga and Matsuo,[121] direct excitation of 2(5*H*)-furanone **97** in isopropanol solution leads to the corresponding adduct **146** in high yields.

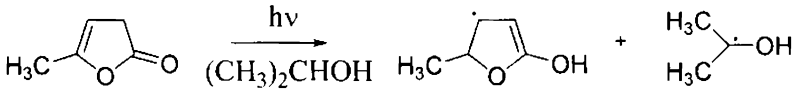


97 **146**

Scheme 42

The quantum yield varies with the lactone concentration and exceeds unity in all cases, indicating that the reaction involves a free radical chain, which may

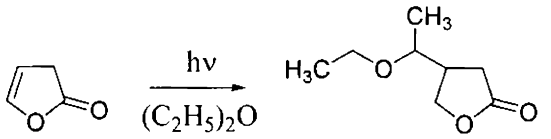
be initiated by the formation of a ketyl radical **148** as a consequence of hydrogen abstraction of the photoexcited carbonyl group from isopropanol.



147 **148** **149**

Scheme 43

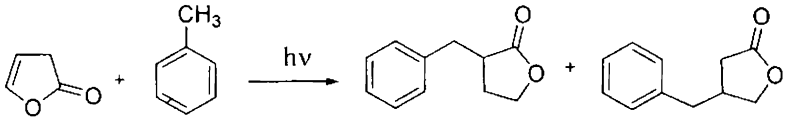
Likewise, the β-adduct **150** is obtained upon irradiation of **114** in ether.[111]



114 **150**

Scheme 44

In cyclohexane or toluene, both α– and β– addition products are formed, but when aromatic ketones are used as photosensitizers predominant formation of the β-adduct is again observed.[122]

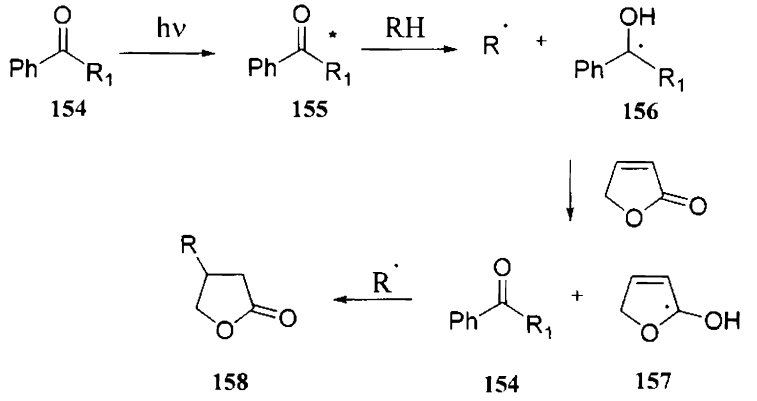


114 **151** **152** **153**

Scheme 45

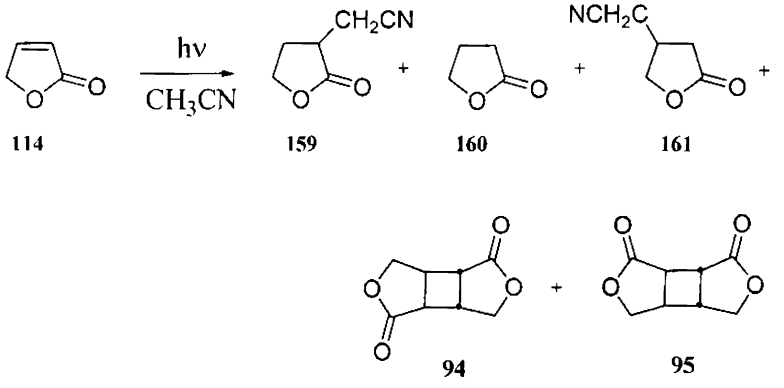
This has been taken as evidence for the involvement of the aromatic ketones as hydrogen transfer agents, as shown below (Scheme 46). Using cyclohexane-d_6 as solvent, it has been demonstrated that the α-adduct arises

via hydrogen abstraction by the β-carbon, on the basis of deuterium incorporation at C-4.[123]



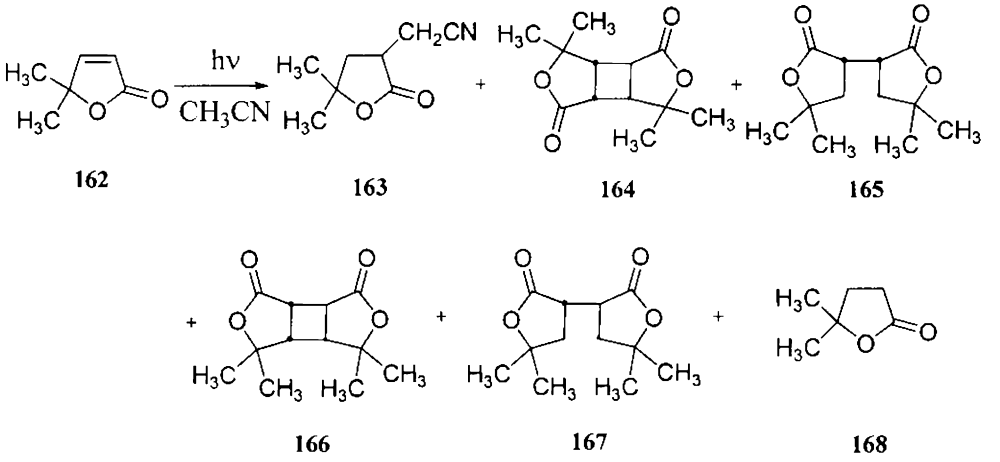
Scheme 46

Anklam and Magaretha[108] have carried out a systematic investigation on the photoreduction of 2(5*H*)-furanone **(114)** and 5,5-dimethyl-2(5*H*)-furanone **(162)** in several solvents. In dilute acetonitrile solution, **114** affords both α and β adducts, **159** and **161** together with the reduction product **160** and the dimers **94** and **95.**



Scheme 47

Under similar conditions, the dimethyl derivative **162** is converted to a mixture of six products, the dimers **164** and **166**, the diastereomeric hydrodimers **165** and **167**, the saturated lactone **168** and the solvent adduct **163**. Analogous results have been obtained in cyclohexane and isopropanol. All these products can be accounted for in terms of hydrogen abstraction by the carbonyl oxygen or by the β-carbon (Scheme 48).



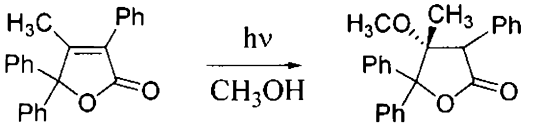
162 **163** **164** **165**

166 **167** **168**

Scheme 48

1.3.7. Addition of Nucleophiles

Methanol addition is observed in the irradiation of 3,5,5-triphenyl-4-methyl-2(5*H*)-furanone **(169)** in methanol.[106]

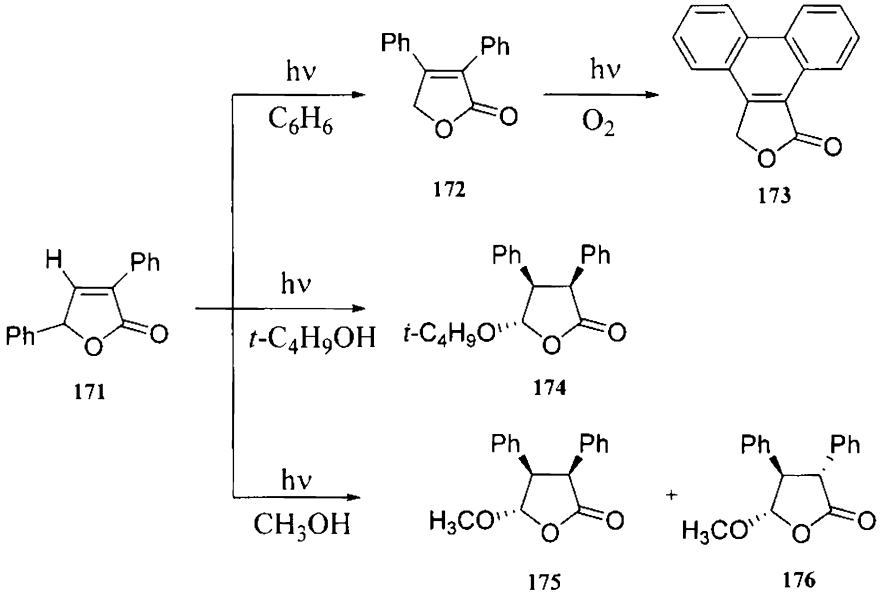


169 **170**

Scheme 49

1.3.8. Substituent Migrations

Padwa and co-workers[106,112,124] have extensively studied this type of reaction for 2(5*H*)-furanones. The irradiation of 3,5-diphenyl-2(5*H*)-furanone (**171**) in benzene through a corex filter for 1.5 h gives 3,4-diphenyl-2(5*H*)-furanone (**172**) in high yields. In the presence of oxygen, **172** further reacts to afford the tetracyclic furanone **173** via the well known stilbene-phenanthrene cyclisation. When *tert*-butyl alcohol is used as the solvent the only product is **174**, while in methanol, a mixture of the isomers **175** and **176** is formed (Scheme 50).

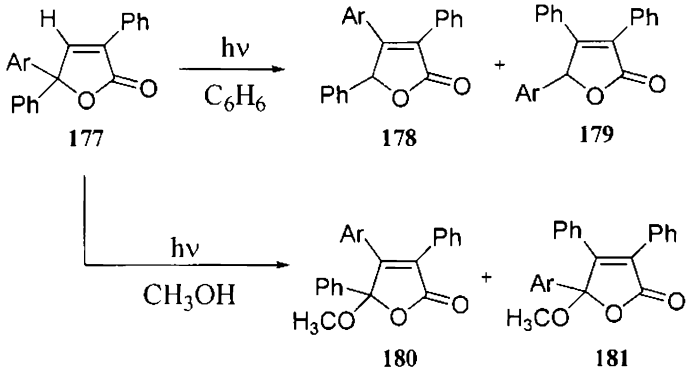


Scheme 50

Similar results have been obtained by irradiation of 3,5,5-triphenyl-2(5*H*)-furanone. In this case a dimerisation process has additionally been observed in concentrated benzene solution. Quantum yields for the direct and sensitized photorearrangements are identical which provides strong evidence for a triplet

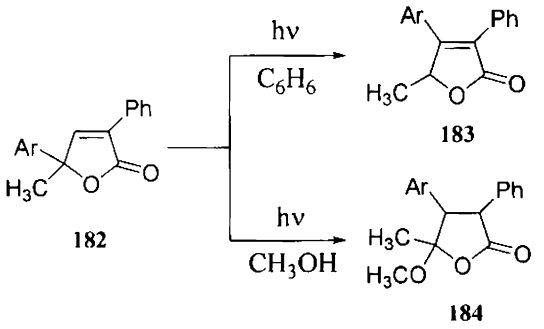
mediated pathway. That the rearrangement is quenched by piperylene furnishes additional confirmation for the triplet state assignment.

Irradiation of 3,5-diphenyl-5-aryl-2(5*H*)-furanone **177** has been also carried out under different conditions, with the aim of determining the relative migratory aptitudes of different aryl groups. The results summarized show that the migration products depend strongly on the nature of the solvent.



Scheme 51

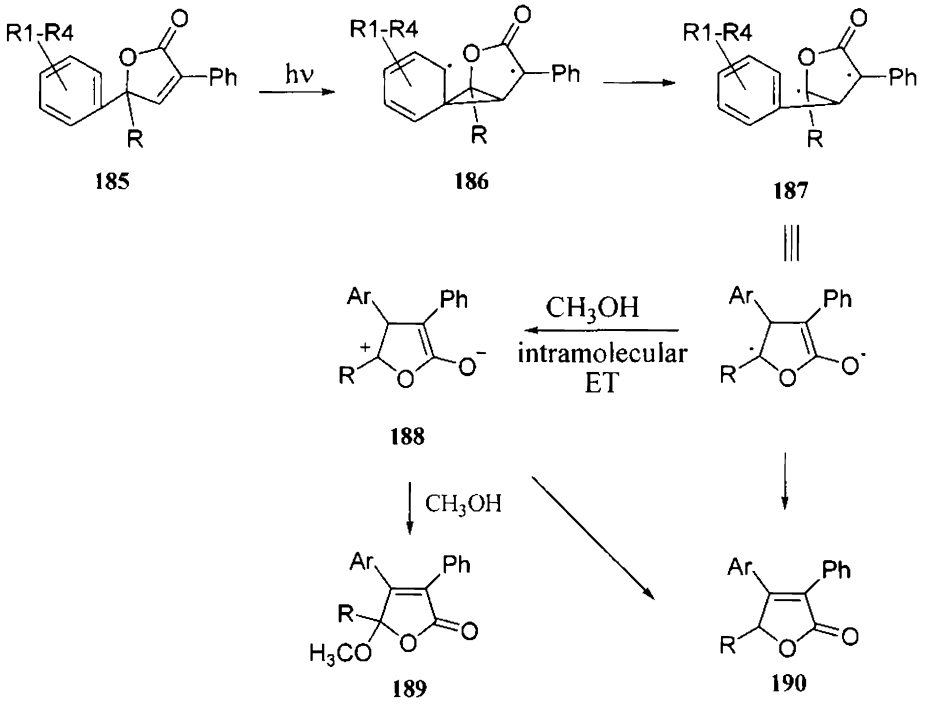
In order to generalize these results, 5-methyl-3,5-diaryl-2(5*H*)-furanone **182** has been irradiated in benzene, whereby only aryl migration has been observed.



Scheme 52

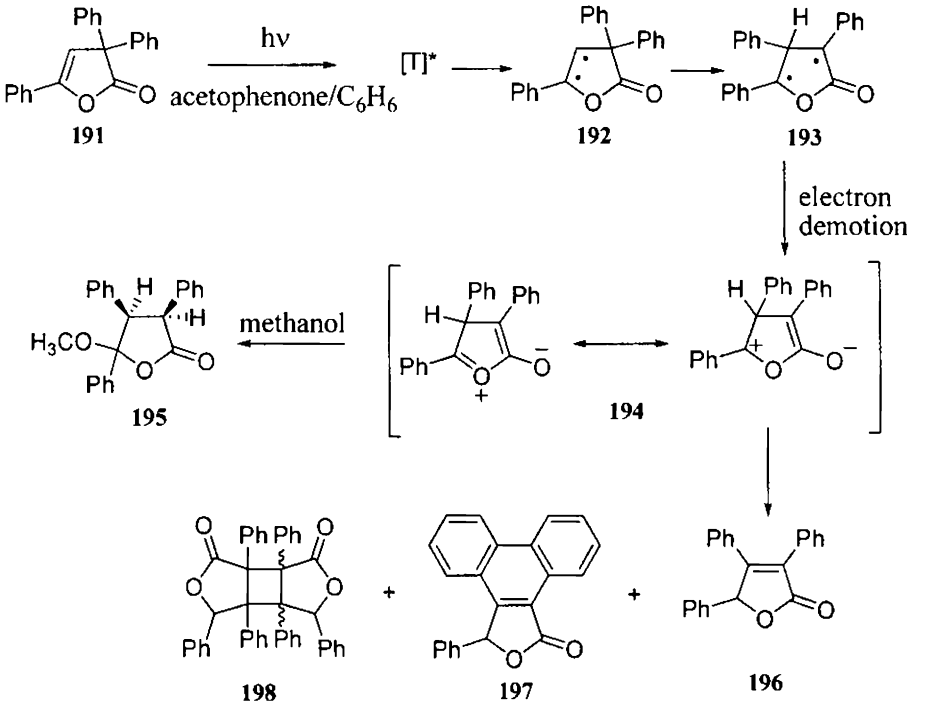
Moreover, 3-phenyl-5,5-dimethyl-2(5*H*)-furanone has been found to be photostable in benzene or methanol solution, thus confirming that aryl groups are the only substituents capable to undergo migration processes. The above results suggests that aryl migrations of 3,5-diaryl-2(5*H*)-furanones take place according to the pathways depicted in Scheme 53.

Formally, the initial steps are simply the same as those of a di-π–methane rearrangement.[125] Subsequently electron demotion proceeds to give a zwitterion which is trapped by the alcoholic solvent. In the absence of a hydroxylic solvent, the zwitterion undergoes a hydride shift to give the observed products.



Scheme 53

Similar aryl migrations have also been reported for 2(3*H*)-furanones by George, Das and their groups.[80-82] The photochemical rearrangement of 2(3*H*)-furanones to give the corresponding 2(5*H*)-furanones and the subsequent formation of the phenanthrofuranone can be explained in terms of a pathway involving triplet excited state[126] (Scheme 54).

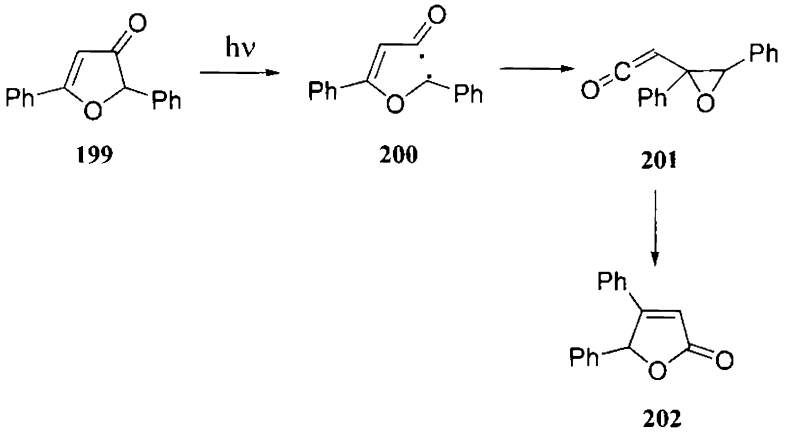


Scheme 54

In the triplet excited state, which can be visualised in terms of a diradical structure, one of the C-3 aryl groups migrates through a bridged transition state to give the rearranged diradical intermediate **193**. Electron demotion in **193** will lead to a zwitterionic intermediate described by structure **194**. In presence of methanol, the zwitterionic intermediate is trapped to give

5-methoxy-3,4,5-triphenyl-2-furanone **(195)**. In the absence of any protic solvents, the zwitterionic intermediate undergoes a hydride shift to give the rearranged 3,4,5-triphenyl-2(5*H*)-furanone **(196)**. This furanone, in turn, absorbs light and undergoes further photocyclisation leading to dihydrophenanthrofuranone **197**. Alternatively, these 2(5*H*)-furanones can undergo photochemical [2+2] cycloaddition leading to the dimer **198**.

Padwa and co-workers[127] in 1976 reported a novel rearrangement, which occurs upon irradiation of 2,5-diphenyl-3(2*H*)-furanone **(199)**. Irradiation of **199** in benzene under argon atmosphere yielded 4,5-diphenyl-2(5*H*)-furanone **(202)** in high yield. An attractive pathway for the formation of **202** involves initial homolytic cleavage of the bond α– to the carbonyl group to give a 1,5-diradical **200**. Subsequent rearrangement of this species to a 1,3-diradical followed by ring closure would yield an epoxy ketene **201**, which rearrange to **202** (Scheme 55).

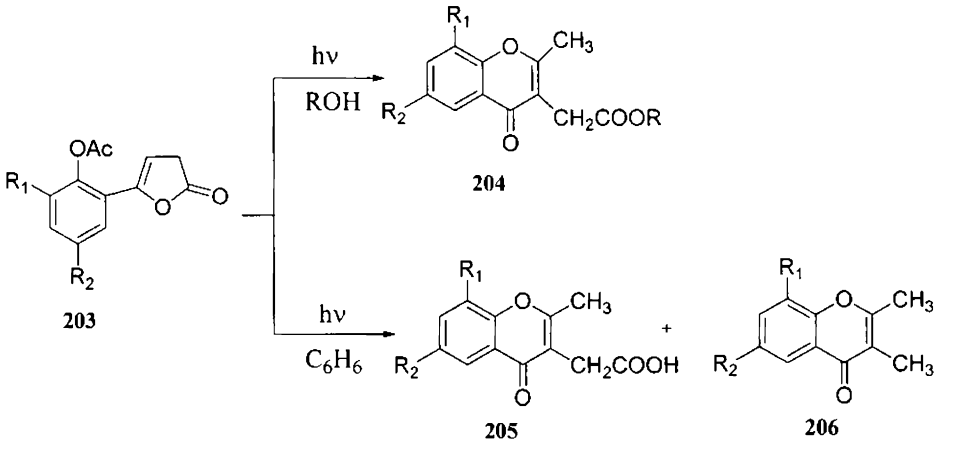


199 **200** **201** **202**

Scheme 55

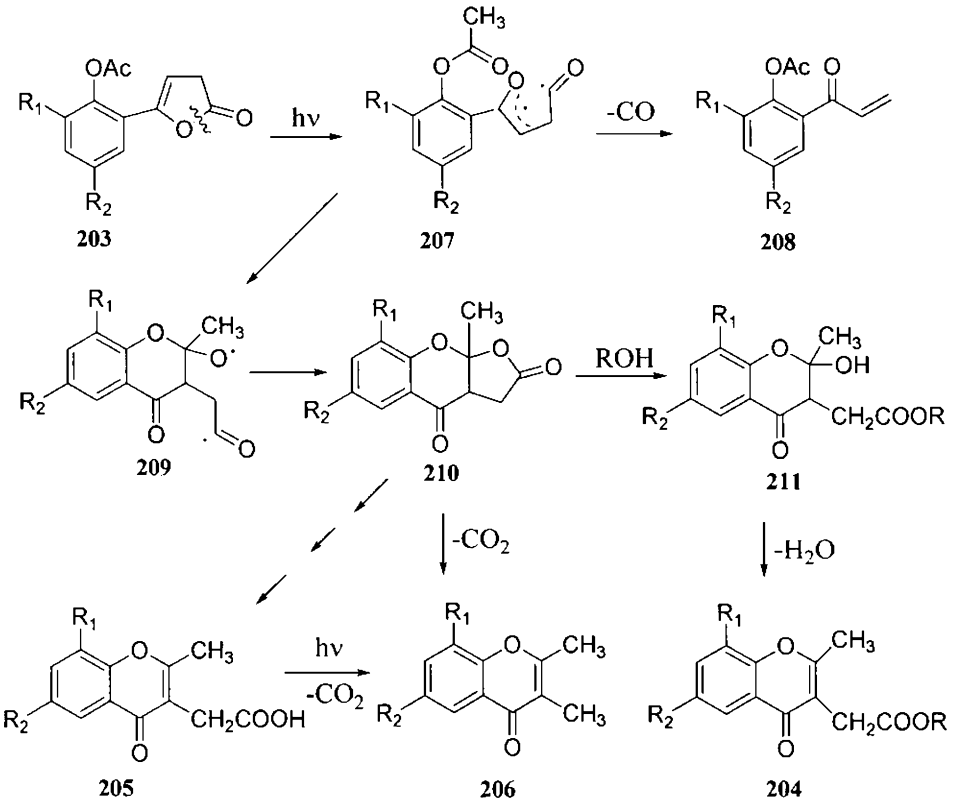
1.3.9. Chromone Formation

Irradiation of **203** in benzene or alcoholic solvents gives, besides the vinyl ketones, the corresponding chromones **204, 205** and **206**[79,83] (Scheme 56).



Scheme 56

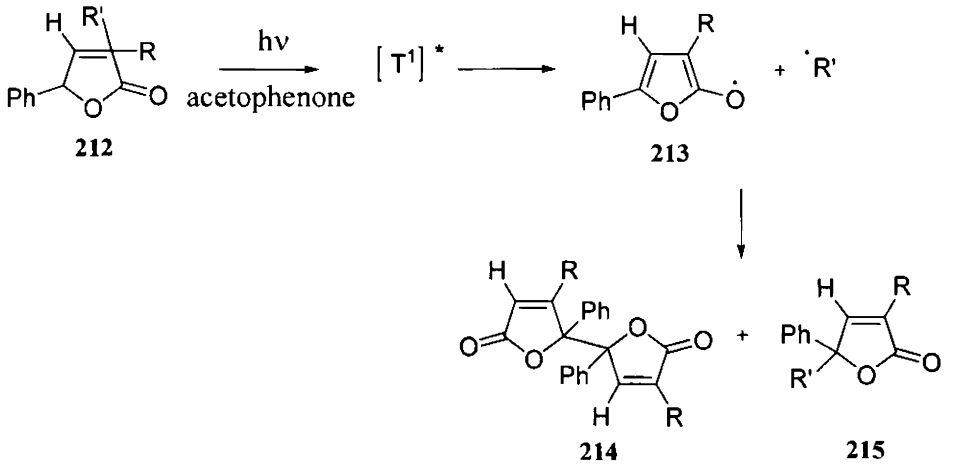
The esters **204** would be formed by solvent addition to intermediate **210** with concomitant ring opening followed by dehydration, while the formation of 2,3-dimethylchromones **206** has been explained by direct decarboxylation of **210**[128,129] or more probably by decarboxylation of the chromoneacetic acids **205** analogous to the well known photodecarboxylation of arylacetic acids (Scheme 57).



Scheme 57

1.3.10. Fragmentation

Some 2(3*H*)-furanones containing a benzyl or benzoyl group at the 3-position undergo facile photochemical cleavage of these groups, upon sensitization with acetophenone, leading to furanoxy radicals **213**. The final products are the rearranged 2(5*H*)-furanones or the bis lactone **214**. The product formed is in support of the pathway shown below (Scheme 58).[91] Under electron transfer conditions, the 2(3*H*)-furanones **212** give rise to the corresponding radical cations, which fragment to the same furanoxy radicals plus benzyl cations.[130]



Scheme 58

1.4. Outline of Research Problem and its Importance

The synthesis and reactions of simple derivatives of 2(3*H*)- and 3(2*H*)-furanones have attracted considerable attention in recent years, primarily in connection with development of routes to antitumor agents that contain this ring as central structural unit. They also serve as useful synthetic building blocks for lactones and furans and are the precursors of a wide variety of biologically important heterocyclic systems. Although a number of syntheses of furanones were known they were in many cases limited to specific substitution patterns. The development of alternative strategies for the preparation of these heterocycles is therefore of considerable importance or continues to be a challenge

We propose to develop new and general approaches to the synthesis of furanone ring systems from simple and readily available starting materials since we were interested in examining their rich photochemistry. The photochemical reactivity of β,γ-unsaturated lactams and lactones is a subject

of current interest. Some of the prominent photoreaction pathways of unsaturated lactones include decarbonylation, solvent addition to double bonds, decarboxylation, migration of aryl substituents and dimerisation. It was reported earlier 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 and 2(3*H*)-furanones possessing this structural requirement undergo facile decarbonylation. But related phenanthrofuranones are isolated as photostable end products upon irradiation. Hence we propose to synthesis a few phenanthro-2(3*H*)-furanones to study the effect of a radical stabilising group at 3-position of furanone ring on photolysis. To explore the triplet-mediated transformations of 2(3*H*)-furanones in polar and nonpolar solvents a few 3,3-bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones and 3,3-di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones were synthesised from the corresponding dibenzoylstyrene precursors by neat thermolysis. Our aim was to study the nature of intermediates involved in these transformations.

We also explored the possibility of developing a new and general approach to the synthesis of 3(2*H*)-furanones from simple and readily available starting materials since such general procedures are not available. The protocol developed by us employs readily available phenanthrenequinone and various 4-substituted acetophenones as starting materials and provides easy access to the required 3(2*H*)-furanone targets. These furanone derivatives have immense potential for further investigations

We also aimed the synthesis of a few dibenzoylalkene-type systems such as acenaphthenone-2-ylidene ketones and phenanthrenone-9-ylidene ketones. These systems were expected to undergo thermal rearrangement to give furanones and spirofuranones. Also these systems can be categorised as quinonemethides which are valuable synthetic intermediates.

1.5. Objectives

1. To synthesise a few 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-ones to assess the role of the 3-methoxy substituent in facilitating light-induced acyl-oxygen bond cleavage
2. To synthesise a few 3,3-bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones and 3,3-di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones to explore the triplet mediated transformations of few 2(3*H*)-furanones in polar and non polar solvents
3. To synthesise a few 2-aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones and to investigate the photochemical transformations
4. To synthesise a few acenaphthenone-2-ylidene ketones and phenanthrenone-9-ylidene ketones
5. Photochemical and thermal studies of acenaphthenone-2-ylidene ketones and phenanthrenone-9-ylidene ketones to establish the generality of dibenzoylalkene rearrangement and to exploit the potential of these systems as *o*-quinonemethides

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Chapter 2

3-Methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-ones: Synthesis and Photochemistry

2.1. Abstract

A number of 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[l]phenanthren-2-ols were synthesised by Claisen-Schmidt condensation reaction between phenanthrenequinone and 4-substituted acetophenones in methanol. Under the influence of heat, these furanols are readily converted to stable 3-methoxy-3-aryl-3H-1-oxacyclopenta[l]phenathren-2-ones. Irradiation of these 2(3H)-furanone derivatives resulted in decarbonylation leading to phenanthrene derivatives. Here our endeavours on the synthesis and photochemistry of 3-methoxy-3-aryl-3H-1-oxacyclopenta[l]phenanthren-2-ones to assess the role of the methoxy substituents in facilitating light-induced acyl-oxygen bond cleavage are depicted.

2.2. Introduction

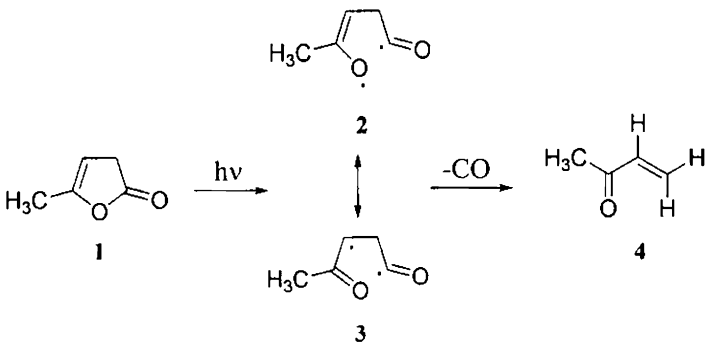
2(3*H*)-Furanones represent an important type of five membered heterocycles of synthetic and biological importance.[1-4] These ring systems serve as important moieties or precursors of several natural products[5-8] (*e.g.*, avenaciolide, plumieride, digitoxin, patulin) and a series of pharmacologically active compounds (digoxin, rofecoxib, protoanemonin, incrustoporine). In light of enormous interest in the versatile utility of these classes of heterocyclic compounds, numerous synthetic efforts have been directed towards these substances. The synthesis of these lactones can be achieved by Baeyer–Villiger oxidation, lactonisation of hydroxy acids, insertion of a

carbonyl group by transition metals, intramolecular cyclisation of 1,4-diones, etc.[9] The methodology that we adopted for the synthesis of 2(3*H*)-furanones involved the Claisen-Schmidt condensation followed by thermal rearrangement.

Claisen-Schmidt condensation[10-16] provides a simple and facile approach for the synthesis of α,β-unsaturated ketones. The reaction involves the nucleophilic addition of enolate ion onto a carbonyl group giving rise to the corresponding aldol which undergoes dehydration to yield the desired α,β-unsaturated carbonyl compound. The base-catalysed reaction between benzil and acetophenone, for example, yields dibenzoylstyrene in excellent yield. We surmised that the reaction between phenanthrenequinone and acetophenones should hence yield the corresponding phenanthrenone-9-ylideneketones. However, condensation of phenanthrenequinone with acetophenones in the presence of a base in methanol yielded 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ols[32] arising through the intermediacy of phenanthrenone-9-ylidene ketones. When heated up to their respective melting points, these dihydrofuranols undergo facile thermal rearrangement to the required 2(3*H*) furanones.

Light induced transformations of β,γ-unsaturated lactones have been the subject of intensive study.[17-22] Depending on the conditions applied, these lactones undergo several phototransformations including decarbonylation,[1] decarboxylation,[23] solvent addition to the double bond,[24] migration of aryl substituents[25] and dimerisation.[26] It has been established that decarbonylation is a singlet-mediated reaction while aryl group migration, dimerisation and solvent addition reactions are triplet mediated.[27,28] Chapman and McIntosh have noted that a critical requirement for clean photochemical cleavage of the acyl-oxygen bond is

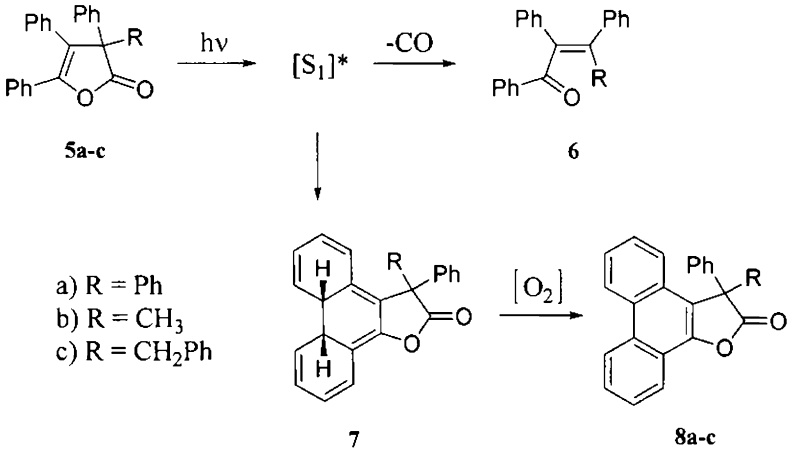
the presence of a double bond adjacent to the ether oxygen.[21] Stabilisation of the incipient oxy radical was considered to be a determining factor in the photocleavage of the bond.



Scheme 1

While 2(3*H*)-furanones possessing this structural requirement undergo facile decarbonylation reaction, 2(5*H*)-furanones are reluctant to undergo decarbonylation. In principle, it should be possible to further enhance the propensity of 2(3*H*)-furanones to undergo decarbonylation by introducing radical-stabilizing groups at appropriate position on the furanone ring. In this chapter, we describe a successful validation of this hypothesis.

Though 3,3,5-triarylfuranones undergo phototransformations characteristic of 2(3*H*)–furanones, related phenanthrofuranones are isolated as photostable end products in certain photochemical transformations.[18-20] Lohray *et al.*[27] found that the photolysis of 3,3,4,5-tetraphenyl-2(3*H*)-furanone **(5a)**, 3-methyl-3,4,5-triphenyl-2(3*H*)-furanone **(5b)**, and 3-benzyl-3,4,5-triphenyl-2(3*H*)-furanone **(5c)** in the presence of oxygen, affords the corresponding phenanthrene derivatives **8a-c**.



Scheme 2

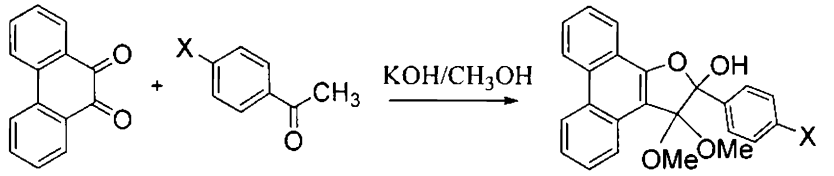
We reasoned that introduction of a radical stabilising methoxy group at the 3-position of phenanthrofuranones should enhance their propensity to undergo decarbonylation by stabilisation of the putative radical center at the 3-position. In the case of carbonyl compounds, Wagner has established that γ-alkoxy substituents enhance the rate of γ-hydrogen abstraction leading to Norrish Type II cleavage and appropriately positioned alkoxy substituents facilitate a rare δ-hydrogen abstraction reaction.[30,31]

In the present study we have examined the photochemistry of a few phenanthro-2(3*H*)-furanones having a methoxy substituent at the 3-position. Required 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-one derivatives **16a-e** were synthesised by the neat thermolysis of the corresponding 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol derivatives **11a-e**, which in turn were generated by the condensation of phenanthrenequinone with acetophenones[32]

2.3. Results and Discussion

2.3.1. Synthesis of 3,3-Dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta-[*l*]phenanthren-2-ols 11a-e.

We employed Claisen-Schmidt condensation for the preparation of desired 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ols **11a-e**. The condensation of phenanthrenequinone **(9)** with acetophenone derivatives **10a-e** in the presence of potassium hydroxide in methanol gave products **11a-e** in 20–50% yield (Scheme 3). Aryl ketones of our choice were acetophenone **(10a),** 4-methylacetophenone **(10b),** 4-methoxyacetophenone **(10c),** 4-chloroacetophenone **(10d)** and 4-phenylacetophenone **(10e).** The structures of **11a-e** were established on the basis of analytical results and spectral data.



9 10a-e 11a-e

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

Scheme 3

UV spectra of all these compounds were dominated by absorption due to the phenanthrene residue present in them. The IR spectra of the products **11a-e** did not indicate the presence of carbonyl groups, but showed absorption at ~ 3400 cm^{-1} indicating the presence of a hydroxy group in the molecule. ^1H NMR spectra of **11a–e** showed the presence of two methoxy groups.

^{13}C NMR spectra also indicated the absence of carbonyl groups in the molecule, but indicated the presence of two signals at ~δ 51.24 and ~ δ 52.31 attributable to methoxy groups and another signal at ~δ 108 attributable to a ketal group. The structure of these compounds was unequivocally determined by single crystal X-ray diffraction analysis (Figure 1) on a representative example **11d.** Crystals suitable for X-ray experiments were obtained by slow evaporation from methanol-dichloromethane mixture (3:2) at room temperature.

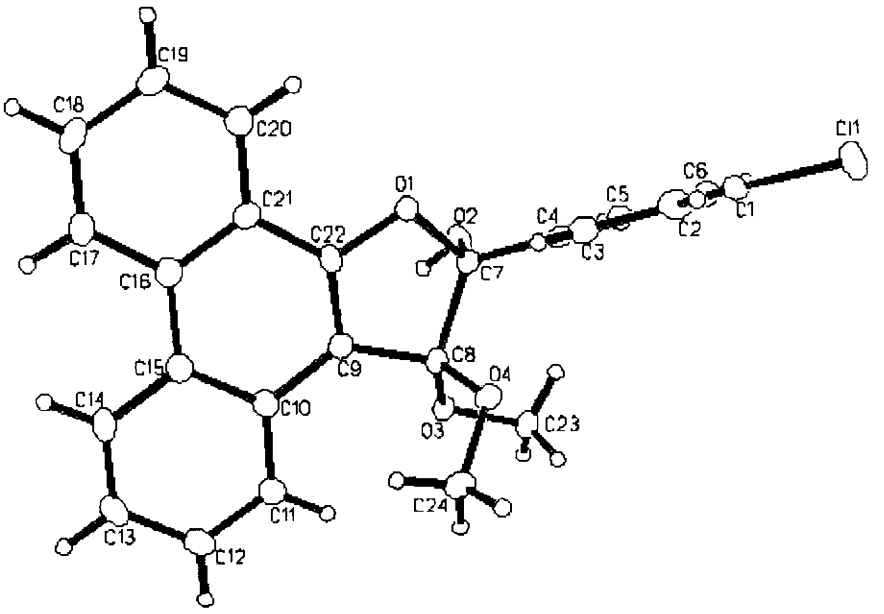
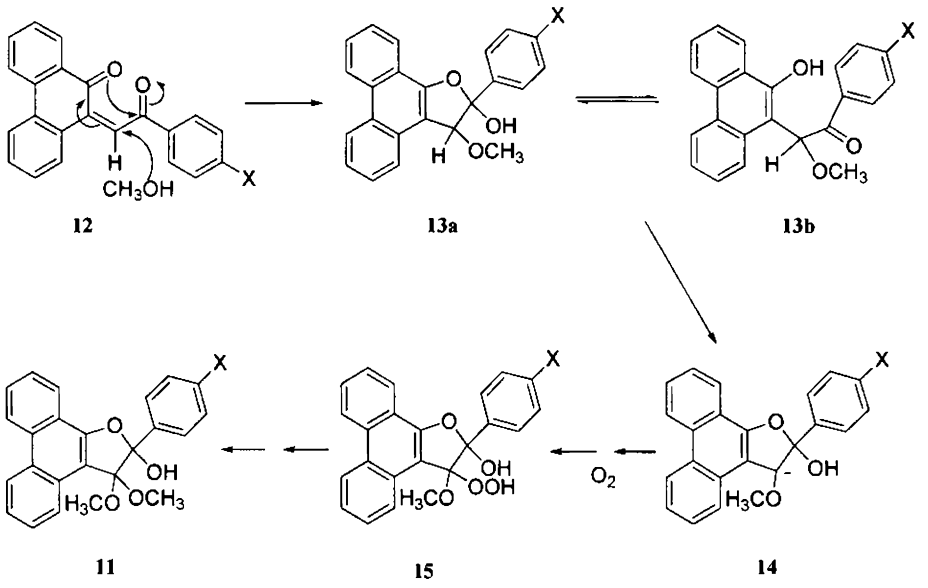


Figure 1. *ORTEP diagram of molecular structure of* ***11d*** *in the crystal*

A possible mechanism for the formation of dihydro-2-furanol **11** involving the intermediacy of phenanthrenone-9-ylidene ketones **12** is presented in Scheme 4. Nucleophilic addition of methanol to **12** leads to the formation of **11.** The carbanion intermediate **14** generated by abstraction of the moderately acidic proton at the 3-position of **13** undergoes oxidation by

the moderately acidic proton at the 3-position of **13** undergoes oxidation by single electron transfer to either oxygen[33] or phenanthrenequinone[34] followed by further transformations to give the hydroperoxide intermediate **15**.[35-37] Under the conditions of work up, **15** is transformed to the dihydrofuranol **11**.[38-40]



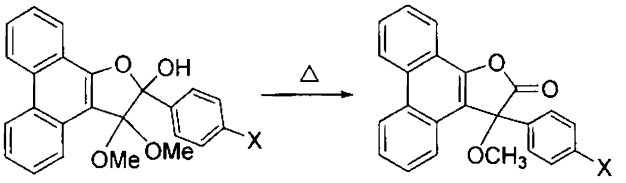
Scheme 4

2.3.2. Synthesis of 3-Methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-ones 16a-e.

The dihydrofuranol derivatives **11a–e** underwent facile thermal rearrangement when heated up to their respective melting points. Neat thermolysis of **11a–e** in sealed tubes gave **16a–e** as colourless crystalline solids in high yield (83%).

The structures of **16a–e** were arrived at on the basis of spectral and analytical data. All the thermolysis products **16a–e** showed strong IR

absorptions at ~ 1813 cm^{-1} indicating the presence of a γ-lactone component in the molecule. UV absorption spectra of these compounds are similar to that of phenanthrene indicating the presence of phenanthrene components. ^1H NMR spectra of **16a–e** showed a singlet at ~ δ 3.4 indicating the presence of a single methoxy group. In the ^{13}C NMR spectra, signals were observed at ~ δ 54 (OCH_3), 85, 114–150 (aromatic) and 175 (C=O). The structures were further confirmed by elemental analysis, which gave acceptable data. Based on these data, the compounds were assigned the 3-methoxy-3-aryl-3*H*-1-oxa-cyclopenta[*l*]phenathren-2-one **16a–e** structures

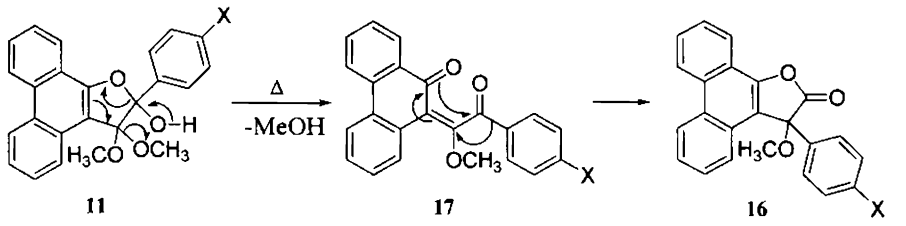


11 **16**

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

Scheme 5

It is interesting to note that the thermal transformation of **11** to **16** may proceed through two distinct pathways. One of mechanisms for the formation of 3-methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenathren-2-one **16a-e** is given in Scheme 6. Upon heating, loss of a molecule of methanol from **11** and consequent bond reorganizations lead to the formation of methoxy-dibenzoylalkene **17**. Subsequently **17** undergoes thermal transformation analogous to that reported for other dibenzoylalkenes to yield the corresponding 2(3*H*)-furanone **16**.[41,42]



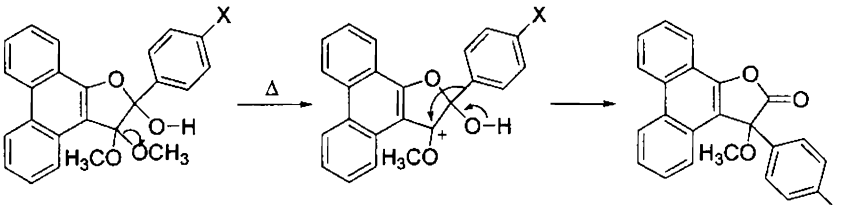
11 17 16

Scheme 6

To support the above proposed mechanism we attempted trapping experiment using dimethyl acetylenedicarboxylate by cycloaddition reaction. The proposed intermediate **17** here is an *o*-quinonemethide and hence may be intercepted by Diels-Alder reaction with a reactive dienophile such as DMAD. But our attempts to trap the intermediate **17** were unsuccesful and an intractable mixture resulted. Furthermore, dibenzoylalkenes rearrange to the corresponding 2(3*H*)-furanones at relatively high temperature. But the rearrangement of furanols **11** to furanones **16** proceeded under mild conditions. These observations cast doubt on the involvement of **17** as an intermediate in the observed transformation.

Alternately a pinacol-pinacolone type mechanism (Scheme 7) can also be suggested for the above formed product **16a-e**. It may be noted that the observed furanol-furanone transformation involves a 1,2-aryl migration step. If the pinacol-pinacolone-type mechanism as depicted in Scheme 7 is operating, the migration step involves 1,2-aryl migration to an electron deficient center and hence a substantial substituent effect is expected. We observed that **11c** having a 4-anisyl substituent is quite unstable and readily rearranges to yield the furanone **16c** whereas **11d** having a 4-chlorophenyl substituent is relatively more stable. These results suggest that 4-anisyl group migrates much faster than a 4-chlorophenyl group and hence a

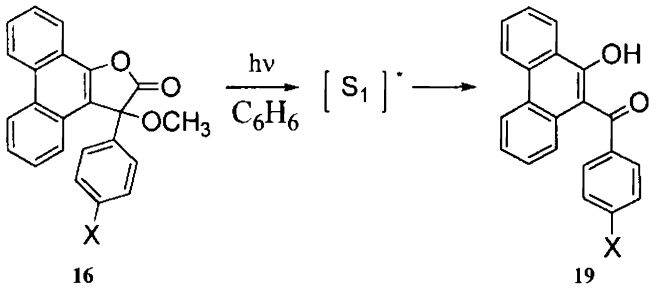
mechanism involving 1,2-aryl migration to an electron deficient center as depicted in Scheme 7 is more satisfactory. So under the reaction condition applied by us, a pinacol-pinacolone type mechanism is a better choice.



Scheme 7

2.3.3. Irradiation of 3-Methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-ones 16a-e.

The photolysis (λ = 300 nm) of 2(3*H*)-furanones **16a-e** in benzene gave 10-hydroxy-phenanthren-9-yl methanone derivatives **19a-e** as yellow crystalline compounds in good yields (64-68%). Structures of these compounds were arrived at on the basis of spectral and analytical data.



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

Scheme 8

IR spectrum of **19a-e** showed the presence of hydroxyl and carbonyl group in the molecule. ^{13}C NMR spectrum also showed a peak at ~ δ 199 confirming the presence of a carbonyl carbon. The structure of these compounds was unequivocally determined by single crystal X-ray diffraction analysis of a representative example such as **19c.** The crystal of this compound was grown in a mixture (3:2) of chloroform and hexane. The crystal data and structural refinement parameters are given in Table 1 at the end of the chapter.

The unusually low carbonyl stretching frequency observed (1620 cm^{-1}) is attributable to strong intramolecular hydrogen bonding interaction between hydroxyl and carbonyl groups present in the molecule. This was further corroborated by the D-H....A distances and angle around H atoms (O1-H1....O2=1.731 Å, 145.9; O1'-H1'....O2'= 1.745 Å, 148.9) as determined from the X- ray structure.

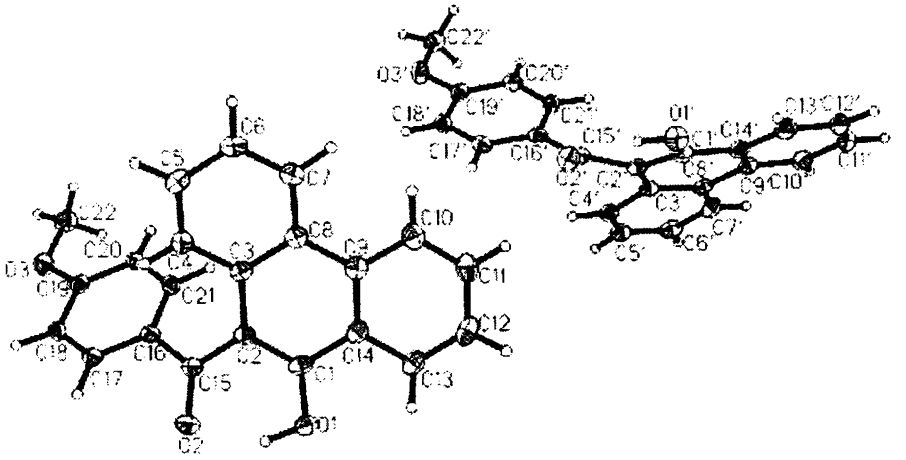


Figure 2. *ORTEP diagram of molecular structure of* ***19c*** *in the crystal*

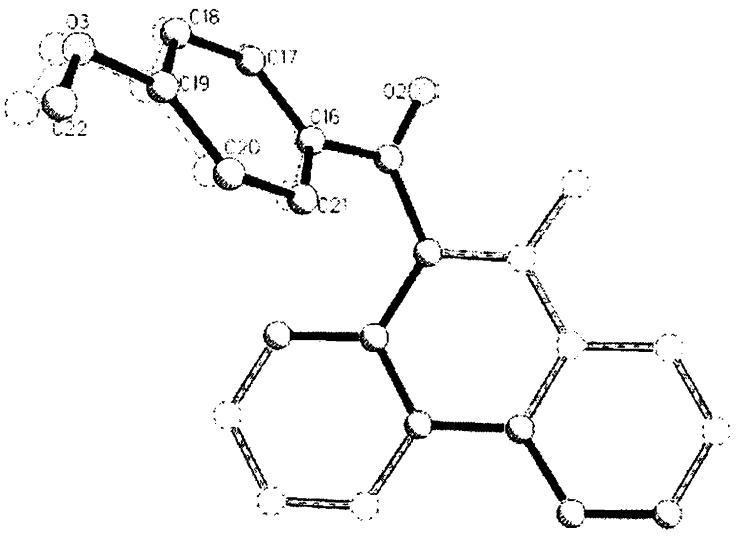


Figure 3. *Overlay of the two unique molecules in* ***19c***
(Solid bonds show the molecule 1 and dotted line bonds represent the 2nd molecule)

The compound crystallises in monoclinic space group $P2_1$ with two unique molecules in the asymmetric unit. As Z'>1, molecular overlay was used to look for differences in the two unique molecules. The overlay (OFIT, Shelxtl) shows that the phenathrene rings match very well (weighted RMS deviation = 0.0174). The molecules start to diverge after the carbonyl group (c16-c16' = 0.143 Å, c19-c19' = 0.415 Å). The two unique molecules in the asymmetric unit use the methoxy oxygen and a H atom of the phenathrene ring to form 1-D chain mediated through C-H...O contacts. These chains are interconnected to form square-like network (Figure 4). Each square is formed by two different symmetry independent molecules and hence the square is not symmetrical [O3'---H11'(x, y-1, z) = 2.465, O3---H12 (x, y-1, z) = 2.688, O2'---H22b (x, y+1,z) = 2.595, O2—

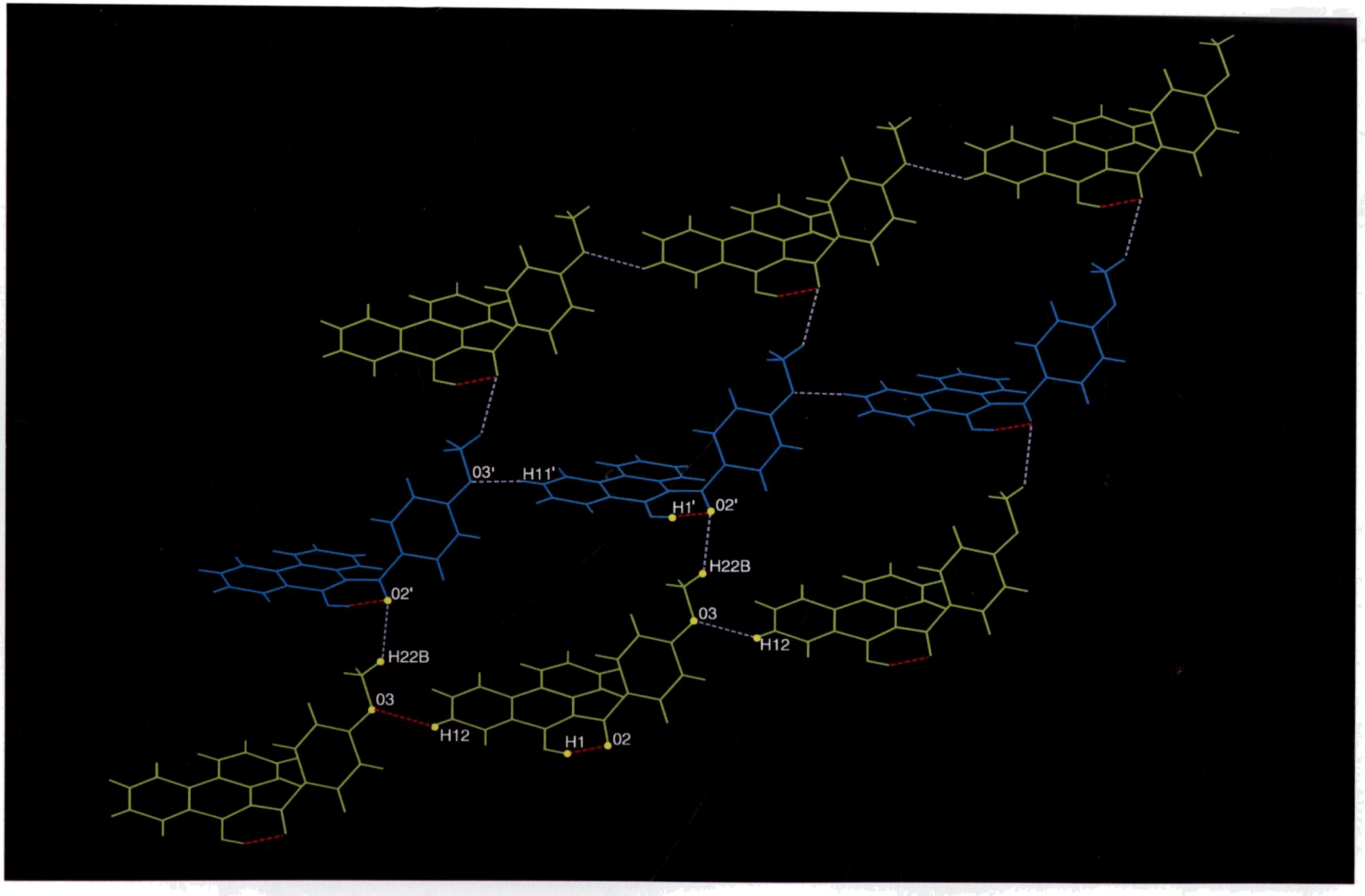
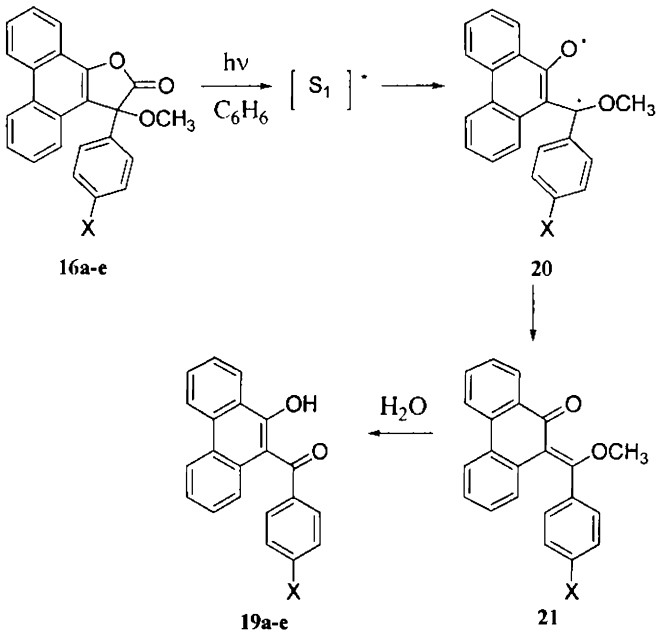


Figure. 4. The Square like network and hydrogen bonding in the crystal lattice of 19c.

H22d (x, y-1, z) = 2.694 Å]. It may be noted that the supramolecular grid like pattern formation is controlled by the methoxy group present on the 9-aroyl substituent.

The formation of photoproducts **19a-e** on irradiation in benzene or acetone can be understood in terms of the pathways shown in Scheme 9).[21,27]



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

Scheme 9

The initial excitation of the 2(3*H*)-furanones to the corresponding singlet excited state resulted in decarbonylation to the diradical intermediate **20** which undergoes bond reorganization to give the quinonemethide intermediate **21**. It appears that the methoxy group has a major role to play on the facile decarbonylation here *vis-à-vis* other

phenanthrofuranones. Hydrolytic elimination of methanol followed by tautomerisation will eventually lead to **19**. Since the phenanthrene-furanones **16a-e** absorbed strongly in the 220 – 400 nm range, it was not feasible to carry out sensitized irradiation of these compounds using common triplet sensitizers.

In order to generate further support for the involvement of intermediates such as **20** and **21**, we carried out traping experiments. Our attempts to trap the quinonemethide intermediate **21** by a 4+2 cycloaddition reaction with DMAD, however, were not successful. We conclude that the hydrolysis of the vinyl ether component in **21** is much faster than the cycloaddition reaction under the reaction conditions applied by us. A good hydrogen atom donor such as 2-propanol was used to trap radical intermediate **20** by *H*-transfer. However, trapping experiment using 2-propanol was unsuccessful indicating the reactive nature of **20**. Though the proposed intermediates could not be intercepted, the photochemical transformation of **16a-e** involving acyl-oxygen bond cleavage appears to be analogous to that of other 2(3*H*)-furanones.[21,22,24,25]

2.4. Conclusion

We have synthesised several 3-methoxy-3-aryl-3*H*-1-oxacyclopenta-[*l*]phenanthren-2-one derivatives and examined their photochemistry. We have demonstrated that the methoxy group in the lactone ring has a profound effect on the acyl-oxygen bond cleavage leading to decarbonylation reaction. Our attempts to trap the proposed intermediates by using DMAD and 2-propanol were unsuccessful presumably due to their reactive nature.

2.5. Experimental

2.5.1. 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 infra red spectra were recorded using ABB Bomem (MB Series) FT-IR spectrometer. All steady state irradiations were carried out using Rayonet Photochemical Reactor (RPR). Solvents for photolysis were purified and distilled before use. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively on a Bruker 300 FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane. Elemental analysis was performed using Elementar Systeme (Vario ELIII) at STIC, Kochi.

2.5.2. Starting Materials: Phenanthrenequinone, acetophenone, 4-methylacetophenone, 4-chloroacetophenone, 4-methoxyacetophenone, 4-chloroacetophenone and 4-phenylacetophenone were purchased from Sigma Aldrich and were used as obtained.

2.5.2.1. 3,3-Dimethoxy-2-phenyl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol (11a): Prepared using a known procedure (30%, mp 116-118 ^{0}C).[32]

2.5.2.2. 3,3-Dimethoxy-2-(4'-methylphenyl)-2,3-dihydro-1-oxacyclopent-a[*l*]phenanthren-2-ol (11b): Prepared using a known procedure (20%, mp 118-120 ^{0}C).[32]

2.5.2.3. 3,3-Dimethoxy-2-(4'-chlorophenyl)-2,3-dihydro-1-oxacyclopenta-[*l*]phenanthren-2-ol (11c): Prepared using a known procedure (25%, mp 142-143 ^{0}C).[32]

2.5.2.4. 3,3-Dimethoxy-2-(4'-methoxyphenyl)-2,3-dihydro-1-oxacyclope-nta[*l*]phenanthren-2-ol (11d): Prepared using a known procedure (40%, mp 136-138 ^{0}C).[32]

2.5.2.5. 3,3-Dimethoxy-2-(4'-phenylphenyl)-2,3-dihydro-1-oxacyclopent-a[*l*]phenanthren-2-ol (11e): Prepared using a known procedure (30%, mp 132-134 ^{0}C).[32]

2.5.3. Synthesis of 3-Methoxy-3-aryl-3*H*-1-oxacyclopenta[*l*]phenanthren-2-ones (16a-e).

Phenanthrenefuranones **16a-e** were synthesised by neat thermolysis of the corresponding phenanthrofuranols **11a-e.**

2.5.3.1. Thermolysis of 11a: A sample of **11a** (100 mg, 0.27 mmol) was thermolysed in a sealed tube at 180 ^{0}C for 6 h. The solid residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (3:2) of hexane and dichloromethane gave **16a** as a white solid.

Compound 16a: (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 3.41 (3H, s, methoxy protons), 7.21-8.93 (13H, m, aromatic

protons) Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.22; H, 4.76.

2.5.3.2. Thermolysis of 11b: A sample of **11b** (100 mg, 0.26 mmol) was thermolysed in a sealed tube at 180 ^{0}C for 6 h. The solid residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (3:2) of hexane and dichloromethane gave **16b** as a white solid

Compound 16b: (81%); mp 160-162 ^{0}C; IR ν_{max} (KBr) 1815 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 208(ε19,600), 223 (ε 14,000), 245 (ε 19,300), 256 (ε 15,900), 276 (ε 7,100), 308 (ε 3,400), 337 (ε 800), 355 nm (ε 700); ^{1}H NMR ($CDCl_3$) δ 2.31 (3H, s, methyl); δ 3.35 (3H, s, methoxy protons); 7.10-8.90 (12H, m, aromatic protons); Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.62; H, 5.34.

2.5.3.3. Thermolysis of 11c: A sample of **11c** (100 mg, 0.22 mmol) was thermolysed in a sealed tube at 180 ^{0}C for 6 h. The solid residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (3:2) of hexane and dichloromethane gave **16c** as a white solid

Compound 16c: (82%); mp 193-194 ^{0}C; IR ν_{max} (KBr) 1813 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 208 (ε 21,400), 245 (ε 21,500), 258 (ε 17,800), 276 (ε 7,900), 308 (ε 24,100), 338 (ε 1000), 354 nm (ε 900); ^{1}H NMR ($CDCl_3$) δ 3.22 (3H, s, methoxy protons), 7.24-8.87 (12H, m, aromatic protons); Anal. Calcd for $C_{23}H_{15}O_3Cl$: C, 73.85; H, 4.03. Found: C, 74.02; H, 4.05.

2.5.3.4. Thermolysis of 11d: A sample of **11d** (100 mg, 0.25 mmol) was thermolysed in a sealed tube at 180 ^{0}C for 6 h. The solid residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (3:2) of hexane and dichloromethane gave **16d** as a white solid

Compound 16d: (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 3.38 (3H, s, methoxy protons), 3.47 (3H, s, methoxy protons), 6.96-8.09 (12H, m, aromatic protons); ^{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, 124.01, 124.19, 126.27, 127.49, 127.51, 127.69, 127.99, 128.32, 128.78, 128.91, 129.18, 132.54, 149.59, 175.28.; Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.9. Found: C, 78.1; H, 4.94.

2.5.3.5. Thermolysis of 11e: A sample of **11e** (100 mg, 0.27 mmol) was thermolysed in a sealed tube at 180 ^{0}C for 6 h. The solid was extracted with dichloromethane. Column chromatography by using a mixture (3:2)of hexane and dichloromethane gave (**16e**) as a white solid

Compound 16e: (81%); mp 152-154 ^{0}C; IR ν_{max} (KBr), 1810 cm^{-1} (lactone C=O); UV λ_{max} (CH_3CN) 207 (ε 41,000), 262 (ε 39,000), 306 (ε 8,000), 342 nm (ε 4,600) 338 (ε 2,800), 356 nm (ε 1,800); ^{1}H NMR ($CDCl_3$) δ 3.35 (3H, s, methoxy protons), 7.31-8.86 (17H, m, aromatic protons); Anal. Calcd for $C_{29}H_{20}O_3$: C, 83.64; H, 4.84. Found: C, 83.48; H, 4.86.

2.5.4. Irradiation of Phenanthrenefuranones 16a-e

Direct irradiation of **16a-e** resulted in the formation of the corresponding 10-hydroxy-phenanthren-9-yl-methanones **19a-e** in good yields.

2.5.4.1. Irradiation of 16a: A benzene solution of **16a** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel.

Compound 19c:(68%); mp 152-154°C; IR ν_{max} (KBr) 3420 cm^{-1} (OH), 1618 cm^{-1}, and 1605 cm^{-1}; UV λ_{max} (CH_3CN) 245 (ε 21,500), 252 (ε 13,000), 290 (ε 4,600), 369 nm (ε 1700); ^1H NMR (300 MHz, $CDCl_3$) δ 7.06-8.80 (m, aromatic and hydroxy protons); Anal. Calcd. for $C_{21}H_{13}O_2$: C, 75.80; H, 3.94. Found: C, 75.69; H, 4.01.

2.5.4.4. Irradiation of 16d: A benzene solution of **16d** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19d** as a yellow crystalline compound.

Compound 19d: (66%); mp 156-157°C; IR ν_{max} (KBr) 3425cm^{-1} (OH), 1615 cm^{-1}, and 1600 cm^{-1}; UV λ_{max} (CH_3CN) 251 (ε 21,000), 293 (ε 9,500), 375 nm (ε 1,500); ^1H NMR ($CDCl_3$) δ 3.76 (3H, s, methoxy), 6.80-8.54 (13H, m, aromatic and hydroxy protons); ^{13}C NMR ($CDCl_3$) δ 55.01, 104.40, 114.03, 122.41, 122.90, 124.46, 125.12, 126.25, 127.50, 127.66, 128.34, 129.43, 130.33, 132.53, 159.78, 199.94; Anal. Calcd. for $C_{22}H_{16}O_3$: C, 80.47; H, 4.9. Found: C, 80.18; H, 4.94.

2.5.4.5. Irradiation of 16e: A benzene solution of **16e** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19e** as a yellow crystalline compound.

Compound 19e: (65%); mp 153-155°C; IR ν_{max} (KBr), 3420 (OH), 1615 cm^{-1}, and 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 6.82-8.59 (m, aromatic and hydroxy protons); Anal. Calcd. for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.38; H, 5.14.

2.5.5. Irradiation of 16a in the presence of Dimethyl acetylenedicarboxylate (DMAD)

A benzene solution of **16a** (0.73 mmol in 150 mL) containing DMAD (590 mg, 4.14 mmol) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 2 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 **19a** (64%).

2.5.6. Irradiation of 16a in the presence of 2-Propanol

A benzene solution of **16a** (0.73 mmol in 150 mL) containing 2-propanol (0.20 mmol) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 2 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 **19a** (60%).

Compound 19c:(68%); mp 152-154°C; IR ν_{max} (KBr) 3420 cm^{-1} (OH), 1618 cm^{-1}, and 1605 cm^{-1}; UV λ_{max} (CH_3CN) 245 (ε 21,500), 252 (ε 13,000), 290 (ε 4,600), 369 nm (ε 1700); ^1H NMR (300 MHz, $CDCl_3$) δ 7.06-8.80 (m, aromatic and hydroxy protons); Anal. Calcd. for $C_{21}H_{13}O_2$: C, 75.80; H, 3.94. Found: C, 75.69; H, 4.01.

2.5.4.4. Irradiation of 16d: A benzene solution of **16d** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19d** as a yellow crystalline compound.

Compound 19d: (66%); mp 156-157°C; IR ν_{max} (KBr) 3425cm^{-1} (OH), 1615 cm^{-1}, and 1600 cm^{-1}; UV λ_{max} (CH_3CN) 251 (ε 21,000), 293 (ε 9,500), 375 nm (ε 1,500); ^1H NMR ($CDCl_3$) δ 3.76 (3H, s, methoxy), 6.80-8.54 (13H, m, aromatic and hydroxy protons); ^{13}C NMR ($CDCl_3$) δ 55.01, 104.40, 114.03, 122.41, 122.90, 124.46, 125.12, 126.25, 127.50, 127.66, 128.34, 129.43, 130.33, 132.53, 159.78, 199.94; Anal. Calcd. for $C_{22}H_{16}O_3$: C, 80.47; H, 4.9. Found: C, 80.18; H, 4.94.

2.5.4.5. Irradiation of 16e: A benzene solution of **16e** (0.73 mmol in 150 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **19e** as a yellow crystalline compound.

Compound 19e: (65%); mp 153-155°C; IR ν_{max} (KBr), 3420 (OH), 1615 cm^{-1}, and 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 6.82-8.59 (m, aromatic and hydroxy protons); Anal. Calcd. for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.38; H, 5.14.

2.5.5. Irradiation of 16a in the presence of Dimethyl acetylenedicarboxylate (DMAD)

A benzene solution of **16a** (0.73 mmol in 150 mL) containing DMAD (590 mg, 4.14 mmol) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 2 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 **19a** (64%).

2.5.6. Irradiation of 16a in the presence of 2-Propanol

A benzene solution of **16a** (0.73 mmol in 150 mL) containing 2-propanol (0.20 mmol) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 2 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 **19a** (60%).

Table 1. Crystal data and structure refinement for compound 19c

Empirical formula	$C_{22}H_{16}O_3$	
Formula weight	328.35	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system, Space group	Monoclinic, $P2_1$	
Unit cell dimensions	a = 7.2298(3) Å	α= 90°.
	b = 13.7492(7) Å	β= 92.621(2)°.
	c = 16.0107(8) Å	γ = 90°.
Volume	1589.86(13) $Å^3$	
Z, Density (calculated)	4, 1.372 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	688	
Crystal size	0.19 x 0.17 x 0.16 mm^3	
Theta range for data collection	1.27 to 27.78°.	
Index ranges	$-9\leq h\leq 9$, $-18\leq k\leq 18$, $-20\leq l\leq 20$	
Reflections collected	27486	
Independent reflections	7421 [R(int) = 0.0496]	
Completeness to theta = 27.78°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9856 and 0.9830	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7421 / 1 / 579	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.0897	
R indices (all data)	R1 = 0.0626, wR2 = 0.0982	
Absolute structure parameter	-1.7(8)	
Largest diff. peak and hole	0.219 and -0.222 $e.Å^{-3}$	

Table 2. Bond lengths (in angstroms) of compound 19c

O(1)-C(1)	1.346(2)	C(11)-C(12)	1.400(4)
O(1)-H(1)	0.97(4)	C(11)-H(11)	0.94(3)
O(2)-C(15)	1.245(2)	C(12)-C(13)	1.368(4)
O(3)-C(19)	1.360(3)	C(12)-H(12)	0.97(2)
O(3)-C(22)	1.431(3)	C(13)-C(14)	1.422(3)
O(1')-C(1')	1.345(3)	C(13)-H(13)	0.99(3)
O(1')-H(1')	0.90(4)	C(15)-C(16)	1.490(3)
O(2')-C(15')	1.243(2)	C(16)-C(17)	1.389(3)
O(3')-C(19')	1.371(3)	C(16)-C(21)	1.399(3)
O(3')-C(22')	1.435(3)	C(17)-C(18)	1.375(3)
C(1)-C(2)	1.381(3)	C(17)-H(17)	1.00(2)
C(1)-C(14)	1.439(3)	C(18)-C(19)	1.395(3)
C(2)-C(3)	1.445(3)	C(18)-H(18)	0.99(2)
C(2)-C(15)	1.471(3)	C(19)-C(20)	1.395(3)
C(3)-C(8)	1.412(3)	C(20)-C(21)	1.387(3)
C(3)-C(4)	1.416(3)	C(20)-H(20)	0.94(2)
C(4)-C(5)	1.371(3)	C(21)-H(21)	0.96(2)
C(4)-H(4)	0.93(3)	C(22)-H(22A)	1.00(3)
C(5)-C(6)	1.402(3)	C(22)-H(22B)	0.99(3)
C(5)-H(5)	0.97(2)	C(22)-H(22C)	0.96(3)
C(6)-C(7)	1.373(3)	C(1')-C(2')	1.385(3)
C(6)-H(6)	0.98(3)	C(1')-C(14')	1.438(3)
C(7)-C(8)	1.414(3)	C(2')-C(3')	1.456(3)
C(7)-H(7)	1.02(3)	C(2')-C(15')	1.475(3)
C(8)-C(9)	1.464(3)	C(3')-C(4')	1.411(3)
C(9)-C(14)	1.408(3)	C(3')-C(8')	1.417(3)
C(9)-C(10)	1.411(3)	C(4')-C(5')	1.373(3)
C(10)-C(11)	1.371(3)	C(4')-H(4')	0.97(2)
C(10)-H(10)	0.98(2)	C(5')-C(6')	1.396(3)

C(5')-H(5')	0.90(3)	C(13')-H(13')	0.99(3)
C(6')-C(7')	1.372(3)	C(15')-C(16')	1.479(3)
C(6')-H(6')	0.94(3)	C(16')-C(21')	1.397(3)
C(7')-C(8')	1.412(3)	C(16')-C(17')	1.398(3)
C(7')-H(7')	0.94(2)	C(17')-C(18')	1.377(3)
C(8')-C(9')	1.451(3)	C(17')-H(17')	0.97(2)
C(9')-C(14')	1.413(3)	C(18')-C(19')	1.395(3)
C(9')-C(10')	1.415(3)	C(18')-H(18')	0.95(2)
C(10')-C(11')	1.375(4)	C(19')-C(20')	1.385(3)
C(10')-H(10')	0.96(3)	C(20')-C(21')	1.393(3)
C(11')-C(12')	1.396(4)	C(20')-H(20')	0.92(2)
C(11')-H(11')	0.97(3)	C(21')-H(21')	0.95(3)
C(12')-C(13')	1.370(3)	C(22')-H(22D)	0.97(3)
C(12')-H(12')	0.96(3)	C(22')-H(22E)	1.04(3)
C(13')-C(14')	1.417(3)	C(22')-H(22F)	0.99(3)

Table 3. Selected Bond angles (in degrees) of compound 19c

C(1)-O(1)-H(1)	107(2)	C(8)-C(3)-C(2)	120.4(2)
C(19)-O(3)-C(22)	117.66(18)	C(4)-C(3)-C(2)	121.4(2)
C(1')-O(1')-H(1')	106(2)	C(5)-C(4)-C(3)	121.8(2)
C(19')-O(3')-C(22')	117.31(17)	C(5)-C(4)-H(4)	118.2(16)
O(1)-C(1)-C(2)	122.9(2)	C(3)-C(4)-H(4)	120.0(16)
O(1)-C(1)-C(14)	115.75(19)	C(4)-C(5)-C(6)	120.0(2)
C(2)-C(1)-C(14)	121.24(19)	C(4)-C(5)-H(5)	116.9(12)
C(1)-C(2)-C(3)	118.9(2)	C(6)-C(5)-H(5)	122.9(12)
C(1)-C(2)-C(15)	117.26(18)	C(7)-C(6)-C(5)	119.6(2)
C(3)-C(2)-C(15)	123.78(19)	C(7)-C(6)-H(6)	118.9(17)
C(8)-C(3)-C(4)	117.99(19)	C(5)-C(6)-H(6)	121.2(17)

C(6)-C(7)-C(8)	121.3(2)	C(19)-C(20)-H(20)	121.0(14)
C(6)-C(7)-H(7)	116.7(14)	C(20)-C(21)-C(16)	120.9(2)
C(8)-C(7)-H(7)	122.0(14)	C(20)-C(21)-H(21)	118.9(14)
C(3)-C(8)-C(7)	119.2(2)	C(16)-C(21)-H(21)	120.2(14)
C(3)-C(8)-C(9)	119.09(19)	O(3)-C(22)-H(22A)	111.2(14)
C(7)-C(8)-C(9)	121.6(2)	O(3)-C(22)-H(22B)	109.3(17)
C(14)-C(9)-C(10)	117.8(2)	H(22A)-C(22)-H(22B)	107(2)
C(14)-C(9)-C(8)	119.1(2)	O(3)-C(22)-H(22C)	109.5(14)
C(10)-C(9)-C(8)	123.0(2)	H(22A)-C(22)-H(22C)	110(2)
C(11)-C(10)-C(9)	121.0(2)	H(22B)-C(22)-H(22C)	110(2)
C(11)-C(10)-H(10)	122.2(15)	O(1')-C(1')-C(2')	123.1(2)
C(9)-C(10)-H(10)	116.8(15)	O(1')-C(1')-C(14')	115.10(19)
C(10)-C(11)-C(12)	121.0(2)	C(2')-C(1')-C(14')	121.71(19)
C(10)-C(11)-H(11)	120.1(15)	C(1')-C(2')-C(3')	118.7(2)
C(12)-C(11)-H(11)	118.9(15)	C(1')-C(2')-C(15')	116.73(19)
C(13)-C(12)-H(12)	121.9(14)	C(3')-C(2')-C(15')	124.48(19)
C(12)-C(13)-C(14)	120.1(2)	C(4')-C(3')-C(8')	118.62(19)
C(14)-C(13)-H(13)	117.1(15)	C(4')-C(3')-C(2')	121.3(2)
C(9)-C(14)-C(1)	119.7(2)	C(8')-C(3')-C(2')	119.98(19)
O(2)-C(15)-C(2)	120.76(19)	C(5')-C(4')-C(3')	121.3(2)
C(2)-C(15)-C(16)	120.62(17)	C(5')-C(4')-H(4')	117.3(13)
C(17)-C(16)-C(15)	119.77(18)	C(3')-C(4')-H(4')	121.4(13)
C(18)-C(17)-C(16)	120.79(19)	C(4')-C(5')-H(5')	118.4(16)
C(16)-C(17)-H(17)	118.8(13)	C(6')-C(5')-H(5')	121.4(16)
C(17)-C(18)-H(18)	121.9(13)	C(7')-C(6')-C(5')	119.7(2)
O(3)-C(19)-C(20)	124.30(19)	C(5')-C(6')-H(6')	120.4(16)
O(3)-C(19)-C(18)	115.76(19)	C(6')-C(7')-C(8')	121.6(2)
C(20)-C(19)-C(18)	119.9(2)	C(6')-C(7')-H(7')	119.4(14)
C(21)-C(20)-C(19)	119.28(19)	C(8')-C(7')-H(7')	118.9(14)
C(21)-C(20)-H(20)	119.7(14)	C(7')-C(8')-C(3')	118.5(2)

C(7')-C(8')-C(9')	122.0(2)	C(21')-C(16')-C(15')	121.2(2)
C(3')-C(8')-C(9')	119.48(18)	C(17')-C(16')-C(15')	119.70(18)
C(14')-C(9')-C(10')	117.4(2)	C(18')-C(17')-C(16')	120.7(2)
C(10')-C(9')-C(8')	122.8(2)	C(18')-C(17')-H(17')	121.9(13)
C(11')-C(10')-C(9')	121.4(2)	C(16')-C(17')-H(17')	117.3(13)
C(9')-C(10')-H(10')	120.9(16)	C(17')-C(18')-C(19')	119.7(2)
C(10')-C(11')-C(12')	120.5(2)	C(17')-C(18')-H(18')	123.1(13)
C(10')-C(11')-H(11')	121.9(15)	C(19')-C(18')-H(18')	117.1(13)
C(12')-C(11')-H(11')	117.6(15)	O(3')-C(19')-C(18')	115.3(2)
C(13')-C(12')-C(11')	120.1(2)	C(20')-C(19')-C(18')	120.8(2)
C(11')-C(12')-H(12')	117.4(15)	C(19')-C(20')-C(21')	119.07(19)
C(12')-C(13')-C(14')	120.2(2)	C(21')-C(20')-H(20')	123.2(14)
C(12')-C(13')-H(13')	123.1(14)	C(20')-C(21')-C(16')	120.8(2)
C(9')-C(14')-C(13')	120.4(2)	C(16')-C(21')-H(21')	119.6(15)
C(9')-C(14')-C(1')	119.20(19)	O(3')-C(22')-H(22D)	105.4(14)
C(13')-C(14')-C(1')	120.4(2)	O(3')-C(22')-H(22E)	109.6(14)
O(2')-C(15')-C(2')	120.3(2)	H(22D)-C(22')-H(22E)	109(2)
O(2')-C(15')-C(16')	118.1(2)	O(3')-C(22')-H(22F)	109.6(16)
C(2')-C(15')-C(16')	121.23(18)	H(22D)-C(22')-H(22F)	114(2)
C(21')-C(16')-C(17')	118.8(2)	H(22E)-C(22')-H(22F)	109(2)

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Chapter 3

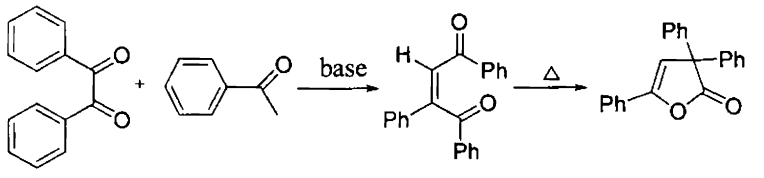
Synthesis and Photochemical Transformations of a Few 3,3,5-Triaryl-3*H*-furan-2-ones

4.1. Abstract

3,3-Bis(4-chlorophenyl)-5-aryl-3H-furan-2-ones and 3,3-di(p-tolyl)-5-aryl-3H-furan-2-ones were synthesised by neat thermolysis of the corresponding (Z)-1,2-bis(4-chlorophenyl)-4-arylbut-2-ene-1,4-dione and (Z)-1,2-di(p-tolyl)-4-arylbut-2-ene-1,4-dione precursors respectively. Irradiation of these furanones were carried out under different conditions. While sensitized irradiation of these furanones in hexane resulted in exclusive formation of dimers, that in acetonitrile did not produce even a trace amount of it: 1,2-aryl migration leading to phenanthrofuranone along with decarbonylation was observed in this case.

4.2. Introduction

The construction of small and medium sized *O*-heterocyclic rings is a cornerstone of natural product synthesis.[1-3] Dibenzoylalkene rearrangement is a useful method for the synthesis of a variety of such heterocyclic derivatives.[4-7] Dibenzoylstyrene (**3**) is conveniently synthesised by the base-catalyzed condensation between benzil and acetophenone. Thermolysis of **3**



1 2 3 4

Scheme 1

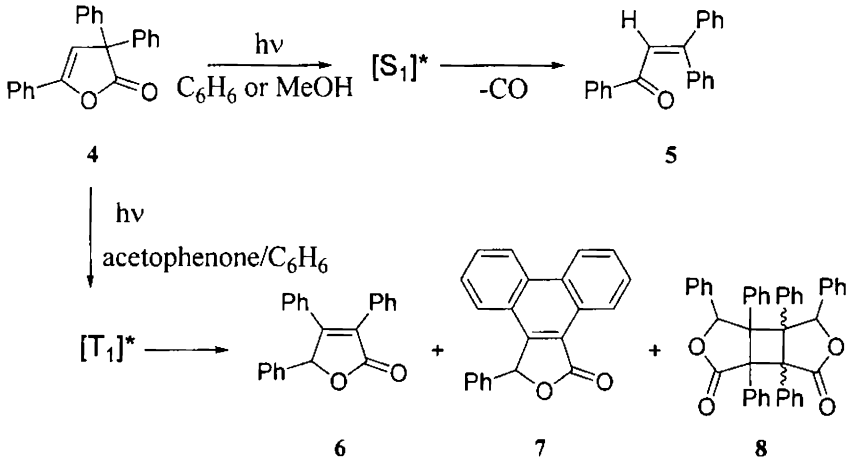
and related systems lead to 2(3*H*)-furanones, which exhibit rich photochemistry (Scheme 1).[8,9] By the application of Claisen-Schmidt condensation we synthesised several dibenzoylstyrene derivatives from 4,4'-dichlorobenzil and 4,4'-dimethylbenzil using appropriate methyl ketones. Since 3,3,5-triphenyl-3*H*-furan-2-one **(4)** could be prepared in good yields by the thermolysis of dibenzoylstyrene **(3)**, we reasoned that our target molecules could also be conveniently synthesised by the same methodology.

Past investigations have shown that unsaturated lactones undergo a variety of phototransformations some of which includes decarbonylation,[10,11] decarboxylation,[12] solvent addition to double bonds,[13,14,15] migration of aryl substituents[15] and dimerisation.[16] Phototransformations of a number of 2(3*H*)-furanones has been studied based on steady state irradiation, product analysis and laser flash photolysis.

For 3,3,5-triphenyl-3*H*-furan-2-one **(4)** the prominent excited state reaction pathways available include singlet mediated decarbonylation to give an α,β-unsaturated carbonyl compound and triplet mediated reaction leading to the formation of 3,4,5-triphenyl-2(5*H*)-furnanone **(6),** and products derived thereof such as 5-phenylphenanthro[9,10-c]furan-2(5*H*)-one **(7)** and a photodimer tentatively identified as **8** (Scheme 2).[16,18,19]

The photochemical rearrangement of 3,3,5-triphenyl-3*H*-furan-2-one **(4)** to give the corresponding 2(5*H*)-furanone **6** and the subsequent formation of the phenanthrofuranone **7** can be explained in terms of a pathway involving triplet-excited state.[20] In the triplet-excited state, which can be visualised in terms of a diradical structure, one of the C-3 aryl groups migrates to C-4 to give the rearranged diradical intermediate. Electron demotion will then lead to a zwitterionic intermediate. In the absence of protic solvents, the zwitterionic

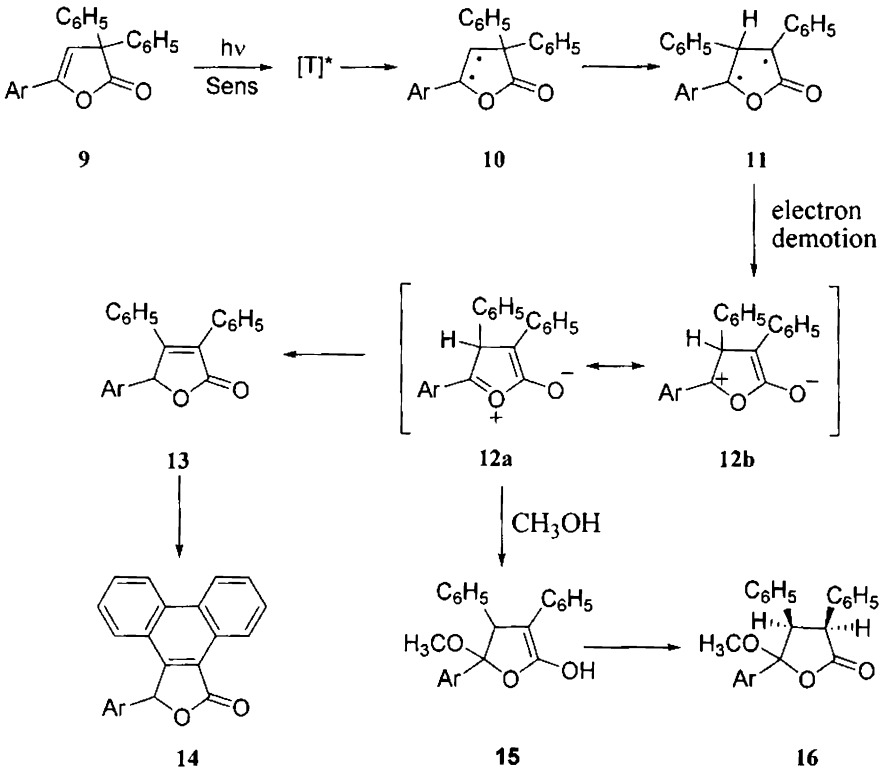
intermediate undergoes a hydride shift to give the rearranged 3,4,5-triphenyl-2(5*H*)-furanone **6** which in turn absorbs light and undergoes further photocyclisation leading to dihydrophenanthrofuranone **7**. Alternatively, the 2(5*H*)-furanone **6** can undergo [2+2] photocycloaddition leading to the dimeric product **8** (Scheme 2).



Scheme 2

The photochemistry of a series of 5-aryl-3,3-diphenyl-3*H*-furan-2-one **9**, containing electron releasing as well as electron withdrawing para substituents on the phenyl group at the C-5 position has been investigated.[20] While photodecarbonylation to 1-aryl-3,3-diphenylprop-2-en-1-ones dominates in the course of direct photolysis in methanol and benzene, triplet sensitization by *p*-methoxyacetophenone results in C_3-C_4 phenyl group migration leading to 5-aryl-3,4-diphenyl-2(5*H*)-furanones **13** and in certain cases in the formation of photodimers. Under exhaustive photolysis, the 2(5*H*)-furanones **13** undergo electrocyclic reactions to dihydrophenanthrene

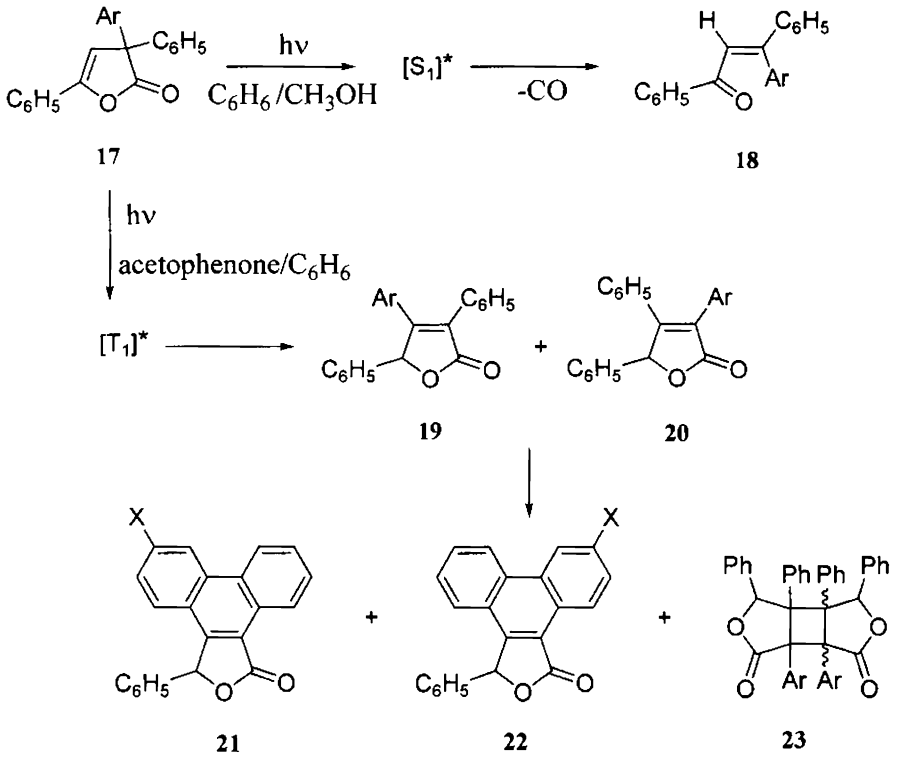
type products which, during workup are oxidised to 3-arylphenanthro[9,10-c]furan-1-(3*H*)-ones **14** (Scheme 3).



9 **10** **11** **12a** **12b** **13** **14** **15** **16**

Scheme 3

Studies on the effects of substituents at the C-3 position of 3-aryl-3,5-diphenyl-3*H*-furan-2-ones reveal that the triplet decay of these photoreactive 2(3*H*)-furanones is predominantly controlled by the aryl group migration.[19] The reaction rate is slowed down by both electron-releasing and electron-withdrawing substituents at the 4-position of the phenyl group at the C-3 position of the aryl substituted 2(3*H*)-furanones (Scheme 4).[20]



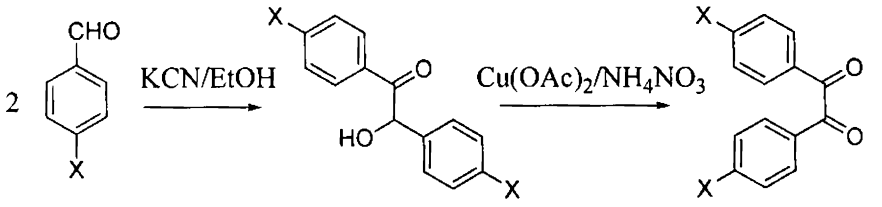
Scheme 4

In the present study, we have examined the sensitized photorearrangements of 3,3-bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones **30a,b** and 3,3-di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones **30c,d** to explore the effect of two aryl groups at the 3-position in controlling the nature of these reactions. The required 2(3*H*)-furanones were synthesised by the cyclisation of (*Z*)-1,2-bis(4-chlorophenyl)-4-arylbut-2-ene-1,4-diones **28a,b** and (*Z*)-1,2-di(*p*-tolyl)-4-aryl-but-2-ene-1,4-diones **28c,d** respectively.

4.3. Results and Discussion

4.3.1. Synthesis of 1,2-Bis(4-chlorophenyl)ethane-1,2-dione (26a), 1,2-Di(*p*-tolyl)ethane-1,2-dione (26b) and 1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (26c).

Benzils and other α-dicarbonyl compounds, in general, are important materials due to their practical applications, i.e. as starting materials for the synthesis of heterocycles[21-23] and as photosensitive agents.[24] Benzoins constitute a convenient intermediate for the preparation of benzils. For the oxidation of benzoins to the corresponding benzils catalytic amount of cupric acetate in the presence of ammonium nitrate was employed. Here the cupric salt is regenerated internally by ammonium nitrate. Since this reaction is run in acetic acid, the solvent performs a duel role by decomposing the formed ammonium nitrite, while serving as an excellent medium to crystallize the diketones. Accordingly 4,4'-dimethoxy, 4,4'-dimethyl and 4,4'-dichloro substituted benzils were prepared from the commercially available aldehydes by benzoin condensation with potassium cyanide in aqueous ethanol[25,26] followed by cupric acetate oxidation of crude benzoins to benzils (Scheme 6).



24a-c **25a-c** **26a-c**

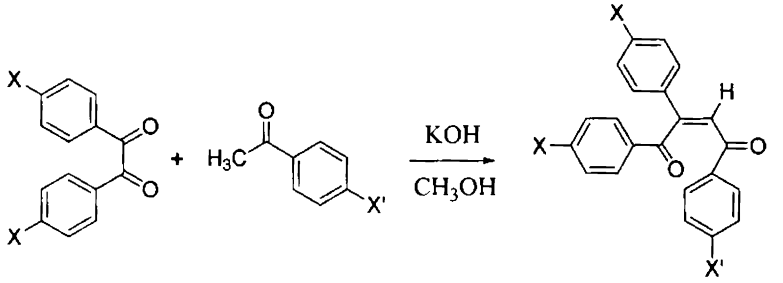
a) X = Cl b) X = Me c) X = OMe

Scheme 5

The structures of product were established on the basis of literature precedence,[27] analytical results and spectral data. The reaction proceeded under mild conditions and only minimal amount of undesirable side-products were formed.

4.3.2. Synthesis of (*Z*)-1,2-Bis(4-chlorophenyl)-4-arylbut-2-ene-1,4-diones (28a, b) and (*Z*)-1,2-Di(*p*-tolyl)-4-arylbut-2-ene-1,4-diones (28c,d)

Claisen–Schmidt condensation is a useful method for the synthesis of α, β-unsaturated ketones.[28,29] It is the condensation of an aromatic aldehyde with an enolate of an aliphatic aldehyde or ketone. By the application of this reaction, we synthesized dibenzoylstyrene derivatives from 1,2-bis(4-chlorophenyl)ethane-1,2-dione **(26a)** and 1,2-di(*p*-tolyl)ethane-1,2-dione **(26b)** using appropriate methyl ketones. The methyl ketones of our interest were acetophenone and 4-chloroacetophenone. The products were obtained in good yields and the structure of compounds was established on the basis of analytical results and spectral data. On the basis of literature precedence, *Z*-configuration was assigned to these molecules.[30]



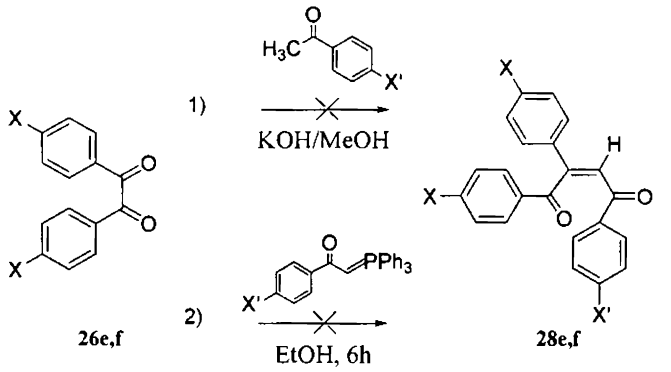
26a-d **27a-d** **28a-d**

a) X = Cl X' = H b) X = Cl X' = Cl c) X = Me X' = H d) X = Me X' = Cl

Scheme 6

Compound *(Z)*-1,2-bis(4-chlorophenyl)-4-phenylbut-2-ene-1,4-dione **(28a)** was obtained in 60% yield and showed strong IR absorptions at 1665 cm^{-1} and 1658 cm^{-1} due to two carbonyl groups present in this molecule. ^1H NMR spectrum showed a multiplet at δ 7.31-8.33 corresponding to thirteen aromatic protons and one vinylic proton in the molecule. Similarly *(Z)*-1,2,4-tris(4-chlorophenyl)but-2-ene-1,4-dione **(28b)** obtained in 58% yield showed strong IR absorptions at 1668 cm^{-1} and 1651 cm^{-1}. ^1H NMR spectrum showed a multiplet at δ 7.12-8.18 corresponding to twelve aromatic protons and one vinylic proton in the molecule. (*Z*)-4-Phenyl-1,2-di(*p*-tolyl)but-2-ene-1,4-dione **(28c)** was also obtained in around 56% yield and showed strong IR absorptions at ~1660 cm^{-1} and ~1655 cm^{-1} due to the two carbonyl groups. ^1H NMR spectrum showed a singlet at δ 2.32 due to six methyl protons and multiplet at ~ δ 7.16-8.24 corresponding to thirteen aromatic and one vinylic proton in the molecule. With (*Z*)-4-(4-chlorophenyl)-1,2-di(*p*-tolyl)but-2-ene-1,4-dione **(28d),** carbonyl groups showed absorptions at 1662 cm^{-1} and 1650 cm^{-1}. In the ^1H NMR spectrum a singlet at δ 2.45 indicates six methyl protons and multiplet at ~ δ 7.31-8.20 corresponds to twelve aromatic and one vinylic proton in the molecule.

Apart from these we also attempted the Claisen–Schmidt condensation of 1,2-bis(4-methoxyphenyl)ethane-1,2-dione **(26c)** with para substituted acetophenones. But the reaction was not successful and **26c** was recovered unchanged. As an alternative, we tried Wittig reaction,[31,32] which is one of the premier methods for the synthesis of alkenes. It uses a carbonyl compound as an electrophile, which is attacked by a phosphorus ylide (the Wittig reagent). Accordingly we carried out Wittig reaction between anisil and phenacyl bromide derived Wittig ylide. But starting diketone was recovered unchanged.



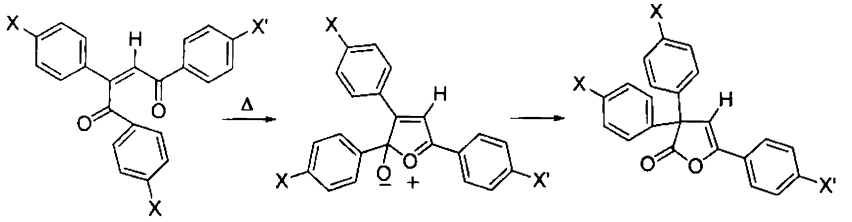
26e,f **28e,f**

e) X = OMe X' = H f) X = OMe X' = Cl

Scheme 7

4.3.3. Synthesis of 3,3-Bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones 30a,b and 3,3-Di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones 30c,d.

Dibenzoylalkenes undergo a variety of striking reactions on thermolysis. These reactions include ring closure, ring opening as well as ring enlargement and contraction.[5,6,7,8] Based on the reports that dibenzoylstyrene and related systems leads to 2(3*H*)-furanones on thermolysis,[33,34] we reasoned that the required compounds can also be conveniently synthesised following the above strategy.



28a-d **29a-d** **30a-d**

a) X = Cl X' = H b) X = Cl X' = Cl c) X = Me X' = H d) X = Me X' = Cl

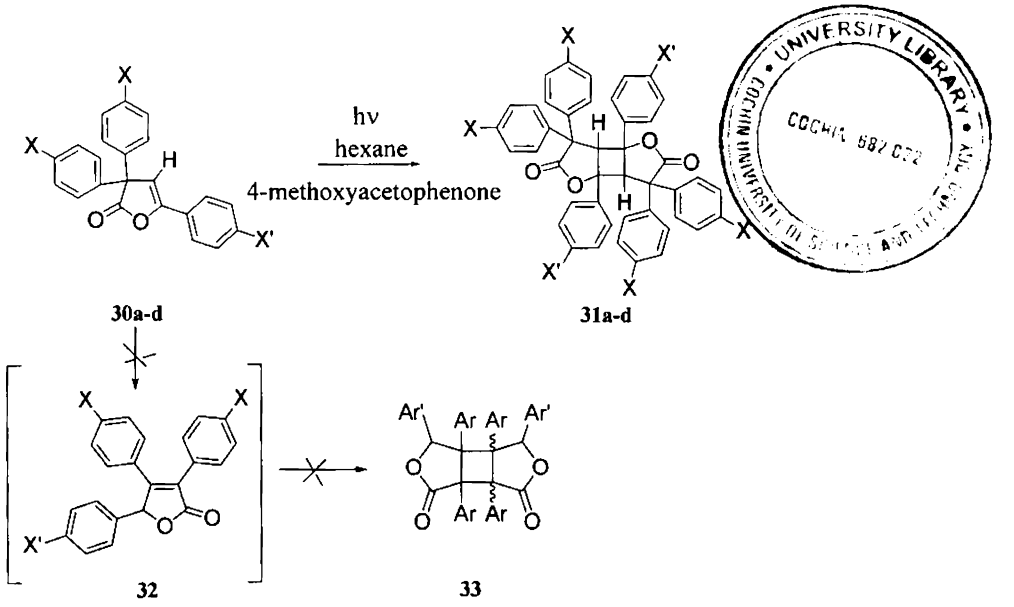
Scheme 8

Based on this assumption, we successfully synthesised a few 3,3-bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones and 3,3-di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones from the corresponding dibenzoylstyrene precursors. The structure of these furanones was confirmed on the basis of spectral and analytical results. 3,3-Bis(4-chlorophenyl)-5-phenyl-3*H*-furan-2-one **(30a)** was obtained in 35% yield and showed strong IR absorptions at 1780 cm^{-1} and 1653 cm^{-1} due to carbonyl group and C=C group respectively in the compound. ^{1}H NMR spectrum showed a singlet at δ 6.20 corresponding to the vinylic proton and a multiplet at δ 7.21-7.60 corresponding to thirteen aromatic protons in the molecule. In ^{13}C NMR spectra signal was observed at δ 60.94 due to methyl carbon. Signals due to aromatic carbons were observed in the region δ 105.65–152.50. The signal observed at δ 176.46 is attributed to carbonyl carbon. Similarly 3,3,5-tris(4-chlorophenyl)-3*H*-furan-2-one **(30b)** obtained in 32% yield showed strong IR absorptions at 1774 and 1650 cm^{-1}. ^{1}H NMR spectrum of this compound showed a singlet at δ 6.00 corresponding to one vinylic proton and a multiplet at δ 7.09-7.62 corresponding to twelve aromatic protons. 5-Phenyl-3,3-di(*p*-tolyl)-3*H*-furan-2-one **(30c)** was obtained in 30% yield and showed strong IR absorptions at 1790 cm^{-1} and 1649 cm^{-1} due to one carbonyl group and C=C group respectively in the compound. In the ^{1}H NMR spectrum, two singlets were observed at δ 2.34 and δ 6.31 indicating the presence of six methyl protons and one vinylic proton respectively. Signals due to aromatic protons were observed in the region δ 7.12–7.56. The ^{13}C NMR spectrum showed peaks at δ 20.99 and δ 177.29 due to methyl and carbonyl carbons. Similarly 5-(4-chlorophenyl)-3,3-di(*p*-tolyl)-3*H*-furan-2-one **(30d)** obtained in 34% yield showed strong IR absorptions at 1771 cm^{-1} and 1658 cm^{-1}. The ^{1}H NMR spectrum of this compound showed a singlet at δ 2.35 corresponding to six methyl protons and a multiplet at δ 7.12-7.69

corresponding to twelve aromatic protons. Signal due to vinylic proton was observed as a singlet in the region δ 6.10. The ^{13}C NMR spectrum also showed data that suit the mentioned compound.

4.3.4. Sensitized Irradiation of 3,3-Bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones 30a,b and 3,3-Di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones 30c,d.

To gain insight into the electronic makeup of the excited state in the photorearrangement of 2(3*H*)-furanones we examined the reactions of different furanones containing various substituents in the para position of phenyl group in polar and nonpolar solvents. Since it is well known that on direct irradiation almost all 2(3*H*)-furanones undergo decarbonylation we attempted a few sensitized irradiation experiments.[10,11,17,18]



a) X = Cl X' = H b) X = Cl X' = Cl c) X = Me X' = H d) X = Me X' = Cl

Scheme 9

The photolysis (λ = 300 nm) of **30a-d** in hexane with 4-methoxyacetophenone as sensitizer yielded product that exhibited poor solubility in common organic solvents and melting above 315 ^{0}C. Earlier reports on aryl substituted 2(3*H*)-furanones[18,19] suggested that these compounds on sensitized irradiation undergo 1,2-phenyl migration leading to 2(5*H*)-furanones which further undergo [2+2] addition to give corresponding dimer. Based on the literature precedence, we tentatively concluded that the product, indeed, is a dimer **31a-d**. Intriguingly, formation of other products arising through aryl migration such as 2(5*H*)-furanones and phenanthrofuranones was not detected. So we decided to examine the structure of the photodimer closely.

Though the products exhibited poor solubility in common solvents, we could record both ^{1}H NMR and ^{13}C NMR spectra of acceptable quality of a representative sample such as **31a**. ^{1}H NMR spectrum of the dimer **31a** showed a sharp singlet at δ 4.93. In the ^{13}C NMR spectrum, signals attributable to aliphatic carbons were observed at δ 62.84, δ 66.13 and δ 88.38. Out of these, the signal observed at δ 62.84 and δ 66.13 corresponds to a CH whereas the signal at δ 88.38 is attributable to the tetrasubstituted carbons. Based on the wide difference in the chemical shift positions of the two tetrasubstituted carbons, we concluded that the signal observed at δ 88.38 is due to a carbon attached to oxygen. If the dimer is arising through the dimerisation of the rearranged 2(5*H*)-furanone the methine signal would have appeared more downfield. Based on these data we concluded that the structure of the dimer is better represented as **31a** arising through the head-to-tail dimerisation of starting 2(3*H*)-furanone. Compounds **31b-d** also showed related ^{1}H NMR results. The structure was further confirmed by elemental analysis, which gave acceptable data.

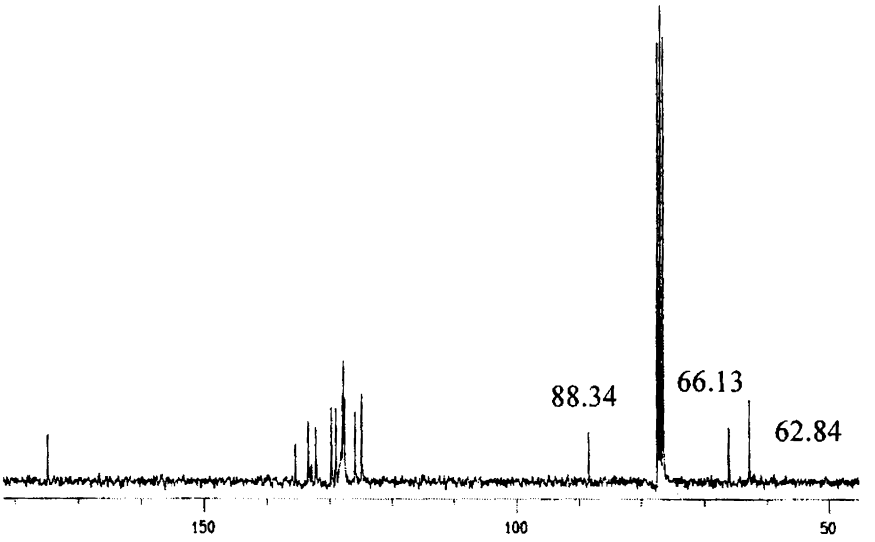
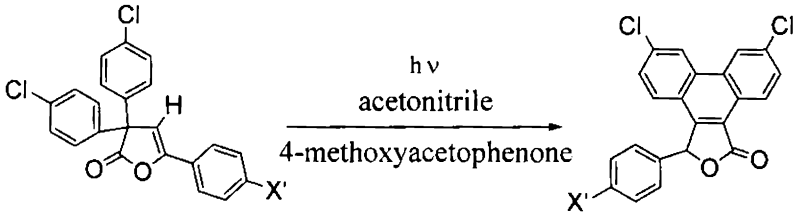


Figure 1: ^{13}C NMR Spectrum of **31a**

Compounds **30a-d** were again subjected to photolysis (λ = 300 nm) under 4-methoxyacetophenone sensitization in acetonitrile. With compounds **30a,b** workup of the photolysate afforded 6,9-dichloro-3-arylphenanthro[9,10-c]furan-1-(3*H*)-one **34a,b** as white solid in moderate yields (~33%). The structure of compounds **34a,b** were established on the basis of analytical results and spectral data. Compound **34a** obtained in 30% yield showed strong absorptions at 1760 cm^{-1} indicating the presence of carbonyl group in the compound. In the ^1H NMR spectrum, singlet at δ 6.64 corresponds to methine proton. Aromatic protons were observed as a multiplet between δ 7.23– 9.14. The structure was further confirmed by elemental analysis, which gave acceptable data. Compound **34b** also showed analogous spectral behaviour. The strong absorption at 1766 cm^{-1} in the IR spectrum showed the presence of carbonyl group in the compound. Here also a singlet at δ 6.36 in the ^1H NMR spectrum corresponds to methine proton. Aromatic protons were

observed as a multiplet between δ 7.16– 9.17. It may be mentioned here that the ^{1}H NMR signal at ~δ 6.36 and carbonyl stretching frequency at ~1760cm^{-1} are characteristic of 3,4,5-triaryl-2(5*H*)-furanone. For 3,3,5-triaryl-2(3*H*)-furanones, the corresponding signals appear at ~δ 6.2 and 1780cm^{-1} respectively. Thus 2(3*H*)-furanone to 2(5*H*)-furanone isomerisation can be conveniently followed by ^{1}H NMR and IR spectral analysis.



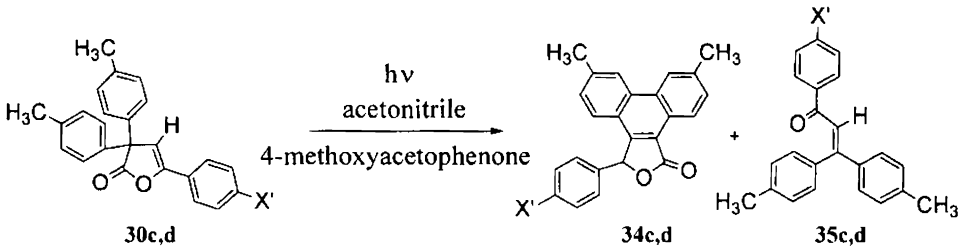
30a,b **34a,b**

a) X' = H b) X' = Cl

Scheme 10

With compounds **30c,d** decarbonylation was also observed resulting in 1-aryl-3,3-di(*p*-tolyl)-propenone **35c,d** apart from photorearrangement to 6,9-dimethyl-3-arylphenanthro[9,10-c]furan-1-(3*H*)-ones **34c,d.** Compound **34c** obtained in 33% yield showed strong absorption at 1768 cm^{-1}indicating the presence of carbonyl carbon. In the ^{1}H NMR spectrum, peak at δ 2.40 corresponds to methyl protons and that at δ 6.67 indicates methine proton. Aromatic protons were observed as a multiplet between δ 7.19– 9.18. Structure of the photoproduct was further confirmed by elemental analysis that gave acceptable data. Compound **34d** also showed related spectral behaviour to that of compound **34c**. Compound **35c** was obtained in 20% yield and showed strong absorptions at 1658 cm^{-1} in the IR spectrum due to carbonyl groups. In the ^{1}H NMR spectrum, methyl protons were observed as a singlet in the region δ 2.45, the vinylic and aromatic

protons were observed as multiplet around ~ δ 7.10– 7.54. Structure of the compound was further confirmed by elemental analysis that gave acceptable data. Compound **35d** also showed analogous spectral behaviour to that of compound **35c.**

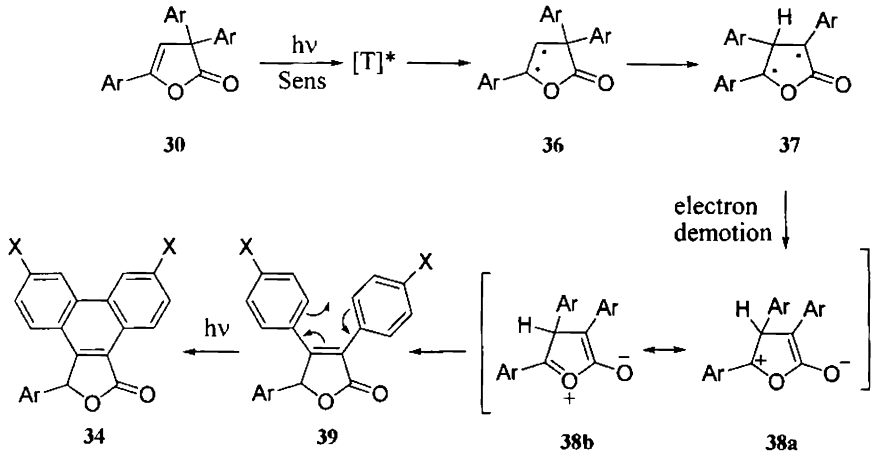


30c,d **34c,d** **35c,d**

c) X = H d) X = Cl

Scheme 11

The triplet sensitized rearrangement of 2(3*H*)-furanones **30a-d** to phenanthrofuranone **34a-d** can be explained in terms of pathway shown in scheme 12.

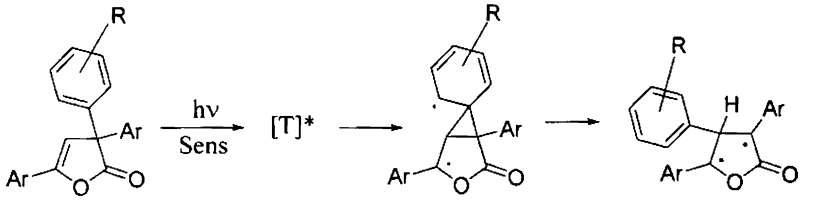


30 **36** **37** **34** **39** **38b** **38a**

Scheme 12

In the triplet excited state having substantial diradical nature, one of the C-3 aryl groups migrates to C-4 to give the rearranged diradical intermediate **37**. Electron demotion in **37** will lead to a zwitterionic intermediate **38** which then undergoes a hydride shift to give the rearranged 3,4,5-triphenyl-2(5*H*)-furanone **39.** Further photocyclisation of this compound occur leading to dihydrophenanthrofuranone **34** which under the condition of workup gave phenanthrofuranone.

Based on the mechanism suggested by Padwa[35,36] to account for analogous 1,2-aryl migration in 3,5-diaryl-2(5*H*)-furanones, a di-π-methane rearrangement type mechanism may also be postulated here for the generation of diradical intermediate **37** (Scheme 13). Based on available data, it is not possible to differentiate between these two possibilities.



30 **40** **37**

Scheme 13

4.4. Conclusion

In summery, 3,3-Bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones and 3,3-di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones were synthesised from (*Z*)-1,2-bis(4-chloro- phenyl)-4-arylbut-2-ene-1,4-dione and (*Z*)-1,2-di(*p*-tolyl)-4-arylbut-2-ene-1,4-dione precursor respectively. Sensitized irradiations of these 2(3*H*)-furanones were carried out in hexane and acetonitrile using

4-methoxyacetophenone as sensitizer. On sensitized irradiation in hexane they underwent [2+2] cycloaddition to yield the dimer whereas in acetonitrile 1,2-aryl migration was the major reaction..

4.5. Experimental

4.5.1. 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. Visualization 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 infra red spectra were recorded using ABB Bomem (MB Series) FT-IR spectrometer. All steady state irradiations were carried out using Rayonet Photochemical Reactor (RPR). Solvents for photolysis were purified and distilled before use. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively on a Bruker 300 FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane. Elemental analysis was performed using Elementar Systeme (Vario ELIII) at STIC, Kochi.

4.5.2. Starting Materials: 4-Chlorobenzaldehyde, *p*-tolualdehyde, *p*-anisaldehyde, acetophenone and 4-chloroacetophenone were purchased from Sigma-Aldrich and were used as obtained.

4.5.2.1. 1,2-Bis(4-chlorophenyl)-2-hydroxyethanone (25a): Prepared using a known procedure (75%, mp 84 ^{0}C).[34]

4.5.2.2. 2-Hydroxy-1,2-di(*p*-tolyl)ethanone (25b): Prepared using a known procedure (70%, mp 66^{0}C).[34]

4.5.2.3. 2-Hydroxy-1,2bis(4-methoxyphenyl)ethanone (25c): Prepared using a known procedure (72%, mp 69^{0}C).[34]

4.5.3. Synthesis of 1,2-Bis(4-chlorophenyl)ethane-1,2-dione (26a)

Cupric acetate (0.07 g, 0.4 mmol), ammonium nitrate (3.6 g, 44.6 mmol), 1,2-bis(4-chlorophenyl)-2-hydroxyethanone (10.0 g, 35.7 mmol) and 30 mL of 80% aqueous acetic acid were taken in a round bottom flask fitted with a water condenser. The mixture was heated with occasional shaking for 1h. The solid separated was collected by filtration and recrystallised from methanol to yield **27a** (68%; mp 196 ^{0}C).

4.5.4. Synthesis of 1,2-Di(*p*-tolyl)ethane-1,2-dione (26b)

Cupric acetate (0.08 g, 0.4 mmol), ammonium nitrate (3.2 g, 39.5 mmol), 2-hydroxy-1,2-di*p*-tolylethanone (10.0 g, 42.0 mmol) and 30 mL of 80% aqueous acetic acid were taken in a round bottom flask fitted with a water condenser. The mixture was heated with occasional shaking for 1h. The solid separated was collected by filtration and recrystallised from methanol to yield **27b** (65%; mp 103 ^{0}C).

4.5.5. Synthesis of 1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (26c)

Cupric acetate (0.07 g, 0.4 mmol), ammonium nitrate (3.5 g, 43.1 mmol), 2-hydroxy-1,2-bis(4-methoxyphenyl)ethanone (10.0 g, 35.5 mmol) and 30 mL of 80% aqueous acetic acid were taken in a round bottom flask fitted with a water condenser. The mixture was heated with occasional shaking for 1 h.

The solid separated was collected by filtration and recrystallised from methanol to yield **27c** (64%; mp 128 ^{0}C).

4.5.6. Synthesis of (*Z*)-1,2-Bis(4-chlorophenyl)-4-arylbut-2-ene-1,4-diones 28a,b

4.5.6.1. (*Z*)-1,2-Bis(4-chlorophenyl)-4-phenylbut-2-ene-1,4-dione (28a): A mixture of 1,2-bis(4-chlorophenyl)ethane-1,2-dione (5.0 g, 17.0 mmol), acetophenone (2.1 g, 18 mmol) and powdered potassium hydroxide (1.0 g) in methanol (60 mL) was stirred around 60 ^{0}C for 1 h and later kept in refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **28a** as a light yellow solid.

Compound 28a (60%); mp 174 ^{0}C; IR (KBr) 1665 and 1658 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-8.33 (m, 14H, aromatic and vinylic protons); Anal. Calcd for $C_{22}H_{14}O_2Cl_2$: C, 69.31; H, 3.70. Found C, 69.28; H, 3.81.

4.5.6.2. (*Z*)-1,2,4-Tris(4-chlorophenyl)but-2-ene-1,4-dione (28b): A mixture of 1,2-bis(4-chlorophenyl)ethane-1,2-dione (5 g, 17.0 mmol), 4-chloroacetophenone (2.6 g, 18 mmol) and powdered potassium hydroxide (1.0 g) in methanol (60 mL) was stirred around 60 ^{0}C for 1 h and later kept in refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **(28b)** as a light yellow solid.

Compound 28b: (58%); mp 172 ^{0}C; IR (KBr) 1668 and 1651 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12-8.18 (m, 13H, aromatic and vinylic protons); Anal. Calcd for $C_{22}H_{13}O_2Cl_3$: C, 63.56; H, 3.15. Found C, 63.51; H, 3.2.

4.5.7. Synthesis of (*Z*)-1,2-di(*p*-tolyl)-4-arylbut-2-ene-1,4-diones 28c,d

4.5.7.1. (*Z*)-4-Phenyl-1,2-di(*p*-tolyl)but-2-ene-1,4-dione (28c): A mixture of 1,2-di(*p*-tolyl)ethane-1,2-dione (5.0 g, 21.0 mmol), acetophenone (2.3 g, 19.5 mmol) and powdered potassium hydroxide (1.0 g) in methanol (60 mL) was stirred around 60 ^{0}C for 1 h and later kept in refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **29c** as a light yellow solid.

Compound 28c: (56%); mp 126 ^{0}C; IR (KBr) 1660 and 1655 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 6H, methyl protons), 7.16-8.24 (m, 14H, aromatic and vinylic protons); Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found C, 84.71; H, 5.60.

4.5.7.2. (*Z*)-4-(4-Chlorophenyl)-1,2-di(*p*-tolyl)but-2-ene-1,4-dione (28d): A mixture of 1,2-di(*p*-tolyl)ethane-1,2-dione (5.0 g, 21.0 mmol), 4-chloroacetophenone (3.0 g, 19.5 mmol) and powdered potassium hydroxide (1.0 g) in methanol (60 mL) was stirred around 60 ^{0}C for 1 h and later kept in refrigerator for 48 h. The solid product that separated out was filtered and purified by recrystallisation from a mixture (2:1) of methanol and dichloromethane to give **28d** as a light yellow solid.

Compound 28d : (58%); mp 133 ^{0}C; IR (KBr) 1662 and 1650 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 6H, methyl protons) 7.31-8.20 (m, 13H, aromatic and vinylic protons); Anal. Calcd for $C_{24}H_{19}O_2Cl$: C, 76.90; H, 5.11. Found C, 76.93; H, 5.09.

4.5.8. Attempted synthesis of 1,2-Bis(4-methoxyphenyl)-4-phenylbut-2-ene-1,4-dione (28e): A mixture of 1,2-bis(4-methoxyphenyl)ethane-1,2-dione

(4.0 g, 14.8 mmol), acetophenone (1.6 g, 13 mmol) and powdered potassium hydroxide (1.0 g) in methanol (60 mL) was stirred around 60 ^{0}C for 1 h and later kept in refrigerator for 48 h. After workup starting compound was recovered unchanged.

4.5.9. Attempted Synthesis of 1,2-Bis(4-methoxyphenyl)-4-phenylbut-2-ene-1,4-dione (28e) by Wittig reaction

A solution of 1,2-Bis(4-methoxyphenyl)ethane-1,2-dione **(26c)** (0.2 g, 0.7 mmol) and triphenylphosphinebenzoylmethylene (0.3 g, 0.7 mmol) in ethanol (30 mL) was stirred at room temperature for 8 h. The starting compound was recovered unchanged at the end of the reaction

4.5.10. Synthesis of 3,3-Bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones 30a,b

4.5.10.1. 3,3-Bis(4-chlorophenyl)-5-phenyl-3*H*-furan-2-one (30a): A sample of **28a** (1.0 g, 2.6 mmol) was thermolysed in a sealed tube at 220 ^{0}C for 6 h. The residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **30a** as a white solid (35%). Further elution of the column with a mixture (3:2) of hexane and dichloromethane gave unchanged **28a**.

Compound 30a: (35%); mp 136 ^{0}C; IR (KBr) 1780 (C=O) and 1653 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20 (s, 1H, vinylic), 7.21-7.60 (m, 13H, aromatic); ^{13}C NMR ($CDCl_3$) δ 60.94, 105.65, 124.73, 125.03, 128.93, 129.04, 129.50, 134.01, 138.42, 140.63, 152.50, 176.46; Anal. Calcd for $C_{22}H_{14}O_2Cl_2$: C, 69.31; H, 3.57. Found C, 69.1; H, 3.53.

4.5.10.2. 3,3,5-Tris(4-chlorophenyl)-3*H*-furan-2-one (30b): A sample of **28b** (1.0 g, 2.4 mmol) was thermolysed in a sealed tube at 240 ^{0}C for 6 h. The residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **30b** as a white solid. Further elution of the column with a mixture (3:2) of hexane and dichloromethane gave unchanged **28b.**

Compound 30b:(32%); mp 152 ^{0}C; IR (KBr) 1774 (C=O) and 1650 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.0 (s, 1H vinylic), 7.09-7.62 (m, 12H, aromatic); Anal. Calcd for $C_{22}H_{13}O_2Cl_3$: C, 63.56; H, 3.15. Found C, 63.51; H, 3.20.

4.5.11. Synthesis of 3,3-Di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones 30c,d

4.5.11.1. 3,3-Di(*p*-tolyl)-5-phenyl-3*H*-furan-2-one (30c): A sample of **28c** (1.0 g, 2.7 mmol) was thermolysed in a sealed tube at 220 ^{0}C for 6 h. The residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave **30c** as a white solid. Further elution of the column with a mixture (3:2) of hexane and dichloromethane gave unchanged **28c**

Compound 30c:(30%); mp 114 ^{0}C; IR (KBr) 1790 (C=O) and 1649 (C=C) cm^{-1}; UV λ_{max} (CH_3CN) 243 (ε 4,520), 250 (ε 4,280), 270 (ε 5,920), 283 (ε 5,590), 298 (ε 1,920), 300 (ε 1,680), 306 (ε 680), 351 (ε 120) nm ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H, methyl protons), 6.31 (s, 1H, vinylic proton), 7.12-7.56 (m, 13H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 20.99, 61.42, 108.07, 124.98, 127.44, 128.11, 128.67, 129.45, 129.80, 137.36, 137.50, 151.50, 177.29 Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found C, 84.50; H, 5.81.

4.5.11.2. 5-(4-Chlorophenyl)-3,3-di(*p*-tolyl)-3*H*-furan-2-one (30d): A sample of **28d** (1.0 g, 2.5 mmol) was thermolysed in a sealed tube at 250 ^{0}C for 6 h. The residue was extracted with dichloromethane and chromatographed over silica gel. Elution with a mixture of (4:1) hexane and dichloromethane gave **30d** as a white solid. Further elution of the column with a mixture (3:2) of hexane and dichloromethane gave unchanged **28d**

Compound 30d:(34%); mp 138 ^{0}C; IR (KBr) 1771 (C=O) and 1658 (C=C) cm^{-1}; UV λ_{max} (CH_3CN) 246 (ε 4,320), 255 (ε 4,460), 266 (ε 5,680), 290 (ε 3,710), 294 (ε 2,760), 302 (ε 1,350), 330 (ε 240), 358 (ε 100) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 6H, methyl protons), 6.10 (s, 1H, vinylic proton), 7.12-7.69 (m, 12H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 22.30, 62.14, 110.92, 124.76, 127.23, 128.56, 129.21, 129.90, 136.9, 137.40, 158.23, 177.85 Anal. Calcd for $C_{24}H_{19}O_2Cl$: C, 76.91; H, 5.11. Found C, 76.80; H, 5.16.

4.5.12. Irradiation of 3,3-Bis(4-chlorophenyl)-5-aryl-3*H*-furan-2-ones 30a,b

4.5.12.1. 3,3-Bis(4-chlorophenyl)-5-phenyl-3*H*-furan-2-one (30a)

4.5.12.1a. Sensitized Irradiation of 30a in Hexane

A solution of **30a** (0.2 g, 0.53 mmol) and *p*-methoxyacetophenone (0.08g, 0.53 mmol) in 130 mL hexane purged with nitrogen for 20 min was irradiated (RPR, 300 nm,) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was washed with a mixture (1:1) of hexane and dichloromethane to give **31a** as white solid.

Compound 31a:(70%); mp > 315 ^{0}C ; IR (KBr) 1774 cm^{-1}(C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.93 (s, 2 H, aliphatic protons), 6.57-7.52 (m, 26 H,

aromatic protons); ^{13}C NMR ($CDCl_3$) δ 62.84, 66.13, 88.38, 124.93, 125.95, 127.70, 127.85, 127.90, 128.01, 128.24, 128.60, 129.11, 129.82, 132.25, 133.49, 135.56, 174.89; Anal. Calcd for $C_{44}H_{28}O_4Cl_4$: C, 69.31; H, 3.70. Found C, 69.24; H, 3.49.

4.5.12.1b. Sensitized Irradiation of 30a in Acetonitrile

A solution of **30a** (0.2 g, 0.53 mmol) and *p*-methoxyacetophenone (0.08g, 0.53mmol) in 130 mL acetonitrile purged with nitrogen for 20 min was irradiated (RPR, 300 nm,) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave unchanged starting material **30a.**

Continued elution of the column with a mixture (1:4) of hexane and dichloromethane yielded **34a** as white solid

Compound 34a: (30%); mp 267 ^0C; IR (KBr) 1760 cm^{-1} (C=O); UV λ_{max} (CH_3CN) 250 (ε 28,400), 256 (ε 29,400), 274 (ε 8,680), 300 (ε 6,850), 311 (ε 4,760), 342 (ε 3,350) 352 (ε 2,150);;^1H NMR (300 MHz, $CDCl_3$) δ 6.64 (s, 1H, aliphatic proton), 7.23-9.14 (m, 11H, aromatic protons); Anal. Calcd for $C_{22}H_{12}O_2Cl_2$: C, 69.67; H, 3.19. Found C, 69.59; H, 3.23.

4.5.12.2. 3,3,5-Tris(4-chlorophenyl)-3*H*-furan-2-one (30b)

4.5.12.2a. Sensitized Irradiation of 30b in Hexane

A solution of **30b** (0.2 g, 0.58 mmol) and *p*-methoxyacetophenone (0.07 g, 0.58 mmol) in hexane (130 mL) purged with nitrogen for 20 min was irradiated (RPR, 300 nm,) for 2 h. Progress of the reaction was monitored by

TLC. Solvent was removed under vaccum and the residue was washed with a mixture (1:1) of hexane and dichloromethane to give **31b** as white solid

Compound 31b: (74%); mp > 315 ^{0}C; IR (KBr) 1779 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.82 (s, 2 H, aliphatic protons), 6.71-7.49 (m, 24 H, aromatic protons); Anal. Calcd for $C_{44}H_{26}O_4Cl_6$: C, 63.56; H, 3.17. Found C, 62.99; H, 3.19.

4.5.12.2b. Sensitized Irradiation of 30b in Acetonitrile

A solution of **30b** (0.2 g, 0.58 mmol) and *p*-methoxyacetophenone (0.07 g, 0.58mmol) in acetonitrile (130 mL) purged with nitrogen for 20 min was irradiated (RPR, 300 nm,) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave unchanged starting material **30b**

Continued elution of the column with a mixture (1:4) of hexane and dichloromethane yielded compound **34b** as a white powder.

Compound 34b:(30%); mp 272 ^{0}C; IR (KBr) 1766 cm^{-1} (C=O); UV λ_{max} (CH_3CN) 253 (ε 27,400), 266 (ε 28,400), 279 (ε 8,560), 306 (ε 7,150), 346 (ε 3,150) 356 (ε 2,350);;^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 (s, 1H, aliphatic proton), 7.16-9.17 (m, 10H, aromatic protons); Anal. Calcd for $C_{22}H_{11}O_2Cl_3$: C, 63.87; H, 2.68. Found C, 63.81; H, 2.53.

4.5.13. Irradiation of 3,3-Di(*p*-tolyl)-5-aryl-3*H*-furan-2-ones 30c,d

4.5.13.1. 3,3-Di(*p*-tolyl)-5-phenyl-3*H*-furan-2-one (30c)

4.5.13.1a. Sensitized Irradiation of 30c in Hexane

A solution of **30c** (0.2 g, 0.58 mmol) and *p*-methoxyacetophenone (0.09 g, 0.58 mmol) in hexane (130 mL) purged with nitrogen for 20 min was irradiated (RPR, 300 nm,) for 2 h. Solvent was removed under vacuum and the residue was washed with a mixture (1:1) of hexane and dichloromethane to give a white solid **31c.**

Compound 31c: (76%); mp > 315 ^{0}C; IR (KBr) 1780 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (s, 6H, methyl protons),4.92(s, 2H, aliphatic protons) 6.5-7.5 (m, 26H, aromatic protons); Anal. Calcd for $C_{48}H_{40}O_4$: C, 68.31; H, 5.92. Found C, 68.2; H, 5.86.

4.5.13.1b. Sensitized Irradiation of 30c in Acetonitrile

A solution of **31c** (0.2 g, 0.58 mmol) and *p*-methoxyacetophenone (0.09 g, 0.58 mmol) in acetonitrile (130 mL) purged with nitrogen for 20 min was irradiated (RPR, 300 nm,) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave unchanged starting material **30c**

.Further elution with a mixture (3:2) of hexane and dichloromethane gave a yellow solid. **35c**. Continued elution of the column with a mixture (1:4) of hexane and dichloromethane yielded compound **34c** as a white powder.

Compound 35c: (20%); mp 110 ^{0}C; IR (KBr) 1658 (C=O) and 1610 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45(s , 6H, methyl protons), 7.10-7.54

(m, 14H, aromatic and vinylic protons); Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found C, 88.39; H, 6.39.

Compound 34c: (31%); mp 254 ^{0}C; IR (KBr) 1768 cm^{-1} (C=O); UV λ_{max} (CH_3CN) 208 (ε 17,200), 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 (300 MHz, $CDCl_3$) δ 2.40 (s, 6H, methyl protons) δ 6.67 (s, 1H, aliphatic proton), 7.19-9.18 (m, 11H, aromatic protons); Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found C, 85.11; H, 5.29.

4.5.13.2. 5-(4-Chlorophenyl)-3,3-di(*p*-tolyl)-3*H*-furan-2-one (30d)

4.5.13.2a. Sensitized Irradiation of 30d in Hexane

A solution of **30d** (0.2 g, 0.53 mmol) and *p*-methoxyacetophenone (0.08 g, 0.53 mmol) in hexane (130 mL) purged with nitrogen for 20 min was irradiated (RPR, 300 nm,) for 2 h. Solvent was removed under vacuum and the residue was washed with a mixture of hexane and dichloromethane (1:1) to give **(31d)** as white solid (78%).

Compound 31d: (78%); mp > 315 ^{0}C; IR (KBr) 1776 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 6H, methyl protons),4.97(s, 2H, aliphatic protons) 6.32-7.61 (m, 24H, aromatic protons); Anal. Calcd for $C_{48}H_{38}O_4Cl_2$: C, 76.93; H, 5.11. Found C, 77.10; H, 5.16.

4.5.13.2b. Sensitized Irradiation of 30d in Acetonitrile

A solution of **30d** (0.2 g, 0.53 mmol) and *p*-methoxyacetophenone (0.08 g, 0.53 mmol) in acetonitrile (130 mL) purged with nitrogen for 20 min was irradiated (RPR, 300 nm,) for 2 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a

column of silica gel. Elution with a mixture (4:1) of hexane and dichloromethane gave unchanged starting material **30d.**

Further elution with a mixture (3:2) of hexane and dichloromethane gave a light yellow solid **35d.** Continued elution of the column with a mixture of (1:4) hexane and dichloromethane yielded compound **34d** as white powder

Compound 35d: (16%); mp 128 ^{0}C; IR (KBr) 1668 (C=O) and 1615 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45(s , 6H, methyl protons), 7.10-7.54 (m, 13H, aromatic and vinylic protons); Anal. Calcd for $C_{23}H_{19}OCl$: C, 79.64; H, 5.52. Found C, 79.69; H, 5.49

Compound 34d: (27%); mp 269 ^{0}C; IR (KBr) 1752 cm^{-1} (C=O); UV λ_{max} (CH_3CN) 208 (ε 21,400), 245 (ε 21,500), 258 (ε 17,800), 276 (ε 7,900), 308 (ε 24,100), 338 (ε 1000), 354 nm (ε 900) ;^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 6H, methyl protons), 6.53 (s, 1H, aliphatic proton), 7.32-9.26 (m, 10H, aromatic protons); Anal. Calcd for $C_{24}H_{17}O_2Cl$: C, 77.31; H, 4.60. Found C, 77.29; H, 4.67.

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Chapter 4

Synthesis and Photochemical Studies of a Few 2-Aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones

4.1 Abstract

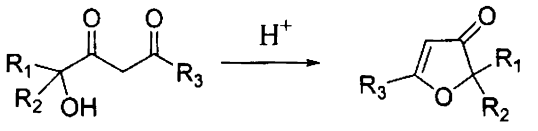
3(2H)-Furanones are valuable synthetic intermediates and key structural subunits of a variety of natural products. This chapter presents our efforts on the development of a new and efficient method for the synthesis of few 2-aryl-2-hydroxy-1-oxacyclopenta[l]phenanthren-3-ones. The protocol developed by us employs readily available phenanthrenequinone and various para substituted acetophenones as starting materials and provides easy access. Our endeavours on the photolysis of above mentioned compounds is also illustrated here. Under the influence of UV radiation these compounds were found to be stable but underwent extensive decomposition to intractable mixture in presence of a tertiary amine.

4.2 Introduction

The 3(2*H*)-furanone ring system is found in a wide variety of natural products including many flavor compounds[1-2] and insect pheromones. Compounds incorporating this functionality or their derivatives have been shown to be biologically active and some display fungicidal, herbicidal, antibiotic, antihelminthic and antitumor activity.[3-8] Natural antitumor agents for example, jatrophone, eremantholides, geiparvarin, chinolone, ciliarin all belong to the group of 3(2*H*)-furanones.[9-12] The potent antitumor properties of many 3(2*H*)-furanones have been associated with their ability to act as Michael acceptors.[13] Apart from the unusual range of biological activity, their

use as reactive intermediates in organic synthesis[14-17] also lent importance to the synthesis of these furanones.

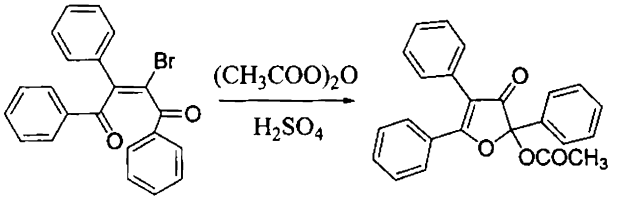
Synthetic approaches to the 3(2*H*)-furanone ring system which vary in their degree of flexibility have appeared in the literature.[18,19] One of the general approaches to the synthesis of these compounds involves the acid catalysed cyclisation–dehydration process of an appropriately substituted α-hydroxy-1,3-diketone (**1**) as in Scheme 1.[21,22,25,26]



1 **2**

Scheme 1

3(2*H*)-Furanones can be easily synthesised from the *cis* isomer of dibenzoylalkenes. *E*-bromodibenzoylstyrenes on addition-cyclisation reaction in presence of acidic reagents yield the corresponding 3(2*H*)-furanones (Scheme 2).[27]

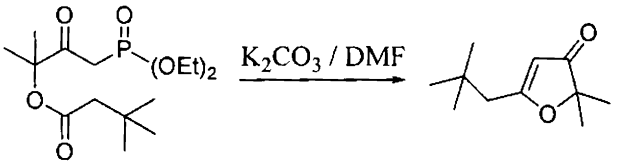


3 **4**

Scheme 2

Sampson *et al.* have utilized a Wadsworth-Emmons type condensation reaction for the key ring formation. When treated with potassium carbonate,

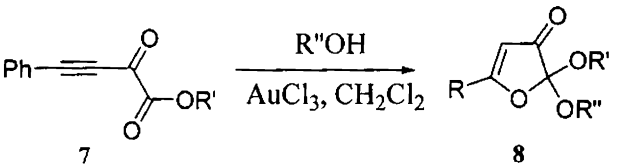
γ-(acyloxy)-β-ketophosphonates **5** undergo an intramolecular condensation to afford 3(2*H*)-furanones.[28]



5 **6**

Scheme 3

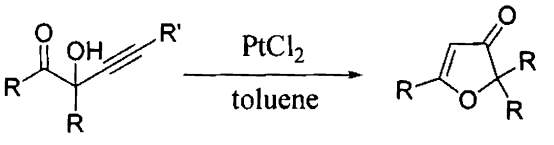
Gold catalysed cyclisations of 2-oxo-3-butynoic esters **7** or disubstituted 1,2-diones with a variety of nucleophiles offer a straightforward route to substituted 3(2*H*)-furanones **8** under mild conditions.[29]



7 **8**

Scheme 4

A novel approach to 3(2*H*)-furanones combines a transition metal catalysed activation of alkynes with a heterocyclisation and subsequent 1,2 alkyl shift.[30]



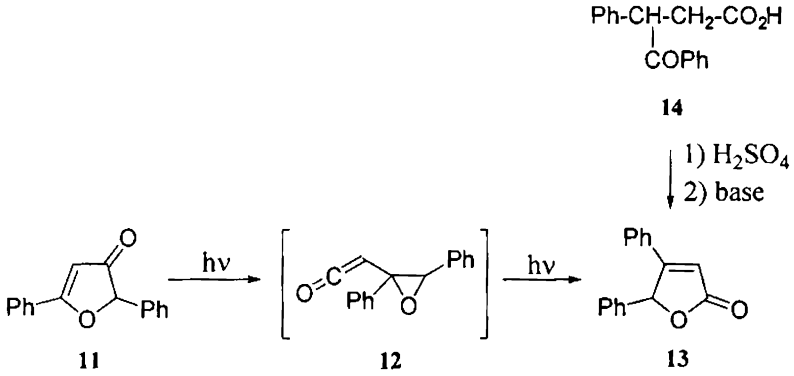
9 **10**

Scheme 5

Although a number of syntheses of 3(2*H*)-furanones were known they were in many cases limited to specific substitution patterns. The development

of alternative strategies for the preparation of these heterocyclics is therefore of considerable importance and continues to be a challenge. In this chapter we present a very facile and efficient procedure which enables the conversion of the easily accessible starting materials into 3(2*H*)-furanones. The protocol developed by as involves a two step process consisting of Claisen-Schmidt condensation of phenanthrenequinone with various para substituted acetophenones followed by acid treatment. Aryl ketones of our choice were acetophenone, 4-methylacetophenone, 4-methoxyacetophenone, 4-chloro-acetophenone and 4-phenylacetophenone.

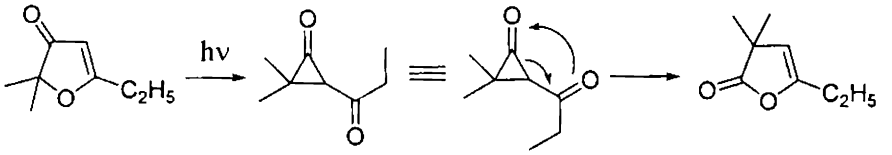
Eventhough the synthesis and reactions of 3(2*H*)-furanones have attracted considerable attention, the intramolecular photochemistry of these compounds, but for a few preliminary examinations, remained largely unexplored. Padwa and coworkers[31] found that irradiation of 2,5-diphenyl-3(2*H*)-furanone **(11)** in benzene under argon atmosphere yielded 4,5-diphenyl-2(5*H*)-furanone **(13)**.



Scheme 6

Agosta and coworkers[32] reported that on irradiation, alkyl-substituted 3(2*H*)-furanone **15** rearranged to the corresponding 2(3*H*)-furanone **17**. The

mechanism involves the formal cyclopentene-vinylcyclopropane rearrangement of **15** to **16** followed by the reverse process with involvement of the other cyclopropane center to yield **17.**



15 **16** **17**

Scheme 7

Highly-crowded 2,2-dimethyl-4,5-di-*tert*-butyl-3(2*H*)-furanone on the other hand gave the decarbonylated product as major and 2,2-dimethyl-4-*tert*-butyl-3(2*H*)-furanone as minor product on irradiation in benzene. The mechanism involves the rearrangement of the furanone to an acylcyclopropanone followed by decarbonylation to yield the product.

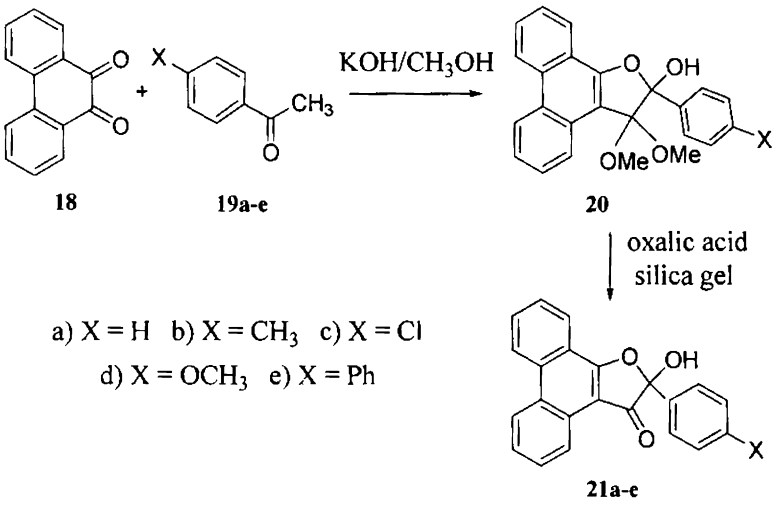
Based on these observations we expected that our systems, 2-aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones would also undergo analogous rearrangements. Our endeavours on the synthesis and photochemistry of these compounds are depicted in this chapter.

4.3 Results and Discussion

4.3.1 Synthesis of 2-Aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones

The condensation of phenanthrenequinone **(18)** with acetophenones **19a-e** in the presence of potassium hydroxide in methanol gave 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ols **20a-e** in 25-40% yields.[33] Close examination of the structural features of these

compounds reveals that it may be regarded as the dimethylketals of 2-aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones **21**. So we attempted the conversion of furanol derivatives to corresponding 3(2*H*)-furanones. Furanol derivatives **20a-e** was dissolved in dichloromethane and oxalic acid adsorbed on silica gel was added. After stirring at room temperature for 12 hours, the product formed was separated by column chromatography and recrystallised from a mixture (2:1) of dichloromethane and hexane to give 2-aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones **21a-e** as white solid.



18 **19a-e** **20** **21a-e**

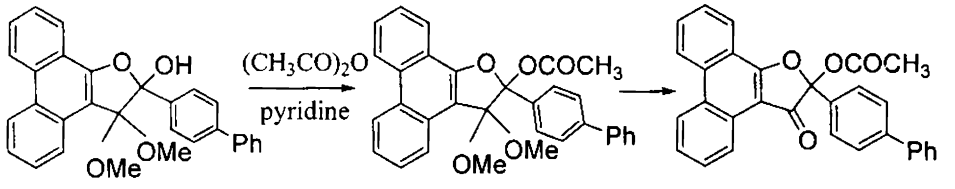
Scheme 8

The structure of these derivatives was arrived at on the basis of spectral and analytical data. 2-Hydroxy-2-phenyl-1-oxacyclopenta[*l*]phenanthren-3-one **(21a)** was obtained in 65% yield and showed strong IR absorptions at 3419 and 1688 cm^{-1} indicating the presence of a hydroxyl and carbonyl group respectively in the molecule. ^1H NMR spectrum of this compound showed a singlet at δ 2.24 corresponding to the hydroxyl proton, and multiplet between

δ 7.20-8.95 corresponding to thirteen aromatic protons. The ^{13}C NMR spectrum showed the carbonyl carbon at δ 197.12. Similarly, 2-hydroxy-2-(*p*-tolyl)-1-oxacyclopenta[*l*]phenanthren-3-one **(21b)** obtained in 67% yield showed strong IR absorptions at 3410 and 1678 cm^{-1} due to hydroxyl and carbonyl groups in the compound. In ^{1}H NMR spectrum the compound showed a singlet at δ 2.29 and δ 2.50 corresponding to the hydroxyl proton and three protons of the methyl group respectively. A multiplet at δ 7.19-8.95 corresponds to twelve aromatic protons. The ^{13}C NMR spectrum showed the carbonyl carbon at δ 196.12. 2-(4-Chlorophenyl)-2-hydroxy-1-oxa-cyclopenta[*l*]phenanthren-3-one **(21c)** obtained in 66% yield shows strong IR absorptions at 3424 and 1672 cm^{-1} due to hydroxyl and carbonyl groups. In the ^{1}H NMR spectrum the compound showed a singlet at δ 2.46 due to hydroxyl proton and multiplet at δ 7.42-8.92 corresponding to twelve aromatic protons. The ^{13}C NMR spectrum showed the carbonyl carbon at δ 196.73. 2-Hydroxy-2-(4-methoxyphenyl)-1-oxacyclopenta[*l*]phenanthren-3-one **(21d)** obtained in 67% yield showed strong IR absorptions at 3415 and 1679 cm^{-1} respectively due to hydroxyl and carbonyl groups. The compound showed a singlet at δ 2.50 corresponding to the proton of hydroxyl group, a singlet at δ 3.72 due to three protons of the methoxy group, and a multiplet at δ 6.96-8.94 corresponding to twelve aromatic protons. The ^{13}C NMR spectrum showed the carbonyl carbon at δ 197.43. 2-Biphenyl-4-yl-2-hydroxy-1-oxa-cyclopenta[*l*]phenanthren-3-one **(21e)** obtained in 68% yield showed strong IR absorptions at 3418 and 1677 cm^{-1} due to hydroxyl and carbonyl groups. The compound showed a singlet at δ 2.38 due to one hydroxyl proton and multiplet between δ 7.35-8.98 corresponding to aromatic protons in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum showed the carbonyl carbon at δ 197.02.

The structures were further confirmed by elemental analysis, which gave acceptable data. The absorption spectra of all these 3(2*H*)-furanones are dominated by the absorption due to the phenanthrene component present in them.

Similarly acetylation of compound **20** using acetic anhydride in pyridine was done on a representative sample **20e.** The structure of the acetoxy furanone derivative **23e** was arrived at on the basis of spectral and analytical data. It seems likely that the initial acetylation product **22** formed underwent hydrolysis during aqueous workup of the reaction mixture. 2-Biphenyl-4-yl-3-oxo-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-yl acetate **(23e),** which was obtained in 63% yield showed prominent peaks at 1770 and 1688 cm^{-1} in the IR spectra indicating the presence of two carbonyl groups in the compound. In the ^{1}H NMR spectrum, one singlet was observed at δ 2.29 due to the presence of three protons of acetoxy group and multiplet at δ 7.35-8.97 corresponding to twelve aromatic protons in the compound. The ^{13}C NMR spectrum showed peaks at δ 172.65 and 197.40 due to carbonyl carbons. As in the case of hydroxyfuranones **21**, the absorption spectrum of **23e** was also dominated by the phenanthrene component.



20 e **22** **23 e**

Scheme 9

4.3.2 Photochemical Transformations

Based on the reports that 3(2*H*)-furanones undergo interesting photochemical transformations, for example rearrangement to 2(5*H*)-furanones, we carried out irradiation experiments on a few representative examples. A solution of 2-hydroxy-2-phenyl-1-oxacyclopenta[*l*]phenanthren-3-one **(21a)** (0.70 mmol in 130 mL) in acetone purged with nitrogen was irradiated (RPR, 350 nm). Even after 18 hours no new products were observed and starting compound recovered unchanged.

The compound was found to be stable under the irradiation condition employed by us. We conclude that the excitation energy in **21** is concentrated in the phenanthrene component. Consequently, **21**, unlike other simple 3(2*H*)-furanones examined by Padwa and Agosta are less likely to undergo photochemical transformations characteristic of the 3(2*H*)-furanone component. So, we explored the possibility of electron transfer mediated phototransformations with a few representative examples. We selected simple tertiary amines as the electron donors to 3(2*H*)-furanones. Photolysis of **21** was carried out in the presence of a tertiary amine, *N*-methylpyrrolidene to examine their electron transfer mediated phototransformation. But the compound underwent extensive decomposition to yield an intractable mixture under the condition applied by us. Since the acetoxy derivative **23e** underwent slow decomposition in solution, we did not examine its photochemistry.

4.4 Conclusion

We have successfully synthesised few 2-aryl-2-hydroxy-1-oxa-cyclopenta[*l*]phenanthren-3-ones from 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ol precursors using a facile and efficient

synthetic strategy. These furanone derivatives have immense potential for further investigations. The photolysis of these compounds resulted in extensive decomposition leading to intractable mixtures in presence of tertiary amine, but are stable towards UV light on direct irradiation in acetone.

4.5. Experimental

4.5.1. 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. Visualization 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 infra red spectra were recorded using ABB Bomem (MB Series) FT-IR spectrometer. All steady state irradiations were carried out using Rayonet Photochemical Reactor (RPR). Solvents for photolysis were purified and distilled before use. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively on a Bruker 300 FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane. Elemental analysis was performed using Elementar Systeme (Vario ELIII) at STIC, Kochi.

4.5.2. Starting Materials: Phenanthrenequinone and acetophenones were purchased from Sigma Aldrich and were used as obtained. 3,3-Dimethoxy-2-

aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ols were synthesised using a known procedure.[33]

4.5.3. Synthesis of 2-Aryl-2-hydroxy-1-oxacyclopenta[*l*]phenanthren-3-ones 21a-e.

4.5.3.1. Synthesis of 2-Hydroxy-2-phenyl-1-oxacyclopenta[*l*]phenanthren-3-one (21a)

A sample of **20a** (5.0 g, 15 mmol) was dissolved in dichloromethane and oxalic acid (5.4 g) adsorbed on silica gel was added. The mixture was stirred at room temperature for 12 h. The progress of the reaction was monitered by using TLC. The product formed was separated by column chromatography and recrystallised from a mixture (2:1) of dichloromethane and hexane gave **21a** as white solid.

Compound 21a (65%); mp 174-176 ^{0}C; IR ν_{max} (KBr) 3419 cm^{-1} (OH), 1688 cm^{-1}(C=O), 1624 cm^{-1} ; 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 2.24 (1H, s, OH), 7.20-8.95 (m, 13H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 106.75, 120.72, 122.62, 123.26, 123.90, 124.39, 126.17, 126.38, 126.47, 126.61, 126.80, 126.95, 127.79, 128.19, 129.02, 129.13, 132.81, 135.58, 139.53, 141.17, 172.64, 197.12.; Anal. Calcd for $C_{22}H_{14}O_3$: C, 80.96; H, 4.32. Found: C, 79.89; H, 4.54.

4.5.3.2. Synthesis of 2-Hydroxy-2-(*p*-tolyl)-1-oxacyclopenta[*l*]phenanthren-3-one (21b)

A sample of **20b** (5.0 g, 14 mmol) was dissolved in dichloromethane and oxalic acid (5.0 g) adsorbed on silica gel was added. The mixture was stirred

at room temperature for 12 h. The progress of the reaction was monitered by using TLC. The product formed was separated by column chromatography and recrystallised from a mixture (2:1) of dichloromethane and hexane gave **21b** as white solid.

Compound 21b (67%); mp 180-182 ^{0}C; IR ν_{max} (KBr) 3410 cm^{-1} (OH), 1678 cm^{-1}(C=O), 1620 cm^{-1} ; UV λ_{max} (CH_3CN) 220 (ε 19,555), 239 (ε 29,040), 256 (ε 21,914), 275 (ε 10,500), 300 (ε 4,930), 340 (ε 2,410), 351 (ε 2,480), 361 nm (ε 2,820); ^{1}H NMR ($CDCl_3$) δ 2.29 (1H, s, OH), 2.50 (s, 3H, methyl protons), 7.19-8.95 (m, 12H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 25.32, 106.19, 121.12, 122.42, 122.26, 123.10, 124.39, 126.37, 126.38, 126.47, 126.60, 126.63, 128.95, 129.11, 129.19, 129.22, 129.53, 129.80, 132.42, 139.50, 140.17, 166.14, 196.12.; Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.16.; H, 4.72. Found: C, 80.20; H, 4.69.

4.5.3.3. Synthesis of 2-(4-Chlorophenyl)-2-hydroxy-1-oxacyclopenta[*l*] phenanthren-3-one (21c)

A sample of **20c** (5.0 g, 13 mmol) was dissolved in dichloromethane and oxalic acid (4.7 g) adsorbed on silica gel was added. The mixture was stirred at room temperature for 12 h. The progress of the reaction was monitered by using TLC. The product formed was separated by column chromatography and recrystallised from a mixture (2:1) of dichloromethane and hexane gave **21c** as white solid.

Compound 21c (66%); mp 214-216 ^{0}C; IR ν_{max} (KBr) 3424 cm^{-1} (OH), 1672 cm^{-1}(C=O), 1626 cm^{-1} ; UV λ_{max} (CH_3CN) 234 (ε 26,215), 246 (ε 24,900), 259 (ε 11,900), 295 (ε 2,890), 302 (ε 2,540), 347 (ε 1569), 354 nm (ε 1,580); ^{1}H NMR ($CDCl_3$) δ 2.46 (1H, s, OH), 7.42-8.92 (m, 12H, aromatic protons);

^{13}C NMR ($CDCl_3$) δ 105.46, 106.63, 120.61, 122.61, 123.22, 123.82, 124.30, 126.16, 126.47, 127.73, 128.10, 128.63, 129.07, 129.44, 131.02, 131.72, 132.75, 134.11, 135.39, 135.56, 139.61, 172.59, 196.73 Anal. Calcd for $C_{22}H_{13}ClO_3$: C, 73.26.; H, 3.62. Found: C, 73.19; H, 3.64.

4.5.3.4. Synthesis of 2-Hydroxy-2-(4-methoxyphenyl)-1-oxacyclopenta[*l*]-phenanthren-3-one (21d)

A sample of **20d** (5.0 g, 14 mmol) was dissolved in dichloromethane and oxalic acid (5.0 g) adsorbed on silica gel was added. The mixture was stirred at room temperature for 12 h. The progress of the reaction was monitered by using TLC. The product formed was separated by column chromatography and recrystallised from a mixture (2:1) of dichloromethane and hexane gave **21d** as white solid.

Compound 21d (67%); mp 132-134 ^0C; IR ν_{max} (KBr) 3415 cm^{-1} (OH), 1679 cm^{-1}(C=O), 1628 cm^{-1} ; UV λ_{max} (CH_3CN) 248 (ε 16,740), 251 (ε 14,980), 256 (ε 11,960), 297 (ε 2,970), 300 (ε 2900), 347 (ε 1,569), 351 (ε 1,380), 356 nm (ε 1690); ^1H NMR ($CDCl_3$) δ 2.50 (1H, s, OH), 3.72 (s, 3H, methoxy protons), 6.96-8.94 (m,12H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 55.27, 106.29, 106.76, 113.99, 120.81, 122.66, 123.26, 123.88, 124.36, 126.12, 126.44, 126.73, 127.26, 127.79, 128.16, 128.44, 129.12, 132.79, 135.55, 160.08, 161.11, 172.50, 197.43; Anal. Calcd for $C_{23}H_{16}O_4$: C, 77.50.; H, 4.51. Found: C, 77.57; H, 4.54.

4.5.3.5. Synthesis of 2-Biphenyl-4-yl-2-hydroxy-1-oxacyclopenta[*l*]phen-anthren-3-one (21e)

A sample of **20e** (5.0 g, 12 mmol) was dissolved in dichloromethane and oxalic acid (4.3 g) adsorbed on silica gel was added. The mixture was stirred

at room temperature for 12 h. The progress of the reaction was monitered by using TLC. The product formed was separated by column chromatography and recrystallised from a mixture (2:1) of dichloromethane and hexane gave **21e** as white solid.

Compound 21e (68%); mp 205-207 ^{0}C; IR ν_{max} (KBr) 3418 cm^{-1} (OH), 1677 cm^{-1}(C=O), 1629 cm^{-1} ; UV λ_{max} (CH_3CN) 251 (ε 14,980), 253 (ε 13,290), 304 (ε 1,879), 350 (ε 1569), 351 nm (ε 1,380); ^{1}H NMR ($CDCl_3$) δ 2.38 (1H, s, OH), 7.35-8.98 (m, 17H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 106.14, 106.76, 120.83, 122.65, 123.35, 123.91, 124.46, 125.71, 126.51, 126.73, 126.76, 128.26, 128.64, 129.21, 129.69, 130.95, 132.87, 133.58, 135.68, 138.91, 160.17, 172.60, 197.02; Anal. Calcd for $C_{28}H_{18}O_3$: C, 83.53.; H, 4.52. Found: C, 83.41; H, 4.54.

4.5.4. Synthesis of 2-Biphenyl-4-yl-3-oxa-2,3-dihydro-1-oxacyclopenta[*l*]-phenanthren-2-yl acetate (23e)

A sample of **20e** (5.0 g, 12 mmol) was dissolved in dichloromethane and pyridine was added. Acetic anhydride was added dropwise to the reaction mixture over a period of 30 minutes and then refluxed for 2 h. The progress of the reaction was monitered by using TLC. After workup the product formed was separated by column chromatography and was then recrystallised from a mixture (2:1) of dichloromethane and hexane to give **23e** as white powder.

Compound 23e (63%); mp 182-184 ^{0}C; IR ν_{max} (KBr) 1770, 1688 cm^{-1}(C=O), 1624 cm^{-1} ; UV λ_{max} (CH_3CN) 205 (ε 25,300), 246 (ε 23,900), 257 (ε 18,000), 304 (ε 8,000), 355 nm (ε 2,000); ^{1}H NMR ($CDCl_3$) δ 2.29 (3H, s, acetoxy), 7.35-8.97 (m, 12H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 20.88, 106.34, 106.78, 1.8,122.69, 123.32, 123.97, 124.45, 125.76, 126.22, 126.51,

126.73, 128.26, 128.60, 129.21, 129.61, 130.09, 132.84, 133.58, 135.61, 138.90, 161.11, 172.65, 197.40.; Anal. Calcd for $C_{30}H_{20}O_4$: C, 81.07; H, 4.54. Found: C, 81.30; H, 4.14.

4.5.4 Irradiation of 2-Hydroxy-2-phenyl-1-oxacyclopenta[*l*]phenanthren-3-one (21a) in acetone

In a typical irradiation experiment, a solution of **21a** in acetone (0.70 mmol in 130 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 18 h. The reaction was monitored by TLC. Solvent was removed and the residue was charged to a column of silica gel. The starting compound **21a** was recovered unchanged. Similar results were obtained with **21b-e**.

4.5.6 Irradiation of 2-Hydroxy-2-phenyl-1-oxacyclopenta[*l*]phenanthren-3-one (21a) in acetone in presence of *N*-Methylpyrrolidine.

In a typical irradiation experiment, a solution of **(21a)** in acetone (0.70 mmol in 130 mL) containing *N*-methylpyrrolidine (542 mg, 6.37 mmol) was purged with nitrogen for 20 min and then irradiated (RPR, 350 nm) for 6 h. The reaction was monitored by TLC. Solvent was removed and the residue was charged to a column of silica gel. An intractable mixture resulted.

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Chapter 5

Synthesis, Photolysis and Solvent Assisted Chemical Transmogrification of Acenaphthenone-2-ylidene ketones

5.1. Abstract

Acenaphthenone-2-ylidene ketones were synthesised via Claisen-Schmidt condensation and Wittig reaction. With a few acetophenones, the initially formed acenaphthenone-2-ylidene ketones underwent a domino Michael-aldol reaction to give dispirocompounds. Isolation of the intermediate acenaphthenone-2-ylidene ketones by Wittig reaction and further reaction on them clearly supports the proposed mechanism for the domino process. E-Z isomerisation was observed with acenaphthenone-2-ylidene ketones under photochemical and Lewis acid catalysed conditions and the E-isomers appear to be more stable than the corresponding Z-isomers. Our attempt towards furanisation of both the isomers resulted in hydrogenation.

5.2. Introduction

Heterocycles form by far the largest of the classical divisions of organic chemistry and are of immense importance biologically, industrially, and indeed to the functioning of any developed human society. The majority of pharmaceuticals and biologically active agrochemicals are heterocyclic,[1] as are countless additives and modifiers used in industries as varied as cosmetics, reprography, information storage, and plastics. Oxygen containing heterocycles are frequent and important targets for synthesis either as final products or as useful synthetic intermediates[2-6] due to their common

occurrence in nature. Dibenzoylalkenes are useful precursors for the synthesis of a variety of heterocyclic compounds.

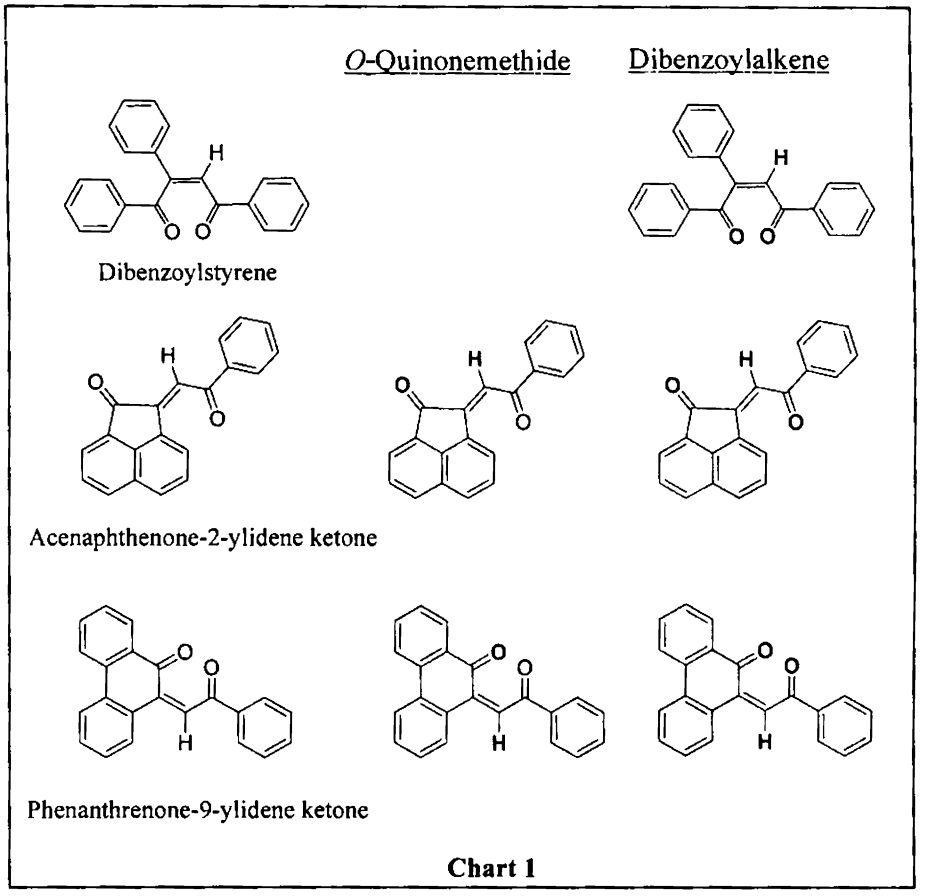
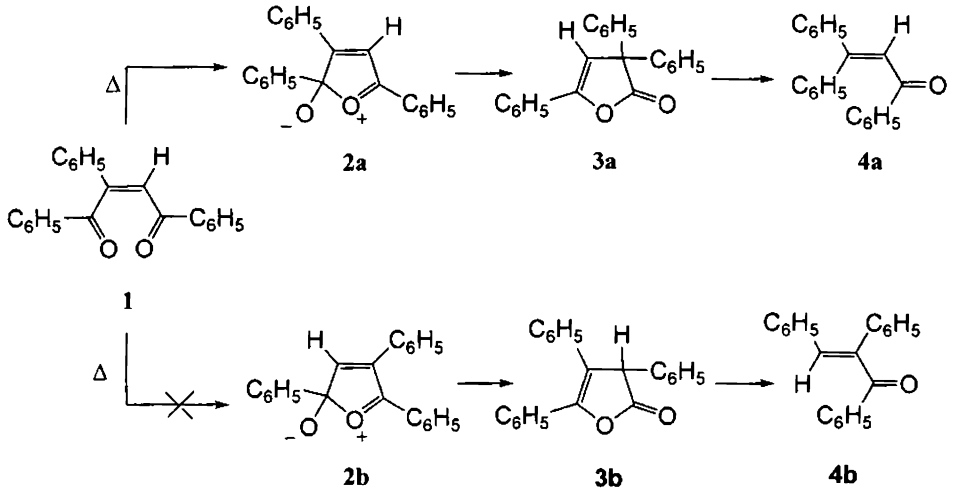


Chart 1

As a logical extension to our continued interest in the synthesis and chemistry of dibenzoylalkene derived furanones, we targeted the synthesis of few acenaphthenone-2-ylidene ketones and phenanthrenone-9-ylidene ketones. These dibenzoylalkene type systems were expected to undergo thermal rearrangement to give spirofuranones and photochemical transformation involving 1,5 - aryl migration. Also acenaphthenone-2-ylidene ketones can be categorised as quinonemethides which are valuable synthetic intermediates.

(Chart 1). They may undergo reactions typical of other *o*-quinonemethides such as Michael type additions, Diels–Alder reaction etc. yielding a variety of heterocycles.

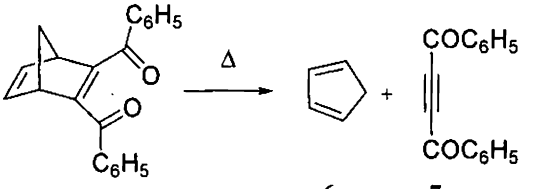
The first reported dibenzoylalkene rearrangement is on the pyrolysis of *cis*-dibenzoylstilbene to tetraphenylcrotonolactone by Zinin in 1872.[7] Subsequently, several other reports on the synthesis and transformations of a variety of dibenzoylalkenes have appeared in literature. *cis*-Dibenzoylstyrene **(1)** on pyrolysis, for example, undergoes ring closure to form triphenylcrotonolactone **(3a)**.[8,9,10] The lactone on further heating undergoes decarbonylation to give β-phenylbenzalacetophenone **(4a)**.[11]



Scheme 1

The preferential formation of the lactone **3a** in the transformation of **1** may be rationalised in terms of greater stability of the zwitterionic intermediate **2a** when compared to the corresponding intermediate **2b** in the alternate route which will lead to the lactone **3b** (Scheme 1).

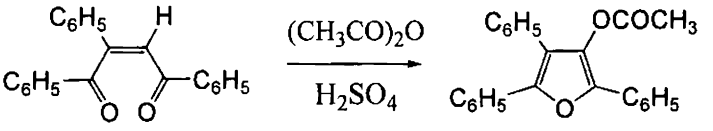
Lahiri *et al.* examined[12] the thermolysis of few *cis*-dibenzoylalkenes having rigid structural features. The thermolysis of 2,3-dibenzoyl-bicyclo[2.2.1]hepta-2,5-diene **(5)**, for example, gave cyclopentadiene **(6)** arising through a retro Diels-Alder reaction (Scheme 2).



5 **6** **7**

Scheme 2

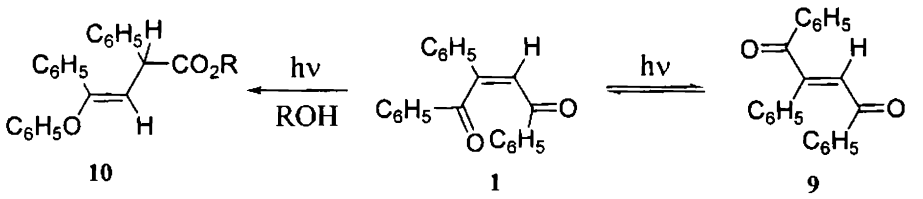
Acid catalysed rearrangements and cyclisation of dibenzoylalkenes are also reported. *cis*-Dibenzoylstyrene **(1)** for example, on treatment with acetic anhydride in presence of H_2SO_4, gave 4-acetoxy 2,3,5-triphenylfuran **(8)**.[13]



1 **8**

Scheme 3

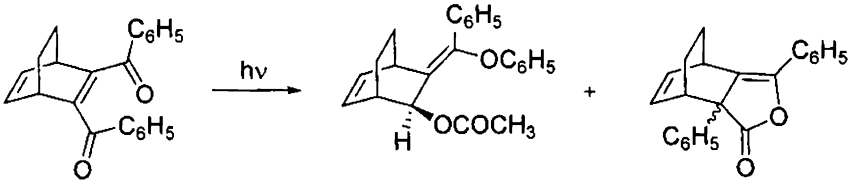
Photorearrangement of dibenzoylalkenes is known to give ketene-derived products and lactones, in addition to cis-trans isomerisation products. When the irradiation is carried out in alcohols as solvents, dibenzoylalkenes undergo intramolecular rearrangement involving 1,5-phenyl migration to oxygen to give the corresponding esters of substituted 3-butenoic acids **10** (Scheme 4).[14,15,16]



10 1 9

Scheme 4

Zimmerman *et al.*[16] had suggested, on the basis of quenching studies that these photoreactions proceed primarily from their singlet excited states. Further studies[17,18] have shown that substrates, wherein the cis-trans isomerisation is prevented through geometrical constraints, undergo predominantly the expected photorearrangements. The photolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene in methanol, for example, gives a mixture of methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-exo-carboxylate **(11)** and the lactone **12** as major products.



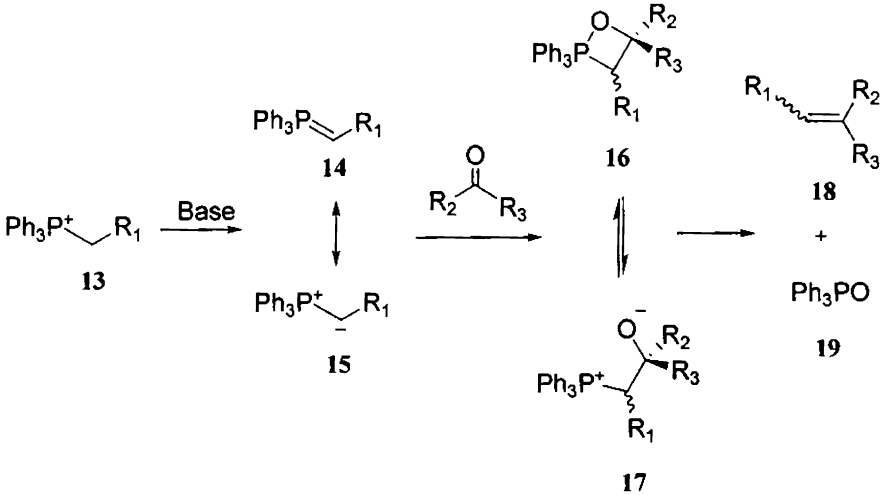
5 11 12

Scheme 5

In this chapter our endeavours on the synthesis and chemical transformations of a few dibenzoylalkene type systems such as acenaphthenone-2-ylidene ketones and phenanthrenone-9-ylidene ketones were presented. Claisen-Schmidt condensation is a useful method for the synthesis of such systems.[19-23] But investigations carried out in our laboratory have revealed that phenanthrenequinone, indeed reacts with acetophenone to

yield phenanthrenone-9-ylidene ketones which undergo further transformation under the reaction conditions to yield phenanthrofuranols. Similarly, condensation of acetophenones with acenaphthenequinione also gave intriguing results. With some acetophenones, acenaphthenone-2-ylidene ketones could be isolated as stable end products, in some cases; the initially formed acenaphthenone-2-ylidene ketones underwent solvent mediated transmogrification to give dispirocompounds. Since Claisen-Schmidt condensation was inadequate for the synthesis of all our required systems we resorted to an alternate method involving a Wittig reaction for the synthesis of target molecules.

The Wittig reaction[24,25] occupies a position of central importance in the assembly of organic molecules as it generates a double bond with high levels of geometric control. In a typical Wittig sequence, triphenylphosphine reacts with an alkyl halide to form a phosphonium halide. The subsequent addition of a strong base eliminates the hydrogen halide to produce an



Scheme 6

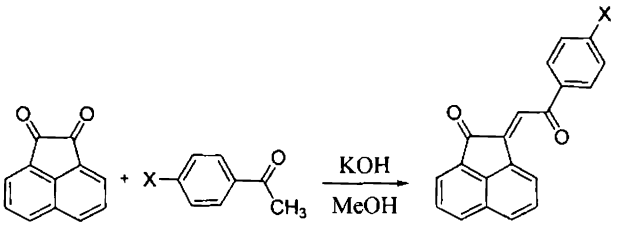
alkylidenephosphorane **14**, otherwise known as an ylide. The carbon of the ylide acts as a nucleophile and adds to the carbonyl group resulting in the production of an alkene **18**. The reaction condition can be manipulated to favour the production of either the *E* or the *Z* isomer by varying a number of parameters such as temperature, solvent, stabilising salts, excess base etc. The overall result of the reaction is thus the replacement of a carbonyl functionality by a carbon carbon double bond. The importance of the method is derived from the fact that only one positional isomer is formed as opposed to elimination methods which generate mixtures of olefinic isomers.

We presume that independent synthesis of our target molecules by Wittig reaction will enable us to study their chemistry in detail and to establish their intermediacy in the formation of unexpected products observed by us. It was also of interest to us to synthesis both the *E* and *Z*-isomers of acenaphthenone-2-ylidene ketones to compare and contrast the reactivity of these isomers towards nucleophilic reagents and with dienophiles.

5.3. Results and Discussion

5.3.1. Synthesis of Acenaphthenone-2-ylidene ketones

In this investigation, we selected those reactions where the required acenaphthenone-2-ylidene ketones were formed in good yields. It has also been established that *E*-isomers are exclusively formed under these conditions.[26] Claisen-Schmidt condensation between acenaphthenequinone **(20)** and acetophenones **21c-f** was carried out in methanol using potassium hydroxide as base. The reaction proceeded smoothly and the required acenaphthenone-2-ylidene ketones **22c-f** were obtained as yellow needles in around 62% yield (Scheme 7). These were purified by recrystallisation from absolute ethanol-chloroform mixture.

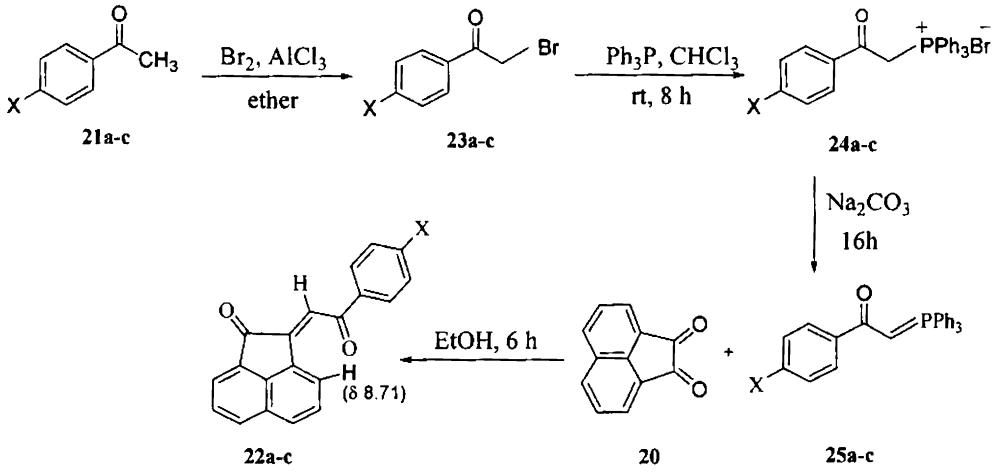


20 **21c-f** **22c-f**

c) X = Cl d) X = Br e) X = OMe f) X = Ph

Scheme 7

With acetophenones **21a,b**, since Claisen-Schmidt condensation reaction was ineffective for our target compounds, Wittig strategy (Scheme 8) was utilised and required products were obtained as yellow needles in ~ 66% yield (Scheme 8).



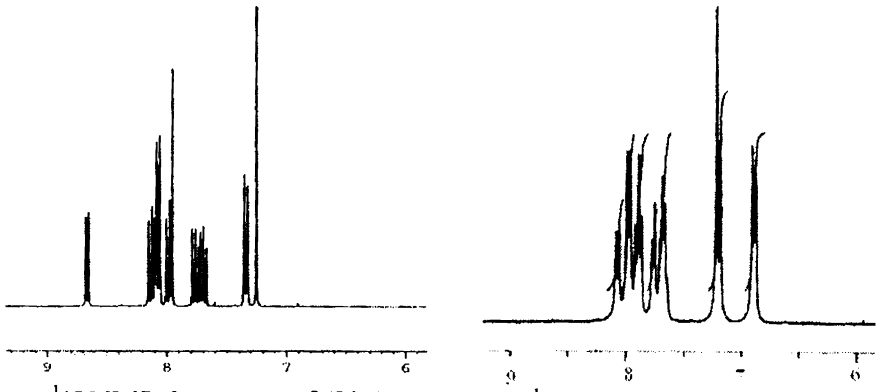
21a-c **23a-c** **24a-c** **22a-c** **20** **25a-c**

a) X = H b) X = CH_3 c) X = Cl

Scheme 8

In the above reaction sequence phenacyl bromides **23a-c** were first synthesised by the bromination of various para substituted acetophenones **21a-c** using diethyl ether as solvent in presence of anhydrous aluminium chloride. These phenacyl bromide derivatives **23a-c** were then converted to corresponding phenacyltriphenylphosphonium bromides **24a-c** by reaction with triphenylphosphine. In presence of the base, sodium carbonate corresponding ylides **25a-c** were formed which then reacts with acenaphthenequinone to form required acenaphthenone-2-ylidene ketones **22a-c**.

The structure of the compounds was established on the basis of literature precedence, analytical results and spectral data. Compound **22a** obtained in 60% yield showed two strong absorptions in the IR spectrum at 1722 and 1671 cm^{-1} due to the presence of two carbonyl groups in the compound. The absorption at 1722 cm^{-1} is assigned to the indenone-type carbonyl group present in this system. In the ^{1}H NMR spectrum, the vinylic and aromatic protons of the compound were observed as a multiplet in the region δ 7.26-8.97. In the ^{13}C NMR spectrum, two signals were observed at δ 199.21 and 200.32 attributable to two carbonyl groups. The structure was further confirmed by elemental analysis which gave acceptable data. Compounds **22b-f** also showed spectral behaviour similar with that of **22a.** Furthermore, the ^{1}H NMR spectra of all these compounds showed a peak around δ 8.71 which is characteristic of the *E*-isomer. Based on these data, *E*-configuration was assigned to these compounds. In other words, the dibenzoylalkene component in **22** has the *trans* configuration which is in contrast to the preferential formation of a product having *cis*-dibenzoylalkene component in the reaction between benzil and acetophenone.



^{1}H NMR Spectrum of **(22a)** ^{1}H NMR Spectrum of **(31a)**

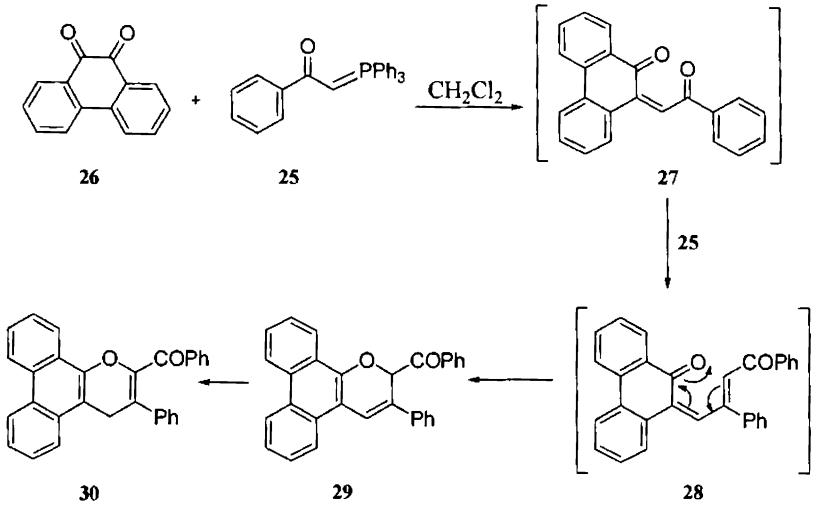
Figure 1

5.3.2. Attempted Synthesis of Phenanthrenone-9-ylidene ketones

As reported earlier, since the base catalysed condensation reaction between phenanthrenequinone **(26)** and acetophenones **21a-f** resulted[27] in 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*l*]phenanthren-2-ols, we resorted to an alternate method involving Wittig reaction. Thus we attempted the Wittig mono olefination of phenanthrenequinone **26** using phenacyl bromide derived ylide **25a** in refluxing dichloromethane for 12 h. However, 2-benzoyl-3-phenyl-4*H*-phenanthro[9,10-b]pyran **(30)** (mp 230-232 ^{0}C) was formed as white crystals in quantitative yields under the condition employed by us. The structure of the compound was established on the basis of literature precedence and analytical results.

The proposed mechanism for the formation of product is shown in Scheme 9. Wittig mono olefination of phenanthrenequinone by triphenyl-phosphinebenzoylmethylene gives phenanthrenone-9-ylidene ketones **27**, which reacts further with a second molecule of ylide **25** to form **28**. The intermediate **28** thus formed then undergo cyclisation to give the pyran

derivative **29** which under the reaction conditions is converted to the final product **30.**



26 25 27 28 29 30

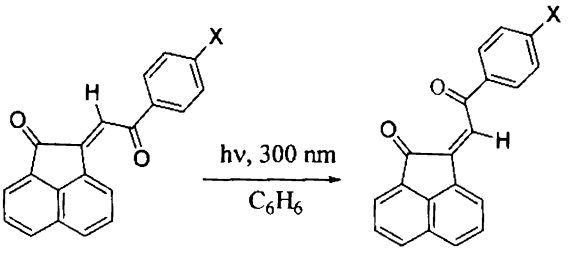
Scheme 9

5.3.3. Photolysis of Acenaphthenone-2-ylidene ketones.

Based on the reports that dibenzoylalkenes undergo interesting photochemical rearrangements[14,15,16,28] we attempted irradiation experiments on the dibenzoylalkene-type systems synthesised by us. A benzene solution of acenaphthenone-2-ylidene ketone **22a,c,e,f** (0.69 mmol, 130 mL) purged with nitrogen was irradiated (RPR, 300 nm) for 12 h. Workup of the photolysate afforded **31a,c,e,f** as yellow solids in ~ 40% yield.

Compound **31a** showed two strong absorptions at 1728 and 1670 cm^{-1} indicating the presence of two carbonyl groups. In the ^1H NMR spectrum, the vinylic and aromatic protons of the compound were observed as multiplet in the region δ 7.16-8.10. Furthermore in the ^1H NMR spectrum, the doublet at ~δ 8.71 which is the characteristic of *E*-isomer was absent. Based on this

observation *Z*-configuration was assigned to the compound. Compounds **31c,e,f** also showed similar spectral behaviour. Thus the only phenomenon observed under the irradiation condition was *E-Z* isomerisation. Products arising through putative 1,5-aryl migration characteristic of simple dibenzoylalkenes were not formed in this case.



22a,c,e,f **31a,c,e,f**

a) X = H c) X = Cl e) X = OMe f) X = Ph

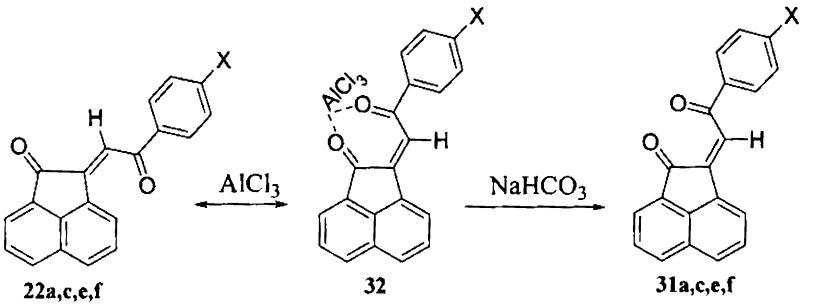
Scheme 10

5.3.4. Thermolysis of Acenaphthenone-2-ylidene ketones

On the basis of the previous reports[8,29] that dibenzoylalkenes undergo thermal rearrangement to 2(3*H*)-furanones, we investigated the thermal rearrangement of our systems by taking **22a** as a representative example. The acenaphthenone-2-ylidene ketone **22a** (100 mg, 0.35 mmol) was heated at 180 ^{0}C in a sealed tube for 4 hours. But the compound decomposed completely during neat thermolysis above the melting point, which is consistent with the observation that *trans*-dibenzoylalkenes fail to undergo such thermal rearrangements. Thermolysis of corresponding *E*-isomer **31a** was also carried out applying the above reaction conditions. But here also an intractable mixture resulted.

5.3.5. Lewis Acid Catalysed Isomerisation

The *E-Z* isomerisation of acenaphthenone-2-ylidene ketones **22a,c,e,f** was accomplished by using anhydrous aluminium chloride as catalyst.[30] Dry dichloromethane was selected as the solvent. The isomerisation proceeded efficiently as indicated by the TLC analysis of reaction mixtures. When the dark solid separated was quenched with saturated sodium bicarbonate solution and extracted with dichloromethane, compounds **31a,c,e,f** were obtained in ~58% yield. The behaviour of the unsaturated dicarbonyl framework in the *Z*-configuration as a bidentate ligand can be the key step of isomerisation. The *Z*-configuration of the products was assigned on the basis of ^{1}H NMR spectrum based on the disappearance of the doublet at ~ δ 8.7 (*vide supra*).



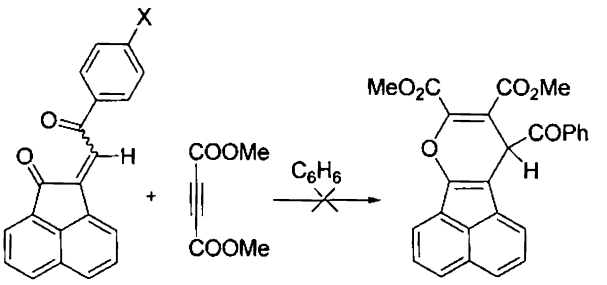
a) X = H c) X = Cl e) X = OMe f) X = Ph

Scheme 11

5.3.6. Attempted Cycloaddition Reaction of Acenaphthenone-2-ylidene ketones

Close examination of the structural features of **31** reveals that it can either be considered as a *cis*-dibenzoylalkene or an *o*-quinonemethide and that they may undergo reactions characteristic of such systems like Diels–Alder

reaction[31-33] yielding a variety of heterocycles. Based on these assumptions we attempted the Diels-Alder reaction of a representative example **31a** with dienophiles. The dienophile of our choice was dimethyl acetylenedicarboxylate (DMAD, **33**). No cycloadduct was formed with the dienophile, the only observed transformation was the *Z-E* isomerisation to a mixture rich in the *E*-isomer **22a.** Above reaction was repeated with the *E* isomer. But no characteristic change was observed and the starting compound recovered unchanged. The mechanism of DMAD-mediated *E-Z* isomerisation is not clearly understood.



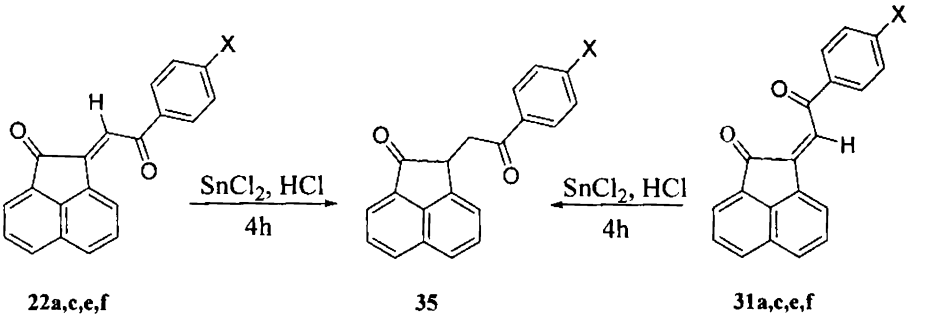
31 & 22 **33** **34**

Scheme 12

5.3.7. Attempted Furanisation of *E* and *Z* - isomers of Acenaphthenone-2-ylidene ketones

Furan is a five membered oxygen containing, unsaturated heterocyclic compound. From a chemical perspective it is the basic ring structure found in a whole class of industrially[34,35] significant products and also found in a large number of biologically active materials.[36-38] It was reported that *cis*-dibenzoylstyrenes[39-42] undergo reductive cyclisation to yield the corresponding furans. From literature it was found that stannous chloride in acetic acid-hydrochloric acid mixture is a useful reagent for the purpose. This reaction

evidently involved first reduction to the saturated diketone which is readily converted to the furan through enol intermediates. In this context we attempted furanisation of both the *E-Z* isomers of acenaphthenone-2-ylideneketones **22a,c,e,f** and **31a,c,e,f** by refluxing in $SnCl_2$ and acetic acid-hydrochloric acid mixture. However our attempts resulted in hydrogenation forming 2-(2-oxo-2-phenylethyl)acenaphthylen-1(2*H*)-one derivatives **35a,c,e,f** in around 70% yield. Since these derivatives **35a,c,e,f** were supposed to be the intermediate in furanisation sequence, above reaction was repeated further on them. But no reaction was observed and **35a,c,e,f** recovered unchanged.



22a,c,e,f **35** **31a,c,e,f**

a) X = H c) X = Cl e) X = OMe f) X = Ph

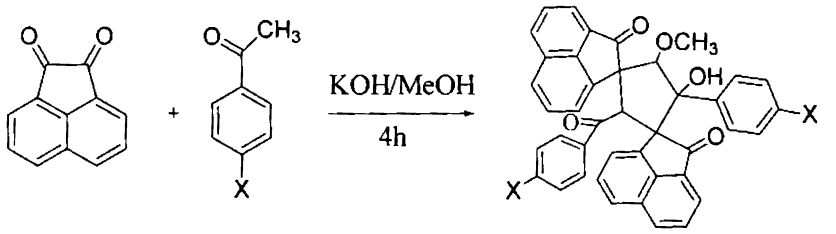
Scheme 13

The product formed was identified on the basis of spectral and analytical data. In the IR spectrum of compound **35a**, strong absorptions were observed at 1724 and 1680 cm^{-1} indicating the presence of two carbonyl groups. The ^1H NMR spectrum exhibited two doublet of doublets at δ 3.42 and 3.91 due to two methylene protons and multiplets at δ 7.23-7.90 due to ten aromatic protons. Another doublet of doublet is also observed at δ 4.26 due to methine proton. In ^{13}C NMR spectrum peaks at δ 200.18 and 204.90 indicates

carbonyl carbons. The structure was further confirmed by elemental analysis, which gave acceptable data. Compounds **35c,e,f** also showed related spectral behaviour.

5.3.8. Synthesis of Dispirocompounds

Domino reaction[43-47] is a process involving two or more bond forming transformations which takes place under the same reaction conditions without adding additional reagents and catalysts, and in which the subsequent reactions result as a consequence of the functionality formed in the previous step. This type of reaction would allow the minimisation of waste, since the amount of solvents, reagents, adsorbants and energy would be drastically decreased and often such reactions are accompanied by dramatic increases in molecular complexity and impressive selectivity.[48-50] In this section a novel domino reaction of acenaphthenequinone **(20)** with acetophenones **21** in methanol that involves aldol and Michael reactions leading to the formation of a highly substituted dispirocompound is depicted.



20 **21a,b** **36a,b**

a) X = H b) X = CH_3

Scheme 14

The Claisen-Schmidt condensation reaction of acenaphthenequinone **20** with acetophenone **(21a)** in 30 mL of methanol in the presence of KOH

gave a colourless amorphous product in around 38% yield. The product showed a broad band at 3345 cm^{-1} in the IR spectrum indicating the presence of a hydroxy group. In addition, two peaks were observed at 1706 and 1682 cm^{-1}. The peak at 1706 cm^{-1} is ascribed to indenone-type carbonyl. In the ^{1}H NMR spectrum, four singlets were observed at δ 2.86 (3H), 5.67 (1H), 5.97 (1H), and 6.19 (1H) along with other signals attributable to aromatic protons. In the ^{13}C NMR spectrum, the signals observed at δ 197.90, 205.21, and 208.75 are attributed to carbonyl carbons. Based on the spectral and analytical data, the compound was identified as the dispirocompound **36a.**

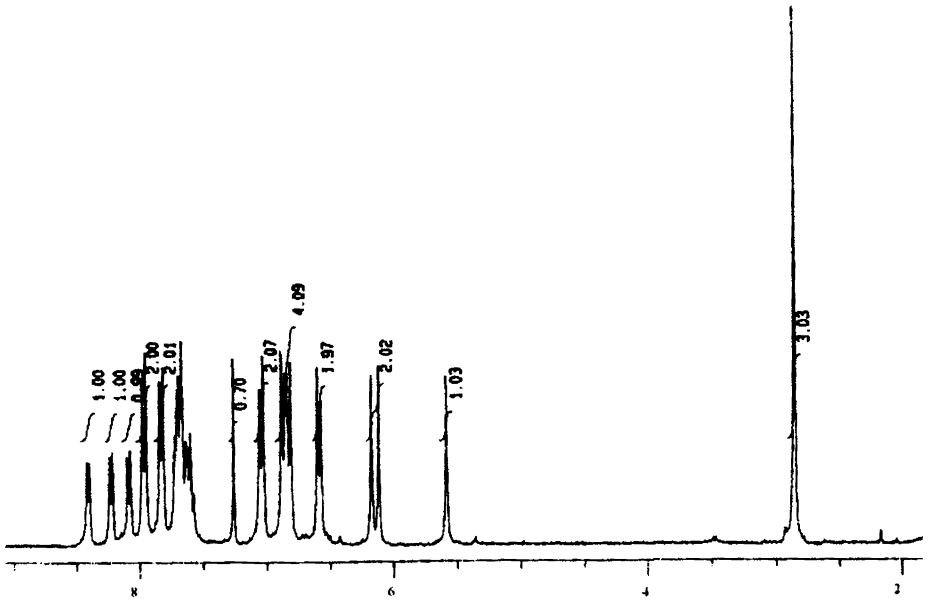


Figure 2: ^{1}H NMR Spectrum of **36c**

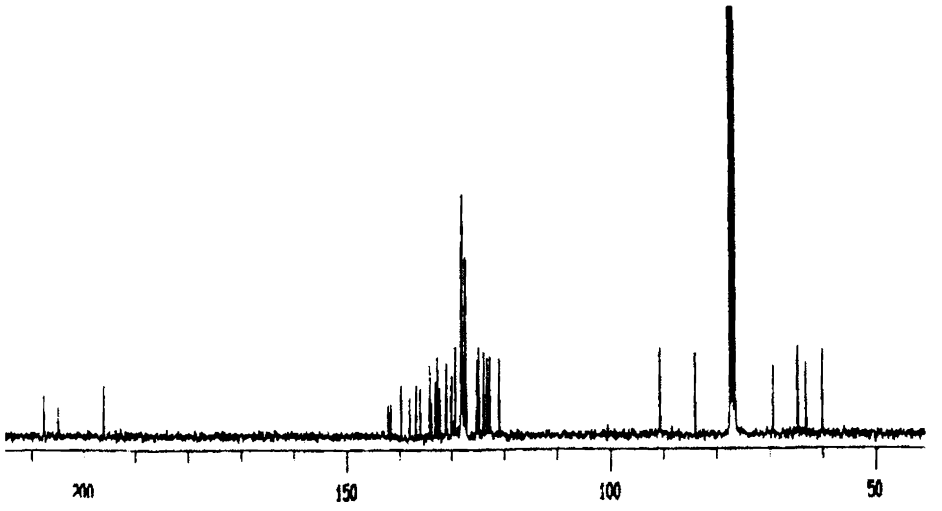
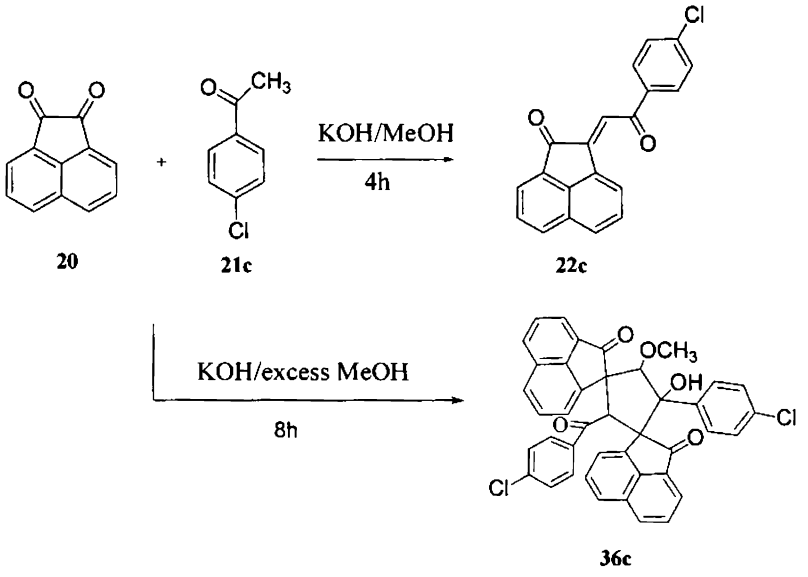


Figure 3: ^{13}C NMR Spectrum of **36c**

Similarly, dispirocompound **36b** was synthesised by the reaction of acenaphthenequinone **20** with 4-methylacetophenone **21b** and it showed analogous spectral behaviour as **36a.**

Interestingly it was found that by condensation reaction with 4-chloroacetophenone (**21c**) both acenaphthenone-2-ylidene ketone **22c** and dispirocompound **36c** were isolated by carefully adjusting the reaction conditions. When the condensation reaction was carried out in 30 mL of methanol for about 4 hours, compound **22c** was isolated whereas in 80 mL of methanol, prolonged refluxing resulted in dispirocompound **36c.** The spectral behaviour depicted by the compound **36c** was analogous to that of **36a** and **36b.** As mentioned earlier condensation of acenaphthenone-2-ylidene ketone with 4-bromoacetophenone, 4-methoxyacetophenone and 4-phenyl-acetophenone resulted in corresponding acenaphthenone-2-ylidene ketones (Scheme 7). We repeated the reaction by changing the molar ratio of reagents,

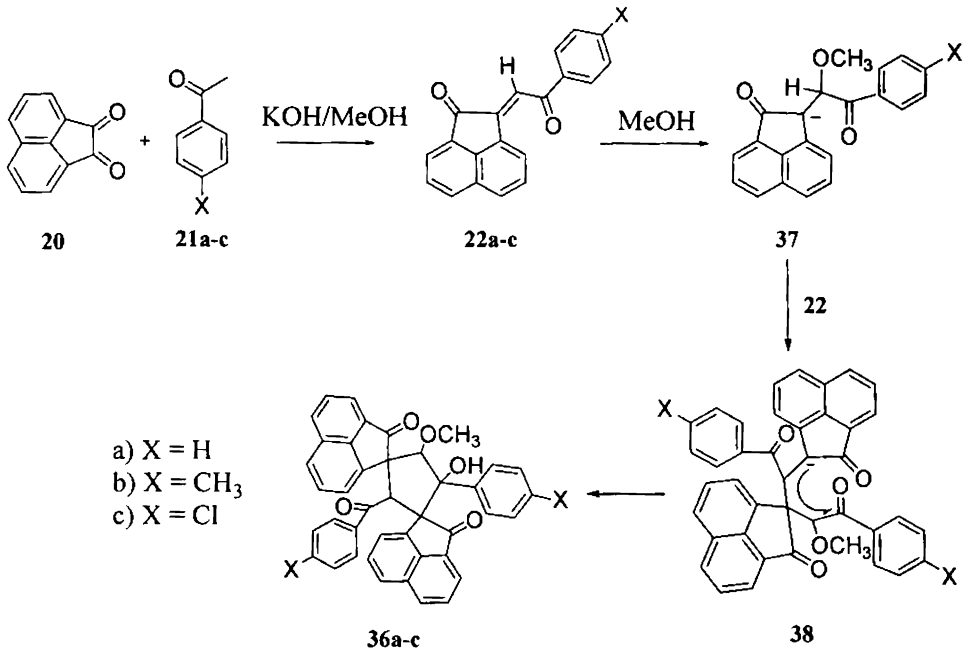
amount of solvent, reaction time etc. But the formation of dispirocompound was not at all observed with acetophenones **21d-f**. With acetophenone and 4-methylacetophenone we got only the dispirocompound **36a,b**.



20 21c 22c 36c

Scheme 15

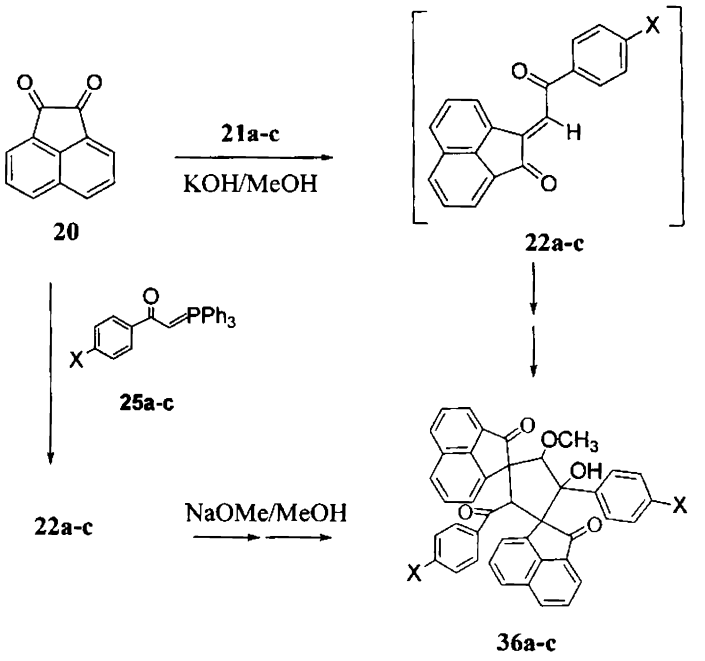
A possible mechanism for the formation of **36** involving a dibenzoylalkene-type intermediate **22** is given in Scheme16. The initial Claisen-Schmidt reaction between acenaphthenequinone **20** and acetophenone **21** gives the acenaphthenone-2-ylidene ketone **22**, which undergoes Michael addition with a molecule of methanol to give the intermediate **37**. Michael addition of **37** to another molecule of **22** followed by cyclisation yields **36**. The driving force behind this domino process is probably the quinonemethide like structure of acenaphthenone-2-ylidene ketones **22a,b,c** which makes them excellent Michael acceptors.



20 **21a-c** **22a-c** **37** **36a-c** **38**

Scheme 16

Our further investigations to unravel the mechanism of the reaction pointed towards a remarkable substituent effect in controlling the reactivity of acenaphthenone-2-ylidene ketones. We have independently synthesised the intermediate acenaphthenone-2-ylidene ketones **22a,b,c** by adopting the Wittig route (Scheme 8) and further reaction with NaOMe in methanol resulted in dispirocompound **36a,b,c**. But no further reaction was observed under the same condition with acenaphthenone-2-ylidene ketones **22d,e,f** even after several hours (Scheme 17). These observations clearly indicate the role of remote substituents in the reactivity of acenaphthenone-2-ylidene ketones.



a) X = H b) X = CH_3 c) X = Cl

Scheme 17

Close examination of the structural features of **36** indicates that the molecule has five asymmetric carbons and hence a maximum of thirty two isomers are possible here. However the ^{13}C NMR and ^{1}H NMR spectra of **36** indicate that the compound prepared by us is homogenous and not a mixture of several isomers. Based on these results, we concluded that solvent assisted transmogrification of the *Z*-isomers **31** should lead to a diastereomer of **36**. So, we repeated the reaction on the *Z*-isomers of acenaphthenone-2-ylidene ketones. Surprisingly, the *Z*-isomers also yielded **36** in comparable yields. We conclude that the *E-Z* isomerisation of acenaphthenone-2-ylidene ketones to give the more stable *E*-isomer is faster than the solvent-mediated transmogrification reaction.

5.4. Conclusion

The condensation of acenaphthenequinone with 4-methoxy-acetophenone and 4-phenylacetophenone gave acenaphthenone-2-ylidene ketones **22e,f** whereas the reaction between acenaphthenequinone and acetophenone and 4-methylacetophenone resulted in domino reaction arising through a novel three-component Michael-aldol tandem reaction. With 4-chloroacetophenone, both acenaphthenone-2-ylidene ketone **22c** and dispirocompound **36c** could be generated by controlling the reaction conditions. By synthesising the intermediate, acenaphthenone-2-ylidene ketones **22a,b,c** by Wittig reaction and doing further reaction on them, their intermediacy in the formation of dispirocompound was confirmed. Our observations clearly indicated the role of substituents in the reactivity of acenaphthenone-2-ylidene ketones. *E-Z* isomerisation was observed with acenaphthenone-2-ylidene ketones under photochemical and Lewis acid catalysed conditions. However, the *E*-isomers appear to be more stable than the corresponding *Z*-isomers. Both these isomers are reluctant to undergo [4+2] cycloaddition under the condition applied. Further our furanisation attempts using stannous chloride-acetic acid-hydrochloric acid mixture resulted in hydrogenation. Our endeavours towards the synthesis of phenanthrenone-9-ylidene ketone resulted in the formation of pyran derivative.

5.5. Experimental

5.5.1. 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 infra red spectra were recorded using ABB Bomem (MB Series) FT-IR spectrometer. All steady state irradiations were carried out using Rayonet Photochemical Reactor (RPR). Solvents for photolysis were purified and distilled before use. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively on a Bruker 300 FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane. Elemental analysis was performed using Elementar Systeme (Vario ELIII) at STIC, Kochi.

5.5.2. Starting Materials: Acenaphthenequinone, acetophenone, 4-methyl-acetophenone, 4-chloroacetophenone, 4-methoxyacetophenone, 4-phenyl-acetophenone were purchased from Sigma Aldrich and were used as obtained.

5.5.2.1. 2-Bromo-1-phenylethanone (23a): Prepared using a known procedure (75%, mp 50 ^{0}C).[50]

5.5.2.2. 2-Bromo-1-(*p*-tolyl)ethanone (23b): Prepared using a known procedure. (73%, mp 48 ^{0}C).[50]

5.5.2.3. 2-Bromo-1-(*p*-chlorophenyl)ethanone (23c): Prepared using a known procedure (76%, mp 85 ^{0}C).[50]

5.5.3. Synthesis of Acenaphthenone-2-ylidene ketones 22a,b,c by Wittig reaction

5.5.3.1. Synthesis of Acenaphthenone-2-ylidene ketone (22a)

5.5.3.1a 2-Bromo-1-phenylethanoyltriphenylphosphonium bromide (24a) 2-Bromo-1-phenylethanone (5.0 g, 25 mmol) was added in portions to a chloroform solution (6 mL) of triphenylphosphine (6.5 g, 25 mmol). The solution was filtered into 1 litre of anhydrous ether. The precipitate thus formed was then collected, dried and recrystallised from water in the form of white powder (68%, mp 267 ^{0}C).

5.5.3.1b Triphenylphosphinebenzoylmethylene (25a): A mixture of 2-bromo-1-phenylethanoyltriphenylphosphonium bromide (7.0 g) and 10% aqueous sodium carbonate (250 mL) was shaken for 15 h. The mixture was filtered and insoluble portion was taken up in hot benzene (200 mL). Some unreacted bromide was removed by filtration; addition of petroleum ether to the benzene filtrate afforded the compound **25a** as white powder (65%, mp 180 ^{0}C).

5.5.3.1c Acenaphthenone-2-ylidene ketone 22a: A solution of acenapthenequinone (5.3 g, 27 mmol) and triphenylphosphine-benzoylmethylene (10.3 g, 27 mmol) in ethanol (30 mL) was stirred at room temperature for 2 h. The solid product that separated out was filtered and purified by recrystallisation from ethanol chloroform mixture to give compound **22a** as yellow needles.

Compound 22a: (60%); mp 108 ^{0}C; IR ν_{max} (KBr), 1722, 1671 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 7.26-8.97 (12H, m, aromatic and vinylic protons); ^{13}C NMR ($CDCl_3$) δ 96.43, 118.29, 123.19, 126.12, 127.62, 128.33, 128.40,

129.23, 130.38, 130.87, 131.02, 133.25, 134.86, 138.10, 140.84, 141.13, 199.21, 200.32; Anal. Calcd for $C_{20}H_{12}O_2$: C, 84.49; H, 4.25. Found: C, 84.43; H, 4.39.

5.5.3.2. Synthesis of Acenaphthenone-2-ylidene ketone 22b

5.5.3.2a 2-Bromo-1-(*p*-tolyl)ethanoyltriphenylphosphonium bromide (24b): 2-Bromo-1-(*p*-tolyl)ethanone (4.0 g, 19 mmol) was added in portions to a chloroform solution (6 mL) of triphenylphosphine (4.9 g, 19 mmol). The solution was filtered into one litre of anhydrous ether. The precipitate was collected, dried and recrystallised from water in the form of white powder (65%, mp 265 ^{0}C).

5.5.3.2b Triphenylphosphine-(*p*-tolyl)methylene (25b): A mixture of 2-bromo-1-(*p*-tolyl)ethanoyltriphenylphosphonium bromide (7.0.g) and 10% aqueous sodium carbonate (250 mL) was shaken for 15 h. The mixture was filtered and insoluble portion was taken up in hot benzene (200 mL). Some unreacted bromide was removed by filtration; addition of petroleum ether to the benzene filtrate afforded the compound **25b** as white powder (67%, mp 178 ^{0}C).

5.5.3.2c Acenaphthenone-2-ylidene ketone 22b: A solution of acenaphthenequinone (5.3 g, 27 mmol) and triphenylphosphine-(*p*-tolyl)methylene (10.7 g, 27 mmol) in ethanol (30 mL) was stirred at room temperature for 2 h. The solid product that separated out was filtered and purified by recrystallisation from ethanol chloroform mixture to give the compound **22b** as yellow needles.

Compound 22b: (64%); mp 144 ^{0}C; IR ν_{max} (KBr), 1710, 1674 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.40(3H, s, methyl protons), 7.21-8.97 (11H, m, aromatic

and vinylic protons); ^{13}C NMR ($CDCl_3$) δ 25.80, 122.52, 126.81, 127.17, 127.50, 129.64, 129.51, 129.80, 130.31, 131.34, 132.01, 134.47, 134.93, 144.29, 153.81, 199.34, 200.16; Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.54; H, 4.74. Found: C, 84.48; H, 4.76.

5.5.3.3. Synthesis of Acenaphthenone-2-ylidene ketone 22c

5.5.3.3a 2-Bromo-1-(chlorophenyl)ethanoyltriphenylphosphonium bromide (24c): 2-Bromo-1-(chlorophenyl)ethanoyltriphenylphosphonium bromide (5.0 g, 22 mmol) was added in portions to a chloroform solution (6 mL) of triphenylphosphine (5.7 g, 22 mmol). The solution was filtered into one litre of anhydrous ether. The precipitate was collected, dried and recrystallised from water in the form of white powder (68%, mp 274 ^{0}C).

5.5.3.3b Triphenylphosphine-(4-chlorophenyl)methylene (25c): A mixture of 2-bromo-1-(chlorophenyl)ethanoyltriphenylphosphonium bromide (7.0.g) and 10% aqueous sodium carbonate (250 mL) was shaken for 15 h. The mixture was filtered and insoluble portion was taken up in hot benzene (200 mL). Some unreacted bromide was removed by filtration; addition of petroleum ether to the benzene filtrate afforded compound **25c** as white powder (64%, mp 194 ^{0}C).

5.5.3.3c Acenaphthenone-2-ylidene ketone 22c: A solution of acenapthenequinone (5.3 g, 27 mmol) and triphenylphosphine-(4-chlorophenyl)methylene (11.2 g, 27 mmol) in ethanol (30 mL) was stirred at room temperature for 2 h. The solid product that separated out was filtered and purified by recrystallisation from ethanol chloroform mixture to give compound **22c** as yellow needles.

Compound 22c: (68%); mp 188^{0}C; IR ν_{max} (KBr), 1716, 1668 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) 7.14-8.81 (11H, m, aromatic and vinylic protons); ^{13}C NMR ($CDCl_3$) δ 96.19, 117.99, 122.09, 126.85, 127.92, 128.39, 128.45, 129.08, 130.18, 130.77, 131.54, 132.05, 134.99, 139.10, 140.14, 140.93, 194.21, 200.4; Anal. Calcd for $C_{20}H_{11}ClO_2$: C, 75.36; H, 3.48. Found: C, 75.39; H, 3.41.

5.5.4. Synthesis of Acenaphthenone-2-ylidene ketones 22c-f by Claisen-Schmidt Condensation

5.5.4.1. Synthesis of Acenaphthenone-2-ylidene ketone 22c

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 at about 60 ^{0}C for 4 h and then kept in a refrigerator for about 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 **22c** as yellow needles (64%, mp 188 ^{0}C).

5.5.4.2. Synthesis of Acenaphthenone-2-ylidene ketone 22d

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 at about 60 ^{0}C for 4 h and then kept in a refrigerator for about 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 **22d** as yellow needles.

Compound 22d: (57%); mp 198 ^{0}C; IR ν_{max} (KBr), 1710, 1663 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 7.12-8.80 (11H, m, aromatic and vinylic protons);

Anal. Calcd for $C_{20}H_{11}BrO_2$: C, 66.14; H, 3.05. Found: C, 66.18; H, 3.11.

5.5.4.3. Synthesis of Acenapthenone-2-ylidene ketone 22e

A mixture of acenapthenequinone (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 at about 60 ^{0}C for 4 h and then kept in a refrigerator for about 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 **22e** as yellow needles.

Compound 22e: (63%); mp 162 ^{0}C; IR ν_{max} (KBr), 1722, 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 3.88 (3H, s, methoxy protons), 6.91-8.84 (11H, m, aromatic and vinylic protons); ^{13}C NMR ($CDCl_3$) δ 55.4096.22, 104.37, 106.09, 107.71, 108.72, 110.99, 113.05, 113.98, 114.13, 114.62, 115.41, 117.69, 121.93, 126.53, 128.37, 129.12, 129.84, 130.47, 130.80, 131.24, 131.31, 132.62, 138.22, 140.70, 164.04, 189.13, 193.66. Anal. Calcd for $C_{21}H_{14}O_3$: C, 84.54; H, 4.73. Found: C, 84.50; H, 4.69.

5.5.4.4. Synthesis of Acenaphthenone-2-ylidene ketone 22f

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 at about 60 ^{0}C for 4 h and then kept in a refrigerator for about 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 **22f** as yellow needles

Compound 22f: (60%); mp 188 ^{0}C; IR ν_{max} (KBr), 1715, 1650 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) 7.25-8.78 (16H, m, aromatic and vinylic protons); ^{13}C NMR ($CDCl_3$) δ 96.22, 108.14, 109.54, 112.89, 117.87, 122.04, 124.04, 126.48,

126.69, 127.114, 127.40, 127.79, 128.23, 128.39, 128.83, 128.94, 129.47, 130.81, 131.43, 132.365, 132.47, 135.31, 140.11, 146.41, 194.87, 201.89. Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.64; H, 4.47. Found: C, 86.68; H, 4.42.

5.5.5. Attempted Synthesis of Phenanthrenone-9-ylidene ketone 27a

A stirred solution of phenanthrenequinone (0.40 g, 2 mmol) and the ylide **26** (0.76 g, 2 mmol) in dry dichloromethane (10 mL) was boiled under reflux for 12 h. After cooling to room temperature compound **30** was precipitated as colourless crystals, which was recrystallised from benzene. (33%, mp 230-232^{0}C)

5.5.6. Irradiation of Acenaphthenone-2-ylidene ketones 22a,c,e,f

5.5.6.1. Photolysis of Acenaphthenone-2-ylidene ketone 22a

A benzene solution of **22a** (0.69 mmol in 130 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 6 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (1:1) of hexane and dichloromethane gave **31a** as a yellow compound. Further elution of the column with a mixture (1:4) of hexane and dichloromethane gave (25%) unchanged **22a.**

Compound 31a: (40%); mp 102^{0}C; IR ν_{max} (KBr), 1728, 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 7.16-8.10 (12H, m, aromatic and vinylic protons); ^{13}C NMR ($CDCl_3$) δ 96.68, 119.29, 123.15, 126.22, 127.62, 128.33, 128.48, 129.23, 130.38, 130.87, 131.02, 132.25, 134.86, 138.10, 139.84, 140.13, 199.29, 200.30; Anal. Calcd for $C_{20}H_{12}O_2$: C, 84.49; H, 4.25. Found: C, 84.43; H, 4.39.

5.5.6.2. Photolysis of Acenaphthenone-2-ylidene ketone 22c

A benzene solution of **22c** (0.62 mmol in 130 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 6 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (1:1) of hexane and dichloromethane gave **31c** as yellow compound. Further elution of the column with a mixture (1:4) of hexane and dichloromethane gave unchanged **22c**.

Compound 31c: (45%); mp 178 ^{0}C; IR ν_{max} (KBr), 1718, 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) 7.2-8.2 (11H, m, aromatic and vinylic protons); ^{13}C NMR ($CDCl_3$) δ 96.19, 117.14, 122.49, 125.85, 127.92, 128.39, 128.74, 129.08, 130.18, 130.77, 131.54, 132.05, 134.99, 139.19, 139.84, 140.93, 194.21, 199.89; Anal. Calcd for $C_{20}H_{11}ClO_2$: C, 75.36; H, 3.48. Found: C, 75.39; H, 3.41.

5.5.6.3. Photolysis of Acenaphthenone-2-ylidene ketone 22e

A benzene solution of **22e** (0.63 mmol in 130 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 6 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (1:1) of hexane and dichloromethane gave **31e** as a yellow compound. Further elution of the column with a mixture (1:4) of hexane and dichloromethane gave unchanged **22e.**

Compound 31e: (40%); mp 152 ^{0}C; IR ν_{max} (KBr), 1722, 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 3.53 (3H, s, methoxy protons), 7.01-8.00 (11H, m, aromatic and vinylic protons); ^{13}C NMR ($CDCl_3$) δ 58.40, 96.62, 105.37,

106.09, 107.71, 108.72, 110.99, 113.05, 113.98, 114.25, 114.68, 115.41, 117.69, 121.86, 126.53, 128.37, 129.12, 129.84, 130.47, 130.80, 131.24, 131.31, 132.62, 138.22, 140.70, 164.04, 189.13, 198.66 Anal. Calcd for $C_{21}H_{14}O_3$: C, 84.54; H, 4.73. Found: C, 84.50; H, 4.69.

5.5.6.4. Photolysis of Acenaphthenone-2-ylidene ketone 22f

A benzene solution of **22f** (0.55 mmol in 130 mL) was purged with nitrogen for 20 min and then irradiated (RPR, 300 nm) for 6 h. Progress of the reaction was monitored by TLC. Solvent was removed under vacuum and the residue was charged to a column of silica gel. Elution with a mixture (1:1) of hexane and dichloromethane gave **31f** as a yellow compound. Further elution of the column with a mixture (1:4) of hexane and dichloromethane gave unchanged **22f.**

Compound 31f: (45%); mp 164 ^{0}C; IR ν_{max} (KBr), 1711, 1656 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) 7.20-8.02 (16H, m, aromatic and vinylic protons); ^{13}C NMR ($CDCl_3$) δ 96.08, 108.24, 109.54, 113.89, 117.36, 122.04, 124.24, 126.48, 126.89, 127.41, 127.46, 127.79, 128.33, 128.39, 129.47, 130.81, 131.43, 132.47, 135.31, 144.11, 148.41, 197.87, 202.01 Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.64; H, 4.47. Found: C, 86.68; H, 4.42.

5.5.7. Isomerisation of Acenaphthenone-2-ylidene ketones 22a,c,e,f catalysed by Lewis Acid

5.5.7.1. Isomerisation of Acenaphthenone -2-ylidene ketone 22a

To a solution of acenaphthenone-2-ylidene ketone **22a** (0.5 g, 1.7 mmol) in dry dichloromethane (30 mL) a slight excess of anhydrous aluminium chloride (0.28 g, 2.2 mmol) was added under stirring at room temperature. After 24 h the reaction was quenched with cold saturated sodium bicarbonate solution

and worked up with dichloromethane. After evaporation of the solvent the residue was column chromatographed over silica gel, eluting with dichloromethane hexane mixture (1:1) gave the product **31a** (55%).

5.5.7.2. Isomerisation of Acenaphthenone -2-ylidene ketone 22c

To a solution of acenaphthenone-2-ylideketone **22c** (0.5 g, 1.57 mmol) in dry dichloromethane (30 mL) a slight excess of anhydrous aluminium chloride (0.25 g, 1.8 mmol) was added under stirring at room temperature. After 24 h the reaction was quenched with cold saturated sodium bicarbonate solution and worked up with dichloromethane. After evaporation of the solvent the residue was column chromatographed over silica gel, eluting with dichloromethane hexane mixture (1:1) gave the product **31c** (58%).

5.5.7.3. Isomerisation of Acenaphthenone -2-ylidene ketone 22e

To a solution of acenaphthenone-2-ylidene ketone **22e** (0.5 g, 1.6 mmol) in dry dichloromethane (30 mL) a slight excess of anhydrous aluminium chloride (0.25 g, 1.9 mmol) was added under stirring at room temperature. After 24 h, the reaction was quenched with cold saturated sodium bicarbonate solution and worked up with dichloromethane. After evaporation of the solvent the residue was column chromatographed over silica gel, eluting with dichloromethane hexane mixture (1:1) gave the product **31e** (57%).

5.5.7.4. Isomerisation of Acenaphthenone-2-ylidene ketone 22f

To a solution of acenaphthenone-2-ylidene ketone **22f** (0.5 g, 1.4 mmol) in dry dichloromethane (30 mL) a slight excess of anhydrous aluminium chloride (0.20 g, 1.5mmol) was added under stirring at room temperature. After 24h the reaction was quenched with cold saturated sodium bicarbonate solution and worked up with dichloromethane. After evaporation of the solvent, the

residue was column chromatographed over silica gel, eluting with dichloromethane hexane mixture (1:1) gave the product **31f** (59%).

5.5.8. Neat Thermolysis of Acenaphthenone-2-ylidene ketones 22a, 31a

5.5.8.1. Acenaphthenone-2-ylidene ketone **22a** (100 mg, 0.35 mmol) was heated to 180 ^{0}C in a sealed tube for 6 h. The progress of the reaction was monitored by TLC. Solvent was removed and the residue was charged to a column of silica gel. An intractable mixture resulted.

5.5.8.2. Acenaphthenone-2-ylidene ketone **31a** (100 mg, 0.35 mmol) was heated to 180 ^{0}C in a sealed tube for 6 h. The progress of the reaction was monitored by TLC. Solvent was removed and the residue was charged to a column of silica gel. An intractable mixture resulted

5.5.9 Synthesis of Dispirocompounds (36a-c)

5.5.9.1. Synthesis of Dispirocompound 36a

5.5.9.1a 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 4 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 **36a** as white powder.

Compound 36a: (40%); mp >300 ^{0}C; IR ν_{max} (KBr) 3345 (OH), 1706 and 1682 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 215 (ε 44,000), 248 (ε 15,000), 341 nm (ε 4,600); ^{1}H NMR ($CDCl_3$) δ 2.86 (s, 3H, methoxy protons), 5.67 (s, 1H), 5.97 (s, 1H, hydroxyl proton), 6.19 (s, 1H), 6.63-8.56 (m, 22H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 60.3 , 63.6 (C), 65.2, 70.0, 84.0, 91.24, 120.82,

123.01, 123.93, 124.26, 125.14, 125.43, 127.28, 127.51, 127.68, 127.71, 128.19, 128.48, 128.80, 129.87, 130.69, 131.23, 132.20, 133.08, 133.12, 134.88, 136.51, 138.07, 138.34, 140.60, 142.22, 142.71, 197.90, 205.21, 208.75 Anal. Calcd for $C_{41}H_{28}O_5$: C, 81.98; H, 4.70. Found: 81.71; H, 4.77.

5.5.9.1b Alternately, to a solution of acenaphtheneone-2-ylidene ketone **22a** (0.36 g, 1.2 mmol) in methanol (synthesised via Wittig route), sodium methoxide (0.06 g) was added and stirred at room temperature for 6 h. The reaction was monitored by TLC. The solid product separated was filtered and purified by recrystallisation from a mixture of methanol and dichloromethane to give compound **36a** as white powder. (45%)

5.5.9.2. Synthesis of Dispirocompound 36b

5.5.9.2a 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 4 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 **36b** as white powder.

Compound 36b: (38%); mp >300 ^{0}C; IR ν_{max} (KBr) 3348 (OH), 1711, and 1676 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 215 (ε 42,000), 251 (ε 16,000), 341 nm (ε 4,600); ^{1}H NMR ($CDCl_3$) δ 1.92 (s, 3H, methyl protons) 2.05 (s, 3H, methyl protons), 2.82 (s, 3H, methoxy protons), 5.63 (s, 1H), 6.03 (s, 1H, hydroxyl proton), 6.21 (s, 1H), 6.41-8.55 (m, 20H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 21.02, 21.28, 60.15, 63.63, 64.92, 69.76, 84.58, 91.12, 120.80, 122.53, 123.35 , 124.11, 124.59, 124.91, 126.7, 127.16, 122.77, 127.84, 128.01, 128.11, 128.43, 129.58, 130.21, 130.30, 130.85, 132.46, 132.89, 133.74, 134.60, 134.83, 136.82, 137.96, 140.52, 142.06, 142.45, 142.68,

197.19, 205.38, 208.34. Anal. Calcd for $C_{43}H_{32}O_5$: C, 82.15; H, 5.13. Found: 82.18; H, 5.19.

5.5.9.2b Alternately, to a solution of acenaphthenone-2-ylidene ketone **22b** (0.36 g, 1.1 mmol) in methanol (synthesised via Wittig route), sodium methoxide (0.05 g) was added and stirred at room temperature for 6 h. The reaction was monitored by TLC. The solid product separated was filtered and purified by recrystallisation from a mixture of methanol and dichloromethane to give compound **36b** as white powder (42%).

5.5.9.3. Synthesis of Dispirocompound 36c

5.5.9.3a 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 (80 mL) was stirred around 60 ^{0}C for 8 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 **36c** as white powder.

Compound 36c: (36%); mp >300 ^{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 2.85 (s, 3H, methoxy protons), 5.58 (s, 1H), 6.11 (s, 1H, hydroxyl proton), 6.17 (s, 1H), 6.57-8.41 (m, 20H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 60.01, 63.17, 64.71, 69.45, 84.02, 90.64, 120.92, 122.70, 123.21, 123.88, 124.79, 125.08, 127.30, 127.48, 127.83, 128.03, 128.14, 128.24, 129.36130.02, 130.10, 131.07, 132.30, 132.81, 133.19, 133.95, 134.28, 136.12, 136.89, 138.14, 139.76, 141.76, 142.16, 196.15, 204.91, 207.69. Anal. Calcd for $C_{41}H_{26}O_5Cl_2$: C, 73.55; H, 3.91. Found: 73.77; H, 4.04.

5.5.9.3b Alternately, to a solution of acenaphthenone-2-ylidene ketone **22c** (0.36 g, 1.10 mmol) in methanol (synthesised via Wittig route), sodium methoxide(0.05 g) was added and stirred at room temperature for 8 h. The reaction was monitored by TLC. The solid product separated was filtered and purified by recrystallisation from a mixture of methanol and dichloromethane to give **36c** as white powder (46%).

5.5.10. Attempted synthesis of Dispirocompounds (22d-f)

5.5.10.1. To a solution of *E*-isomer of acenaphthenone-2-ylidene ketone **22d** (0.35 g, 1 mmol) in methanol (synthesised via Wittig route), sodium methoxide (0.52 g) was added and stirred at room temperature for 12 h. TLC showed no new product formation. Unchanged acenaphthenone-2-ylidene ketone **22d** was obtained in quantitative yield

5.5.10.2. To a solution of *E*-isomer of acenaphthenone-2-ylidene ketone **22e** (0.35 g, 1.1 mmol) in methanol (synthesised via Wittig route), sodium methoxide (0.52 g) was added and stirred at room temperature for 12 h. TLC showed no new product formation. Unchanged acenaphthenone-2-ylidene ketone **22e** was obtained in quantitative yield

5.5.10.3. To a solution of *E*-isomer of acenaphthenone-2-ylidene ketone **22f** (0.35 g, 1 mmol) in methanol (synthesised via Wittig route), sodium methoxide (0.53 g) was added and stirred at rt for 12 h. TLC showed no new product formation. Unchanged acenaphthenone-2-ylidene ketone **22f** was obtained in quantitative yield.

Above reaction was repeated with the *Z*-isomers **31a,c,e,f** also and the starting compound recovered unchanged.

5.5.11. Attempted Furanisation of Acenaphthenone-2-ylidene ketones

5.5.11.1. Synthesis of 2-(2-Oxo-2-phenylethyl)acenaphthylen-1(2*H*)-one (35a)

A solution of acenaphthenone-2-ylidene ketone **22a** (3.0 g, 11 mmol) in 10 mL of glacial acetic acid was poured into a warm mixture of 10 mL of glacial .acetic acid, 10mL of conc. hydrochloric acid and stannous chloride (11.7 g, 52 mmol). Progress of the reaction was monitored by TLC. After refluxing for 4 h and cooling, the product precipitated and was collected on a filter and recrystallised from hexane dichloromethane mixture (1:1) to give compound **35a** as white powder.

Compound 35a: (68%); mp 128-130 ^{0}C; IR ν_{max} (KBr), 1724, 1680 (C=O), 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.42 (1H, dd, methylene proton), 3.91 (1H, dd, methylene proton), 4.26 (1H, dd, methine proton) 7.23-7.90 (m, 11H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 39.81, 49.95, 123.91, 126.34, 126.82, 127.35, 128.71, 128.80, 131.56, 133.28, 133.58, 133.71, 136.84, 143.48, 143.65, 200.18, 204.90, Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.94. Found: C, 83.88; H, 4.98.

5.5.11.2. Synthesis of 2-(2-Oxo-2-(4-chlorophenyl)ethyl)acenaphthylen-1(2*H*)-one (35c)

A solution of acenaphthenone-2-ylidene ketone **21c** (3.0 g, 9 mmol) in 10 mL of glacial acetic acid was poured into a warm mixture of 10 mL of glacial acetic acid, 10 mL of conc. hydrochloric acid and stannous chloride (10.5 g, 46 mmol). After refluxing for 4 h and cooling, the product precipitated and was collected on a filter and recrystallised from hexane dichloromethane mixture (1:1) to give compound **35c** as white powder.

Compound 35c: (70%); mp 150-152 ^{0}C; IR ν_{max} (KBr), 1728, 1676 (C=O), 1607 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.46 (1H, dd, methylene proton), 3.94 (1H, dd, methylene proton), 4.35 (1H, dd, methine proton) 7.26-8.13 (m, 10H, aromatic protons); Anal. Calcd for $C_{20}H_{13}ClO_2$: C, 74.89; H, 4.08. Found: C, 74.80; H, 3.99.

5.5.11.3. Synthesis of 2-(2-Oxo-2-(4-methoxyphenyl)ethyl)acenaphthyl-en-1(2*H*)-one (35e)

A solution of acenaphthenone-2-ylidene ketone **21e** (3.0 g, 10 mmol) in 10mL of glacial acetic acid was poured into a warm mixture of 10mL of glacial acetic acid, 10 mL of conc. hydrochloric acid and stannous chloride (10.6 g, 47 mmol). After refluxing for 4 h and cooling, the product precipitated and was collected on a filter and recrystallised from hexane dichloromethane mixture (1:1) to give compound **35e** as white powder.

Compound 35e: (72%); mp 148 ^{0}C; IR ν_{max} (KBr), 1712, 1673 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 3.45 (3H, s, methoxy), δ 3.50 (1H, dd, methylene proton), 3.98 (1H, dd, methylene proton), 4.45 (1H, dd, methine proton) 7.20-8.37 (10H, m, aromatic protons); Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.68; H, 4.96.

5.5.11.4. Synthesis of 2-(2-Oxo-2-(4-phenylphenyl)ethyl)acenaphthylen-1(2H)-one (35f)

A solution of acenaphthenone-2-ylidene ketone **22f** (3.0 g, 8 mmol) in 10mL of glacial acetic acid was poured into a warm mixture of 10 mL of glacial acetic acid, 10mL of conc. hydrochloric acid and stannous chloride (9.2 g, 41 mmol). After refluxing for 4 h and cooling, the product precipitated and was

collected on a filter and recrystallised from hexane dichloromethane mixture (1:1) to give compound **35f** as white powder

Compound 35f: (74%); mp 158^{0}C; IR ν_{max} (KBr), 1720, 1681 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 3.54 (1H, dd, methylene proton), 4.01 (1H, dd, methylene proton), 4.39 (1H, dd, methine proton) 7.42-8.07 (15H, m, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 40.22, 47.28, 96.20, 121.34, 121.62, 124.22, 127.29, 127.32, 128.00, 128.29, 128.66, 128.83, 128.97, 130,85, 131.57, 133.73, 135.18, 139.31, 139.83, 142.01, 146.11, 196.69, 204.71 Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 86.20; H, 5.18.

With *Z*-isomers **31a,c,e,f** related reaction was observed resulting in the formation of compounds **35a,c,e,f** respectively.

5.5.12. Attempted Cycloaddition Reaction of Acenaphthenone-2-ylidene Ketone 22d and 31a with DMAD.

5.5.12.1. A mixture of acenaphthenone-2-ylidene ketone **22a** (100 mg, 0.3 mmol) and dimethyl acetylenedicarboxylate (44.0 mg, 0.3 mmol) dissolved in benzene was placed in a round bottom flask fitted with a reflux condenser. The mixture was heated under reflux for 6 h and the reaction was monitored by TLC. No new product was formed and starting compound **22a** recovered unchanged.

5.5.12.2. A mixture of acenaphthenone-2-ylidene ketone **31a** (100 mg, 0.3 mmol) and dimethyl acetylenedicarboxylate (44.0 mg, 0.3 mmol) dissolved in benzene was placed in a round bottom flask fitted with a reflux condenser. The mixture was heated under reflux for 6 h and the reaction was monitored by TLC. The reaction mixture was separated by column chromatography over silica gel using a mixture (2:1) of dichloromethane and hexane. On elution,

the *E*-isomer **22a** (38%) separated out first followed by the *Z*-isomer **31a** (18%).

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