

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[*f*]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[*f*]phenanthren-3-ones. **Chapter 5** mainly deals with synthesis, photolysis and solvent assisted chemical transmigration 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).

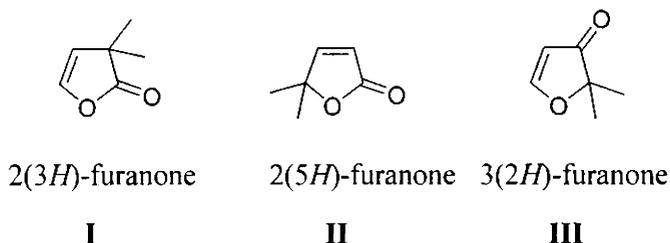
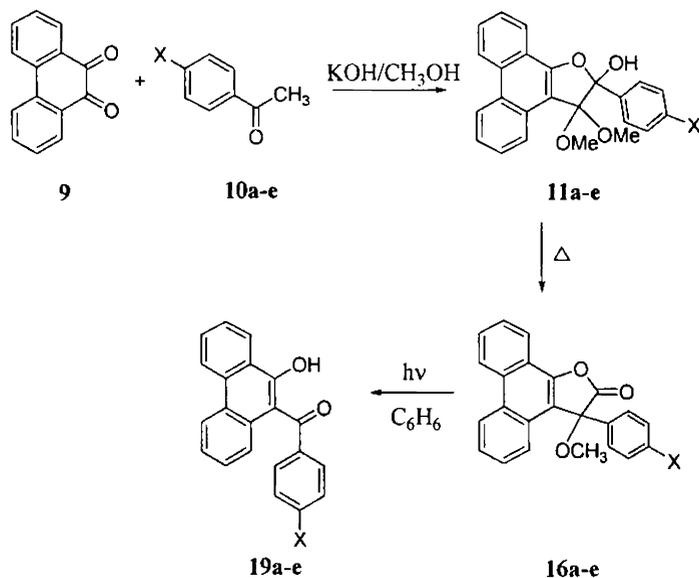


Figure 1

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



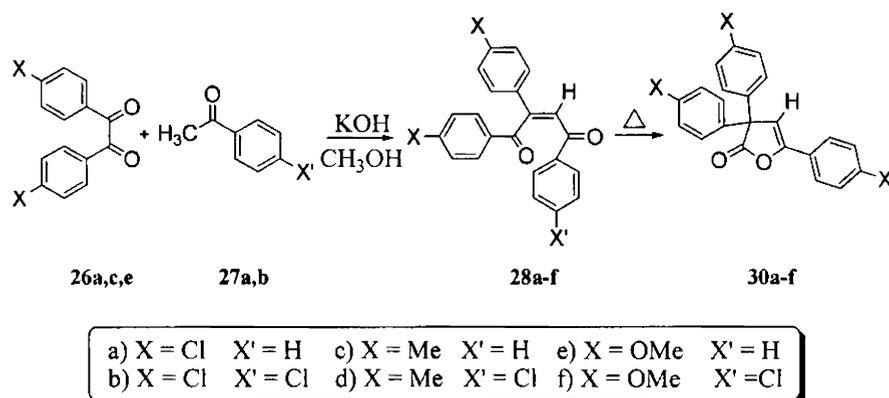
a) X = H b) X = CH₃ c) X = OCH₃ d) X = Cl e) X = Ph

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[*f*]phenanthren-2-ones from 3,3-dimethoxy-2-aryl-2,3-dihydro-1-oxacyclopenta[*f*]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.

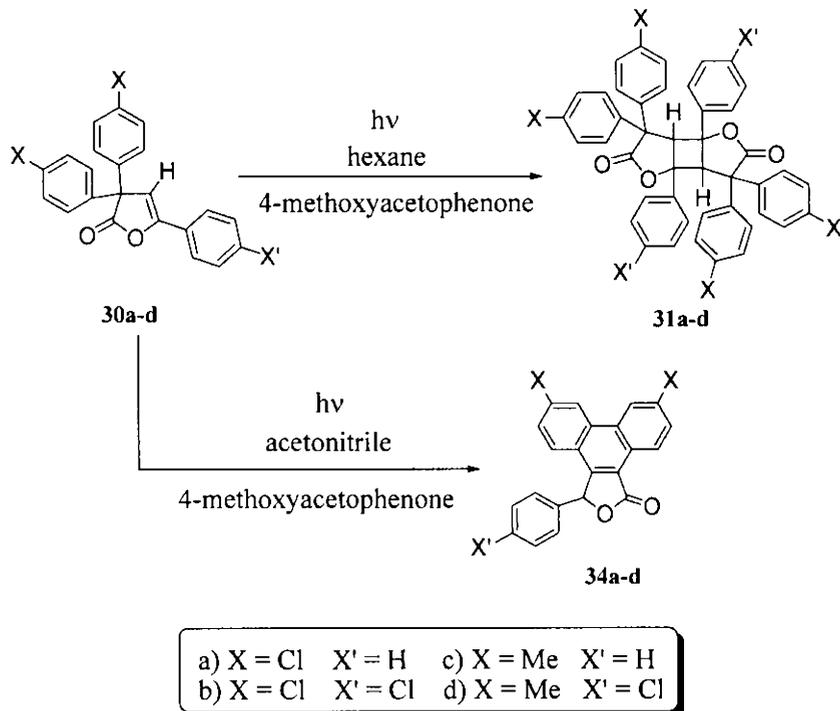
Chapter 3: Synthesis and Photochemical Transformations of a Few 3,3,5-Triaryl-3*H*-furan-2-ones

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



Scheme A 2

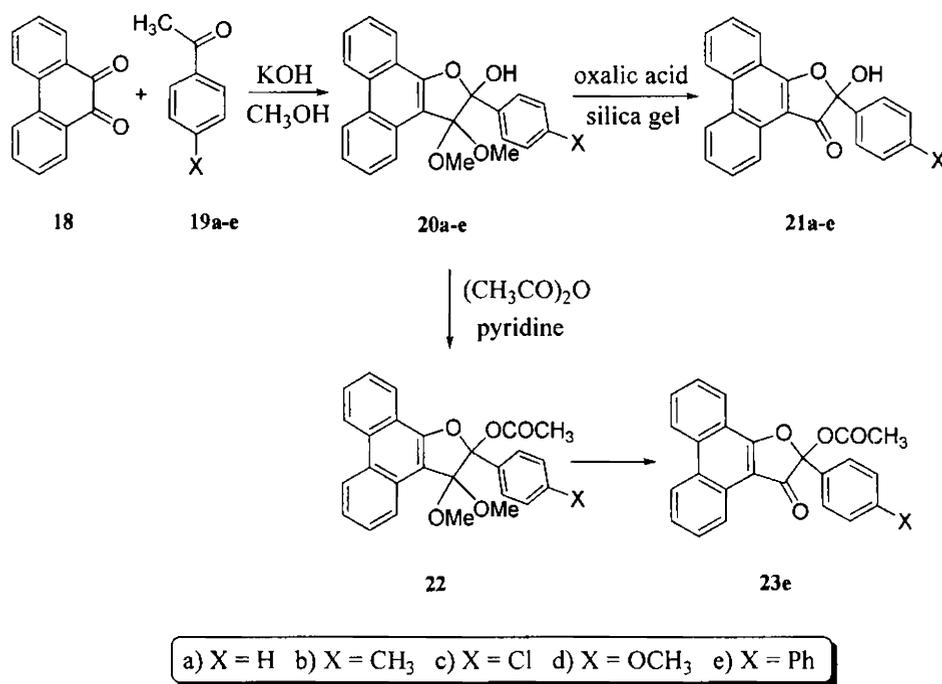
condensation of 4,4'-disubstituted benzils with suitably-substituted acetophenones to give diarylstyrenes which upon thermolysis yield the corresponding 2(3*H*)-furanones (Scheme A2). Our observations clearly indicated that with 4-methoxyacetophenone as sensitizer, irradiation in acetonitrile, lead to 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.



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.

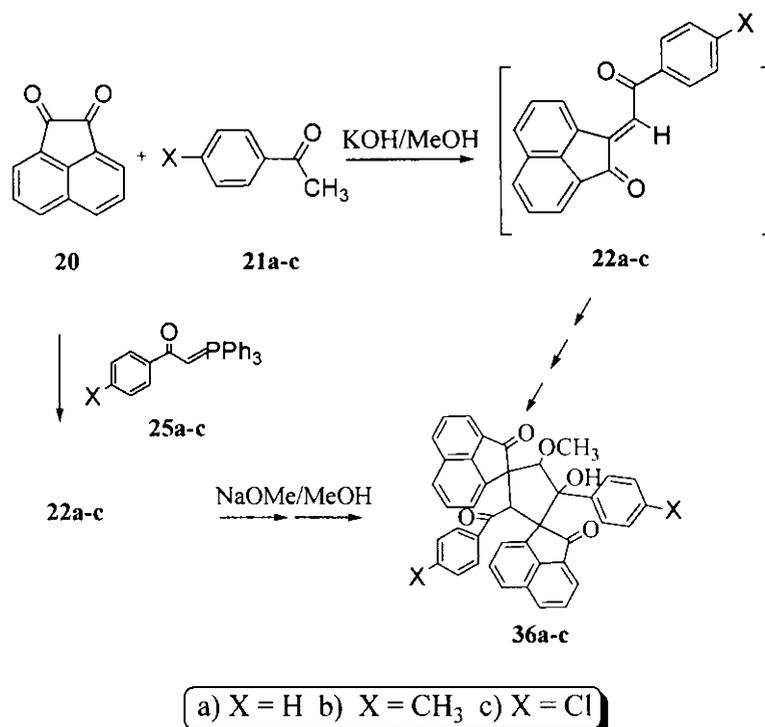


Scheme A 4

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[7]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[7]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.
