Chapter 1

A Preamble on Furanones: Synthesis and Photochemistry

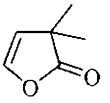
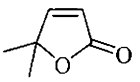
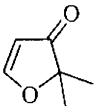
1.1. Introduction

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

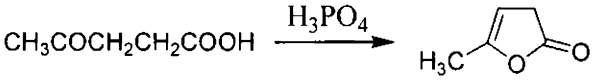
Furanones are of valuable synthetic and biological importance. They serve as useful synthetic building blocks for lactones and furans and comprise an important heterocyclic incorporated in natural products. The products of ring opening of these compounds with nucleophiles are the precursors of a wide 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).



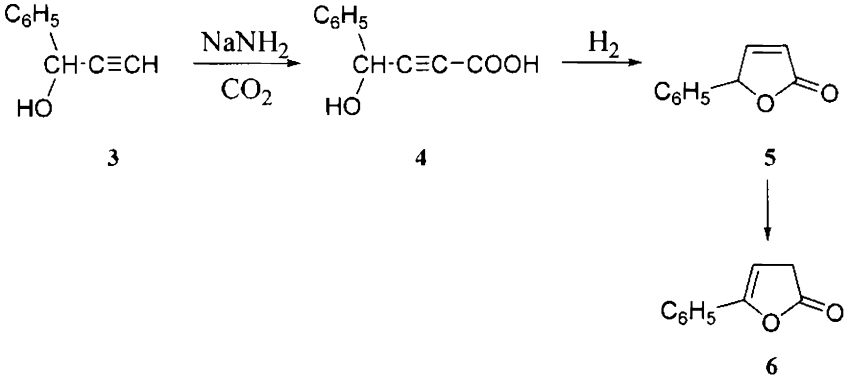
1 2

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



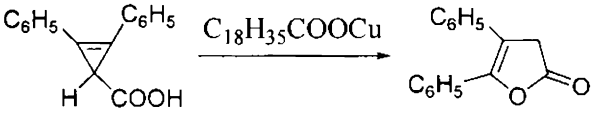
3 4 5 6

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.

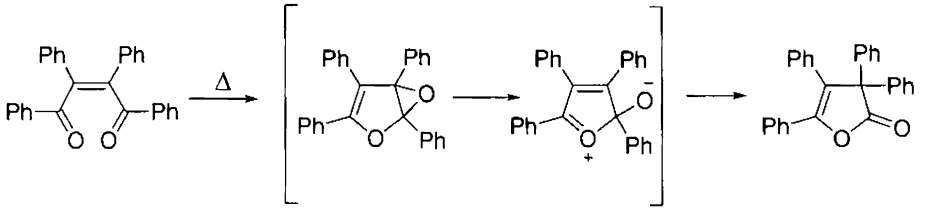


7 **8**

Scheme 3

1.2.1.4.Thermal Rearrangement

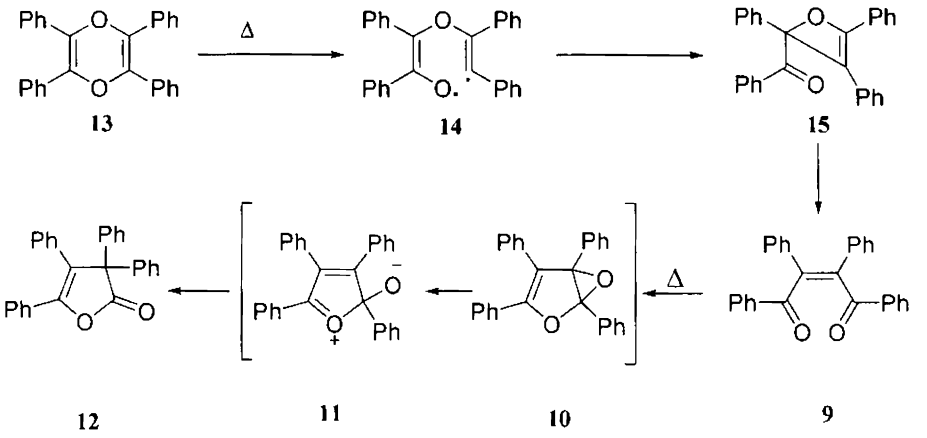
Zenin in 1872 reported the thermal rearrangement of *cis*-dibenzoyl-stilbene **(9)** to tetraphenylcrotonolactone **(12)** (Scheme 4).[27-29]



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

Scheme 4

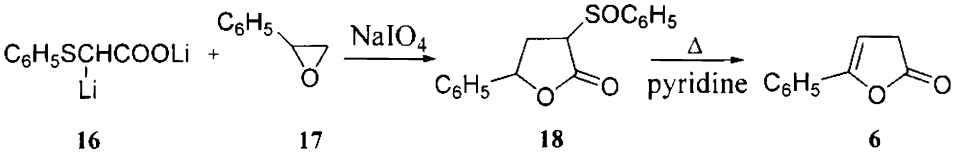
Later Berger and Summerbell observed similar thermal rearrangements with tetraphenyl-*p*-dioxadiene **(13)**. Upon pyrolysis around 250 ^{0}C, **13** rearranges to tetraphenylcrotonolactone **(12)** through the intermediacy of dibenzoyl-stilbene **(9)**.[30,31]



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]



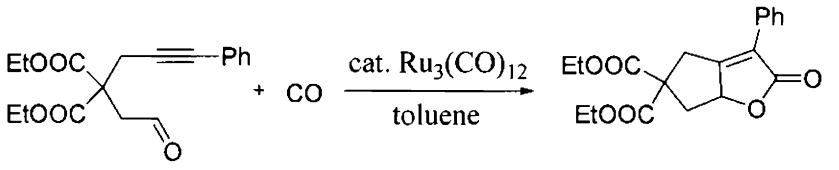
Scheme 6

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

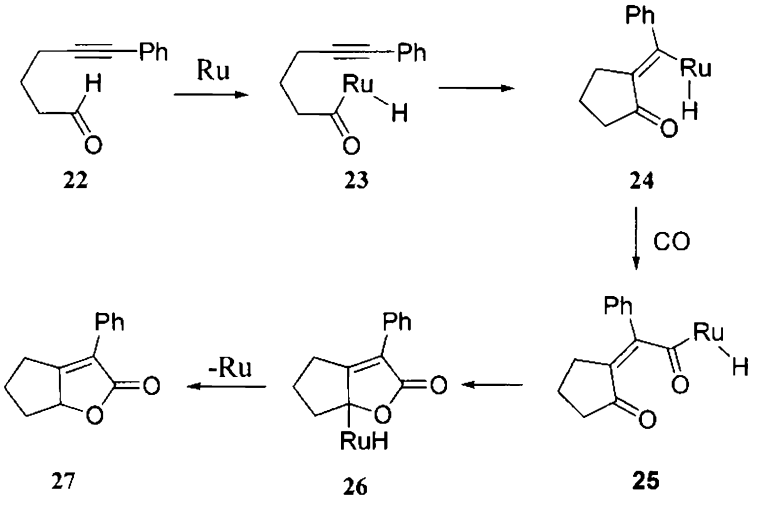
toluene in the presence of a catalytic amount of $Ru_3(CO)_{12}$ gave the corresponding bicyclic lactone **21** in high yields (Scheme 7).



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** **27** **26** **25**

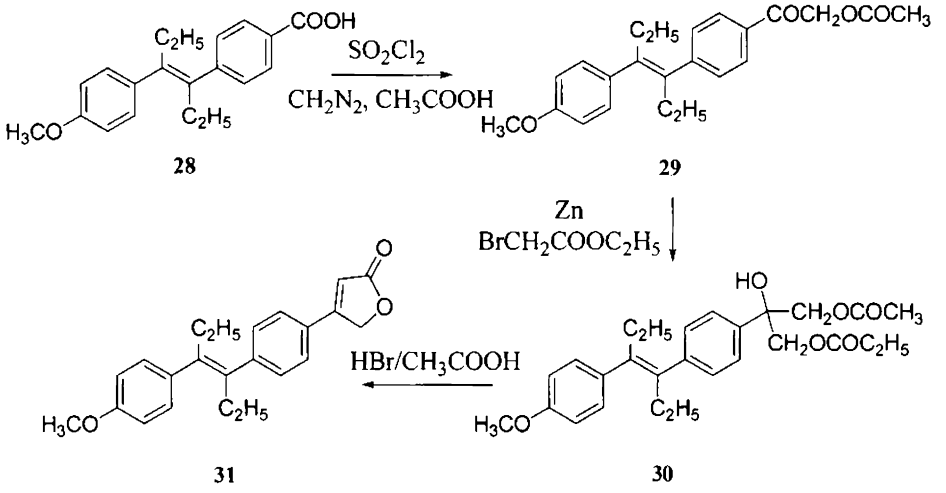
Scheme 8

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).

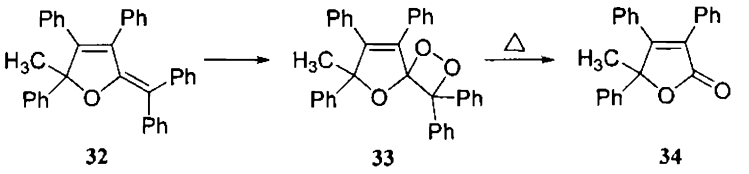


Scheme 9

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]

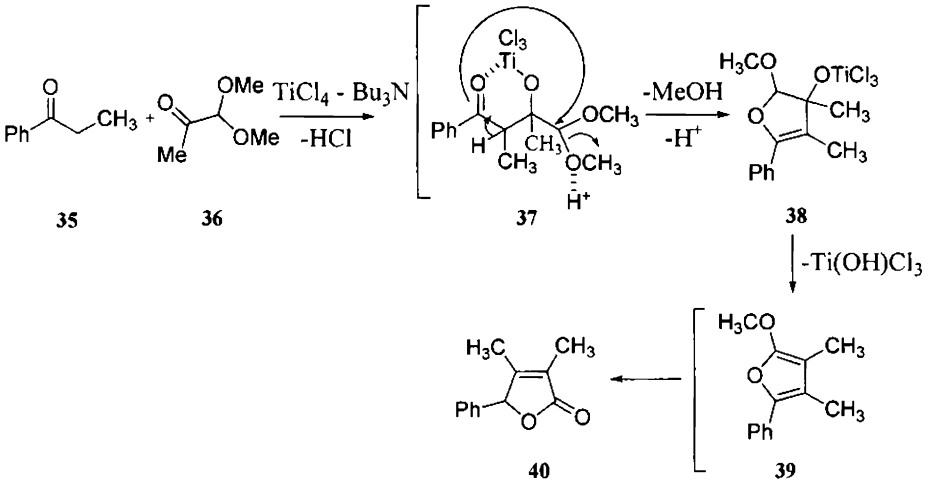


Scheme 10

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]

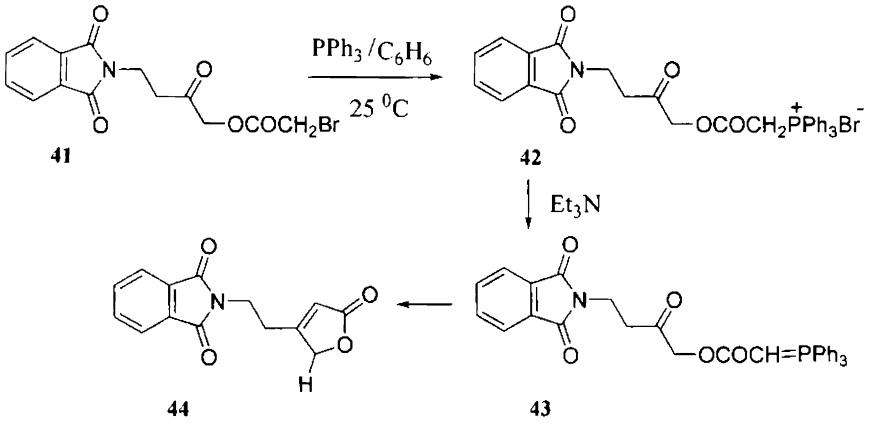


Scheme 11

$TiCl_4$-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]

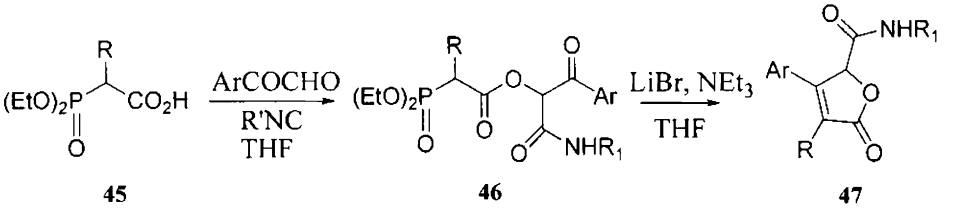


Scheme 12

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).



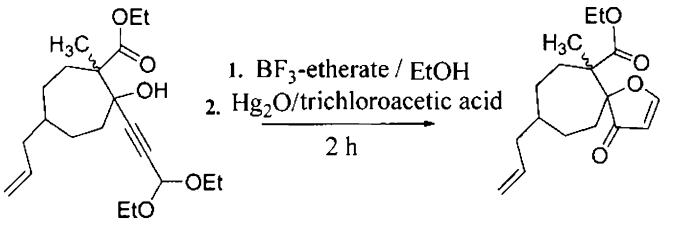
45 **46** **47**

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]

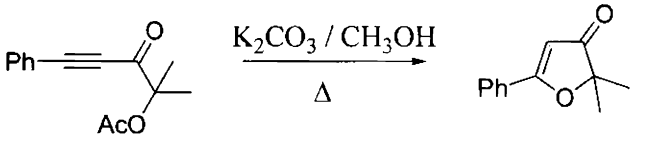


48 **49**

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.

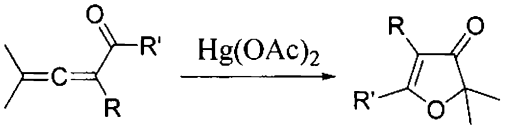


50 **51**

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).

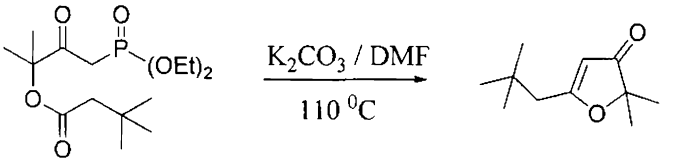


52 **53**

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).

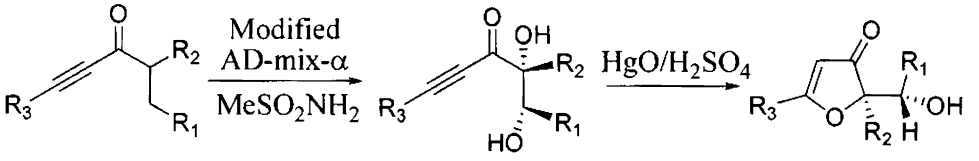


54 **55**

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

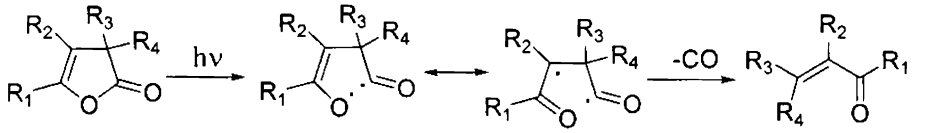
The required enynone precursors were obtained by addition of a terminal alkynyllithium to the appropriate 2-alkenal in THF to give the corresponding enynol which was oxidized to the requisite enynone **56** using MnO_2. The dihydroxy-ynones **57** were obtained from Sharpless asymmetric dihydroxylation 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

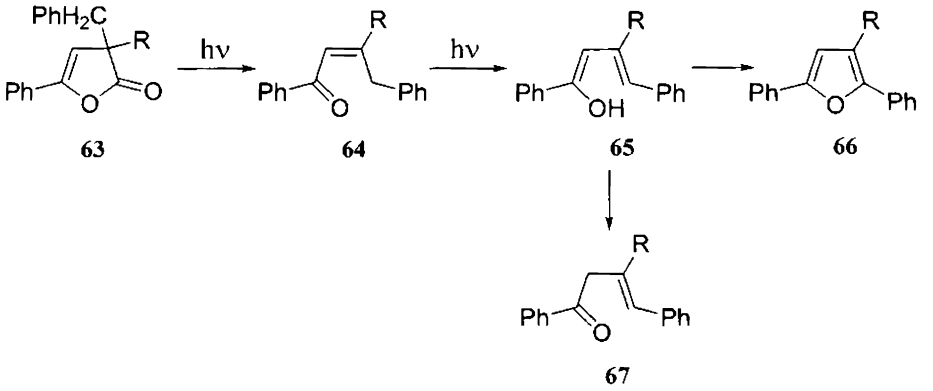
The photochemical decarbonylation of enol lactones has been reported to give the corresponding vinylketones.[77-83] It appears to occur from their lowest lying singlet states, through a primary cleavage of the carbonyl–oxygen bond. This leads to the formation of diradical intermediates which can be stabilised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



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

Scheme 19

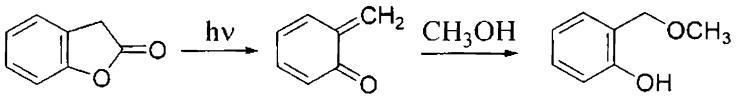
In the case of the 3-benzyl derivatives decarbonylation followed by double bond isomerisation and/or cyclisation to furan derivatives **66** was observed.[91]



63 **64** **65** **66** **67**

Scheme 20

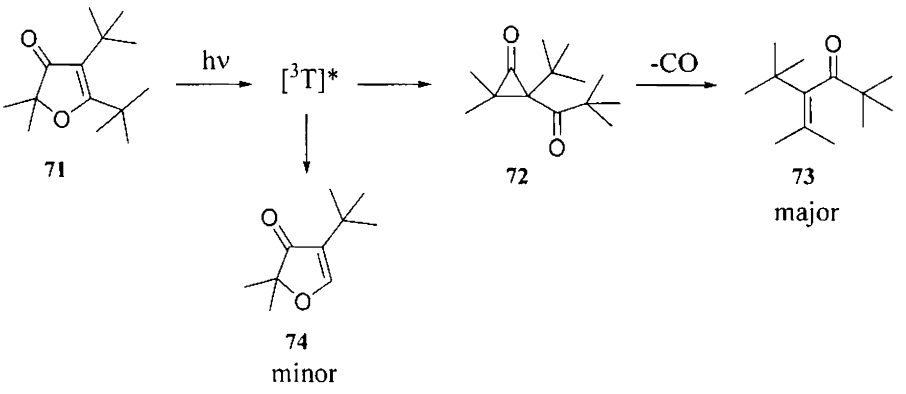
Chapman and McIntosh[92] have described a photodecarbonylation of benzofuran-2(3*H*)-one which upon irradiation in methanol affords *o*-hydroxybenzyl methyl ether **(70)** via the intermediacy of **69**. Analogous results are observed with substituted derivatives.[93-97]



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).

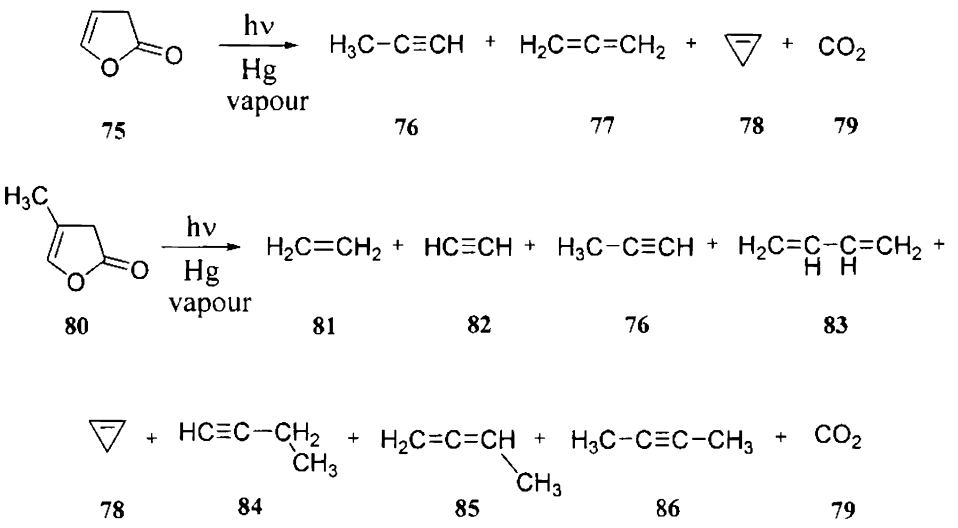


Scheme 22

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.

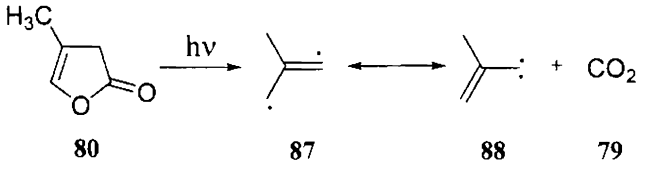
1.3.2. Decarboxylation

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]

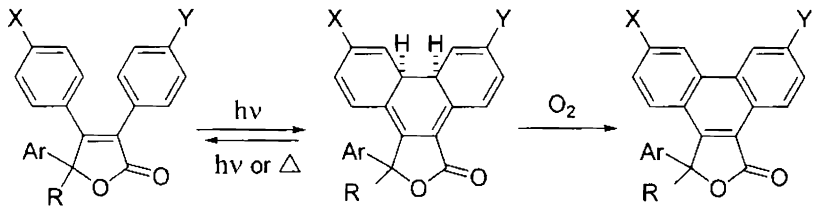


Scheme 24

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**.

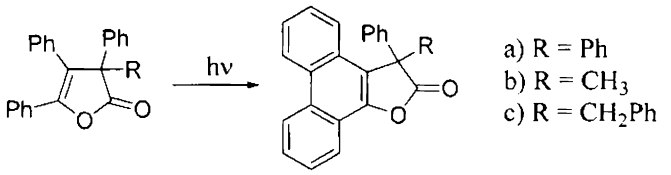


89 **90** **91**

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.

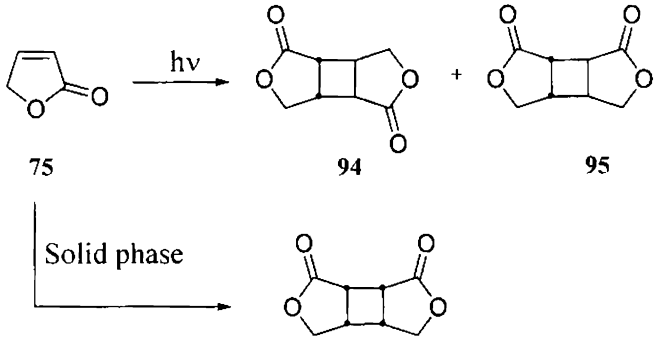


92 **93**

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]



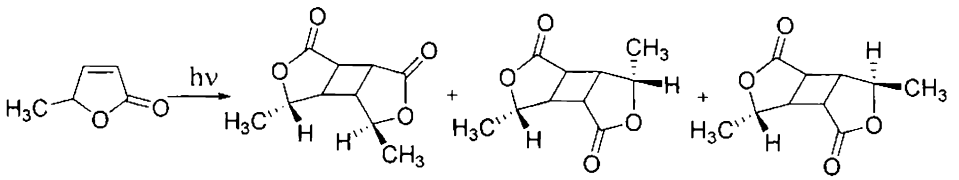
75 **94** **95**

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.

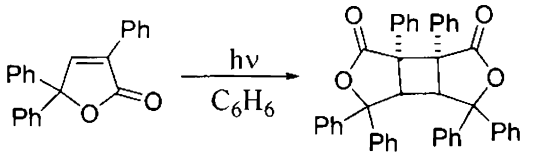


97 **98** **99** **100**

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.

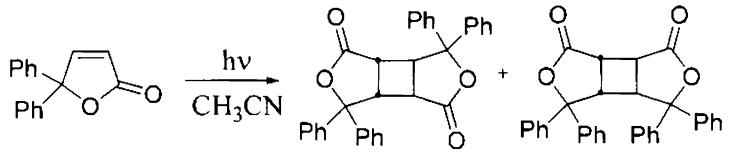
Padwa and co-workers[106] have studied the irradiation of 3,5,5-triphenyl-2(5*H*)-furanone **(101)** in concentrated benzene solution (Scheme 29). Under these conditions the formation of a dimer **(102)** tentatively assigned as syn-head-to-head has been observed.



101 **102**

Scheme 29

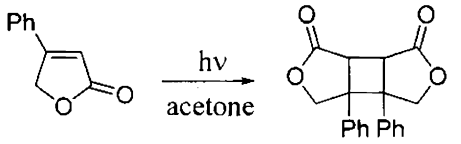
Likewise, irradiation of 5,5-diphenyl-2(5*H*)-furanone **(103)** in acetonitrile affords a mixture of the anti-head-to-tail and head to head dimers **104** and **105** as the only photoproducts.[106,107] In more dilute solutions, solvent addition products are also formed.



103 **104** **105**

Scheme 30

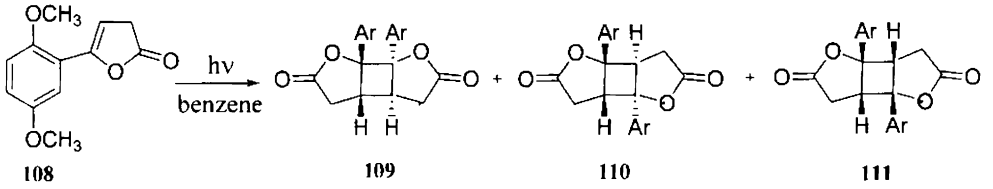
A cyclobutane dimer **107** has been also isolated upon irradiation of 4-phenyl-2(5*H*)-furanone **(106)** in acetone[108], although the syn/anti nature could not be determined.



106 **107**

Scheme 31

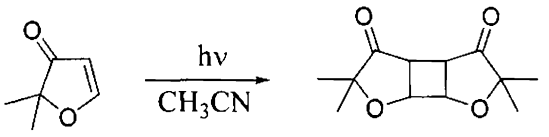
Martinez-Utrilla and Miranda[79] have reported a photodimerisation of enol lactone. Thus irradiation of 5-(2',5'-dimethoxyphenyl)-2(3*H*)-furanone **(108)** in benzene under nitrogen gives the anti-head-to-head dimer **109** and anti and syn head-to-tail isomers **110** and **111** respectively.



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

Scheme 32

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

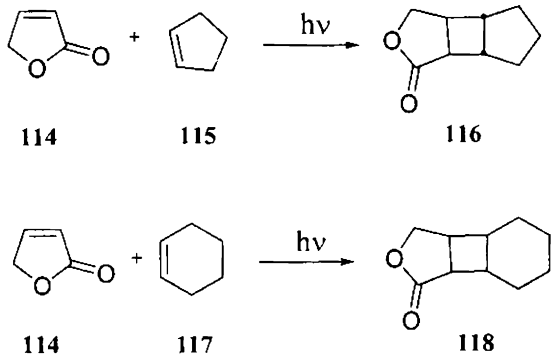


112 **113**

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.



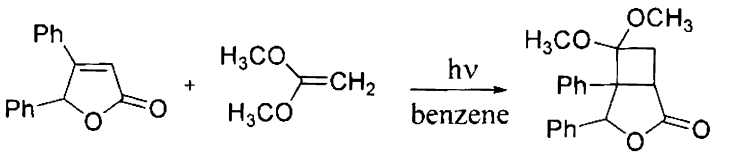
114 **115** **116**

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.

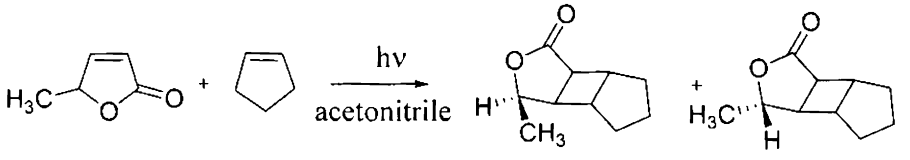
A similar photochemical reaction between dimethoxyethene and 3,5-diphenyl-2(5*H*)-furanone in benzene has been reported by Padwa and Dehm (Scheme 35).[112] Usual phenyl migration was not observed under this condition.



119 **120** **121**

Scheme 35

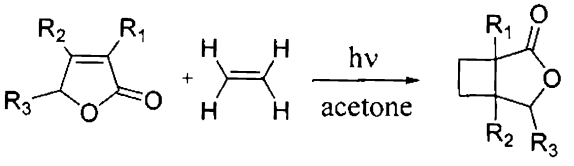
The photochemical addition of cyclopentene to 5-methyl-2(5*H*)-furanone has been studied by Ohga and Matsuo.[105] Using excess of cyclopentene, the irradiation of this lactone in acetonitrile under oxygen gives two isomeric cycloadducts (Scheme 36).



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.

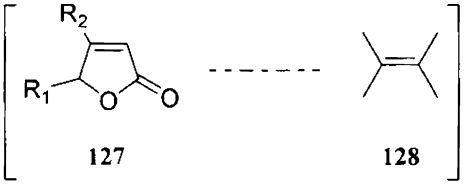


124 **125** **126**

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)

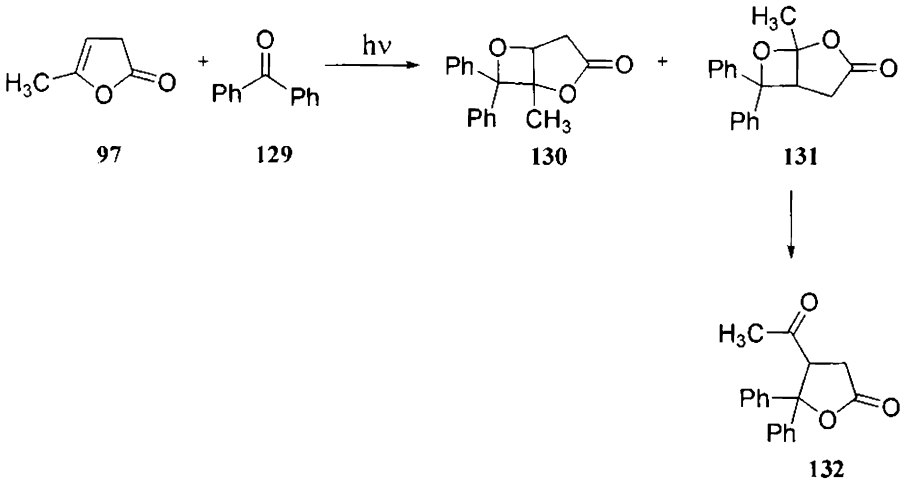
a) $R_1 = CH_2OOCC(CH_3)_3$ b) $R_2 = CH_3$, H

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.

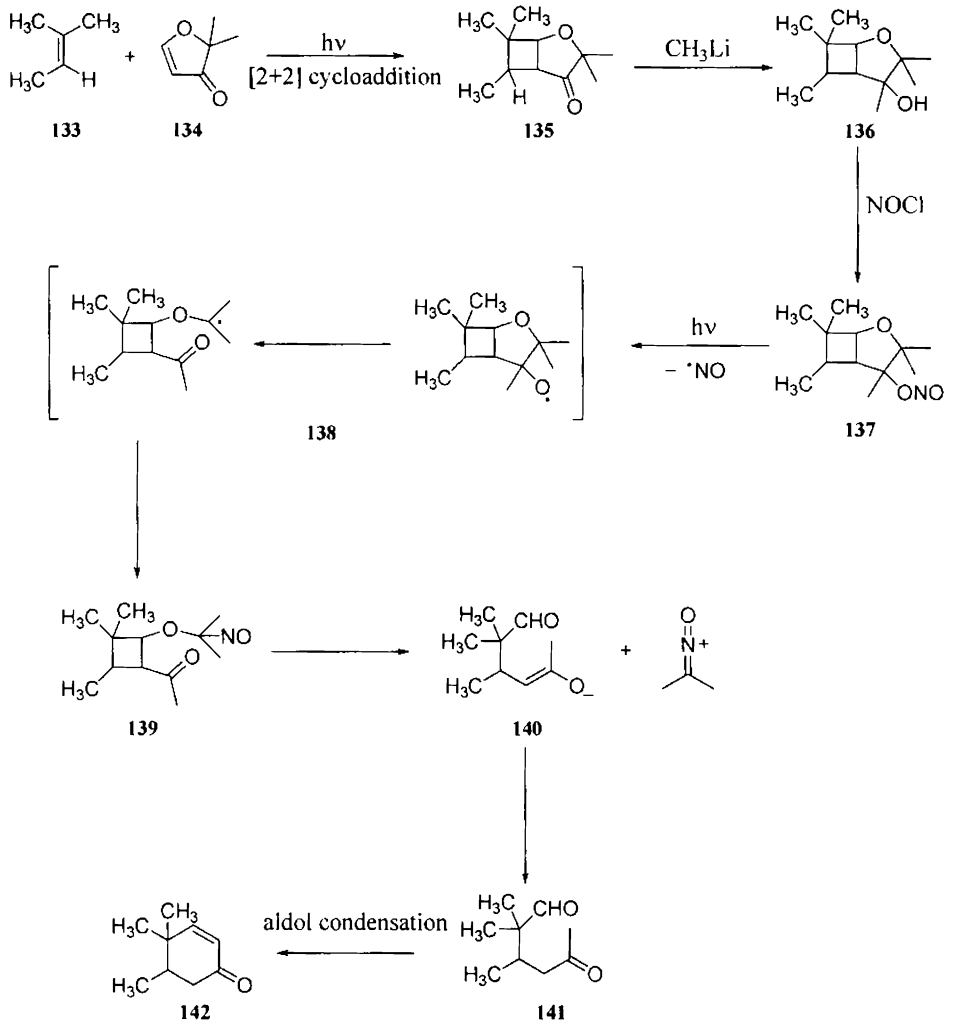
The photoreaction of 2(3*H*)-furanones that can be included in this section is the formation of oxetanes **130** and **131** through Paterno-Buchi addition of 5-methyl-2(3*H*)-furanone **(97)** and benzophenone (Scheme 39).[115] Compound **130** is thermally stable, but **131** react further to give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

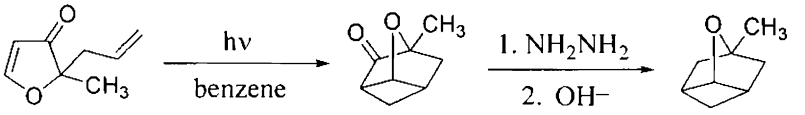


Scheme 40

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).

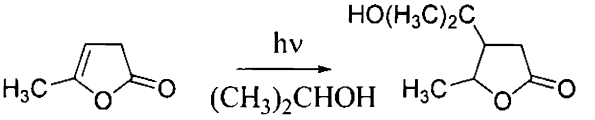


143 **144** **145**

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.

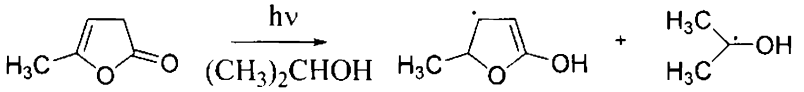


97 **146**

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

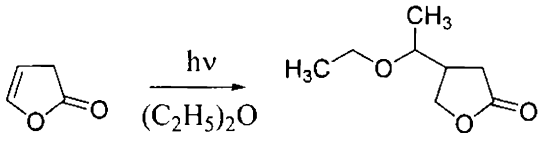
be initiated by the formation of a ketyl radical **148** as a consequence of hydrogen abstraction of the photoexcited carbonyl group from isopropanol.



147 **148** **149**

Scheme 43

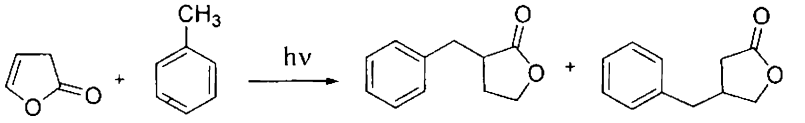
Likewise, the β-adduct **150** is obtained upon irradiation of **114** in ether.[111]



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]

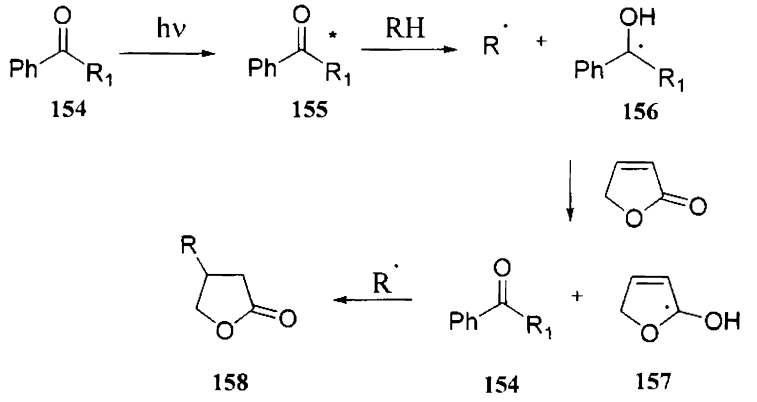


114 **151** **152** **153**

Scheme 45

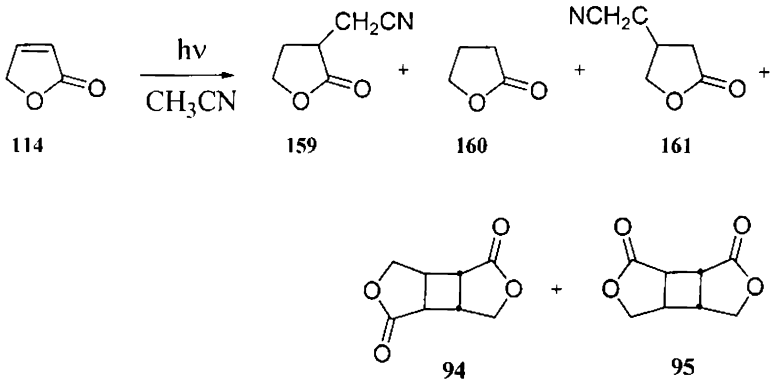
This has been taken as evidence for the involvement of the aromatic ketones as hydrogen transfer agents, as shown below (Scheme 46). Using cyclohexane-d_6 as solvent, it has been demonstrated that the α-adduct arises

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



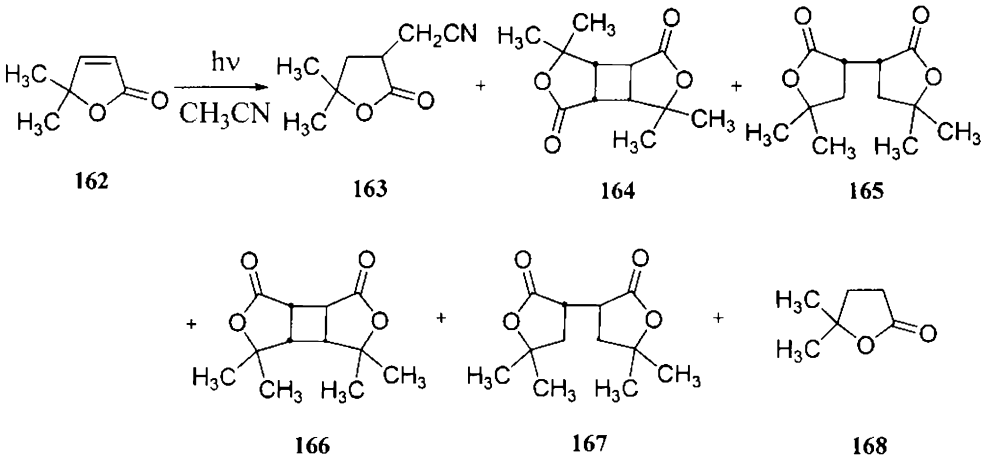
Scheme 46

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).



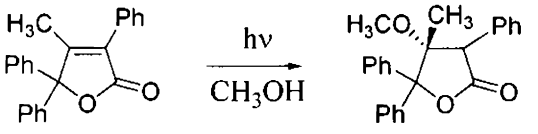
162 **163** **164** **165**

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]

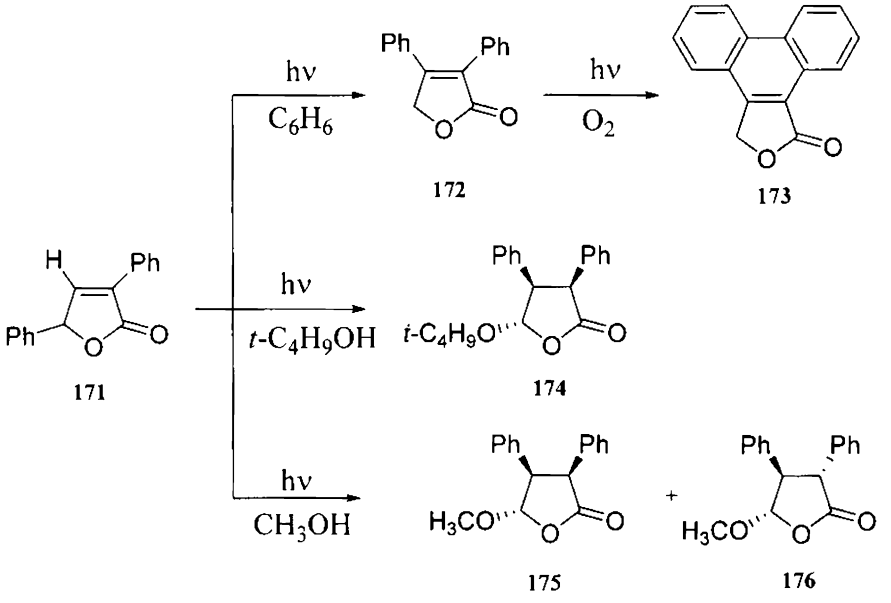


169 **170**

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).

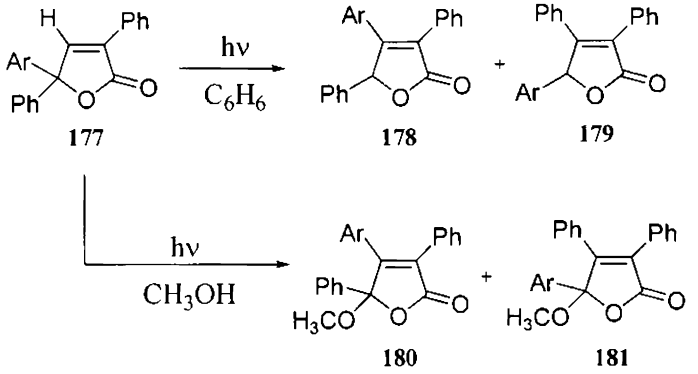


Scheme 50

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

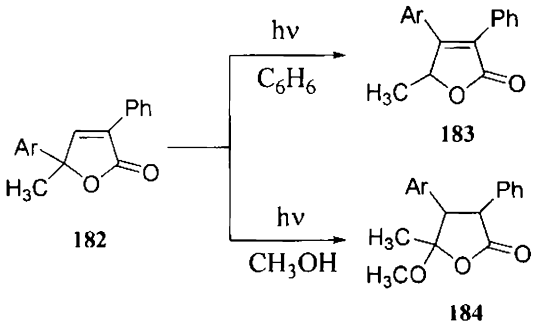
mediated pathway. That the rearrangement is quenched by piperylene furnishes additional confirmation for the triplet state assignment.

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

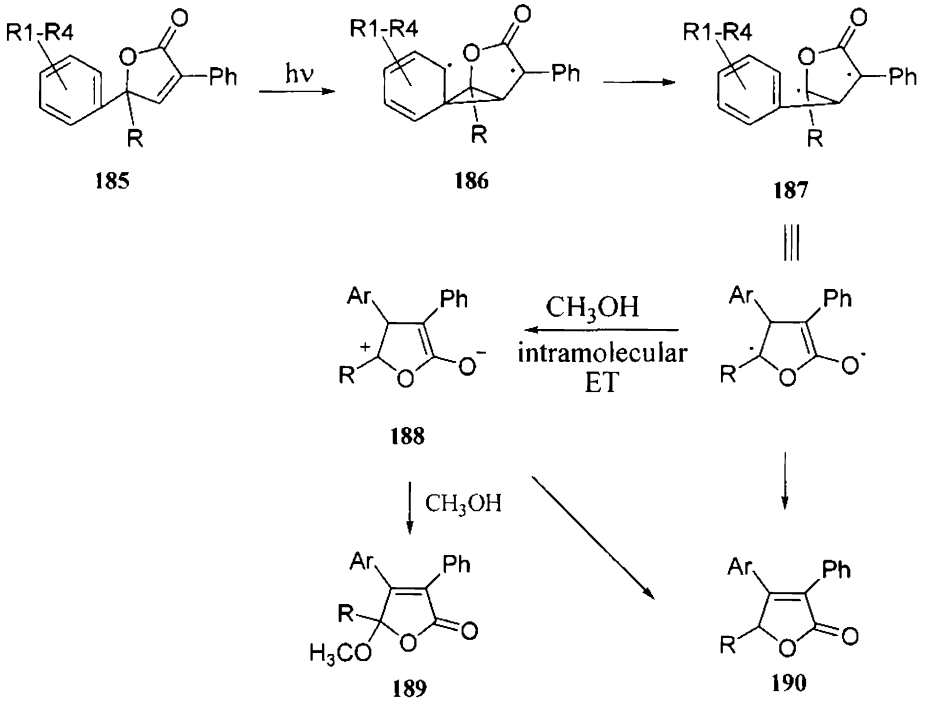
In order to generalize these results, 5-methyl-3,5-diaryl-2(5*H*)-furanone **182** has been irradiated in benzene, whereby only aryl migration has been observed.



Scheme 52

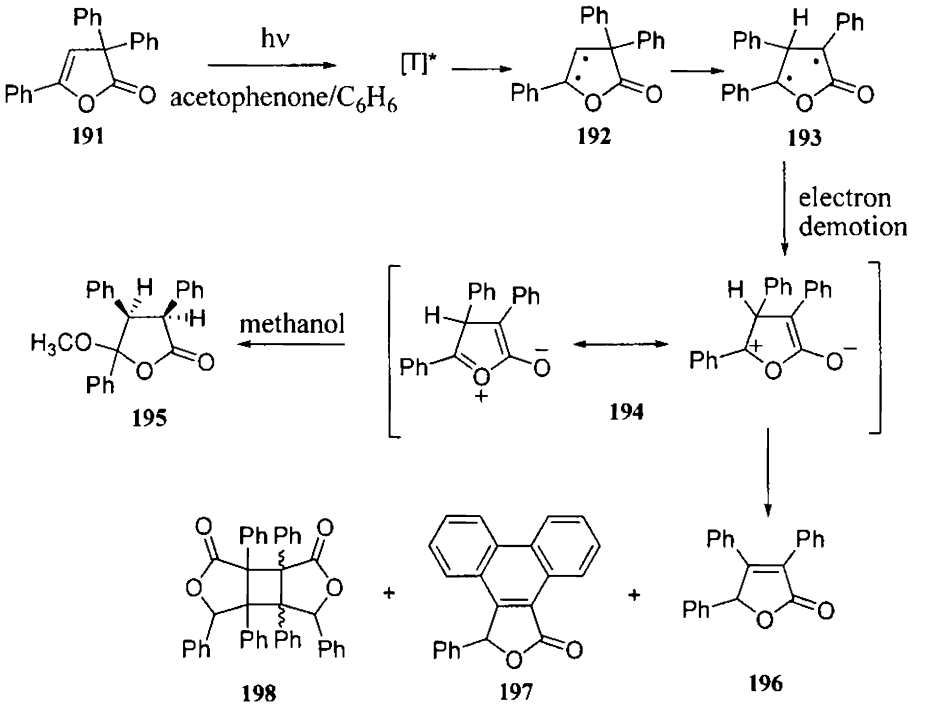
Moreover, 3-phenyl-5,5-dimethyl-2(5*H*)-furanone has been found to be photostable in benzene or methanol solution, thus confirming that aryl groups are the only substituents capable to undergo migration processes. The above results suggests that aryl migrations of 3,5-diaryl-2(5*H*)-furanones take place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

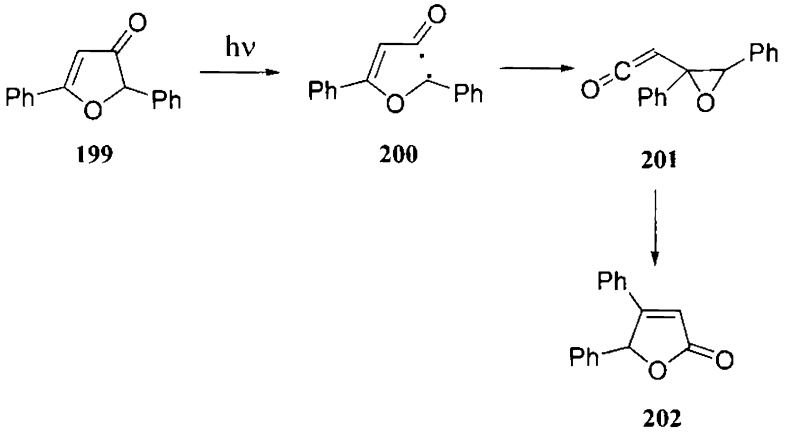


Scheme 54

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).

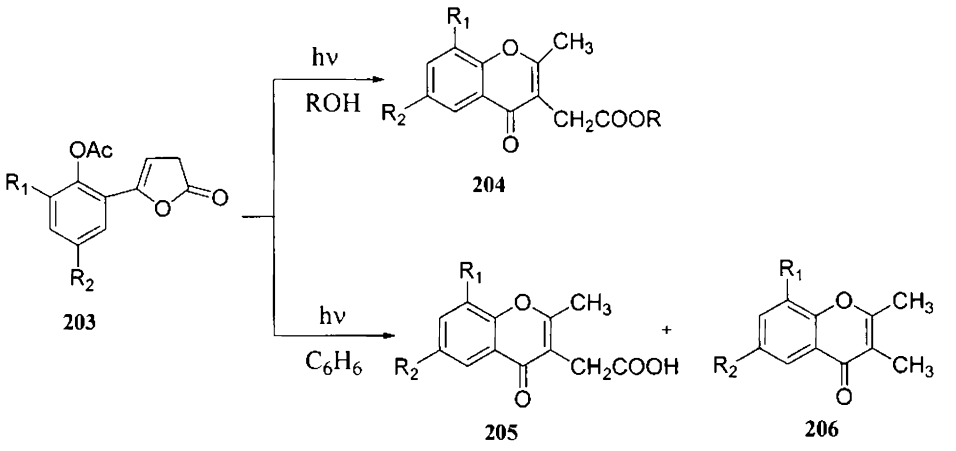


199 **200** **201** **202**

Scheme 55

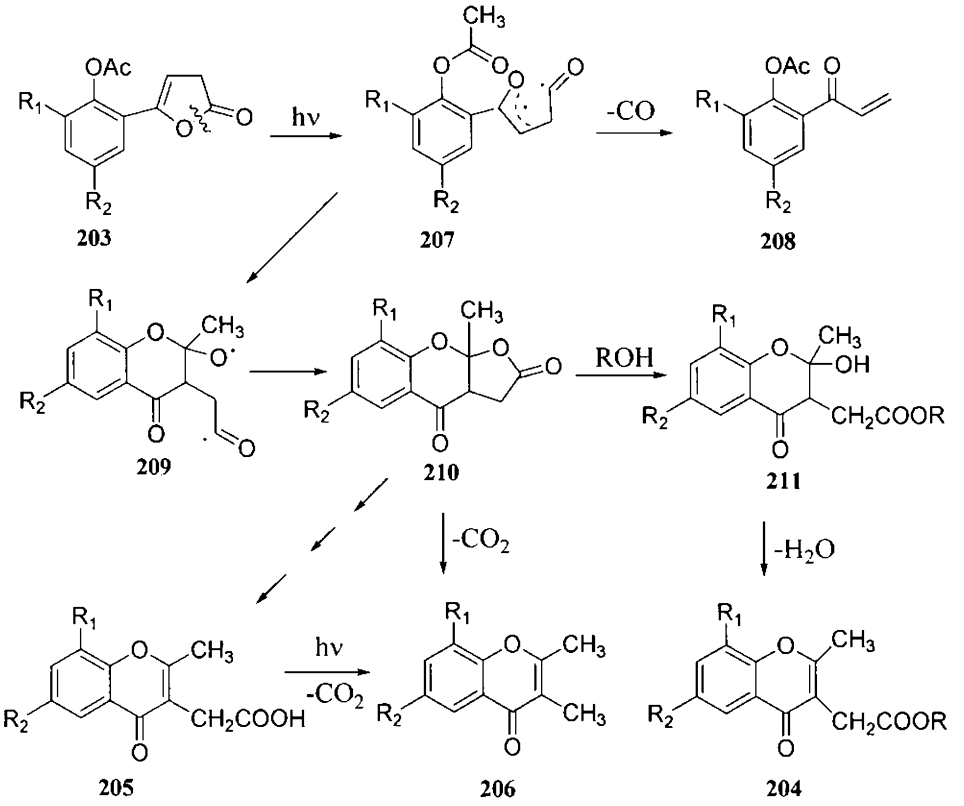
1.3.9. Chromone Formation

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

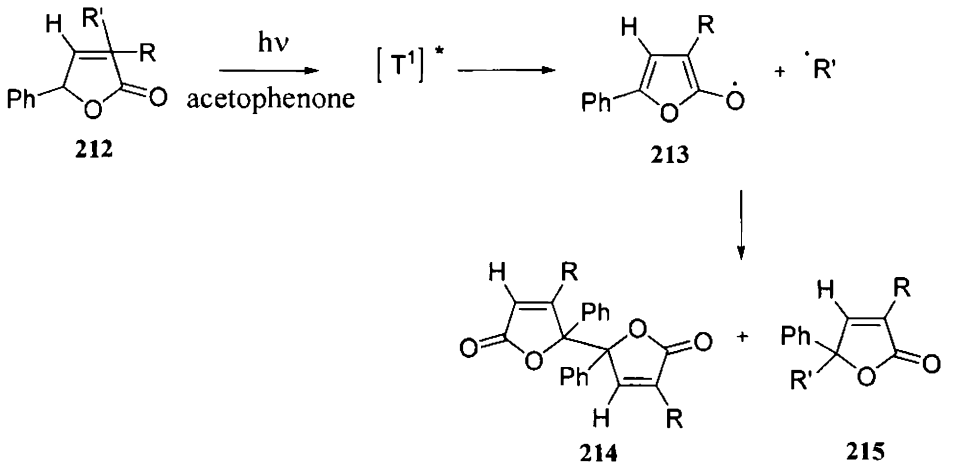
The esters **204** would be formed by solvent addition to intermediate **210** with concomitant ring opening followed by dehydration, while the formation of 2,3-dimethylchromones **206** has been explained by direct decarboxylation of **210**[128.129] or more probably by decarboxylation of the chromoneacetic 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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