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# PHOTOCHEMISTRY OF 2(3H)- AND 2(5H)-FURANONES

Luis Fillol[a], Miguel A. Miranda[a*], Isabel M. Morera[b], and Hamid Sheikh[a]

[a]Departamento de Química Orgánica, Facultad de Farmacia, Avenida Blasco Ibañez, 13, 46010-Valencia, Spain

[b]Departamento de Química, E.T.S.I. Industriales, Universidad Politécnica, Apartado 22012, 46071-Valencia, Spain

Abstract - *The most general photoreaction of 2(3H)-furanones* **1** is singlet mediated decarbonylation to vinyl ketones, although in some cases the formation of cyclobutane dimers and oxetanes has been observed. On the other hand, 2(5H)-furanones **2** preferentially undergo dimerization, 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 appropiate substituents, are stilbene-phenanthrene cyclization or substituent migrations (from **1** and **2**), as well as chromone formation or fragmentation (from **1**).

The present review deals with the photochemical transformations of 2(3H)-furanones **1** and 2(5H)-furanones **2**.

Scheme 1

The main photochemical processes which have been described for these compounds are as below:

A) Decarbonylation

B) Decarboxylation

C) Stilbene-phenanthrene-like cyclization

D) Dimerization

E) Cycloaddition

F) Hydrogen abstraction

G) Addition of nucleophiles

H) Substituent migrations

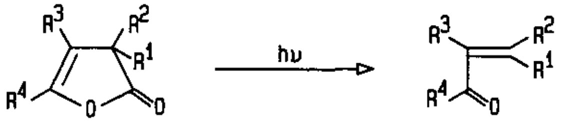
I) Chromone formation

J) Fragmentation

The results published so far are summarized below, arranged according to the above classification. When two or more processes are involved in the formation of a product, the first one has been used for classification.

## A) DECARBONYLATION

The photochemical decarbonylation of enol lactones **1a-t** has been reported to give the corresponding vinyl ketones **3a-t**.[1-7]

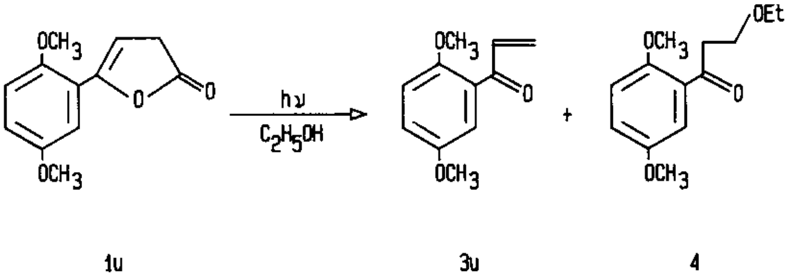


**1** **3**

a: $R^1=R^2=R^3=H$; $R^4=CH_3$
b: $R^1=R^4=CH_3$; $R^2=R^3=H$
c: $R^1=R^2=R^3=H$; $R^4=Ph$
d: $R^1=R^4=Ph$; $R^2=R^3=H$
e: $R^1=R^2=R^4=Ph$; $R^3=H$
f: $R^1=R^2=R^3=R^4=Ph$
g: $R^1=R^2=Ph$; $R^3=H$; $R^4=p\text{-}CH_3Ph$
h: $R^1=R^2=Ph$; $R^3=H$; $R^4=p\text{-}CH_3OPh$
i: $R^1=R^2=Ph$; $R^3=H$; $R^4=p\text{-}C_2H_5OPh$
j: $R^1=R^2=Ph$; $R^3=H$; $R^4=p\text{-}PhPh$
k: $R^1=R^2=Ph$; $R^3=H$; $R^4=p\text{-}ClPh$
l: $R^1=R^2=Ph$; $R^3=H$; $R^4=p\text{-}CNPh$
ll: $R^1=R^4=Ph$; $R^3=H$; $R^2=Ph$
m: $R^1=R^4=Ph$; $R^3=H$; $R^2=p\text{-}CH_3Ph$
n: $R^1=R^4=Ph$; $R^3=H$; $R^2=p\text{-}CH_3OPh$
o: $R^1=R^4=Ph$; $R^3=H$; $R^2=p\text{-}CNPh$
p: $R^1=R^4=Ph$; $R^3=H$; $R^2=p\text{-}ClPh$
q: $R^1=R^2=R^3=H$ $R^4=2\text{-}AcO\text{-}5\text{-}CH_3Ph$
r: $R^1=R^2=R^3=H$ $R^4=2\text{-}AcO\text{-}3,5\text{-}(CH_3)_2Ph$
s: $R^1=R^2=R^3=H$ $R^4=2\text{-}AcO\text{-}5\text{-}CH_3OPh$
t: $R^1=R^2=R^3=H$ $R^4=2,5\text{-}(AcO)_2Ph$

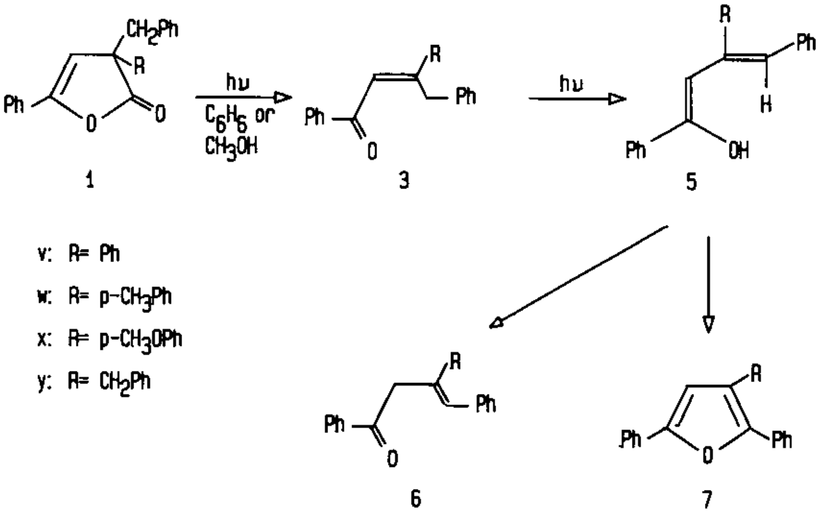
Scheme 2

The irradiation of **1u** in ethanol gives the aryl vinyl ketone **3u** and also 2,5-dimethoxyphenyl-2-ethoxyethyl ketone **4** as the result of a secondary solvent addition.[3]



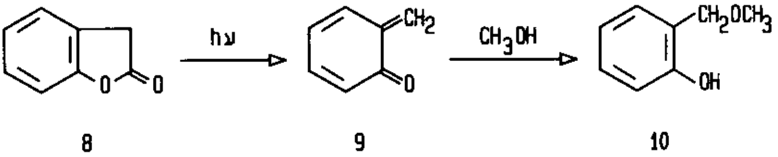
Scheme 3

In the case of the 3-benzyl derivatives **1v-y** decarbonylation is followed by double bond isomerization to **6v-y** and/or cyclization to furan derivatives **7v-y.**[8]



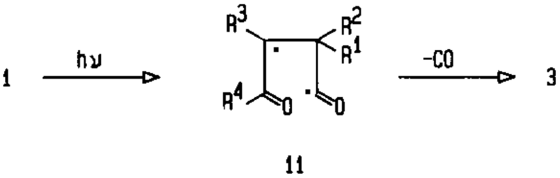
Scheme 4

Chapman and McIntosh[9] have described a similar photodecarbonylation of benzofuran-2(3H)-one (**8**) which upon irradiation in methanol affords o-hydroxybenzyl methyl ether **10** via the intermediate **9**. Analogous results have been obtained with substituted derivatives.[10-14]



Scheme 5

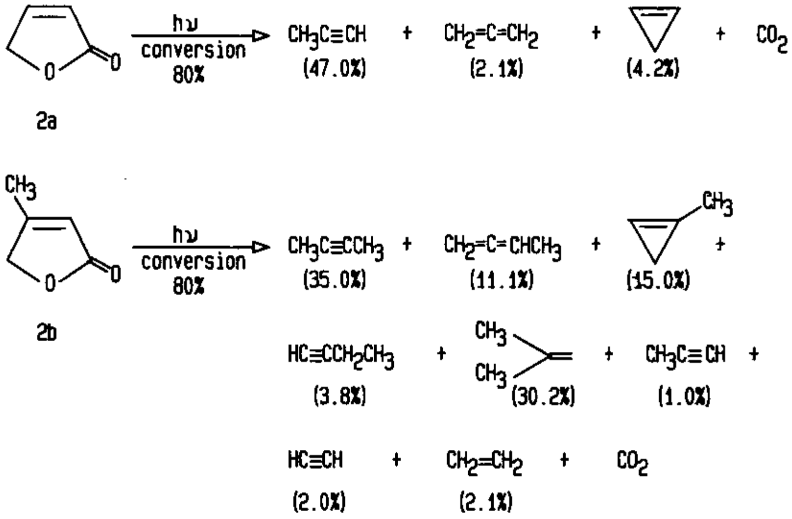
In general, decarbonylation of enol lactones **1** appears to occur from their lowest lying singlet states, through a primary cleavage of the carbonyl-oxygen bond, similar to that previously postulated in the case of enol esters.[15-21] This leads to the formation of diradical **11**, which can be stabilized by loss of carbon monoxide.



Scheme 6

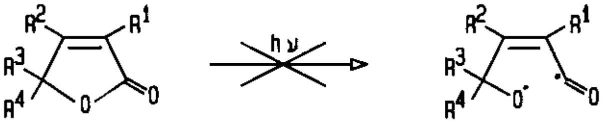
## B) DECARBOXYLATION

Krull and Arnold[22] have studied the mercury sensitized vapor phase photochemistry of 2(5H)-furanone (**2a**) and 4-methyl-2(5H)-furanone (**2b**). The photolysis of **2a** gives methylacetylene, allene and cyclopropene. However **2b** leads to a complex mixture of primary and secondary photoproducts.



Scheme 7

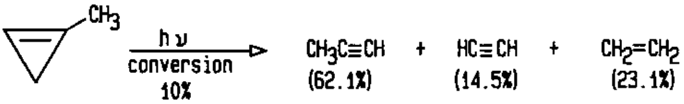
It must be mentioned that 2(5H)-furanones (**2**) do not undergo cleavage of the carbonyl-oxygen bond, since the $sp^3$ hybridized C-5 does not allow resonance stabilization of the intermediate **12**.



**2** **12**

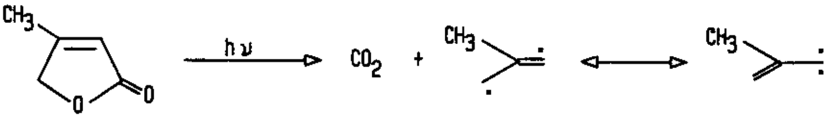
Scheme 8

The formation of 1-butyne and 1,2-butadiene was first thought to be a secondary reaction of 1-methylcyclopropene, but this hypotesis was questioned after studying the chemical reactivity of the latter compound, which gave rise only to propyne, acetylene and ethylene.



Scheme 9

Hence it can not be ruled out the posibility of the formation of some 1-butyne and/or 1,2-butadiene through a 1,2-methyl migration in the intermediate **13**, previously postulated by Closs to account for the photodenitrogenation of 3H-pyrazoles.[23]

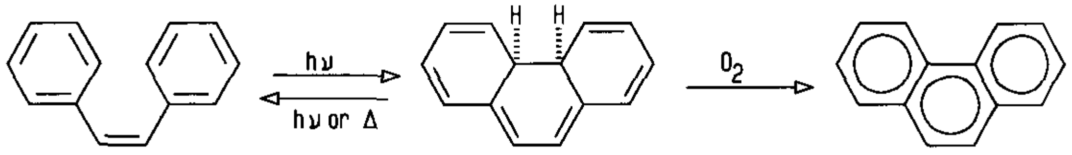


**2b** **13**

Scheme 10

C) STILBENE-PHENANTHRENE-LIKE CYCLIZATION

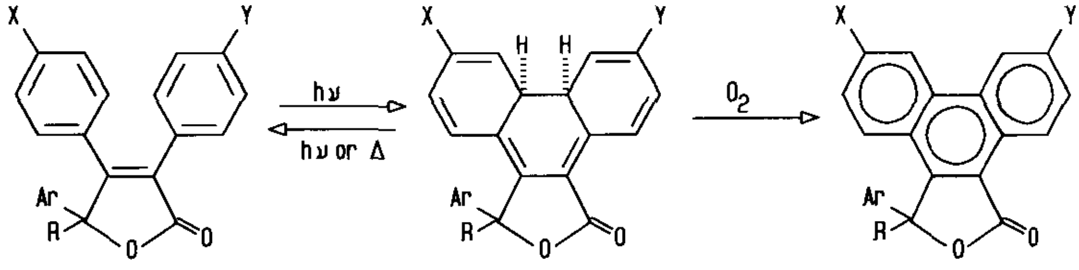
The photocyclization of cis-stilbene **14** to phenanthrene **15** is a well known reaction.[24,25]



14 15

Scheme 11

Rio and Hardy[26], Lohray et al.[4], Gopidas et al.[5], and Pratapan et al.[6], have studied the photochemistry of lactones **2**, which posses a cis-stilbene moiety. Thus, when the lactones **2c-n** are irradiated in the presence of oxygen, in chloroform or benzene as solvent, a cyclization to the corresponding phenanthrene derivatives **17** is observed to take place. In these experiments a wood glass filter (310nm<λ<390nm) was used, in order to irradiate selectively at the absorption bands of compounds **2c-n**.



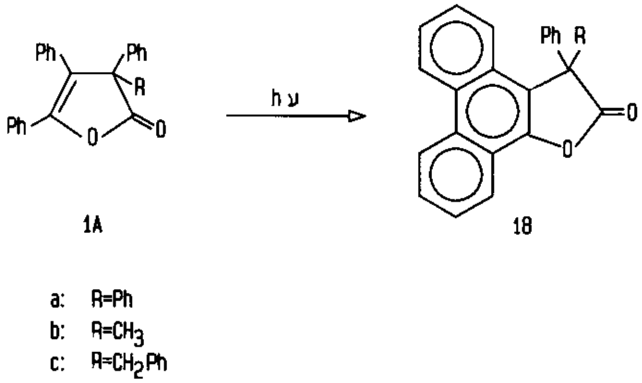
2 16 17

c: Ar=Ph; R=X=Y=H
d: Ar=Ph; X=Y=H; R=OH
e: Ar=Ph; X=Y=H; R=$OCH_3$
f: Ar=Ph; X=Y=H; R=$OCOCH_3$
g: R=H; Ar=Ph; X=$CH_3$; Y=H
h: R=H; Ar=Ph; X=$OCH_3$; Y=H
i: R=H; Ar=Ph; X=CN; Y=H
j: R=H; Ar=Ph; X=Cl; Y=H
k: R=H; Ar=Ph; X=H; Y=$CH_3$
l: R=H; Ar=Ph; X=H; Y=$OCH_3$
ll: R=H; Ar=p-$CH_3$Ph; X=H; Y=H
m: R=H; Ar=p-$C_2H_5$OPh; X=H; Y=H
n: R=H; Ar=Ph; X=H; Y=H

Scheme 12

If oxygen is slowly bubbled through the solutions, a photochromism phenomenon is observed, due to the intermediates **16.** The filter does not allow to irradiate these intermediates. However, in the absence of the filter, the production of phenanthrenes **17** is very slow, due to the reverse reaction of the intermediates **16** to the starting compounds **2.**

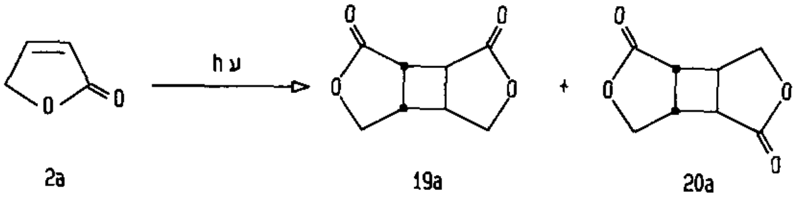
Similar processes have been reported for 2(3H)-furanones. So, Lohray et al.[4] found that the photolysis of 3,3,4,5-tetraphenyl-2(3H)-furanone (**1Aa**), 3-methyl-3,4,5-triphenyl-2(3H)-furanone (**1Ab**) and 3-benzyl-3,4,5-triphenyl-2(3H)-furanone (**1Ac**) in the presence of oxygen, affords the corresponding phenanthrene derivatives **18Aa, 18Ab** and **18Ac.** Laser flash photolysis leads to spectral changes that suggest the involvement of excited singlet states in these cyclizations.



Scheme 13

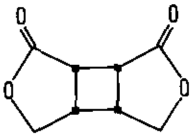
D) DIMERIZATION

Irradiation of 2(5H)-furanone (**2a**) in solution leads to the formation of anti-photodimers **19a** and **20a.**



Scheme 14

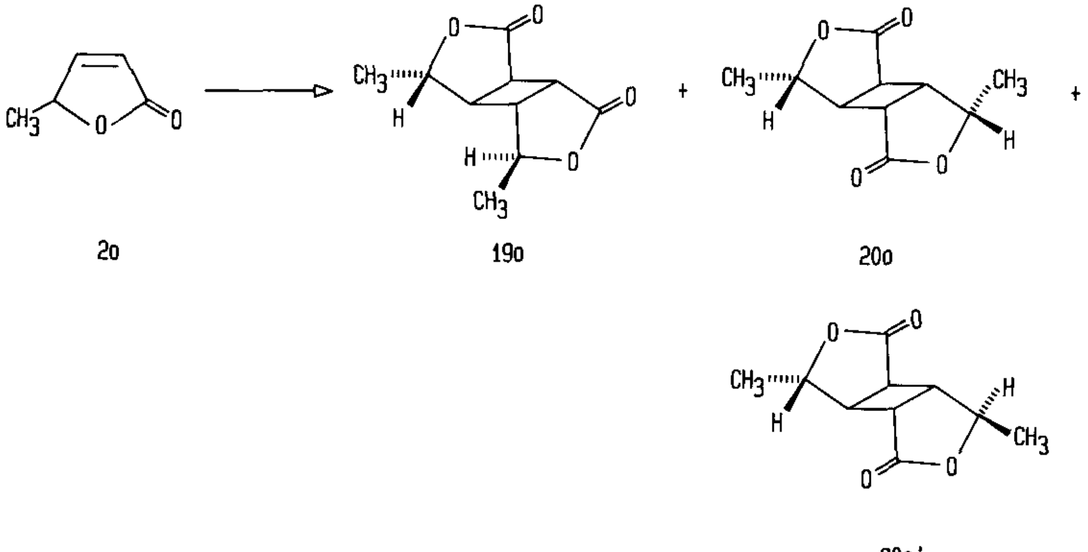
Compound **19a** is the result of a head-to-head dimerization while **20a** arises from a head-to-tail dimerization. On the other hand, irradiation of 2(5H)-furanone (**2a**) in solid phase at low temperature gives a head-to-head dimer (**21a**).[27]



**21a**

Scheme 15

The photodimerization of substituted 2(5H)-furanones has also been *observed*.[28] Thus, irradiation of 5-methyl-2(5H)-furanone (**2o**) in acetonitrile with 254nm light gives a mixture of compounds **19o**, **20o** and **20o'** with the relative yields 3:0.9:3.



**2o** **19o** **20o**

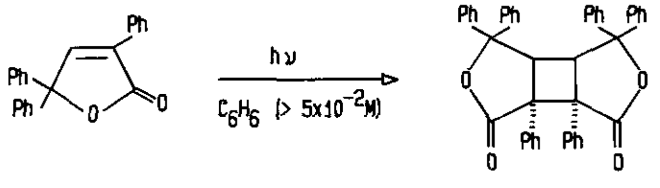
**20o'**

Scheme 16

The solvent effects on the yield of each isomer have been studied. In this way, it has been found that the ratio **19o/20o'** decreases from 3 to 1 on going from acetonitrile to benzene, while the ratio **20o/20o'** remains essentially unchanged.

This is in accordance with the expectations based on the higher dipole moments of the head-to-head dimers. Furthermore the photodimerization of **2o** can be sensitized by ketones with triplet energies higher than that of xanthone and quenched by 1,3-pentadiene, which suggests that the three photodimers are formed through an excited triplet state, whose estimated energy level is about 70 Kcal/mol.

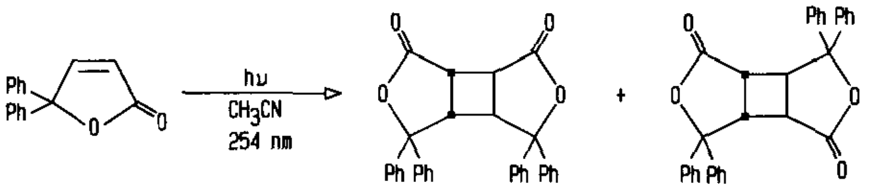
The irradiation of 3,5,5-triphenyl-2(5H)-furanone (**2p**) in concentrated benzene solution ($5\times10^{-2}$ M) has been studied by Padwa and his co-workers.[29] Under these conditions the formation of a dimer, tentatively assigned as syn-head-to-head (**21p**) has been observed.



**2p** **21p**

Scheme 17

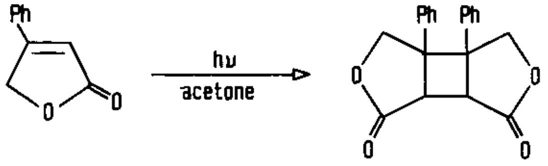
Likewise, irradiation (λ = 254 nm) of 5,5-diphenyl-2(5H)-furanone (**2q**) in acetonitrile (1M solution) affords a mixture of the anti-head-to-tail and head-to-head dimers **20q** and **19q** as the only photoproducts.[30,31] In more dilute solutions, solvent addition products are also formed.



**2q** **19q** **20q**

Scheme 18

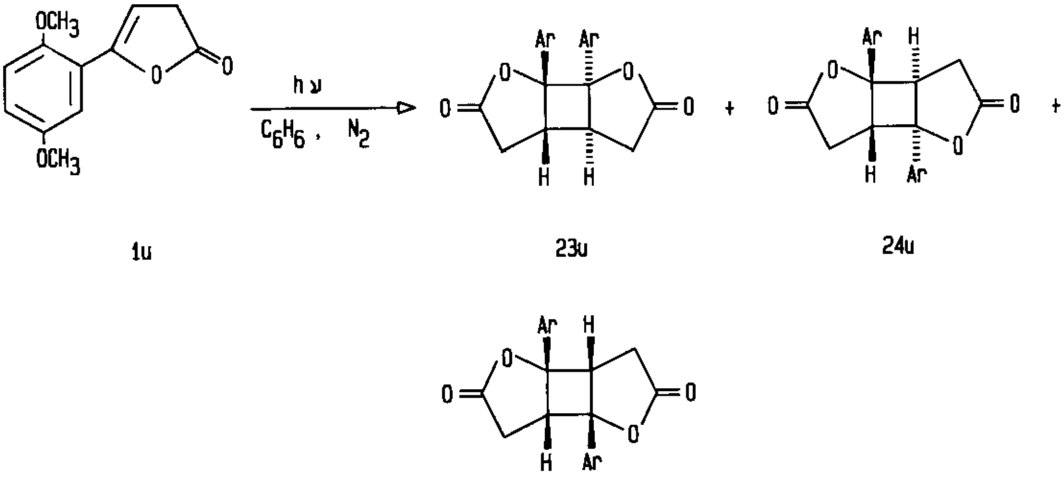
A cyclobutane dimer **22r** has been also isolated upon irradiation of 4-phenyl-2(5H)-furanone (**2r**) in acetone, although the syn/anti nature could not be determined.[32]



2r 22r

Scheme 19

Martínez-Utrilla and Miranda[3] have reported a photodimerization of enol lactones. Thus irradiation of 5-(2',5'-dimethoxyphenyl)-2(3H)-furanone (**1u**) in benzene under nitrogen gives the anti-head-to-head dimer **23u** and both anti- and syn- head-to-tail isomers **24u** and **25u**.



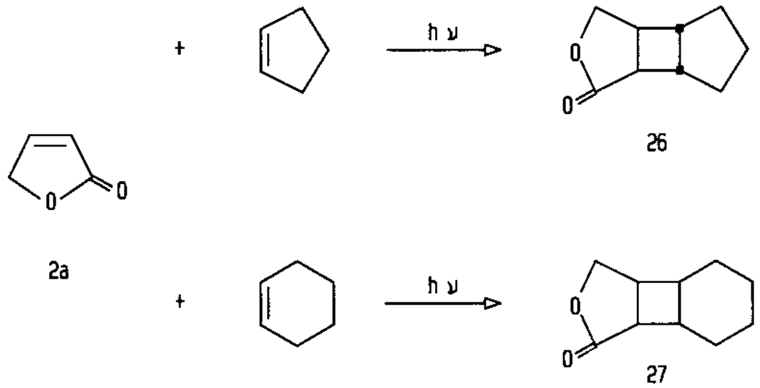
1u 23u 24u

25u

Scheme 20

### E) CYCLOADDITIONS

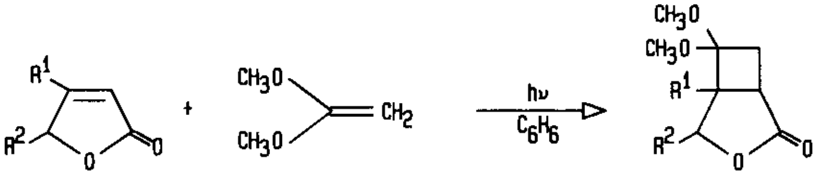
Tada and his co-workers[33] have observed a photoaddition of cyclopentene and cyclohexene to 2(5H)-furanone (**2a**), to give **26** and **27** (mixture of three stereoisomers), respectively.



Scheme 21

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.

However, more recent work by Kosugi et al.[32] has proven that dimethoxyethene does not actually quench the reaction but it adds to 2(5H)-furanone (**2a**), 4-phenyl-2(5H)-furanone (**2r**) and 5-n-butyl-2(5H)-furanone (**2s**) to give **28a**, **28r** and **28s**. Acetone was not used as solvent because of the easy formation of the oxetane derivative with dimethoxyethene.

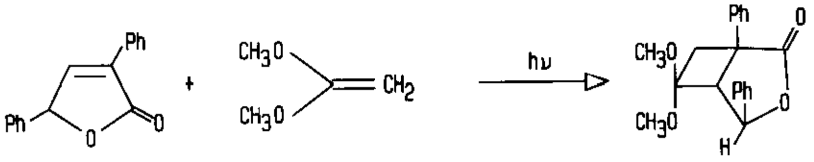


**2** **28**

a: $R^1 = R^2 = H$
r: $R^1 = Ph;\ R^2 = H$
s: $R^1 = H;\ R^2 = n\text{-}C_4H_9$

Scheme 22

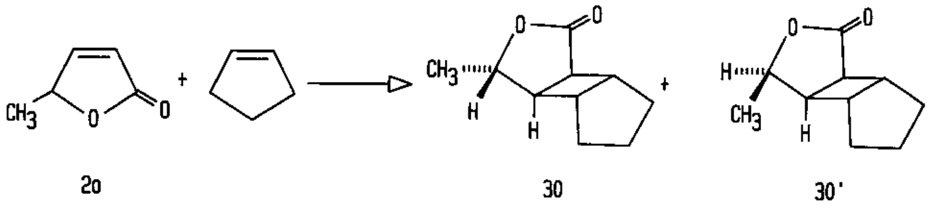
A similar photochemical reaction between dimethoxyethene and 3,5-diphenyl-2(5H)-furanone (**2t**) in benzene has been reported by Padwa and Dehm,[34] who did not observe under these conditions the usual phenyl-migration (see part H).



**2t** **29**

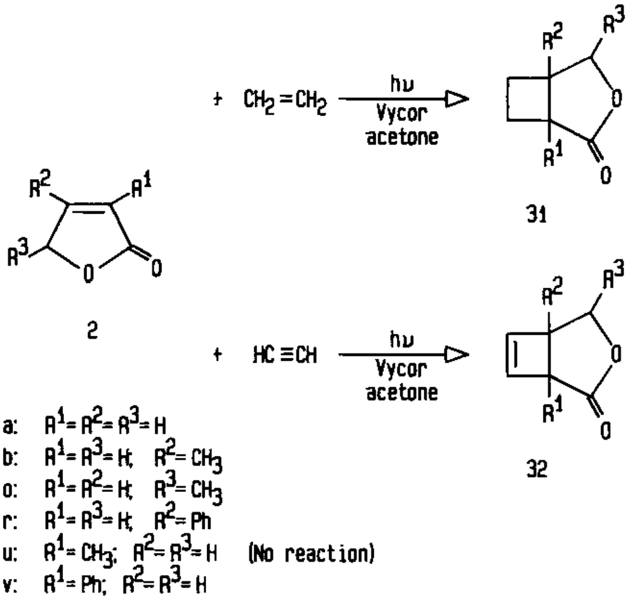
Scheme 23

The photochemical addition of cyclopentene to 5-methyl-2(5H)-furanone (**2o**) has been studied by Ohga ad Matsuo.[28] Using excess of cyclopentene, the irradiation of this lactone in acetonitrile under oxygen gives two isomeric cycloadducts **30** (36%) and **30'** (24%).



Scheme 24

In the above mentioned work of Kosugi et al.[32] the addition of ethene and acetylene to a series of 2(5H)-furanones has been studied.



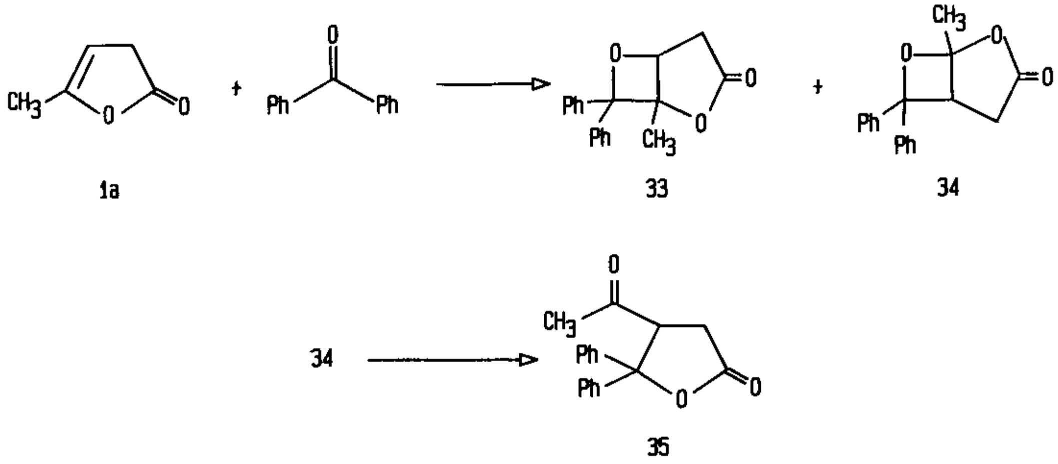
Scheme 25

The irradiation of **2a** with ethene gives the cycloaduct **31a** in high yield (70% at room temperature and more that 80% at -50°C). Acetone is the best solvent and it seems to act as a sensitizer. In the same way, the photocycloaddition of **2b**, **2o**, **2r** and **2v** to ethene in acetone affords the corresponding adducts in 44, 49, 52 and 35% respectively.

It is worth mentioning that 3-methyl-2(5H)-furanone (**2u**) does not give the adduct **31u**, in contrast with the behavior of the analogous 3-phenyl substituted furanone **2v**. This fact suggests that the electronic effect of the conjugated phenyl group plays an important role in this reaction.

The adducts **32** are produced in the same way by irradiation of **2a**, **2b**, **2o**, **2r** and **2v** with ethyne (yields: 54, 29, 8, 23 and 14% respectively), whereby the lack of reactivity of **2u** is confirmed.
A competing dimerization occurs in the case of 4-phenyl-2(5H)-furanone (**2r**) (see section D).

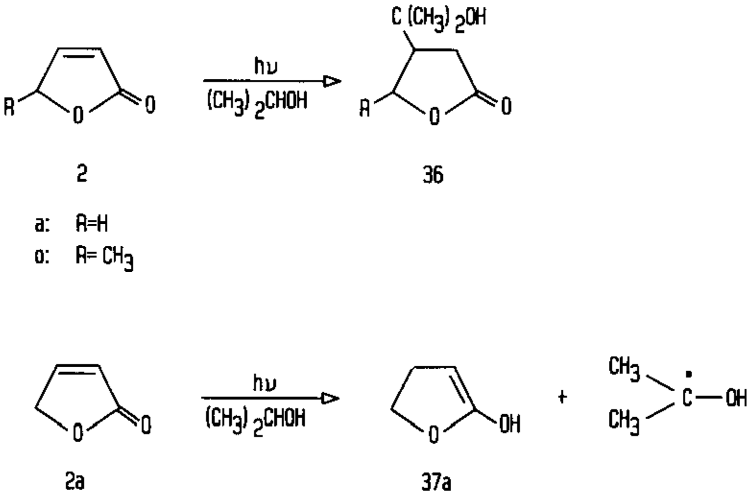
The only photoreaction of 2(3H)-furanones that can be formally incluced in this section is the formation of oxetanes **33** and **34** through Paterno-Büchi addition of 5-methyl-2(3H)-furanone (**1a**) and benzophenone.[35] Compound **33** is thermally stable, but **34** reacts further to give the saturated lactone **35**.



Scheme 26

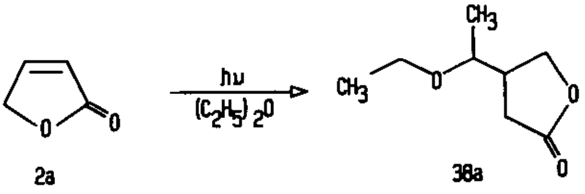
## F) HYDROGEN ABSTRACTION

According to Ohga and Matsuo,[36] direct excitation of 2(5H)-furanones **2a** and **2o** in isopropanol solution leads to the corresponding adducts **36a** and **36o** in yields suitable for high scale synthesis. 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 (**37**) as a consequence of hydrogen abstraction of the photoexcited carbonyl group from isopropanol.



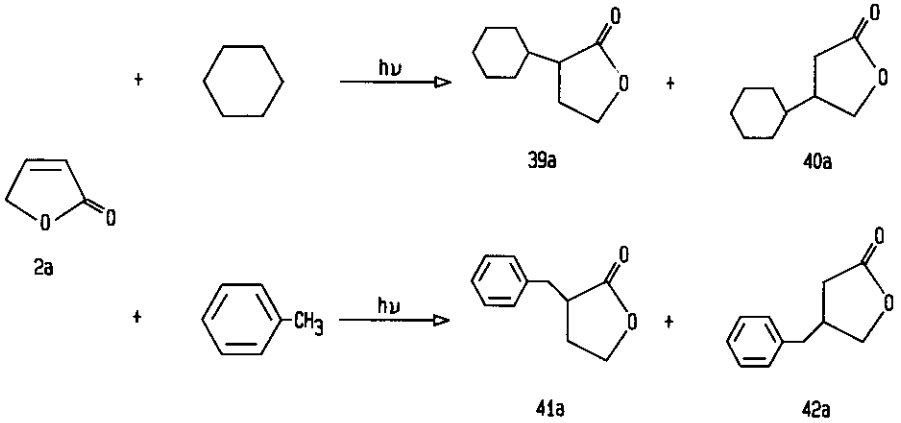
Scheme 27

Likewise, the $\beta$-adduct **38a** is obtained upon irradiation of **2a** in ether.[32]



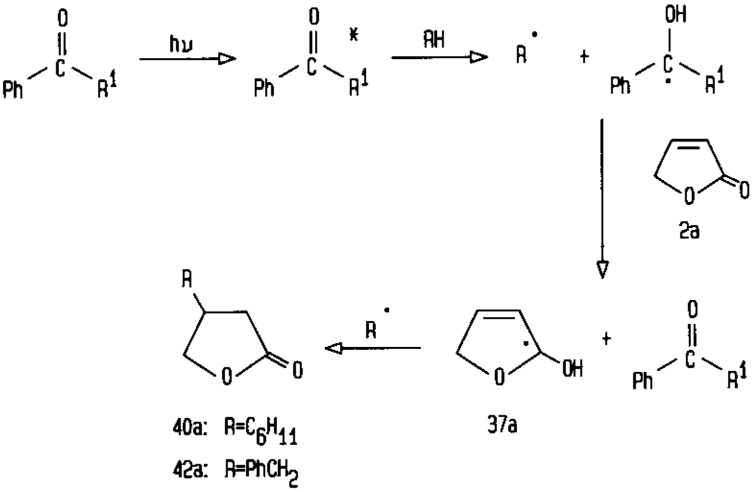
Scheme 28

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-adducts is again observed.[37]



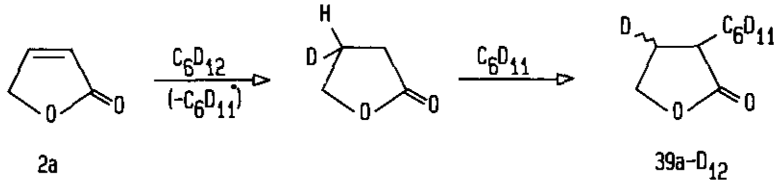
Scheme 29

This has been taken as evidence for the involvement of the aromatic ketones as hydrogen transfer agents, as shown below.



Scheme 30

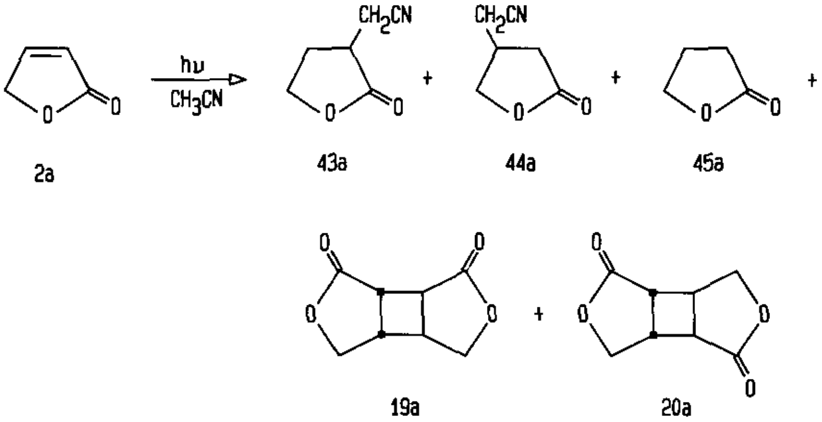
Using perdeuterated cyclohexane as solvent it has been demonstrated that the α-adduct arises via hydrogen abstraction by the β-carbon, on the basis of deuterium incorporation at the C-4.[38]



Scheme 31

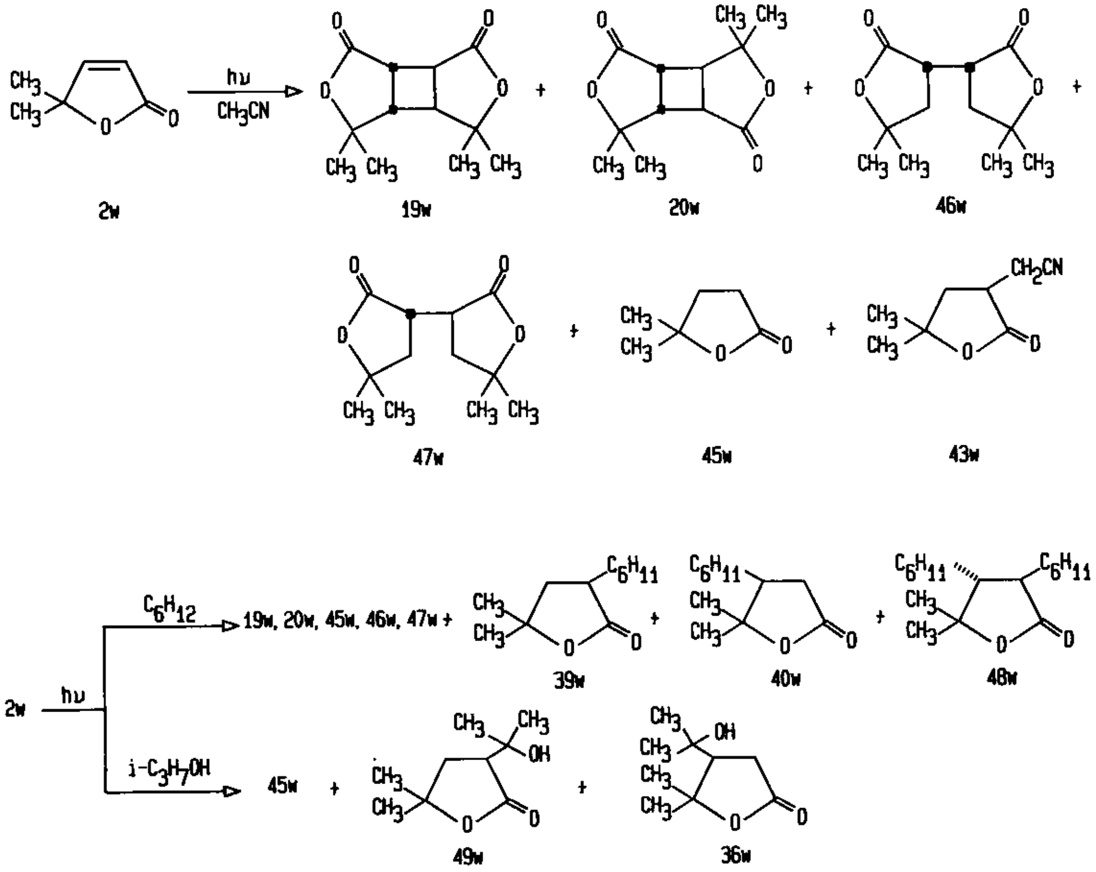
This occurs in a non-stereospecific manner, a fact that allows to rule out the possibility that α-solvent addition is a concerted process.

Anklam and Margaretha[31] have carried out a systematic investigation on the photoreduction of 2(5H)-furanone (**2a**) and 5,5-dimethyl-2(5H)-furanone (**2w**) in several solvents. In dilute (ca. $10^{-2}$ M) acetonitrile solution, **2a** affords both α- and β-adducts (**43a** and **44a**) together with the reduction product **45a** and the dimers **19a** and **20a** (see section D).



Scheme 32

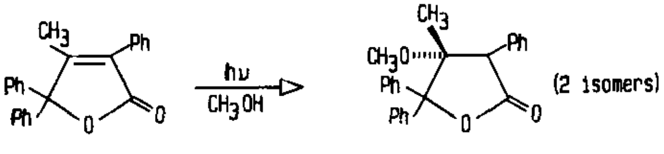
Under similar conditions, the dimethyl derivative **2w** is converted into a mixture of six products, the dimers **19w** and **20w**, the diastereomeric hydrodimers **46w** and **47w**, the saturated lactone **45w** and the solvent adduct **43w**. Analogous results have been obtained in cyclohexane and isopropanol (see Scheme 33). All these products can be accounted for in terms of hydrogen abstraction by the carbonyl oxygen or by the β-carbon, as discussed above for the parent compound.



Scheme 33

## G) ADDITION OF NUCLEOPHILES

Methanol addition is observed in the irradiation of 3,5,5-triphenyl-4-methyl-2(5H)-furanone (**2x**) in this solvent.[29]

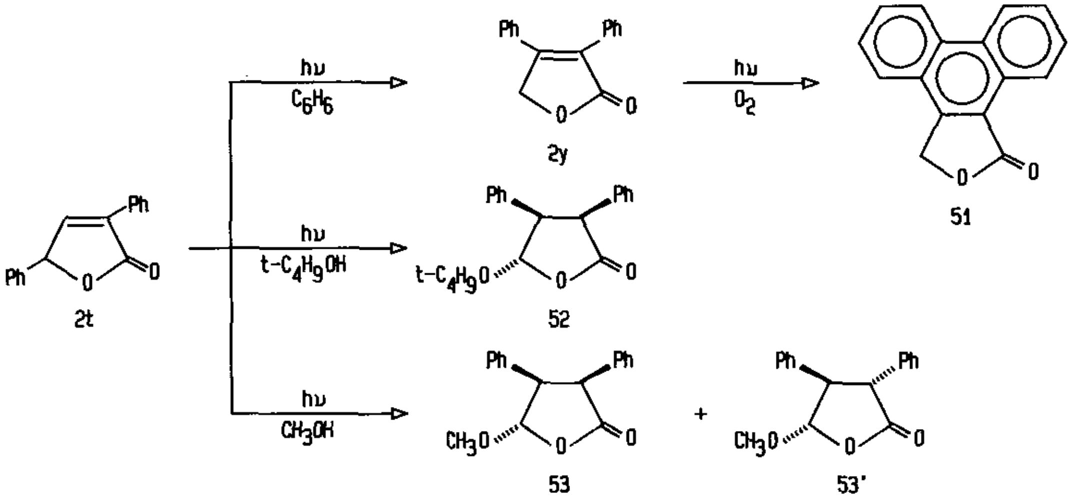


**2x** **50x**

Scheme 34

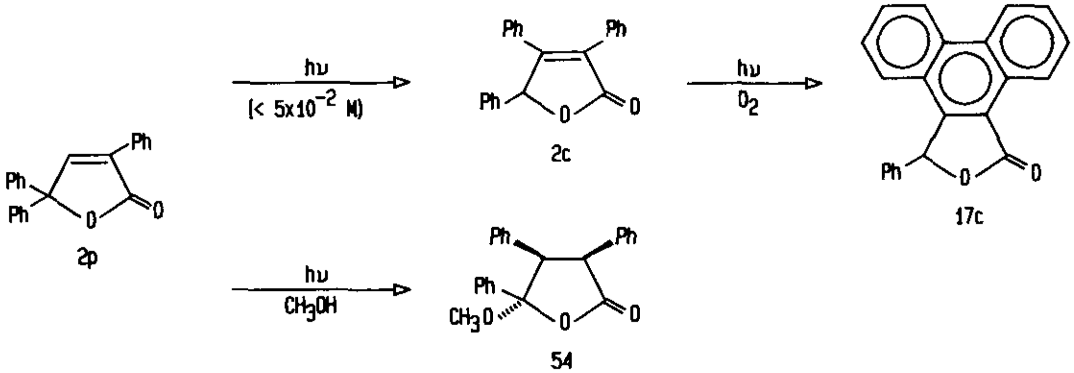
## *H) SUBSTITUENT MIGRATIONS*

This type of reaction for 2(5H)-furanones has been widely studied by Padwa and co-workers.[29,34,39] The irradiation of 3,5-diphenyl-2(5H)-furanone (**2t**) in benzene through Corex filter for 1.5 h gives 3,4-diphenyl-2(5H)-furanone (**2y**) in high yield. In the presence of oxygen, **2y** further reacts to afford the tetracyclic furanone **51** via the well known stilbene-phenanthrene cyclization (see part C). When tert-butyl alcohol is used as the solvent the only product is **52,** while in methanol, a mixture of the isomers **53** (30%) and **53'**(45%) is formed.



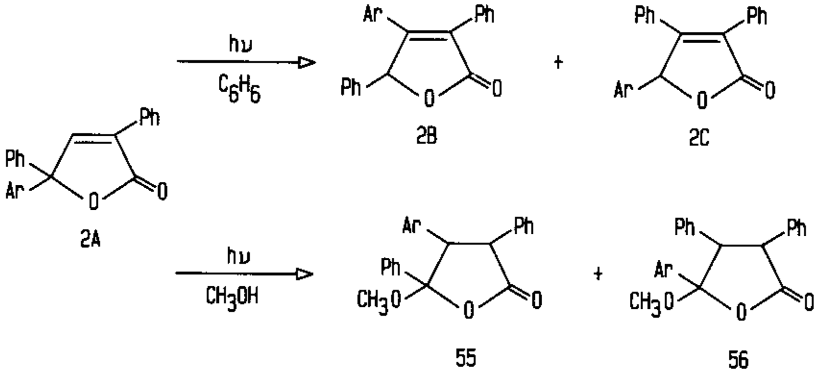
Scheme 35

Similar results have been obtained by irradiation of 3,5,5,-triphenyl-2(5H)-furanone (**2p**). In this case a dimerization process has additionally been observed in concentrated benzene solution. Direct and sensitized quantum yields of the photorearrangement are identical, which provides strong evidence for a triplet excited state. That the rearrangement is quenched by piperylene *furnishes* additional confirmation for the triplet state assignment.



Scheme 36

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



Scheme 37

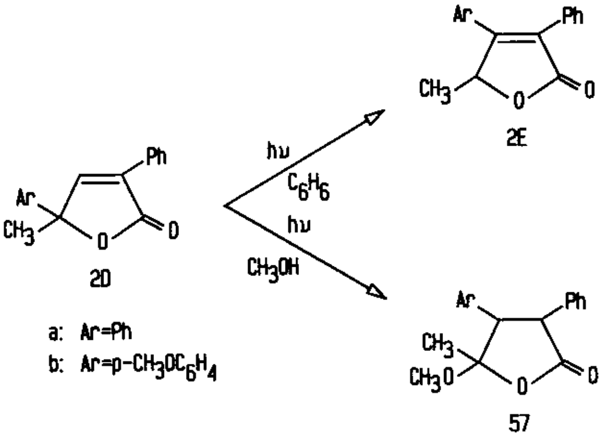
TABLE I. Migratory aptitude of aryl groups in the irradiation of compounds **2A**

| Ar | ratio[a] 2B/2C | ratio[b] 55/56 |
|---|---|---|
| $p\text{-}CH_3OC_6H_4$ | 16.0 | 0.72 |
| $p\text{-}NCC_6H_4$ | 3.5 | 4.5 |
| $m\text{-}CH_3OC_6H_4$ | 1.5 | 0.95 |
| $p\text{-}CH_3C_6H_4$ | 3.5 | 0.81 |

[a] Benzene as solvent.

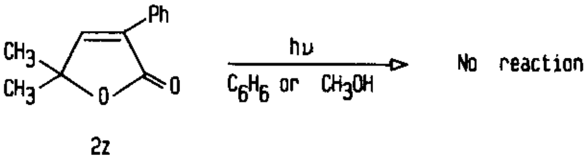
[b] Methanol as solvent.

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



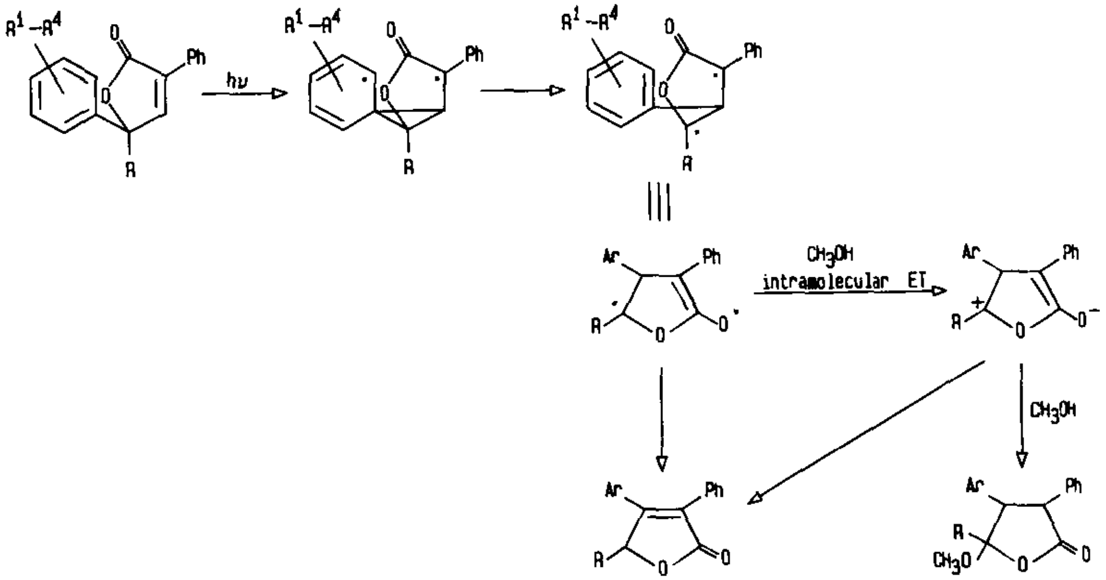
Scheme 38

Moreover, 3-phenyl-5,5-dimethyl-2(5H)-furanone **2z**, 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.



Scheme 39

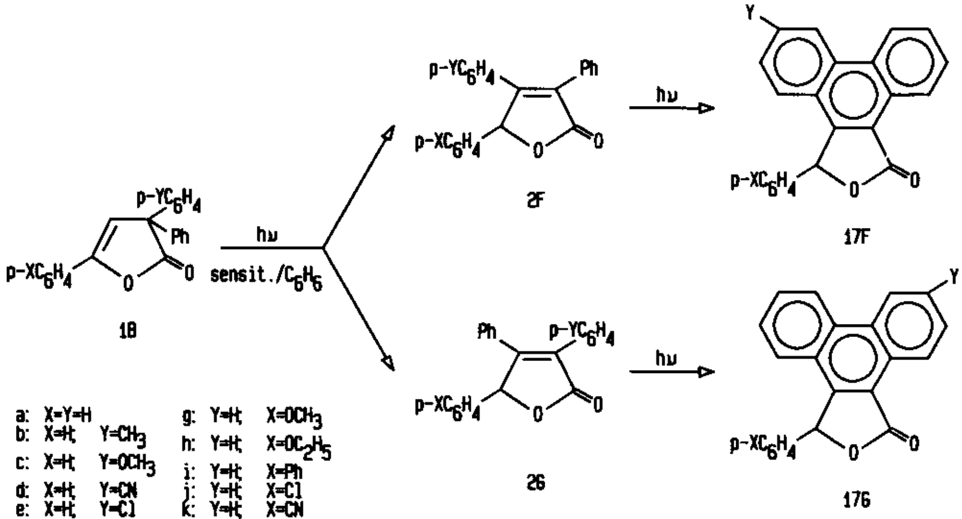
The above results suggest that aryl migrations of 3,5-diaryl-2(5H)-furanones take place according to the following Scheme.



Scheme 40

Formally the initial steps are simply the same as those of a di-π-methane rearrangement.[40] 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.

Similar aryl migrations have also been reported for 2(3H)-furanones by George, Das and their groups.[4-6] The migratory aptitudes of different aryl groups at C-3 and the effect of nonmigrating aryl groups at C-5 on the photorearrangement are illustrated as follows:



a: X=Y=H
b: X=H, Y=$CH_3$
c: X=H, Y=$OCH_3$
d: X=H, Y=CN
e: X=H, Y=Cl
f: Y=H, X=$CH_3$
g: Y=H, X=$OCH_3$
h: Y=H, X=$OC_2H_5$
i: Y=H, X=Ph
j: Y=H, X=Cl
k: Y=H, X=CN

| | 2F | 26 | 17F | 176 |
|---|---|---|---|---|
| 18a** | 48% [a] | | 9% | |
| 18b** | 18% | 12% | 27% | 18% |
| 18c** | 11% | 18% | 20% | 30% |
| 18d** | 16% [a] | – | 18% | – |
| 18e** | 13% [a] | – | 13% | – |
| 18f* | 40% [a] | | 18% | |
| 18g* | 19% [a] | | 9% | |
| 18h* | 12% [a] | | 6% | |
| 18i* | 12% | | 40% | |
| 18j* | 39% [a] | | 16% | |
| 18k* | 52% | | 10% | |

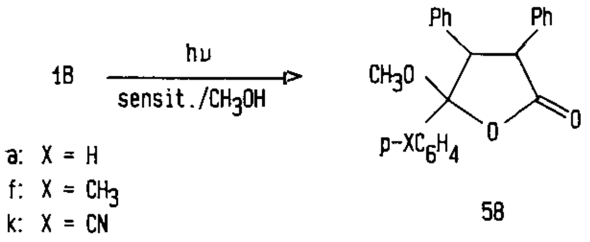
[a] Varying amounts of a non-fully characterized dimer were also obtained.

* Sensitized by p-$CH_3OPhCOCH_3$

** Sensitized by $PhCOCH_3$ or $CH_3COCH_3$

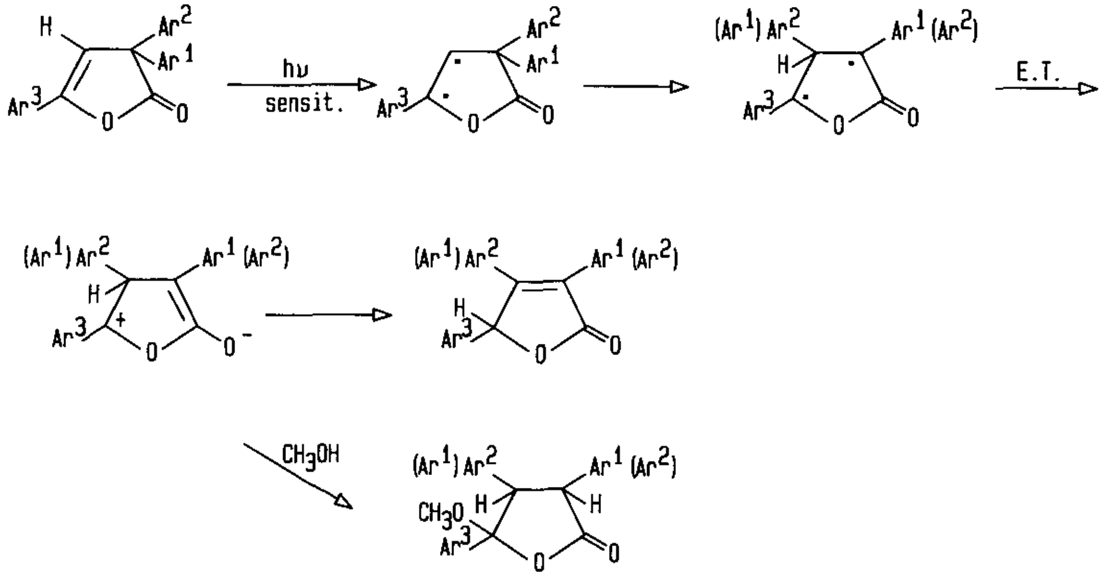
Scheme 41

In methanol, aryl migration is followed by nucleophilic solvent addition, as evidenced by the isolation of **58a,f,k** starting from **1Ba,f,k**.[5,6]



Scheme 42

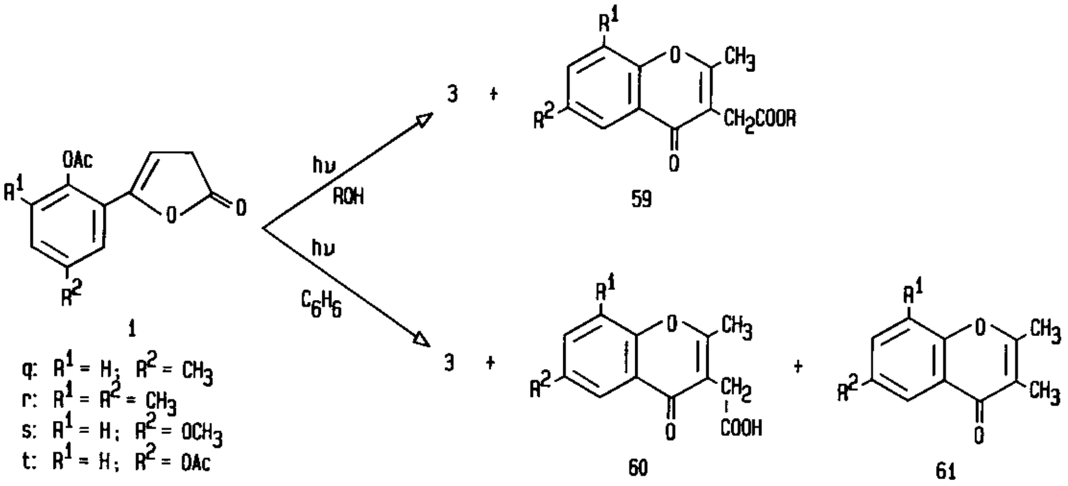
These results can be explained in terms of the pathway shown in the Scheme below, involving an excited triplet state, visualized as a 1,2-diradical structure. The individual steps of the proposed mechanism are analogous to those mentioned in the aryl migration of 2(5H)-furanones.



Scheme 43

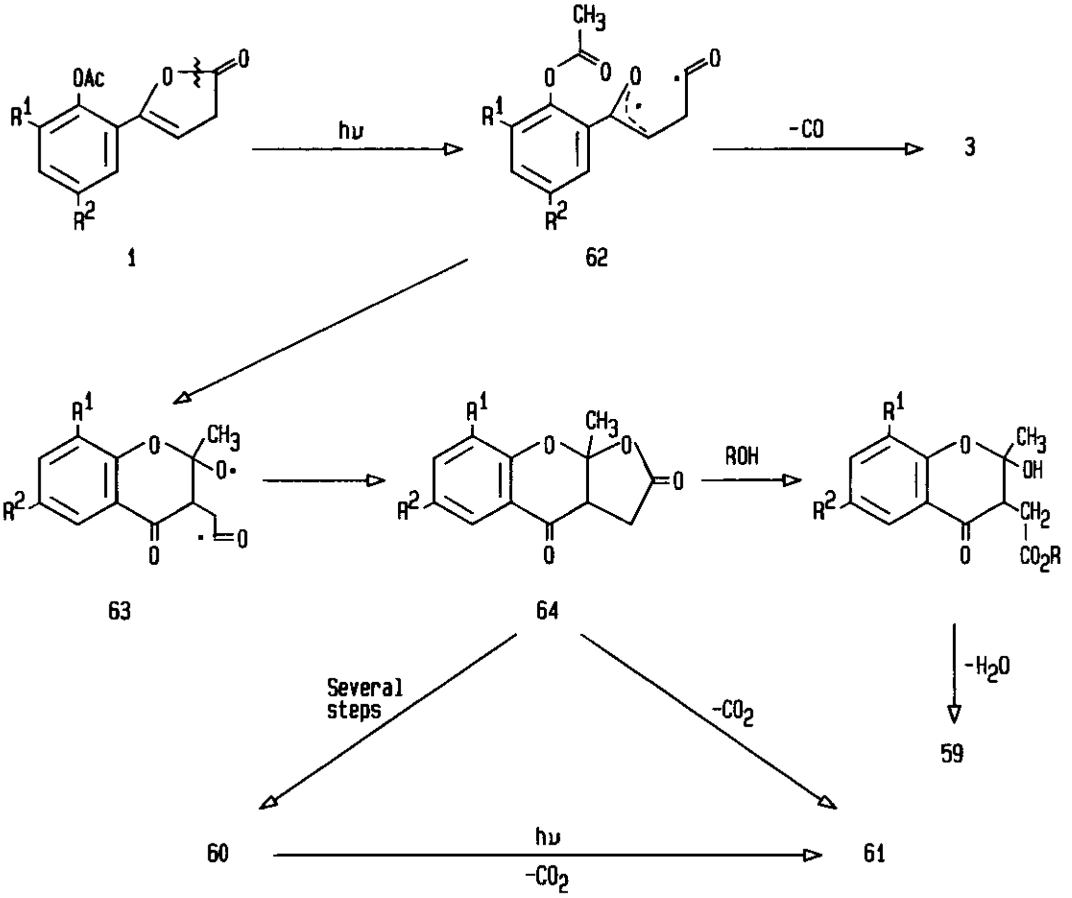
## I) CHROMONE FORMATION

The irradiation of **1q**, **1r**, **1s** and **1t** in benzene or alcoholic solvents gives besides the vinyl ketones **3q**, **3r**, **3s** and **3t** (see section A) the corresponding chromones **59**, **60** and **61**.[3,7]



Scheme 44

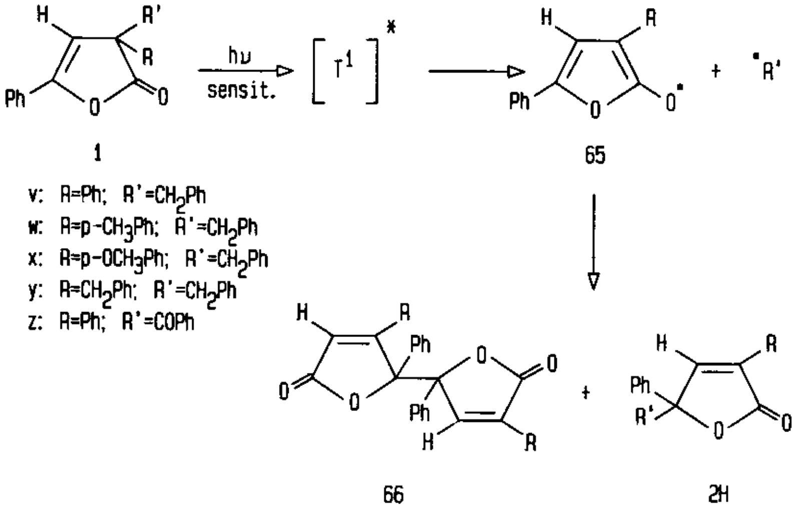
The formation of these products has been rationalized by assuming a primary cleavage of the O-CO bond, followed by decarbonylation or intramolecular radical addition (Scheme 45). The esters **59** would be formed by solvent addition to intermediate **64** with concomitant ring opening followed by dehydration, while the formation of 2,3-dimethylchromones **61** has been explained by direct decarboxylation of **64**,[41,42] or more probably by decarboxylation of the chromoneacetic acids **60**,[7] analogous to the well known photodecarboxylation of arylacetic acids.[43]



Scheme 45

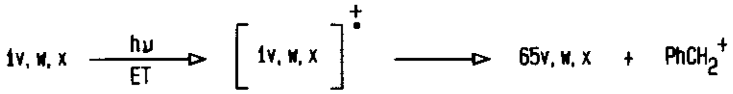
## J) FRAGMENTATION

Some 2(3H)-furanones containing a benzyl (**1v,1w,1x** and **1y**) or benzoyl (**1z**) group at the 3-position undergo facile photochemical cleavage of these groups, upon sensitization with acetophenone, leading to furanoxy radicals **65**. The final products are the rearranged 2(5H)-furanones **2H** or the bis lactones **66**. A small amount of bibenzyl could be isolated in the case of **1x**, which is in support of the pathway shown in the Scheme below.[8]



Scheme 46

Under electron transfer conditions, the 2(3H)-furanones **1v**, **1w** and **1x** give rise to the corresponding radical cations, which fragment to the same furanoxy radicals **65** plus benzyl cations.[44]



Scheme 47

ACKNOWLEDGEMENTS

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