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# Heterocyclic Photochemistry. 2. 4-Pyrones. A Mechanistic Study

## John A. Barltrop,* A. Colin Day, and Christopher J. Samuel[1]

*Contribution from the Dyson Perrins Laboratory, Oxford University, Oxford, England. Received August 13, 1978*

**Abstract:** The phototransposition of 4-pyrones into 2-pyrones in neutral solvents is shown to follow the sequence (4-pyrone)* → oxabicyclohexenyl zwitterion (e.g., **14**) → cyclopentadienone epoxide (e.g., **15**) + $h\nu$ → 2-pyrone. The oxabicyclohexenyl zwitterion derived from 3,5-dimethyl-4-pyrone has been trapped as a [4 + 3] cycloadduct with furan and the corresponding cyclopentadienone epoxide has been isolated and shown to rearrange photochemically to 2-pyrone. The zwitterion also reacts with hydroxylic solvents to give derivatives of cyclopentenone-4,5-diols and of furfuraldehyde. The effect of substituents in the 4-pyrone and of solvents on the photochemical behavior is rationalized.

## Introduction

The history of pyrone photochemistry is a long one, dating back to the early days of photochemistry when Paterno in 1914 reported a photodimer of 2,6-dimethyl-4-pyrone (**1a**).[2] The structure of this dimer was not correctly assigned,[3] however, until 1958, when Yates and Jorgenson[4] showed it to have the head-to-tail cage structure (**2a**). Under conditions of low



1
a, R = Me
b, R = Et
c, R = Ph
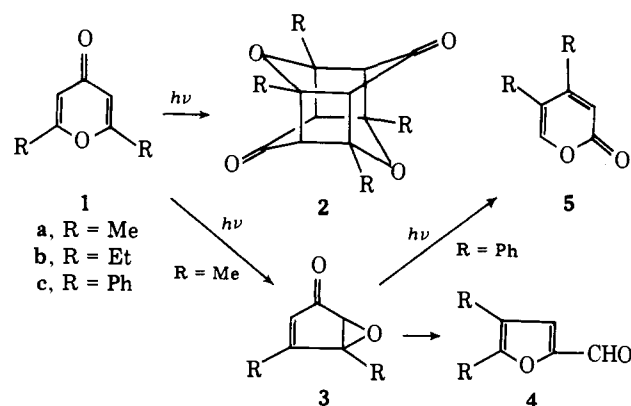
concentration, chosen to retard dimerization, Yates and Still[5] observed the first monomeric product, finding that irradiation of **1a** in water afforded ca. 1% yield of 4,5-dimethylfurfural-

dehyde (**4a**) which they suggested was formed via an epoxide (**3a**).
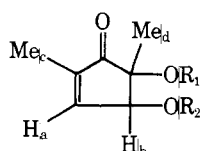
Padwa and Hartman showed that 2,6-diphenylpyrone (**1c**) gave a photodimer, to which they assigned a similar cage structure (**2c**), but no monomeric photoproducts. However, they did show that epoxide (**3c**), synthesized independently, gave **4c** on treatment with acid and the transposed **5c** on irradiation.[6]

More recently, appropriately substituted 4-pyrones have been found to rearrange photochemically to 2-pyrones,[7,8] and, again, epoxides such as **3** have been postulated as intermediates. In concentrated sulfuric acid, where pyrones are protonated and are best described as hydroxypyrylium cations, this rearrangement to 2-pyrones occurs almost regardless of substitution pattern;[8,9] our studies of this system are described in the accompanying paper.[10] Since we began this work, reports have appeared of solvent adducts (**7**) formed in competition with 2-pyrones (**8**) in alcoholic solvents (eq 1).[11,12]



(1)
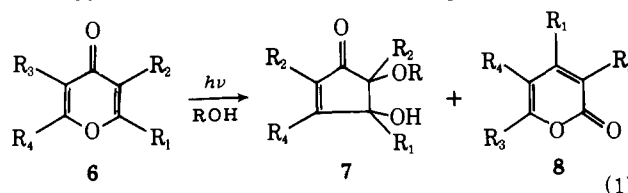
Further studies on the photodimerization have appeared, including reports of the dimer of 2,6-diethyl-4-pyrone (**1b**)[13]

**Table I.** NMR Data for



| R$_1$ | R$_2$ | solvent | $\tau_a$ | $\tau_b$ | $\tau_c$ | $\tau_d$ | $J_{ab}$ | $J_{ac}$ | $J_{bc}$ |
|---|---|---|---|---|---|---|---|---|---|
| CH$_2$CF$_3$ | H | CCl$_4$ | 2.97 | 5.31 | 8.22 | 8.72 | 2.3 | 1.5 | 1.8 |
| CH$_3$ | H | CCl$_4$ | 2.95 | 5.29 | 8.20 | 8.75 | 2.2 | 1.4 | 1.8 |
| H | H | CDCl$_3$ | 2.88 | 5.24 | 8.19 | 8.72 | 2.1 | 1.4 | 1.9 |
| epoxide | | CCl$_4$ | 2.91 | 6.31 | 8.27 | 8.46 | 1.6 | 1.7 | <0.2 |

and of cyclobutane dimers (**9** and **10**).[14] A single report of [2 + 2] photocycloaddition of acetylenes to a pyrone to give cyclobutenes (**11**) has also appeared.[15]
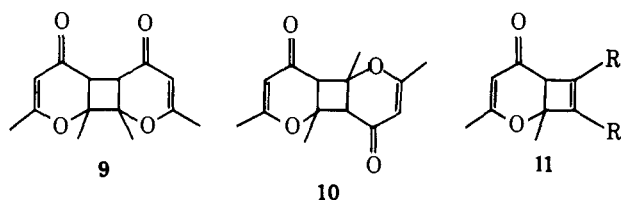


The presence of a 3-hydroxyl group in 4-pyrones permits facile rearrangement to hydroxycyclopentenediones (**13**) (eq 2)[16] and Barton has made use of this reaction in a synthesis of the mould metabolite, terrein, from kojic acid.[17]



$$\text{(2)}$$
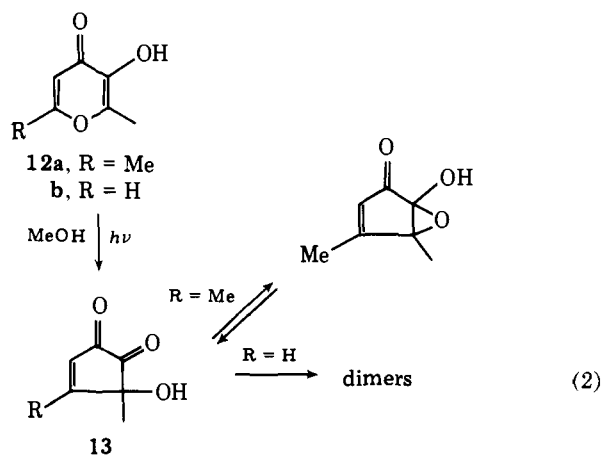
Our working hypothesis in this study has been that the phototranspositions observed with 4-pyrones have as their initial steps the sequence outlined in eq 3 involving initial 2,6



$$\text{(3)}$$
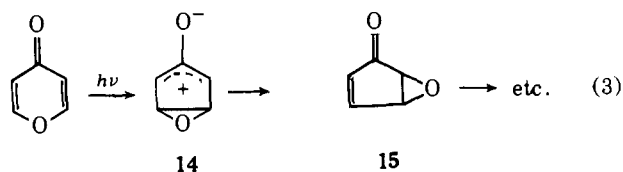
bonding in the excited state to form zwitterion **14**, followed by an oxygen walk to give the cyclopentadienone epoxide (**15**) which can then lead to the other products.

**Irradiation of 3,5-Dimethyl-4-pyrone in Trifluoroethanol.** For reasons to be discussed below, the most informative system proved to be 3,5-dimethyl-4-pyrone in trifluoroethanol (TFE). Irradiation of a 1% solution at 254 nm afforded a number of products, isolated by PLC on silica gel, whose structures and yields are discussed in order of decreasing $R_f$ on TLC.

The fastest running component (1%) was a crystalline compound, mp 160 °C, the mass spectrum of which showed a molecular ion at $m/e$ 248 and a base peak at $m/e$ 125,

implying a dimer. The simplicity of the NMR spectrum, which showed only four signals, indicates an element of symmetry. The two six-proton singlets at $\tau$ 8.64 and 8.93 are both attributable to methyl groups attached to saturated carbon atoms and the pair of two-proton doublets at $\tau$ 3.89 and 5.53 ($J = 3$ Hz) together with a strong IR band at 1644 cm$^{-1}$ suggests an enol ether. The 1749-cm$^{-1}$ band implies a strained ketone, so we assign structure **16a** or **16b**. The presence of the angular
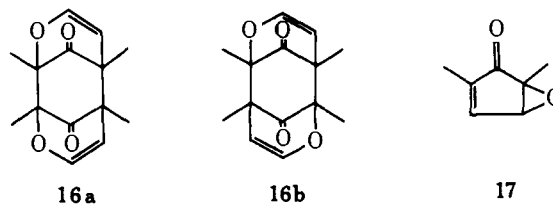


methyl groups restricts the NMR coupling data available and does not permit a distinction to be made between these alternatives or between possible stereoisomers.

The next compound (3%) was shown by mass spectrometry to be an isomer of starting material. On catalytic hydrogenation, it gave a mixture of *cis*- and *trans*-2,5-dimethylcyclopentanones, synthesized independently by the method of House and Trost,[18] thereby defining its carbon skeleton. The IR (1732 (s) and 1629 (w) cm$^{-1}$) and UV (234 and 267 (sh) nm) spectra indicated a bicyclohexenone, and the NMR spectrum (see Table I) was in accord with the structure assignment as the epoxide **17**. Note, in particular, the high-field resonance of the 4 proton at $\tau$ 6.31 compared with analogous compounds lacking the epoxide ring.

A second crystalline compound (0.5%, mp >200 °C) was shown to be a dimer by mass spectrometry (molecular ion at $m/e$ 248, base peak at $m/e$ 125). The presence of only four signals in the NMR spectrum again indicated an element of symmetry. The slightly broadened signals at $\tau$ 3.24 (2 H) and 8.09 (6 H), their IR bands at 1686 (s) and 1649 (w) cm$^{-1}$, and the UV absorption at 231 nm[19] are all in accord with an $\alpha$-methyl unsaturated ketone moiety with the allylic coupling unresolved but responsible for the broadening of the NMR signals. The other CH signals at $\tau$ 5.66 must be vicinal to the enone CH ($J = 3$ Hz) and the other unsplit methyl group ($\tau$ 8.84) must be attached to a saturated carbon atom, so we assign the structure as **18a** or **18b**.
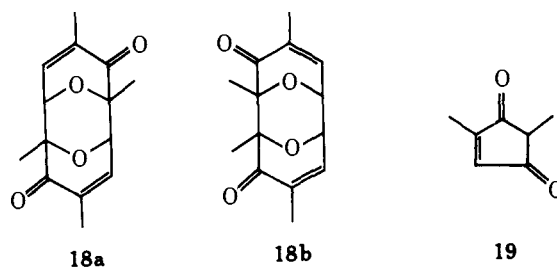


The next component was a pale yellow oil (2%) shown by mass spectrometry to be isomeric with starting material. This compound was unique in this study in showing a vicinal coupling constant of 7.5 Hz between a saturated methyl group at $\tau$ 8.79 and a one-proton signal at $\tau$ 7.44 indicating a CH$_3$CH fragment. The signals at $\tau$ 3.13 (1 H) and 7.91 (3 H) are coupled ($J = 1.5$ Hz) and suggest a methylenone fragment. We assign the cyclopentenedione structure (**19**). The UV and IR spectra and the yellow color are all in accord with this assignment.[20]

The next two components were 3,6-dimethyl-2-pyrone[10,21] (**20**, 46%) and recovered starting material (**21**).

The final product to be isolated (14%) was shown by mass spectrometry to be an adduct of starting materials and TFE. The $^{19}$F NMR spectrum showed a triplet ($J = 8.9$ Hz), 75.8

ppm upfield from CFCl₃ and the ¹H NMR spectrum showed a quartet ($J = 8.9$ Hz) at $\tau$ 5.99, implying a trifluoroethyl ether. ¹H NMR signals at $\tau$ 2.97 (1 H) and 8.22 (3 H) ($J = 1.9$ Hz) together with the IR (1726 (s) and 1645 (w) cm⁻¹) and UV (225 nm) spectra indicated a 2-methylcyclopent-2-enone moiety, and the presence of a broad singlet at $\tau$ 7.5 and a broad band at 3490 cm⁻¹ indicated a hydroxyl group. The other one-proton signal, at $\tau$ 5.31, is coupled to that at $\tau$ 2.97 ($J = 2.3$ Hz) and must be vicinal, so we assign the gross structure as of the type 22 or 23.



**20**     **21**     **22**     **23**
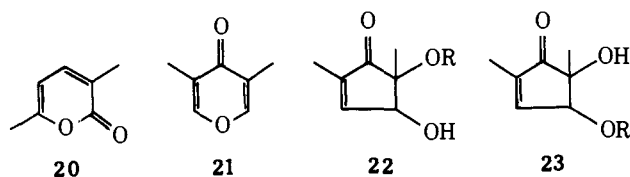
a, R = CH₂CF₃
b, R = CH₃
c, R = H

The NMR spectrum in Me₂SO-$d_6$ did not show any coupling between the hydroxyl proton and an adjacent CH that would be expected for 22a.[22] Also the compound did not undergo a Norrish type II fragmentation such as that reported by Pavlik for 24 (eq 4).[12] In neither case, however, can a neg-



(4)

**24**
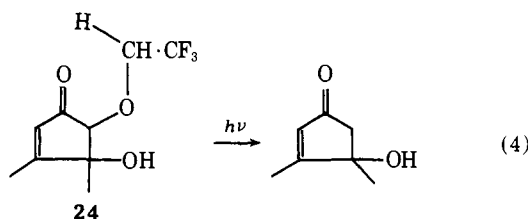
ative result be considered significant. We were able to distinguish between 22 and 23 by treatment of the compound with chromium trioxide–pyridine complex in methylene chloride,[23] which gave a single yellow product, isolated by PLC, which showed a mass spectrometric molecular weight of 222, showing loss of two units during the oxidation. The IR spectrum showed no hydroxyl stretch and the NMR spectrum showed the absence of the 4 proton, ca. $\tau$ 5-6, suggesting the expected diketone (25). Bands in the IR spectrum at 1763 (w), 1718 (s), and 1616 (w) cm⁻¹ and in the UV spectrum at 229 nm are all consistent with this cyclopentenedione structure, as are the NMR data. This establishes the gross structure of the initial adduct as 22a.

In the IR spectrum of 22a in carbon tetrachloride, the 3100-3700-cm⁻¹ region is strongly concentration dependent. At higher concentrations it showed a sharp band at 3622 cm⁻¹ and a broad band centered around 3460 cm⁻¹. On dilution, the relative intensities of the bands changed, and the broad, low-frequency band almost disappeared. Since only free and intermolecularly hydrogen bonded O–H absorptions are observed, the hydroxyl and trifluoroethyl groups must be trans.[12,24] The absence of intramolecular hydrogen bonding also provides confirmatory evidence that the hydroxyl is not adjacent to the carbonyl group as in 23. The epoxide 17 was stable thermally in TFE for the duration of the experiment and also on GLC injection, though it decomposed slowly over the course of several days. Irradiation of its solution in TFE, however, gave the $\alpha$-pyrone 20 and dione 19, but none of the TFE adduct 22a. The dimers would not have been observed on the scale used.

Gas chromatographic monitoring of formation of monomeric products from pyrone 21 vs. irradiation time at low conversions (<1%) showed that the epoxide 17 and TFE ad-

duct 22a were primary products and the dione 19 and $\alpha$-pyrone 20 were secondary.

Irradiation of 22a gave 25 but epoxide 17, dione 19, and pyrones 20 and 21 were absent.

**Furan Trapping Experiments.** In the initial attempt to trap the postulated zwitterion, based on the known cycloaddition of oxyallyl zwitterions and cyclopropanones to dienes,[25] 3,5-dimethyl-4-pyrone (21) was irradiated in furan, and a product was isolated by PLC and shown by mass spectrometry to be a 1:1 adduct.

Spin decoupling of the NMR spectrum showed the presence of three independent systems in the molecule: (1) a three-proton singlet at $\tau$ 8.69, implying a methyl group attached to a saturated center, (2) a one-proton quartet at $\tau$ 3.01 and a three-proton doublet at $\tau$ 8.39 ($J = 0.8$ Hz), which together with IR bands at 1666 and 1603 cm⁻¹ are most reasonably assigned to an $\alpha$-methyldihydropyrone part structure (26), and



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



**28**
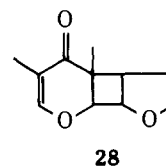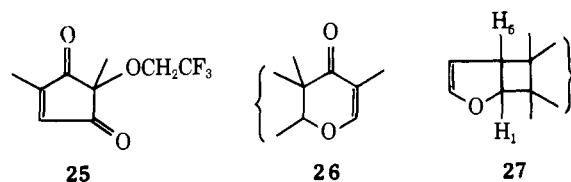
(3) five one-proton signals extensively coupled to one another. Four of these last, at ca. $\tau$ 3.69, 4.93, 4.81, and 6.39, are appropriate for a 2-oxabicyclo[3.2.0]hept-3-ene part structure (27), as are the values of the coupling constants.[26] The remaining proton in the third group, at $\tau$ 5.40, shows coupling constants of 4.2 Hz to H₁ and 1.6 Hz to H₅. Thus, it must be vicinal to H₁, but neither of these coupling constants can establish the stereochemistry reliably. They do show, however, that the fragments are joined as shown in 28.

In addition, a 2:1 adduct was isolated, but not fully characterized. Its NMR spectrum indicated that it was of this same [2 + 2] type.

Irradiation of the pyrone in a 4% solution of furan in TFE gave, as the major photoproduct, a crystalline compound (mp 105–107 °C, 26%) to which the structure 29 was readily as-



**29**     **30**
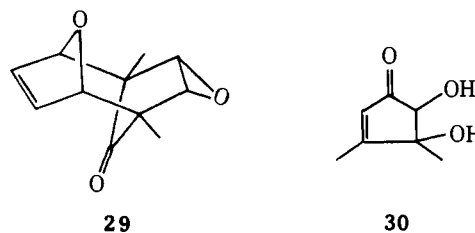
signed. Elemental and mass spectrometric analysis showed it to be a 1:1 adduct of furan and dimethylpyrone. The presence of only six signals in the ¹³C NMR spectrum and the simplicity of the ¹H NMR spectrum imply an element of symmetry in the molecule. The broad signals at $\tau$ 3.77 and 5.51 are typical of [4 + 2] adducts to the 2,5 positions of furan.[25] The UV [277 nm ($\epsilon$ 31) and end absorption only] and IR (1776 cm⁻¹) spectra imply a highly strained, unconjugated ketone and thus the gross structure must be as shown in 29. It is not possible to assign the stereochemistry from the spectra but analogy and argument from steric hindrance suggest that it is as shown.

The [2 + 2] adduct (28) was also present in this photolysis

**Table II.** Percentage Yields of Products from Irradiation of **21** in Various Solvents

| solvent | 28 | 29 | 22 | 20 |
|---|---|---|---|---|
| TFE | 0 | 0 | 7 | 46 |
| TFE + 4% furan | 4 | 26 | trace | 25 |
| TFE + 20% furan | 18 | 37 | | 14 |
| furan | 60 | 0 | 0 | 0 |
| methanol | 0 | 0 | 80 | 5 |
| water | 0 | 0 | 76 | |

and the yield of this latter compound increased with percentage of furan as shown in Table II.

**Irradiation in Other Solvents.** Irradiation of 3,5-dimethyl-4-pyrone in a more nucleophilic solvent than TFE increased the yield of solvent adduct at the expense of α-pyrone (see Table II). Thus irradiation of 3,5-dimethyl-4-pyrone (ca. $10^{-3}$ M) in methanol gave only 5% α-pyrone together with 80% of another compound whose molecular weight showed that it was an adduct of the pyrone and methanol. The similarity of its spectroscopic data, including the concentration-dependent OH region of the IR spectrum, to those of the TFE adduct (**22a**)' showed it to be the corresponding methanol adduct (**22b**). At higher concentrations, the reaction was slow and the yield much reduced. Irradiation of a 0.3 M solution in methanol-$d_4$ in a quartz NMR tube showed slow disappearance of starting material, less than 10% yield of the methanol adduct, and only diffuse absorption at high field, with no other sharp signals, suggesting that the reaction was giving polymer rather than a discrete dimer.

Similarly, irradiation of 3,5-dimethyl-4-pyrone in water (0.08 M) gave a product whose molecular weight showed it to be a 1:1 adduct of the pyrone and water. The similarity of its UV and NMR spectra to those of **22a** and **22b** showed it to be related water adduct (**22c**). The carbonyl stretch which appears at 1726 and 1724 cm$^{-1}$ in **22a** and **22b**, respectively, is lowered to 1717 cm$^{-1}$ in **22c**, possibly due to intramolecular hydrogen bonding. The 2-pyrone **20** could not be detected in the NMR spectrum of the crude photolysate (i.e., <5% yield).

The preceding results suggested that irradiation of 2,6-dimethyl-4-pyrone in water, under the conditions of Yates and Still,[5] should have yielded a water adduct with a cyclopentenone structure (**30**). A preliminary experiment involving irradiation of a $10^{-4}$ M aqueous solution did, indeed, show formation of a product absorbing at 228 nm, which did not correspond either to cage dimer or to furfural (**4a**) but which was appropriate for a β-methylcyclopentenone. Irradiation under the conditions of Yates and Still (0.2%, medium-pressure mercury lamp), followed by ether extraction gave mostly cage dimer together with ca. 1% of furfural, exactly as they found, but no product absorbing at 228 nm. However, by continuously extracting with ethyl acetate for 10 days the water adduct was isolated in 10% yield. Its structure is established by the following considerations. Elemental and mass spectrometric analysis showed the compound to be an adduct of water and the starting pyrone. A one-proton quartet at τ 4.12 and a three-proton doublet at τ 7.89 ($J$ = 1.4 Hz) indicate a β-methylenone system and the IR (1712 (s) and 1620 (m) cm$^{-1}$) and UV (228 nm) spectra imply that it is in a five-membered ring. The sharpness of the signal at τ 5.86, showing the absence of allylic coupling, implies structure **30**. A tenfold further reduction in concentration and irradiation with low-pressure mercury lamps resulted in the formation of almost no dimer and the isolation of water adduct **30** in 60% yield, together with 1% furfural (**4a**) and also 1% 4,5-dimethyl-2-pyrone (**5a**). Careful examination of mother liquors and PLC fractions did not reveal the presence of the $C_5$ epimer of **30**.

## Discussion

**Mechanisms.** All the results for 3,5-dimethyl-4-pyrone can be discussed in terms of Scheme I. Firstly, the alkyl-4-pyrones fluoresce only very weakly, or not at all, at room temperature;[27a] the lowest excited state is therefore very short lived. Nonetheless, in furan solution, a [2 + 2] photoadduct is formed. Thus there must be a shallow potential energy minimum on the $S_1$ surface at approximately the $S_0$ equilibrium geometry which preserves the excited state long enough for it to react with furan.[27b] Secondly, a key result is the isolation of the [4 + 2] adduct (**29**). Cycloaddition of oxyallyl systems

**Scheme I**
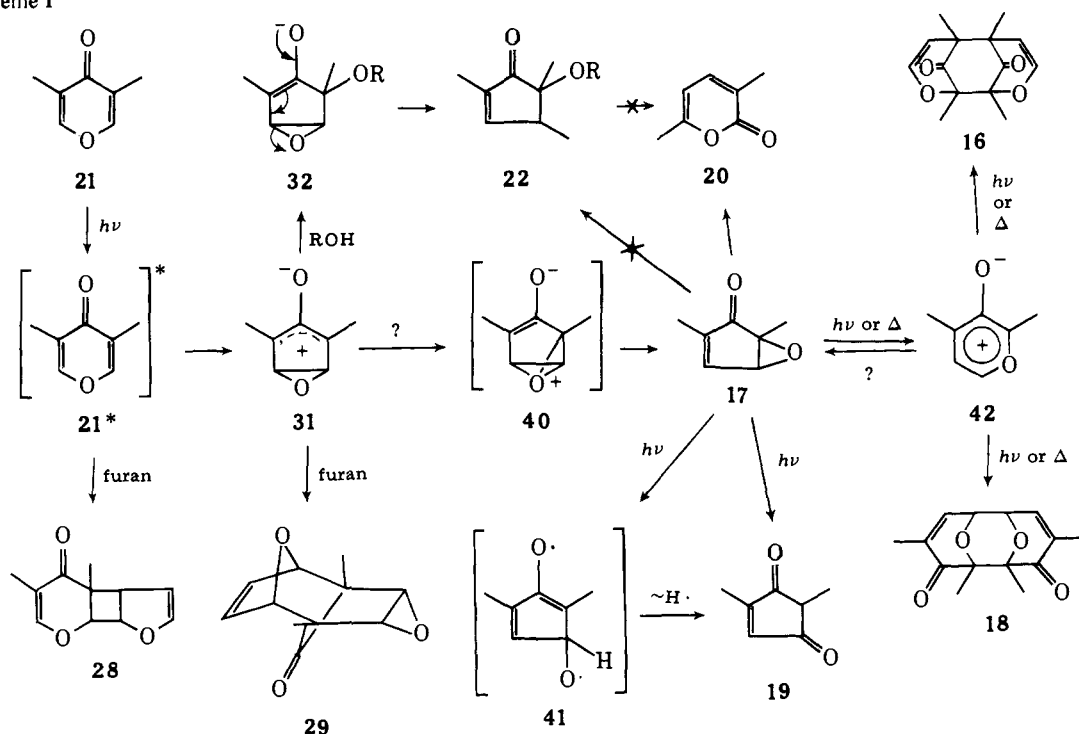
to furan is a well-studied reaction,[25] so formation of this adduct establishes the involvement of zwitterion **31** in 4-pyrone photochemistry.

The displacement of the product distribution (see Table II) from α-pyrone **20** toward the [4 + 2] adduct **29** and then toward [2 + 2] adduct **28** as the concentration of furan increased supports the product–precursor relationship indicated; the higher the concentration of furan, the earlier on the reaction coordinate it can trap intermediates.

The TFE adduct **22a** is not formed from the epoxide **17**. It is a primary photoproduct and is thus best formulated as deriving from nucleophilic attack of solvent on the oxyallyl zwitterion **31** followed by opening of the epoxide ring, as shown, in the enolate **32** or the corresponding enol.

The solvent would be expected to attack the zwitterion **31** from the less hindered side, i.e., trans to the epoxide ring, thus resulting in the observed adduct stereochemistry (eq 5). Sim-

$$(5)$$
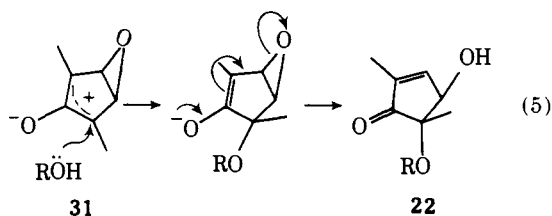
ilarly cycloaddition of furan would be expected to occur from the same side and for this reason the adduct **29** is drawn with the epoxide and carbonyl group syn to one another.

Similar solvent adducts are known in cyclohexadienone photochemistry; Schuster et al.[28] have isolated adducts of methanol to the type A zwitterion **33** (see Scheme II). The nature of the product depends on whether the solvent is acidified or not. Presumably the difference is that, whereas the enolate **34** can expel chloride as shown, to give **35**, in the presence of acid the enol **36** ketonizes, giving **37**. The analogue of **37** in the pyrone case, i.e., **38**, would be unlikely to be stable, in view of the known acid and base lability of **39**.[29]

**38**         **39**
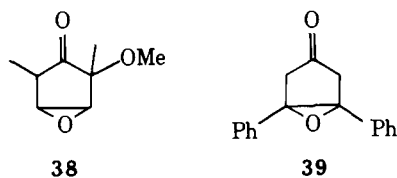
On the other hand, intramolecular nucleophilic attack on the oxyallyl zwitterion **31** by the lone pair of the ether oxygen atom would lead to the epoxide **17** via oxoniabenzvalene (**40**) as a transition state or an intermediate. Such an epoxide was first postulated as an intermediate in 1963,[5] but this is the first direct evidence for its involvement.

The dione **19** and α-pyrone **20** are both secondary products and both are formed on irradiation of the epoxide. Formation of the former is a standard reaction of α,β-epoxy ketones proceeding via C–O homolysis to diradical **41** and hydrogen atom shift.[30] The mechanism of formation of the latter is not so obvious and is presently under study, but a possible formulation is given.

( * = · or ± )
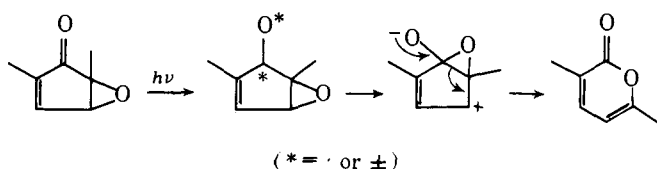
Regardless of the stereochemistry or regiochemistry of the dimers, their immediate precursor is obviously the 3-oxidopyrylium betaine (**42**). The scarcity of the epoxide **17** pre-

**Scheme II**
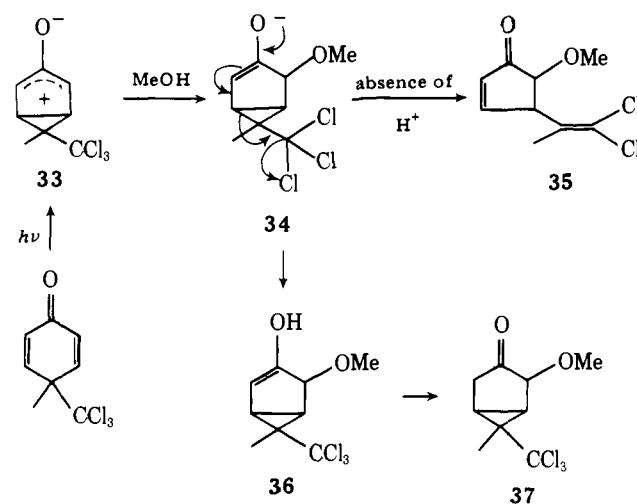
cluded further study of their formation and, in particular, it could not be established whether the processes shown in Scheme I were thermal or photochemical.

In their related study[31] of 3-oxidopyridinium betaines (**43**), Katritzky et al., by considering the frontier molecular orbitals, predicted that their betaines should dimerize thermally at the 2,4-2′,6′ positions to give unsymmetrical dimers of the form **44**, as observed, whereas photochemically they should undergo

**43**                        **44**

**45**                        **46**
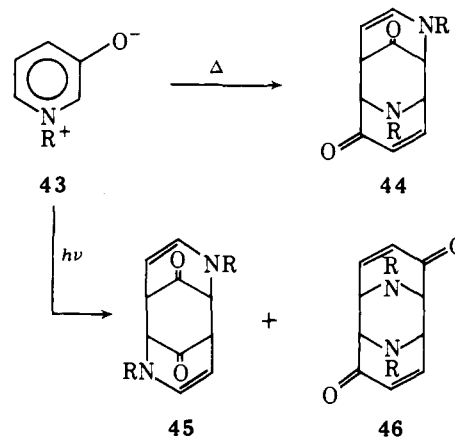
2,4-2′,4′ or 2,6-2′,6′ dimerization to give symmetrical dimers of types **45** and **46**, though only the former was observed.

Assuming the change in heteroatom to have only a quantitative effect, our finding of symmetrical dimers implies that they were formed photochemically and suggests the possibility of interconversion of **17** and **42** with either absorbing light to give its characteristic photoproducts.

In the more nucleophilic solvent, methanol, the rate of intermolecular trapping of zwitterion by solvent is enhanced over the rate of intramolecular rearrangement to epoxide, resulting in about a 100-fold increase in the ratio of solvent adduct **22** to α-pyrone **20**.

Turning to the aqueous irradiations of 2,6-dimethyl-4-pyrone, we note a general similarity between our results and those of Yates and Still,[5] but with some significant differences. The most important of these was our isolation of dihydroxy-cyclopentenone (**30**). This was very soluble in water and almost insoluble in ether, so the earlier failure to observe it is explained. The enhanced yield at lower concentration is just as expected for a competition between unimolecular reaction and bimolecular dimerization.

We considered the possibility that furfural (**4a**) and α-pyrone **5a** were derived from the water adduct **30** by a second photochemical step, or were artifacts of an acidic or basic

**Scheme III**
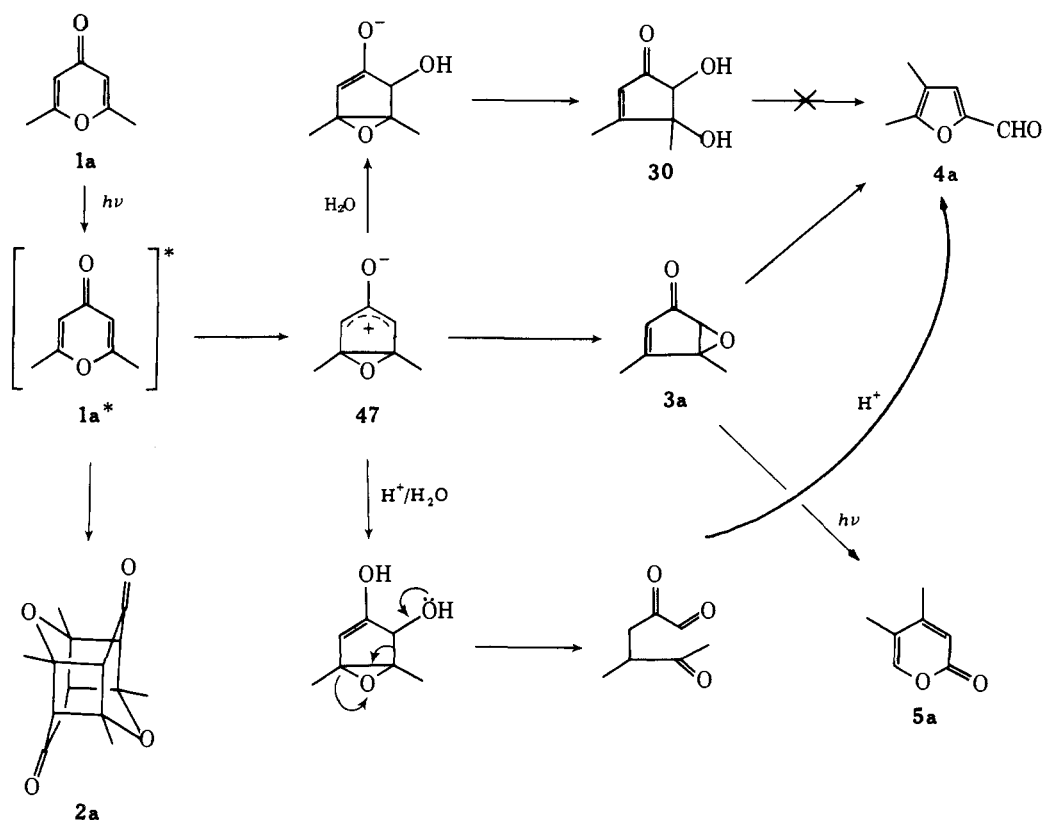


workup, but control experiments ruled out these possibilities. The diol was stable under conditions of acidity or basicity far outside those likely to be met with adventitiously during workup, and irradiation gave neither furfural nor pyrone.

In the light of these results and our conclusions concerning irradiation of 3,5-dimethyl-4-pyrone in TFE, we postulate Scheme III for 2,6-dimethyl-4-pyrone in water involving similar competitions between 2,6 bonding and a bimolecular process and between intramolecular rearrangements and solvent trapping of the oxyallyl zwitterion **47**.

**Effect of Solvents and Substituents.** Ishibe et al., finding that only those 4-pyrones with phenyl groups in both the 3 and 5 positions rearranged to 2-pyrones, suggested[ƒ] that the controlling factor was steric hindrance to dimerization. Pavlik and Kwong, on the other hand, finding that even some pyrones lacking 3,5-diphenyl substitution rearranged in TFE, argued against this and suggested that the controlling factor was the nature of the lowest excited state.[8] The ordering of states could well be solvent dependent, as Hart concluded for some 2,4-cyclohexadienones,[32] but this rationale cannot account systematically for the effect of substituents.

We believe that we can account for all these effects within a unified framework. The oxyallyl zwitterion is an established intermediate so we suggest that the main controlling factor is stabilization of this species by (1) electron-donating groups in the 3 and 5 positions or (2) polar solvents.

Thus groups such as phenyl or methyl at 3 or 5 should facilitate 2,6 bonding, whereas such groups at 2 or 6 might be expected to oppose this process because of losing the conjugation present in the excited state.

Thus, whereas 3,5-dimethyl-4-pyrone (**21**) gives only monomeric photoproducts in water or TFE even at high concentration (≥0.1 M), 2,6-dimethyl-4-pyrone (**1a**) gives appreciable quantities of dimer in the same solvents even at low concentration[12] (ca. $10^{-2}$ M). Failure to observe monomeric photoproducts from 2,6-diphenyl-4-pyrone[33] (**1c**), other than those from photooxidation,[34] is consistent with this picture.

In terms of this argument, the hydroxyl groups in 3-hydroxy-4-pyrones (**12a** and **12b**) would be particularly effective at stabilizing the zwitterion, and 2,6 bonding followed by loss of a proton would provide a facile pathway to the observed products[16] (eq 6), whereas, under the same conditions, the



**12a, R = Me**
**b, R = H**

$$(6)$$
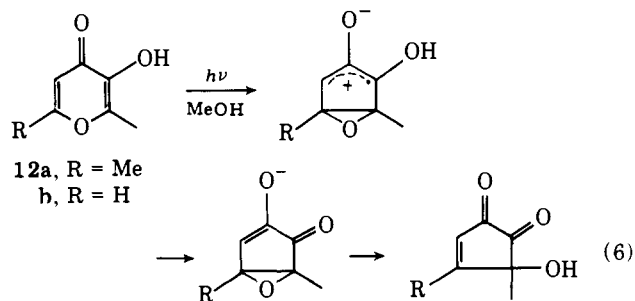
compound lacking the hydroxyl group (i.e., **1a**) affords cage dimer almost exclusively.[4]

It would also be expected that more polar solvents would stabilize the zwitterion and thus facilitate formation of products derived from 2,6 bonding. Thus, whereas tetraphenyl- and 3,5-diphenyl-2,6-dimethyl-4-pyrone (**48a** and **48b**, respec-
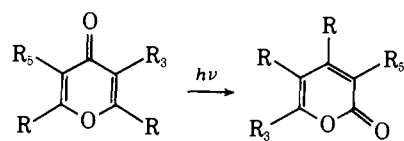


**48a, R = Ph; $R_3$ = $R_5$ = Ph**
**b, R = Me; $R_3$ = $R_5$ = Ph**
**c, R = Me; $R_3$ = Ph; $R_5$ = H**
**d, R = $R_3$ = $R_5$ = Me**

tively) rearrange even in methylene chloride solution, 3-phenyl-2,6-dimethyl-4-pyrone (**48c**) fails to do so even in acetonitrile and only does so in TFE.[8] Also, whereas tetramethyl-

4-pyrone (**48d**) rearranges in acetonitrile, 2,6-dimethyl-4-pyrone (**1a**) requires water or TFE to do so.

Thus, while 2,6-dimethyl-4-pyrone (**1a**) gives only dimers in solvents less polar than TFE or water, in these solvents it also forms monomeric products.[5,12] Similarly, while 3,5-dimethyl-4-pyrone (**21**) only gives monomeric products in methanol at high dilution (ca. $10^{-3}$ M), in TFE or water good yields of monomeric products are obtained even at higher concentrations ($\geq 0.1$ M).

## Conclusions

The evidence presented in this paper strongly suggests that the multifarious products formed by irradiating 4-pyrones under various conditions are all derived from an oxabicyclohexenyl zwitterion (such as **31** or **47**), the primary ground-state intermediate to which photoexcited 4-pyrones relax. This conclusion is supported by detailed MO calculations.[36]

## Experimental Section

Unless otherwise stated, the following procedures apply. Irradiations were carried out using quartz test tubes fitted with serum caps, NMR tubes, or UV cells in a Rayonet RPR-100 reactor fitted with 254-nm lamps. Gas chromatography was carried out using one of the following columns: A, 5% silicone oil; B, 10% PEGS; C, 20% Carbowax 20M. Preparative thin layer chromatography (PLC) was carried out using 200 × 200 × 1 mm layers of Kieselgel, eluting with the indicated percentage of ether in petroleum ether (bp 30–40 °C), the indicated number of times. Bands absorbing 254-nm light are recorded in order of decreasing $R_f$. Trifluoroethanol was Koch-Light puriss. and was used without further purification. Furan, from various suppliers, was redistilled before use. Melting points were measured on a Kofler block and are uncorrected. Compounds for which high-resolution mass spectra are given were pure by NMR and homogeneous by TLC and GC.

**Irradiation of 3,5-Dimethyl-4-pyrone in TFE.** The pyrone[35] (2.00 g) in TFE (200 mL) was irradiated for 3 h, concentrated in vacuo, and subjected to PLC (5% ether, four times), which gave four bands. Band 1 (10 mg) crystallized on standing, and was triturated with petrol and recrystallized from the same solvent (three times) to give dimer **16**, mp 160 °C. The spectral data follow: NMR ($CCl_4$) $\tau$ 3.89 (d, 2 H, $J = 6$ Hz), 5.53 (d, 2 H, $J = 6$ Hz), 8.64 (s, 6 H), 8.93 (s, 6 H); IR ($CCl_4$) 1749 (s), 1644 (s) $cm^{-1}$; mass spectrum $m/e$ 248 (1), 125 (100), 124 (11), 43 (8), 41 (12), 39 (7). Anal. ($C_{14}H_{16}O_4$) C, H. Band 2 (29 mg) contained 1,3-dimethyl-6-oxabicyclo[3.1.0]hex-3-en-2-one. The spectral data follow: NMR (Table 1); IR (film) 1732 (s), 1629 (w) $cm^{-1}$; UV $\lambda_{max}$ (EtOH) 234, 267 (sh) nm; mass spectrum $m/e$ 124 (49), 96 (23), 82 (27), 68 (62), 67 (35), 56 (25), 55 (26), 53 (31), 43 (24), 40 (44), 39 (100); high-resolution mass spectrum $m/e$ 124.0524 (calcd for $C_7H_8O_2$, $m/e$ 124.0524). Band 3 was resubjected to PLC (10% ether, six times), which gave three fractions. Band 3a (5 mg) crystallized on standing, was triturated with petrol, and had mp >200 °C, dimer **18**. The spectral data follow: NMR ($CDCl_3$) $\tau$ 3.24 (br d, 2 H, $J = 3$ Hz), 5.66 (d, 2 H, $J = 3$ Hz), 8.09 (br s, 6 H), 8.84 (s, 6 H); IR ($CHCl_3$) 1686 (s), 1649 (w) $cm^{-1}$; UV $\lambda_{max}$ (EtOH) 231 nm; mass spectrum $m/e$ 248 (5), 125 (100), 124 (5), 43 (6), 41 (8), 39 (5). Band 3b (21 mg) contained 2,4-dimethylcyclopent-4-ene-1,3-dione as a yellow oil. The spectral data follow: NMR ($CCl_4$) $\tau$ 3.13 (q, 1 H, $J = 1.5$ Hz), 7.44 (q, 1 H, $J = 7.5$ Hz), 7.91 (d, 3 H, $J = 1.5$ Hz), 8.79 (d, 3 H, $J = 7.5$ Hz); IR (film) 1747 (m), 1702 (s), 1618 (m) $cm^{-1}$; UV $\lambda_{max}$ (EtOH) 230 nm; mass spectrum $m/e$ 124 (49), 96 (23), 95 (11), 82 (27), 68 (62), 67 (35), 56 (25), 55 (26), 53 (31), 43 (24), 40 (44), 39 (100); high-resolution mass spectrum $m/e$ 124.0524 (calcd for $C_7H_8O_2$, 124.0524). Band 3c (461 mg) contained 3,6-dimethyl-2-pyrone.[10,21] Band 4 was resubjected to PLC (20% ether, four times), which gave two fractions. Band 4a (183 mg) contained recovered starting material. Band 4b (142 mg) contained 4-hydroxy-2,5-dimethyl-5-trifluoroethoxy-2-cyclopentenone. The spectral data follow: NMR (Table 1); IR ($CCl_4$) 3620 (m), 3490 (br m), 1726 (s), 1645 (w), 1280 (s), 1162 (s) $cm^{-1}$; UV $\lambda_{max}$ (EtOH) 225 nm; mass spectrum $m/e$ 224 (19), 125 (100), 124 (60), 96 (29), 43 (86); high resolution mass spectrum $m/e$ 224.0661 (calcd for $C_9H_{11}F_3O_3$, $m/e$ 224.0660).

**Hydrogenation of the Epoxide.** The epoxide (9 mg) in methanol (2 mL) was hydrogenated for 24 h under ambient conditions over 10%

palladium on barium sulfate (10 mg). Filtration and concentration in vacuo gave a residue which was identical in spectroscopic (NMR and IR) and chromatographic (GC on column B, 110 °C) behavior with authentic 2,5-dimethylcyclopentanone.[18]

**Irradiation of the Epoxide.** The epoxide (18 mg) in TFE (3 mL) was irradiated for 1 h. Analysis by GC (column A, 100 °C) and NMR revealed the presence of 3,6-dimethyl-2-pyrone and the cyclopentenedione and the absence of the TFE adduct.

**Irradiation of the TFE Adduct. Run 1.** The adduct (8 mg) in TFE (3 mL) was irradiated. GC analysis (column C, 140 °C) revealed the absence of any volatile product other than the oxidation product described below.

**Run 2.** The adduct (65 mg) in benzene (6.5 mL) was irradiated for 9 h in a test tube adjacent to a 250-W medium-pressure mercury lamp in a Pyrex water-cooled housing. GC analysis (column C, 140 °C) showed only a single volatile product. The solution was concentrated in vacuo and subjected to PLC (25% ether, five times), which gave two bands. Band 1 (4.1 mg) was identical with the oxidation product described below. Band 2 (38.2 mg) was recovered starting material.

**Oxidation of the TFE Adduct.** The TFE adduct (100 mg) in dichloromethane (2 mL) was added dropwise to a solution of chromium trioxide (0.6 g) and pyridine (0.97 mL) in methylene chloride (15 mL). The mixture was stirred for 16 h, filtered, concentrated in vacuo, and subjected to PLC (25% ether, three times), which gave two bands. Band 1 (22 mg) contained 2,4-dimethyl-2-trifluoroethoxycyclopent-4-ene-1,3-dione. The spectral data follow: NMR ($CCl_4$) $\tau$ 2.98 (q, 1 H, $J = 1.5$ Hz), 6.08 (q, 2 H, $J = 8.3$ Hz), 7.83 (d, 3 H, $J = 1.5$ Hz), 8.57 (s, 3 H); UV $\lambda_{max}$ (Et OH) 227 nm; IR ($CCl_4$) 1763 (w), 1718 (s), 1616 (w), 1284 (s), 1160 (s) $cm^{-1}$; high-resolution mass spectrum $m/e$ 222.0505 (calcd for $C_9H_9F_3O_3$, 222.0504). Band 2 (41 mg) contained recovered starting material.

**Irradiation of 3,5-Dimethyl-4-pyrone in Furan.** The pyrone (196 mg) in furan (25 mL) was irradiated for 29 h. The solution was concentrated in vacuo and subjected to PLC (10% ether, four times), which gave three bands. Band 1 (15 mg) contained a 2:1 adduct. The spectral data follow: NMR ($CCl_4$) $\tau$ 3.60 (dd, 2 H, $J = 1.6, 2.9$ Hz), 5.08 (br, 2 H, $J = 2.9$), 5.44 (dd, 2 H, $J = 1.4, 8.2$ Hz), 5.77 (br s, 2 H), 6.15 (d of m, 2 H, $J \sim 8$ Hz), 8.75 (s, 6 H). Band 2 was resubjected to PLC (alumina, 5% ether, three times), which gave two bands. Band 2a (151 mg) was pure 1,10-dimethyl-5,8-dioxatricyclo[5.4.0.0$^{2,6}$]-undeca-3,9-dien-11-one. The spectral data follow: NMR ($CCl_4$) $\tau$ 3.01 (q, 1 H, $J = 0.8$ Hz), 3.69 (dd, 1 H, $J = 1.7, 2.8$ Hz), 4.81 (dd, 1 H, $J = 4.2, 8.6$ Hz), 4.93 (t, 1 H, $J = 2.8$ Hz), 5.40 (dd, 1 H, $J = 1.6, 4.2$ Hz), 6.39 (br d, 1 H, $J = 8.6$ Hz), 8.39 (d, 3 H, $J = 0.8$ Hz), 8.69 (s, 3 H); IR ($CCl_4$) 1666 (s), 1628 (s), 1603 (m) $cm^{-1}$; UV $\lambda_{max}$ (EtOH) 211, 252, 287 nm; mass spectrum $m/e$ 192 (10), 125 (63), 124 (46), 113 (100), 86 (36), 85 (35), 68 (53), 57 (38); high-resolution mass spectrum $m/e$ 192.0786 (calcd for $C_{11}H_{12}O_3$, $m/e$ 192.0786). Band 2b (43 mg) contained the same [2 + 2] adduct contaminated with a different 2:1 adduct. Band 3 (11 mg) contained recovered starting pyrone.

**Irradiation of 3,5-Dimethyl-4-pyrone in TFE Containing 4% Furan.** The pyrone (200 mg) in TFE (24 mL) and furan (1 mL) was irradiated for 35 h, concentrated in vacuo, and subjected to PLC (25% ether, four times), which gave five bands. Band 1 (12 mg) contained [2 + 2] adduct. Band 2 (45 mg) contained 3,6-dimethyl-4-pyrone. Band 3 (77 mg) contained 1,6-dimethyl-9,11-dioxatetracyclo-[4.3.1.1$^{2,5}$.0$^{7,9}$]undec-3-en-10-one, which crystallized on standing (mp 81–96 °C); recrystallization from petrol gave mp 105–107 °C. The spectral data follow: NMR ($CCl_4$) 3.77 (br s, 2 H), 5.51 (br s, 2 H), 6.48 (s, 2 H), 8.93 (s, 6 H); UV $\lambda_{max}$ (EtOH) 277 (31) nm; IR ($CCl_4$) 1776 $cm^{-1}$; mass spectrum $m/e$ 192 (5), 177 (11), 163 (17), 147 (23), 125 (16), 124 (75), 119 (36), 96 (19), 95 (100), 91 (12), 69 (17), 68 (43), 67 (23), 41 (31), 39 (40). Anal. ($C_{11}H_{12}O_3$) C, H. Band 4 (4 mg) contained recovered starting pyrone. Band 5 (6 mg) contained TFE adduct.

**Irradiation of 3,5-Dimethyl-4-pyrone in TFE Containing 20% Furan.** The pyrone (200 mg) in TFE (20 mL) and furan (5 mL) was irradiated for 70 h, concentrated in vacuo, and subjected to PLC (10% ether, five times), which gave four bands. Band 1 (53 mg) contained [2 + 2] furan adduct. Band 2 (27 mg) contained 3,6-dimethyl-2-pyrone. Band 3 (110 mg) contained [4 + 3] furan adduct. Band 4 (14 mg) contained recovered starting pyrone.

**Irradiation of 3,5-Dimethyl-4-pyrone in Methanol. Run 1.** The pyrone (100 mg) in methanol (1.0 L) was irradiated in a Hanovia 1-L PCR fitted with a low-pressure mercury lamp for 3.5 h. The solution

was concentrated in vacuo and the crude photolysate was subjected to PLC (25% ether, four times), which gave three bands. Band 1 (5 mg) contained 3,6-dimethyl-2-pyrone. Band 2 (95 mg) contained 4-hydroxy-5-methoxy-2,5-dimethyl-2-cyclopentenone. The spectral data follow: NMR (CCl$_4$) $\tau$ 2.96 (dq, 1 H, $J$ = 1.8, 2.3 Hz), 5.16 (1 H, dq, $J$ = 1.2, 2.3 Hz), 6.2 (br s, 1 H), 6.70 (s, 3 H), 8.21 (dd, 3 H, $J$ = 1.2, 1.8 Hz), 8.75 (s, 3 H); IR (CCl$_4$) 3480 (br m), 1724 (s), 1649 (w) cm$^{-1}$; UV $\lambda_{max}$ (EtOH) 224 nm; mass spectrum $m/e$ 156 (13), 141 (10), 125 (32), 124 (49), 96 (43), 95 (22), 88 (29), 81 (15), 73 (21), 69 (20), 68 (10), 67 (20), 43 (100). Band 3 (5 mg) contained recovered starting pyrone.

**Run 2.** The pyrone (15 mg) in methanol-$d_4$ (0.5 mL) was irradiated in a quartz NMR tube for 44 h. Integration of the spectrum with respect to the −CHD$_2$ signal of solvent showed ca. 8% residual starting material, ca. 8% methanol adduct, and otherwise only broad, featureless signals.

**Irradiation of 3,5-Dimethyl-4-pyrone in Water.** The pyrone (102 mg) in water (10.2 mL) was irradiated for 4.5 h. The solution was concentrated in vacuo and subjected to PLC (50% ether, four times), which gave two bands. Band 1 (24 mg) was recovered starting pyrone. Band 2 (70 mg) was 4,5-dihydroxy-2,5-dimethyl-2-cyclopentenone. Short-path distillation (100 °C, 0.02 mm) gave an oil, which crystallized on standing (mp 80–87 °C). Recrystallization from petrol–chloroform gave mp 89–90 °C. The spectral data follow: NMR (CDCl$_3$) Table 1; (Me$_2$SO-$d_6$) $\tau$ 2.89 (br s, 1 H), 4.59 (d, 1 H), 4.74 (s, 1 H), 5.62 (m, 1 H), 8.33 (br s, 3 H), 8.98 (s, 3 H); IR (CHCl$_3$) 3600 (sh), 3550 (sh), 3380 (br m), 1717 (s), 1638 (w) cm$^{-1}$; UV $\lambda_{max}$ (MeOH) 224 nm; mass spectrum $m/e$ 142 (15), 141 (10), 127 (60), 125 (80), 124 (90), 109 (75), 96 (40), 95 (35), 81 (35), 74 (30), 71 (40), 69 (40), 53 (35), 43 (100). Anal. (C$_7$H$_{10}$O$_3$) C, H.

**Irradiation of 2,6-Dimethyl-4-pyrone in Water. Run 1.** The pyrone (0.84 g) in water (420 mL) was irradiated in an immersion well apparatus through quartz with a 450-W Hanovia medium-pressure mercury lamp for 4.5 h. The solution was continuously extracted for 24 h with ethyl acetate which was concentrated in vacuo to yield a yellow oil (1.08 g). This was triturated with ether to give a solid (0.26 g, mp 240–250 °C) presumed to be cage dimer. The mother liquors were subjected to PLC (100% ether, twice), which gave two bands. Band 1 (10 mg) contained 4,5-dimethylfurfuraldehyde. Band 2 (96 mg) contained water adduct.

**Run 2.** The pyrone (1.00 g) in water (5.0 L) was irradiated in five batches, each for ca. 5 h, in a Hanovia 1-L PCR fitted with a low-pressure mercury lamp. The solution was continuously extracted for 10 days with ethyl acetate which was concentrated in vacuo. The semisolid residue was triturated with ether to give crystals of the water adduct (0.515 g) and mother liquors (0.657 g) which were subjected to PLC (100% ether, twice) which gave four bands. Band 1 (10 mg) contained 4,5-dimethylfurfuraldehyde. Band 2 (9 mg) contained 4,5-dimethyl-2-pyrone. Band 3 (63 mg) contained further water adduct. Band 4 (11.5 mg) contained recovered starting pyrone. The total yield of water adduct was 0.578 g (50.5%); recrystallized from petrol–chloroform, it had mp 111–112 °C. The spectral data follow: NMR (CD$_3$OD) $\tau$ 4.12 (q, 1 H, $J$ = 1.4 Hz), 5.86 (s, 1 H), 7.89 (d, 3 H, $J$ = 1.4 Hz), 8.73 (s, 3 H); (Me$_2$SO-$d_6$) $\tau$ 4.15 (q, 1 H, $J$ = 1.5 Hz), 4.39 (d, 1 H, $J$ = 6.5 Hz), 4.65 (s, 1 H), 6.04 (d, 1 H, $J$ = 6.5 Hz), 7.97 (d, 3 H, $J$ = 1.5 Hz), 8.88 (s, 3 H); IR (CHCl$_3$) 3680 (w), 3600 (w), 3400 (br m), 1712 (s), 1620 (m) cm$^{-1}$; UV $\lambda_{max}$ (H$_2$O) 228 nm; mass spectrum $m/e$ 142 (13), 127 (20), 125 (17), 124 (32), 96 (32), 53 (25), 43 (70), 28 (100). Anal. (C$_7$H$_{10}$O$_3$) C, H.

**Reactions of Water Adduct. With Acid.** The water adduct in 20% sulfuric acid (10$^{-4}$ M) was allowed to stand at room temperature. No change in the UV spectrum was observed after 24 h.

**With Base.** One drop of 1 M sodium hydroxide was added to the water adduct in water (10$^{-4}$ M). The absorption at 228 nm decreased with a half-life of ca. 20 h.

**Irradiation.** The water adduct in water (ca. 10$^{-4}$ M) was irradiated (conditions A). The absorption at 228 nm decreased over the course of 0.5 h. No other absorption appeared.

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