Evidence for a Zwitterionic 2,6-Bonded Intermediate in 4-Pyrone Photochemistry. Following the Time Evolution of an Excited State

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Summary By selective trapping experiments involving furan, trifluoroethanol, and methanol, it is shown that the photochemically reactive state of 3,5-dimethyl-4-pyrone evolves sequentially into a zwitterionic intermediate and 3,6-dimethyl-2-pyrone.

A number of groups[1–3] have contributed to our knowledge of the photochemistry of 4-pyrones, obtaining a wide variety products: dimers, 2-pyrones, furancarbonyl derivatives, acetylene adducts, and solvent adducts. We report here the formation of two different 1:1-adducts of furan and 3,5-dimethyl-4-pyrone and discuss their implications for the mechanism of formation of other products.

Table. Percentage yields[a] of products from irradiation of (**1**) in various solvents

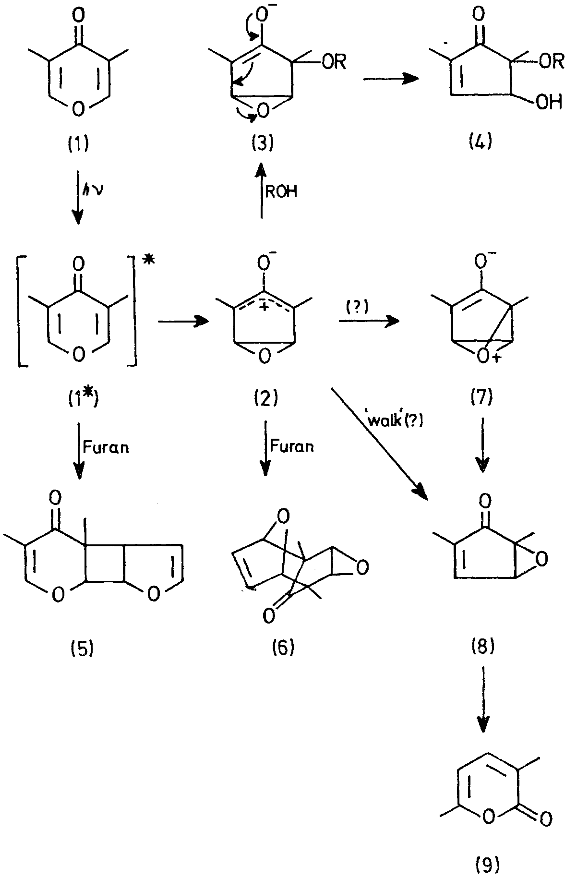
	Products			
Solvent	(**5**)	(**6**)	(**4**)	(**9**)
TFE	0	0	7	46
TFE + 4% furan	4	26	trace	25
TFE + 20% furan	18	37	—	14
Furan	60	0	0	0
Methanol	0	0	80	5

[a] These figures represent isolated yields and reflect product ratios estimated from the n.m.r. spectra of the crude photolysates.

Irradiation[†] of 3,5-dimethyl-4-pyrone (**1**) in trifluoroethanol (TFE) containing 4% furan gave, as the major product a crystalline compound, m.p. 105—107 °C, to which the structure (**6**) was assigned. Elemental and mass spectrometric analysis showed it to be a 1:1-adduct of furan and the dimethylpyrone. The presence of only six signals in the ^{13}C n.m.r. spectrum (δ 202·5, 135·4, 85·3, 59·5, 58.8, and 10·1 p.p.m.) and the simplicity of the ^{1}H n.m.r. spectrum [τ 3·77 (2H, br s), 5·51 (2H, br s), 6·48 (2H, s), and 8·93 (6H, s)] imply an element of symmetry in the molecule. The broad signals at τ 3·77 and 5·51 are typical of 4 + 3 adducts to the 2,5-positions of furan.[4] The u.v. [277 nm (ϵ 31) and end absorption only] and i.r. (1776 cm^{-1}) spectra imply a highly strained unconjugated carbonyl group and thus the gross structure must be as shown in (**6**). It is not possible to assign the stereochemistry from the spectra. Considerable analogy[5] suggests that (**6**) was formed by cycloaddition of furan to the oxyallyl zwitterion (**2**) (see Scheme).

In the presence of higher concentrations of furan, a second adduct was formed, to which the structure (**5**) was assigned.[‡] This must be formed by reaction of furan with the excited state of the pyrone before it undergoes 2,6-bonding. (A dark control reaction showed that neither adduct is formed by a thermal process.)

Irradiation in TFE in the absence of furan afforded two products. The major was 3,6-dimethyl-2-pyrone[3a] (**9**) and the minor was assigned the solvent adduct structure (**4**, R = CH_2CF_3).[§] The formation of the latter can be rationalised most simply in terms of attack by solvent, acting as an external nucleophile, on the oxyallyl system (**2**) followed by epoxide cleavage facilitated by the adjacent enolate unit. Formation of the 2-pyrone (**9**) can be considered as involving attack of the epoxide oxygen in (**2**), acting as an internal nucleophile, on the oxyallyl system, to give the oxoniabenzvalene (**7**) which would be expected to undergo C–O bond cleavage to give (**8**). Alternatively,



Scheme

[†] All irradiations were at 254 nm and, except for that in methanol which was at 8 × 10^{-4}M, were at *ca.* 0·06M.

[‡] N.m.r.: τ (CCl_4) 3·01 (1H, q, *J* 0·8 Hz), 3·69 (1H, dd, *J* 1·7 and 2·8 Hz), 4·81 (1H, dd, *J* 4·2 and 8·6 Hz), 4·93 (1H, t, *J* 2·8 Hz), 5·40 (1H, dd, *J* 1·6 and 4·2 Hz), and 6·39 (1H, dm, *J* 1·6, 1·7, 2·8, and 8·6 Hz); i.r. (CCl_4) 1666, 1628, and 1603 cm^{-1}; u.v. (EtOH) 252 and 287 nm; *m/e* 192.

[§] N.m.r.: τ (CCl_4) 2·97 (1H, dq, *J* 1·6 and 2·3 Hz), 5·31 (1H, dq, *J* 1·9 and 2·3 Hz), 5·99 (2H, q, *J* 8·9 Hz), 7·5 (1H, br s), 8·22 (3H, dd, *J* 1·6 and 1·9 Hz), and 8·72 (3H, s); ^{19}F n.m.r. (CCl_4) 75·8 p.p.m. upfield from $CFCl_3$ (t, *J* 8·9 Hz); i.r. (CCl_4) 3490, 1726, and 1645 cm^{-1}; u.v. (EtOH) 225 nm; *m/e* 224.

(**2**) could bypass (**7**) and give (**8**) directly by a walk mechanism analogous to that operative in cyclohexadienone photochemistry.[6]

In the more nucleophilic solvent, methanol, irradiation of (**1**) gave predominantly the methanol adduct (**4**, R = Me)¶ together with traces of the 2-pyrone (**9**).

We have thus demonstrated the formation of an oxyallyl zwitterion (**2**) by light-induced 2,6-bonding of a 4-pyrone and shown that it can react in at least three ways; (i) it can be trapped with furan, (ii) it can react with an external nucleophile to give a solvent adduct, and (iii) it can rearrange in an intramolecular manner to give a 2-pyrone. In the light of this it is easy to understand why phenyl substitution at positions 3 and 5 of the 4-pyrone should facilitate formation of the zwitterion and therefore the transposition products. Arguments about steric hindrance[2] are unnecessary.

This paper also illustrates a new approach for following the time-evolution of an excited species. Irradiation in neat furan gives a product presumably derived by trapping the excited state of the pyrone. At lower concentrations of furan, the excited state has time to evolve into the zwitterion before it is trapped by the furan.

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¶ N.m.r.: τ (CCl_4) 2·96 (1H, dq, *J* 2·3 and 1·8 Hz), 5·16 (1H, dq, *J* 2·3 and 1·2 Hz), 6·2 (1H, br s), 6·70 (3H, s), 8·21 (3H, dd, *J* 1·8 and 1·2 Hz), and 8·75 (3H, s); i.r. (CCl_4) 3480, 1724, and 1649 cm^{-1}; u.v. (EtOH) 224 nm; *m/e* 156.

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