4-Pyrone Photochemistry. The Intermediacy of a Cyclopentadienone Epoxide

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Summary 2,5-Dimethylcyclopentadienone epoxide has been isolated from trifluoroethanol solutions of 3,5-dimethyl-4-pyrone after irradiation at 254 nm and shown to be an intermediate in the photochemical conversion of the latter compounds into 3,6-dimethyl-2-pyrone.

CYCLOPENTADIENONE epoxides have frequently been postulated as intermediates in the photoisomerisation of 4-pyrones to 2-pyrones,[1–3] and it has been shown[4] that such epoxides do afford 2-pyrones on irradiation. However, no direct evidence has yet been presented for their involvement in 4-pyrone photochemistry. We report here the formation of a cyclopentadienone epoxide (**3**) upon irradiation[†] of 3,5-dimethyl-4-pyrone (**1**) and give evidence for the intermediacy of this epoxide in the photochemical conversion of the 4-pyrone (**1**) into 3,6-dimethyl-2-pyrone (**6**).

Recently, we found that irradiation of 3,5-dimethyl-4-pyrone (**1**) in trifluoroethanol (TFE) gave two products, the 2-pyrone (**6**) and the TFE adduct (**4b**).[2] Further study of this system has revealed the presence of two minor, but mechanistically significant, products, which were isolated by preparative-layer chromatography on silica gel and shown by mass spectrometry to be isomeric with the starting material. The isomer of lower R_F was identified from spectroscopic data[‡] as 2,4-dimethylcyclopent-4-ene-3,5-dione (**5**).

The isomer of higher R_F gave, upon catalytic hydrogenation, a mixture of *cis*- and *trans*-2,5-dimethylcyclopentanones, thereby revealing its carbon skeleton, and is formulated as 1,3-dimethyl-6-oxabicyclo[3.1.0]pent-3-en-2-one (**3**) on the basis of spectroscopic evidence. The i.r. (1732s and 1629w cm^{-1}) and u.v. (234 and 267sh nm) spectra indicated a bicyclohexenone, and the n.m.r. spectrum [τ (CCl_4) 2·91 (1H, dq, J 1·6 and 1·8 Hz), 6·31 (1H, d, J 1·6 Hz), 8·27 (3H, d, J 1·8 Hz), and 8·46 (3H, s)] resembled those of the alcohol adducts (**4**)[2] except for the appearance of the saturated methine signal at higher field (τ 6·31) than the corresponding signals in the alcohol adducts (**4a**: τ 5·31; **4b**: 5·16), as expected for an epoxide proton. Also, the absence of observable coupling between this methine proton and the

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[†] All irradiations were at 254 nm and *ca.* 1% concentration.

[‡] N.m.r. data: τ (CCl_4) 3·13 (1H, q, J 1·5 Hz), 7·44 (1H, q, J 7·5 Hz), 7·91 (3H, d, J 1·5 Hz), and 8·79 (3H, d, J 7·5 Hz); i.r. (liq. film) ν_{max} 1746 m, 1702s, and 1617m cm^{-1}; u.v. (EtOH) λ_{max} 230 nm; m/e 124.

allylic methyl group at τ 8·27 is indicative of a conformation different from that of the adducts (**4**), as is understandable for a strained bicyclic structure. Finally, an i.r. band at 862 cm^{-1} is consistent with the presence of an epoxide ring.

Independent irradiation† of the epoxide (**3**) in TFE rapidly afforded the 2-pyrone (**6**) and the cyclopentenedione (**5**), but not the TFE adduct (**4b**). The possibility, suggested by this observation, that (**3**) is the precursor of (**5**) and (**6**) in the photoisomerisation of the 4-pyrone (**1**) was confirmed by g.l.c. analysis of the photolysate from (**1**)† at low conversions ($< 1\%$), which showed that the epoxide (**3**) and the TFE adduct (**4b**) were both primary photoproducts, and the cyclopentenedione (**5**) and the 2-pyrone (**6**) secondary. Control experiments indicated that (**3**) was thermally stable and (**4b**) photochemically stable under the irradiation conditions. Also, since the TFE adduct (**4b**) is a primary photoproduct, and not formed from the epoxide (**3**), this adduct must have arisen directly by attack of TFE on the oxyallyl zwitterion (**2**), as suggested in our previous paper.[2]

Our mechanistic conclusions are summarised in the Scheme. Formation of the cyclopentenedione (**5**) from the epoxide (**3**) is a typical reaction of $\alpha\beta$-epoxyketones,[4] involving C$_\alpha$–O cleavage to form a diradical (**8**), followed by hydrogen shift. Also isolated from the photolysate were two crystalline photodimers, the structures of which reflect two of the possible modes of dimerisation of the oxypyrylium tautomer of the epoxide.[5]

In conclusion, we have demonstrated the involvement of a cyclopentadienone epoxide in the photochemistry of a 4-pyrone, an involvement first postulated 14 years ago,[1] and confirmed our previous mechanistic proposals.[2]

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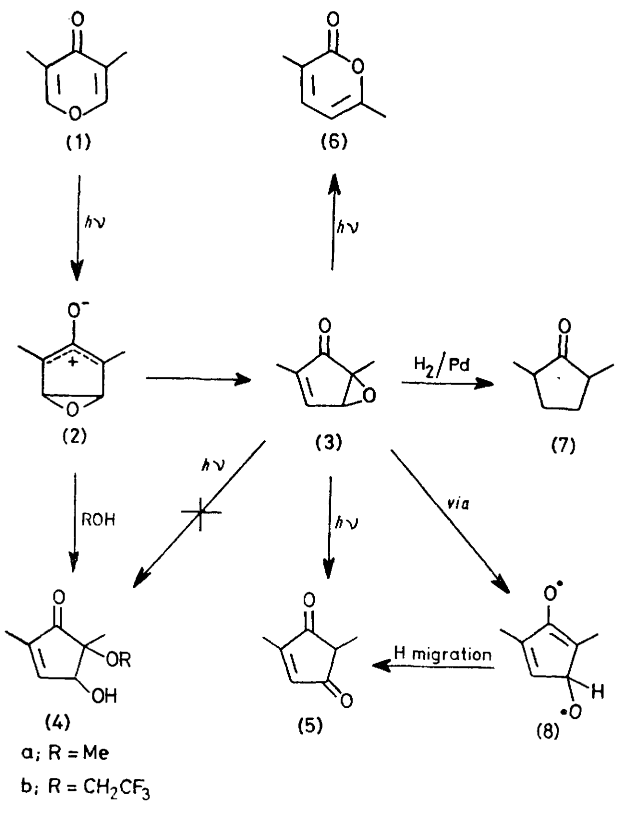

SCHEME

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[5] *Cf.* related results of N. Dennis, A. R. Katritzky, and H. Wilde, *J.C.S. Perkin I*, 1976, 2338.