Hydroxypyrylium Photochemistry. A New Intermediate

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Summary The photochemical conversion of 4-hydroxy-3,5-dimethylpyrylium cation into the 2-hydroxy-3,6-dimethyl isomer in sulphuric acid is shown to involve a cyclic sulphate as an intermediate.

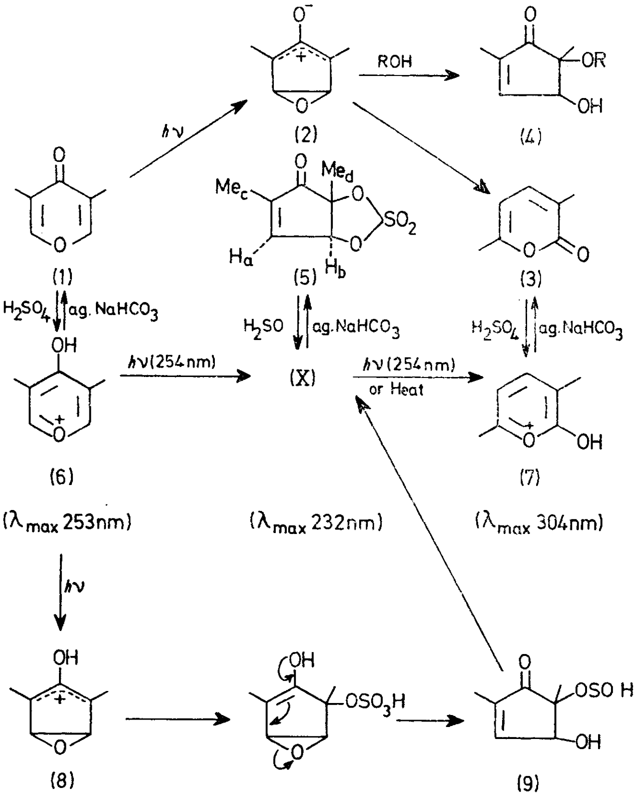
In the preceding communication,[1] we have shown that the primary process leading from the excited state of the 4-pyrone (**1**) is 2,6-bonding to form an oxyallyl zwitterion (**2**) which can react further, either in an intramolecular manner to give the 2-pyrone (**3**) or with a nucleophilic solvent to a cyclopentenone derivative (**4**).

By analogy, in sulphuric acid, where pyrones are protonated, one might expect light-induced 2,6-bonding to give a hydroxyallyl cation (protonated **2**) which could undergo nucleophilic attack, leading to a 4,5-dioxygenated cyclopentenone derivative.

We report here that such species are produced, and are, in fact, hitherto unsuspected intermediates in the photochemical conversion of 4-hydroxy- into 2-hydroxy-pyrylium cations.[2,3] Thus, we have recently reported[3] that irradiation of 3,5-dimethyl-4-pyrone (**1**) in sulphuric acid gave 3,6-dimethyl-2-pyrone (**3**) and show here that, under modified conditions, it is possible to isolate the cyclic sulphate (**5**) in 43% yield.

Irradiation of a stirred 0·3M solution† of the pyrone (**1**) in sulphuric acid followed by injection of the acid solution through a fine needle into stirred saturated aqueous $NaHCO_3$, ether extraction, and preparative layer chromatography on silica gel afforded (**5**) as a colourless crystalline compound, m.p. 73—74 °C.

Elemental and mass spectrometric analysis showed (**5**) to be a formal adduct of the starting material and sulphur



Scheme

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† Stirring was necessary to prevent secondary photolysis of (X) before it could diffuse away from the walls of the vessel.

trioxide. Hydrogenation over palladium on barium sulphate gave 2,5-dimethylcyclopentanone as a mixture of isomers identical with an authentic mixture of isomers synthesised independently,[4] thus establishing the carbon skeleton. The i.r. (1744 and 1641 cm^{-1}) and u.v. [223 nm (ϵ 8440) and 339 nm (42·3)] spectra implied a conjugated cyclopentenone, and the n.m.r. spectrum (see Table) confirms (**5**) as the only possible structure.

Irradiation of a solution of the 4-pyrone (**1**) in sulphuric acid in a quartz n.m.r. tube showed, in addition to a decrease in the signals due to (**6**) and an increase in those due to (**7**), the appearance of other signals identical with those of a solution of (**5**) in sulphuric acid. These last signals increased initially, and then, either (a) on further irradiation or (b) on standing in the dark at room temperature, decreased with corresponding increases in the signals due to (**7**) with a half-life for the dark reaction of 45 h. Similarly, irradiation of a solution of (**1**) in sulphuric acid (*ca.* 10^{-4}M) in a u.v. cell showed successive shifts in the absorption maxima: $252 \xrightarrow{h\nu} 232 \xrightarrow{h\nu \text{ or heat}} 304$ nm. Thus the cyclic sulphate is established as an intermediate, and as a thermal and photochemical precursor to the 2-hydroxypyrylium cation (**7**).

TABLE. N.m.r. data for the cyclic sulphate (**5**).

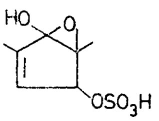
Solvent	τ_a	τ_b	τ_c	τ_d	J_{ab}	J_{ac}	J_{bc}
$CDCl_3$[a]	2·69	4·57	8·03	8·28	2·6	1·5	2·3
H_2SO_4[b]	2·35	4·29	7·99	8·20	2·7	1·3	0·9

[a] Relative to $Me_4Si = \tau$ 10. [b] Relative to $CH_2Cl_2 = \tau$ 4·74.

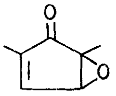
What then is the structure (X) of (**5**) in sulphuric acid? The similarity of the n.m.r. coupling pattern in deuteriochloroform and sulphuric acid (see Table) implies that the 4,5-dioxygenated cyclopentenone structure is preserved, while downfield shifts suggest protonation. The proton cannot be on the carbonyl oxygen since *O*-protonation of $\alpha\beta$-unsaturated ketones shifts the u.v. absorption maximum about 50 nm to the red,[5] and it is thus presumably on one of the sulphate oxygen atoms, possibly with opening of the sulphate ring to form a species such as (**9**).

By analogy with the processes in neutral solution, formation of (**5**) is most simply rationalised in terms of light-induced 2,6-bonding leading to a hydroxyallyl cation (**8**) which is trapped as the cyclic sulphate as outlined in the Scheme.

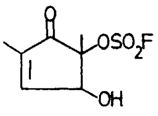
Although there is as yet no evidence concerning the mechanisms for the conversion of the cyclic sulphate into the 2-pyrone, it would be reasonable to invoke intermediates such as (**10**) or (**11**).



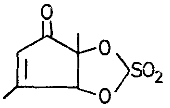
(10)



(11)



(12)



(13)

Transient signals have also been observed when irradiation of other systems has been monitored by u.v. or n.m.r. spectroscopy. Thus 3,5-dimethyl-4-pyrone in fluorosulphonic acid shows transient n.m.r. signals at τ 1·80, 4·15, 7·81, and 8·06 which decay with a half-life of *ca.* 1 h. These data are consistent with structure (**12**). 2,5-Dimethyl-4-pyrone in sulphuric acid shows n.m.r. signals at τ 3·08, 4·29, 7·38, and 8·23 and u.v. absorption at *ca.* 240 nm which decay with a half-life of *ca.* 3 h. These data are consistent with a structure related to (**13**). 2,6-Dimethyl-4-pyrone in sulphuric acid shows transient u.v. absorption at *ca.* 240 nm which decays within 1 h. In none of these cases, however, has the species responsible yet proved isolable. Nonetheless, these observations do suggest the generality of the sort of process described in the Scheme.

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[5] J. Rosenbaum, M. Rosenbaum, and M. C. R. Symons, *Mol. Phys.*, 1960, **3**, 205.