Carbonium-ion Photochemistry: the Photoisomerisation of Protonated Cyclohexadienones and Phenols[1]

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Summary Alkylated hydroxybenzenonium cations undergo a reversible photoisomerisation in FSO$_3$H to give the corresponding 2-hydroxybicyclo[3,1,0]hexenyl cations.

SOLUTIONS of polymethylbenzenonium cations in fluorosulphuric acid undergo upon irradiation a symmetry allowed disrotatory closure to give the corresponding bicyclo[3,1,0]hexenyl cations.[2] In view of the widespread interest in cyclohexadienone photochemistry[3] we have explored the photochemistry of some protonated cyclohexadienones and phenols in fluorsulphuric acid and have found that both the cations corresponding to the cyclohexa-2,4- and -2,5-dienones undergo light-induced isomerisations.

The hydroxybenzenonium cation[4] (1) underwent a clean isomerisation to give (2) upon irradiation of its long-wavelength absorption (λ_{max} 400 nm) in FSO$_3$H at low temperatures. The irradiation was carried out in a regular clear-wall n.m.r. tube using the apparatus previously described[5] and the reaction monitored by low-temperature n.m.r. observation. Provided that light with wavelength greater than 380 nm was used, the only product detected was the bicyclic cation (2). The structure of (2) was established by the identity of its n.m.r. spectrum with that of authentic protonated hexamethylbicyclo[3,1,0]hexenone (3). Quenching of the irradiated solution in aqueous potassium carbonate at 0° gave (3), identical with material prepared by the procedures described by Hart.[6]

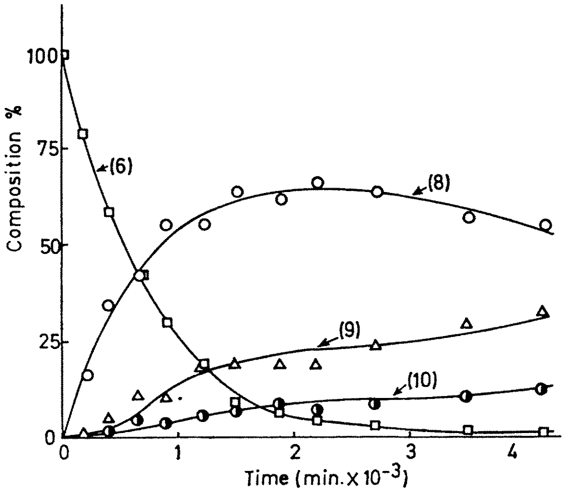
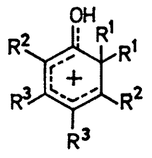


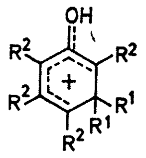
FIGURE. *Irradiation of* (6) *in* FSO$_3$H *at* −85°, *wavelength* > 325 *nm, Bausch and Lomb* HP 100 *mercury light source.*

Cation (2) was also produced by irradiation, through a Pyrex filter, of (4) (λ_{max} 341 nm) at low temperatures in FSO$_3$H.[4] A photostationary state was reached under these conditions which consisted of equal amounts of (2) and (4) and no detectable (1). The same photostationary state was reached by irradiating either (2) (λ_{max} 340 nm) or (1) in FSO$_3$H with a Pyrex filter.

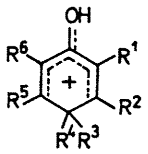
Any mechanism involving an initial thermal rearrangement can be discounted, as at −60° the cations (1), (2), and (4) are all thermally stable. Thus the isomerisation of (1) and (4) to (2) cannot involve the thermal production of (5) followed by a photochemical closure of (5) to (2), but must be initiated by a photochemical step. The excited state involved in the isomerisations of these protonated ketones is certainly not a n,π^* singlet or triplet state. The lack of any difference in rate of isomerisation of rigorously degassed or oxygen-saturated FSO$_3$H solutions of (1) would suggest but not establish that the reaction proceeds through the first π,π^* singlet state.



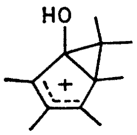
	R^1	R^2	R^3
(1)	Me	Me	Me
(6)	Me	H	H
(9)	H	H	Me



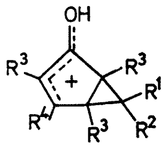
	R^1	R^2
(5)	Me	Me
(12)	Me	H



	R^1	R^2	R^3	R^4	R^5	R^6
(4)	Me	Me	Me	Me	Me	Me
(7)	H	H	Me	Me	H	H
(10)	Me	Me	H	H	H	H
(11)	H	Me	H	H	Me	H
(13)	H	Me	Me	H	H	H



(15)



	R^1	R^2	R^3	R^4
(2)	Me	Me	Me	Me
(8)	Me	Me	H	H
(14)	Me	H	H	Me

To test for photochemically induced alkyl shifts and the generality of these isomerisations, the dimethyl cations (6) and (7) were prepared by protonation of the corresponding dienones[7] with FSO$_3$H. Irradiation of (6) (λ_{max}

363 nm) below −60° with light of wavelength greater than 325 nm caused it to isomerise to (8), which underwent a further slow photochemical reaction to form (9) and (10) in a 3 : 1 ratio[8] (see Figure). The cation (7) (λ_{max} 298 nm) behaved in a similar manner except that at the wavelength of the light used (λ > 275 nm) the bicyclic material (8) readily isomerised to (9), (10), and (11). At −60° all these cations were thermally stable.

^{1}H *n.m.r. data for cations,* −55° *in* FSO_3H[a]

Cation	Vinyl H	Methylene H	Bridgehead H	Methyl H
(2)	—	—	—	1·24 1·43 1·53 1·57 1·91 2·33
(6)	8·58(h) 7·62(q) 7·12(m2H)	—	—	1·64
(7)	8·31(d) 7·15(d)	—	—	1·51
(8)	8·50(m) 7·79(d)	—	3·53(m) 4·10(m)	1·46 1·68
(9)	7·32(bs) 7·05	4·41	—	2·26 2·67
(10)	8·25(d) 7·16(d)	4·15	—	2·22 2·54
(11)	6·94	3·99	—	2·51

[a] All chemical shifts in p.p.m. referred to internal tetramethylammonium chloride taken as 3·1 p.p.m.; h heptet, m multiplet, d doublet, bs broad singlet.

It is clear from these results that no methyl group migration occurs during the transformation of (6) and (7) to (8), but that these migrations are involved in the subsequent photoisomerisations of (8). The photochemical reactions of (8) may best be understood in terms of symmetry-allowed breaking of the C-1–C-5 bond in its first excited state to give the cation (12), which would be expected to undergo rapid thermal 1,2 alkyl shifts and proton reorganization to give either (9) or (10). Similarly, (2) could ring-open to give (5), which is known[4] to rearrange to (4).

One significant difference between the photoreactions of (6) and (7) is that (11) is only obtained as one of the products when (7) and not (6) is irradiated. The conditions used for these two reactions only differ in wavelength of the light used and it is found with the shorter-wavelength light needed to excite (7) that (9) is photochemically labile, being transformed into (11). 3,4-Dimethylphenol is largely protonated at C-6 in FSO_3H and this cation (9) (λ_{max} 361 nm) has a very similar u.v. spectrum to that of (6). However, a small proportion is protonated at C-4, and the cation (13) by comparison with other *para*-protonated phenols[9] is expected to absorb at *ca.* 290 nm. It would appear that (13) is undergoing the photoisomerisation, probably to give the bicyclic cation (14) which would, under these conditions, be photochemically transformed to (11).

Although a clear distinction cannot yet be made between the several possible mechanisms for the protonated cyclohexadienone photoisomerisations, a two-step process involving an initial photochemical valence isomerisation followed by a thermal cyclopropyl migration is particularly attractive. The photochemical isomerisation of, for example (1) to (15) has precedent in the analogous photoisomerisation of the benzenonium ions to bicyclo[3,1,0]-hexenyl cations, a reaction which has been shown to occur by way of an electrocyclic pathway rather than the alternative symmetry allowed [$\sigma^2a + \pi^2a$] cycloaddition mechanism.[2] Cation (15) is known to be thermally accessible from, and to revert to, (2) by what is formally a suprafacial 1,4-sigmatropic shift.[10] The rate of this cyclopropyl migration around the cyclopentenyl ring is very dependent upon the charge stabilizing ability of the substituents upon C-6 and it is interesting that while (13) is photochemically labile, (9) would appear to be stable.[2,11]

Through the use of silica gel slurries or trifluoroethanol, Hart[12] has been able to invert the energies of the π,π^* and n,π^* states of certain cyclohexa-2,4-dienones and has shown that keten formation does not occur from the π,π^* state. Whereas in these media the energies of the n,π^* and π,π^* states of 6,6-dimethylcyclohexa-2,4-dienone are not reversed, in FSO_3H solution no such limitation applies.

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