The Photoisomerization of Some Tropylium Cations and Protonated Tropone

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Summary The use of FSO_3H as a solvent enabled the photoisomerization of tropylium, methyl-, hydroxy-, and methoxy-tropylium cations to be carried out giving in high yield either the bicyclo[3,2,0]heptadienyl or norbornadien-7-yl cations.

DESPITE the detailed attention which has been given to the elucidation of the chemistry of carbonium ions, very little information is available on their photochemical reactions. Solid tropylium salts have been reported[1] to be light sensitive and bicyclo[3,2,0]hepta-3,6-dien-2-ol together with the corresponding ether have been isolated by van Tamelen and his co-workers[2] from the photolysis of tropylium fluoroborate in dilute aqueous acid. Rather than use a solvent in which any product cations are likely to be unstable with respect to covalent material we have investigated fluorosulphuric acid as a solvent[3] and report the results of preliminary studies on the photochemistry of several tropylium cations.

Irradiation of tropylium fluoroborate, (λ_{max} 217 and 273 nm)[4] dissolved in fluorosulphuric acid, in a quartz n.m.r. tube with a Bausch and Lomb HP 100 mercury light source induced a clean isomerization of the tropylium ion to the norbornadien-7-yl cation[5] (I). The irradiation was carried out at temperatures below −60° by focussing the light with a series of lenses on to the n.m.r. tube contained in a quartz Dewar flask. The reaction was monitored and the product identified by n.m.r.,† comparison being made to an authentic sample of the norbornadien-7-yl cation (I)[5] prepared by protonation of norbornadien-7-ol. (I) was the sole product detected and with prolonged irradiation the reaction could be driven to completion.

The most reasonable mechanism for this rearrangement is an initial light-induced isomerization of the tropylium ion to give the bicyclo[3,2,0]heptadienyl cation (II) followed by a thermal conversion of this into (I). The isomerization of (II) to (I) in FSO_3H has been reported[5] as being a very rapid process at temperatures below −60°. This mechanism is in accord with that suggested by van Tamelen *et al.*[2] for the photolysis in dilute acid, in that Story[6] has shown that capture of (II) competes effectively with isomerization in nucleophilic solvents. It is interesting to note that the

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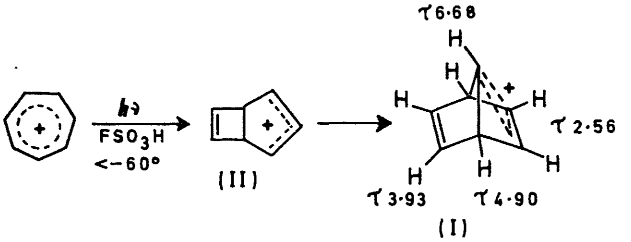
† Chemical shifts of all cations are referred to internal methylene chloride taken as τ 4·70.

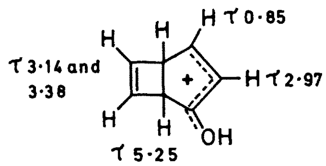
norbornadien-7-yl cation isomerizes thermally to the tropylium cation at +47°.[5]

Irradiation of methyltropylium ion[4] at −85° yielded the 2-methylnorbornadienyl cation[7] together with other minor products. No isomerization of the phenyltropylium cation[8] upon prolonged irradiation of the long-wavelength absorption could be detected.

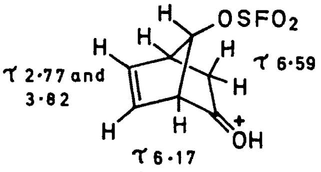
Of particular interest in view of the wide-spread attention that the photochemical reactions of tropone have received[9] is the photoisomerization of protonated tropone. The hydroxytropylium cation (λ_{max} 229 and 306 nm) produced upon solution of tropone in FSO_3H, underwent a clean isomerization upon irradiation of the long-wavelength absorption in a regular clear-wall n.m.r. tube at −75°. Two products were detected and identified by their n.m.r. spectra;† protonated bicyclo[3,2,0]hepta-3,6-dienone (III)[10] and the protonated norbornenone derivative (IV)[11]‡ were formed in equal amounts. Both of these products (III) and (IV) are known to be stable in FSO_3H at low temperatures, and not to rearrange further.[10,11] It is likely that (III) and the corresponding 3-hydroxy-cation (V) are the primary photoproducts and that (V) undergoes subsequent rearrangement and reaction with acid to give (IV).



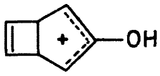
(II) (I)



(III)



(IV)



(V)

The possibility that it is not the hydroxytropylium ion undergoing the photoreaction but unprotonated tropone is very unlikely in view of the acidity of FSO_3H. Further evidence against this possibility is that the methoxytropylium cation[4] undergoes an analogous photoisomerization to give the methoxy-cations corresponding to (III) and (IV) upon irradiation in FSO_3H.

The high yield of monomeric products on irradiation of the hydroxytropylium cation is in marked contrast to the low yield of [6 + 6] dimer obtained by irradiation of tropone in 2N-H_2SO_4.[12] It would appear that in the latter reaction at least one of the tropone reactants must be unprotonated.

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‡ Alternatively (IV) could exist as a di-cation (ref. 11).

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