Carbonium-ion Photochemistry: the Benzenonium–Bicyclo[3,1,0]hexenyl Cation Photoisomerisation

By R. F. CHILDS* and B. PARRINGTON

(*Department of Chemistry, McMaster University, Hamilton, Ontario, Canada*)

Summary The photochemical conversion of protonated durene in fluorosulphuric acid into a bicyclo[3,1,0]-hexenyl cation has been shown to proceed by a symmetry-allowed disrotatory closure rather than by a $[\sigma 2a + \pi 2a]$-cycloaddition reaction.

IT has been previously reported[1] that certain methyl-substituted benzenonium cations could be induced to undergo a photochemical isomerisation upon irradiation in FSO_3H, and that provided the temperature at which the reaction was carried out was kept sufficiently low the product bicyclo[3,1,0]hexenyl cations could be observed and characterized by n.m.r.

Of the possible mechanisms for this reaction a symmetry-allowed photochemical disrotatory closure of the 4π pentadienyl cation was considered to be likely. However, a $[\sigma 2a + \pi 2a]$ cycloaddition reaction is an alternative process which cannot be ruled out on the basis of the known isomerisations. Distinction between these two alternatives is of interest in that such a cycloaddition, involving antarafacial addition at the double bond and inversion at the migrating saturated carbon, has been recently suggested to account for multitudinous photochemical rearrangements of the cyclohexadienones and cyclohexenones.[2]

Protonation of durene in fluorosulphuric acid[3] at −78° gave the tetramethylbenzenonium cation (1). Upon irradiation of the long-wavelength absorption[4] of (1) at −90°, using a Pyrex filter and the apparatus previously described,[5] a new cation was produced, which was stable at low temperatures. The structure of the photoproduct was established as (2) on the basis of its n.m.r. spectrum,† which shows a striking resemblance to that of the pentamethylbicyclo[3,1,0]hexenyl cation.[1]

Not only are the methyl and methylene proton resonances consistent with such an assignment but the position of the proton upon the cyclopentenyl ring (3·09) is typical for a similarly situated proton on a cyclopropyl conjugated allyl cation.[6]

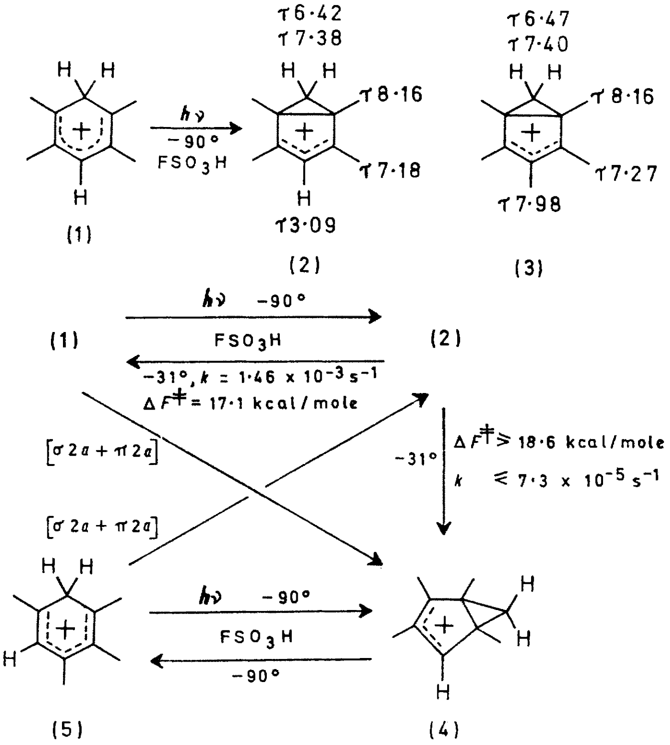
Upon increasing the length of the irradiation time, a photostationary state was reached between (1) and (2). The position of the photostationary state was dependant upon the type of lamp and filters used, consisting, for example, of (2) (60%) and (1) (40%) with a Pyrex filter and Phillips SP 500 w high-pressure mercury light source.

Heating‡ the fluorosulphuric acid solution of the photoproduct (2) to −31° caused it to undergo a clean isomerisation back to protonated durene (1), with a first-order rate constant of $1{\cdot}46 \times 10^{-3}\ \mathrm{s}^{-1}$ ($\Delta F^{\ddagger} = 17{\cdot}1$ kcal/mole). A thermal suprafacial sigmatropic 1,4-shift of the methylene group of (2) would give rise to the bicyclic cation (4) or its expected thermal progeny, protonated isodurene (5). As less than 5% of (5) and no (4) were detected as products of this thermal reaction the rate of the sigmatropic 1,4-shift must be less than $7{\cdot}3 \times 10^{-5}\ \mathrm{s}^{-1}$ ($\Delta F^{\ddagger} \gg 18{\cdot}6$ kcal/mole).

It is interesting that the rate of cyclopropyl migration around the cyclopentenyl ring is very dependent upon the state of substitution of C-6, implying that in the transition state C-6 bears considerable positive charge. Thus for 6,6-dimethyl substituted[1b] $\Delta F^{\ddagger} = 9{\cdot}0$ kcal/mole; 6-*exo*-monomethyl[1c,7] $\Delta F^{\ddagger} = 12{\cdot}0$ kcal/mole; 6-*endo*-monomethyl[7] $\Delta F^{\ddagger} \gg 15{\cdot}4$ kcal/mole, and in this work, 6-unsubstituted $\Delta F^{\ddagger} \gg 18{\cdot}6$ kcal/mole.

If the photoisomerisation of (1) had occurred by way of a $[\sigma 2a + \pi 2a]$ cycloaddition reaction, the bicyclic product formed would be (4). During the attainment of the photostationary state between (1) and (2), no peaks attributable to (4) could be detected. It is conceivable, particularly considering the methyl substitution pattern of (4), that (4) would be thermally labile under the reaction and observation conditions. As the thermal isomerisation of (2) → (1) is a symmetry-forbidden breaking of the C-1–C-5 bond, (4) would be expected to give (5) thermally,[8] especially in view of the high basicity of isodurene compared with durene.[4] Less than 5% of (5) could be detected in the photostationary state obtained by irradiating (1).

Irradiation of the long-wavelength band of protonated isodurene[4] in FSO_3H at −90° for comparable times to those used for (1) → (2) conversions gave no detectable product, which again points to the thermal instability of electrocyclic product (4) and lack of a $[\sigma 2a + \pi 2a]$ cycloaddition to give (2).



Although the results reported seem to indicate clearly that the preferred path of photoisomerisation of benzenonium cation to a bicyclohexenyl cation is by a disrotatory electrocyclic ring closure rather than $[\sigma 2a + \pi 2a]$ cycloaddition reaction, we have found that upon prolonged irradiation of an equilibrium mixture of (1) and (2), small quantities of protonated isodurene are formed. Similarly, extensive irradiation of (5) produces a small amount of the mixture of (1) and (2). It is conceivable that these could arise from an inefficient cycloaddition reaction; however, there are several alternative processes which must also be considered.

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† All chemical shifts are referred to internal tetramethylammonium chloride taken as τ 6·9.

‡ At higher temperatures, ring sulphonation of durene occurred in this medium.

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