Photolysis of Pentamethylcyclopentadiene in the Presence of Trifluoroacetic Acid: Generation and E.s.r. Spectrum of the Pentamethylcyclopentadiene Radical Cation

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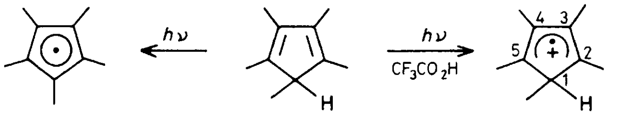
The e.s.r. spectrum of the pentamethylcyclopentadiene radical cation, $Me_5C_5H^{\cdot+}$, is observed when pentamethylcyclopentadiene is photolysed in trifluoroacetic acid.

Most types of organic radical cations (**2**) can be regarded as the conjugate acids of neutral radicals (**1**), which are usually more familiar. We report the exploitation of this principle for preparing a diene radical cation in fluid solution.

$$\underset{(1)}{R^{\cdot}} + H^{+} \leftrightharpoons \underset{(2)}{RH^{\cdot+}}$$

The penta-alkylcyclopentadienes, such as pentamethylcyclopentadiene (**3**) are remarkable among hydrocarbons in that, when they are irradiated with u.v. light, hydrogen is evolved and the e.s.r. spectrum of the corresponding penta-alkylcyclopentadienyl radical *e.g.* [(**4**); a(15H) 6.35 G, Q_{Me} 32.75 G†], can be observed.[1]

If pentamethylcyclopentadiene is irradiated with u.v. light (unfiltered, or filtered through Pyrex glass), using trifluoroacetic acid as solvent, the spectrum shown in Figure 1 is observed. This can be simulated using the hyperfine coupling constants a(6H) 15.0, a(6H) 4.0, a(1H) 1.6, a(3H) 0.8 G, and we assign it to the pentamethylcyclopentadiene radical cation (**5**) in which the cyclopentadienyl ring is η^1-bonded to the hydrogen atom, and the structure is non-fluxional on the e.s.r. time scale.



(**4**) (**3**) (**5**)

The SOMO (ψ_2) of the diene has the Hückel coefficients $|c|_{2,5}$ 0.602 and $|c|_{3,4}$ 0.372; if we use the Q_{Me} value taken from the radical (**4**), and ignore any 'excess charge effect,' the Heller–McConnell equation predicts the values $a(Me_{2,5})$ = 11.8 and $a(Me_{3,4})$ 4.5 G. The hydrogen atom on C-1 lies in the nodal plane of ψ_2 and should show hyperfine coupling only by the spin polarisation mechanism and not through hyperconjugation; the magnitude would be predicted to be about 1 G.

A similar analysis has been proposed for the e.s.r. spectrum of the cyclopentadiene radical cation [$a(H_{2,5})$ 11.6, $a(H_{3,4})$

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† 1 G = 10^{-4} T.

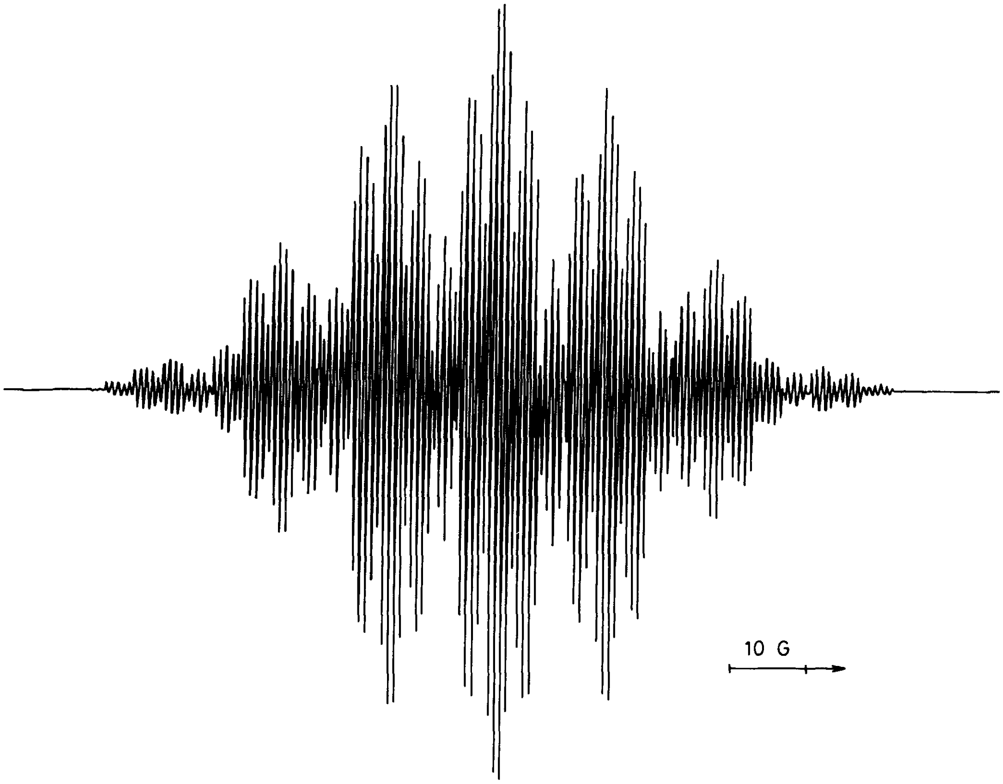

Figure 1. E.s.r. spectrum of the radical cation (**5**), obtained by photolysis of a solution of pentamethylcyclopentadiene (10 μl) in degassed trifluoroacetic acid (0.5 cm^3) at −10 °C.

3.5, a(2-H$_1$) < 2 G], which was observed from γ-radiolysis of cyclopentadiene in a matrix of Cl_3CF.[2] The only 1,3-diene radical cation which has been observed previously in fluid solution is the hexamethylbutadiene radical cation, which was prepared by treating hexamethylbutadiene or di-t-butylacetylene in dichloromethane with aluminium chloride.[3]‡

This general technique of inducing the homolysis of a substrate under acid conditions should provide a route to a variety of types of radical cation which have not hitherto been accessible.

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‡ We take this opportunity to correct an unfortunate expression in ref. 3, in which the rearrangement was referred to as being electrophilic. The aluminium chloride acts as an electrophile, but the rearrangement itself is nucleophilic.

References

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