The Electron Spin Resonance Spectrum of the Hexamethylbutadiene Radical Cation, and Evidence for a New Molecular Rearrangement of Acetylenes

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The e.s.r. spectrum of the hexamethylbutadiene radical cation, $Me_2C{=}CMeCMe{=}CMe_2^{\cdot +}$, is observed when either hexamethylbutadiene or di-t-butylacetylene is treated with aluminium chloride in dichloromethane; the latter reaction implies a novel molecular rearrangement.

The reaction which is recognised to occur between di-t-butylacetylene (**1**) and aluminium chloride in dichloromethane is the formation of a tetra-t-butylcyclobutadiene–aluminium chloride σ-complex, which, on photolysis, gives the tetra-t-butylcyclobutadiene radical cation, with the e.s.r. hyperfine coupling constant *a*(36 H) 0.27 G†.[1]

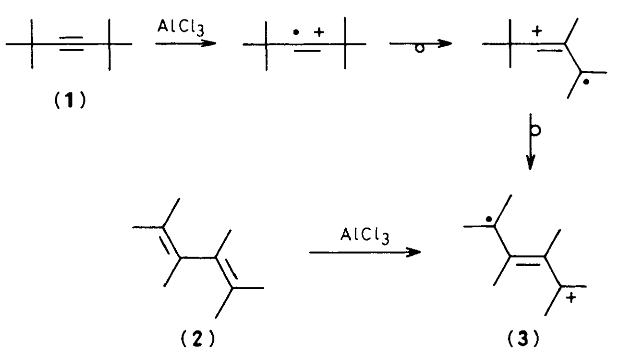
Before the mixture is photolysed, however, a spectrum can be observed, which can be simulated using the hyperfine coupling constants *a*(6H) 4.2 G, *a*(6H) 10.55 G, *a*(6H) 10.7 G; *g* 2.0028.

The same spectrum is observed when hexamethylbutadiene[2] (**2**) is treated under the same conditions. The reagents were mixed at −100 °C, and reacted at this temperature, or when they were allowed to warm briefly. With both the alkyne and the diene, an orange-brown colour developed as the e.s.r. spectrum became apparent, and if the solutions were kept below −20 °C, the spectra persisted for some hours.

We ascribe this spectrum to the hexamethylbutadiene radical cation (**3**). The hyperfine coupling constants which are predicted for (**3**) on the basis of the Hückel–McConnell model (taking a *Q* value, from the $CH_3CH_2^{\cdot}$ radical, of 54 G), are *a*(6H) 3.7 G, and *a*(12H) 9.8 G.

No spectra of 1,3-diene radical cations have previously been observed in fluid solution, but the radical cation of buta-1,3-diene itself has been recorded on γ-radiolysis of the diene adsorbed on silica gel,[3] or in a solid fluorocarbon matrix.[4] Hexa-alkylation of the diene may be assumed to lower its ionization potential, and to increase the persistence of the radical cation.

We were unable to detect the presence of any hexamethylbutadiene in the di-t-butylacetylene, which was prepared by two different routes[5,6] and purified by g.l.c. We conclude that, apart from the dimerization reaction, aluminium chloride induces an electrophilic rearrangement of the acetylene to give the diene. One possible mechanism is illustrated in Scheme 1. No such rearrangement appears to be reported in the literature.



Scheme 1

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† 1 G = 10^{-4} T

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