## The Generation of Azulene Radical Cations from Arylalkynes

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Arylalkynes  $ArC \equiv CR$  (R = alkyl or aryl) undergo one-electron oxidation with dimerization and rearrangement to show the e.s.r. spectra of the corresponding azulene radical cations.

Two types of radical cation have hitherto been identified from the one-electron oxidation of alkynes in solution. First, many primary, secondary, and tertiary dialkylalkynes have been shown to react with aluminium chloride under irradiation with u.v. light<sup>1</sup> (or in a few cases under other conditions)<sup>2</sup> with dimerization to yield the corresponding tetra-alkylcyclobutadiene radical cations (equation 1).

Secondly, a few di-t-alkylalkynes have been shown to react with aluminium chloride, or with mercury( $\Pi$ ) trifluoroacetate in trifluoroacetic acid, with rearrangement, to give hexaalkylbutadiene radical cations (equation 2).<sup>3,4</sup> We now report a third type of behaviour, involving both dimerization and rearrangement, which can be observed with arylalkynes.

Our attempts to oxidise diphenylethyne by u.v. irradiation in the presence of aluminium chloride gave only a weak



**Figure 1.** E.s.r. spectrum of the 1,2,3-triphenylazulene radical cation in dichloromethane at 208 K.

spectrum which could not be analysed; with aluminium bromide under similar conditions, Broxterman and Hogeveen obtained a radical which was presumed to be the tetraphenylcyclobutadiene radical cation.<sup>5</sup>

However, if diphenylethyne in trifluoroacetic acid containing mercury(II) trifluoroacetate is irradiated with Pyrexfiltered u.v. light, the new complicated e.s.r. spectrum shown in Figure 1 is obtained. ENDOR and TRIPLE e.s.r. spectroscopy yielded the hyperfine coupling constants given below.

Quenching the solution with water gave bright blue 1,2,3-triphenylazulene in 38% yield, and treatment of this with  $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{++}$  SbCl<sub>6</sub><sup>-</sup>, or photolysis of a solution in trifluoroacetic acid, regenerated the original spectrum.

We therefore assign this spectrum to the triphenylazulene radical cation (1) (equation 3).

The SOMO has a node passing through C-2 and C-6,<sup>6</sup> and comparison of the hyperfine coupling constants with the spin densities obtained from M.O. calculations<sup>7</sup> suggests the following assignment of the observed coupling constants: a(2H) + 0.67 (4-,8-H), a(2H) - 4.13 (5-,7-H), a(1H) + 0.07 (6-H), a(4H) - 1.16 (2'-,6'-,2"-,6"-H), a(4H) + 0.59 (3'-,5',-3"-,5"-H), and a(2H) - 1.24 G (4-,4'-H).†

Under similar conditions, bis(4-t-butylphenyl)ethyne gives the radical cation (2), and 1-phenylpropyne gives the unsymmetrically substituted radical cation (3), and from both of these, the parent azulenes have again been isolated.

Reaction (3) involves both the dimerization which characterises reaction (1) and the 1,2-rearrangement of the  $\sigma$ -bonding electron pair which occurs in reaction (2).



 $\dagger 1G = 10^{-4} T.$ 



This remarkable expansion of the benzene ring to give a seven-membered ring when diphenylethyne is treated with a Lewis acid is a known reaction,<sup>8</sup> and various reasonable mechanisms have been put forward which involve either a monomeric or dimeric form of the alkyne.

(4)

Our results raise the further possibility that the reaction might proceed through a radical cation rather than a simple cation,‡ and a reasonable mechanism which emphasises the

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analogy with the mechanism which was illustrated for reaction (2) (cf. ref. 3) is shown in equation (4).§

We acknowledge the support of the S.E.R.C.

Received, 16th December 1985; Com. 1771

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