Generation of Azulene Radical Cations from Arylalkynes

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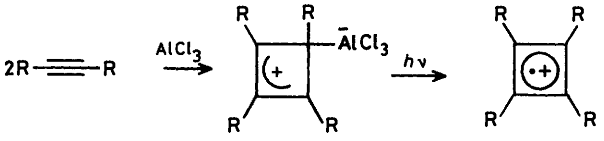
If a diarylalkyne 4-$XC_6H_4C{\equiv}CR$ (R = Ph, 4-MeC_6H_4, or 4-$Bu^tC_6H_4$) or 1-phenylpropyne in trifluoroacetic acid containing mercury(II) trifluoroacetate is irradiated with u.v. light filtered through Pyrex glass, the e.s.r. spectrum of the corresponding azulene can be observed. The azulenes have been isolated and converted back into their radical cations by irradiation in trifluoroacetic acid, or in dichloromethane containing $(4\text{-}BrC_6H_4)_3N^{+\bullet}$ or $(2,4\text{-}Br_2C_6H_3)_3N^{+\bullet}$. Possible mechanisms by which the azulenes are formed from the alkynes are discussed.

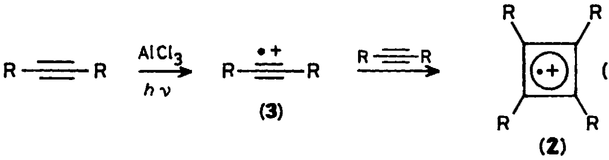
Two types of radical cation have been reported to be formed when dialkylalkynes are subjected to one-electron oxidation.

First, if a mixture of a dialkylalkyne and aluminium chloride in dichloromethane is irradiated at low temperature with u.v. light, the e.s.r. spectrum of the corresponding tetra-alkylcyclobutadiene radical cation (**2**) can be observed, and some 40 examples of this behaviour have been reported.[1] Two alternative mechanisms have been considered for the reaction, and each can probably operate under the appropriate conditions. In one mechanism, the alkyne may react with the aluminium chloride to form a zwitterionic complex (**1**) between the tetra-alkylbutadiene and aluminium chloride. Irradiation of this then induces homolysis of the carbon–metal bond, with the formation of the radical cation [equation (1)].[2] In the other, the alkyne may undergo initial one-electron oxidation to give the alkyne radical cation (**3**), which then gives a cycloaddition reaction with a second alkyne molecule to generate the cyclobutadiene radical cation (**2**) [equation (2)].[3] A few alkynes carrying tertiary alkyl groups have also been converted into the corresponding cyclobutadiene radical cations by irradiation in trifluoroacetic acid solution.[4]



(1)

(**1**) (**2**)

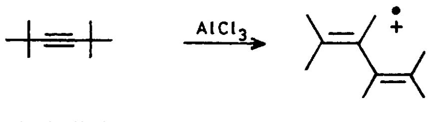


(**3**)

(2)

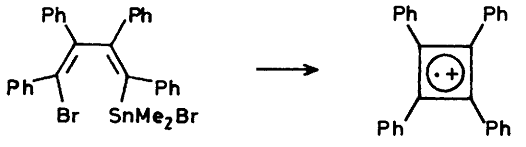
(**2**)

Secondly, if di-t-butylacetylene is treated with aluminium chloride in dichloromethane, an oxidative rearrangement may occur prior to photolysis to generate the radical cation of hexamethylbutadiene [equation (3)].[5]



(3)

Relatively little work has been carried out on the generation of radical cations from arylalkynes. Sandel and Freedman[6] studied the e.s.r. spectra of products obtained from the pyrolysis of the tetraphenylbutadienyltin compound (**4**), and obtained an intermediate with a spectrum which could be interpreted in terms of four equivalent phenyl groups, and which might be the tetraphenylcyclobutadiene radical cation [equation (4)].



(**4**)

(4)

In exploratory experiments, Broxterman obtained a spectrum from the low-temperature irradiation of diphenylacetylene and aluminium chloride in dichloromethane.[7] This spectrum was presumed to relate to the tetraphenylcyclobutadiene radical cation, but attempts to extend this work to t-butyl-(3,5-di-t-butylphenyl)acetylene were unsuccessful.

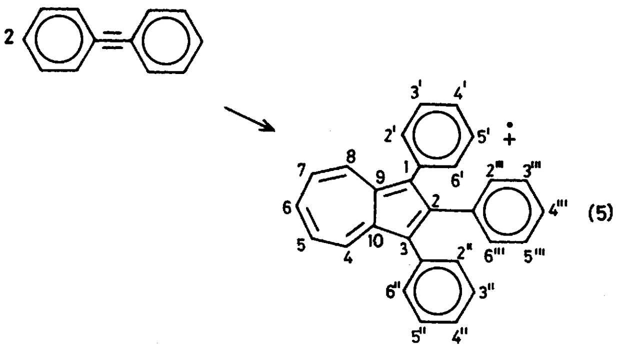
Results

A solution of diphenylacetylene (*ca.* 0.05 g) in trifluoroacetic acid (*ca.* 1 cm^3) containing mercury(II) trifluoroacetate (*ca.* 0.1 g) was irradiated in an e.s.r. cavity with light from a high-pressure mercury arc filtered through Pyrex glass. The solution developed a strong yellow colour, and the spectrum shown in Figure 1(a) was observed. The same spectrum, but weaker, was obtained when the sample was merely exposed to the light of the laboratory, but it was destroyed when the sample was irradiated with unfiltered u.v. light.

The spectrum could not be analysed in terms of any compound which might be formed by either of the two reactions [equations (1) and (3)] which are recognised to occur when dialkylalkynes are oxidised. The reaction was therefore carried out on a preparative scale without irradiation and quenched with water, and the product was isolated by chromatography on alumina. A deep blue crystalline solid was isolated in 38% yield, and was identified as the known 1,2,3-triphenylazulene.[8]

When this azulene was treated with the one-electron oxidant $(4\text{-}BrC_6H_4)_3N^{+\bullet}$ $SbCl_6^-$ or $(2,4\text{-}Br_2C_6H_3)_3N^{+\bullet}$ $SbCl_6^-$ in dichloromethane or was irradiated in trifluoroacetic acid with u.v. light filtered through Pyrex glass, the same spectrum as in Figure 1(a) was generated. We therefore assign this spectrum to the 1,2,3-triphenylazulene radical cation (**5**), as shown in equation (5).

Analysis of the spectrum by ENDOR (see Figure 2) and TRIPLE spectroscopy yielded the following hyperfine coupling constants, the assignment of which is discussed later: *a*(H-4,8) +0.67 G, *a*(H-5,7) −4.13 G, *a*(H-6) +0.07 G, *a*(H-2′,6′,2″,6″)

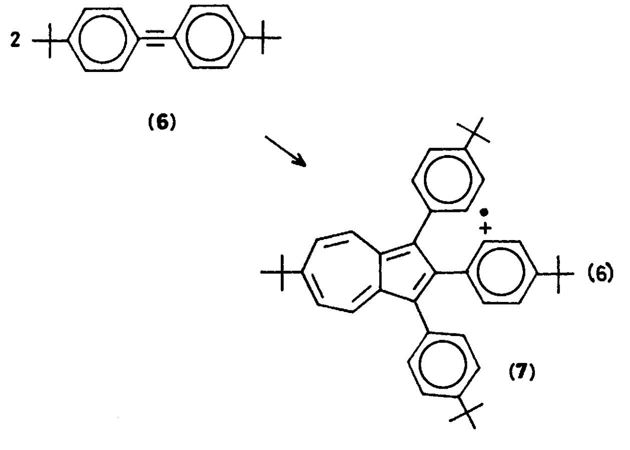


(5)

−1.16 G, a(H-3′,5′,3″,5″) +0.59 G, a(H-4′,4″) −1.24 G, g 2.0027. By using these coupling constants, the simulation in Figure 1(b) was obtained.

The triphenylazulene in tetrahydrofuran was also reduced over a potassium mirror to give the e.s.r. spectrum of the radical anion shown in Figure 3, which yields the hyperfine coupling constants a(H-4,8) 6.25 G, a(H-5,7) 0.72 G, a(H-6) 8.77 G, a(H-2‴, 4‴, 6‴) 1.43 G, g 2.0028.

With similar photolysis, bis-(4-t-butylphenyl)acetylene (**6**) in CF_3CO_2H–$Hg(OCOCF_3)_2$ gave the simpler spectrum [Figure 4(a) and (b)] of the radical cation of 6-t-butyl-1,2,3-tris-(4-t-butylphenyl)azulene (**7**), with the hyperfine coupling constants a(H-4,8) 0.67 G, a(H-5,7) 3.80 G, a(H-2′,6′,2″,6″) 1.20 G, a(H-3′,5′,3″,5″) 0.59 G, g 2.0030. The azulene was isolated and characterised, and converted back into the radical cation by irradiation in trifluoroacetic acid, or in dichloromethane containing $(2,4\text{-}Br_2C_6H_3)_3N^{+\bullet}$ $SbCl_6^-$, with u.v. light filtered through Pyrex glass.



(6)

(7)

In the same way, bis-(4-methylphenyl)acetylene (**8**) gave the spectrum of the azulene radical cation (**9**) as shown in Figure 5(a), which was analysed with the help of ENDOR spectroscopy. The simulation shown in Figure 5(b) was obtained using the hyperfine couplings constants 3.87 G (2 H), 1.69 G (6 H), 1.19 G (2 H), 1.04 G (2 H), 0.715 G (2 H), 0.56 G (2 H), and 0.975 G (2 H), but we do not believe that this necessarily implies that there is restricted rotation about the bonds to the phenyl groups. The ENDOR signals relating to the coupling constants 1.04 and 1.19 G, and 0.56 and 0.75 G appear as a pair of broad doublets, and though we have not been able to find it, a simulation which assumes equivalence of the *ortho*-positions and of the *meta*-positions may be possible.

The azulene was isolated, and from it the radical cation was regenerated as before.

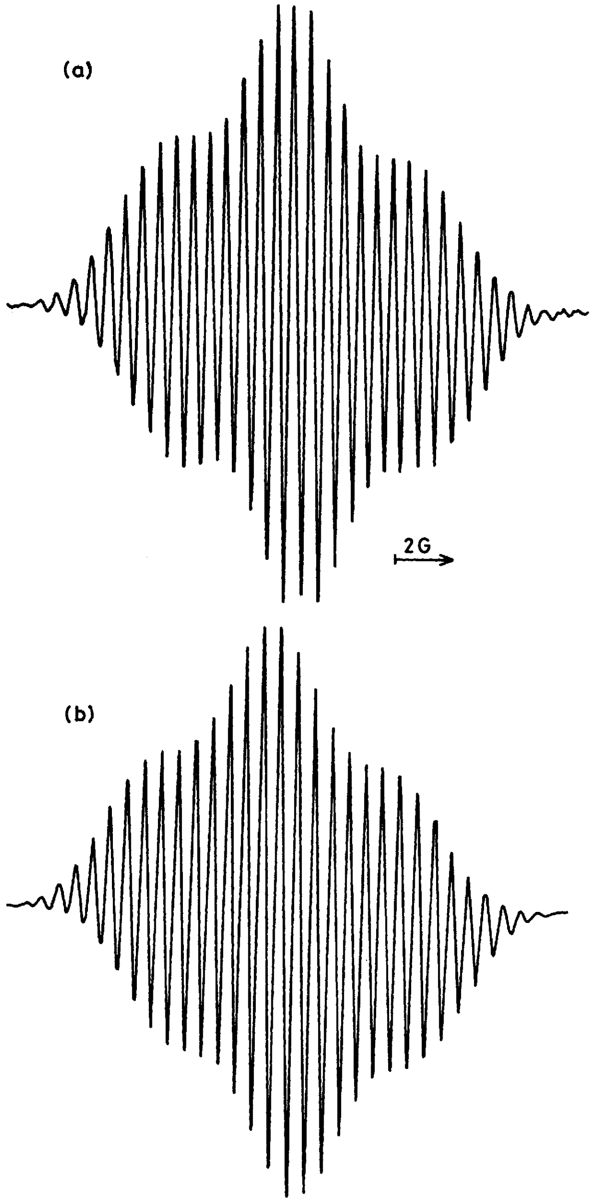
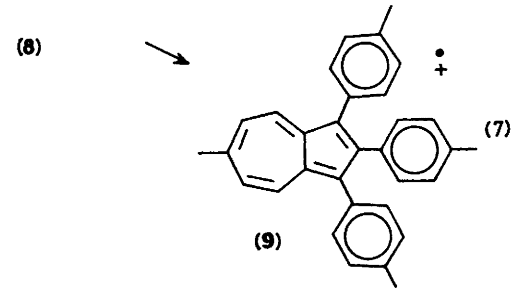


Figure 1. (a) Observed e.s.r. spectrum of the triphenylazulene radical cation (**5**) in CF_3CO_2H at 265 K; (b) simulation, ΔH_{pp} 0.17 G



(8)

(9)

1-Phenylpropyne (**10**) was treated similarly. The spectrum can be analysed in terms of hyperfine coupling by only one methyl group (see Discussion section) and we ascribe it to the radical cation of 1,2-dimethyl-3-phenylazulene (**11**), with $a(CH_3\text{-}1)$ 10.60, a(H-4,8) 0.65, a(H-5,7) 5.00, a(H-2′,6′,2″,6″) 1.30, a(H-4′,4″) 1.30 G, g 2.0028.

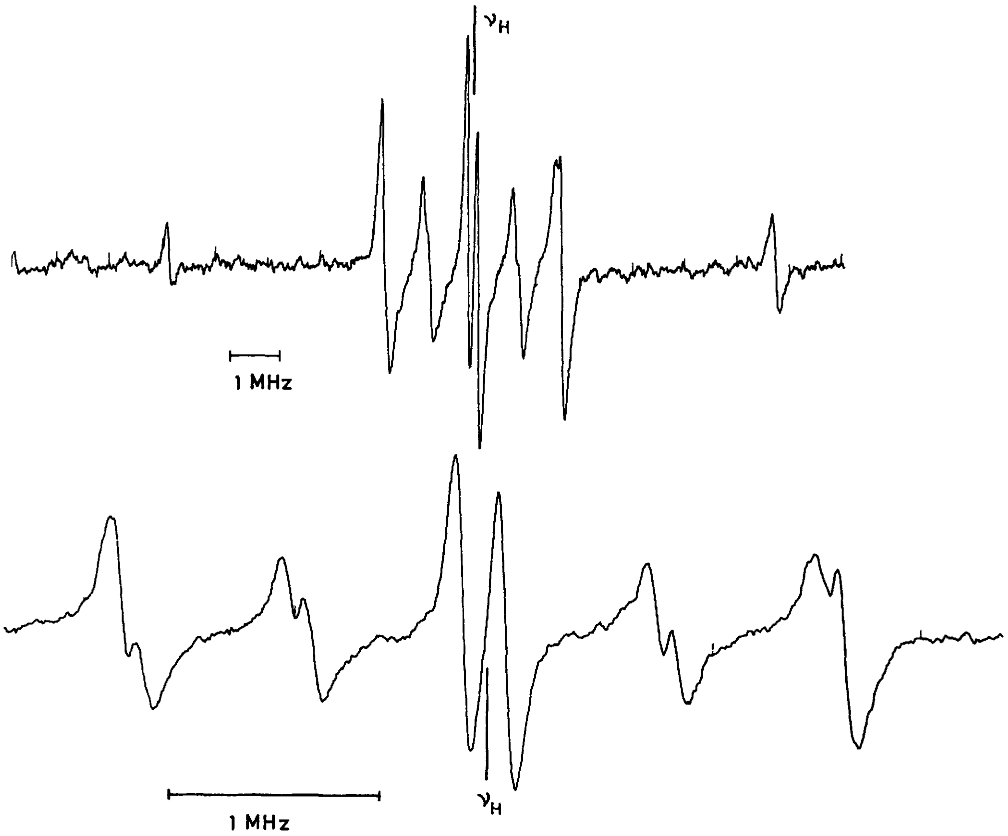


Figure 2. ENDOR spectrum of the triphenylazulene radical cation in CF_3CO_2H at 268 K; the lower spectrum shows an expansion of the central region of the upper one

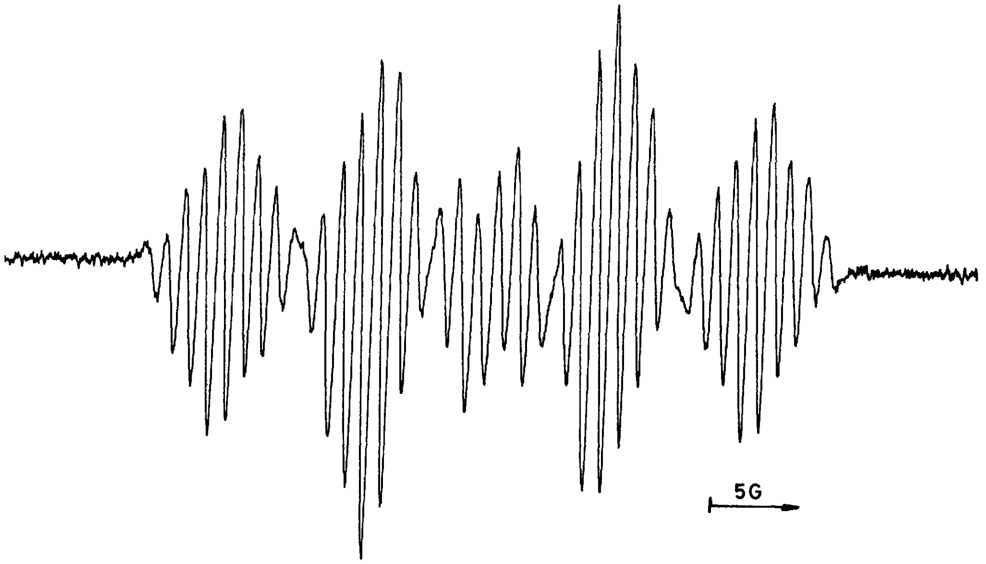
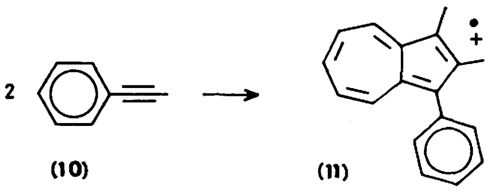


Figure 3. E.s.r. spectrum of the triphenylazulene radical anion in tetrahydrofuran at 173 K

The known azulene[9] was isolated, and the radical cation was regenerated as before (Figure 6).

Bis-(2,4,6-trimethylphenyl)acetylene behaved differently. When it was irradiated in the presence of mercury trifluoroacetate in trifluoroacetic acid, a simple strong spectrum with broad lines was generated. Most of the lines can be accommodated in terms of a doublet of quartets, a(H) 3.5 G, a (3 H)



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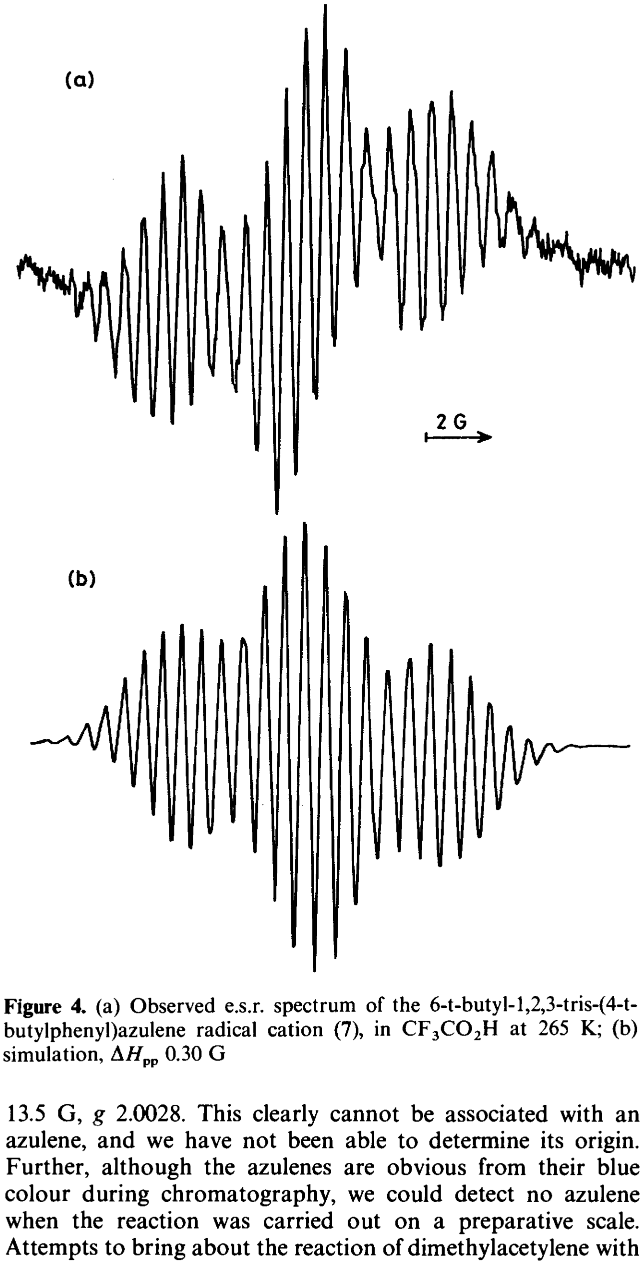


Figure 4. (a) Observed e.s.r. spectrum of the 6-t-butyl-1,2,3-tris-(4-t-butylphenyl)azulene radical cation (7), in CF_3CO_2H at 265 K; (b) simulation, ΔH_{pp} 0.30 G

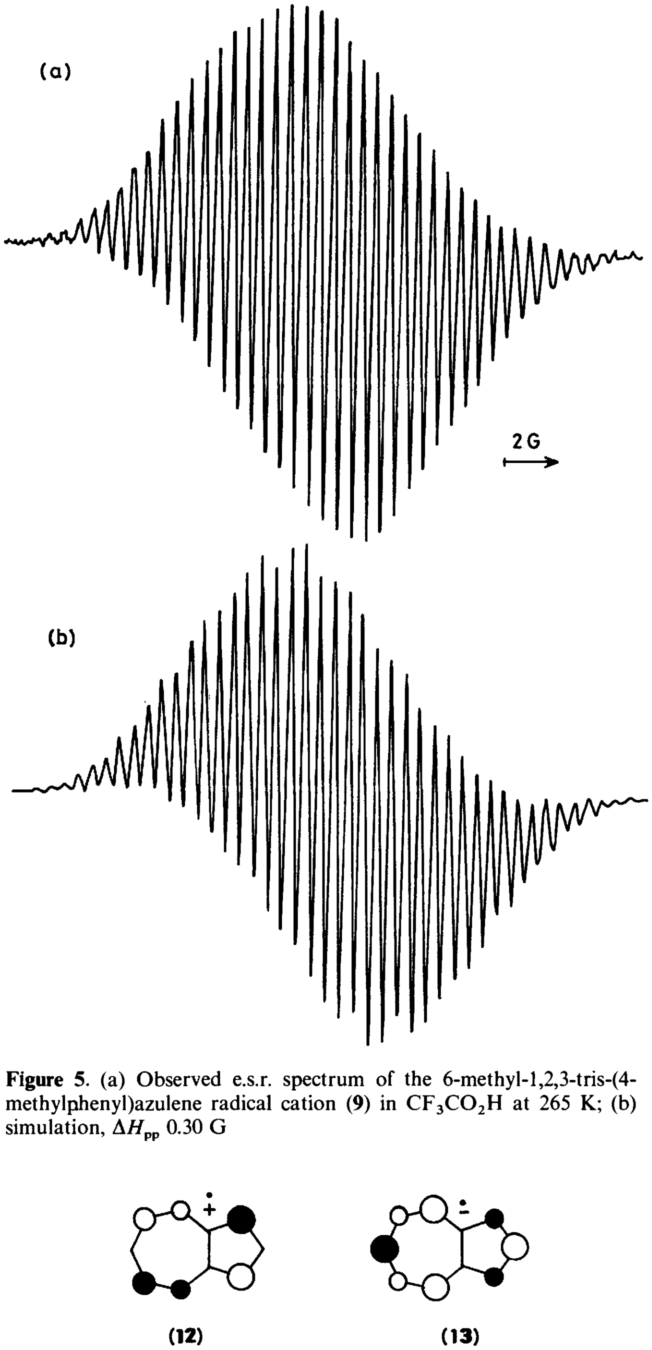
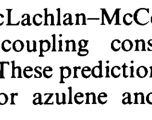


Figure 5. (a) Observed e.s.r. spectrum of the 6-methyl-1,2,3-tris-(4-methylphenyl)azulene radical cation (9) in CF_3CO_2H at 265 K; (b) simulation, ΔH_{pp} 0.30 G



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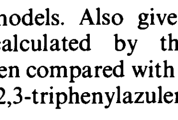


(13)

13.5 G, *g* 2.0028. This clearly cannot be associated with an azulene, and we have not been able to determine its origin. Further, although the azulenes are obvious from their blue colour during chromatography, we could detect no azulene when the reaction was carried out on a preparative scale. Attempts to bring about the reaction of dimethylacetylene with diphenylacetylene gave only material with the spectrum of the triphenylazulene radical cation (**5**); neither the tetramethylcyclobutadiene radical cation (**2**; R = Me) nor the dimethylphenylazulene radical cation (**11**) was detected.

Efforts to generate a radical cation from phenylacetylene were similarly unsuccessful. When the reagents were mixed an exothermic reaction occurred and the solution turned black. On irradiation, an e.s.r. spectrum was observed, but it was too weak and complex to permit interpretation.

Discussion

E.s.r. Spectra.—The e.s.r. spectra of the radical anion of azulene[10] and of four substituted azulenes[11] have been reported, but the only radical cations that have been detected are those of azulene itself and 2,4,8-trimethylazulene, which were generated by Dessau and Shih[12] by oxidising the azulenes with cobalt(III) acetate in trifluoroacetic acid in a flow system.

The form of the SOMO of the azulene radical cation (ψ_5) is illustrated in (**12**), and that of the radical anion in (**13**). For the radical cation, the Table lists the values of the Hückel coefficients (*c*) and the derived electron densities (c^2) and McLachlan spin densities (ρ), followed by the hyperfine coupling constants calculated on the Hückel–McConnell and Hückel–McLachlan–McConnell models. Also given are the hyperfine coupling constants calculated by the INDO method.[12] These predictions are then compared with the values observed for azulene and for 1,2,3-triphenylazulene radical cations.

It will be seen that there is a reasonable correspondence between the observed spectrum and that calculated, particularly by the McLachlan and the INDO methods. Dougherty, Lewis, Naumann, and McGlynn have shown by photoelectron spectroscopy that methylation or phenylation has little effect on the π-electron distribution,[13] and our assignment of the hyperfine coupling constants in the substituted azulene radical cations is

Table. Predicted and observed hyperfine coupling constants (G) in azulene radical cation

	Position							
	1	2	3	4	5	6	7	8
c	0.543	0	−0.543	0.160	0.335	0	−0.335	−0.160
c^2	0.295	0	0.295	0.026	0.112	0	0.112	0.026
ρ	0.403	−0.097	0.403	0.006	0.125	−0.042	0.125	0.006
$a_{calc.}(H)^a$	−7.85	0	−7.85	−0.69	−2.97	0	−2.97	−0.69
$a_{calc.}(McL)^b$	−10.72	+2.58	−10.72	−0.15	−3.33	+1.12	−3.33	−0.15
$a_{calc.}(INDO)^c$	−9.98	2.91	−9.98	−0.60	−3.90	1.99	−3.90	−0.60
$a_{obs.}(azulene^{+\cdot})^d$	10.65	1.52	10.65	0.38	4.15	1.12	4.15	0.38
$a_{obs.}$(**5**)				+0.67	−4.13	+0.07	−4.13	+0.67

[a] H = Hückel; Q taken to be −26.6 G from $C_6H_6^{+\cdot}$. [b] McL = McLachlan; $\lambda = 1.1$, $Q = -26.6$ G. [c] Ref. 12, using the geometry derived from *X*-ray diffraction. [d] Ref. 12.

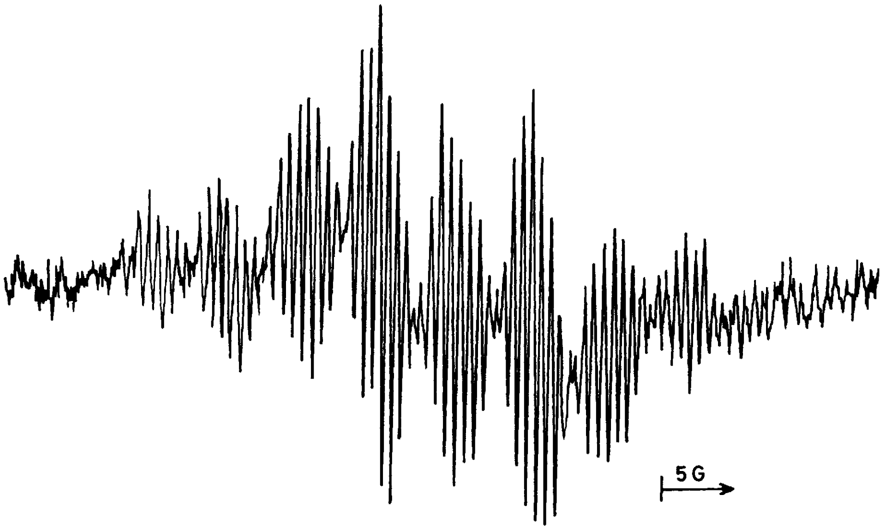


Figure 6. Observed e.s.r. spectrum of the 1,2-dimethyl-3-phenylazulene radical cation (**11**) in CH_2Cl_2 at 253 K

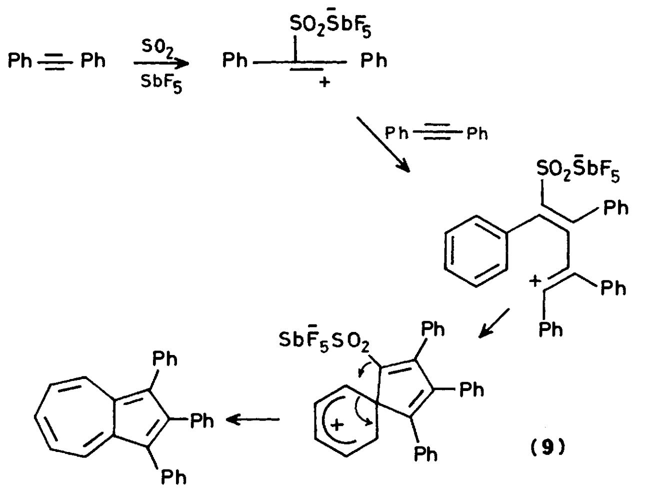
based on the correspondence of their spectra with that of azulene radical cation itself, as illustrated in the Table for 1,2,3-triphenylazulene.

The most prominent feature of the SOMO of the azulene radical cation (**12**) is that a node passes through positions 2 and 6, and that the largest coefficients are at positions 1 and 3. This is reflected in the spectrum of the radical cation of 1,2-dimethyl-3-phenylazulene (**11**), where the methyl substituent at position 1 shows a coupling of 10.60 G, whereas the coupling for the methyl group at position 2 is undetectable.

Our assignment of the hyperfine coupling constants in the 1,2,3-triphenylazulene radical anion is based on a similar comparison with the calculated and observed spectra of the azulene radical anion.

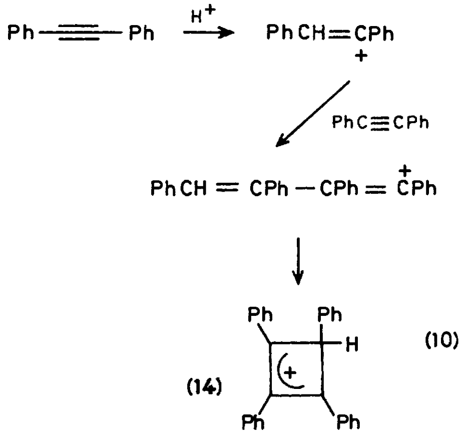
Mechanism of Azulene Formation.—The remarkable ring expansion involved in the conversion of diphenylacetylene into 1,2,3-triphenylazulene is well documented, though it apparently has not been observed before with other arylacetylenes, nor has the presence of the azulene radical cations been noted. The reaction occurs in the presence of 2,4-dinitrobenzenesulphenyl chloride and aluminium chloride,[8] or of triethylaluminium and aluminium chloride,[14] or of antimony pentafluoride in sulphur dioxide,[15] or on irradiation,[16] but not in the presence of the sulphenyl chloride alone, or of aluminium bromide, or of zinc chloride.[8] Breslow and Battiste[17] obtained the same product when diphenyl-(2,3-diphenylcycloprop-2-enyl)methanol was treated with acetic anhydride and sodium acetate, or with phenyl isocyanate.

The suggested mechanism of Fan, Dickstein, and Miller for the reaction induced by SbF_5 in SO_2 is illustrated in equation (9).[15]



(9)

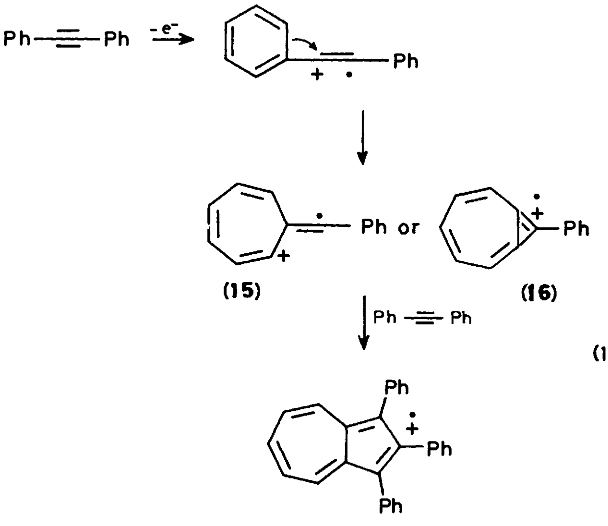
In contrast the ring expansion does not appear to occur in the presence of a protic acid. In fluorosulphonic acid (without irradiation), simple protonation and cyclodimerization occur to give the tetraphenylcyclobutenyl cation (**14**) as shown in equation (10). Trifluoroacetic acid apparently will not induce this reaction with diphenylacetylene, though it will with some other diarylacetylenes.[18]



(10)

Our observation of the formation of radical cations requires that, further to the steps involving addition, cyclisation, and rearrangement, a fourth step needs to be considered, which involves one-electron oxidation. It is possible that this occurs last and is irrelevant to the formation of the azulene, but it is interesting that the foregoing conditions which lead to the formation of triphenylazulene are indeed those which are most conducive to the formation of radical cations.

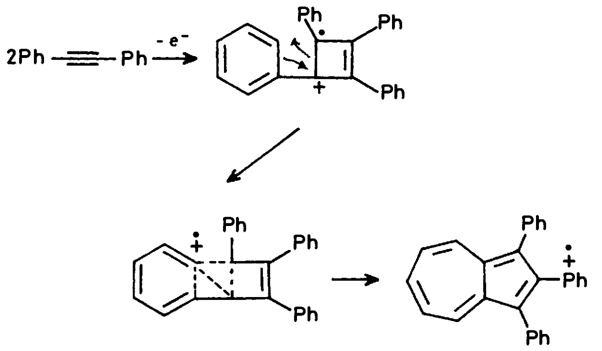
We therefore represent in equation (11) a further mechanism by which the azulenes might be formed, where the ring expansion occurs in a radical cation. The rearranged radical cation (**15**) might alternatively be represented as the bicyclooctatetraene radical cation (**16**), as MNDO calculations suggest that this structure may be relatively stable.[19]



(11)

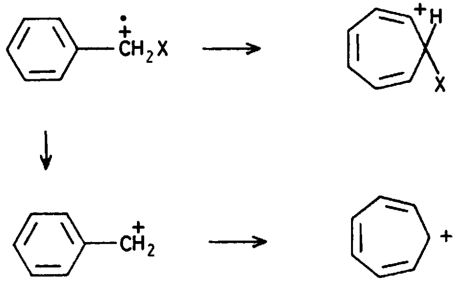
If this were the mechanism, the substitution pattern in the dimethylphenylazulene (**11**) would be determined in the final step of the reaction. We have calculated by the MNDO method the energies of the optimised structures for 1,2-dimethyl-3-phenylazulene (80.51 kcal mol^{-1}) * and its radical cation (250.54 kcal mol^{-1}), and for 1,3-dimethyl-2-phenylazulene (80.74 kcal mol^{-1}) and its radical cation (248.93 kcal mol^{-1}): the differences between the isomeric pairs are too small for any inference regarding the mechanism to be drawn.

A sequence of steps in which the addition and cyclisation precede the rearrangement, and the ring expansion occurs on the tetraphenylcyclobutadiene radical cation [equation (12)], would be equally acceptable. By this route, the substitution pattern in the dimethylphenylazulene (**11**) would be determined in the initial step, and would require the intermediacy of the *cis*-isomer of $Me_2Ph_2C_4^{+\cdot}$. Mixed dialkylacetylenes, $RC\equiv CR'$, usually generate the *cis*- and *trans*-isomers of $R_2R'_2C_4^{+\cdot}$ in approximately equal amounts,[1] but we do not know what the regioselectivity of the dimerisation of methylphenylacetylene would be.



(12)

The expansion of the benzene ring which occurs in the reactions discussed here has an interesting analogy in mass spectrometry where benzyl cations or the radical cations of benzyl compounds give rise to the corresponding derivatives of cycloheptatriene [equation (13)].[20] The tetraphenylcyclobutadiene and diphenylacetylene radical cations have recently been detected by mass spectrometry [reaction (14)],[21] but there appears to be no evidence regarding their possible rearrangement.



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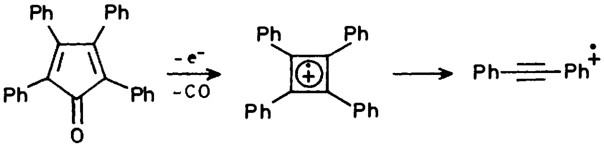

(14)

An interesting comparison can be drawn between the rearrangements discussed here, and that of the tetramethylcyclobutadiene radical cation [reaction (9)] reported by Broxterman and Hogeveen.[7] The former reaction can be represented [equation (12)] as a six-membered ring bonded to a four-membered ring rearranging to a seven-membered ring fused to a five-membered ring. In a similar way, reaction (9) can be represented as the rearrangement of a four-membered ring bonded to a four-membered ring, to give two five-membered rings [equation (15)].

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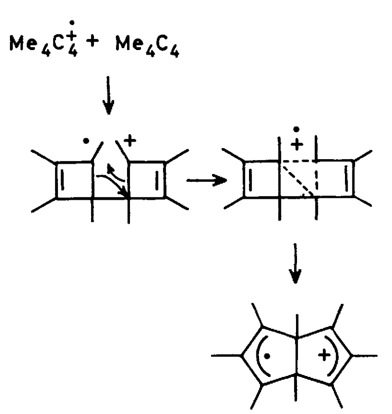
* 1 cal = 4.184 J.



(15)

Experimental

Diphenylacetylene, bis-(4-methylphenyl)acetylene, and methylphenylacetylene were commercial products (Aldrich).

Bis-(4-*t-butylphenyl*)*acetylene* (**6**).—1-Methyl-4-t-butylbenzene was irradiated in the presence of bromine to give 1-dibromomethyl-4-t-butylbenzene, which was treated with copper in toluene to give 1,2-dibromo-1,2-bis-(4-t-butylphenyl)-ethane. This was heated under reflux with potassium hydroxide in dioxane yielding bis-(4-t-butylphenyl)acetylene (**6**), m.p. 176—177 °C (lit.,[22] 177—178 °C); δ(^{1}H) ($CDCl_3$) 1.30 (s 18 H, Bu^t) and 7.43 (s 8 H, ArH); *m*/*z* 290 (*M*, 60%), 275 (*M* − Me, 100), 260 (*M* − 2 Me, 1.5), and 245 (*M* − 3 Me, 4.4).

Bis-(2,4,6-*trimethylphenyl*)*acetylene*.—The Friedel–Crafts reaction between mesitylene and tetrachlorocyclopropene gave dimesitylcyclopropenone, which was decarbonylated over alumina yielding the alkyne, m.p. 128 °C (lit.,[23] 130 °C); δ(^{1}H) ($CDCl_3$) 2.30 (s, 6 H, *p*-Me), 2.50 (s, 12 H, *o*-Me), and 6.93 (s, 4 H, ArH).

E.s.r. Spectroscopy.—E.s.r. spectra were recorded using a Varian E4 or E109 instrument, fitted with a 500 W high-pressure mercury arc focused on the cavity. ENDOR spectra were obtained using a Bruker accessory interfaced to an E109 spectrometer.

Preparation of Azulenes.—(*a*) A solution of diphenylacetylene (1.78 g, 0.01 mol) in trifluoroacetic acid (20 cm^3) containing mercury(II) trifluoroacetate (4.26 g, 0.01 mol) was stirred under argon for 1 h at room temperature under ambient illumination. The mixture was poured into water (100 cm^3), and the organic product extracted into dichloromethane, and isolated by chromatography on basic alumina (eluant 3:1 pentane–dichloromethane). Recrystallisation from pentane gave 1,2,3-triphenylazulene as deep blue crystals (0.68 g, 38%), m.p. 208 °C (lit.,[15] 209—210 °C; lit.,[16] 216—217 °C) (Found: C, 93.9; H, 5.75. Calc. for $C_{28}H_{20}$: C, 94.3; H, 5.65%).

Initial identification was made by ^{1}H and ^{13}C n.m.r. with the INEPT and DANTE pulse sequences, and with the addition of chromium acetylacetonate (*ca.* 0.04M) as a relaxant. Peaks were assigned using the data in ref. 24: δ(^{1}H) (C_6D_6) (i) 6.74 (t, *J* 9.93 Hz), (ii) 6.9 (2 H, d, with further coupling), (iii) 7.18 (11 H, m, but includes C_6D_5H), (iv) 7.33 (2 H, dd), (v) 7.36 (4 H, dd, *J* 1.8 and 8.2 Hz), (vi) 8.35 (2 H, d, *J* 9.21 Hz) [homonuclear correlated 2D n.m.r. established the couplings (ii)—(iv), (iii)—(v), and (iii)—(i)—(vi)]; δ(^{13}C) ($CDCl_3$) 123.8 (C-5,7), 126.3 (C-4′,4″), 126.6 (C-4‴), 127.6 (C-3″,5″), 128.1 (C-3′,5′,3‴,5‴), 129.0 (unprotonated C), 131.4 (C-2″,6″), 131.6 (C-2′,6′,2‴,6‴), 135.9 (C-4,8′), 136.3 (unprotonated C), 136.4 (unprotonated C), 137.4 (unprotonated C), and 138.1 (C-6).

(*b*) In a similar reaction bis-(4-t-butylphenyl)acetylene (**6**) gave 6-t-butyl-1,2,3-tris-(4-t-butylphenyl)azulene (43%) as a blue solid which decomposed on melting; δ(^{1}H) ($CDCl_3$) 1.30 (s, 18 H, 1,3-Bu$^t_2$), 1.34 (s, 9 H, Bu^t), 1.50 (br s, 9 H, Bu^t), and 7.2 (m, 16 H, ArH); *m*/*z* 581 (*M* + 1, 25%), 580 (*M*, 54), 161 (100), and 57 (Bu^t, 63).

(*c*) Similarly bis-(4-methylphenyl)acetylene (**8**) gave the blue 6-methyl-1,2,3-tris-(4-methylphenyl)azulene (46%), m.p. 163—164 °C; δ(^{1}H) ($CDCl_3$) 2.35 (m, 12 H, 4 Me), 7.0 (m, 14 H), and 8.15 (m, 2 H).

(*d*) Similarly 1-phenylpropyne (**10**) gave the blue 1,2-dimethyl-3-phenylazulene, m.p. 79—80 °C (lit.,[9] 80—81 °C) (Found: C, 92.9; H, 7.1. Calc. for $C_{18}H_{16}$: C, 93.1; H, 6.9%); δ(^{1}H) ($CDCl_3$) 2.47 (s, 3 H, Me), 2.56 (s, 3 H, Me), 6.88 (m, 2 H), 7.33 (m, 6 H), 7.88 (d, 1 H), and 8.05 (d, 1 H).

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