The Formation of Cyclobutadiene Radical Cations by the Cycloaddition of an Alkyne and Alkyne Radical Cation

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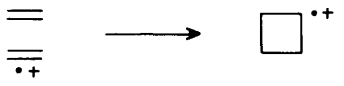
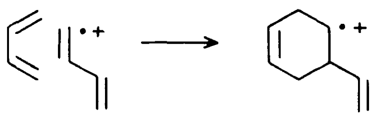
The formation of cyclobutadiene radical cations by the cycloaddition reaction between an alkyne and an alkyne radical cation has been established by solid state e.s.r. spectroscopy.

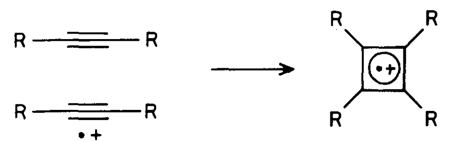
Ledwith[1] and Bauld[2,3] have established reactions in which an alkene or a diene reacts with the corresponding alkene or diene radical cation, to give a cyclobutane, equation (1), or a cyclohexene, equation (2), respectively. We now report e.s.r. studies which establish that a similar cycloaddition will occur between an alkyne and an alkyne radical cation to give a cyclobutadiene radical cation (**1**).

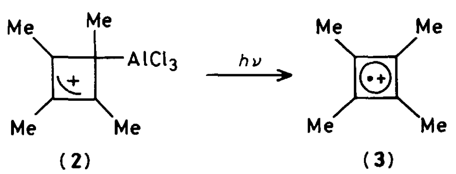
The tetramethylcyclobutadiene radical cation (**3**) was prepared by Hogeveen[4] by the photolysis in fluid solution of the σ-complex (**2**), which was derived from but-2-yne and aluminium chloride.[3] We simplified this procedure by photolysing a mixture of the alkyne and aluminium chloride in CH_2Cl_2,[5] and this reaction generates the cyclobutadiene radical cation even when there is no evidence for the formation of a σ-complex analogous to (**2**).[6]

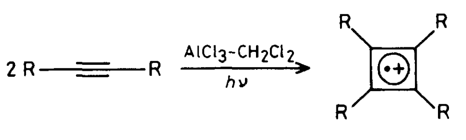
The $AlCl_3$–CH_2Cl_2 reagent is known to oxidise π-electron systems to the corresponding radical cations,[7] and we speculated that reaction (5) might proceed through reaction between the alkyne and alkyne radical cation, equation (3), rather than through the σ-complex, equation (4).


(1)


(2)

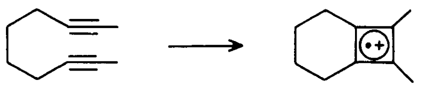

(**1**) (3)


(**2**) (**3**) (4)


(5)

γ-Irradiation of a 10^{-3} mol dm^{-3} solution of but-2-yne in a solid matrix of $CFCl_3$ at 77 K does not give rise to any significant spectrum. There is extensive evidence that γ-irradiation of frozen Freon solution converts a solute into the corresponding radical cation.[8] We suggest that our inability to observe the spectrum of the species $\mathrm{MeC{\equiv}CMe^{\bullet+}}$ results from the fact that the formal degeneracy of the π-orbitals, which would be expected to be lifted by the fixed orientation of the methyl groups, nevertheless leads to considerable *g*-anisotropy.†

If the irradiated sample is then annealed in the e.s.r. cavity up to *ca.* 150 K, a strong spectrum of the tetramethylcyclobutadiene radical cation (**1**; R = Me) appears, *a*(12H) 8.70 G, *g* 2.0030.‡


(**4**) (**5**) (6)

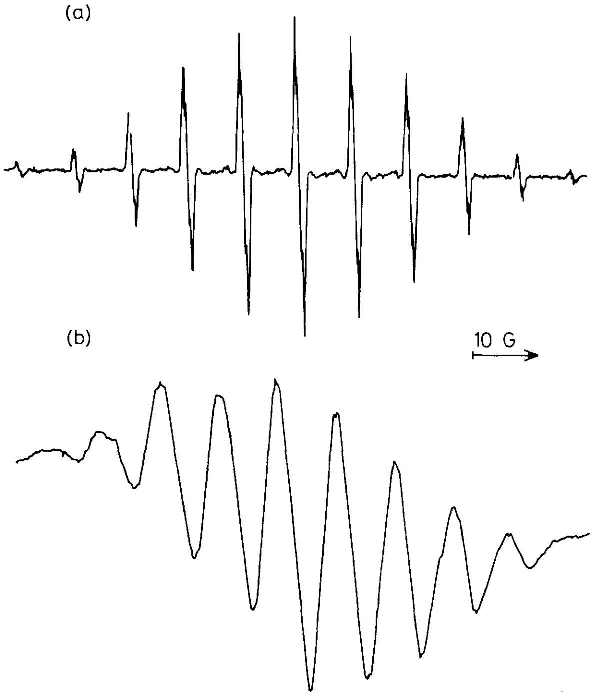


Figure 1. E.s.r. spectra of the radical cation (**5**), prepared (a) in liquid CH_2Cl_2 solution by reaction (6) at 181 K, and (b) in solid $CFCl_3$ solution by γ-irradiation at 77 K.

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† Spectra at 4 K have been obtained, but remain poorly defined. We note that Shiotani and his co-workers have announced the detection of this cation, and its dimer, using other Freon solvents (M. Shiotani, reported at the 23rd Japanese E.S.R. Symposium, 1984).

‡ 1G = 10^{-4} T.

We conclude that the alkyne radical cation is formed during the radiolysis; on annealing, migration of solute molecules occurs through the matrix, and reaction between the alkyne and the alkyne radical cation generates the cyclobutadiene radical cation by reaction (3).

This conclusion is supported by the behaviour of deca-2,8-diyne (**4**) in fluid solution; Figure 1 shows the e.s.r. spectrum of the cyclobutadiene radical cation (**5**) formed, reaction (6), a(6H) 8.75, a(2H) 8.95, a(2H) 8.60, a(2H) 0.34, a(2H) 0.36 G, g 2.0030, at 183 K.

γ-Irradiation of the diyne (**4**) in $CFCl_3$ at 77 K gives rise directly to the spectrum of (**5**), which within the limitation imposed by the line width in the solid state, is the same as the spectrum obtained in fluid solution (Figure 1). The alkyne and alkyne radical cation units are now part of the same molecule, and intramolecular cycloaddition can occur without the necessity for molecular migration through the lattice.

These results leave open the interesting question of the timing of the two bond-forming processes in reaction (3). Consideration of orbital correlation diagrams suggests[9,10] that a [$2\pi s + 1\pi s$] cycloaddition should be symmetry forbidden, and MNDO and MINDO/3 calculations on the reaction between ethene and the ethene radical cation are in favour of a non-synchronous, but concerted mechanism.[9]

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