

Photoaddition of Acetylenes to Benzene

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Summary Acetylene photoadds to benzene giving cyclo-octatetraene; the corresponding addition of dimethyl acetylenedicarboxylate occurs *via* intermediate (I), and the addition of methyl phenylpropiolate involves photo-excitation of the acetylene rather than the benzene.

VARIOUS conjugated acetylenes are known to photoadd to benzene, forming the corresponding cyclo-octatetraenes.^{1,2} The corresponding addition of acetylene itself has been reported only tentatively, and it was thought possible that the product arose from tetramerisation of acetylene.^{2,3} We now report that irradiation (253.7 nm) of acetylene-saturated benzene under nitrogen at 20° gives small amounts (quantum yield estimated to be <0.001) of cyclo-octatetraene (identified by g.l.c. and mass spectrometry) as the

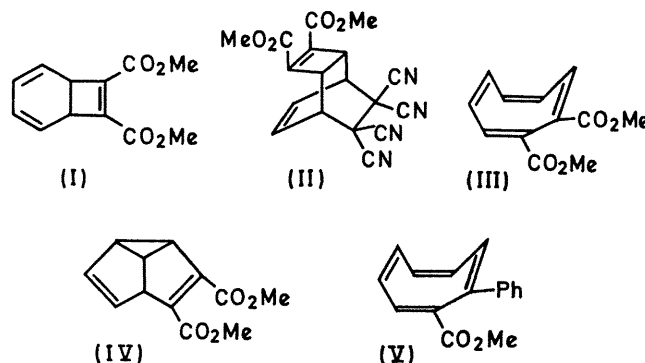
only C₈ product. Specifically, no trace of semibullvalene was found, so it seems very unlikely that this compound was a precursor of the cyclo-octatetraene. Hexadeuterio-benzene likewise gives 1,2,3,4,5,6-hexadeuteriocyclo-octatetraene; hence, tetramerisation of acetylene is excluded. Similarly, *t*-butylacetylene and hex-1-yne both form 1:1 adducts with benzene, and it has been shown in the latter case at least that the product is *n*-butylcyclo-octatetraene rather than the 1,3-addition product previously thought possible.^{4b}

Very little has been reported on the mechanism of the addition of acetylenes to benzene, and although the possibility of an initial 1,2-cycloaddition was suggested earlier,^{1,2} alternatives are readily envisaged. Trapping studies have now shown that the photoaddition of dimethyl acetylenedicarboxylate to benzene does proceed by way of the

bicyclo[3,2,0]octatriene (I) previously suggested^{1,2†}. Thus, irradiation (253.7 nm) in the presence of tetracyanoethylene at 20° led to formation of a 1:1:1 adduct (II) (m.p. 209–211°) at the expense of the cyclo-octatetraene (III). Control experiments established that adduct (II) did not arise by addition of tetracyanoethylene to the cyclo-octatetraene (III) under the conditions employed. This result also excludes the intermediacy of the 1,3-adduct (IV), although mono-olefins⁴ are known to photoadd 1,3 to benzene[‡].

The excited species, previously unidentified, has been shown to be the acetylene rather than the benzene in the case of addition of methyl phenylpropiolate to benzene to form the cyclo-octatetraene (V). In this case the reaction still proceeds readily behind a filter transmitting at wavelengths >290 nm where only the acetylene absorbs to a significant degree. Further, solutions of methyl phenylpropiolate in benzene show no appreciable charge-transfer absorption in this region. In view of this result, it is specially interesting that an analysis of orbital-symmetry

relationships has indicated the possibility of concerted *cis*- or *trans*-1,2-addition of S_1 acetylene to S_0 benzene, but not of S_1 benzene to S_0 acetylene.⁶



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† Later results (D Bryce-Smith, R Deshpande, A Gilbert, and J Grzonka, *Chem Comm*, in the press) suggest strongly that the initial product is not compound (I) but a zwitterion or related species having a significant degree of dipolar character which subsequently transforms into (I).

‡ Liu obtained a mixture of three isomeric semibullvalenes from vapour-phase irradiation of mixtures of hexafluorobut-2-yne and benzene (ref. 5). Since the ratio of these products was similar to that obtained by sensitised photoisomerisation of the corresponding thermal 1,4-adduct of the acetylene and benzene, the semibullvalenes may not have resulted from direct 1,3-addition to benzene.

¹ E Grovenstein and D V Rao, *Tetrahedron Letters*, 1961, 148.

² D Bryce Smith and J E Lodge, *Proc Chem Soc*, 1961, 333; *J Chem Soc*, 1963, 695.

³ Z Kuri and S Shida, *Bull Chem Soc Japan*, 1952, **25**, 116; Z Kuri, *J Chem Soc Japan*, 1955, **76**, 944.

⁴ (a) K E Wilzbach and L Kaplan, *J Amer Chem Soc*, 1966, **88**, 2066; (b) D Bryce-Smith, A Gilbert, and B H Orger, *Chem Comm*, 1966, 512.

⁵ R S H Liu and C G Krespan, *J Org Chem*, 1969, **34**, 1271.

⁶ D Bryce-Smith, *Chem Comm*, 1969, 806.