

ARYNE CHEMISTRY PART VI¹

THE REACTION OF TETRAHALOGENOBENZYNES WITH
BICYCLOHEPTA [2,2,1] DIENE.

H.Heaney and J.M.Jablonski,

Department of Chemistry,

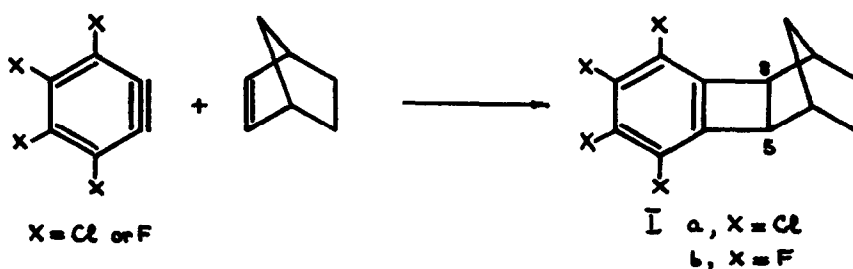
Loughborough University of Technology,

Leicestershire, England.

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The absence of rearranged products in the reaction of benzyne with bicyclohept [2,2,1] ene led to the suggestion that the isolated product arose by a concerted mechanism.² However, this process is not allowed, for thermal cyclisations, by the Woodward-Hoffman rules.³ There is no clear evidence which supports the formulation of benzyne as a triplet di-radical; electron paramagnetic resonance spectra have not been observed using a wide range of benzyne precursors.⁴ In view of the high reactivity of highly halogenated benzynes in addition reactions,^{5,6} we decided to investigate the reactions of tetrachloro-, and tetrafluorobenzyne with bicyclohept [2,2,1] ene, and with bicyclohepta [2,2,1] diene. The yields of adducts were, as expected, higher than with benzyne.

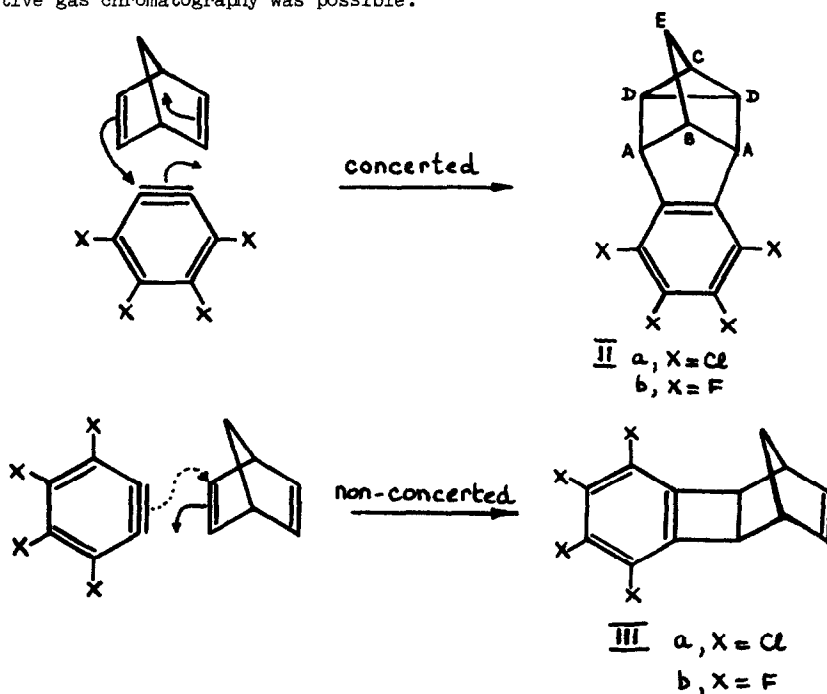
With bicyclohept [2,2,1] ene we have only isolated one adduct (I a and b) in each reaction, and these have been shown to be the exo-adducts by proton magnetic resonance (p.m.r.) spectroscopy since the resonance due to the protons at positions 5 and 8 appear as a sharp singlet;⁸ at τ 6.83 in I a, and at τ 6.75 in I b.



Tetrachlorobenzene, generated from pentachlorophenyl-lithium gave a good yield of crystalline material with bicyclohepta [2,2,1] diene, which was shown to be a mixture by thin layer chromatography on silica gel/silver nitrate. Column chromatography on silica gel/silver nitrate gave two fractions (a) compound (IIa), m.p. 190° (22%), and (b) compound (IIIa), m.p. 102° (50%). The structure of (IIIa) follows from the fact that (Ia) is obtained on hydrogenation in the presence of a palladium on carbon catalyst.

The structure of (IIa) was assigned on the following evidence. Elemental analysis and molecular weight determination showed the compound to be isomeric with (IIIa). The absence of resonances due to olefinic protons in the p.m.r. spectrum proves that one additional ring is present in (IIa) as compared with (IIIa). The symmetrical nature of (IIa) is evident from the relative simplicity of the p.m.r. spectrum which shows the following resonances: τ 6.61 (2 protons) unresolved, protons A; τ 7.58 (1 proton) unresolved, proton B; τ 8.05 (1 proton, triplet), proton C ($J_{CD} = 6$ c./sec.); τ 8.28 (2 protons), protons E unresolved; and τ 8.58 (2 protons, doublet), protons D ($J_{DC} = 6$ c./sec.).

Analogous compounds have been isolated from reactions of tetrafluorobenzene with bicyclohept [2,2,1] ene, and bicyclohepta [2,2,1] diene. In the latter reactions analytical, and preparative gas chromatography was possible.



The most likely mechanism of formation of (II) is a concerted addition of the aryne across the 2, and 6 positions of the diene. The similar addition of maleic anhydride, and tetracyanoethylene was suggested as occurring by a concerted mechanism.⁷ Nevertheless the formation of (III) should occur by a non-concerted mechanism. The ratio of (IIb) to (IIIb) when the reaction was carried out in ether was 1:6, while in cyclohexane the ratio was 1:4. We suggest that this solvent effect supports our suggested mechanisms.

We are at present investigating the reactions of highly halogenated arynes with other strained olefins and dienes.

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References.

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