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THE REACTION OF BENZYNE WITH CYCLOHEPTATRIENE

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A recent paper on the title subject by Tabushi et al[1] prompts us to record our results in this area. Thermal decomposition of o-benzenediazonium carboxylate in the presence of cycloheptatriene yields two $C_{13}H_{12}$ isomers. One of these is 7-phenylcycloheptatriene 2, and the other, a cycloadduct to which Tabushi et al assigned structure 8, we assign structure 3 on the basis of the evidence presented below.

Our spectral data for the cycloadduct are in reasonable agreement with those reported by Tabushi et al, and there is no doubt that we are dealing with the same compound. The p.m.r. spectrum of the cycloadduct is reproduced in the Figure. The unsymmetrical appearance of this spectrum immediately suggests that a symmetrical structure such as 8 is unlikely. In our hands the claim[1] that irradiation of the signal at δ 3.95-4.35 caused the multiplet at δ2.2-2.6 to simplify to an AB quartet could not be substantiated. This is the only evidence in the paper by Tabushi et al for structure 8, and which led these workers to dismiss structure 3, and on the basis of our results seems to be in error.

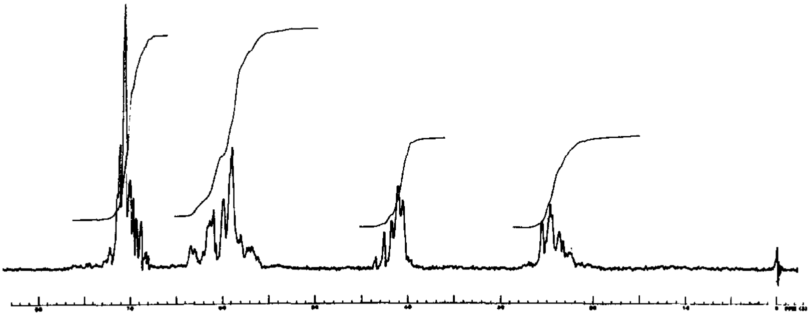
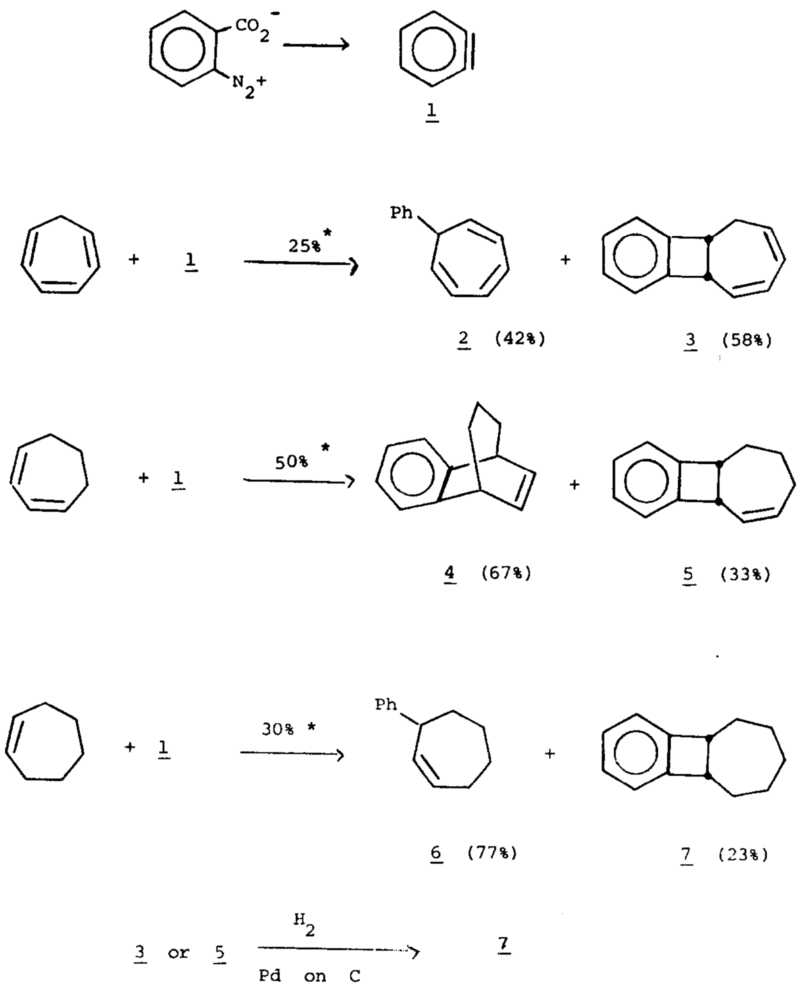


Figure. 60 MHz spectrum of cycloadduct 3 in CCl_4

Hydrogenation of the cycloadduct 3 proceeded with the uptake of two molar equivalents of hydrogen to give a single product 7, δ 7.02 (symm. m, 4H, aromatic), 3.80-3.37 (m, 2H, cyclobutyl), 2.33-1.0 (m, 10H, aliphatic methylene). The u.v. spectrum of 7 is characteristic of a benzocyclobutene[2]: $\lambda_{max}^{cyclohexane}$ (log ε) 261 (3.18), 267 (3.36), 274 (3.31) nm. The ring skeleton of 7, and hence of 3, was firmly established when it was found that 7 was formed together with 3-phenylcycloheptene[3] 6 in the reaction of benzyne with cycloheptene (Scheme 1). We assign structure 3 rather than 9 to the cycloadduct from cycloheptatriene since in the p.m.r. spectrum (Figure) the cyclobutyl protons appear as two overlapping multiplets at δ 3.95-4.35. In structure 9 the corresponding signal should have a more symmetrical appearance, since the



Scheme 1

* Yield based on anthranilic acid used to prepare o-benzenediazonium carboxylate.

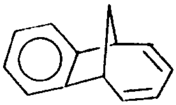
cyclobutyl protons here are chemically equivalent. The ring fusion in 7 is believed to be cis since the cyclobutyl proton region in the p.m.r. spectrum corresponds closely to that described for the corresponding cis-fused adduct obtained from benzyne and cis-cyclooctene.[2]

Reaction of benzyne with 1,3-cycloheptadiene gave the Diels Alder adduct 4, and the 2+2 cycloadduct 5 (Scheme 1). No "ene" product was detected. The structure of 4 follows from its p.m.r. spectrum: δ 7.02 (s, 4H, aromatic), 6.37 (apparent d of d, "J" = 4.8, 3.1 Hz, 2H, vinyl), 3.58-3.18 (m, 2H, bridgehead) 1.82 - 1.20 (m, 6H, methylene). Irradiation of the signal due to the bridgehead protons caused the vinyl multiplet to collapse to a singlet. Hydrogenation of 4 gave benzobicyclo [3.2.2]non-6-ene, δ 6.99 (m, 4H, aromatic), 2.97 (m, 2H, bridgehead) 2.12-1.10 (m, 10H, methylene). Cycloadduct 5 was shown to possess the benzocyclobutene chromophore: $\lambda_{max}^{cyclohexane}$ 261(3.28), 267 (3.37), 274 (3.29)nm; p.m.r. δ 7.30-6.82 (m, 4H, aromatic), 5.95-5.26 (m, 2H, vinyl), 4.49-4.24 (m, 1H, allylic cyclobutyl), 3.75-3.35 (5 line m, 1H, cyclobutyl), 2.52-1.40 (m, 6H, methylene). Hydrogenation of 5 gave 7. Thus 2+2 cycloaddition to give 5 competes to a significant extent with 2+4 cycloaddition in the reaction of benzyne with 1,3-cycloheptadiene.[4]

The 2+4 cycloaddition of benzyne with 1,3-dienes has been shown to be stereospecific, while the 2+2 cycloaddition of benzyne with acyclic alkenes proceeds with loss of stereochemistry.[5] These results are most simply interpreted in terms of benzyne being in the symmetric, singlet ground state, and that 2+4 cycloaddition is concerted, and 2+2 cycloaddition is step-wise.[5] With non-polar alkenes, the 2+2 cycloaddition probably proceeds via a diradical[2] and this mechanism can be assumed to operate in the formation of 3, 5 and 7 from cycloheptatriene, 1,3-cycloheptadiene and cycloheptene, respectively.

The formation of 3 as the only[6] cycloadduct from cycloheptatriene is surprising. Although attack on the 1,2- and 5,6- double bonds is statistically favoured over attack on the 3,4-double bond, some product derived from the latter mode of reaction might reasonably be expected. Work is in progress to determine the reason for the observed selectivity.

The predominant formation of 2+4 cycloadduct 11 from benzyne and tropone,[7] but 2+2 cycloadduct from benzyne and cycloheptatriene is readily explained by the fact that tropone is planar,[8] while cycloheptatriene[9] is not. The observation that adducts 8 and 10[10] are not formed in the cycloheptatriene reaction suggests that the diradical 12 in which C_2 - C_6 are coplanar, cannot be a long-lived intermediate. Molecular models suggest that in one conformer of 12, bonding of the aromatic σ-radical to C_4 or C_6 could readily lead to 10 and 8 , respectively.



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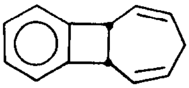

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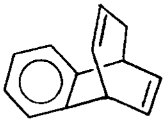

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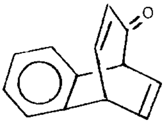

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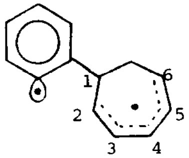

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References and Footnotes

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