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Predominant 2+6 Cycloaddition of Benzyne with Cycloheptatriene[1]

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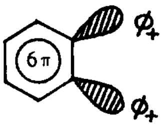
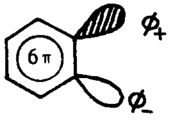
Chemistry of benzyne has attracted increasing attention of organic and/or physical organic chemists.[2] The most important discussion in this stage about the state of benzyne seems to be going on the problem whether it has a bonding (or symmetric, 1a) or antibonding (or antisymmetric, 1b) interaction between in-plane-orbitals at C_1 and C_2.[3]



1a (S-benzyne)

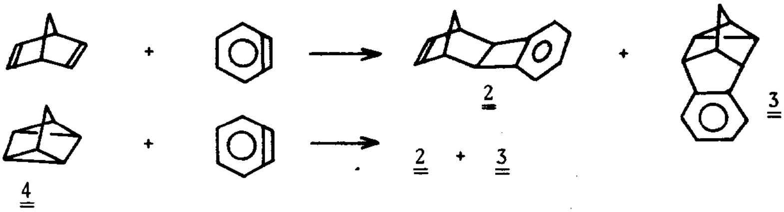


1b (A-benzyne)

Cycloadditions of benzyne with conjugated dienes were found to be stereospecific,[4] indicating that the reaction was concerted, so that it is allowed. This implies that benzyne has the symmetric electronic state (1a).

Now we wish to report the predominant 2+6 cycloaddition of benzyne with cycloheptatriene. The present results seem to afford an experimental evidence for the important (or exclusive) contribution of A-benzyne in its 2+6 cycloaddition with cycloheptatriene, the conclusion is in accord with our observation on cycloaddition of benzyne with norbornadiene or quadricyclane.[5]

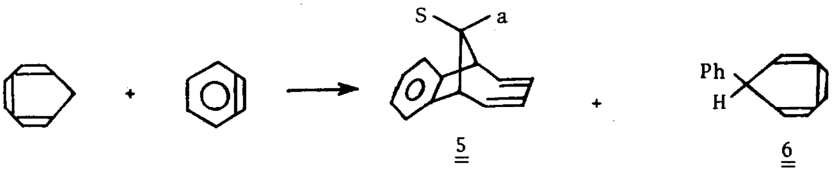
Cycloaddition of benzyne with norbornadiene gave 2 and 3 in ca. 73 and 27% of the total adduct,[6] respectively, where 2 is expected to result from the interaction of A-benzyne (1b) and a homoconjugated diene system.[7] Quadricyclane (4) also gave 2 and 3 in ca. 67 and 33% of the total adduct, respectively.[5] Two reasonable explanations can be made: a) The rigioselectivity resulted from the competition between S- and A-benzyne, the latter converting to the former or b) benzyne can behave as A- and S- form at the same time. Since neither an appreciable dilution effect on the product composition nor a substrate reac-



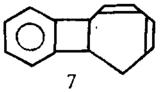
(1)

tivity vs. benzyne state relationship[8)] was observed, mechanism b) should be more plausible.[9)] In these circumstances, investigation of the cycloaddition of benzyne with a conjugated triene seems to be necessary and important.

Cycloaddition of cycloheptatriene (5g) and benzyne generated from thermolysis of benzenediazoniumcarboxylate[10)] (started from 3g of anthranilic acid) in refluxing methylene chloride gave a crude mixture of adducts (ca. 50% yield, bp 62-69° at 8 mmHg) which consisted of two compounds 5 and 6, in 52 and 48% of the total products, respectively.



Spectral data of isolated 5 (a colorless liquid) are as follows: Mass spectrum, m/e (relative intensity); 168 (98), 167 (100), 165 (40), 153 (63), 152 (41); uv spectrum, λ_{max} (C_2H_5OH) mμ (approximate ε); 241 (4,000), 247 shoulder, 259 shoulder, 266 (2,500), 272.5 (2,000); nmr spectrum ($CDCl_3$, TMS); τ 7.4-7.8 (multiplet, H_{9s} and H_{9a}), τ 5.65-5.97 (multiplet, H_1 and H_6), τ 3.65-4.45 (multiplet, H_2, H_3, H_4 and H_5), τ 2.95 (multiplet, aromatic H). Spin decoupling experiment showed that the peak at τ 5.65-5.97 changed to singlet by irradiation near 7.5τ and did not change by irradiation near 4.0τ and that the peak at τ 7.4-7.8 changed to AB quartet (J_{AB} = 11 cps) by irradiation near 5.9τ. This decoupling excluded the structure of 2+2 cycloadduct 7 which is the only remaining alternative to fit to uv and nmr data.



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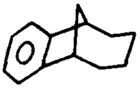
Hydrogenation of 5 on a palladium catalyst afforded the corresponding saturated compound 8. Mass spectrum; 172 (37), 143 (35), 131 (36), 130 (48), 129 (100) 128 (44) and 115 (53); nmr spectrum (CCl_4); τ 7.95-9.0 (broad multiplet, 10H), τ 6.25-6.60 (multiplet, 2H) and τ 2.99 and 3.03 (4H). Compound 8 was different from known 9 (from the corresponding ketone[13]). Compound 6 is known[11] and our spectral data were quite consistent with reported data.



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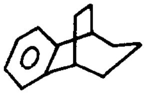

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Formation of 6 is understood as a result of ene-type reaction which is well known for allyl compound.[12] Most important to note is that 5, a 2+6 cycloadduct, was the only detectable cycloadduct in the benzyne-conjugated triene system although 2+2 and 2+4 were structually possible.[13] The observed regioselectivity strongly suggests that the present cycloaddition is not two step process which should give a 2+4 cycloadduct (and/or a 2+2 cycloadduct) in an appreciable amount (the 2+4 adduct was obtained for azodicarboxylate). A concerted 2+6 cycloaddition requires that benzyne should be an A-form on the basis of orbital symmetry consideration.

Thus, a major contribution of A-benzyne (1b) was clearly detected. Considering that an almost exclusive contribution of S-benzyne (1a) was confirmed by independent experiments by Jones[4a] and Atkins,[4b] one can accept a general mechanism a, of concurrent contribution of S- and A-benzyne. For example, in the norbornadiene or quadricyclane case, the concurrent contribution of both forms was considered to interpret the observed regioselectivity. This mechanism is valid if the energy difference between the two state of benzyne is smaller than that between two approaching processes i.e., homo-end-approach and exo-2+2-approach (the energy difference may be estimated by the perturbation theory.)

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3) R. Hoffmann, A. Imamura, W. J. Hehre, J. Am. Chem. Soc., 90, 1499 (1968). Beside 1a and 1b, a polar form is often important in the reactions with polar substrates.

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6) Product 2 was determined by Simmons; H. E. Simmons, J. Am. Chem. Soc., 83, 1657 (1967). Formation of 3 as well as 2 was reported later; L. Friedman, R. L. Rice, See ref. 2 p. 235. Our experiments under different conditions gave a similar product distribution.

7) Calculation of homoconjugation; R. Hoffmann, E. Heilbronner, R. Gleiter, J. Am. Chem. Soc., 92, 706 (1970). There are many references reporting homo-Diels Alder cycloaddition of norbornadiene with common dienophiles.

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9) More detailed discussion on the point will be made in a full paper.

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12) Substituent effects and deuterium isotope effects of the ene reaction will be reported soon.

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