

THE ADDITION OF BENZYNE TO

1,2-DIDEUTERIOCYCLOHEXENE*

Göran Ahlgren and Björn Åkermark
Department of Organic Chemistry
Royal Institute of Technology
S-100 44 Stockholm 70, Sweden

(Received in UK 22 May 1970; accepted for publication 25 June 1970)

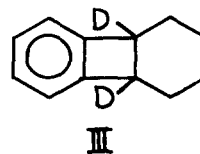
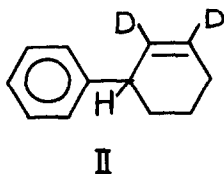
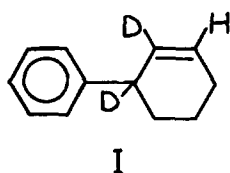
The mechanism of the 2+2 cycloaddition of benzyne to olefins has recently attracted considerable interest. Since the reaction is not stereospecific, it can not be a 2_s+2_a concerted reaction but should proceed in a stepwise manner.

Whether the addition has diradical (1) or dipolar character (2) has been a matter of dispute.

Depending on the nature of the olefin and on the reaction conditions, a number of reagents, e.g. chlorine (3), N-bromosuccinimide (4) and azoesters (5) have been shown to add to olefins in either a radical or a polar type of reaction. The first excited triplet level of benzyne is probably very close to the ground state (6). Benzyne might therefore be expected to add to olefins as either a diradical or a dipolar reagent.

The reaction between benzyne and cyclohexene has been reported to give both the ene-adduct, 3-phenylcyclohexene (7) and the cycloadduct, 1,2-phenylenecyclohexane (8) (cf., however 1d). The hydrogen atoms are very readily removed from the allylic positions of cyclohexene to give cyclohexenyl radicals (9). If the ene reaction between benzyne and 1,2-dideuteriocyclohexene had radical character, it should proceed via cyclohexenyl radicals. Equal amounts of the two adducts (I) and (II) would then be formed (5a). When benzyne (10) was reacted with 1,2-dideuteriocyclohexene, only the "true" ene-adduct (I), presumably formed in a concerted reaction, was obtained. None of the isomeric ene-adduct (II) could be detected and, contrary to the earlier report, none of the cyclo-adduct (III) was formed.

* Cycloaddition reactions, part 4. Part 3: Ref. (11).



This result may be compared with the addition of triplet excited maleate to 1,2-dideuteriocyclohexene, which yielded the two possible ene-adducts and the cycloadduct in a ratio of 1:1:2 (11). It seems safe to conclude that benzyne has relatively small tendency to react as a diradical.

This conclusion is further supported by the fact that benzyne gives dipolar adducts with weak nucleophiles like ethers (12) rather than abstracting hydrogen atoms from them.

Financial support from the Swedish Board for Technical Development is gratefully acknowledged.

- 1a. I. Tabushi, K. Okazaki and R. Oda, Tetrahedron **25**, 4401 (1969).
- b. M. Jones, Jr. and R. H. Levin, J. Am. Chem. Soc., **91**, 6411 (1969).
- c. L. Friedman, R. J. Osiewicz and P. W. Rabideau, Tetrahedron Lett., 5735 (1968).
- d. P. G. Gassman and H. P. Benecke, Tetrahedron Lett., 1089 (1969).
2. H. H. Wasserman, A. J. Solodar and L. S. Keller, Tetrahedron Lett., 5597 (1968).
3. M. L. Poutsma, J. Am. Chem. Soc., **87**, 2161 (1965).
- 4a. C. Walling, A. L. Rieger and D. D. Tanner, J. Am. Chem. Soc. **85**, 3129 (1963).
- b. E. E. Van Tamelen and T. J. Curphey, Tetrahedron Lett., 121 (1962).
- 5a. G. Ahlgren and B. Åkermark, Acta Chem. Scand., **22**, 1129 (1968).
- b. E. Koerner von Gustorf, D. V. White, B. Kim, D. Hess and J. Leitch, J. Org. Chem. **35**, 1155 (1970).
6. T. Yonezawa, H. Konishi and H. Kato, Bull. Chem. Soc. Japan, **42**, 933 (1969).
7. H. E. Simmons, J. Am. Chem. Soc., **83**, 1657 (1961).
8. "Dehydrobenzene and cycloalkynes", R. W. Hoffman, Ed. Academic Press, New York, N. Y., 1967, p. 201.
9. C. Walling and W. Thaler, J. Am. Chem. Soc., **83**, 3877 (1961).
10. Benzyne was generated by diazotization of anthranilic acid with isoamyl nitrite in refluxing methylene chloride/acetone solution in the presence of 1,2-dideuteriocyclohexene according to the procedure of L. Friedman and F. M. Logullo, J. Org. Chem., **34**, 34, 3089 (1969).
11. G. Ahlgren and B. Åkermark, Tetrahedron Lett., 1885 (1970).
12. Ref. 8, p. 177.