

## Stereochemistry of 1,4-Cycloaddition of Benzyne

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WE report the first demonstration of the concerted nature of a Diels–Alder reaction of benzyne.

The 2+2 cycloaddition of benzyne to mono-enes<sup>1</sup> is stereoselective but not stereospecific; this indicates a two-step mechanism, in agreement with Woodward–Hoffmann predictions, with formation of the second bond competing with bond rotation. This is reasonable for the highly reactive intermediates involved.

In the 2+4 cycloaddition of benzyne to conjugated dienes† there is the positive prediction of a concerted and hence stereospecific process for ground-state singlet benzyne with the two electrons in the lower symmetric orbital.<sup>2</sup> In complete agreement with expectation for a concerted cyclo-addition, we find<sup>3</sup> that benzyne, generated by the oxidation of 1-aminobenzotriazole in methylene chloride at 25°, added stereospecifically to *trans,trans*-hexa-2,4-diene to give *cis*-1,4-dihydro-1,4-dimethylnaphthalene (60%) and biphenylene (6%). The structure and stereochemistry of the adduct followed from its simple <sup>1</sup>H n.m.r. spectrum (CCl<sub>4</sub>): 8.70 (d, 6H, *J* 7 c./sec.), 6.35–6.93 (m, 2H), 4.30 (d, 2H, *J* 2.5 c./sec.), and 2.91 (s, 4H). It

was dehydrogenated with palladium on charcoal to 1,4-dimethylnaphthalene (50%). None of the isomeric *trans*-adduct could be detected.

With *cis,trans*-hexa-2,4-diene coplanarity, and hence concerted cycloaddition, is severely hindered. In the same reaction conditions with this isomer much more biphenylene (70%) was formed together with a small amount (9%) of a complex mixture of products of which only 8%, *i.e.* less than 1% overall, could be the Diels–Alder adduct (n.m.r. analysis). This large difference in reactivity of benzyne towards the *trans,trans*- and the *cis,trans*-diene also argues strongly against a non-concerted mechanism.

Our results exactly parallel those of Bartlett and Schueller<sup>4</sup> for the reaction of ethylene with the same pair of dienes; the *trans,trans*-isomer gave *cis*-3,6-dimethylcyclohexene stereospecifically (60%) whilst the *cis,trans*-isomer gave no cycloadduct.

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† Most Diels–Alder reactions reported for benzyne have been with cyclic dienes constrained in, or near, the required planar conformation, though lower yield cycloadditions to acyclic dienes are well known (R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967, p. 210). Wittig and Dürr first reported the addition of benzyne to buta-1,3-diene in 10% yield (G. Wittig and H. Dürr, *Annalen*, 1964, **673**, 55); curiously this reaction has just been rediscovered (9%) (L. F. Hatch and D. Peter, *Chem. Comm.*, 1968, 1499). We have observed the same reaction, with benzyne generated from 1-aminobenzotriazole at –80°, in 90% yield.

<sup>1</sup> I. Tabushi, R. Oda, and K. Okazaki, *Tetrahedron Letters*, 1968, 3743; M. Jones and R. Levin, *ibid.*, p. 5593; H. Wassermann, A. J. Solodar, and L. S. Keller, *ibid.*, p. 5597; L. Friedman, R. J. Osiewicz, and P. W. Rabideau, *ibid.*, p. 5735.

<sup>2</sup> R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499.

<sup>3</sup> Report to the American Chemical Society Petroleum Research Fund, Sept., 1968.

<sup>4</sup> P. D. Bartlett and K. E. Schueller, *J. Amer. Chem. Soc.*, 1968, **90**, 6071.