

THE CYCLOADDITION OF *o*-BENZYNE TO
(E)-DEUTERIO-*trans*-BUTYLETHYLENE

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The mechanism of the thermal, homopolar, $2\pi + 2\pi$ reaction is central to the theory of cycloaddition chemistry. Unfortunately, a lack of reactivity towards such processes among the appropriate olefinic systems has precluded a thorough analysis of the controlling factors.

Results from our laboratory, as well as the work of others, support the classification of *o*-benzyne as a highly reactive, but otherwise quite typical homopolar, 2π reaction partner.^{1,2} Hence, a study of the addition of *o*-benzyne to other nonpolar 2π components could lead to a clearer understanding of the intricate details of these cycloaddition reactions. Indeed, several reports on the stereochemistry of *o*-benzyne - olefin cycloadditions have appeared and retention of configuration in the benzocyclobutenyl fragment derived from the olefin is generally observed.^{2,3} While such results are in accord with a rotationally-non equilibrated biradical intermediate, they suffer from the traditional drawback of also being consistent with a blend of mechanisms. For example, a mixture of concerted $2\pi S + 2\pi S$ and $2\pi S + 2\pi A$ pathways could serve equally well to produce the observed results.^{4a}

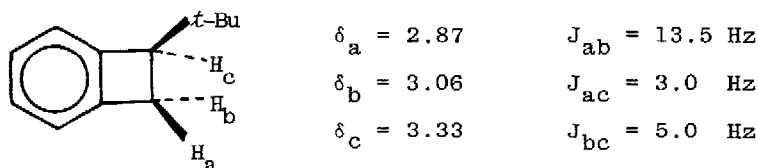
As all of the previous studies have involved 1,2-disubstituted olefins, the reaction of *o*-benzyne with an appropriately deuterated, but otherwise monsubstituted olefin would be of considerable interest. As Table I reveals, cycloaddition of *o*-benzyne to a *trans*-disubstituted olefin results in stereoretention, generally to the extent of ca. 70-80%.⁵ If the biradical explanation is correct, then

Table I: The Stereochemistry of *o*-Benzyne-Olefin Cycloadditions

Olefin	% <i>trans</i> -benzocyclo- butene (Stereoretention)	% <i>cis</i> -benzocyclo- butene (Stereo-inversion)	Ref.
<i>trans</i> -dichloroethylene	80	20	3a
<i>trans</i> -ethyl propenyl ether	79	21	3b
<i>trans</i> -cyclooctene	78	22	3e
<i>trans</i> -acetoxy propene	69	31	3c
<i>trans</i> -methyl propenyl ether	53	47	3c

predominant stereoretention would again be expected from a similar deuterio-olefin. On the other hand, if the dual-pathway mechanism is operative, a considerably different stereochemical outcome should result. This expectation is based on the premise that the sterically demanding $2\pi S + 2\pi A$ inversion mode should play an increased role with the less encumbered olefin, resulting in enhanced stereoinversion.⁴

In order to explore these considerations, the reaction of *o*-benzyne with (E)-deuterio-*tert*-butylethylene was investigated. This olefin was selected as it has been shown to react with *o*-benzyne only by 2+2 cycloaddition.^{2a} The labelled olefin was prepared according to the method of Brown and Gupta.⁶ The 100 MHz pmr spectrum of *tert*-butylbenzocyclobutene was readily decomposed to yield the data contained in the figure below.⁷ It was then a straightforward matter to cycloadd *o*-benzyne to the labelled *tert*-butylethylene and determine the relative amounts of protium residing at H_a and H_b in the adduct.



An excess (2.5 equiv.) of the (E)-deuterio-*tert*-butylethylene sample (88.5% d₁; 11.5% d₀)⁸ was reacted with *o*-benzyne⁹ (1 equiv.) and the resultant 1-deuterio-2-*tert*-butylbenzocyclobutene was isolated in 9% yield after distillation

Notes and References

1. R. W. Hoffmann, Ed., "Dehydrobenzene and Cycloalkynes", Academic Press, New York, N. Y., 1967.
2. a) M. Jones, Jr. and R. H. Levin, J. Amer. Chem. Soc., 91, 6411 (1969); b) R. W. Atkin and C. W. Rees, Chem. Commun., 152 (1969).
3. a) M. Jones, Jr. and R. H. Levin, Tetrahedron Lett., 5593 (1968); b) H. Wasserman, A. J. Solodar and L. S. Keller, ibid., 5597 (1968); c) L. Friedman, R. J. Osiewicz and P. W. Rabideau, ibid., 5735 (1968); d) J. Tabushi, R. Oda and K. Ikazaki, ibid., 3743 (1968); e) P. G. Gassman and H. P. Benecke, ibid., 1089 (1969); f) P. G. Gassman, H. P. Benecke and T. J. Murphy, ibid., 1649 (1969).
4. a) N. D. Epiotis, J. Amer. Chem. Soc., 94, 1935 (1972); b) N. D. Epiotis, R. L. Yates, D. Carlberg and F. Bernardi, ibid., 98, 453 (1976).
5. *cis*-olefins are less appropriate models since initial non-bonded attractions or repulsions may affect the stereochemical outcome.
6. H. C. Brown and S. K. Gupta, J. Amer. Chem. Soc., 97, 5249 (1975). Note that the boiling point of this olefin is incorrectly reported as 58°C at 750 mm; the correct boiling point is 41°C at 760 mm.
7. These assignments are completely consistent with general observations from similar systems that $J_{cis} > J_{trans}$ and that a proton *cis* to a substituent resonates at higher field than one positioned *trans*.^{3a,b,d}
8. Determined by low ionization mass spectral analysis.
9. *o*-Benzynes were generated *via* thermal decomposition of benzenediazonium-2-carboxylate hydrochloride salt according to the method of Friedman, as described by Dittmer, et. al.¹⁰
10. D. C. Dittmer and E. S. Whitman, J. Org. Chem. 34, 2004 (1969).
11. Low ionization mass spectral analysis of the benzocyclobutene product revealed it to be 89.0% d₁ and 11.0% d₀. This indicates the absence of a significant secondary isotope for the cycloaddition step and allows this type of numerical analysis.
12. P. Dervan and T. Uyehara, J. Amer. Chem. Soc., 98, 1262 (1976).
13. A. T. Bowne, unpublished observation.