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

Arlyce T. Bowne, Theodore A. Christopher and Ronald H. Levin* Department of Chemistry, Harvard University Cambridge, Massachusetts 02138, U.S.A.

(Received in USA 19 July 1976; received in UK for publication 1 October 1976)

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 <u>ca</u>. 70-80%.⁵ If the biradical explanation is correct, then

4111

Olefin	% trans-benzocyclo- butene (Stereoretention)	% cís-benzocyclo- butene (Stereoinversion)	Ref
trans-dichloroethylene	80	20	3a
trans-ethyl propenyl ether	79	21	3b
trans-cyclooctene	78	22	3e
trans-acetoxy propene	69	31	3c
trans-methyl propenyl ether	53	47	3c

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

predominant stereoretention would again be expected from a similar deutero-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-*text*-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 *text*-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 *text*-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-*text*-butylethylene sample (88.5% d_1 ; 11.5% d_0)⁸ was reacted with *o*-benzyne⁹ (1 equiv.) and the resultant 1-deu-terio-2-*text*-butylbenzocyclobutene was isolated in 9% yield after distillation

(bp 29°C at 0.05 mm). Expansion and repeated integration of the cyclobutenyl protons gave rise to an $H_a:H_b:H_c$ ratio of $(0.74:0.32:1.05) \pm 0.05$. After correction for the 11.5% text-butylethylene-d₀ contaminant, an $H_a:H_b$ ratio of $(0.75:0.25) \pm 0.07$ resulted.¹¹



The net stereochemical result of predominant retention of configuration argues convincingly for the biradical mechanism and finally lays to rest the possibility of dual concerted pathways in the thermal $2\pi + 2\pi$ cycloaddition of simple olefins. Furthermore, the striking similarity between our stereochemical ratio and the data contained in Table I is consistent with initial bonding between the arynic carbon atom and the sterically less hindered olefinic carbon atom. This would transform the remaining olefinic center into a secondary radical. If the relative rate of bond rotation to ring closure in the biradical, and hence the stereochemical outcome, is controlled by radical stability and rotational barrier heights,¹² then all of the reported studies should, indeed, lead to similar stereochemical outcomes.

In a parallel study, we have found that o-benzyne reacts with ethylene to yield benzocyclobutene.¹³ In order to probe what may well be the simplest, thermally accessible, homopolar $2\pi + 2\pi$ cycloaddition, and to test the above radical stability-rotational barrier interpretation, we are investigating the cycloaddition of o-benzyne to a stereospecifically labelled dideuterioethylene.

<u>Acknowledgement</u> is made to the E. I. duPont de Nemours Company for a Young Faculty Grant to R. H. L. The Harvard University Chemistry Department also assisted this investigation through its undergraduate research program (T. A. C.).

Notes and References

- R. W. Hoffmann, Ed., "Dehydrobenzene and Cycloalkynes", Academic Press, New York, N. Y., 1967.
- a) M. Jones, Jr. and R. H. Levin, <u>J. Amer. Chem. Soc.</u>, <u>91</u>, 6411 (1969); b) R.
 W. Atkin and C. W. Rees, <u>Chem. Commun.</u>, 152 (1969).
- a) M. Jones, Jr. and R. H. Levin, <u>Tetrahedron Lett</u>., 5593 (1968); b) H.
 Wasserman, A. J. Solodar and L. S. Keller, <u>ibid</u>., 5597 (1968); c) L. Friedman,
 R. J. Osiewicz and P. W. Rabideau, <u>ibid</u>., 5735 (1968); d) J. Tabushi, R. Oda
 and K. Ikazaki, <u>ibid</u>., 3743 (1968); e) P. G. Gassman and H. P. Benecke, <u>ibid</u>.,
 1089 (1969); f) P. G. Gassman, H. P. Benecke and T. J. Murphy, <u>ibid</u>., 1649 (1969).
- 4. a) N. D. Epiotis, <u>J. Amer. Chem. Soc</u>., <u>94</u>, 1935 (1972); b) N. D. Epiotis, R. L. Yates, D. Carlberg and F. Bernardi, <u>ibid</u>., <u>98</u>, 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, <u>J. Amer. Chem. Soc.</u>, <u>97</u>, 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-Benzyne was 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% d_1 and 11.0% d_0 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, <u>J. Amer. Chem. Soc.</u>, <u>98</u>, 1262 (1976).
- 13. A. T. Bowne, unpublished observation.