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ON THE MECHANISM OF THE NORBORNADIENE-t-BUTYL PERBENZOATE REACTION

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THE cuprous bromide catalyzed reaction of norbornadiene and t-butyl perbenzoate in benzene has been shown to give 7-t-butoxynorbornadiene as the only substitution product in about 25 per cent yield.[1] This reaction was originally devised as a promising synthetic route to 7-substituted norbornadienes[2] because of the intriguing possibility of hydrogen abstraction at C.7 to give an intermediate, non-classical radical, i.e. homoallylicly-assisted hydrogen abstraction analogous to homoallylicly-assisted ionization at C.7.[3] An alternative mechanism involving rearrangement of the bicyclic nucleus was also considered.[2]

It has now been found by deuterium labeling that the reaction proceeds via rearrangement of the norbornadiene skeleton and the general olefin-perester mechanism proposed by Kochi[4] is suggested as being the most reasonable path.

Norbornadiene labeled in the two position (I), rather than 7-deuterionorbornadiene as originally intended,[5] was chosen to elucidate the mechanism because it could be obtained in higher yield and could be purified more readily. 2-Deuterionorbornadiene was prepared by the method of Streitweiser,[6]

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[1] P.R. Story, J. Amer. Chem. Soc. **82**, 2085 (1960).

[2] P.R. Story, J. Org. Chem. **26**, 287 (1961).

[3] S. Winstein and M. Shatavsky, J. Amer. Chem. Soc. **78**, 592 (1956).

[4] J.K. Kochi, J. Amer. Chem. Soc. **83**, 3162 (1961).

[5] P.R. Story, J. Amer. Chem. Soc. **83**, 3347 (1961).

[6] Private communication. The author thanks Professor Streitweiser for prior disclosure of the details of this preparation.

involving deuterium oxide (99.7 per cent) treatment of the 2-norbornadienyl anion prepared by a modification of Wittig's method.[7] Nuclear magnetic resonance spectral analysis of the gas phase chromatographically (GPC) pure material indicated that 24.7 per cent of the olefinic hydrogens were replaced by deuterium.

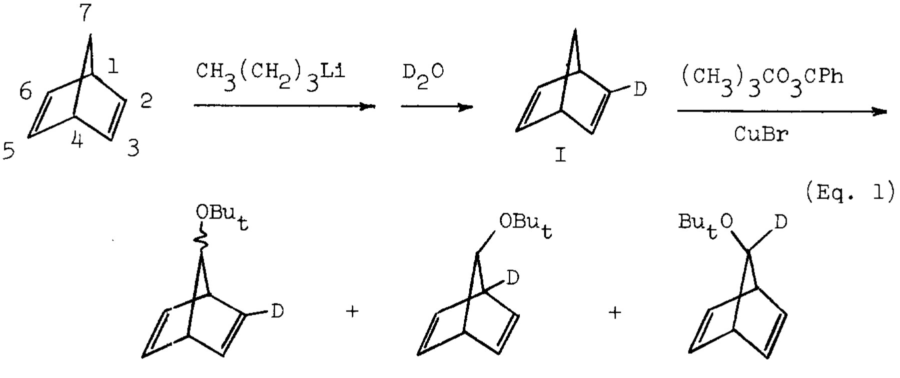
TABLE 1

Distribution of the Deuterium in 7-t-Butoxynorbornadiene prepared from 2-Deuterionorbornadiene*

C.7 position (bridge)	0.22 D
C.1 and C.4 positions (bridgeheads)	0.32 D
one double bond	0.25 D
other double bond	0.18 D
total deuterium	0.97

* The values given are the average of 8-9 determinations and represent the diminution of peak areas as compared to an authentic undeuterated sample. The author thanks E.W. Anderson for the NMR determinations.

The deuterated norbornadiene (I) was treated with t-butyl perbenzoate in the usual way[2] to yield deuterated 7-t-butoxynorbornadiene (II) which was purified by preparative scale GPC and examined by NMR. Careful integration of the peak areas and comparison with an authentic undeuterated



I

(Eq. 1)

IIa IIb IIc

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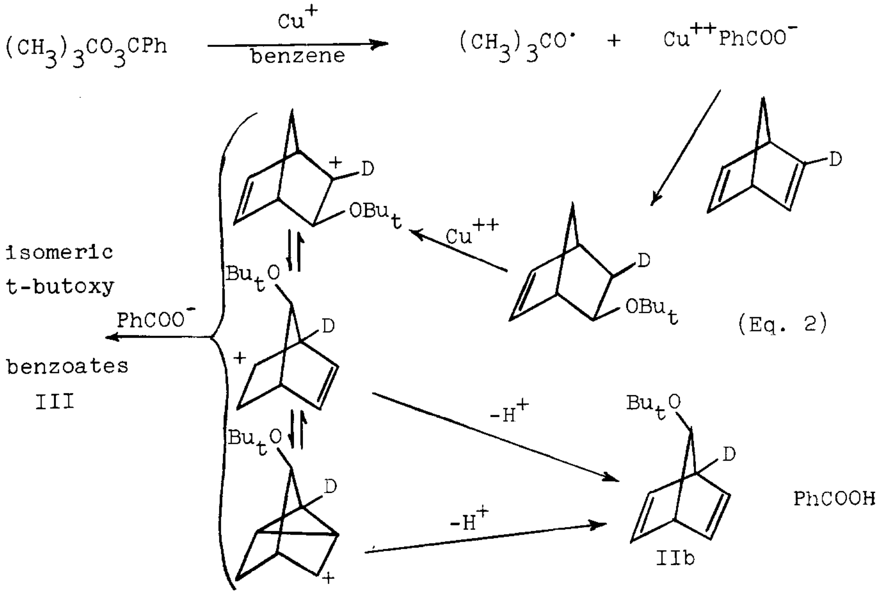
[7] G. Wittig and E. Hahn, Angew. Chem. **72**, 781 (1960).

sample showed deuterium at all skeletal positions in an approximately statistical distribution as shown in Table 1.

These data thus rule out hydrogen abstraction at C.7 and are consistent with the Kochi-type[4] mechanism outlined in equation (2) which shows that part of the reaction which leads to deuterium at C.1 and C.4 (IIb). The deuterium is distributed approximately statistically, according to this mechanism, by attack of the t-butoxy radical at all four olefinic carbons. It is possible that part of the isomeric mixture of t-butoxy benzoates (III)[8] may have arisen by strictly radical paths.



The possibility that the ether (II) is produced by benzoic acid elimination from one or more t-butoxy benzoate is held unlikely because of the insensitivity of the yield of the ether (II) to reaction reflux time.

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[8] The structures of the t-butoxy benzoates (III) are, so far, unknown. The mixture has been characterized by infrared spectral and GPC data which shows two major and two minor components. This reaction also gives some polymeric material.

Further, several allylic benzoates[4] including 1-phenylprop-3-en-1-yl benzoate[9] have been shown not to rearrange under these reaction conditions.

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[9] M.S. Kharasch, G. Sosnovsky and N.C. Yang, J. Amer. Chem. Soc. **81**, 5819 (1959).