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CYCLIZATION OF DIENES VIA HYDROBORATION: SILVER ION INDUCED INTRAMOLECULAR ALKYL COUPLING

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The cyclization of dienes or polyenes is a synthetically useful process, and has been achieved in a number of ways, among which the most widely used are thermal rearrangements,[1] cyclizations induced by protic or Lewis acids,[2] transition metals[3] or by radical means.[4] The type of cyclized product depends on the method used. We wish to report a further method of cyclization, based on the silver ion induced oxidation of organoboranes.

The coupling of hydroborated olefins <u>in situ</u> by alkaline silver nitrate[5,6] has proved a synthetically valuable procedure for the conversion of branched and unbranched olefins into symmetrical hydrocarbons (Scheme 1). **Transalkylation** from boron to silver is believed[7] to generate unstable alkyl silver intermediates, which decompose to give radical species. These may then undergo normal radical coupling.

$$R_3B \xrightarrow[\text{Base}]{AgNO_3} [R{-}Ag] \longrightarrow R^{\cdot} \xrightarrow{R^{\cdot}} R{-}R \qquad \text{(Scheme 1)}$$

The proximity of the radical centres generated in this manner from hydroborated dienes should favour intramolecular coupling. Thus it was expected that dienes would yield mainly cyclized products, and these expectations have generally been realized (Table).

TABLE

Products of Reaction of Dienes with Diborane Followed by Alkaline Silver Nitrate

Diene	Cyclic Products[a]	Yield (%)[b]
2,3-Dimethyl-1,3-butadiene	*trans*-Dimethylcyclobutane[c,d]	79
2-Methyl-1,4-pentadiene	Methyl cyclopentane	85
1,5-Hexadiene	Cyclohexane[e]	66
	Methylcyclopentane[e]	17
2,5-Dimethyl-1,5-hexadiene	1,4-Dimethylcyclohexane, *trans*	49
	cis	33
1,6-Heptadiene	Cycloheptane	67
1,7-Octadiene	Cyclooctane	42
1,5-Cyclooctadiene[f]	*cis*-[3,3,0]-Bicyclooctane[c]	19
	Cyclooctene	19
	Cyclooctanone[g]	43
Geranyl acetate	*trans*-*p*-Menthane	83
Linalyl acetate	1-Hydroxy-*p*-menthane, *trans*	36
	cis	36

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[a] Products were identified by g.l.c. comparison (Carbowax 20M; Silicon XE-60) with authentic samples.

[b] Yields were determined by g.l.c. using n-undecane as internal standard.

[c] Characterized by g.l.c.-mass spectrometry.

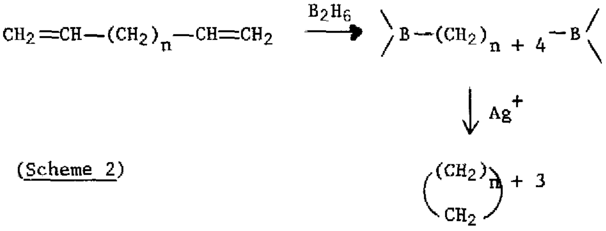
[d] Propylene was identified as a minor product, formed by fragmentation of the diradical intermediate.

[e] Product composition was unaffected by heating the intermediate borane at 65° for 1 h.

[f] The equilibrated hydroboration product, 9-borabicyclo-[3,3,1]-nonane[8] was used.

[g] The origin of this product is under investigation.

Although the hydroboration of dienes is complex, giving rise to mixtures of cyclic and acyclic boranes,[9] there is no requirement in this reaction for the borane to be cyclic. This is shown by the reaction of 1,5-hexadiene (Table). Brown[10] has shown that this yields mainly polymeric borane at 0°, which slowly rearranges to the cyclic borepane at 65°. Treatment of hydroborated 1,5-hexadiene before and after isomerization, however, gives identical products. This suggests that, although boron prefers to form 5,6 and 7-membered rings, the cyclization should be capable of extension to larger rings (Scheme 2).



(Scheme 2)

This is illustrated in the products obtained from 1,6-heptadiene and 1,7-octadiene. The product distributions follow the trends observed for the position of hydroboration of the dienes.[11] We believe the reason for the exclusive terminal cyclization in the case of heptadiene and octadiene is that hydroboration of both double bonds occurs essentially independently, and only in cases where cyclic borane formation is thermodynamically favourable will non-terminal cyclization products arise. The product observed from geranyl acetate arises as a result of cis-elimination[12] within the first-formed cyclic borane.[13] This results in generation of a terminal olefin, which undergoes intramolecular hydroboration to give a seven-membered cyclic borane.

A typical procedure is as follows. The diene (10 mmole) in THF (15 ml) under a nitrogen atmosphere was cooled to 0°. Diborane (10 mmole) in THF was added slowly over 30 min. with vigorous stirring. The solution was maintained at 0° for 2 h and then allowed to warm to room temperature. Methanolic potassium hydroxide (2M, 20 ml) was added slowly, followed by aqueous silver nitrate (5M, 7.5 ml). The mixture was stirred for 1 h at room temperature, centrifuged and the clear supernatant analysed by g.l.c. Products were isolated, where possible, by ether extraction and distillation.

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References

1. See V.N. Ipatiev, W.D. Huntsman, and H. Pines, J.Amer.Chem.Soc., 1953, 75, 6222; H. Pines, N.E. Hoffman, and V.N. Ipatiev, J.Amer.Chem.Soc., 1954, 76, 4412, and J.M. Coxon, R.P. Garland, and M.P. Hartshorn, Aust.J.Chem., 1972, 25, 353, for leading references.

2. See E.E. van Tamelen, Acc.Chem.Res., 1975, 8, 152; W.S. Johnson, Acc.Chem.Res., 1968, 1, 1, for pertinent examples.

3. F.J. McQuillen, and D.G. Parker, J.C.S., Perkin I, 1974, 809.

4. M. Julia, F. LeGoffic, and L. Katz, Bull.Soc.Chim.France, 1964, 1122; T.W. Sam, and J.K. Sutherland, J.C.S.Chem.Comm., 1971, 970; A.L.J. Beckwith and G. Phillipou, J.C.S.Chem.Comm. 1973, 280.

5. H.R. Snyder, J.A. Kuck, and J.R. Johnson, J.Amer.Chem.Soc., 1938, 60, 105.

6. H.C. Brown, and C.H. Snyder, J.Amer.Chem.Soc., 1961, 83, 1001, 1002.

7. J.R. Johnson, M.G. Van Campen, Jr., and O. Grummitt, J.Amer.Chem.Soc., 1938, 60, 111.

8. E.F. Knights, and H.C. Brown, J.Amer.Chem.Soc., 1968, 90, 5280.

9. H.C. Brown, and E. Negishi, J.Amer.Chem.Soc., 1967, 89, 5475.

10. P.L. Burke , E. Negishi, and H.C. Brown, J.Amer.Chem.Soc., 1973, 95, 3654.

11. H.C. Brown, E. Negishi, and P.L. Burke, J.Amer.Chem.Soc., 1972, 94, 3561.

12. H.C. Brown, and R.M. Gallivan, J.Amer.Chem.Soc., 1968, 90, 2906.

13. R. Murphy and R.H. Prager, Aust.J.Chem., in the press.