A New Approach to Medium-ring 1,5-Dienes *via* Alkylborane Fragmentation

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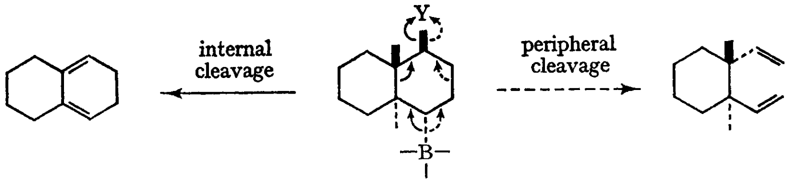
WE wished to learn whether the fragmentation of alkylboranes[1] as in Scheme 1 could be employed to prepare *trans, trans*-cyclodeca-1,5-dienes.[2] Unlike their previously studied counterparts,[1,3] the decalylborane derivatives required for this purpose could fragment either by internal cleavage or by peripheral cleavage.

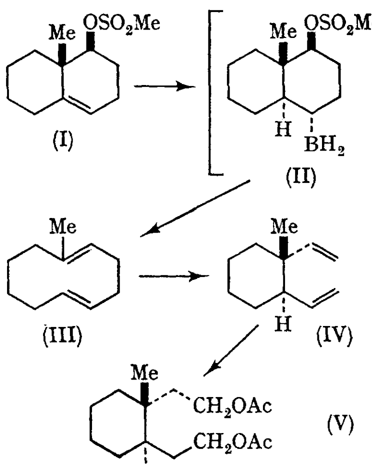


SCHEME 1

Our preliminary work, summarized in Scheme 2, has shown that such reactions exhibit a remarkably high preference for internal cleavage, and thus admirably serve as a means of preparing certain cyclodeca-1,5-dienes.[4]

The methanesulphonate derivative (I) on treatment with a tenfold molar excess of 0·6M-diborane in tetrahydrofuran[5] gave the alkylborane derivative [principally (II)] which on treatment with refluxing aqueous sodium hydroxide in tetrahydrofuran gave the hydrocarbon (III) [78% yield of distilled material, b.p. (bath temp.) 75—85%/10 min.]; λ_{max}(film) 6·00 (C=C), 9·60, 10·20, 10·40 (*trans*-CH=CH), 10·60, 11·20, 11·71, and 12·10 μ; δ (CCl_4, with Me_4Si as reference) 5·05—4·60 (vinyl H, broad, unresolved) and 1·32 (vinyl CH_3). The structure of the diene (III) follows from its method of preparation,[1,3] and is supported by the spectral data. When (III) was pyrolyzed (320°) in the injection port of a gas chromatograph, the material eluted differed markedly from (III) and showed the properties expected for the Cope rearrangement product,[6] diene (IV), λ_{max}(film) 3·26 (vinyl H), 6·09 (C=C), 10·0, and 10·96 μ ($C=CH_2$); δ (CCl_4, Me_4Si reference) 6·0—4·6 (vinyl H, complex pattern (6H), and 0·89 (angular CH_3) (3H). Rearrangements of this type have previously been observed with cyclodeca-1,5-dienes.[7]

The stereochemistry of the diene (IV) was



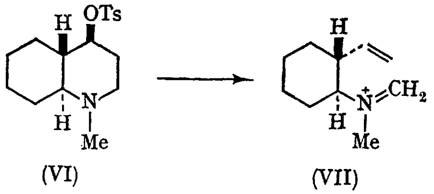
SCHEME 2

established as follows. Hydroboration with disiamylborane[8] followed by oxidation with alkaline hydrogen peroxide afforded a mixture of primary and secondary alcohols from which the diacetate (V), λ_{max}(film) 5·75 (CO), 8·05, 9·47, and 9·64 μ; δ (in CCl_4, Me_4Si reference) 4·06 (CH_2OAc triplet, J 8·0 c./sec.) (4H), 1·97 ($CH_3{\cdot}CO$) (6H), and 0·85 (angular CH_3) (3H), could be isolated by preparative gas chromatography after acetylation. It was identical with an authentic specimen.

The fragmentation leading to the diene (III) is highly selective, since the i.r. spectrum of a distilled sample of the product exhibits only a weak shoulder at 10·96 μ, whereas the isomeric divinyl compound (IV) shows its strongest absorption band at this position.

The preference displayed here by the methanesulphonate (I) contrasts sharply with the findings of Grob and his co-workers for the seemingly analogous decahydroquinoline (VI),[9] which undergoes only peripheral cleavage to the vinyl compound (VII).

Further examples of internal cleavage reactions will be reported in our full Paper.



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[1] *cf.* J. A. Marshall and G. L. Bundy, *J. Amer. Chem. Soc.*, 1966, **88**, 4291; C. A. Grob and P. W. Schiess, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1.

[2] This diene system commonly occurs in the medium-ring sesquiterpenes. For a Review, see F. Šorm, *Fortschr. Chem. org. Naturstoffe*, 1961, **1**.

[3] G. L. Bundy, unpublished results.

[4] For an alternative route to these compounds, see E. J. Corey and A. G. Hortmann, *J. Amer. Chem. Soc.*, 1965, **87**, 5736.

[5] H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover, and G. Zweifel, *J. Amer. Chem. Soc.*, 1960, **82**, 4233.

[6] *cf.*, W. von E. Doering and W. R. Roth, *Angew. Chem. Internat. Edn.*, 1963, **2**, 115.

[7] *cf.*, I. Ognjanov, V. Herout, M. Horák, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2371; G. Ohloff, *Angew. Chem.*, 1959, **71**, 162; C. A. Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, 1963, **46**, 483.

[8] H. C. Brown and G. Zwiefel, *J. Amer. Chem. Soc.*, 1960, **82**, 3222.

[9] C. A. Grob, H. R. Kiefer, H. J. Lutz, and H. J. Wilkens, *Helv. Chim. Acta*, 1967, **50**, 416.