The Stereochemistry of Alkylboronate 1,3-Elimination Reactions

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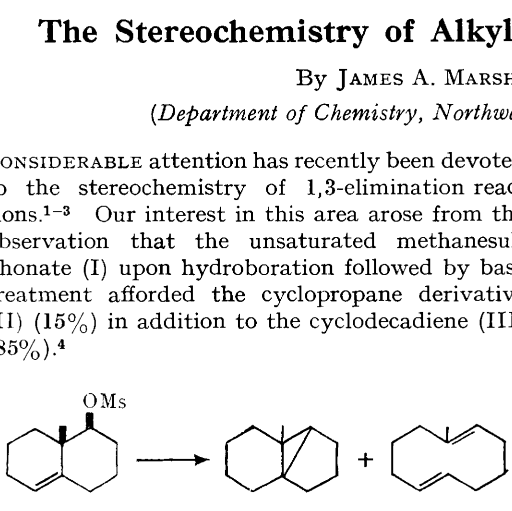
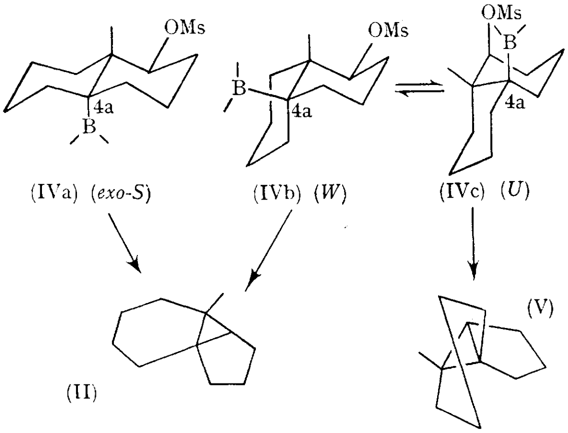
CONSIDERABLE attention has recently been devoted to the stereochemistry of 1,3-elimination reactions.[1–3] Our interest in this area arose from the observation that the unsaturated methanesulphonate (I) upon hydroboration followed by base treatment afforded the cyclopropane derivative (II) (15%) in addition to the cyclodecadiene (III) (85%).[4]



(I) (II) (III)

Previous work clearly indicates that (II) must arise *via* a 1,3-elimination reaction of the tertiary boronate derivative (IV).[5] The question here pertains to the stereochemistry of the process leading from the boronate (IV) to the hydrocarbon (II). Three arrangements can be envisioned for the present case, the *exo-S* (IVa), the *W* (IVb), and the *U* (IVc).[1]

Both the *exo-S* (IVa) and *W* (IVb) arrangements could directly afford the cyclopropane (II), the former with retention of configuration at C(4a) and inversion of configuration at C(1) and the latter with inversion of configuration at both C(4a) and C(1).[1] Cyclization *via* the *U* form (IVc) with retention of configuration at C(4a) and C(1) can be excluded since this process would afford the highly strained hydrocarbon (V) with a *trans*-fused bicyclo[4,1,0]heptane ring system. The problem then is to differentiate between the *exo-S* and -*W* modes of cyclization.



This problem was easily resolved through oxidation[6] of the alkylborane mixture derived from the hydroboration of unsaturated mesylate (I). The resulting mixture was treated directly with Li–NH_3–EtOH to effect hydrogenolysis of the methyl sulphonate grouping. The material thereby secured in 75% overall yield contained 12% of the *cis*-tertiary decalol (VI)[7] and 88% of an inseparable mixture of the secondary *cis*- and *trans*-decalols (VII) and (VIII).† Decalol (VI) was isolated and identified by comparison with an authentic sample.[7] None of the isomeric

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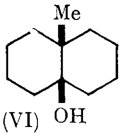
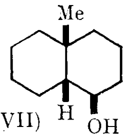
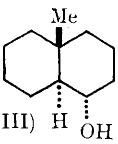
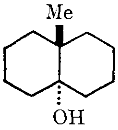
† An 18 ft. by ¼ in. column of Carbowax 20-M on 60—80 mesh Chromosorb W was employed for this gas chromatographic analysis. At 188° with a helium flow rate of 98 cc./min., the following retention times were observed: (VI), 8·6 min.; (VII) and (VIII), 14·0 min.; (IX), 8·0 min. As little as 1% of (IX) could have been detected in the mixture had it been present.


(VI)


(VII)


(VIII)


(IX)

trans-tertiary decalol (IX) was detected by gas chromatography.†

These results indicate that basic 1,3-eliminations of boronates proceed readily *via* the *W* orientation with inversion at both carbon atoms.‡

We gratefully acknowledge support from the National Science Foundation and the National Institutes of Health.

(*Received, May 27th,* 1968; *Com.* 678.)

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‡ Matteson and Talbot[2] have shown that electrophilic attack of norborn-5-ene-2-boronic acid by mercuric chloride likewise preferentially occurs with double inversion to yield nortricyclylmercuric chloride .

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[2] D. S. Matteson and M. L. Talbot, *J. Amer. Chem. Soc.*, 1967, **89**, 1119, 1123.
[3] F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, in the press.
[4] J. A. Marshall and G. L. Bundy, *J. Amer. Chem. Soc.*, 1966, **88**, 4291.
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[6] *Cf.* G. Zweifel and H. C. Brown, *Org. Reactions*, 1963, **13**, 22.
[7] J. A. Marshall and A. R. Hochstetler, *J. Org. Chem.*, 1966, **31**, 1020.