Peripheral Bond Fission in the Alkylboronate Fragmentation of the 1,1,4a-Trimethyldecalin System

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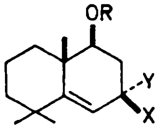
Summary In the alkylboronate fragmentation of the 1,1,4a-trimethyldecalin system, hydroxy-groups cause peripheral fission.

ALKYLBORONATE fragmentation provides a useful synthesis of dienes, especially cyclodecadienes.[1] It has been reported that when two pathways are possible in the fragmentation, the more highly substituted C–C bond preferentially undergoes cleavage (*e.g.* ref. 2).

We report a peripheral fission in the boronate fragmentation of the 1,1,4a-trimethyldecalin system. As a model experiment for the preparation of the *trans,trans*-cyclodecadienone[3] (IIb), the mesylate[4] (Ib) of alcohol[5] (Ia) was hydroborated and then treated with NaOH in tetrahydrofuran, to give, as expected, a single olefin (IIa) [67% from (Ia)]. When heated (IIa) rearranged readily into the divinylcyclohexane (IIIa) quantitatively.

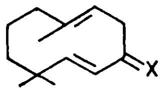
Attempted preparations of the octalin derivatives, appropriately functionalised at C-3, from the acetoxy-octalone[5] (Ic) proceeded as follows: (Ic) was reduced ($NaBH_4$) to the corresponding alcohol (Id) (79%), m.p. 75—76°, which was then treated with dihydropyran-phosphorus oxychloride. Removal of the acetyl group of the product by reduction ($LiAlH_4$) and subsequent mesylation gave the mesylate

(Ie) [93% from (Id)]. The desired hydroxy-mesylate (If) was obtained from (Ie) by hydrolysis with toluene-*p*-sulphonic acid in aqueous methanol.



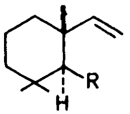
(I)

a; X = Y = H, R = H
b; X = Y = H, R = Ms
c; X,Y = O, R = Ac
d; X = OH, Y = H, R = Ac
e; X = OTHP, Y = H, R = Ms
f; X = OH, Y = H, R = Ms



(II)

a; X = H_2
b; X = O
c; X = H,OH



(III)

a; R = CH=CH_2
b; R = CH_2CHO

THP = tetrahydropyranyl;
Ms = mesyl

The mesylate (If) was hydroborated, and excess of the reagent was removed by addition of methanol. Treatment of the alkylborane obtained with NaOH caused an unexpected fragmentation to give the aldehyde (IIIb) (40%) as sole volatile product. Since the cyclodecadienol (IIc), obtained from the corresponding ketone (IIb)[3] by reduction with $LiAlH_4$, was recovered unchanged under the reaction conditions, internal fission followed by Cope rearrangement was not responsible for the formation of (IIIb).[†]

All new compounds gave satisfactory elemental analyses and showed expected spectroscopic properties.

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[†] (IIc) rearranged into (IIIb) at elevated temperatures.

[1] For a review, see J. A. Marshall, *Synthesis*, 1971, 229.
[2] J. A. Marshall and G. L. Bundy, *Chem. Comm.*, 1967, 854.
[3] This compound has been synthesised by an alternative route: M. Miyashita and A. Yoshikoshi, *Chem. Comm.*, 1971, 1091.
[4] Boronate fragmentation of this mesylate has also been described: see ref. 1.
[5] P. Beak and B. M. Monroe, *J. Org. Chem.*, 1967, **32**, 2778.