Tetrahedron Letters No. 24, pp. 2153-2156, 1971. Pergamon Press. Printed in Great Britain.

REACTION OF ALLYLBORANES WITH METHYLCYCLOPROPENE

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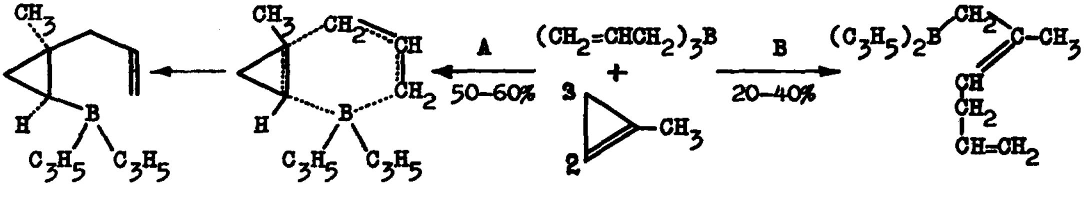
(Received in UK 29 April 1971; accepted in UK for publication 13 May 1971)

Allylboranes were previously reported to give addition products with terminal acetylenes[I-3], allenes[4] and vinyl ethers[5]. It was of interest to study their behaviour with regard to cyclopropenes, since the double bond in the latter readily adds Grignard reagents[6], whereas allylboranes display sometimes the properties of organometallic compounds[7].

We investigated the reaction of I-methylcyclopropene with triallylborane and found it to proceed along the two paths:



I

II

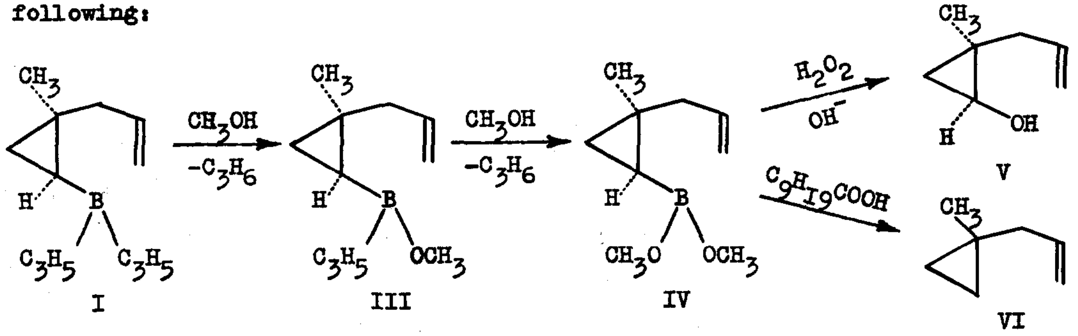
The first one (A) is a cis-addition of allyl- and allylboron fragments of triallylborane molecule to the double bond of cyclopropene, the boron atom being added to the unsubstituted carbon atom. The second way (B) involves the cleavage of the C_2-C_3 bond of the cyclopropene ring followed by allyl- and allylboron fragments addition to C_2 and C_3 respectively.

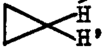
It should be noted that all the three B-C bonds of triallylborane are able to take part in this reaction, if cyclopropene is in excess.

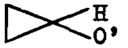
The reaction was carried out by introducing gaseous I-methylcyclopropene into cooled (-70 to 0°C) triallylborane, the process being exothermic.

I-Methylcyclopropene containing 3-20% of methylenecyclopropane was used. The latter was shown to be inert towards triallylborane (20-I40°).

Distillation of the reaction products (ratio of initial compounds I:I) resulted in diallyl(I-methyl-I-allylcyclopropyl-2)borane (I[8], 50-60%, b.p. 50-5I°/2 mm, n_D^{I9} I.4755). The structure of borane I was evidenced by the following:

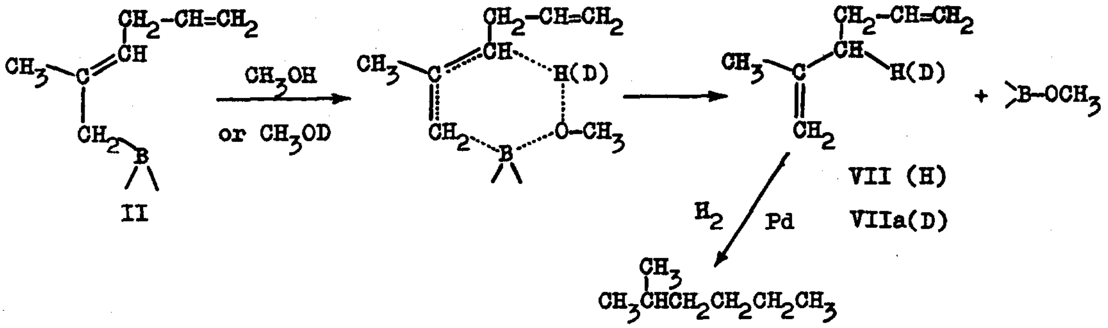


One allyl-B bond of borane I is rapidly cleaved by action of methanol to yield monomethoxyborane (III[8], 6I%, b.p. 38-40°/2 mm, n_D^{I9} I.4545). The compound I (or III) was refluxed with an excess of methanol (5-I0 h) to give dimethoxyborane IV[8] (90%, b.p. 60.5-6I°/I0 mm, n_D^{2I} I.435I), PMR ($CHCl_3$, TMS, δ=0): -0.38, -0.28, -0.25, -0.I4 (, I H), 0.32-0.78 (m, , 2 H), I.I0 (CH_3, 3 H), 2.08 (d, J=7 Hz, C-CH_2-C=, 2 H), 3.57 (B-OCH_3, 6 H), 4.52-5.I5 (m, CH_2=C, 2 H), 5.35-6.03 (m, =CH-, I H).

Oxidation of borane IV with hydrogen peroxide in alkaline solution afforded I-methyl-I-allylcyclopropanol-2 (V[8], 89%, b.p. 58-59°/II mm, n_D^{22} I.4500), PMR ($CHCl_3$): 0.32-0.55 (4 bands, , 2 H), 0.89 (CH_3, 3 H), 2.I3 (d, J=7 Hz, C-CH_2-C, 2 H), 3.I4, 3.I9, 3.24, 3.30 (, I H), 4.82-5.33 (m, CH_2=C, 2 H), 5.56-6.I7 (m, C=CH, I H), 4.27 (O-H, I H).

I-Methyl-I-allylcyclopropane (VI) was obtained by heating the compound IV with capric acid (I:4) at I30-I80° (VI[8], 86%, b.p. 85-87°/742 mm, n_D^{22} I.4II8), PMR ($CHCl_3$, δ): 0.26 (CH_2-CH_2, 4 H), I.02 (CH_3, 3 H), I.97 (d, J=7 Hz, CH_2-C, 2 H), 4.75-5.22 (m, CH_2=C, 2 H), 5.42-6.I9 (m, C=CH-, I H).

No compounds of type II were isolated. Their formation was proved in the following way



A crude mixture of products of the reaction of triallylborane with I-methylcyclopropene was refluxed for 5-I2 h with an excess of methanol, giving after distillation in vacuo diene VII (20-40% yield) and borane IV (50-60%).

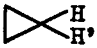
The pure diene VII was obtained by reaction of allylmagnesiumchloride with 2-methylallylbromide. IR-, PMR spectra as well as other physical properties of pure diene are completely identical with those of the sample obtained from II (b.p. 86-86.5°, n_D^{20} I.4I90), PMR ($CHCl_3$, δ): I.67 (t, J=I.2 Hz, CH_3, 3 H), 2.05 ($-CH_2-CH_2-$, 4 H), 4.65 (d, J=0.8 Hz, $CH_2=C<^{C}_{C}$, 2 H), 4.70-5.I0 (m, $CH_2=C-C$, 2 H), 5.40-6.I0 (m, $=CH-$, I H).

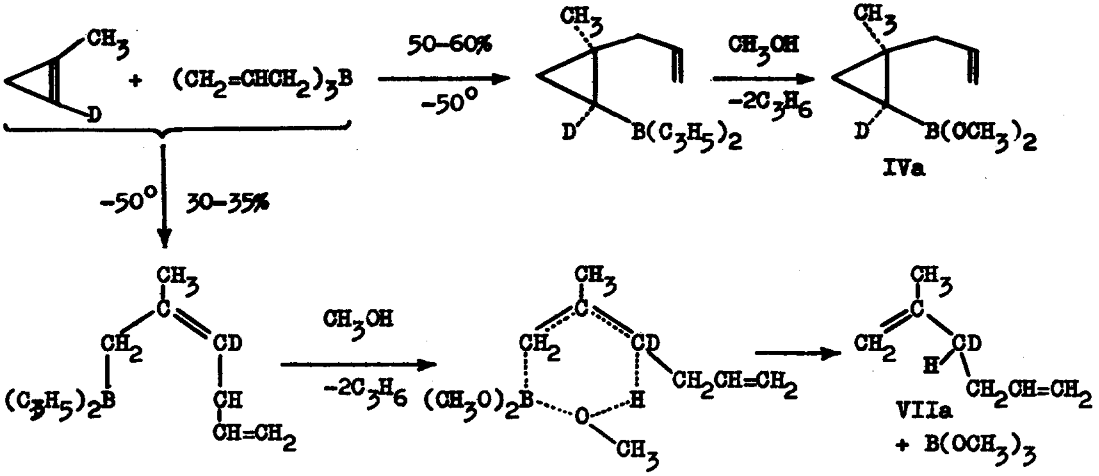
Hydrogenation of diene VII (Pd-black) resulted in 2-methylhexane.

The location of the double bond in compound VII at $C_I=C_2$ instead of $C_2=C_3$ is due to allyl rearrangement during alcoholysis[9], as was demonstrated by means of alcoholysis with CH_3OD. PMR spectrum of diene VIIa (b.p. 87-89°, $n_D^{2I.5}$ I.4I89) differed from that of VII only in the signal shape at 2.05 ppm ($-CH_2-CHD-$, 3 H).

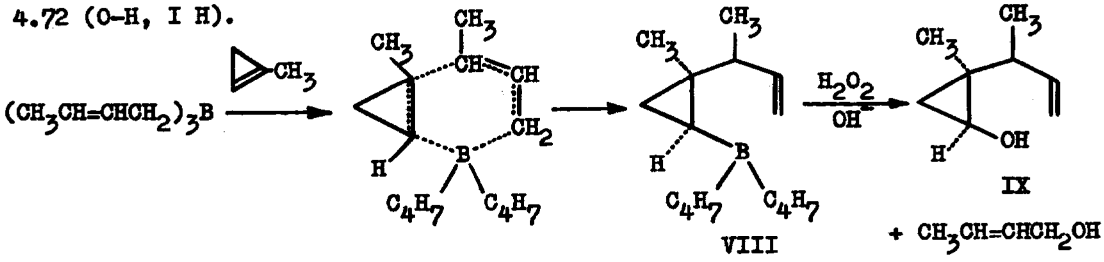
As a result of the reaction of I-methyl-2-deuterocyclopropene with triallylborane (I:2) followed by methanolysis of the reaction mixture, 2-methyl-3-deuterohexa-I,5-diene (VIIa, 30-35%) and dimethoxy(I-methyl-I-allyl-2-deuterocycloprop-2-yl)borane (IVa, 50-60%) were obtained.

The cis-addition of allylboranes to the double bond of cyclopropene proceeds along with allyl rearrangement that is confirmed by formation of VIII in the reaction of I-methylcyclopropene with tri(2-butenyl)borane.

Oxidation of borane VIII (H_2O_2, OH^-) gave carbinol IX[8] (88% yield, b.p. 64-65°/IImm, n_D^{20} I.4566), PMR (liquid, δ): 0.28-0.50 (m,  , 2 H), 0.72



(CH$_3$–◁ , 3 H), I.06 (d, J=7 Hz, CH$_3$–C–, 3 H), 2.I0 (m, CH–, I H), 2.05–2.30 (4 bands, –O–C–H, I H), 4.70–5.I2 (m, CH$_2$=C–, 2 H), 5.62–6.23 (m, =CH–, I H), 4.72 (O–H, I H).



Allylboranes react with other cyclopropene compounds in similar way.

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8. Satisfactory elemental analysis was obtained.
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