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THE REACTION OF BICYCLO/1,1,0/BUTANE WITH ORGANOBORANES

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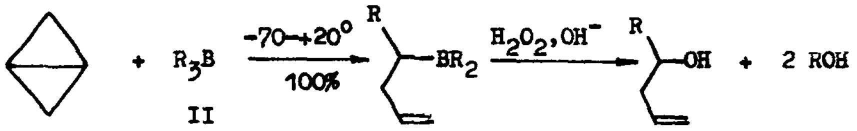
Bicyclobutane is a high-strained compound, its chemical properties being like those of unsaturated systems [1-3]. The typical reaction for this compound is an addition to the central bond, whereas little is known about the reactivity of the side bonds [1]. In this paper we wish to report on our studies of the reaction of bicyclobutane with organoboranes which seems to be one of few cases including the side bonds reactions.

We have studied the reaction of bicyclobutane (I) with tri-n-propyl-(IIa), triallyl- (IIb) and tri(2-butenyl)borane (IIc) and found it to lead to butenyl derivatives of boron of type III.



I III IV

IIa, R= $n-C_3H_7$
b, R= $CH_2=CH-CH_2$
c, R= $CH_3-CH=CH-CH_2-$

This reaction is highly exothermic and occurs at -70- +20°. The reaction products, being unsymmetrical boranes (IIIa-c), were not isolated, but their formation was proved on the basis of PMR and IR spectroscopy data. For example, there were characteristic bands of the terminal double bond $CH_2=CH-$ in the IR-spectrum of IIIa.

Oxidation of products III with H_2O_2 (OH^-) led to allylcarbinols of type IV and to alcohols ROH. In all cases, the oxidation products consisted of only IV and ROH together with less than one percent of an impurity, probably $R-CH_2-CH_2-CH=CH_2$. Thus the reaction of bicyclobutane with organoboranes seems to be highly selective. Oxidation of the products of bicyclobutane:tri-

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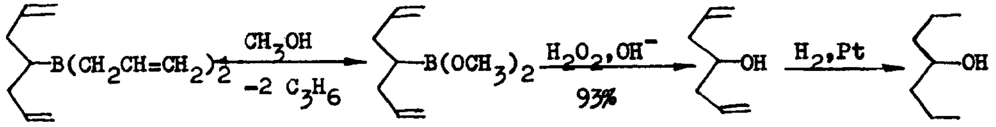
n-propylborane reaction afforded n-propanol and 1-hepten-4-ol in 79% yield, b.p. 52-52.5°/11 mm, n_D^{20} 1.4334 (lit.4): b.p. 66°/20 mm, n_D^{20} 1.4342).

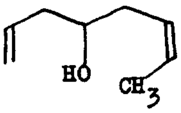
Methanolysis of compound IIIb gave propylene and dimethoxyborane V in 94.8% yield (with respect to I), b.p. 71-72.5°/23 mm; PMR (CCl_4, δ, TMS): 1.30 (m, 4 lines, CH-B, 1H), 2.08 (t, J=7 Hz, CH_2, 4H), 3.48 (s, CH_3-OB, 6H), 4.64-5.10 and 5.39-6.12 (2 m, CH_2=C, 4H, and C=CH, 2H).



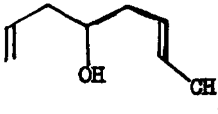
IIIb V IVb VI

Oxidation of V (H_2O_2, OH^-) afforded 1,6-heptadien-4-ol (IVb), b.p. 44-44.5°/9 mm, n_D^{20} 1.4512. Hydrogenolysis of IVb (Pt) yielded 4-heptanol (VI), b.p. 62.5-63°/15 mm, n_D^{20} 1.4196 (lit.5): b.p. 63.8°/16 mm, n_D^{20} 1.4205).

As has been previously shown6), the allylic rearrangement takes place in nearly all reactions of allyl type boranes, the only exception being the cleavage of cyclopropene single bond which occurs without the rearrangement7). Since both alkylboranes and triallylborane react with I in a similar way, we believed allylboranes to react with I without the rearrangement. In order to check this conception, the reaction of I with tricrotylborane (IIc) was performed. Oxidation of a crude reaction mixture afforded isomeric butenols and the mixture of cis- and trans-IVc, b.p. 59.6-60.5°/9 mm, n_D^{21} 1.4578, yield 90%. IR: 970, 1641, 1660, 1670, 1828, 3008, 3024, 3081 (C=C), 3380 cm^{-1}; PMR (CCl_4, δ, TMS): 1.62 (CH_3, 3H), 3.30-3.60 (m, CH-O, 1H), 5.27-5.55 (m, CH=CH, 2H). For the mixture of IVc thus obtained, the ratio of cis:trans isomers is equal to approximately 1:4, i.e. the same as in starting tricrotylborane8). Hence the reaction of allylboranes with I occurs without the rearrangement.

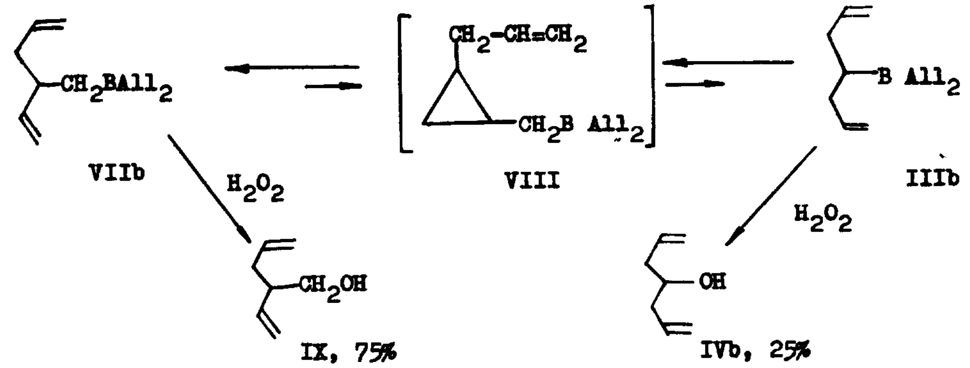


cis-IVc (30%)



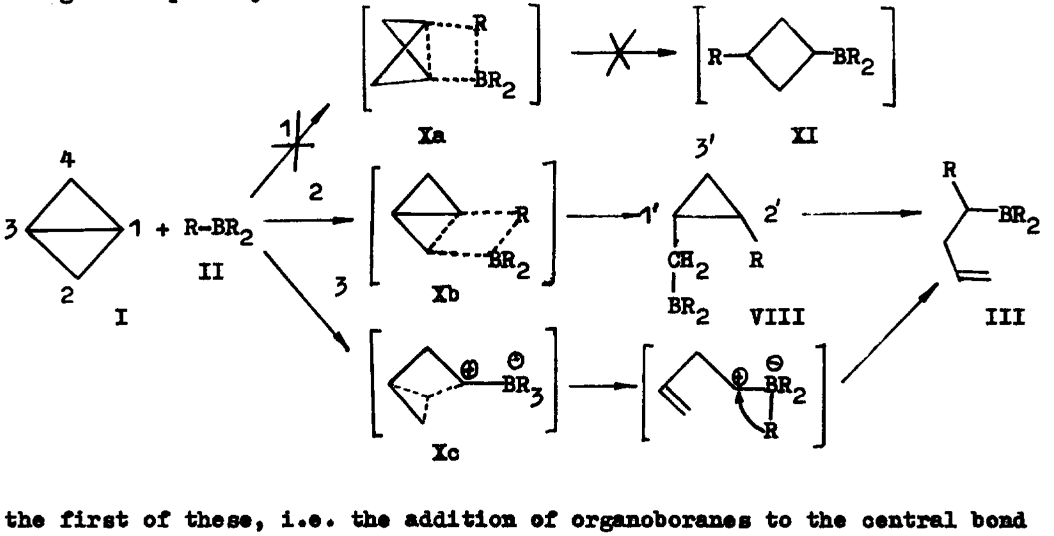
trans-IVc (70%)

It is known that butenyl derivatives of metals can undergo the rearrangements which include intermediate cyclopropylcarbinyl compounds 9-11). So we believed the butenylboranes of type III having the boron atom attached to the secondary carbon atom to have to isomerize into boranes of type VII which include boron atom attached to the terminal carbon atom. The boranes VII are more thermodynamically stable. Really, as was shown in the case of reaction of I with triallylborane, the isomerization proceeds slowly at 20° and rapidly at heating. Thus compound IIIb was converted into VIIb in approximately 75% yield when heated for 5h at 95°. The ratio IIIb:VIIb (75:25) appears to be equilibrium because it does



not change after heating the mixture for 10h at 95°. For watching the course of isomerization, PMR-spectroscopy was used. PMR-spectrum of IIIb includes three multiplets: 1.35-2.58 ($B-CH_2-C=C$, $B-CH(CH_2-C=C)_2$), 4.50-5.05 ($CH_2=C$), and 5.30-6.27 ($C=CH$). After heating IIIb at 95° the doublet at 1.29 ppm appeared in the spectrum. Oxidation of the equilibrium mixture gave rise to the mixture of alcohols IVb and IX (1:4). These carbinols were separated by use of GLPC. Unsaturated alcohol IX had n_D^{21} 1.4540; PMR (CCl_4, δ, TMS): 1.83-2.55 (m, CH_2-CH, 3H), 3.42 (d, J=6 Hz, CH_2-O, 2H), 3.98 (s, OH, 1H), 4.73-5.19 and 5.33-6.10 (2 m, $CH_2=C$, 4H, and $C=CH$, 2H).

The reaction of bicyclobutane with organoboranes may be thought to occur along three pathways:



the first of these, i.e. the addition of organoboranes to the central bond C_1-C_3, is probably unlikely since the resulting cyclobutylboranes (XI) are stable nearly up to 100° 12), and cannot give III under the used conditions. In our opinion, the second route is most likely. In this case the reaction occurs with cleavage of the side bond C_1-C_2 in I, organoboron fragment adding to C_2, and R - to C_1. That leads to cyclopropylmethyl derivatives of boron (VIII). The latter are unstable and must rearrange rapidly to form the mixture of butenyl compounds III and VII. A simple calculation shows that the energy of breaking of $C_1-C_{2'}$ bond (according to the second pathway, VIII   III) is at least 2-3 kcal/mole less than that of $C_1-C_{3'}$ bond (VIII ⟶ VII). An attempt to detect the intermediate compound VIII by carrying out the reaction directly within a NMR-spectrometer tube resulted in failure: even at -60^{o} the only reaction product was compound III. Thus it is not possible to eliminate the third pathway completely. This route involves simultaneous breaking of C_1-C_2 and C_1-C_3 bonds of bicyclobutane and addition of both boron and alkyl fragments to the same C_1 atom (Xc).

Although the data reported herein do not permit to elucidate a correct mechanism of the reaction of bicyclobutane with organoboranes, it is possible to claim with certainty that the breaking of the bicyclic system involves either the side bond cleavage only (scheme 2), or simultaneous breaking of both the central and the side bonds (scheme 3).

For all compounds described correct elemental analyses were obtained. IR and PMR spectra of these compounds are in good agreement with their structures. Moreover, the structure of carbinol IX was confirmed by means of double proton-proton resonance.

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