Tetrahedron Letters No. 45, pp 4627 - 4632, 1972. Pergamon Press. Printed in Great Britain.

REACTION OF TRIALKYLBORANES WITH 1-METHYLCYCLOPROPENE: A NEW METHOD FOR INTRODUCING OF THE METHALLYL FRAGMENT INTO THE CARBON CHAIN OF OLEFINS AND ALKYL HALIDES

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(Received in UK 25 September 1972; accepted for publication 4 October 1972)

It has been already shown that triallyl- and tricrotylborane react with 1-methylcyclopropene along two directions (A and B), the first of which (A) is cis-addition of the allyl and boryl fragments of the allylborane molecule to the double bond of cyclopropene. It has been also shown that the cis-addition occurs with allyl rearrangement [1,2]. The second direction (B) was described by only one example, namely by the reaction of triallylborane with 1-methylcyclopropene [1,2]. This reaction involves the cleavage of the ordinary C_2-C_3 bond of the cyclopropene ring and formation of the compound in which allyl radical is attached to C_2 and boryl fragment - to C_3 atom. As it was shown in the subsequent investigation [2] the scission of the C_2-C_3 bond occurs without the allyl rearrangement.* Thus, 1-butene, dimethoxyborane (II, 80-85%) and 2-methyl-1,5-heptadiene (III, 10-15%) were obtained from the products of reaction between tricrotylborane and 1-methylcyclopropene after alcoholysis which included the allyl rearrangement [1,2]. Diene III is the mixture of cis- and trans-isomers (the ratio is 25:75), i.e. the diene keeps the stereochemistry of crotyl radicals of the initial borane (in the latter, by nmr data [3], this ratio is nearly equal 30:70).

In the light of all mentioned above it was rather interesting to study reaction of cyclopropenes with trialkylboranes. Since the latter cannot add to acetylenes [4] and olefins [5,6], it was to be expected that trialkylbo-

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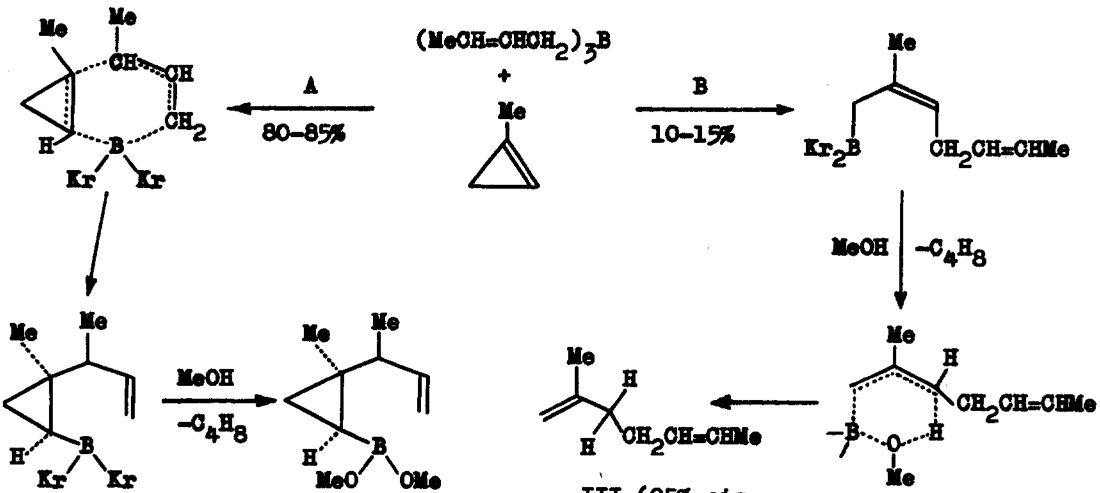
*It is for the first time that the reaction of allylboranes occuring without the allyl rearrangement is described.



I

II

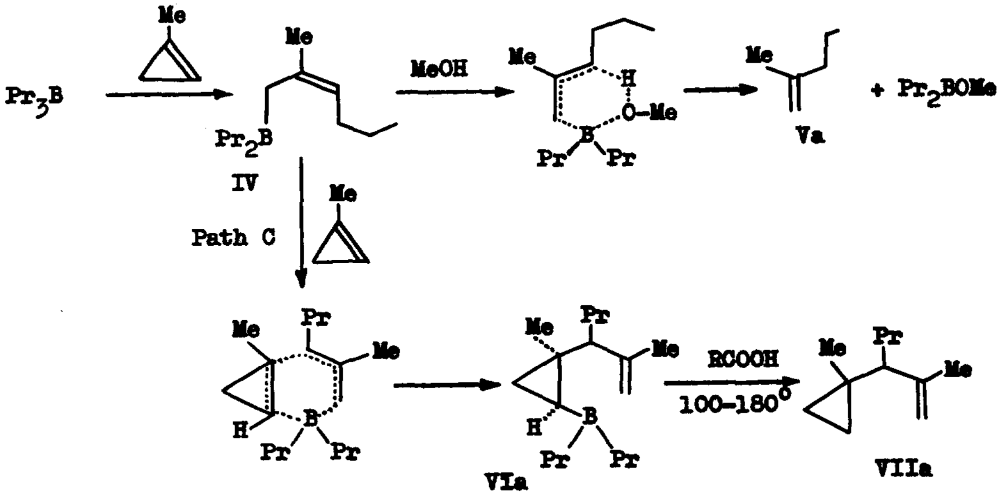
III (25% cis
75% trans)

Kr = $MeCH{=}CHCH_2$

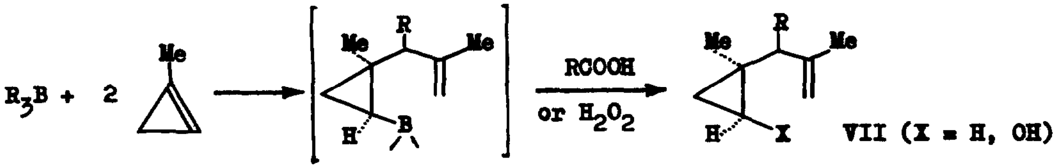
ranes would react with cyclopropenes only by means of cleavage of the ordinary bond C_2-C_3 of the latter (the direction B). It turned out that the reaction between tri-n.-propylborane and 1-methylcyclopropene was exothermic at -50 -20° and resulted in di-n.-propyl(2-methylhex-2-en-1-yl)borane (IV). However, duting the first run the yield of hydrocarbon Va (after methanolysis) did not exceed 15%. The low yield of Va is clearly explained by the fact that the compound IV, which is an allyl type borane, reacts with 1-methylcyclopropene more rapidly than the initial tripropylborane and results in the compound VIa.

The reaction of tri-n.-propylborane with 1-methylcyclopropene in the ratio 1:2 (without any solvent) afforded a cyclopropyl derivative which gave rise, on heating with stearic acid, to hydrocarbon VIIa in 50% yield, b.p. 45-45.5°/7 mm, n_D^{20} 1.4550; M 152 (mass-spectr.); PMR ($CHCl_3$, TMS, $\delta=0$): 0.10-0.42 (m, $\overset{\frown}{CH_2-CH_2}$, 4H), 0.80 ($CH_3-\triangleleft$), 1.69 ($CH_3-C{=}$), 4.59, 4.73 ($CH_2{=}C$, 2H).

Thus, the reaction between trialkylboranes and 1-methylcyclopropene in the ratio 1:2 may be regarded as a method for preparation of cyclopropane derivatives of type VII containing an alkyl radical R in α-position to the double bond (the Scheme 3).



Scheme 3



It is well known that trialkylboranes are not able to react with alkohols if the temperature is below 150°[7], while the allyl derivatives of boron are easily splittered by alkohols at 0–60° [1,2]. So, for the purpose of inhibiting the reaction along the pathway C and increasing of the yield of olefin V, we have carried out a series of reactions between trialkylboranes and 1-methylcyclopropene in an excess of alcohol (methanol or butanol). In this case the intermediate compound (VIII) reacts immediately after formation with an alcohol, and as a result olefin of type V is formed (allyl rearrangement takes place during the alcoholysis). The yield is 60–98%, with respect to one B–C bond of the initial trialkylborane.

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