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A METHOD FOR PREPARATION OF 1,4-DIENES VIA ALLYLBORATION OF VINYL ETHERS

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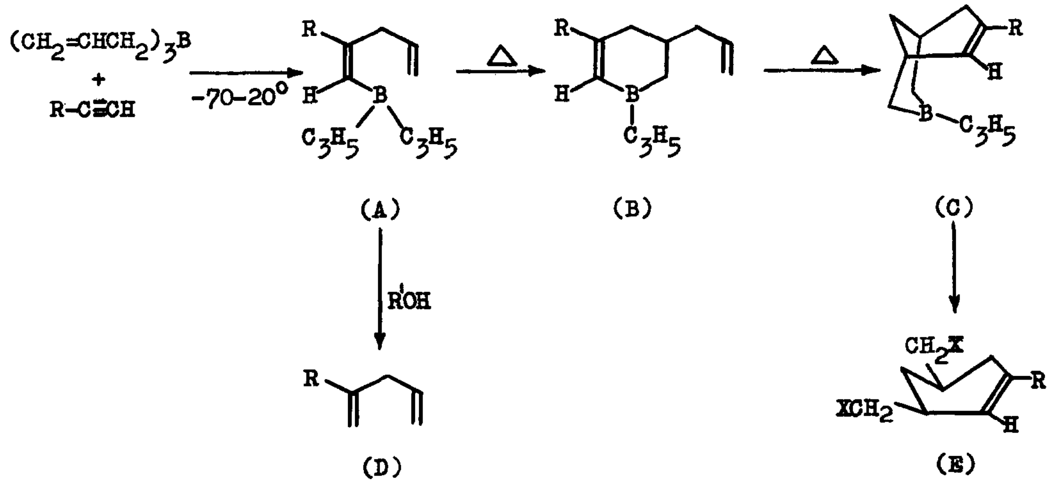
The reaction of allylboranes with acetylene and its derivatives was earlier shown to proceed through three consequent stages[1-6] and to lead to derivatives of pentadienylborane (A) and 1-boracyclohex-2-ene (B) or to the bicyclic compounds (C) depending on the conditions of the reaction, e.g.

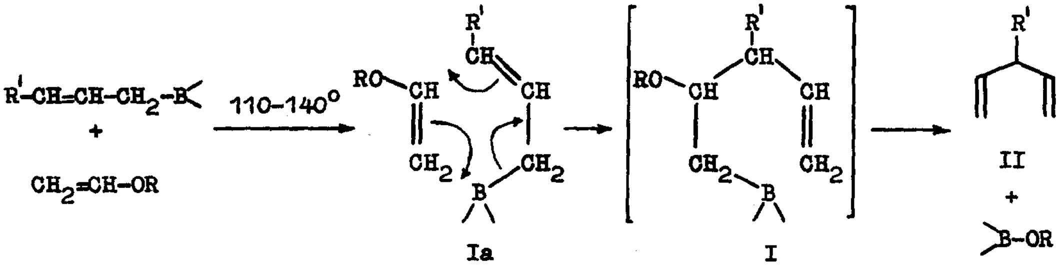


R = H, D, Alkyl, Aryl, R'O, Me_3Si, etc.
C_3H_5 = Allyl; X = H, OH

The first stage of this reaction, called "allylboron-acetylene condensation", is a cis-addition of the allyl and allylboron fragments of the allylborane molecule to the triple bond of the acetylene. The addition occurs with allylic rearrangement[4]. The products of the condensation were used to obtain different classes of organic compounds, such as penta-1,4-dienes of type D[4,6], unsaturated diols and alcohols, levulinic acid derivatives, cis-3,5-disubstituted cyclohexenes of type E[1-3], etc.

In the course of our subsequent research we found allylboranes to be able to react with activated olefins. Thus, as a result of the interaction of allylboranes and vinyl ethers 1,4-dienic compounds are formed.

On heating triallylborane with butyl vinyl ether at 110-140°C penta-1,4-diene is obtained (IIa, b.p.26-27°C, n_D^{20} 1.3839), the yield being more than 80%(per two boron-allyl bonds of the initial borane).



$R = C_2H_5$, $n\text{-}C_4H_9$; IIa, $R' = H$ (80%)

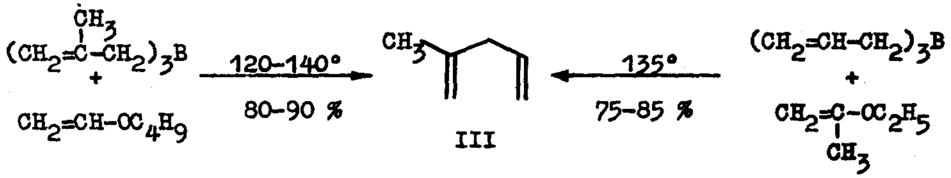
IIb, $R' = CH_3$ (50%)

At first the addition of the allyl and allylboron fragments to the double carbon-carbon bond seems to be realized to yield 2-alkoxypent-4-enyl-1-borane (I) which gives diene IIa as a result of the β-elimination of a B-OR-fragment. This type of β-elimination reaction has been observed in the hydroboration of vinyl alkyl ethers[7].

The reaction of tri(2-butenyl)borane[8] with butyl vinyl ether affords 3-methylpenta-1,4-diene (IIb, b.p. 51-52°C at 734 mm, n_D^{22} 1.3968), the formation of which shows that a rearrangement of allylic type (probably through cyclic electron transfer, Ia) takes place in this process.

Since only two B-C bonds take part in the above reactions the ratio of vinyl ether to borane must be 1-2:1. The preparation of the compounds II is conveniently carried out in a distillation flask equipped with a Hempel column, butyl vinyl ether being added to allylborane at 120-135°C. The diene II thus obtained distilled off into the receiver. When using the low boiling ethyl vinyl ether, the reaction should be conducted in a tube or an autoclave.

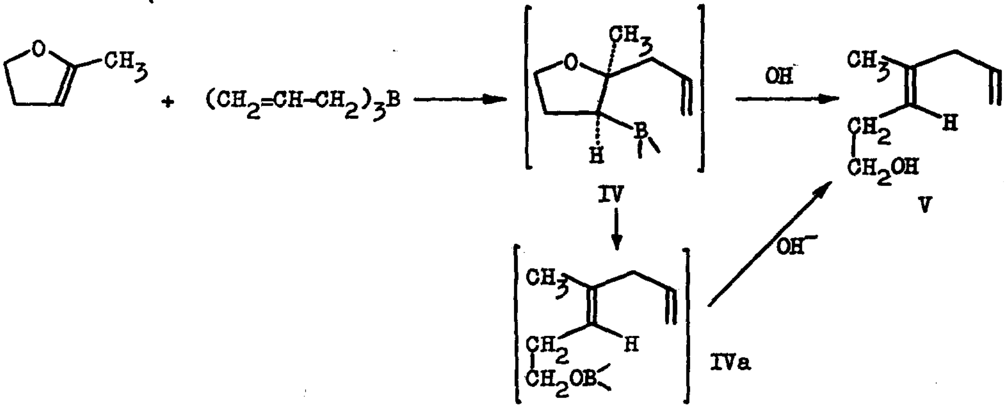
2-Methylpenta-1,4-diene (III, b.p. 57.5-58°C, n_D^{21} 1.4065) is obtained similarly from butyl vinyl ether and trimethallylborane as well as by the interaction of triallylborane and isopropenyl ethyl ether (the ratio 1.5:1, a sealed tube, 135-140°C, 5 hrs, yield 75-85%).



In the latter case diene III is separated from the unreacted isopropenyl ethyl ether by shaking with 3% hydrochloric acid.

The described procedure permits one to obtain pure 1,4-dienes since no isomers were observed in all cases studied.

The reaction of triallylborane with 4,5-dihydrosilvan proceeds smoothly even at room temperature (for about 2 days), while at 80-100°C it is completed within minutes. Alkaline hydrolysis of the products (IV or IVa) gives pure 4-methylhepta-3,6-dien-1-ol (V, yield 75-80%, b.p. 78-79°C at 9 mm, n_D^{20} 1.4661, d_4^{20} 0.8781).



The PMR spectrum (TMS, δ=0, ppm, 50% solution in CCl_4): 1.66 (d, J=1.5 cps, 3 H, CH_3), 2.20 (q - two triplets, J=7 cps, 2 H, $=C-CH_2-C$), 2.77 (d, J=7cps, 2 H, $=C-CH_2-C=$), 3.50 (t, J=7 cps, 2 H, $-CH_2-O$), 4.64 (s, 1 H, OH), 4.78-5.40 (m, 3 H, $CH_2=C$, $C-CH=C\lessgtr^{C}_{C}$), 5.40-6.18 (m,1 H, C=CH).

Hence the reaction of allylboranes with open-chain and cyclic vinyl ethers represents a convenient method for the synthesis of 1,4-dienes and their functional derivatives.

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