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SYNTHESIS OF ORGANOBORANES VIA ORGANOALUMINUMS. A CONVENIENT ROUTE TO TRIALKENYLBORANES FROM NONCONJUGATED DIOLEFINS

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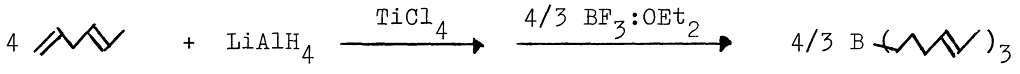
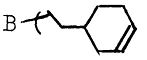
Hydroalumination of olefins followed by treatment with boron trifluoride etherate provides a convenient and selective method for the preparation of organoboranes.
Trialkenylboranes are obtained in excellent yields from nonconjugated diolefins.

Diborane usually doubly metalates diolefins so that it is not possible to prepare trialkenylborane by the usual hydroboration.[1] Recently it was shown that hydroalumination of nonconjugated diolefins with $LiAlH_4$ proceeds readily in the presence of $TiCl_4$ as a catalyst to give lithium tetraalkenylaluminums in which aluminum is connected to the less hindered C=C bond of the diolefin.[2] Also trialkylaluminums were shown to react with boron trifluoride etherate or borate esters under mild conditions to give the corresponding trialkylboranes in excellent yields.[3] Therefore, hydroalumination of diolefins followed by treatment with $BF_3:OEt_2$ appeared to be a promising route to trialkenylboranes. This procedure has in fact proved quite satisfactory.

Preparation of trialkenylborane was accomplished as follows. 1,4-Hexadiene (2.6 g, 32 mmol) and $TiCl_4$ (86 mg, 0.45 mmol) were added to a clear solution of $LiAlH_4$ in THF (30 ml of 0.26 molar, 7.8 mmol) under nitrogen atmosphere. After 12 hours at room temperature, $BF_3:OEt_2$ (1.6 g, 11 mmol) was added and the reaction mixture was then heated under reflux for 5 hours. Oxidation of the resulting organoborane by alkaline hydrogen peroxide produced 4-hexen-1-ol in 88% yield from 1,4-hexadiene (GLC analysis).[4]



Similarly B)$_3$ and B)$_3$ were obtained from 4-vinyl-1-cyclohexene and 2-methyl-1,5-hexadiene, respectively, in excellent yields. (see Table 1).

This one-pot synthesis of trialkenylboranes may have a wide applicability in organic syntheses, as organoboranes of the type BR_3 undergo many interesting reactions.[5]

α,ω-Dialuminoalkanes formed preferentially from the dihydroalumination of α,ω-dienes,[6] on treatment with $BF_3:OEt_2$ also gave organoboranes in which boron atoms are attached to the terminal carbon atoms of the dienes.

Some selective hydroboration reagents, such as disiamylborane or 9-BBN, have been explored. The results summarized in Table 1 show that the regioselectivity of these reactions is as high as that of the hydroboration reaction using disiamylborane as the reagent.[7)]

Table 1. PRODUCTS OF OXIDATION WITH ALKALINE HYDROGEN PEROXIDE AFTER TRANSMETALLATION TO BORON

Diolefin	Product distribution[a]	Yield[b] %
1,4-Hexadiene	4-Hexen-1-ol	88
2-Methyl-1,5-hexadiene	5-Methyl-5-hexen-1-ol	92
4-Vinyl-1-cyclohexene	2-(3-Cyclohexenyl)ethanol	86
1,4-Pentadiene[c]	1,4-Pentanediol (24%) 1,5-Pentanediol (76%)	84
1,5-Hexadiene[d]	1,5-Hexanediol (11%) 1,6-Hexanediol (89%)	92
1,7-Octadiene	1,7-Octanediol (9%) 1,8-Octanediol (91%)	64

[a] Identified by GLC and ^{1}H NMR. [b] GLC analysis and based on diolefin. [c] Hydroboration with BH_3 afforded 62% of 1,4- and 38% of 1,5-pentanediol,[1)] while hydroboration with disiamylborane gave 15% of 1,4- and 85% of 1,5-pentanediol.[7)] [d] Hydroboration with disiamylborane gave 93% of 1,6-hexanediol with 7% of other diols.[7)]

In conclusion, the sequence of hydroalumination of olefins followed by treatment with BF_3:OEt_2 provides a convenient and selective method for the preparation of organoboranes.

References and notes

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2) F. Sato, S. Sato, and M. Sato, J. Organometal. Chem., 131, C26 (1977).
3) K. Ziegler, in H. Zeiss (Ed.), " Organometallic Chemistry ", Reinhold Publishing Corp., New York, 1960, p. 244-246, and references cited therein.
4) Conversion of organoboranes into alcohols by oxidation with alkaline hydrogen peroxide is usually applied to determine their structures; see ref. 5. Oxidation with alkaline hydrogen peroxide of the reaction products of $LiAlH_4$ with 1,4-hexadiene gave 4-hexen-1-ol in only 5-8% yield.
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