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Preliminary communication

THERMALLY STABLE α-METHYLALLYLBORANES

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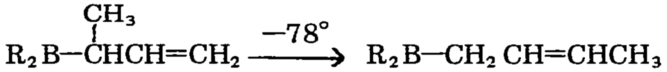
Summary

Syntheses are described for but-1-en-3-ylbis(dimethylamino)borane and but-1-en-3-yl(dimethylamino)methoxyborane, the first α-methylallylboranes inert to thermal allylic rearrangement at ambient temperatures.

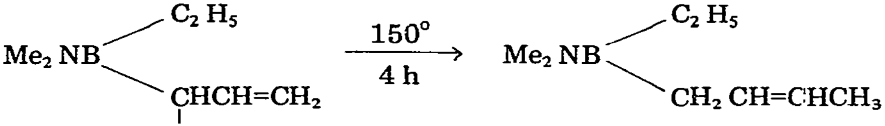
A recent review [1] has documented the broad synthetic applicability of allylboranes, but has also noted the limitations caused by high thermal reactivity with respect to allylic rearrangement. The unusually high degree of thermal instability is measured by the minimal (10-11 kcal·mol^{-1}) activation energies determined for "permanent allylic rearrangement" of triallylboranes [1] and by observations that α-methylallyldialkylboranes (I) rearrange spontaneously to the crotyl isomers (II) even at —78° [2]. We recently reported the synthesis and reorganization kinetics of but-1-en-3-yl(dimethylamino)ethylborane (III),



$$R_2B{-}\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2 \xrightarrow{-78^\circ} R_2B{-}CH_2CH{=}CHCH_3$$

(I) (II)

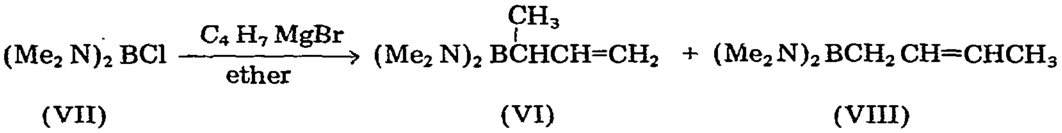
for which rearrangement to the but-2-en-1-yl isomer (IV) was sufficiently inhibited to allow III a chemically useful, but still limited half-life of 62 h at 100°, and ca. 2 months at room temperature [3]. The only other report of even a somewhat stable α-methylallylborane had been the di-n-hexyl butenylboronates (V), formed as a 77/23 inseparable mixture of but-1-en-3-yl and but-2-en-1-yl isomers, in which the α-methylallyl isomer rearranged completely over several weeks to the crotyl isomer [4].



(III) (IV)

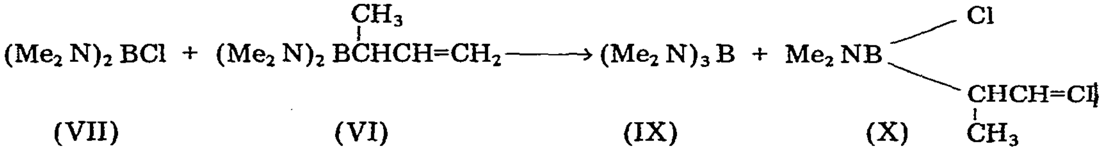
We have subsequently prepared two substituted α-methylallylboranes which, when carefully purified, appear to have indefinite shelf life at room temperature (no isomerization over five months) and cannot be thermally isomerized readily even near their boiling points.

But-1-en-3-ylbis(dimethylamino)borane (VI) was prepared by treatment of bis(dimethylamino)chloroborane (VII) [5] with the Grignard reagent from 1-bromo 2-butene [6]. The reaction yielded VI and the but-2-en-1-yl isomer VIII in an 84/16 ratio:



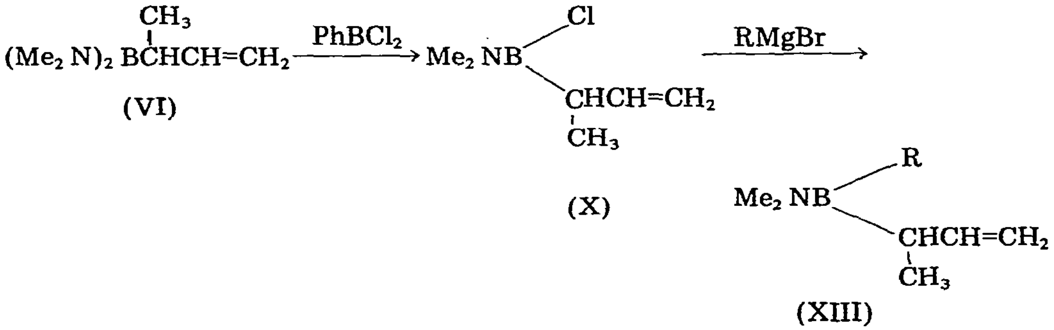
$$\underset{\text{(VII)}}{(Me_2N)_2BCl} \xrightarrow[\text{ether}]{C_4H_7MgBr} \underset{\text{(VI)}}{(Me_2N)_2B\overset{\overset{CH_3}{|}}{C}HCH{=}CH_2} + \underset{\text{(VIII)}}{(Me_2N)_2BCH_2CH{=}CHCH_3}$$

Spinning-band distillation allowed separation of pure (99+%) VI, b.p. 89° (48 mm)*, but VIII could not be quantitatively removed from a high-boiling impurity. Tris(dimethylamino)borane (IX) and but-1-en-3-yl(dimethylamino)-chloroborane (X) were the major side-products, shown to arise from disproportionation of VII and VI. Similar disproportionations occur in closely analogous systems[5,7].



$$\underset{\text{(VII)}}{(Me_2N)_2BCl} + \underset{\text{(VI)}}{(Me_2N)_2B\overset{\overset{CH_3}{|}}{C}HCH{=}CH_2} \longrightarrow \underset{\text{(IX)}}{(Me_2N)_3B} + \underset{\text{(X)}}{Me_2NB}\begin{matrix} Cl \\ \underset{\underset{CH_3}{|}}{C}HCH{=}C \end{matrix}$$

The increased synthetic utility accompanying inertness towards thermal allylic reorganization is illustrated by the fact that isomerically pure VI can be treated with one equivalent of either phenylboron dichloride (XI) or chloro(dimethylamino)phenylborane (XII) to give isomerically pure X without rearrangement of the allyl function. Grignard coupling of X according to the general



$$\underset{\text{(VI)}}{(Me_2N)_2B\overset{\overset{CH_3}{|}}{C}HCH{=}CH_2} \xrightarrow{PhBCl_2} \underset{\text{(X)}}{Me_2NB}\begin{matrix} Cl \\ \underset{\underset{CH_3}{|}}{C}HCH{=}CH_2 \end{matrix} \xrightarrow{RMgBr} \underset{\text{(XIII)}}{Me_2NB}\begin{matrix} R \\ \underset{\underset{CH_3}{|}}{C}HCH{=}CH_2 \end{matrix}$$

method of Niedenzu and Dawson [8] can then be used to generate a variety of alkyl-substituted (amino)-α-methylallylboranes (XIII) of high isomeric purity,

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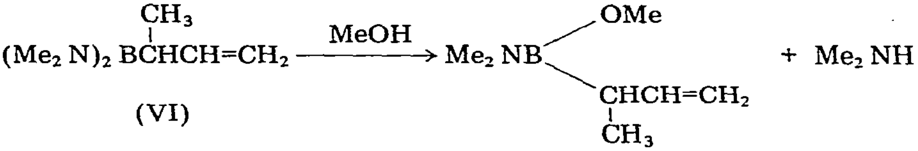
* Satisfactory elemental analyses and spectral data were obtained for new compounds.

while bypassing less satisfactory alternative synthetic routes involving, for example, pyrophoric alkylboranes.

Bis(dimethylamino)but-1-en-3-ylborane (VI) is stable even at 200°. At 225° some isomerization of VI to VIII is detected, but with accompanying decomposition. With added magnesium chloride or zinc chloride [3,4] allylic rearrangement of VI to VIII is catalyzed. Magnesium chloride (10% by weight) proved the milder, but more satisfactory catalyst, causing 13% VI → VIII isomerization in 24 h at 170°. Under comparable conditions, 10% zinc chloride caused total isomerization, but with accompanying decomposition (to IX among other products).

Treatment of VI with one equivalent of anhydrous methanol [9] yielded the second extraordinarily stable allylborane, but-1-en-3-yl(dimethylamino)-methoxyborane (XIV), b.p. 60—63° (25 mm), in 90% yield, isomerically pure. Thus methanolysis causes no allylic rearrangement.



$$(Me_2N)_2\underset{(VI)}{B\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2} \xrightarrow{MeOH} Me_2NB\begin{cases} OMe \\ \underset{CH_3}{\underset{|}{C}}HCH{=}CH_2 \end{cases} + Me_2NH$$

(VI)

(XIV)

Attempts to isomerize XIV, either neat or in n-dodecane solution, failed up to 150°. At 170°, slow reorganization gave 1—2% of the crotyl isomer after 24 h. As with VI, isomerization of XIV could be catalyzed by addition of anhydrous magnesium or zinc chlorides; the latter was more effective, but also induced decomposition.

Allyl(amino)boranes VI and XIV represent the only known examples of α-substituted, terminal-olefin allylboranes which are completely stable to allylic rearrangement at laboratory temperatures, and thus appear to constitute a useful pair of synthetic intermediates. Further synthetic applications of these stable allylboranes are under development.

Acknowledgment

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