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Preliminary communication

A STEREOSELECTIVE SYNTHESIS OF *cis*-ALKENYLBORANES

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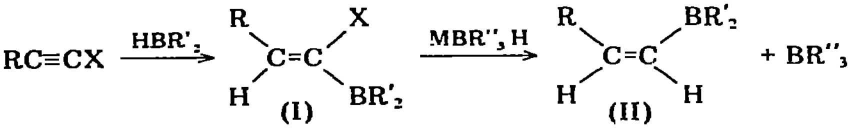
Summary

The reaction of 1-halo-1-alkynes with dialkylboranes followed by treatment with either lithium triethylborohydride or potassium tri-s-butylborohydride produces *cis*-alkenylboranes in high yields in a highly stereoselective manner.

The *cis* nature of hydroboration [1] permits the ready formation of alkenylboranes in which the boron atom and the vicinal alkyl group are *trans* to each other. Using such stereochemically defined alkenylboranes, a number of unique olefin syntheses have been developed which provide stereoselective routes to monoolefins [2], α,β-unsaturated carbonyl derivatives [3], vinyl halides [2a,4], alkenylmercury derivatives [5], conjugated dienes and enynes [6] and cumulenes [7]. However, the lack of convenient procedures for the synthesis of *cis*-alkenylboranes has considerably restricted their synthetic applicability.

We have found that the reaction of 1-halo-1-alkenylboranes (I) with either lithium triethylborohydride or potassium tri-s-butylborohydride* produces the desired *cis*-alkenylboranes (II) in high yields (eqn. 1).



(1)

R, R', R'' = alkyl, X = halogen, M = Li or K

The experimental procedure is quite simple as exemplified by the following preparation of *cis*-1-hexenylbis(3-methyl-2-butyl)borane (III). To a dry, nitrogen-flushed 300-ml flask equipped with a septum inlet, a magnetic stirring bar and a mercury-sealed outlet were introduced sequentially borane

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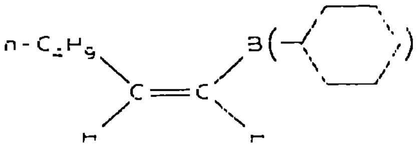
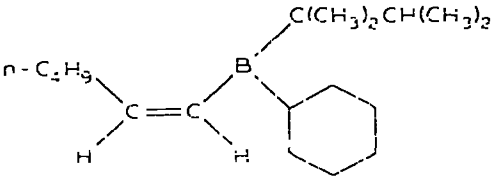
[*] Available from Aldrich Chemical Co., Milwaukee, Wisconsin. For a review on these compounds, see ref. 8.

in THF (2.56 *M*, 19.6 ml, 50 mmol), 2-methyl-2-butene (7.0 g, 100 mmol, 0°, 1 h), freshly distilled 1-iodo-1-hexyne (10.4 g, 50 mmol, 0°, 1 h) and lithium triethylborohydride in THF (1.09 *M*, 46 ml, 50 mmol, −25° then warmed to 25° over 1 h). Triethylborane[*] and THF were evaporated in vacuo, and the residue was extracted with petroleum ether. Evaporation of the petroleum ether produced III: NMR (CCl_4, TMS) δ 0.7-1.15 (m, ca. 21H), 1.15-2.4 (m, ca. 10H) and 5.85-6.05 (m, ca. 2H) ppm. The yield by NMR using benzene as an internal standard was 91%. The essential absence (< 2-3%) of the *trans* isomer was established by the comparison of the NMR data with those of the *trans* isomer obtained by the reaction of 1-hexyne with bis(3-methyl-2-butyl)borane which exhibited an entirely different pattern in the olefinic region [NMR (CCl_4, TMS) δ 0.7-1.15 (m, 21H), 1.15-2.5 (m, 10H), 6.25 (d, 1H, J = 18 Hz), 6.5-7.15 (dt, 1H, J = 18 and 6Hz) ppm]. The stereochemical results are consistent with the intramolecular migration of hydrogen from boron to carbon with inversion of configuration at the sp^2 hybridized α carbon center, analogous to the previously observed alkyl migration [2]. After oxidation of a sample of III with sodium hydroxide and 30% hydrogen peroxide, GLC examination[**] indicated the formation of 3-methyl-2-butanol (95% yield) and only a very minor amount (2% yield) of 2,3-dimethyl-4-nonanone which can be formed via the competitive alkyl transfer. This indicates that the migratory aptitude of the hydridic hydrogen relative to that of the 3-methyl-2-butyl group, after correction for the statistical factor, is ca. 100.

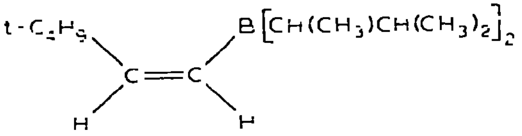
Quite analogously, IV-VI were obtained in 80-95% yields.



(IV)



(V)



(VI)

Although potassium tri-s-butylborohydride reacts similarly, the ease of removal of triethylborane makes lithium triethylborohydride the reagent of choice. Saline hydrides such as lithium hydride and potassium hydride are not

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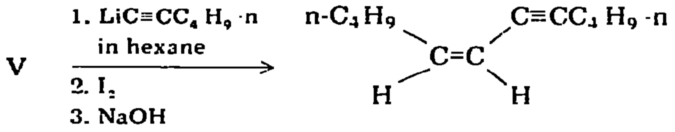
[*] Triethylborane is pyrophoric. The trapped solution containing triethylborane must therefore be treated with due caution.

[**] Hexanal, which was formed as one of the main products, was not analyzed quantitatively by GLC.

satisfactory, producing *cis*-alkenylboranes in much lower yields at much slower rates over the temperature range of −25 to 65°.

The removal of the trialkylborane by-product and the inorganic salt may be omitted in many cases in which the *cis*-alkenylboranes are used as synthetic intermediates. For example, a 10-mmol aliquot of the solution containing III obtained as described above was treated with 6 *N* sodium hydroxide (6.8 ml, 40 mmol), and iodine dissolved in THF was added until the brown color of iodine began persisting for several minutes (ca. 27 mmol). GLC examination indicated the formation of *trans*-2,3-dimethyl-4-nonene* in 82% yield (stereoisomeric purity ⩾ 98%). Unlike the previously developed *trans*-olefin synthesis via 1-halo-1-alkenylboranes [2], the procedure reported here does not involve protonolysis of organoboranes with carboxylic acids at high temperatures and should be capable of accommodating various acid-sensitive functional groups.

A unique synthetic application of *cis*-alkenylboranes is their conversion to conjugated *cis*-enynes. In a manner analogous to the synthesis of conjugated *trans*-enynes [6b], V was converted in a highly stereospecific manner to *cis*-5,7-dodecenyne* in 51% yield (eqn. 2).



(2)

> 98% *cis*

Use of III or IV in place of V resulted in the formation of the *cis*-enyne in lower yields.

Acknowledgment

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[*] Identified by comparing spectral and chromatographic behavior with those of an authentic sample.