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## A Convenient Stereoselective Synthesis of Substituted Alkenes *via* Hydroboration–Iodination of Alkynes[1]

*Sir:*

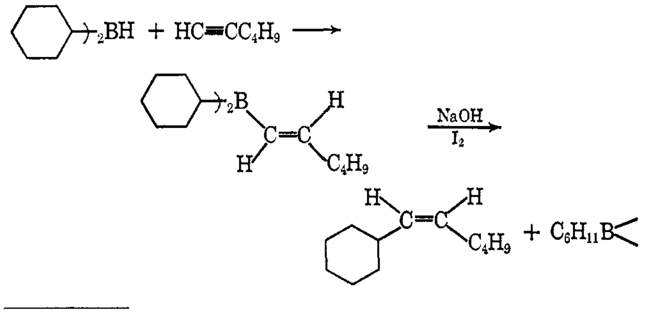
The addition of bromine to vinylboronic esters results in the formation of 1,2-dibromoalkaneboronic esters. These may be converted to vinyl bromides by treatment with water or sodium hydroxide.[2] Matteson and Liedtke[3] have suggested that bromine adds *trans* to the vinylboronic esters. Also, they have established that the deboronobromination involves a stereospecific *trans* elimination. In concurrence with these results, Brown and Bowman[4] have reported that bromination of the vinylborane derived from hydroboration of 1-hexyne with bis(3-methyl-2-butyl)borane yields *cis*-1-bromo-1-hexene on work-up.

**Table I.** Conversion of Vinylboranes into Olefins by Iodine in the Presence of Sodium Hydroxide

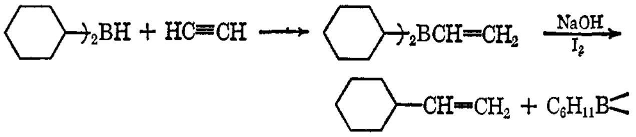
| Vinylborane derived from | Olefin produced (isomeric purity, %[a]) | Yield, %[b] |
|---|---|---|
| $(C_6H_{11})_2BH$ + acetylene | Vinylcyclohexane | 83[c] |
| + 1-hexyne | *cis*-1-Cyclohexyl-1-hexene (99) | 75 |
| + cyclohexylacetylene | *cis*-1,2-Dicyclohexylethylene (92) | 77 |
| + 3-hexyne | 3-Cyclohexyl-3-hexene[d] | 85 |
| $((CH_3)_2CHCHCH_3)_2BH$ + 1-hexyne | *cis*-2,3-Dimethyl-4-nonene (98) | 63 |

[a] The analytical and spectral data for each of these products are consistent with their structures. [b] The yields are based on the theoretical production of 1 mole of olefin from 1 mole of dialkylborane. [c] By glpc analysis. [d] The configuration of this olefin has not been established.

We now wish to report that iodination of vinylboranes does not afford the corresponding vinyl iodides, but results in a transfer of one alkyl group from boron to the adjacent carbon to give high yields of substituted olefins. Thus, addition of iodine to the vinylborane derived from the hydroboration of 1-hexyne with dicyclohexylborane gives an 81% yield of *cis*-1-cyclohexyl-1-hexene with 92% isomeric purity. If sodium hydroxide is added prior to the iodination step, a 75% yield of pure *cis* olefin (99%) is obtained.



The hydroboration of acetylene with dicyclohexylborane in tetrahydrofuran proceeds readily to the vinylborane stage,[5] and iodination of this organoborane in the presence of sodium hydroxide produces 83% of vinylcyclohexane.



Finally, vinylboranes derived from the hydroboration of disubstituted alkynes with dialkylboranes may be converted by this procedure to trisubstituted olefins. The experimental results are summarized in Table I.

It is apparent that the utility of this reaction depends on the availability of the starting dialkylboranes.[6] Fortunately, most cyclic and many acyclic olefins are readily converted to substituted boranes.[7] Consequently, the iodination of vinylboranes offers a novel route for the introduction of olefinic side chains onto both cyclic and acyclic systems.

The following procedure for the synthesis of *cis*-1-cyclohexyl-1-hexene is representative. A solution of 4.1 g (50 mmoles) of cyclohexene in tetrahydrofuran (20 ml) was placed in a 100-ml flask equipped with a thermometer, a pressure-equalizing funnel, and a magnetic stirrer. The flask was immersed in an ice–water bath and hydroboration was achieved by the dropwise addition of 13.9 ml of a solution of borane (25 mmoles) in tetrahydrofuran. The precipitate formed ($R_2BH$) was stirred at 0–5° for 1 hr, and then the reaction mixture was diluted with 2.05 g of 1-hexyne (25 mmoles) in 10 ml of tetrahydrofuran while the temperature was maintained at 15–20°. After the precipitate had dissolved, the resulting solution was stirred for an additional 30 min at room temperature. To this mixture was then added at −10° 15 ml of 6 *N* sodium hydroxide, followed by the dropwise addition of a solution of iodine (6.35 g, 25 mmoles) in tetrahydrofuran (10 ml) over a period of 15 min. After the reaction mixture had warmed up to room temperature, any excess iodine was decomposed by adding a small amount of aqueous sodium thiosulfate. The olefin product was extracted into pentane and dried. Distillation gave 3.1 g of *cis*-1-cyclohexyl-1-hexene (75%), bp 44–45° (1 mm), $n^{20}$D 1.4586.

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[1] This research was supported by National Science Foundation Grant No. GP-6633.

[2] B. M. Mikhailov and P. M. Aronovich, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 927 (1961); *Chem. Abstr.*, **55**, 24541 (1961); D. S. Matteson and K. Peacock, *J. Org. Chem.*, **28**, 369 (1963); W. G. Woods and I. S. Bengelsdorf, *ibid.*, **31**, 2769 (1966).

[3] D. S. Matteson and J. D. Liedtke, *J. Am. Chem. Soc.*, **87**, 1526 (1965).

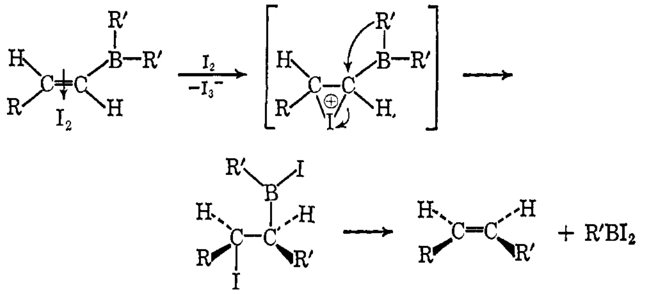
[4] H. C. Brown, private communication.

[5] H. Arzoumanian, unpublished results.

[6] We are currently exploring the possibility of using monoalkylboranes for the iodination reaction.

[7] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

Although our efforts were mainly directed toward the practical application of this novel reaction, we have also carried out a brief mechanistic investigation of the reaction of iodine with *trans*-1-hex-1-enyl-bis(dicyclohexyl)borane[8] in tetrahydrofuran in the absence of base. Ultraviolet examination of the vinylborane–iodine solution indicated that the halogen reacted rapidly with the organoborane. Likewise the strong infrared absorption band of the *trans* double bond (1604 cm$^{-1}$) disappeared on adding a stoichiometric amount of iodine. Finally, examination of the organoborane–iodine solution by nmr revealed that 1-cyclohexyl-1-hexene (92% *cis* and 8% *trans*) is formed during the iodine-addition step, and not during the work-up. The formation of the olefin from the iodoorganoborane may be rationalized in terms of an initial fast base or solvent-assisted migration of a cyclohexyl group from boron to the adjacent carbon. The intermediate $\beta$-iodoorganoborane then undergoes deboronoiodination to give the *cis* olefin. It should be noted that all of the reactions leading to the *cis* olefins must be stereoselective.[9]



Migrations of alkyl substituents from boron to the $\alpha$-carbon in $\alpha$-haloorganoboranes[10] and deboronohalogenation of $\beta$-haloorganoboranes[2,3] are well documented.

(8) Derived from the hydroboration of 1-hexyne with dicyclohexylborane.

(9) Several possible mechanistic variations not explicitly considered herein will be discussed in the full paper.

(10) D. S. Matteson and R. W. H. Mah, *J. Am. Chem. Soc.*, **85**, 2599 (1963); G. Köbrich and M. R. Merkle, *Angew. Chem. Intern. Ed. Engl.*, **6**, 74 (1967).

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## Mass Spectrometric Study of Tetrakis(trifluorophosphine)nickel(0)[1]

*Sir:*

Previous studies[2-4] of various transition metal carbonyls have indicated a consecutive unimolecular fragmentation of the parent-molecule ions formed upon electron impact. Because CO and $PF_3$ are rather different molecules, but yet bond to transition metals in similar fashion, we have initiated a mass spectrometric study of various $PF_3$-substituted metal carbonyls. We wish to report herein preliminary results of our studies of tetrakis(trifluorophosphine)nickel(0) that indicate several close similarities to the metal carbonyl systems and at least one significant difference.

Tetrakis(trifluorophosphine)nickel(0), $Ni(PF_3)_4$, was prepared approximately as described earlier.[5] About 2 g of $Ni(CO)_4$ was vacuum distilled into a 150-ml stainless-steel pressure vessel along with a quantity of purified[6] $PF_3$ adequate to yield a pressure of 300 psi at room temperature. The vessel was heated to 125–150° for 12 hr and then cooled to −195°, and the CO that was formed was removed by vacuum. This was continued through about four cycles until the amount of CO formed in the successive steps was approaching the point of diminishing return.

The product was a mixture of about 80% $Ni(PF_3)_4$ and 20% $Ni(CO)(PF_3)_3$ and no more than a trace of any of the other trifluorophosphinenickel carbonyl species. The tetraphosphine was isolated by preparative-scale gas–liquid chromatography using an Autoprep A-700 gas chromatograph. A 7.5 m × 0.25 in. column of 40% DC-702 silicone oil[7] on Kromat FB was used with helium as the carrier at a flow of about 60 cc/min. Temperatures of 25–40° were satisfactory using injections of about 30 $\mu$l. The product, which was trapped at −78°, was dried by vacuum distillation through a bed of 4A molecular sieves. The product was chromatographically pure when tested by glpc on an analytical scale and was found by low-voltage mass spectrometry to contain no discernible impurities.

The compound was introduced easily at room temperature to the ion source of the mass spectrometer. Operating pressures were about 2–5 × $10^{-6}$ torr. The 70-ev mass spectrum, appearance potentials, clastogram, and metastable transitions were determined with a time-of-flight mass spectrometer described previously.[8] The modifications made to this instrument for metastable transition studies and the data interpretation are reported elsewhere.[9] No thermal decomposition was noted in these studies, and no contamination of the source or detector components was found.

The 70-ev mass spectrum (monoisotopic) is given in Table I. This table also contains the appearance potentials determined by the energy compensation technique[10] with mercury (IP = 10.43 ev) as the calibrant. In these measurements, the nickel-58 isotope was used throughout.

A comparison of the relative abundances in Table I for the ions formed from tetrakis(trifluorophosphine)nickel(0) and those produced from $Ni(CO)_4$[2] indicates a significant similarity of these two molecules, although the $Ni(PF_3)_3^+$ and $Ni(PF_3)_4^+$ ions are much less abun-

(1) Taken in part from the M.S. thesis submitted by M. A. Krassoi to the Graduate School of Kansas State University, Manhattan, Kan.

(2) R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **3**, 699 (1964); **4**, 157 (1965); *J. Phys. Chem.*, **69**, 1618, 3198 (1965); *J. Organometal. Chem.* (Amsterdam), **4**, 190 (1965); *J. Chem. Phys.*, **44**, 1964 (1966).

(3) R. E. Winters and J. H. Collins, *J. Phys. Chem.*, **70**, 2057 (1966).

(4) A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, *Z. Physik. Chem.* (Frankfurt), **45**, 79 (1965); S. Pignataro, A. Foffani, F. Grasso, and B. Cantone, *ibid.*, **47**, 106 (1965); B. Cantone, F. Grasso, and S. Pignataro, *J. Chem. Phys.*, **44**, 3115 (1966); S. M. Schildcrout, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, **89**, 1617 (1967); and D. R. Bidinosti, and N. S. McIntyre, *Can. J. Chem.*, **45**, 641 (1967).

(5) R. J. Clark and E. O. Brimm, *Inorg. Chem.*, **4**, 651 (1965).

(6) R. J. Clark and P. I. Hoberman, *ibid.*, **4**, 1771 (1965).

(7) The high oil loading (calculated on the basis of dry support) is important. In contrast to the normal behavior, the resolution for many of these metal carbonyl–trifluorophosphine species decreases on going to loading lower than this.

(8) E. J. Gallegos and R. W. Kiser, *J. Am. Chem. Soc.*, **83**, 773 (1961); *J. Phys. Chem.*, **65**, 1177 (1961).

(9) D. L. Dugger and R. W. Kiser, submitted for publication.

(10) R. W. Kiser and E. J. Gallegos, *J. Phys. Chem.*, **66**, 947 (1962).