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The Reactions of (1-Halo-1-alkenyl)dialkylboranes with Lead(IV) Acetate or (Diacetoxyiodo)benzene. A Stereoselective Synthesis of 1-Halo-1,2-dialkylethylenes

Yuzuru Masuda, Akira Arase,* and Akira Suzuki**
Department of Applied Chemistry, Kitami Institute of Technology, Kitami 090
***Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060*
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The reaction of (1-halo-1-alkenyl)dialkylboranes with lead(IV) acetate or (diacetoxyiodo)benzene was studied. (1-Bromo-1-alkenyl)dialkylboranes gave 1-bromo-1,2-dialkylethylenes. When alkyl groups on the boron atom of vinylboranes were bulky or the reaction temperatures were low, *Z*-isomers were afforded, whereas when alkyl groups on the boron atom were small or the reaction temperatures were relatively high, *E*-isomers were afforded as the main products. (1-Chloro-1-alkenyl)dialkylboranes gave (*Z*)-1-chloro-1,2-dialkylethylenes regardless of the reaction conditions. (1-Iodo-1-alkenyl)dialkylboranes failed to give satisfactory yields of 1-iodo-1,2-dialkylethylenes.

The authors previously reported a stereospecifically defined synthesis of 1-bromo-1,2-dialkylethylenes by the reaction of (1-bromo-1-alkenyl)dialkylboranes with lead(IV) acetate (LTA) or (diacetoxyiodo)benzene (DIB).[1]

$$\mathrm{R_2BCBr{=}CHR'} \xrightarrow{\mathrm{Pb(OAc)_4\ or\ PhI(OAc)_2}} \mathrm{RCBr{=}CHR'}\ (Z\text{ or }E)$$

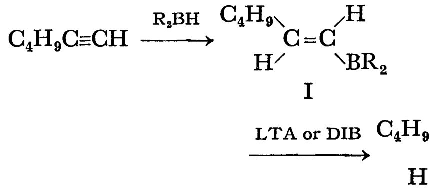
Alkenyl halides are potentially important compounds in organic synthesis because of their wide use as reaction intermediates for introduction of some substituents to alkenyl group *via* alkenylmagnesiums,[2] lithiums,[3] and coppers.[4] Several synthetic methods for alkenyl halide have hitherto been reported. Brown and his co-workers described a route to terminal and internal alkenyl halides from alkynes by the reaction of alkenyldialkylborane[4] and alkenylboronic ester[5] with molecular halogen. In these reactions, "anti-Markownikoff" addition of hydrogen halide to alkyne was realized. On the other hand the reaction reported by us,

$$\mathrm{RC{\equiv}CR'} \xrightarrow{\mathrm{HBR_2''}} \mathrm{RCH{=}CR'BR_2''} \xrightarrow{\mathrm{X_2}} \mathrm{RCH{=}CR'X}$$

involves a migration of an alkyl group from the boron atom to the alkenyl carbon atom. Thus the latter reaction has a great advantage in that the several types of internal alkenyl bromide can be synthesized almost arbitrarily by selecting the combination of starting alkyne and alkene. Thus in this report, more detailed studies including some related reactions are presented.

Results and Discussion

The reactions of organoborane with oxidizing agents at times give peculiar reaction products. Among those, the reaction with LTA or DIB is one of interesting classes, because in the reaction with such reagent, trialkylborane affords corresponding alkyl acetate,[6] whereas in the reaction of 1-alkenyldialkylborane (I) an intramolecular migration of one alkyl group from boron atom to the alkenyl carbon atom adjacent to the boron atom occurs to give a corresponding *E*-alkene (II) (Table 1).



IIa R=cyclohexyl
IIb R=1,2-dimethylpropyl

Although stereoselective syntheses of internal alkene from alkenyldialkylboranes have been achieved by Zweifel *et al.*,[7] Negishi *et al.*,[8] and Yatagai *et al.*,[9] these reactions are carried out under strong basic conditions. Consequently, they can not be used when organoboranes have alkyl groups sensitive to base. In contrast, there are no problems even for such organoboranes in the present reaction, because the reaction proceeds under almost neutral conditions. Further, our findings suggest the possibility that a combination of alkyl group with haloalkenyl group occurs by the reaction of (1-halo-1-alkenyl)dialkylboranes with above reagents.

Thus, 1-bromo-1-hexyne, readily prepared from 1-hexyne in a high yield,[10] was hydroborated by dicyclohexylborane or bis(1,2-dimethylpropyl)borane to (1-bromo-1-hexenyl)dialkylborane (III),[7a,8] and LTA or DIB was added to the reaction mixture. As was expected, (*Z*)-1-bromo-1-cyclohexyl-1-hexene (IVa) or 4-bromo-2,3-dimethyl-4-nonene (IVb) was obtained in a moderate yield with a high stereoselectivity (Table 2).

Table 1. Reaction[a] of 1-hexenyldialkylboranes with LTA or DIB

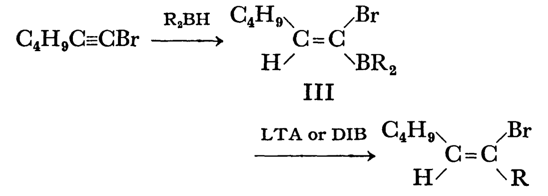
R	Reagent	Solvent	Product (*E* : *Z*)	Yield/%[b]
Cyclohexyl	DIB	$CHCl_3$	IIa (92 : 8)	60 (54)[c]
	LTA	C_6H_6	IIa (85 : 15)	45
1,2-Dimethylpropyl	LTA	CH_2Cl_2	IIb (93 : 7)	53 (50)[c]

a) Carried out at 0—25 °C for 4 h. Mole ratio; organoborane/reagent=1. b) Determined by GLPC based on BH_3 employed. c) Isolated by elution with hexane on silica-gel column.

Table 2. Reaction[a] of (1-bromo-1-hexenyl)dialkylboranes, derived from sterically hindered olefin, with LTA or DIB

R	Reagent	Solvent	Temp/°C	Time/h	Product (*Z* : *E*)	Yield/%[b]
Cyclohexyl	DIB	CH_2Cl_2	0	4	IVa (95 : 5)	55 (51)[c]
	DIB	CH_2Cl_2	−25	4	IVa (98 : 2)	58 (54)[c]
	LTA	CH_2Cl_2	−50	8	IVa (98 : 2)	43
1,2-Dimethylpropyl	DIB	CH_2Cl_2	−25	4	IVb (96 : 4)	42
	LTA	CH_2Cl_2	−50	8	IVb (98 : 2)	56 (50)[c]
	LTA	C_6H_6 n-C_6H_{14}	0	4	IVb (97 : 3)	40

a) Mole ratio; organoborane/reagent=1. b) Determined by GLPC based on BH_3 employed. c) Isolated by elution with hexane on silica-gel column.



III

IVa, R=cyclohexyl
IVb, R=1,2-dimethylpropyl

It is apparent that the utility of this reaction depends on the availability of the starting dialkylborane. However, dialkylboranes prepared by the simple hydroboration of alkenes with borane in THF is limitted to only sterically hindered olefins such as cyclohexene, 2-methyl-2-butene, and α-pinene.[11] Several methods for the general synthesis of dialkylboranes have been proposed.[12] However, they did not give satisfactory results in the present reaction, probably because of the complexity of the procedure or contaminations of some compounds which were liable to inhibit the reactions.

Accordingly, we employed another easier procedure for the synthesis of dialkylborane. Brown *et al.*[13] have reported that the reaction of 2 mol of 1-pentene and 1 mol of borane in THF at room temperature results in the formation of a mixture containing 63.3% of dipentylborane. Consequently, the introduction of a solution of such a hydroboration stage to our reaction

$$\underset{(1\text{ mol})}{BH_3} \xrightarrow[\text{THF}]{\text{1-pentene (2 mol)}} \underset{2.0\%}{BH_3} + \underset{22.0\%}{H_2BR} + \underset{63.3\%}{HBR_2} + \underset{12.7\%}{R_3B}$$

seemed togive corresponding alkenyl bromides. Actually, acceptably pure 1-bromo-1,2-dialkylethylenes (IVc, IVd, and IVe) were obtained in about 50—60% yields uncontaminated with by-products which obstructed the isolation of the alkenyl bromides in column chromatography. The results are summarized in Table 3.

$$2\ \alpha\text{-olefin} \xrightarrow[\text{THF}]{BH_3} \xrightarrow{C_4H_9C{\equiv}CBr} \xrightarrow{\text{LTA or DIB}} C_4H_9CH{=}CRBr$$

IVc, R=hexyl
IVd, R=octyl
IVe, R=2-methylpentyl

The most important feature in the results is the fact that stereospecifically defined bromoalkenes were obtained by merely controlling the reaction conditions, such as temperature and solvent, when LTA was employed. That is, (*Z*)-(1-bromo-1-hexenyl)dialkylborane, obtained *via* the hydroboration of 1-bromo-1-hexyne with dialkylborane, gave (*Z*)-6-bromododecene at −50 °C in dichloromethane, while the same organoborane gave *E*-isomer at 0 °C in a mixture of benzene and hexane (1: 1). Similar results were obtained when 1-octene and 2-methyl-1-pentene were employed as the starting alkene, suggesting the wide applicability of the

Table 3. Reaction of (1-bromo-1-hexenyl)dialkylboranes, derived from 1-alkyne, with LTA or DIB

R	Reagent[a]	Solvent	Temp/°C	Time/h	Product (*Z* : *E*)	Yield/%[b]
Hexyl[d]	DIB	CH_2Cl_2	0	4	IVc (48 : 52)	40
	DIB	CH_2Cl_2	−50	4	IVc (49 : 51)	10
	LTA	CH_2Cl_2	0	4	IVc (21 : 79)	36
	LTA	CH_2Cl_2	−50	4	IVc (96 : 4)	65 (56)[c]
	LTA	C_6H_6 n-C_6H_{14}	0	4	IVc (5 : 95)	55 (52)[c]
Octyl[d]	LTA	CH_2Cl_2	−50	4	IVd (97 : 3)	(54)[c]
	LTA	C_6H_6 n-C_6H_{14}	0	4	IVd (4 : 96)	(45)[c]
2-Methylpentyl[e]	LTA	CH_2Cl_2	−50	4	IVe (97 : 3)	54 (51)[c]
	LTA	C_6H_6 n-C_6H_{14}	0	4	IVe (10 : 90)	42 (35)[c]

a) Mole ratio; organoborane/reagent=1. b) Determined by GLPC based on BH_3 employed. c) Isolated by elution with hexane on silica-gel column. d) Carried out by using a following solution; 2×1-alkene+BH_3: THF $\xrightarrow{25\,^\circ\text{C, 24 h}}$ R_2BH (63%). e) Carried out by using a following solution; 2×2-methyl-1-pentene+BH_3: THF $\xrightarrow{0\,^\circ\text{C, 2 h}}$ (2-methylpentyl)$_2$BH (60—70%).

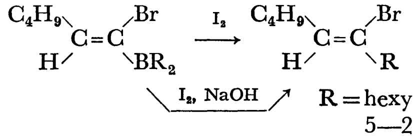
TABLE 4. REACTION OF (1-CHLORO-1-HEXENYL)DIALKYLBORANES WITH LTA OR DIB

R	Reagent[a]	Solvent	Temp/°C	Time/h	Product (Z : E)	Yield/%[b]
Cyclohexyl	DIB	CH_2Cl_2	−50—0	8	VIa (97 : 3)	55 (52)[c]
	LTA	CH_2Cl_2	−50	4	VIa (97 : 3)	48
1,2-Dimethyl propyl	LTA	CH_2Cl_2	−50—0	8	VIb (97 : 3)	42 (40)[c]
Hexyl	LTA	CH_2Cl_2	−50—0	8	VIc (97 : 3)	53 (51)[c]
	LTA	$\left[\begin{array}{l}C_6H_6\\ n\text{-}C_6H_{14}\end{array}\right.$	0	4	VIc (97 : 3)	31

a) Mol ratio; organoborane/reagent = 1. b) Determined by GLPC based on BH_3 employed. c) Isolated by elution with hexane on silica-gel column. d) Carried out by using a following solution: 2 × 1-hexene + BH_3 : THF $\xrightarrow{25\,°C,\ 24\,h}$ $(hexyl)_2BH$ (63%).

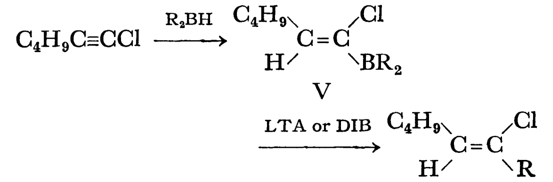
present reaction for the syntheses of several types of 1-bromo-1,2-dialkylethylene.

On the other hand, in the Zweifel reaction,[7] the migration of alkyl group from the boron atom of 1-alkenyldialkylborane to the alkenyl carbon atom adjacent to the boron atom with iodine under alkaline solutions, was applied on the same (1-bromo-1-hexenyl)-dialkylborane, but only a small amount of the corresponding Z-isomer was found to be obtained.



R = hexyl, yield, 5—28%

Then we undertook the reaction of (1-chloro-1-alkenyl)dialkylborane(V), obtained from 1-chloro-1-hexyne[14] and dialkylboranes, with LTA or DIB. The results are shown in Table 4. In all cases examined, corresponding (Z)-1-chloro-1,2-dialkylethylenes were afforded in moderate yields with high stereoselectivities. Unfortunately, E-isomers could not be obtained as predominant products, even by controlling the reaction conditions, such as temperature and solvent.



V

VIa, R = cyclohexyl
VIb, R = 1,2-dimethylpropyl
VIc, R = hexyl

(1-Iodo-1-hexenyl)dialkylborane failed to give satisfactory yields of 1-iodo-1,2-dialkylethylenes in the similar treatment with LTA. In these cases appreciable amounts of by-products, such as alkyl acetate and trisubstituted alkene, presumably formed by a migration of two alkyl groups, were contaminated.

$$C_4H_9C{\equiv}CI \xrightarrow{R_2BH} \xrightarrow{LTA} C_4H_9CH{=}CRI$$

R = cyclohexyl, VIIa, yield, 24%

$$+\ ROAc + C_4H_9CH{=}CR_2$$

25% 20%
(Z, 98%; E, 2%)

$$2\ C_4H_9CH{=}CH_2 \xrightarrow{BH_3} \xrightarrow{C_4H_9C\equiv CI} \xrightarrow{LTA} C_4H_9CH{=}CRI + ROAc$$

R = hexyl, VIIb, yield, 16% 30%
(Z, 15%; E, 85%)

The present reaction provides a new method for the stereoselective synthesis of (Z)- or (E)-1-bromo-1,2-dialkylethylene, and also of (Z)-1-chloro-1,2-dialkylethylene. It is interesting that sterically defined (Z)- or (E)-1-bromo-1,2-dialkylethylene is obtained by controlling the reaction conditions when LTA is used. The manner of the elimination of the dialkylboryl group from the carbon atom seems to influence the stereochemistry of the product. A further work involving such a mechanistic study is now under investigation.

Experimental

Instruments. IR spectra (film) were recorded by using a Hitachi-285 spectrometer. PMR (CCl_4, TMS) were run on a Hitachi R-20A spectrometer. Mass spectra were recorded by using a Hitachi M-52 mass spectrometer.

Reagents. Cyclohexene, 1-hexene, and 1-octene were distilled under argon stream after drying over lithium aluminium hydride. Commercial 2-methyl-2-butene, 2-methyl-1-pentene, and 1-hexyne were used without any purification. Solvents were purified by appropriate methods respectively and they were distilled before use. 1-Chloro-1-hexyne,[14] 1-bromo-1-hexyne,[10] and 1-iodo-1-hexyne[15] were prepared by the methods described in the literatures. Borane in THF,[11c] lead (IV) acetate,[16] above 98% purity,[17] and (diacetoxyiodo)benzene[18] were prepared by the methods described in the literatures.

Identification of the Products. E- and Z- isomers were isolated respectively from the reaction mixture by repeated applications on the column chromatography, and subjected to the analysis. They were identified by reference to literatures.[2,19]

1-Bromo-1-cyclohexyl-1-hexene (IVa). A 100-ml round bottomed flask, equipped with a gas inlet for argon, a sample inlet with a serum cap, a dropping funnel and a magnetic stirring bar, was flushed with argon, and then in the flask dicyclohexylborane was prepared by the addition of cyclohexene (1.64 g, 20 mmol) to BH_3 (10 mmol) in THF. To the solution, 1-bromo-1-hexyne (1.61 g, 10 mmol) was slowly added at −10 °C and then the solution was stirred for 3 h at 0 °C. Then DIB (3.2 g, 10 mmol) in dichloromethane (30 ml) was dropped at −25 °C and the reaction mixture was stirred at the same temperature. After completion of the reaction, hexane (20 ml) was added, and the solution was washed with NaCl-saturated water once and then dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the reaction mixture was put on a column packed with silica gel (Wako gel Q-50) giving 1.32 g (5.4 mmol, 54%) of IVa (Z, 98%; E, 2%) by elution with benzene. Z-Isomer was isolated by repeated applications on column chromatography of the above mixture: n_D^{20} 1.4940; PMR δ 5.52 (t, 1H); [2,19] IR $\nu_{c=c}$ 1655 cm^{-1};[2] mass spectrum *m/e* 244, 246 (M$^+$). Found: C, 59.11; H, 8.69%. Calcd for $C_{12}H_{21}Br$: C, 58.78; H, 8.63%.

4-Bromo-2,3-dimethyl-4-nonene (IVb). To the solution of (1-bromo-1-hexenyl)bis(1,2-dimethylpropyl)borane, obtained in the similar manner as described above, LTA (4.5 g, 10 mmol) in dichloromethane (50 ml) was dropped at −50 °C and the stirring was continued for 8 h at the same temperature. Then, water (5 ml) and hexane (20 ml) were added to the solution at 0 °C. By the same procedure as described in the synthesis of IVa, 1.17 g (5.0 mmol, 50%) of IVb (Z, 98%; *E*, 2%) was obtained. *Z*-isomer was isolated by column chromatography of the above mixture: n_D^{20} 1.4638; PMR δ 5.53 (t, 1H);[2,19] IR $\nu_{c=c}$ 1655 cm^{-1};[2] mass spectrum *m/e* 232, 234 (M$^+$). Found: C, 56.50; H, 9.02%. Calcd for $C_{11}H_{21}Br$: C, 56.66; H, 9.08%.

*(*Z*)-6-Bromo-5-dodecene (IVc-*Z*).* In the same reaction apparatus as described above, flushed with argon, 1-bromo-1-hexyne (1.61 g, 10 mmol) was placed, and then the solution, prepared by the hydroboration (25 °C, 24 h) of 1-hexene (1.68 g, 20 mmol) with BH_3 (10 mmol, in THF), was dropped into the flask by using a syringe at −25 °C followed by the stirring for 2 h at −10 °C. Then LTA (4.5 g, 10 mmol) in dichloromethane (50 ml) was slowly added at −65 °C and the solution was stirred at −50 °C for 4 h. After the reaction, a mixture of water (3 ml) and THF (5 ml) was added to the solution at −50 °C, and then the solution was allowed to return to room temperature. By the same procedure as described in the synthesis of IVa, 1.38 g (5.6 mmol, 56%) of IVc (*Z*, 96%; *E*, 4%) was obtained. *Z*-isomer was isolated by column chromatography: n_D^{20} 1.4682; PMR δ 5.51 (t, 1H);[2,19] IR $\nu_{c=c}$ 1655 cm^{-1};[2] mass spectrum *m/e* 246, 248 (M$^+$). Found: C, 58.46; H, 9.29%. Calcd for $C_{12}H_{23}Br$: C, 58.30; H, 9.38%.

*(*Z*)-6-Bromo-5-tetradecene (IVd-*Z*).* This compound was obtained in the similar manner as described in the synthesis of IVc-*Z*; PMR δ 5.51 (t, 1H);[2,19] IR $\nu_{c=c}$ 1660 cm^{-1};[2] mass spectrum *m/e* 274, 276 (M$^+$). Found: C, 61.18; H, 9.80%. Calcd for $C_{14}H_{27}Br$: C, 61.09; H, 9.89%.

*(*Z*)-6-Bromo-8-methyl-5-undecene (IVe-*Z*).* This compound was obtained in the similar manner as described in the synthesis of IVc-*Z*; PMR δ 5.52 (t, 1H);[2,19] IR $\nu_{c=c}$ 1660 cm^{-1};[2] mass spectrum *m/e* 246, 248 (M$^+$). Found: C, 58.39; H, 9.36%. Calcd for $C_{12}H_{23}Br$: C, 58.30; H, 9.38%.

*(*E*)-6-Bromo-5-dodecene (IVc-*E*).* To the solution of (1-bromo-1-hexenyl)dialkylborane, prepared by the procedure as described in the synthesis of IVa, a mixture of benzene (20 ml) and hexane (20 ml) was added, and then powdered LTA (4.5 g, 10 mmol) was introduced slowly to the solution at −10 °C, followed by stirring for 4 h at 0 °C. Then, water (5 ml) was added. By the similar procedure as described in the synthesis of IVa, 1.28 g (5.2 mmol, 52%) of a mixture (*Z*, 5%; *E*, 95%) was obtained. *E*-Isomer was isolated by column chromatography: n_D^{20} 1.4718; PMR δ 5.71 (t, 1H);[2,19] IR $\nu_{c=c}$ 1645 cm^{-1};[2] mass spectrum *m/e* 246, 248 (M$^+$). Found: C, 58.48; H, 9.31%. Calcd for $C_{12}H_{23}Br$: C, 58.30; H, 9.38%.

*(*E*)-6-Bromo-5-tetradecene (IVd-*E*).* This compound was obtained in the similar manner as described in the synthesis of IVc-*E*; PMR δ 5.72 (t, 1H);[2,19] IR $\nu_{c=c}$ 1645 cm^{-1};[2] mass spectrum *m/e* 246, 248 (M$^+$). Found: C, 58.35; H, 9.38%. Calcd for $C_{12}H_{23}Br$: C, 58.30; H, 9.38%.

*(*Z*)-1-Chloro-1-cyclohexyl-1-hexene (VIa), (*Z*)-4-Chloro-2,3-dimethyl-4-nonene (VIb), (*Z*)-6-Chloro-5-dodecene (VIc), (*Z*)-1-Iodo-1-cyclohexyl-1-hexene (VIIa) and (*E*)-6-Iodo-5-dodecene (VIIb).* These compounds were synthesized in the similar manners as described in the syntheses of the corresponding bromo compounds. Analytical data are as follows.

VIa: PMR δ 5.31 (t, 1H);[2,19] IR $\nu_{c=c}$ 1660 cm^{-1};[2] mass spectrum *m/e* 200, 202 (M$^+$). Found: C, 71.87; H, 10.53%. Calcd for $C_{12}H_{21}Cl$: C, 71.80; H, 10.54%.

VIb: PMR δ 5.31 (t, 1H);[2,19] IR $\nu_{c=c}$ 1660 cm^{-1};[2] mass spectrum *m/e* 188, 190 (M$^+$). Found: C, 70.03; H, 11.16%. Calcd for $C_{11}H_{21}Cl$: C, 70.00; H, 11.21%.

VIc: PMR δ 5.03 (t, 1H);[2,19] IR $\nu_{c=c}$ 1655 cm^{-1};[2] mass spectrum *m/e* 202, 204 (M$^+$). Found: C, 71,12; H, 11.41%. Calcd for $C_{12}H_{23}Cl$: C, 71.08; H, 11.43%.

VIIa: PMR δ 5.30 (t, 1H);[2,19] IR $\nu_{c=c}$ 1640 cm^{-1};[2] mass spectrum *m/e* 292 (M$^+$). Found: C, 49.38; H, 7.20%. Calcd for $C_{12}H_{21}I$: C, 49.33; H, 7.24%.

VIIb: PMR δ 6.03 (t, 1H);[2,19] IR $\nu_{c=c}$ 1630 cm^{-1};[2] mass spectrum *m/e* 294(M$^+$). Found: C, 49.03; H, 7.84%. Calcd for $C_{12}H_{23}I$: C, 48.99; H, 7.88%.

References

1) Y. Masuda, A. Arase, and A. Suzuki, *Chem. Lett.*, **1978**, 665.

2) T. H. Chan, P. W. Law, and W. Mychajlowsky, *Tetrahedron Lett.*, **1977**, 3317

3) a) J. F. Normant, *Synthesis*, **1972**, 63; b) G. Cahiez, D. Bernard, and J. F. Normant, *ibid.*, **1976**, 245.

4) H. C. Brown, D. H. Bowman, S. Misumi, and M. K. Unni, *J. Am. Chem. Soc.*, **89**, 4531 (1967).

5) H. C. Brown, T. Hamaoka, and N. Ravindran, *J. Am. Chem. Soc.*, **95**, 5786, 6456 (1973).

6) Y. Masuda and A. Arase, *Bull. Chem. Soc. Jpn.*, **51**, 901 (1978).

7) a) G. Zweifel, H. Arzomanian, and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 3652 (1976); b) G. Zweifel, R. P. Fischer, J. T. Snow, and C. C. Whitney, *ibid.*, **93**, 6309 (1971).

8) E. Negishi, J. J. Katz, and H. C. Brown, *Synthesis*, **1972**, 555.

9) H. Yatagai, Y. Yamamoto, K. Maruyama, A. Sonoda, and S. Murahashi, *J. Chem. Soc., Chem. Commun.*, **1977**, 852.

10) K. E. Schulte and M. Goes, *Arch. Pharm.*, **290**, 118 (1959).

11) a) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York (1962); b) G. M. L. Cragg, "Organoboranes in Organic Synthesis," Marcel Dekker, New York (1973); c) H. C. Brown, "Organic Syntheses *via* Boranes," J. Wiley and Sons, New York (1975).

12) a) H. C. Brown, E. Negishi, and S. K. Gupta, *J. Am. Chem. Soc.*, **92**, 6648 (1970); b) H. C. Brown and S. K, Gupta, *ibid.*, **93**, 1818 (1971); c) A. Pelter, K. Rowe, and K. Smith, *J. Chem. Soc., Chem. Commun.*, **1975**, 531.

13) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Am. Chem. Soc.*, **82**, 4703 (1960).

14) a) H. Normant and T. Cuvigny, *Bull. Soc. Chim. F.*, **1957**, 1447; b) D. J. Pflaum and H. H. Wenzke, *J. Am. Chem. Soc.*, **56**, 1106 (1934).

15) P. L. Southwick and J. R. Kirchiner, *J. Org. Chem.*, **27**, 3305 (1962).

16) J. C. Bailar, Jr., *Inorg. Synth.*, Vol. 1, 47 (1939).

17) L. F. Fieser and M. Fieser, "Reagent for Organic Synthesis," J. Wiley and Sons, New York (1967) Vol. 1, p. 537.

18) K. H. Pausker, *J. Chem. Soc.*, **1953**, 107.

19) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2 nd ed, Pergamon, Oxford (1969), p. 184.