Reaction of Organoboranes with Lithium Aldimines. A New Procedure for the Synthesis of Unsymmetrical Ketones[1)]

Yoshinori Yamamoto,* Kaoru Kondo, and Ichiro Moritani[2)]
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

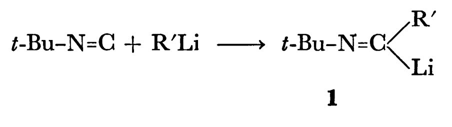
(Received June 26, 1975)

Unsymmetrical ketones are obtained in good yields *via* the reaction of dialkylchloroboranes with lithium aldimines followed by treatment with (i) thioglycolic acid and (ii) H_2O_2–NaOH. The reaction permits the introduction of both primary and secondary alkyl groups into R and R′ substituents of ketones (RR′C=O), and can even be extended to the accommodation of a functional group. The reaction of B-*n*-hexyl-9-borabicyclo[3.3.1]-nonane with lithium aldimine derived from *n*-butyllithium also gives unsymmetrical ketone, 5-undecanone, upon treatment with H_2O_2–NaOH.

In recent years, various procedures for the synthesis of ketones *via* organometallics have been developed.[3)] The synthesis through organoboranes is the most useful and convenient. Symmetrical ketones are obtained from the reaction of trialkylboranes with carbon monoxide in the presence of water[4)] or with sodium cyanide and trifluoroacetic anhydride,[5)] or *via* the reaction of dialkylborinates with α,α-dichloromethyl methyl ether and lithium triethylcarboxide.[6)] Unsymmetrical ketones are available *via* the reaction of thexyldialkylboranes with carbon monoxide[7)] or with sodium cyanide,[8)] *via* the reaction of trialkylboranes with α,β-unsaturated carbonyl derivatives,[9)] α-bromoketones,[10)] diazoketones,[11)] α-lithio derivative of 1,1-bis(phenylthio)pentane,[12)] or α-azidostyrene,[13)] or *via* the reaction of lithium alkynyltrialkylborates with electrophilic reagents.[14)] Although thexylborane can combine two different olefins with a different reactivity toward the B–H bonds, union of two different olefins with similar reactivity such as 1-hexene and 1-butene is unsuccessful.[15)] This causes an unsatisfactory result for the union of two primary alkyl groups such as *n*-hexyl and *n*-butyl in the unsymmetrical ketone synthesis.[15)] We report a new synthesis of unsymmetrical ketones *via* the reaction of organoboranes with lithium aldimines.

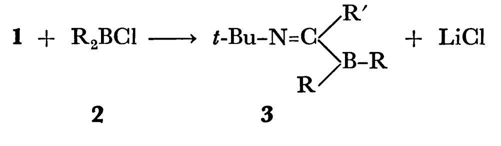
Results and Discussion

Lithium aldimines (**1**) are obtained by addition of alkyllithiums to isocyanides which do not contain α-hydrogens[16)] (Scheme 1). The reaction of dialkylchloroboranes (**2**) with **1** gives the corresponding adduct (**3**) (Scheme 2).



$$t\text{-Bu-N=C} + \text{R}'\text{Li} \longrightarrow t\text{-Bu-N=C}\begin{smallmatrix}\diagup \text{R}' \\ \diagdown \text{Li}\end{smallmatrix} \quad (1)$$

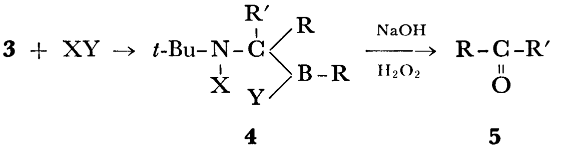
1



$$\mathbf{1} + \text{R}_2\text{BCl} \longrightarrow t\text{-Bu-N=C}\begin{smallmatrix}\diagup \text{R}' \\ \diagdown \text{B-R} \\ \text{R}\diagup \end{smallmatrix} + \text{LiCl} \quad (2)$$

2 **3**

It was anticipated that such a compound as **3** can react with an electrophile to induce alkyl transfer from boron to carbon,[17)] in which case alkaline hydrogen peroxide oxidation of **4** might give ketone (**5**), where the one alkyl group (R) arises from **2** and the other (R′) from alkyllithium (Scheme 3).



$$\mathbf{3} + \text{XY} \rightarrow t\text{-Bu-}\underset{\text{X}}{\underset{|}{\text{N}}}\text{-}\overset{\text{R}'}{\overset{|}{\text{C}}}\begin{smallmatrix}\diagup \text{R} \\ \diagdown \text{B-R} \\ \text{Y}\diagup\end{smallmatrix} \xrightarrow[\text{H}_2\text{O}_2]{\text{NaOH}} \text{R-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-R}' \quad (3)$$

4 **5**

As a typical case we examined the reaction of di-*n*-hexylchloroborane (10 mmol) with lithium aldimine derived from *n*-butyllithium (10 mmol) and *t*-butylisocyanide (10 mmol). The borane was added to the lithium aldimine at 0 °C, trifluoroacetic anhydride (20 mmol) then being added to the resultant mixture as an electrophile. After being stirred for 1 hr at room temperature, the mixture was subjected to alkaline hydrogen peroxide oxidation, giving 5-undecanone. However, it was obtained in a relatively low 56% yield. This was apparently due to the improper choice of reaction temperature since boranes similar to **3** undergo dimerization.[18)] When the reaction was performed at −78 °C, the ketone was obtained in a remarkably improved 95% yield. Various ketones prepared are listed in Table 1.

Unsymmetrical ketones can be prepared by utilizing olefins and alkyl halides as building blocks that can be varied independently. There appears no difficulty in introducing a primary alkyl group containing a functional substituent. However, isopropyl cyclopentyl ketone (**12**) is obtained in only 44% yield, suggesting that the combination of two secondary alkyl groups proceeds with some difficulty under the reaction conditions. This might be due to the difficulty for the transfer of sterically bulky alkyl groups. The relative migratory aptitudes of alkyl groups in the related boranes are in the order primary>secondary>tertiary.[19)] We selected several electrophiles and examined the yield of **12** in order to find the best reagent in the present reaction system. The results are summarized in Table 2.

Thioglycolic acid is recommended as a reagent inducing the migration. The present procedure offers the following advantages over the previous methods;[7,8)] (i) accommodation of an alkyl group such as isopropyl which can not be introduced *via* the hydroboration methods, (ii) the combination of two different alkyl groups such as *n*-hexyl and *n*-butyl which is not attainable through thexylborane. The only disadvantage is the loss of one alkyl group (R) (Scheme 3). This

---

* To whom correspondence should be addressed.

TABLE 1. SYNTHESIS OF UNSYMMETRICAL KETONES *via* THE REACTION OF **1** WITH **2**

Olefin	Alkyllithium	Ketone	Yield, %
1-Hexene	*n*-Butyllithium	5-Undecanone (**6**)	95
1-Hexene	3-Methylbutyllithium	2-Methyl-5-undecanone (**7**)	92
1-Hexene	Ethyllithium	3-Nonanone (**8**)	86
1-Hexene	*iso*-Propyllithium	2-Methyl-3-nonanone (**9**)	71
5-Bromo-1-pentene	*n*-Butyllithium	10-Bromo-5-undecanone (**10**)	61
Cyclopentene	*n*-Butyllithium	*n*-Butyl cyclopentyl ketone (**11**)	63
Cyclopentene	*iso*-Propyllithium	*iso*-Propyl cyclopentyl ketone (**12**)	44

TABLE 2. EFFECTIVENESS OF ELECTROPHILES IN THE SYNTHESIS OF UNSYMMETRICAL KETONES

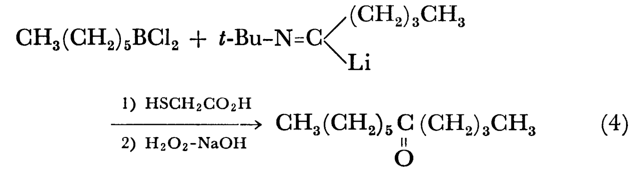
Electrophile	$PhSO_3H$	CH_3SOCl	$(CF_3CO)_2O$	H_2S	CF_3CO_2H	$(CH_3)_2SO_4$	PhSH	$HSCH_2CO_2H$
12 (Yield, %)	26	44	44	45	54	58	64	91

TABLE 3. EFFECTIVENESS OF ADDITIVES IN THE REACTION OF *n*-HEXYLDICHLOROBORANE WITH *n*-BUTYLLITHIUM ALDIMINE

Additive	$PhNH_2$	$(CF_3CO)_2O$	PhSH	C_2H_5SH	C_2H_5SNa-C_2H_5SH	$HSCH_2CO_2H$
6 (Yield, %)	28	29	45	49	49	50

may be overcome by utilizing $RBCl_2$ instead of R_2BCl.

We examined the reaction of *n*-hexyldichloroborane with lithium aldimine derived from *n*-butyllithium (Scheme 4).



$$CH_3(CH_2)_5BCl_2 + t\text{-Bu-N=C}\begin{smallmatrix}(CH_2)_3CH_3\\ Li\end{smallmatrix} \xrightarrow[2)\ H_2O_2\text{-NaOH}]{1)\ HSCH_2CO_2H} CH_3(CH_2)_5\underset{\underset{O}{\|}}{C}(CH_2)_3CH_3 \quad (4)$$

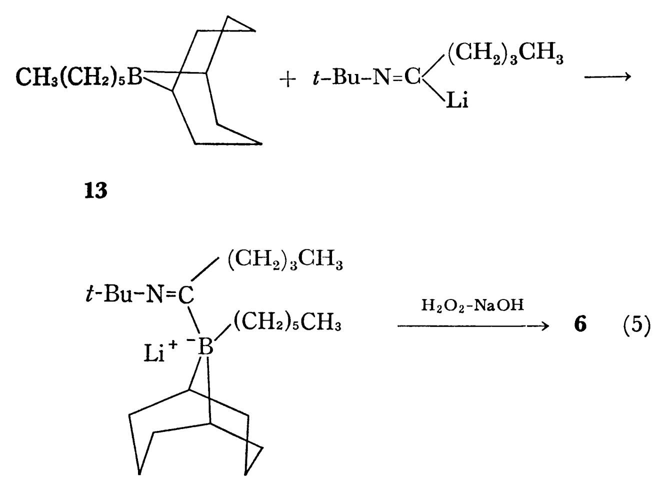
6　50%

The yield of product (**6**) depends upon the additive (Table 3), thioglycolic acid giving the best result. However, the yield never exceeded 50%, the reason not being clarified.

Additives such as $HSCH_2CO_2H$, C_2H_5SH, PhSH, and $(CF_3CO)_2O$ may act as electrophiles in the manner described above (Scheme 3). The other additives ($PhNH_2$ and C_2H_5SNa–C_2H_5SH) are not electrophilic, but nucleophilic. It seems that these reagents attack the electron deficient boron atom, inducing the migration of hexyl group *via* the borate complex. We might conclude that such a borane as **3** undergoes rearrangement under the influence of both electrophilic and nucleophilic reagents, though the latter agents are less effective. In fact, such rearrangement under electrophilic and nucleophilic conditions is observed in the case of α-bromoboranes.[20]

We then tried the reaction of *n*-hexyl-9-borabicyclo-[3.3.1]nonane (*n*-hexyl-9-BBN) (**13**) with lithium aldimine derived from *n*-butyllithium (Scheme 5).

The simple oxidation of reaction mixture gave **6** in 69% yield. When thioglycolic acid was employed before the oxidation, **6** was produced in only 4% yield. Instead, a large amount of diol was detected by glpc analysis, which presumably arose from the migration of 9-BBN ring. This suggests that the borate intermediate (**14**) undergoes rearrangement more easily than the borane intermediate (**3**); presumably the migration in **14** proceeds without assistance of electrophilic or nucleophilic reagents to produce the borane intermediate.[21]



14

The reaction of trialkylboranes with lithium aldimines was in sharp contrast with that of dialkylchloroboranes. In the case of R_2BCl, the migration of second alkyl group (R) was very difficult under the conditions (i) $HSCH_2CO_2H$–(ii) H_2O_2–NaOH (Scheme 3). On the other hand, in the case of R_3B, the migration was very facile, leading to the trialkylcarbinylborane ($R_2R'C$–B<).[22] However, this was avoided by the removal of thioglycolic acid as shown in Scheme 5. In contrast to **13**, the reaction with tri-*n*-hexylborane with *n*-butyllithium aldimine followed by treatment with H_2O_2–NaOH gave 7-*n*-butyl-7-tridecanol in 19% yield along with **6**.[22] This can be explained by the fact that the ease of migration of the primary alkyl group (*e.g.* *n*-hexyl) is greater than that of the secondary one (*e.g.* 9-BBN ring).

In conclusion, the reaction of dialkylchloroboranes with lithium aldimines is recommended for the synthesis of unsymmetrical ketones. When the loss of one alkyl group in R_2BCl causes a serious problem, the utilization of 9-borabicyclo[3.3.1]nonane derivatives might remove the difficulty.

Experimental

All boiling points are uncorrected. The IR spectra were obtained on a Hitachi 215 spectrophotometer. The NMR spectra were obtained on a JEOL JNM-MH-60 spectrometer, TMS being chosen as an internal standard. The elemental analysis was performed by Mr. Y. Harada in our Department. Glpc analyses were carried out on a Yanagimoto GCG 550T using a 2 m column packed with Carbowax 20 M or SE-30 10 wt% on Celite 545 AW.

Materials. Reagent grade solvents were purified by standard techniques and kept over a drying agent. B_2H_6: THF, $BH_2Cl : OEt_2$, $BHCl_2 : OEt_2$, dialkylchloroboranes, tri-*n*-hexylborane, *n*-hexyl-9-borabicyclo[3.3.1]nonane, and *n*-hexyldichloroborane were prepared according to the known procedures.[23] Commercial 1-hexene, cyclopentene, the electrophiles, and *n*-butyllithium in hexane were used. Other alkyllithiums were prepared by standard procedures (ethyllithium in ether,[24] isoamyllithium in ether,[24] and isopropyllithium in pentane[25]). Titration was performed according to the method of Gilman and Haubein[26] or that of Watson and Eastham.[27] 5-Bromo-1-pentene[28] and *t*-butylisonitrile[29] were prepared according to the methods previously reported.

Reaction of Lithium Aldimine with Dialkylchloroborane. General Procedure: In a 200-ml flask maintained under N_2 and fitted with a septum inlet, magnetic stirrer, and reflux condenser, were placed *t*-butylisonitrile (3.6 ml, 30 mmol) and dry ether (60 ml). The solution was cooled to 0 °C and a solution of alkyllithium (30 mmol) was added dropwise. The mixture was stirred for 30 min at 0 °C and then cooled to −78 °C with a dry-ice acetone bath. Dialkylchloroborane (30 mmol) was added, and the resulting mixture was kept at −78 °C for 30 min. Thioglycolic acid (4.2 ml, 60 mmol) or trifluoroacetic anhydride (8.4 ml, 60 mmol) was then added, the temperature being regulated to reach room temperature over 1 hr. Oxidation was accomplished by the addition of 6 M aqueous NaOH (10 ml)–30% H_2O_2 (10 ml). The organic phase was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over anhydrous K_2CO_3. The solvent was removed under reduced pressure and the product was filtered through the column of silica (*ca.* 200 g). The ketones were eluted with benzene in substantially pure form. The ketones were then distilled under reduced pressure and/or subjected to a preparative glpc to obtain analytically pure materials. Alcohols were removed from the column with ether. No attempt was made to attain optimum yields of individual ketones, but all were subjected to the general procedure described above. The spectral data, boiling points and n_D are summarized in Table 4. Authentic samples of **6** and **8**, commercially available, were used. The other authentic samples (**7**, **9**, **11**, and **12**) were independently prepared by the reported procedures (Table 4). Elemental analysis was performed on the unknown compound (**10**); (Found: C, 51.40; H, 8.33; Br, 33.00%. Calcd for $C_{10}H_{19}BrO$: C, 51.07; H, 8.14; Br, 33.98%). For the synthesis of **6**—**11** except **12**, trifluoroacetic anhydride was utilized as an electrophile, satisfactory results being obtained. Utilization of thioglycolic acid in these cases improved the yields. Pronounced effect of this reagent was observed in the preparation of **12** (Table 2).

*Reaction of Di-*n*-hexylchloroborane with* n*-Butyllithium Aldimine. Temperature Effect.* Lithium aldimine was prepared as described above. Di-*n*-hexylchloroborane (10 mmol, 2.4 ml) was added at 0 °C to the solution of lithium aldimine. The resulting mixture was stirred for 30 min at 0 °C. Trifluoroacetic anhydride (20 mmol, 2.8 ml) was then added. The mixture was allowed to reach room temperature over 1 hr. Oxidation was accomplished in the normal way. The aqueous layer was saturated with K_2CO_3 and the organic layer was analyzed by glpc with *n*-dodecane as an internal standard. The reaction at −78 °C was carried out according to the general procedure.

*Check for the Effectiveness of Electrophiles in the Preparation of **12**.* All reactions (10 mmol scale) were carried out according to the general procedure. Neat electrophiles (20 mmol) (Table 2) were added directly to the reaction mixture, except that H_2S dissolved in ether was added. After oxidation, the aqueous layer was saturated with K_2CO_3 and the organic layer was analyzed by glpc with *n*-dodecane as an internal standard. Increase in the amount of electrophiles did not significantly improve the yield of **12**, though a decrease in the amount lowered the yield.

Table 4. Spectral and physical data of products

Compd No.	Bp, °C/mmHg (lit)	n_D^{20} (lit)	IR(neat) (ν_{max}, cm^{-1})	NMR (δ in CCl_4, J=Hz)
6	82—83/5 (227/760)[30]	1.4287 (n_D^{18} 1.4275)[30]	1710	0.90 (t, 6H, J=6), 1.26 (broad s, 12H), 2.30 (t, 4H, J=7)
7	84—85/4 (126—128/23.5)[31]	1.4308 (1.4307)[31]	1710	0.88 (d, 6H, J=6), 0.88 (t, 3H, J=6), 1.10—1.70 (m, 11H), 2.29 (t, 4H, J=7)
8	67—68/10 (187/751)[32]	1.4210 (1.4208)[32]	1710	0.88 (t, 3H, J=6), 0.97 (t, 3H, J=6), 1.30 (broad s, 8H), 2.33—2.50 (m, 4H)
9	50—51/2 (77/4)[33]	1.4228 (1.4226)[33]	1716	0.88 (t, 3H, J=6), 1.03 (d, 6H, J=7), 1.22—1.65 (m, 8H), 1.96—2.78 (m, 3H)
10	90—91/1	1.4667	1710	0.90 (t, 3H, J=6), 1.11—2.01 (m, 10H), 2.34 (t, 4H, J=7), 3.33 (t, 2H, J=6)
11	77—78/4 (104—106/25)[34]	1.4477 (n_D^{23} 1.4479)[34]	1710	0.89 (t, 3H, J=6), 1.15—1.90 (m, 12H), 2.35 (t, 2H, J=7), 2.65—2.90 (m, 1H)
12	50—52/3 (84/30)[35]	1.4444	1714	1.03 (d, 6H, J=7), 1.61 (broad s, 8H), 2.32—3.16 (m, 2H)

Reaction of n-*Hexyldichloroborane with* n-*Butyllithium Aldimine.* The reaction (10 mmol scale) was carried out according to the general procedure, except for the utilization of *n*-hexyldichloroborane (10 mmol, 1.8 ml) and of pentane as the solvent. Various additives (20 mmol) to induce the migration were examined (Table 3). Analyses were performed by glpc.

Reaction of n-*Hexyl-9-borabicyclo*[*3.3.1*]*nonane with* n-*Butyllithium Aldimine.* Lithium aldimine (10 mmol) was prepared as described above. To this solution was added *n*-hexyl-9-borabicyclo[3.3.1]nonane (**13**) prepared from 1-hexene (10 mmol, 1.25 ml) and 9-borabicyclo[3.3.1]nonane (10 mmol) at −78 °C and the resulting mixture was kept at this temperature for 30 min. Oxidation was accomplished after the reaction was allowed to reach room temperature over 1 hr. Analysis was carried out by glpc. Ketone (**6**) was produced in 69% yield.

Thioglycolic acid (20 mmol, 1.4 ml) was added at −78 °C before oxidation. Oxidation and subsequent analysis were performed according to the general procedure. Along with the minor product (**6**, 4%), a large peak with longer retention time was detected in glpc, the precise structure of which was not determined.

References

1) For a preliminary communication, see Y. Yamamoto, K. Kondo, and I. Moritani, *Tetrahedron Lett.*, **1974**, 793.

2) Present address, Kuraray Co. Ltd., Osaka.

3) D. T. Thompson and R. Whyman, "Transition Metals in Homogeneous Catalysis," ed. by G. N. Schrauzer, Marcel Dekker, New York (1971), p. 149.

4) H. C. Brown and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 2738 (1967).

5) A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Commun.*, **1970**, 1529; A. Pelter, K. Smith, M. G. Hutchings, and K. Rowe, *J. Chem. Soc. Perkin I*, **1975**, 129.

6) B. A. Carlson and H. C. Brown, *J. Amer. Chem. Soc.*, **95**, 6876 (1973).

7) H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967); H. C. Brown and E. Negishi, *ibid.*, **89**, 5285 (1967).

8) A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Commun.*, **1971**, 1048.

9) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967); G. W. Kabalka, H. C. Brown, A. Suzuki, S. Homma, A. Arase, and M. Itoh, *ibid.*, **92**, 710 (1970); H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 712 (1970); A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, G. W. Kabalka, and G. W. Holland, *ibid.*, **92**, 3503 (1970); H. C. Brown and E. Negishi, *ibid.*, **93**, 3777 (1971); A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, E. Negishi, and S. K. Gupta, *Chem. Commun.*, **1969**, 1009.

10) H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **90**, 6218 (1968); H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969); H. C. Brown and M. M. Rogić, *ibid.*, **91**, 4304 (1969); H. C. Brown, H. Nambu, and M. M. Rogić, *ibid.*, **91**, 6852 (1969).

11) J. Hooz and S. Linke, *ibid.*, **90**, 5936 (1968); J. Hooz and D. M. Gunn, *Chem. Commun.*, **1969**, 139; J. Hooz, D. M. Gunn, and H. Kono, *ibid.*, **49**, 2371 (1971); D. J. Pasto and P. W. Wojikowski, *J. Org. Chem.*, **36**, 1790 (1971); D. J. Pasto and K. McReynolds, *Tetrahedron Lett.*, **1971**, 801.

12) S. Yamamoto, M. Shiono, and T. Mukaiyama, *Chem. Lett.*, **1973**, 961.

13) A. Suzuki, M. Tabata, and M. Ueda, *Tetrahedron Lett.*, **1975**, 2195.

14) a) M. Naruse, T. Tomita, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, **1973**, 795; *Tetrahedron*, **30**, 835 (1974); M. Naruse, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, **1973**, 2741; *Tetrahedron*, **30**, 3037 (1974). b) A. Pelter, C. R. Harrison, and D. Kirkpatrick, *Chem. Commun.*, **1973**, 544; *Tetrahedron Lett.*, **1973**, 4491; A. Pelter, K. J. Gould, and L. A. P. K-Maguire, *Chem. Commun.*, **1974**, 1029. c) *via* other borate complexes, E. Negishi, A. Abramovitch, and R. E. Merrill, *ibid.*, **1975**, 138; E. Negishi, K-W. Chiu, and T. Yoshida, *J. Org. Chem.*, **40**, 1676 (1975); see also, E. Negishi and T. Yoshida, *Chem. Commun.*, **1973**, 606.

15) E. Negishi and H. C. Brown, *Synthesis*, **1974**, 77.

16) H. M. Walborsky and G. E. Niznik, *J. Amer. Chem. Soc.*, **91**, 7778 (1969); G. E. Niznik, W. H. Morrison, III, and H. M. Walborsky, *J. Org. Chem.*, **39**, 600 (1974).

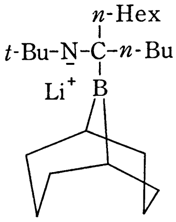
17) G. Hesse, H. Witte, W. Gulden, *Angew. Chem.*, **77**, 591 (1965); *Tetrahedron Lett.*, **1966**, 2707.

18) J. Casanova, Jr., "Isonitrile Chemistry," ed. by I. Ugi, Academic, New York (1971), p. 109.

19) A. Pelter, M. G. Hutchings, K. Smith, and D. J. Williams, *J. Chem. Soc. Perkin I*, **1975**, 145.

20) H. C. Brown and Y. Yamamoto, *J. Amer. Chem. Soc.*, **93**, 2796 (1971); *Chem. Commun.*, **1972**, 71.

21) We assume that a borane intermediate such as **15** is involved in the reaction. The oxidation leads to the formation of **6**. The treatment with $HSCH_2CO_2H$ presumably induces the migration of 9-BBN ring. However, these are assumptions, and no evidence has so far been obtained.



15

22) Y. Yamamoto, K. Kondo, and I. Moritani, *J. Org. Chem.*, in press.

23) H. C. Brown, "Organic Syntheses *via* Boranes," Wiley, New York (1975).

24) The same procedure as that for the preparation of *n*-butyllithium was employed ("Organic Reactions," Vol. 6 (1951), p. 352).

25) H. Gilman, F. W. Moore, and O. Baine, *J. Amer. Chem. Soc.*, **63**, 2479 (1941).

26) H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

27) S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 165 (1967).

28) J. I. G. Cadogan, D. H. Hey, and S. H. Ong, *J. Chem. Soc.*, **1965**, 1932.

29) The same method as that for the preparation of 1,1,3,3-tetramethylbutylisonitrile was employed "Organic Syntheses," Vol. 51 (1971), p. 31).

30) "Handbook of Chemistry and Physics," 53rd ed., The Chemical Rubber Company, Cleveland ,1973.

31) S. G. Powell and F. Hagemann, *J. Amer. Chem. Soc.*, **66**, 374 (1944).

32) E. Vogel, *J. Chem. Soc.*, **1948**, 613.

33) H. H. Morris and R. H. Young, Jr., *J. Amer. Chem. Soc.*, **77**, 6678 (1955).

34) G. Vavon and A. Guedon, *Bull. Soc. Chim.*, **47**, 901 (1930).

35) J. Crouzet, L. Giral, G. Cauquil, and J. Rouzaud, *Bull. Soc. Chim. Fr.*, **1967**, 3722.