δ 216.7, 160.30, 72.14, 55.70, 52.69, 52.18, 49.23, 44.16, 42.67, 39.46, 39.66, 34.03, 32.88, 32.12, 16.88; HRMS calcd for $C_{15}H_{22}O_3$ 250.1563, found 250.1569.

(1β,5α,6β,7β,9β)-7-Hydroxy-3,3,9-trimethyltricyclo[4.3.2.0^{1,5}]undecan-11-one (32e): ^1H NMR ($CDCl_3$) δ 3.90 (m, 1 H, CHO), 2.52 (d, J = 3.5 Hz, 1 H, CHC=O), 2.2–0.9 (m, 11 H), 1.13 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 0.86 (d, J = 6.7 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 219.58, 71.37, 59.40, 53.06, 52.51, 49.21, 44.40, 42.90, 39.66, 39.45, 38.37, 32.84, 32.18, 16.85; HRMS calcd for $C_{14}H_{22}O_2$ 222.1614, found 222.1606.

9-(Formyloxy)bicyclo[4.3.0]nonan-2-one (29f): ^1H NMR ($CDCl_3$) δ 8.02 (s, 1 H, CHO), 5.10 (m, 1 H, CHO), 2.75 (t, J = 3 Hz, 1 H, CHC=O), 2.4–1.5 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 160.03, 74.60, 51.88, 43.78, 29.64, 29.38, 27.99, 27.06, 24.07, 20.99; HRMS calcd for $C_{10}H_{14}O_3$ 182.0939, found 182.0933.

9-(*p*-Tolylthio)bicyclo[4.3.0]nonan-2-one (30f): ^1H NMR ($CDCl_3$) δ 7.27 (d, J = 8 Hz, 2 H, ortho H), 7.05 (d, J = 8 Hz, 2 H, meta H), 3.77 (t, J = 9 Hz, 1 H, CHS), 2.6–1.4 (m, 12 H), 2.31 (s, 3 H, para CH_3); ^{13}C NMR ($CDCl_3$) δ 211.62, 137.70, 133.40, 131.31, 129.65, 57.56, 51.33, 37.43, 36.11, 31.08, 30.84, 29.18, 26.08, 21.07; HRMS calcd for $C_{16}H_{20}OS$ 260.123, found 260.1222.

1(9)-Bicyclo[4.3.0]nonen-2-one (31f):[21] ^1H NMR ($CDCl_3$) δ 6.62 (s, 1 H, =CH), 2.86–1.22 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 199.51, 144.94, 138.38, 45.72, 40.27, 33.11, 31.75, 31.52, 24.02; HRMS calcd for $C_9H_{12}O$ 136.0885, found 136.0872.

Acknowledgment. We gratefully acknowledge the financial support from the National Science Foundation (CHE-8419265) and the National Institute of General Medical Sciences (GM36336). We thank Professor Kiitiro Utimoto for obtaining the elemental analysis, Dr. Sadahiko Iguchi for measuring the high-resolution mass spectra and Professor Joseph Paukstelis for taking the 2D NOESY NMR spectra.

---

[21] Bal, S. A.; Marfat, A.; Helquist, P. *J. Org. Chem.* **1982**, *47*, 5045.

Addition Compounds of Alkali-Metal Hydrides. 30. Rapid Reaction of Trialkylboranes with Lithium Aluminum Hydride. A Novel and Quantitative Synthesis of Lithium Dialkylborohydrides

Herbert C. Brown,* Milind V. Rangaishenvi, and Uday S. Racherla

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

Received August 26, 1986

For the first time, a wide variety of lithium dialkylborohydrides have been synthesized via a rapid, general, and quantitative reaction of trialkylboranes with lithium aluminum hydride in anhydrous ether at 25 °C. A new generation of lithium dialkylborohydrides such as the lithium dimethylborohydride ($LiMe_2BH_2$) and lithium diisopropylborohydride ($Li\text{-}i\text{-}Pr_2BH_2$) can now be routinely prepared in large quantities for studies on the reductions of organic functional groups. More importantly, since the dialkylborohydrides can also serve as masked intermediates for dialkylboranes, the present procedure provides easy access to a variety of dialkylboranes which cannot be obtained by direct hydroboration.

The importance of trialkylborohydrides as valuable selective reducing agents in organic synthesis is well-established.[1] In the past, several methods were reported for the synthesis of many hindered and even highly hindered trialkylborohydrides.[2] Surprisingly, very little is known about lithium borohydrides containing less than three alkyl groups on boron, a deficiency which can be primarily attributable to the instability of dialkylboranes and the lack of general procedures for their preparation.

Earlier, lithium dialkylborohydrides were prepared in a quantitative manner by the reduction of triethylenediamine–dialkylborane complexes with lithium aluminum hydride in anhydrous ether at 0 °C[3] (eq 1). Unfortunately,

$$R_2BH{\cdot}TED + LiAlH_4 \rightarrow LiR_2BH_2 + AlH_3{\cdot}TED\downarrow \qquad (1)$$

this method is limited only to those dialkylboranes which can be prepared by direct hydroboration.[4] More recently, the synthesis of lithium dialkylborohydrides was achieved via a reduction of dialkylborinates with lithium monoethoxyaluminohydride in ether at 0 °C[5] (eq 2). Although

$$R_2BOMe + LiAlH_3(OEt) \rightarrow LiR_2BH_2 + AlH(OMe)(OEt)\downarrow \qquad (2)$$

this procedure is general and efficient, it requires the prior preparation of the dialkylborinates[6] as well as lithium monoethoxyaluminohydride,[7] not always convenient because the dialkylborinates are not readily available in all cases.[8,9]

During a routine preparation of organoboranes for our isomerization studies,[10] we discovered that triisopropyl-

---

[1] Krishnamurthy, S. *Aldrichimica Acta* **1974**, *7*, 55.

[2] Brown, H. C.; Singaram, B.; Singaram, S. *J. Organomet. Chem.* **1982**, *239*, 43 and references cited therein.

[3] Brown, H. C.; Singaram, B.; Mathew, C. P. *J. Org. Chem.* **1981**, *46*, 4541.

[4] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.

[5] Singaram, B.; Cole, T. E.; Brown, H. C. *Organometallics* **1984**, *3*, 1520.

[6] Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1979**, *44*, 2417.

[7] Brown, H. C.; Shoaf, C. J. *J. Am. Chem. Soc.* **1964**, *86*, 1079.

[8] (a) Lappert, M. F. *Chem. Rev.* **1956**, *56*, 959. (b) Mikhailov, B. M. *Usp. Khim.* **1959**, *28*, 1450.

[9] (a) Mikhailov, B. M.; Aronovich, P. M. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1956**, 322. (b) Mikhailov, B. M.; Vaver, V. A. *Ibid.* **1957**, 989. (c) Köster, R. *Angew. Chem.* **1959**, *71*, 31; (d) *Ibid.* **1961**, *73*, 66. (e) Köster, R.; Grassberger, M. A. *Ann.* **1968**, *719*, 169. (f) Mikhailov, B. M.; Vasil'ev, L. S. *Zh. Obshch. Khim.* **1965**, *35*, 928.

[10] Brown, H. C.; Racherla, U. S.; Rangaishenvi, M. V., unpublished results.

0022-3263/87/1952-0728$01.50/0

Table I. Preparation of Lithium Dialkylborohydrides via a Rapid Reduction of Trialklylboranes with Lithium Aluminum Hydride in Ether at 25 °C[a]

			^{11}B NMR (in ether)		
trialkylborane	time, h	product	chem shift (δ)[b] (mult)	J_{BH}, Hz	% isol[c] yield
Me_3B	0.25	$LiMe_2BH_2$	−21.80 (t)	64	99 (85)[d]
Et_3B	0.25	$LiEt_2BH_2$	−14.20 (t)	67	98
n-Pr_3B	0.25	Li-n-Pr_2BH_2	−11.53 (t)	67	98
i-Pr_3B	0.25	Li-i-Pr_2BH_2	−7.59 (t)	62	100 (99)[d]
n-Bu_3B	0.25	Li-n-Bu_2BH_2	−16.07 (t)	61	99
sec-Bu_3B	0.25	Li-*sec*-Bu_2BH_2	−9.62 (t)	68	99
i-Bu_3B	0.25	Li-i-Bu_2BH_2	−19.09 (t)	67	100
$Cpnt_3B$[e]	0.25	$LiCpnt_2BH_2$[e]	−11.24 (t)	68	100
$chpt_3B$[f]	0.25	$LiChpt_2BH_2$[f]	−13.83 (t)	67	99
$Coct_3B$[g]	0.25	$LiCoct_2BH_2$[g]	−14.70 (t)	68	99
Bnz_3B[h]	1.50	$LiBnz_2BH_2$[h]	−12.88 (t)	72	100

[a] All reactions were done at 0.5 M concentration. [b] Relative to $BF_3{\cdot}OEt_2$, $\delta = 0$ ppm. [c] All reactions were performed on a 10-mmol scale. [d] 100-mmol scale isolation experiments. [e] Cpnt = cyclopentyl. [f] Chpt = cycloheptyl. [g] Coct = cyclooctyl. [h] Bnz = benzyl.

borane undergoes a rapid reaction with $LiAlH_4$ in anhydrous ether at 25 °C and cleanly affords lithium diisopropylborohydride (eq 3). Indeed, we had earlier noted

$$i\text{-}Pr_3B + LiAlH_4 \rightarrow Li\text{-}i\text{-}Pr_2BH_2 + i\text{-}PrAlH_2 \quad (3)$$

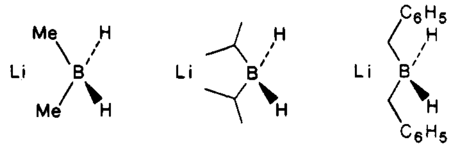
and reported that triethylborane and similar boranes with primary alkyl groups react with lithium aluminum hydride to give the lithium dialkylborohydride but had circumvented this reaction by carrying out the treatment with lithium aluminum hydride in the presence of triethylenediamine in order to achieve a general synthesis of the lithium trialkylborohydrides.[11]

Results and Discussion

To a solution of triethylborane (10 mmol) in anhydrous ether (10 mL) was added lithium aluminum hydride (10 mmol) in ether dropwise at 25 °C, and the solution was stirred for 15 min. The reaction mixture was then cooled to 0 °C and a solution of triethylenediamine (5 mmol) in ether was slowly added to it. Instantly, a white precipitate of bis(monoethylalane)–triethylenediamine complex was thrown out of solution. The reaction mixture was stirred for an additional 15 min and centrifuged. The clear supernatant ether layer was then transferred into a measuring cylinder. The precipitate was washed thoroughly with a known volume of ether and centrifuged, and the ethereal layer was transferred once again into the measuring cylinder. The solution was then analyzed by ^{11}B NMR and hydride analysis. Thus, finally, ^{11}B NMR showed a clean triplet (δ −14.2, J = 67 Hz) corresponding to the lithium diethylborohydride (LDEBH) and hydride analysis established its yield to be 99%. In this fashion, a wide variety of lithium dialkylborohydrides were synthesized in quantitative yields (eq 4). Table I summarizes our results.

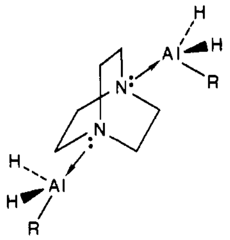
$$R_3B + LiAlH_4 \xrightarrow[\text{2. 0.5 equiv TED, 0 °C, 15 min}]{\text{1. } Et_2O\text{, 25 °C, 15 min}} \underset{98\text{–}100\%}{LiR_2BH_2} + RAlH_2{\cdot}{}^1/_2TED\downarrow \quad (4)$$

The present method for the preparation of lithium dialkylborohydrides is general, highly convenient, and quantitative and is significantly better than any of the previous methods[4,6,14] because it utilizes readily available starting materials. As a result of the present study, a new generation of lithium dialkylborohydrides (such as shown below) are made available, which may indeed be highly



useful for selective reductions of organic functional groups. For this purpose, we also demonstrated that $LiMe_2BH_2$ and $Li(i\text{-}Pr)_2BH_2$ could be conveniently prepared on a large scale, starting from Me_3B and i-Pr_3B.[13]

Further, the byproducts in the above synthesis are bis(monoalkylalane)–triethylenediamine complexes.



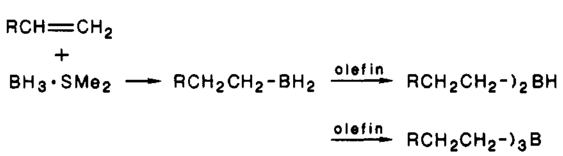
These are highly crystalline, nonpyrophoric substances, which can be isolated in essentially quantitative yields. Hence, a variety of monoalkylalanes are now available as stable adducts of triethylenediamine.

The lithium dialkylborohydrides are very stable and can be stored at 25 °C (under nitrogen) for extended periods of time without any hydride loss, redistribution, or isomerization. Further, by using simple and convenient procedures, it is possible to liberate the free dialkylboranes from the lithium dialkylborohydrides[15] (eq 5 and 6).

$$LiR_2BH_2 + CH_3I \rightarrow R_2BH + LiI + CH_4\uparrow \quad (5)$$

$$LiR_2BH_2 + HCl \rightarrow R_2BH + LiCl + H_2\uparrow \quad (6)$$

Dialkylboranes are synthetically highly useful boron intermediates.[16] In the past, many dialkylboranes (such as the disiamylborane and dicyclohexylborane) were prepared by direct hydroboration of hindered alkenes with $BH_3{\cdot}SMe_2$.[4] However, with less hindered alkenes, it is difficult to cleanly stop the hydroboration at the dialkylborane stage (eq 7) and consequently such dialkyl-



$$\begin{array}{l} RCH{=}CH_2 \\ + \\ BH_3{\cdot}SMe_2 \longrightarrow RCH_2CH_2\text{-}BH_2 \xrightarrow{\text{olefin}} (RCH_2CH_2\text{-})_2BH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \xrightarrow{\text{olefin}} (RCH_2CH_2\text{-})_3B \end{array} \quad (7)$$

boranes could not be prepared by direct hydroboration. Since the dialkylborohydrides are stable, masked inter-

---

[11] Brown, H. C.; Hubbard, J. L.; Singaram, B. *Tetrahedron* **1981**, *37*, 2359.

[12] Brown, H. C.; Zaidlewicz, M.; Negishi, E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1984; Vol. 7.

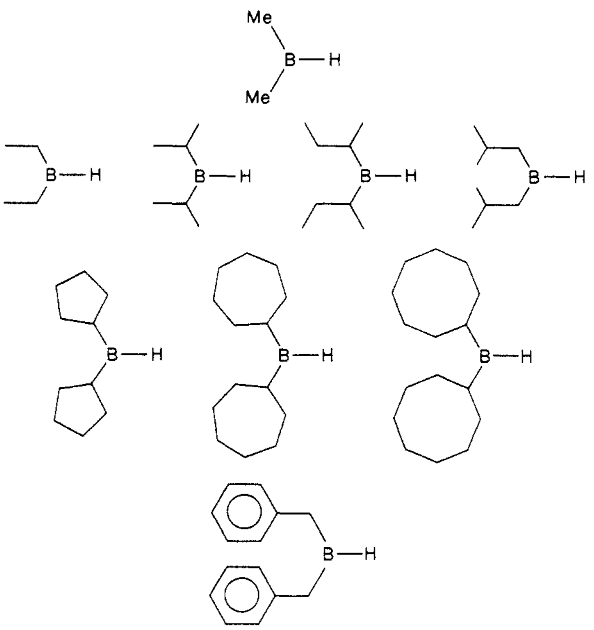
[13] Brown, H. C.; Racherla, U. S. *J. Org. Chem.* **1986**, *51*, 427.

[14] Brown, H. C.; Singaram, B.; Mathew, C. P. *J. Org. Chem.* **1981**, *46*, 2712.

[15] For experimental procedures, see ref 5 and Cole, T. E.; Bakshi, R. K.; Sbrenik, M.; Singaram, B.; Brown, H. C. *Organometallics*, in press.

[16] (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834. (b) Brown, H. C.; Knights, E. F.; Coleman, R. A. *Ibid.* **1969**, *91*, 2144. (c) Brown, H. C.; Rhodes, S. P. *Ibid.* **1969**, *91*, 4306. (d) Zweifel, G.; Polston, N. L. *J. Am. Chem. Soc.* **1970**, *92*, 4068. (e) Zweifel, G.; Arzoumanian, H.; Whitney, C. C. *Ibid.* **1967**, *89*, 3652. (f) Zweifel, G.; Arzoumanian, H. *Ibid.* **1967**, *89*, 5086.

Chart I



mediates for dialkylboranes, the present procedure provides, for the first time, a general and convenient access to a wide variety of highly desirable dialkylboranes (such as shown in Chart I).

Experimental Section

General. All of the manipulations involving air-sensitive substances were carried out under nitrogen according to standard procedures.[4] The ^{11}B NMR spectra of all compounds were recorded on a Varian FT-80A spectrometer. All hydride analyses were performed on the gasimeter.[4]

Materials. Tri-*sec*-butylborane and tricyclopentylborane were prepared by the hydroboration of *cis*-2-butene and cyclopentene with $BH_3 \cdot SMe_2$ in THF.[4] All other triorganylboranes used in the above procedure were made via our modified organometallic route.[13] Anhydrous ethyl ether from Mallinckrodt (+99.9%) was directly used in all of the experiments. $LiAlH_4$ was purchased from Alfa. A glycerol–water–THF (1:1:1) mixture was used as the hydrolysis solution for the hydride estimation of the lithium dialkylborohydrides.

General Procedure for the Preparation of LiR_2BH_2. The following procedure for the preparation of lithium diisopropylborohydride is representative.

To a well-stirred solution of triisopropylborane[13] (14.0 g, 100 mmol) in anhydrous ether (100 mL) was added $LiAlH_4$ in EE (100 mL, 1.0 M, 100 mmol) dropwise at 25 °C over a period of 0.5 h. The resulting homogeneous mixture was stirred for an additional 15 min and cooled to 0 °C, and then a solution of triethylenediamine in EE (100 mL, 0.5 M, 50 mmol) was slowly added to it. A white precipitate of bis(monoisopropylalane)–triethylenediamine was instantly thrown out of solution. The reaction mixture was stirred vigorously at 25 °C for 15 min and then allowed to settle overnight. The clear supernatant ether layer was then transferred into another flask and the precipitate was washed with anhydrous ether (2 × 50 mL). The washings were once again transferred into the other flask. The ^{11}B NMR analysis of the ethereal solution confirmed the formation of $Li(i\text{-}Pr)_2BH_2$ (δ −7.6, t, J = 62 Hz), while hydride analysis established its yield to be 99%.

Preparation of $LiMe_2BH_2$. Me_3B was first prepared directly from a mixture of methyl iodide, Mg turnings, and $BF_3 \cdot OEt_2$ according to our modified organometallic method[13] and collected as a gas into anhydrous ether at 0 °C. Subsequently, $LiAlH_4$ in EE (100 mL, 1.0 M, 100 mmol) which was initially cooled to 0 °C was added dropwise while stirring the solution. The reaction mixture was thus stirred for 15 min at 0 °C and then a cooled solution of triethylenediamine in EE (100 mL, 0.5 M, 100 mmol) was slowly added to it. A voluminous white precipitate of bis(monomethylalane)–triethylenediamine was instantly thrown out of solution. The reaction mixture was vigorously stirred for 15 min at 0 °C and then allowed to settle overnight at room temperature. The supernatant ether layer was transferred into another flask and the precipitate was thoroughly washed with ether (2 × 50 mL). The washings were next combined with the ethereal solution already separated into another flask. Once again, the ^{11}B NMR analysis of the ethereal solution confirmed the formation of $LiMe_2BH_2$ (δ −21.8, t, J = 64 Hz) while its yield was established to be 85% by the hydride analysis.

Acknowledgment. We thank the National Science Foundation (Grant CHE 8414171) for the financial support of this research.

Polar Effects in Free-Radical Reactions. Solvent and Isotope Effects and Effects of Base Catalysis on the Regio- and Chemoselectivity of the Substitution of Protonated Heteroaromatic Bases by Nucleophilic Carbon-Centered Radicals

Francesco Minisci,* Elena Vismara,* Francesca Fontana, Giampiero Morini, and Marco Serravalle

Dipartimento di Chimica del Politecnico, 20133 Milano, Italy

Claudio Giordano

Zambon Chimica S.p.A., Cormano (MI), Italy

Received October 17, 1986

The substitutions of protonated pyridine, quinaldine, lepidine, and 3-cyano- and 4-cyanopyridine by Ph, Me, *n*-Pr, *n*-Bu, *i*-Pr, *t*-Bu, α-tetrahydrofuranyl (α-THF), dioxanyl, and benzyl radicals are affected by the nature of the solvent as concerns the regioselectivity and the relative rates. The isotope effect is negligible with the phenyl radical, but it is significant and solvent-dependent with isopropyl and α-THF radicals. The effect of the solvent increases by increasing the nucleophilic character of the carbon-centered radicals. The results support a strong influence of the reversibility and of the polar effect on the substitutions of protonated heteroaromatic bases by nucleophilic carbon-centered radicals.

Few cases are known[1] where solvents do have a significant effect on the rates and selectivity of free-radical reactions.

The best known and striking example of solvent effect

0022-3263/87/1952-0730$01.50/0 © 1987 American Chemical Society