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FACILE REACTION OF POTASSIUM HYDRIDE WITH TRIALKYLBORANES, A CONVENIENT GENERAL SYNTHESIS OF SIMPLE AND HINDERED POTASSIUM TRIALKYLBOROHYDRIDES UNDER EXCEPTIONALLY MILD CONDITIONS *

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Summary

The reaction of potassium hydride in tetrahydrofuran with simple and hindered trialkylboranes proceeds readily at 25°C ($\leqslant$0.5 h) with the formation of the corresponding trialkylborohydrides. Even some highly hindered trialkylboranes react smoothly under these conditions. This reaction provides a convenient synthesis in high yields of such hindered and highly hindered potassium trialkylborohydride under very mild reaction conditions.

Introduction

In recent years, potassium hydride has emerged as an excellent reagent for the metalation of a variety of organic compounds, such as highly hindered alcohols, phenols, amines, ketones, sulfoxide, etc. [1]. In such reactions, potassium hydride has been demonstrated to be far superior to the alkali metal hydrides of lithium and sodium. Further, the reactivity of potassium hydride surpasses even finely divided potassium as a base, while possessing none of the latter's electron transfer properties. A number of organopotassium derivatives synthesized by this procedure have found major applications in organic synthetic transformations [2]. Preliminary investigations indicated potassium

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* Dedicated to Professor Herbert C. Brown in recognition of his contributions to chemistry.

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hydride also to be highly reactive towards weak Lewis acids of boron, e.g., trialkylboranes, producing the corresponding addition compounds potassium trialkylborohydrides [3]. Trends in lattice energy of saline hydrides suggest that reactivity should increase rapidly in the series lithium hydride < sodium hydride < potassium hydride [1a]. This has been supported by studies of reactions of hydrides with Brønsted acids. A recent study of reactions of lithium hydride and sodium hydride with organoboranes of increasing steric requirement also supports this trend. Lithium hydride was virtually inert toward hindered trialkylboranes, even in refluxing tetrahydrofuran (THF). Sodium hydride was found to be more reactive with hindered trialkylboranes but required reflux to react with tri-sec-butylborane; sodium hydride was inert toward exceptionally hindered boranes such as tris(3-methyl-2-butyl)borane [4]. Reactions of potassium hydride with trialkylboranes have been examined in hydrocarbon solvents; yields were poor in many cases [5]. Only a few reactions of potassium hydride with trialkylboranes have been examined; however, results suggest that the predicted ordering of reactivity is supported.

Recent studies have shown that the hindered and highly hindered trialkylborohydride anions are capable of introducing remarkable steric control in the reduction of cyclic ketones [3,6]. Consequently, the development of a general procedure for the synthesis of such hindered trialkylborohydrides under relatively mild conditions should be highly useful. We undertook a systematic study of the reaction in tetrahydrofuran of potassium hydride with representative trialkylboranes of increasing steric requirements with respect to rate, stoichiometry and products of the reaction.

Results and discussion

A representative series of trialkylboranes of increasing steric requirements (comprising unhindered, hindered, and highly hindered trialkylboranes) were selected for this study [7]. Their rates of reactions with potassium hydride in tetrahydrofuran at 25°C was examined. The stoichiometry of the reactions, and spectral (IR and ^{11}B NMR) and chemical characteristics of the resulting trialkylborohydrides were determined.

Reaction conditions and general procedure for the rates of reaction of potassium hydride with representative trialkylboranes in tetrahydrofuran

Commercially available potassium hydride (22—25% suspension in mineral oil, ~50% over that required by the stoichiometry) was placed in the reaction flask and the oil coating was removed by washing with n-pentane. Reactions were generally run with the potassium hydride suspended in a 1.0 *M* solution of the trialkylborane in THF; in some cases, low solubility of the trialkylborane required use of 0.5 *M* concentration. Reaction mixtures were prepared either by addition of pure trialkylborane to sufficient THF to produce a 1.0 *M* (or 0.5 *M*) solution or by addition of a solution of organoborane (produced in situ by hydroboration) in THF to dry powdered potassium hydride. Reactions were studied at room temperature with vigorous stirring under inert dry atmosphere. Trialkylborohydride formation was monitored by withdrawing known aliquots of the reaction mixture at various intervals of time and treating with an equiv-

TABLE 1

REACTION OF POTASSIUM HYDRIDE WITH REPRESENTATIVE TRIALKYLBORANES IN TETRAHYDROFURAN AT 25°C [a]

Trialkylborane	Trialkylborohydride formed (%) [b]								
	$\frac{1}{4}$h	$\frac{1}{2}$h	1h	2 h	3 h	6 h	12 h	24 h	72 h
Triethylborane	93	96	96						
Tri-n-butylborane	95	98	98						
Triisobutylborane	96	100	99						
Tri-sec-butylborane	82	93	100	100					
Tricyclopentylborane	100		95						
Tricyclohexylborane [c]	96	96	96						
Tri-*exo*-2-norbornylborane [d]	100	100							
Perhydro-9b-boraphenalene	92	98	98						
Tris(*trans*-2-methylcyclopentyl)borane					10	20		50	73
Trisiamylborane			2		4			9	

[a] Unless otherwise indicated, solutions were 1.0 *M* in R_3B and approximately 50% excess of potassium hydride was utilized. [b] Monitored by GLC by measuring the n-octane formed after quenching with n-octyl iodide or, in some cases, by hydrolysis of the clear reaction mixture after filtration. [c] 0.47 *M* in R_3B. [d] 0.6 *M* in R_3B.

alent amount of n-octyl iodide. GLC examination for n-octane formed (utilizing an internal standard) indicated the extent of the reaction [8]. Alternatively, the reaction course can be monitored by measuring the hydrogen evolved on hydrolysis of a known aliquot of the solution (centrifuged to remove suspended potassium hydride). The results are summarised in Table 1.

Effect of structure of the trialkylborane

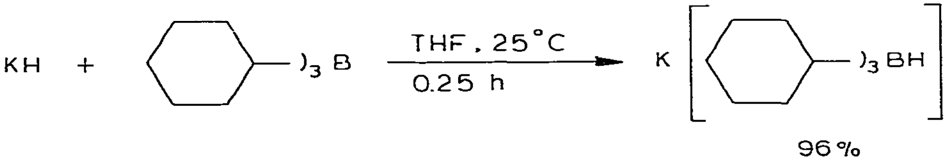
Unhindered trialkylboranes such as perhydro-9b-boraphenalene, triethyl-, tri-n-butyl-, and triisobutylboranes react with potassium hydride almost instantly and quantitatively in THF at 25°C (eq. 1). Indeed, reactions were so

$$\text{KH} + \text{i-Bu}_3\text{B} \xrightarrow[<0.5\text{ h}]{\text{THF, }25^\circ\text{C}} \underset{100\%}{\text{K-i-Bu}_3\text{BH}} \qquad (1)$$

rapid and vigorous that care was needed to control the reaction by (i) adding the trialkylborane slowly and/or (ii) effectively cooling the reaction flask in a water bath (ca. 20°C).

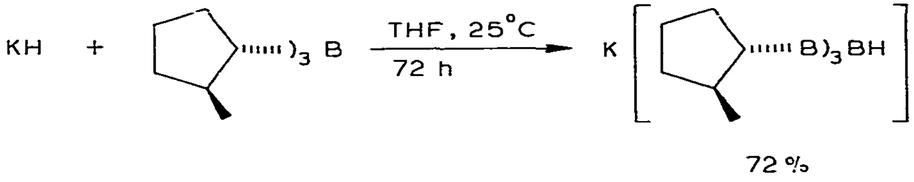
All of the hindered trialkylboranes examined, tri-sec-butyl-, tricyclopentyl-, tricyclohexyl-, and tri-*exo*-2-norbornylborane, react rapidly (0.25—1.0 h) and quantitatively at 25°C (eq. 2, 3).

$$\text{KH} + \text{sec-Bu}_3\text{B} \xrightarrow[1\text{ h}]{\text{THF, }25^\circ\text{C}} \underset{100\%}{\text{K-sec-Bu}_3\text{BH}} \qquad (2)$$



(3)

The reaction of highly hindered trialkylboranes with potassium hydride was quite sluggish. Thus, the reaction of tris(*trans*-2-methylcyclopentyl)borane proceeds to the extent of 50% in 24 h at 25° C; in 72 h period 73% of reaction was realized. Trisiamylborane [tris(3-methyl-2-butyl)borane] was essentially inert towards potassium hydride under these conditions (eq. 4, 5).



(4)

$$\mathrm{KH} + \mathrm{Sia_3B} \xrightarrow[24\ \mathrm{h}]{\mathrm{THF},\ 25^{\circ}\mathrm{C}} \underset{9\ \%}{\mathrm{KSia_3BH}} \qquad (5)$$

Comparison of the reactivity of potassium hydride vs. those of lithium and sodium hydrides

As is shown by reaction with tri-sec-butylborane: lithium hydride, 0% in 24 h; sodium hydride, 8% in 2 h; potassium hydride, 100% in 1 h (see Fig. 1), potassium hydride is exceptionally reactive. Very likely this is due to lower

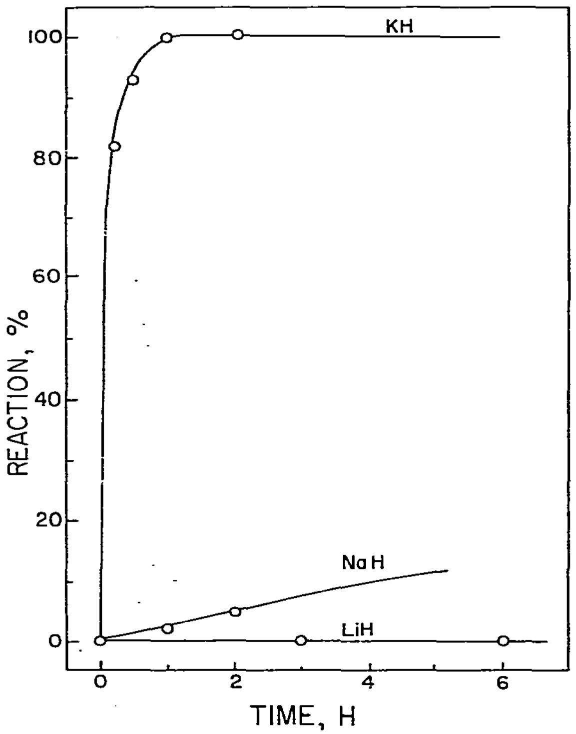


Fig. 1. Reaction of tri-sec-butylborane with saline hydrides in tetrahydrofuran at 25° C.

crystal lattice energy of the KH which would facilitate the reaction with trialkylboranes [1a].

Stoichiometry of the reaction

In the presence of excess potassium hydride, trialkylboranes appear to undergo a simple Lewis acid base reaction in 1/1 ratio to form a molecular addition compound (eq. 6).

$$\underset{\text{solid}}{KH} + \underset{\text{solution}}{R_3B} \rightarrow \underset{\text{solution}}{KR_3BH} \qquad (6)$$

Based on this stoichiometry, the ratio of K/B/H in solution should be 1/1/1. We undertook to analyze representative solutions of potassium trialkylborohydrides for potassium, boron, and hydride (Table 2). Indeed, such analyses revealed a 1/1/1 ratio.

Concentration of potassium was determined by hydrolyzing a known aliquot of the solution with water and titrating the base formed against standard acid. Boron was determined by GLC analysis of the alcohols produced by oxidation of the trialkylboranes to the corresponding alcohols. Hydride concentration was estimated by measuring the hydrogen evolved on hydrolysis of a known aliquot of the solution. Further, the observed concentration of the borohydride solution agreed quite well with the concentration calculated on the basis of the amount of trialkylborane and the total volume of the reaction mixture. The results summarized in Table 2 clearly establish the stoichiometry of the reaction between potassium hydride and trialkylborane to be 1/1 (eq. 6).

Infrared spectra

Tetrahydrofuran solutions of potassium trialkylborohydrides exhibit a strong and broad absorption in the infrared region around 2000 cm^{-1} due to the B—H stretching vibration in the borohydride anion. Similar observations have been recorded for the corresponding lithium and sodium analogs (4,5]. The exact frequency is dependent on the nature of the alkyl group on boron. The results are summarized in Table 3.

^{11}B NMR spectra

Solutions of potassium trialkylborohydrides in tetrahydrofuran exhibit clean sharp doublets (due to boron—hydrogen coupling) in the upfield region (relative to $BF_3 \cdot Et_2O$). In this respect, potassium trialkylborohydrides resemble sodium trialkylborohydrides [4]. It should be pointed out that the solutions of lithium trialkylborohydride exhibit sharp singlets rather than the expected doublets attributed to the presence of a minute quantity of free trialkylborane which rapidly exchanges with the trialkylborohydride. It is evident that, unlike lithium trialkylborohydride, the potassium derivatives do not have any tendency to dissociate into free trialkylborane and potassium hydride even to a slight extent. Indeed, fast exchange between unhindered potassium trialkylborohydrides and trialkylboranes (e.g., KEt_3BH/Et_3B system) has been observed in our laboratory [10]. The results are summarized in Table 4.

Stability of potassium trialkylborohydride solutions

Under dry nitrogen or argon atmosphere, solutions of potassium trialkyl-

(continued on p. 118)

TABLE 2

ANALYSIS OF POTASSIUM TRIALKYLBOROHYDRIDE SOLUTIONS IN TETRAHYDROFURAN

KH (mmol)	R_3B (mmol)	Total volume [a] (ml)	Time (h)	Temp (°C)	K^+ concn. [b] (*M*)	R_3B concn. [c] (*M*)	H^- concn. [d] (*M*)	Ratio			KR_3BH concn. Calc. [e]
								K	B	H	
45	i-Bu_3B(30)	30	4	25	1.00	0.95	0.98	1.05	1.00	1.03	1.00
45	s-Bu_3B(30)	30	4	25	1.05	0.99	1.00	1.06	1.00	1.01	1.00

[a] Final volume of the reaction mixture. [b] Determined by titration against standard acid. [c] Determined by GLC analysis of alcohol produced after oxidation. [d] By hydrolysis and measuring the hydrogen evolved. [e] Calculated from the amount of R_3B and the total volume of the reaction mixture.

TABLE 3

INFRARED SPECTRA OF POTASSIUM TRIALKYLBOROHYDRIDES IN TETRAHYDROFURAN

Trialkylhydride	ν(B—H) (cm^{-1})
Potassium triethylborohydride	2020
Potassium tri-n-butylborohydride	2015
Potassium triisobutylborohydride	2040
Potassium tri-sec-butylborohydride	2030
Potassium tricyclopentylborohydride	2040
Potassium tricyclohexylborohydride	2030
Potassium tri-*exo*-2-norbornylborohydride	2025
Potassium perhydro-9b-boraphenalylhydride	2030
Potassium tris(*trans*-2-methylcyclopentyl)borohydride)	2050

TABLE 4

^{11}B NMR SPECTRA OF POTASSIUM TRIALKYLBOROHYDRIDES IN TETRAHYDROFURAN

Trialkylborohydride	Chemical shift, [a] δ (ppm) (multiplicity)	J(B—H) (Hz)
Potassium triethylborohydride	—12.83(d)	70
Potassium tri-n-butylborohydride [b]	—15.46(d)	78
Potassium triisobutylborohydride	—18.44(d)	68
Potassium tri-sec-butylborohydride	—7.53(d)	68
Potassium tricyclopentylborohydride	—10.65(d)	65
Potassium tricyclophenylborohydride	—8.01(d)	70
Potassium tri-*exo*-2-norbornylborohydride	—9.46(d)	65
Potassium perhydro-9b-boraphenalylhydride [d]	—10.55(d)	70
	—11.77(d)	70
Potassium tris(*trans*-2-methylcyclopentyl)borohydride [e]	—12.22(d)	69

[a] All chemical shifts are relative to $BF_3 \cdot Et_2O$ with chemical shifts upfield from $BF_3 \cdot Et_2O$ assigned as negative. [b] Decoupled spectrum also showed a resonance at δ —12.6 ppm due to the presence of about 6% K(s-Bu)(n-Bu)$_2$BH. [d] Isomeric pairs. [e] Diastereomeric pairs.

TABLE 5

STABILITY OF POTASSIUM TRI-sec-BUTYLBOROHYDRIDE SOLUTION IN TETRAHYDROFURAN AT 25°C [a]

Experimental conditions	Hydride remaining (%)									
	0 h	$\frac{1}{2}$h	1 h	3 h	6 h	12 h	24 h	7 d	15 d	30 d
Dry nitrogen	1.05 (100)						1.05 (100)			1.04 (99)
Dry air	1.05 (100)		0.98 (93)	0.90 (86)			0.62 (59)			
Air and moisture	1.05 (100)	0.87 (83)	0.76 (72)	0.58 (55)	0.11 [b] (10)	0.0 [c] (0)				

[a] Figures in parentheses are percentages of hydride concentration compared with (0 h) concentration. [b] Solution becomes orange. [c] Solution turns dark red.

borohydrides are indefinitely stable. On exposure to air and moisture, they tend to lose hydride activity. However, the exposure to dry air destroys the hydride activity rather slowly (Table 5). Apparently these complex hydrides are more sensitive to moisture (hydrolysis) than to air (oxidation).

Conclusions

Potassium hydride reacts rapidly and quantitatively with almost all of the trialkylboranes examined. The reactivity of potassium hydride in these reactions is far greater than that of lithium and sodium hydrides. The reaction is exceptionally clean, proceeding in 1/1 stoichiometry forming the corresponding trialkylborohydride in excellent yields. The present reaction provides a simple and convenient route to many hindered and highly hindered trialkylborohydrides, highly useful for the stereoselective reduction of ketones.

Experimental

General comments

All glassware was dried at least 4 h at 140°C, assembled hot, and cooled under a stream of dry nitrogen or argon. All reactions were carried out under a dry nitrogen or argon atmosphere. All additions of liquids, trialkylboranes, solvents were carried out with oven-dried, nitrogen purged hypodermic syringes fitted with stainless steel needles.

Materials

Tetrahydrofuran, trialkylboranes, and potassium hydride were stored under nitrogen. Tetrahydrofuran was distilled from excess lithium aluminum hydride. The isomeric tributylboranes (Callery Chemical Co.) were distilled before use and triethylborane was used as such. All other trialkylboranes utilized in this study were prepared by the hydroboration of corresponding olefins with $BH_3 \cdot THF$ or with $BH_3 \cdot Me_2S$ dissolved in THF [10]. The majority of the olefins and alkanes employed in this study were from the Phillips Petroleum Company. Potassium hydride (24% mineral oil) used was obtained from the Ventron Corporation. It was separated from the oil matrix by washing three times with dry (Molecular Sieve) n-pentane.

Spectra

Infrared spectra were recorded in Perkin—Elmer grating spectrometers using sealed liquid cells [10]. ^{11}B NMR spectra were recorded on a Varian XL-100-15 spectrometer (32.1 MHz) fitted with a Nicolet 1080 data acquisition system. Results with this system confirmed earlier preliminary studies with continuous wave spectroscopy at 32.1 MHz using a Varian HA-100 in HR mode. All chemical shifts are relative to $BF_3 \cdot OEt_2$ [δ 0 ppm] with chemical shifts downfield from $BF_3 \cdot OEt_2$ assigned as positive.

GLC analyses

GLC analyses were carried out with a Varian Model 1200 FID Chromatograph.

Rates of reaction of potassium hydride with trialkylboranes in tetrahydrofuran at 25°C

A. Triisobutylborane. An oven-dried, 50-ml flask, equipped with a Teflon stopcock, a Silicone rubber stopple, and a magnetic stirring bar, connected to a mercury bubbler was cooled to room temperature under a stream of dry nitrogen. The flask was immersed in a water bath (ca. 25°C). In the flask was placed 5.3 g (33 mmol) of potassium hydride in mineral oil. The mineral oil was removed by washing with 3 × 30-ml of dry n-pentane. The last traces of pentane were removed by blowing with a dry stream of nitrogen. Tetrahydrofuran, 15 ml, was injected into the reaction flask. Then 5 ml (20 mmol) of triisobutylborane was added slowly (~1 min) and the resulting mixture was stirred well. A vigorous reaction began immediately and the disappearance of potassium hydride can be visibly seen. The resulting mixture is 1.0 *M* in triisobutylborane.

At the end of 15 min, 0.5 ml (0.5 mmol) of the reaction mixture was withdrawn using a syringe and injected into a 5-ml flask equipped with a magnetic stirring bar and maintained under a static pressure of nitrogen at 25°C. THF (1 ml) followed by 0.5 mmol of n-octyl iodide and 0.5 mmol of n-nonane were introduced. After stirring for 10 min, 1 ml of water was added and the THF layer was subjected to GLC analysis on a 5% SE-30 column, 6 ft × 0.125 in on Chromosorb W. There was present 96% of n-octane corresponding to the presence of 96% potassium triisobutylborohydride.

Similarly, the reaction was checked at 0.5 h (100%) and 1 h (100%). The reaction mixture was filtered to separate the excess potassium hydride giving a crystal clear solution of potassium triisobutylborohydride in THF, 1.05 *M* in hydride concentration. ^{11}B NMR δ — 18.44 ppm (d, *J* 68 Hz); IR: 2040 cm^{-1} (B—H).

B. Tri-sec-butylborane. The experimental set-up was the same as in the previous experiment. In the flask was placed 5.3 g (33 mmol) of potassium hydride and it was freed from the oil coating by washing with n-pentane. THF (15 ml) was injected into the reaction flask. The flask was immersed in a water bath (ca. 25°C). Then tri-sec-butylborane, 5 ml (20 mmol) was added slowly (~1 min). Immediately vigorous exothermic reaction was observed. The mixture was stirred vigorously. The reaction was monitored periodically by n-octyl iodide reduction technique, 0.25 (82%), 0.5 (93%), and 1 h (100%). Excess potassium hydride was removed by filtration and the clear solution exhibited hydride concentration of 1.0 *M* (100% yield). ^{11}B NMR δ — 7.53 ppm (d, *J* 68 Hz); IR: 2030 cm^{-1} (B—H).

C. Tricyclohexylborane. In a typical experiment, 5 g (30 mmol) of the potassium hydride dispersion was placed in a 100-ml flask as described in the previous experiment. The remainder of the apparatus was assembled and potassium hydride was freed of oil as before. Tricyclohexylborane, 42.6 ml (20 mmol) of a 0.47 *M* solution in THF, was added using a double-ended needle and the resulting mixture was stirred well. Periodically, the rate of reaction was monitored by the n-octyl iodide reduction method. The results summarized in Table 1 indicate that reaction was complete in 15 min producing potassium tricyclohexylborohydride in quantitative yield. ^{11}B NMR δ — 8.01 ppm (d, *J* 70 Hz); IR: 2030 cm^{-1} (B—H).

D. Tris(trans-2-methylcyclopentyl)borane. A typical reaction set-up was assembled and 13.3 g (75 mmol) of potassium hydride in mineral oil was placed in the reaction flask. It was freed from the oil matrix by washing with 3 X 40-ml portions of n-pentane. To this dry KH, 50 ml (50 mmol) of a 1 *M* solution of tris(*trans*-2-methylcyclopentyl)borane in THF was added. The resulting mixture was stirred well. At appropriate intervals of time 3-ml aliquots of the reaction mixture were withdrawn and centrifuged to separate the potassium hydride. The clear THF layer was hydrolyzed and the hydrogen evolved was measured.

Reaction was checked at 3 (19%), 6 (20%), 24 (50%), and 72 h (73%). ^{11}B NMR δ +83.5(s), −12.22(d, *J* 70 Hz), −13.45 (d, *J* 66 Hz). IR: 2050 cm^{-1} (B—H).

E. Trisiamylborane. Potassium hydride, 7.1 g (37.5 mmol) was treated with trisiamylborane (25 ml, 25 mmol) in THF at 25°C. The reaction was monitored periodically by the appearance of hydride concentration in the solution phase with time. In a 24 h period, only 9% of the reaction had taken place.

Stoichiometry. Ratio of K/B/H

Analysis of potassium tri-sec-butylborohydride solution in THF is representative. In a typical experiment, a 2-ml aliquot of the crystal clear solution of potassium tri-sec-butylborohydride, approximately 1.0 *M*, was hydrolyzed (THF + water 3 glycerine in 1/1 ratio) and the hydrogen evolved (52 ml) was measured. This indicated hydride concentration to be 1.0 *M*.

Potassium was determined by injection of 0.25 ml of the hydride solution into 3 ml water and titration of the released base with standard hydrochloric acid (0.2394 *M*) to a phenolphthalein endpoint. It required 1.10 ml of the acid, indicating the concentration of potassium to be 1.05 *M*.

Boron was determined by oxidation of 2 ml of the hydride solution using 1 ml of 3 *M* sodium hydroxide and 1.5 ml of 30% hydrogen peroxide. GLC analysis using n-dodecane as an internal standard revealed 5.94 mmol of 2-butanol. This corresponds to a boron concentration of 0.99 *M*.

The ratio of $K^+/B/H^-$ is thus 1.06/1.00/1.01, indicating 1/1/1 stoichiometry.

Similarly, analysis of potassium triisobutylborohydride solution in THF also revealed such a 1/1/1 stoichiometry. The results are summarized in Table 2.

Stability of potassium trialkylborohydrides

A. Dry nitrogen. Solutions of potassium tri-sec-butylborohydride were analyzed for the hydride concentration periodically by hydrolysis technique. The results clearly indicate that under dry nitrogen these reagents are indefinitely stable.

B. Effect of dry air. A 50-ml flask with a sidearm was fitted with a condenser protected by a drying tube (filled with Drierite^R) and flushed with dry air. Potassium tri-sec-butylborohydride, 20 ml (20 mmol) was introduced and allowed to stand exposed to dry air with constant stirring. At appropriate intervals, aliquots were removed and analyzed for residual hydride. Thus, in 1 h, only 7% hydride loss was observed and in 24 h 41% hydride had been destroyed.

C. Effect of air and moisture. Potassium tri-sec-butylborohydride solution, 15 ml, was introduced into a 50-ml flask. The flask was covered with a lid which had an opening 0.25″ in diameter. Periodically, aliquots were removed and analyzed for the residual hydride.

Results are summarized in Table 5.

References

1 (a) C.A. Brown, J. Org. Chem., 39 (1974) 3913 and the ref. cited therein; (b) idem, J. Amer. Chem. Soc., 95 (1973) 982; (c) idem, Synthesis, (1974) 427; (d) C.A. Brown, D. Barton and S. Sivaram, ibid., (1974) 434.

2 (a) C.A. Brown and A. Yamashita, J. Amer. Chem. Soc., 97 (1975) 591; (b) C.A. Brown and A. Yamashita, Chem. Commun., (1976) 959.

3 C.A. Brown, J. Amer. Chem. Soc., 95 (1973) 4100.

4 H.C. Brown, S. Krishnamurthy and J.L. Hubbard, manuscript submitted for publication.

5 P. Binger, G. Benedikt, G.W. Rotermund and R. Köster, Ann. Chem., 717 (1968) 21.

6 (a) S. Krishnamurthy, Aldrichimica Acta, 7 (1974) 55; (b) H.C. Brown and W.C. Dickason, J. Amer. Chem. Soc., 92 (1970) 709; (c) H.C. Brown and S. Krishnamurthy, ibid., 94 (1972) 7159; (d) S. Krishnamurthy and H.C. Brown, ibid., 98 (1976) 3383.

7 H.C. Brown, Boranes in Organic Chemistry, Cornell University Press, Ithaca, New York, 1972.

8 H.C. Brown and S. Krishnamurthy, J. Amer. Chem. Soc., 95 (1973) 1669.

9 C.A. Brown, Abstr. 172nd Nat. Meeting Amer. Chem. Soc., San Francisco, CA, September 1976 (ORGIN 153).

10 H.C. Brown, G.W. Kramer, A.B. Levy and M.M. Midland, Organic Syntheses via Boranes, Wiley—Interscience, New York, 1975.