ν_1 case, the concentration fluctuation has been found to be a dominant line broadening mechanism for the ν_3 mode of acetonitrile in CCl_4 solution.

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Attempts on the Preparation of Lithium Trialkoxyborohydrides. Stability and Stereoselective Reduction of Cyclic Ketones

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The reaction of potassium trialkoxyborohydrides of varying steric requirements with lithium chloride in tetrahydrofuran(THF) was examined in detail to establish the generality of this synthesis of the corresponding lithium trialkoxyborohydrides. The metal ion exchange reaction between potassium triisopropoxyborohydride and lithium chloride in THF proceeded instantly at room temperature and the corresponding lithium salt was very stable toward disproportionation. However, for R=*s*-Bu, *t*-Bu and 2-methylcyclohexyl, with increasing steric requirement, the lithium derivatives were unstable and thus dissociated into $(RO)BH_3^-$ and $(RO)_4B^-$. The stereoselectivity of lithium triisopropoxyborohydride(LIPBH) in the reduction of representative cyclic ketones was examined and compared with that of the potassium derivative.

Introduction

On effort to develop the new selective reducing agents possessing unique reducing characteristics, the method for preparation of potassium triisopropoxyborohydride(KIPBH) from triisopropoxyborane and potassium hydride was recently developed (eq 1).[1] This reagent is very stable toward disproportionation at room temperature when stored over an excess amount of potassium hydride.

$$KH + (i\text{-}PrO)_3B \xrightarrow[\text{reflux, 24h}]{\text{THF}} K(i\text{-}PrO)_3BH \quad (1)$$

The systematic study on the reaction of KIPBH with representative organic compounds under standardized conditions revealed that the reagent is a very mild reducing agent which can reduce only aldehydes, ketones and disulfides, and shows an excellent degree of stereoselectivity in the reduction of cyclic ketones.[2] Accordingly, development of a general procedure for the syntheses of potassium trialkoxyborohydrides in tetrahydrofuran(THF) has been of considerable interest. Recently, a general synthesis of potassium trialkoxyborohydrides by treating the corresponding trialkoxyboranes with excess potassium hydride in THF was reported (eq 2).[3]

$$KH + (RO)_3B \xrightarrow{\text{THF}} K(RO)_3BH \quad (2)$$

R=*i*-Pr, *s*-Bu, *t*-Bu, phenyl, cyclopentyl, 2-methylcyclohexyl

However, there has been no reports on the synthesis of stable lithium trialkoxyborohydrides. So far it has been known that the metal ion of borohydrides plays an important role in the reduction of organic compounds.[4] Thus, it is expected that

potassium and lithium ion in trialkoxyborohydrides would show different reducing characteristics. Preliminary experiments revealed that the reaction of trialkoxyboranes with excess lithium hydride did not proceed to the formation of lithium trialkoxyborohydrides. However, the metal exchange reaction seemed to be promising. Accordingly, we studied the reaction of stable potassium trialkoxyborohydrides with lithium chloride in the hopes of synthesis of stable lithium trialkoxyborohydrides as the following equation (eq 3).

$$K(RO)_3BH + LiCl \xrightarrow{THF} Li(RO)_3BH + KCl \downarrow \quad (3)$$

And also we examined the reducing characteristics of the stable lithium derivative in the reduction of cyclic ketones.

Results and Discussion

Representative trialkoxyboranes, such as triisopropoxyborane, tri-*sec*-butoxyborane, tri-*tert*-butoxyborane, and tris(2-methylcyclohexoxy) borane, were prepared from the corresponding alcohols and borane-methyl sulfide (BMS) according to the established procedure (eq 4).[3]

$$3ROH + BH_3 \cdot SMe_2 \xrightarrow{\Delta} (RO)_3B + 3H_2 \uparrow + SMe_2 \quad (4)$$

Potassium trialkoxyborohydrides were synthesized from the corresponding trialkoxyboranes and commercially available potassium hydride (22-25% suspension in mineral oil) after removing the oil by washing the reagent with THF, according to the published procedure (eq 2).[3] The infrared and ^{11}B NMR spectral data of potassium trialkoxyborohydrides are summarized in Table 1 for comparison with those of lithium derivatives.[3]

Reactions of potassium trialkoxyborohydrides and lithium chloride were generally carried out by adding lithium chloride solution in THF to the THF solution of potassium trialkoxyborohydrides at room temperature with stirring.

The white precipitate of potassium chloride was settled down immediately. The formation and stability of lithium trialkoxyborohydrides was monitored by infrared and ^{11}B NMR spectroscopy. The results are summarized in Table 2.

The reaction of metal ion exchange between potassium triisopropoxyborohydride(KIPBH) and lithium chloride in THF proceeded instantly to form the corresponding lithium derivative (LIPBH) at room temperature. The reagent, LIPBH, was very stable toward disproportionation at room temperature (eq 5). As far as we know, it is the first stable lithium trialkoxyborohydride to be prepared.

$$K(i\text{-}PrO)_3BH + LiCl \xrightarrow{THF} Li(i\text{-}PrO)_3BH + KCl \downarrow \quad (5)$$

It is evident that, in the presence of excess lithium chloride, potassium triisopropoxyborohydride undergoes a simple metal ion exchange reaction, forming the corresponging lithium derivative (eq 5). Analyses of the solution thus formed of

Table 1. Stability of Potassium Trialkoxyborohydrides, and Their Infrared and ^{11}B NMR Spectra

Trialkoxyborohydrides	Stability at room temperature	IR		^{11}B NMR	
		$\nu_{(B-H)}$ cm^{-1}	$\nu_{(B-O)}$ cm^{-1}	Chemical shift[c] δ(ppm) (Multiplicity)	$J_{(B-H)}$ (Hz)
Potassium triisopropoxyborohydride[a]	stable with KH[b]	2210	1375	6.1(d)	118
Potassium tri-*sec*-butoxyborohydride[a]	Stable with KH[b]	2220	1385	6.6(d)	119
Potassium tri-*tert*-butoxyborohydride	stable with or without KH	2200	1365	6.0(d)	113
Potassium tris(2-methylcyclohexoxy)borohydride	stable with KH	2160	1370	6.2(s)[d]	

[a]All trialkoxyboranes were consumed even at room temperature to produce the corresponding $K(RO)_3BH$ with a minor impurity of $K(RO)_4B$ (KIPBH: 2h; KSBBH:24h). However, refluxing was required for 24h to remove the impurity. [b]The potassium trialkoxyborohydrides were slowly dissociated when kept without potassium hydride. [c]All chemical shifts are relative to $BF_3 \cdot OEt_2$ with chemical shifts downfield from $BF_3 \cdot OEt_2$ assigned as positive. [d]Broad singlet.

Table 2. ^{11}B NMR Spectra of Lithium Trialkoxyborohydrides and Their Stability in Tetrahydrofuran

Lithium Salts[a]	IR		^{11}B NMR		Stability at room temperature
	$\nu_{(B-H)}$ cm^{-1}	$\nu_{(B-O)}$ cm^{-1}	Chemical shift[b] δ(ppm) (Multiplicity)	$J_{(B-H)}$ (Hz)	
Triisopropoxyborohydride	2220	1380	5.6(d)	125	stable
Tri-*sec*-butoxyborohydride			5.8(d)	124	slowly dissociated
Tri-*tert*-butoxyborohydride			4.4(d)	130	unstable
Tris(2-methylcyclohexoxy)-borohydride			4.7(s)[c]		unstable

[a]All potassium salts reacted with lithium chloride and the precipitate of potassium chioride was deposited immediately. [b]All chemical shifts are relative to $BF_3 \cdot OEt_2$ with chemical shifts downfield from $BF_3 \cdot OEt_2$ assigned as positive. [c]Broad singlet.

lithium triisopropoxyborohydride in THF for lithium, boron, and hydride using the standard method revealed that the ratio of Li/B/H in solution is 1/1/1.

The formation of hindered lithium trialkoxyborohydrides, such as tri-*sec*-butoxy-, tri-*tert*-butoxy- and tris(2-methylcyclohexoxy) borohydrides, was also completed immediately. However, these hindered lithium trialkoxyborohydrides thus formed were unstable under these experimental conditions. The ^{11}B NMR spectra of the reaction mixture of, for example, potassium tri-*sec*-butoxyborohydride and lithium chloride exhibited the presence of a considerable amount of Li(*s*-BuO)BH_3, Li(*s*-BuO)$_4$B and (*s*-BuO)$_3$B together with Li(*s*-BuO)$_3$BH, the expected product. Moreover, the products from the more hindered trialkoxyborohydrides, such as tri-*tert*- butoxy- and tris(2-methylcyclohexoxoy) borohydrides, underwent immediate redistribution. We suggest the dissociation involves the following mechanism (eq 6-9).

$$K(s\text{-BuO})_3BH + LiCl \rightarrow Li(s\text{-BuO})_3BH + KCl \downarrow \quad (6)$$

$$2\,Li(s\text{-BuO})_3BH \rightleftharpoons [Li(s\text{-BuO})_2BH_2] + Li(s\text{-BuO})_4B \quad (7)$$

$$[Li(s\text{-BuO})_2BH_2] + Li(s\text{-BuO})_3BH \rightleftharpoons Li(s\text{-BuO})BH_3 + Li(s\text{-BuO})_4B \quad (8)$$

$$Li(s\text{-BuO})_4 \rightleftharpoons (s\text{-BuO})_3B + s\text{-BuOLi} \quad (9)$$

It is evident that the stability of lithium trialkoxyborohydrides depends on the bulkiness of borohydrides. Thus, as increasing the steric requirements of alkoxyl group, the stability of lithium derivatives decreases. This phenomenon exhibits a striking contrast to that of potassium derivatives.[3] In the case of potassium trialkoxyborohydrides, the stability of these reagents increases as the bulkiness of alkoxyl group increases.

Lithium triisopropoxyborohydride in THF exhibits a strong and broad absorption around 2220 cm^{-1} in the infrared region, attributed to the B-H stretching vibration in the borohydride anion, but they do not show any boron-hydrogen bridge absorption band around 1550 and 2100 cm^{-1}.[5] ^{11}B NMR spectra of the solution of lithium trialkoxyborohydrides in THF exhibit clean, sharp doublets in slightly downfield region relative to $BF_3 \cdot OEt_2$, including other peaks due to the dissociated products except for the case of LIPBH. However, lithium tris (2-methylcylohexoxy) borohydride shows broad singlet in the upfield region, same as potassium derivative. The streoselectivity of lithium triisopropoxyborohydride toward representative cyclic ketones was studied, and the results are summarized in Table 3.

LIPBH reduced norcamphor and camphor, rigid bicyclic ketones, with somewhat higher degree of stereoselectivity than that of KIPBH, giving 97% and 96% of less stable isomers respectively. However, in the cases of reduction toward monocyclic ketones, LIPBH exhibited much less degree of stereoselectivity than KIPBH.

The reducing power of LIPBH appeared to be much stronger than that of KIPBH. However, LIPBH is still a mild hydride reducing agent. Thus, the reagent can not reduce amides, esters, epoxides, and other readily reducible functional structures. In addition to that, LIPBH, unlike KIPBH,[2] showed the possibility for selective reduction of nitriles to the corresponding aldehydes. Preliminary experiments revealed that LIPBH reduced benzonitrile to benzaldehyde in the yield of 70% within 24 h at room temperature. These selective reducing characteristics toward organic compounds are of interest and hence the further study is under investigation.

Conclusion

Lithium triisopropoxyborohydride(LIPBH) can be prepared cleanly from the corresponding potassium derivative and lithium chloride in tetrahydrofuran at room temperature (or 0°C), but the reaction fails in the cases of more hindered trialkoxyborohydrides, such as tri-*sec*-butoxy-, tri-*tert*-butoxy-, and tris (2-methylcyclohexoxy) borohydrides, where rapid disproportionation of the product occurs.

LIPBH shows much less degree of stereoselectivity than potassium triisopropoxyborohydride(KIPBH) in the case of reduction toward monocyclic ketones. However, the reagent shows a same or higher degree of stereoselectivity than KIPBH in the reduction of rigid bicyclic ketones.

In addition, LIPBH is a mild reducing agent, possessing an unique reducing characteristics toward organic compounds, even though its reducing power is much stronger than KIPBH. Furthermore, since the structure of LIPBH is very similar to one of the intermediates on the reaction of aldehydes or ketones with lithium borohydride, LIPBH is expected to contribute for the mechanistic study on the borohydride reduction.

Experimental

All glassware used was dried in an oven, assembled hot and cooled with a stream of nitrogen. All reactions were carried out under nitrogen atmosphere. Experimental techniques used in handling air-sensitive materials are described elsewhere.[6] Tetrahydrofuran was dried over a 4-Å molecular sieve and distilled from sodium benzophenone ketyl prior to use. Potassium hydride(Alfa) was freed from the mineral oil

Table 3. Stereoselective Reaction of Lithium Triisopropoxyborohydride with Cyclic Ketones in Tetrahydrofuran at 0°

Ketone	H^-/comp.	Reaction time(h)	Less stable isomer(%)[a]	
			LIPBH[c]	KIPBH[b]
2-methylcyclohexanone	2/1	5	68	91
3-methylcyclohexanone	2/1	5	45	74
4-methylcyclohexanone	2/1	5	24	66.5
4-*t*-butylcyclohexanone	2/1	24	28	53.0
3,3,5-trimethylcyclohexanone	2/1	24	93	95.5
norcamphor	2/1	5	97	95.5
camphor	2/1	48	96	91[c]

[a]The yields of alcohols were quantitative. [b]Data taken from ref (2). [c]Present study.

according to the published procedure.[3] All trialkoxyboranes, prepared from the corresponding alcohols and borane–methyl sulfide, were distilled from a small piece of potassium metal. ^{11}B NMR spectra were recorded on a Varian FT-80, and all chemical shifts were reported in δ (ppm) relative to $BF_3 \cdot OEt_2$. IR spectra were recorded on a Perkin-Elmer 1330 spectrophotometer. GC analyses were performed using a Hewlett-Packard 5790 FID chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter. The alcohol products were analyzed using a 12ft × 0.125 in. column packed with 15% THEED on 100/120 mesh Supelcoport or 10% Carbowax 20M on 100/120 mesh Supelcoport with the use of a suitable internal standard and authentic mixture.

Preparation of Tri-sec-butoxyborane (Representative).

The trialkoxyborane was prepared according to the established procedure.[3] An oven-dried, 1-*l*, round-bottom flask with side arm, condenser tube, and adaptor was attached to a mercury bubbler. The flask was flushed with dry nitrogen and maintained under static pressure of nitrogen and was charged with 100 m*l* of 10M borane–methyl sulfide complex (1 mol) and kept at room temperature by using a water bath. A total of 226g (3.05 mol) of *sec*-butyl alcohol was added dropwise to the borane–methyl sulfide complex *via* a double-ended needle while the mixture was stirred at room temperature. After completion of addition, the reaction mixture was brought to a gentle reflux to evolve all of the hydrogen (2 h). The ^{11}B NMR spectrum of the reaction mixture showed a single peak at δ17.5 corresponding to tri-*sec*-butoxyborane. The trialkoxyborane was further purified by distillation from a small piece of potassium metal: bp 99–99.5°C (29mm); n_D^{20} 1.3941.

Preparation of Potassium Tri-sec-butoxyborohydride (KSBBH).

The preparation of KIPBH, prepared according to the published procedure,[3] is representative. An oven-dried 2-*l* round-bottom flask with side arm, condenser tube, and adaptor was attached to a mercury bubbler. The flask was flushed with dry nitrogen and maintained under a static pressure of nitrogen. To this flask was added 60g of KH(1.5 mol) as an oil dispersion with the aid of a double-ended needle. The mineral oil was removed with THF (3×50 m*l*). To this pure KH was added ca. 500 m*l* of freshly distilled THF. The suspended KH was kept at room temperature by using a water bath. A total of 172.6g (0.75 mol) of distilled tri-*sec*-butoxyborane was added to the KH suspension in THF *via* a double-ended needle while the mixture was stirred vigorously. After completion of addition, the reaction mixture was brought to gentle reflux over the excess KH. The ^{11}B NMR spectrum of the mixture after 24 h showed a clean doublet centered at δ6.55 (J_{B-H} = 119 Hz), indicating the formation of pure potassium tri-*sec*-butoxyborohydride.

Reaction of KSBBH with Lithium Chloride in THF (Representative)

A 50-m*l* centrifuge vial fitted with a rubber septum and magnetic stirring bar was charged with 20 m*l* of 0.95 M KSBBH–THF solution (19 mmol) at room temperature. To this was added 21 m*l* of 0.95 M lithium chloride–THF solution (20 mmol, 5% excess) dropwise with stirring. A white precipitate, presumably potassium chloride, was formed immediately. After the addition of lithium chloride, the stirring was continued for 1 h at room temperature. The supernatant solution was transferred by using a double-ended needle and subjected to ^{11}B NMR analysis. ^{11}B NMR spectra at this time showed a major peak at δ 5.8(J_{B-H} = 124 Hz), assigned to Li(*s*-BuO)$_3$ BH, the expected product, along with a minor one at δ17.5, assigned to (*s*-BuO)$_3$B. However, the spectra changed slowly with time, showing a new peak at δ2.8 of Li(*s*-BuO)$_4$B and at δ-13 of Li(*s*-BuO)BH_3 (multiplicity), along with a peak of (*s*-BuO)$_3$B increased.

General procedure for Stereoselective Reaction

The reaction of norcamphor with LIPBH is representative. To a 50-m*l* round-bottom flask fitted with a side arm and capped by a rubber septum was added a 2.2 m*l* solution of LIPBH in THF (2.0 mmol in hydride). The flask was kept at 0°C with the aid of an ice-water bath. To this was added 1.0 m*l* of a norcamphor in THF (1.0 M in ketone). The reaction mixture was kept at 0°C for 5 h. It was then hydrolyzed by addition of 2 m*l* of 2 N HCl solution. The aqueous layer was saturated with anhydrous potassium carbonate, and the organic layer was analyzed by GC.

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