Raman-scattered radiation was observed at 45° to the laser beam or 90° to the sample tube. Low-temperature spectra were recorded by mounting the sample vertically in an unsilvered Pyrex glass Dewar filled with liquid nitrogen.

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Registry No. $Xe(OTeF_5)_4$, 66255-64-9; $FXe(OTeF_5)_3$, 91002-50-5; *trans*-$F_2Xe(OTeF_5)_2$, 91002-51-6; *cis*-$F_2Xe(OTeF_5)_2$, 91108-44-0; $F_3Xe(OTe_5)$, 91002-52-7; XeF_4, 14989-42-5; $OXe(OTeF_5)_4$, 68854-32-0; $OXeF(OTeF_5)_3$, 68854-36-4; *trans*-$OXeF_2(OTeF_5)_2$, 68889-95-2; *cis*-$OXeF_2(OTeF)_2$, 68854-35-3; $OXeF_3(OTeF_5)$, 91108-43-9; $OXeF_4$, 13774-85-1; $O_2Xe(OTeF_5)_2$, 91002-53-8; $O_2XeF(OTeF_5)$, 91002-54-9; O_2XeF_2, 13875-06-4; ^{18}O, 14797-71-8; ^{17}O, 13968-48-4; ^{129}Xe, 13965-99-6.

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Addition Compounds of Alkali-Metal Hydrides. 24. A General Method for Preparation of Potassium Trialkoxyborohydrides. A New Class of Reducing Agents

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The generality of the synthesis of potassium triisopropoxyborohydride, stabilized toward disproportionation by storing over excess potassium hydride, was examined with seven additional organoborates of varying steric requirements. The reaction of trimethoxy- and triethoxyborane with potassium hydride proceeded readily at room temperature, but the products could not be stabilized by the presence of excess potassium hydride. Triphenoxyborane reacted readily, even at −10 °C, and stabilization was achieved. Tri-*sec*-butoxy- and tricyclopentoxyborane required refluxing in THF for 12–24 h, and the products were stabilized over potassium hydride. Finally, the reactions of tris(2-methylcyclohexoxy)- and tri-*tert*-butoxyborane were even slower, requiring a number of days for completion. Both products were stabilized toward disproportionation over potassium hydride. Indeed, potassium tri-*tert*-butoxyborohydride was quite stable toward disproportionation without excess potassium hydride. The stereoselectivities of these reagents in the reduction of representative cyclic ketones were examined. The stereoselectivities varied in an erratic manner with the steric requirements of the alkoxy group and did not approach the stereoselectivities previously achieved with lithium tri-*sec*-butylborohydride and lithium trisiamylborohydride.

Recently we reported an improved method for preparation of potassium triisopropoxyborohydride (K(IPBH)) from triisopropoxyborane and potassium hydride[2] (eq 1). Moreover,

$$(i\text{-PrO})_3B + KH \rightarrow K(i\text{-PrO})_3BH \quad (1)$$

K(IPBH), thus prepared, is stable toward disproportionation at room temperature when maintained over a small excess of potassium hydride.

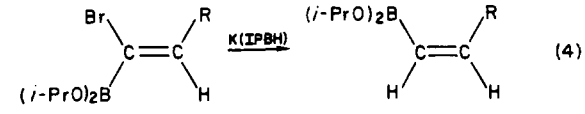
The reagent, K(IPBH), is a very mild reducing agent and, unlike sodium and potassium borohydrides, shows a high degree of stereoselectivity toward cyclic ketones.[3]

K(IPBH) readily transfers hydride to dialkylhaloboranes or trialkylboranes to produce the corresponding dialkylboranes and trialkylborohydrides, respectively[4,5] (eq 2 and 3).

$$R_2BX + K(i\text{-PrO})_3BH \rightarrow R_2BH + KX + (i\text{-PrO})_3B \quad (2)$$

$$R_3B + K(i\text{-PrO})_3BH \rightarrow KR_3BH + (i\text{-PrO})_3B \quad (3)$$

It also provides a valuable procedure for the synthesis of *cis*-vinylboronic esters[6] (eq 4).



(4)

Table I. ^{11}B NMR Spectra and Physical Properties of Trialkoxyboranes

trialkoxyborane	^{11}B NMR chem shift,[a] δ	bp, °C (*P*, torr)	$n^{20}D$
trimethoxyborane	18.3	68.5–70 (748)	1.3555
triethoxyborane	17.8	43 (40)	1.3732
triisopropoxyborane	17.5	60 (42)	1.3741
tri-*sec*-butoxyborane	17.5	99–99.5 (29)	1.3941
tri-*tert*-butoxyborane	15.6	85 (42)	1.3871
tricyclopentoxyborane	17.8	132–133 (3.7)	1.4571
tris(2-methylcyclohexoxy)-borane[b]	18.6	162–164 (0.4)	
triphenoxyborane[c]	16.8[d]	232–234 (2.8)	

[a] All chemical shifts are reported relative to $BF_3 \cdot OEt_2$ with chemical shifts downfield from $BF_3 \cdot OEt_2$ assigned as positive. [b] Very viscous liquid. [c] Solid, mp 99–101 °C. [d] In THF.

These unique characteristics of K(IPBH) stimulated us to investigate other members of the potassium trialkoxyborohydride family. Accordingly, we undertook a study to develop a general procedure for the synthesis of potassium trialkoxyborohydrides in tetrahydrofuran (THF) with representative trialkoxyboranes of different steric requirements and to examine their stereoselectivities in the reduction of cyclic ketones.

Results and Discussion

Trialkoxyboranes were prepared from the corresponding alcohols and borane–methyl sulfide complex (BMS) according to the published procedure with a slight modification[7] (eq 5).

$$3ROH + BH_3 \cdot SMe_2 \xrightarrow{\Delta} (RO)_3B + 3H_2\uparrow + SMe_2 \quad (5)$$

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(6) Research in progress with T. Imai.
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Table II. Reaction of Potassium Hydride with Representative Trialkoxyboranes in Tetrahydrofuran[a] and Stability of the Potassium Trialkoxyborohydrides at Room Temperature

trialkoxyborane	temp	time	stability of $K(RO)_3BH$ at room temp
trimethoxyborane	RT	instantly	unstable
triethoxyborane	RT	instantly	unstable
triisopropoxyborane[b]	reflux	24 h	stable with KH[d]
tri-*sec*-butoxyborane[b]	reflux	24 h	stable with KH[d]
tri-*tert*-butoxyborane	reflux	5 days	stable with or without KH
tricyclopentoxyborane	RT	12 h	stable with KH[d]
tris(2-methylcyclohexoxy)-borane	reflux	12 days	stable with KH[d]
triphenoxyborane[c]	−10 °C	instantly	stable with KH[d]

[a] Solutions were 1.0 M in $(RO)_3B$, and an approximately 100% excess of potassium hydride was utilized. [b] All trialkoxyboranes were consumed even at room temperature to produce the corresponding $K(RO)_3BH$ with a minor impurity of $K(RO)_4B$ (K(IPBH) 2 h; K(SBBH) 24 h). However, refluxing was required to remove the impurity. [c] The solubility of $K(C_6H_5O)_3BH$ in THF is low (0.7 M at 25 °C; 0.35 M at 0 °C; almost insoluble at −25 °C). [d] The potassium trialkoxyborohydrides slowly dissociated when kept without potassium hydride.

The ^{11}B NMR spectra and physical properties of various trialkoxyboranes, prepared in this study, are summarized in Table I.

Potassium trialkoxyborohydrides were prepared 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 (eq 6).

$$KH + (RO)_3B \xrightarrow{THF} K(RO)_3BH \qquad (6)$$

Reactions were generally carried out by adding trialkoxyborane to potassium hydride (100% excess over the stoichiometric amount) suspended in sufficient THF to produce a nearly 1.0 M potassium trialkoxyborohydride solution. Reactions were studied at various temperatures (−10 °C, 0 °C, room temperature, or under reflux). The formation of trialkoxyborohydride was monitored by ^{11}B NMR spectroscopy to establish the approximate rate and stability under these experimental conditions. The results are summarized in Table II.

Unhindered trialkoxyboranes such as trimethoxy- and triethoxyboranes react with potassium hydride rapidly. However, the corresponding potassium trialkoxyborohydrides are unstable under these experimental conditions. The ^{11}B NMR spectra of the reaction mixture of trimethoxyborane with potassium hydride exhibited the presence of a considerable amount of $K(CH_3O)BH_3$ and $K(CH_3O)_4B$[8] together with $K(CH_3O)_3BH$, the expected product.

The formation of hindered potassium trialkoxyborohydrides, such as triisopropoxyborohydride (K(IPBH)), tri-*sec*-butoxyborohydride (K(SBBH)), and tri-*tert*-butoxyborohydride (K(TBBH)) in high purity, from the reaction of the corresponding trialkoxyboranes with potassium hydride required refluxing in THF for 1–5 days. These borohydrides are stable for more than 6 months at room temperature when stored over a small excess of potassium hydride. Especially, K(TBBH), the most hindered one in this series, is so stable that no potassium hydride is necessary to keep it in pure form.

Of the tricycloalkoxyboranes examined, tricyclopentoxyborane reacts with potassium hydride at a moderate rate with the reaction being complete in 12 h at room temperature. However, the reaction of tris(2-methylcyclohexoxy)borane with potassium hydride was very slow, requiring approximately 12 days for completion, even under reflux.

Table III. Infrared and ^{11}B NMR Spectra of Potassium Trialkoxyborohydrides in Tetrahydrofuran

	IR		^{11}B NMR	
trialkoxyborohydride	ν(B–H), cm^{-1}	ν(B–O), cm^{-1}	chem shift,[a] δ (multiplicity)	J(B–H), Hz
potassium triisopropoxy-borohydride	2210	1375	6.1 (d)	118
potassium tri-*sec*-butoxy-borohydride	2220	1385	6.6 (d)	119
potassium tri-*tert*-butoxyborohydride	2200	1365	0.0 (d)	113
potassium tricyclo-pentoxyborohydride	2145	1365	6.2 (s)[b]	
potassium tris(2-methyl-cyclohexoxy)-borohydride	2160	1370	6.7 (s)[b]	
potassium triphenoxy-borohydride	2370	1330	4.5 (s)	

[a] All chemical shifts are relative to $BF_3{\cdot}OEt_2$ with chemical shifts downfield from $BF_3{\cdot}OEt_2$ assigned as positive. [b] Broad singlet.

Triphenoxyborane reacts with potassium hydride almost instantly, even at −10 °C, to produce potassium triphenoxyborohydride precipitating from the solution. This borohydride exhibits a very low solubility in THF, especially at lower temperature. It is also stable when maintained over potassium hydride at room temperature.

It is evident that, in the presence of excess potassium hydride, many trialkoxyboranes undergo a simple addition reaction in a 1/1 molar ratio, forming the corresponding molecular addition compound (eq 6). Analyses of the solutions thus formed of potassium trialkoxyborohydrides in THF for potassium, boron, and hydride using the standard method[9] revealed that the ratio of K/B/H in solution is always 1/1/1. These results clearly establish the stoichiometry of the reaction between potassium hydride and trialkoxyborane to be 1/1.

Potassium trialkoxyborohydrides in THF exhibit a strong and broad absorption around 2200 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}.[10] ^{11}B NMR spectra of the solutions of K(IPBH), K(SBBH), and K(IBBH) in THF exhibit clean, sharp doublets in the same or slightly downfield region relative to $BF_3{\cdot}OEt_2$. However, both potassium tricycloalkoxyborohydrides and potassium triphenoxyborohydride show broad singlets in the upfield region, suggesting either that the reactions have not gone to completion or that these borohydrides must be slightly dissociated into free trialkoxyborane and potassium hydride. In the presence of a small quantity of free trialkoxyborane, an exchange reaction would convert the usual doublet into a singlet. These results are summarized in Table III.

The stereoselectivity of these trisubstituted borohydrides toward representative cyclic ketones was studied, and the results are summarized in Table IV. K(SBBH) showed a greater degree of stereoselectivity than K(IPBH). However, the bulkier borohydride, K(TBBH), did not show any higher degree of stereoselectivity than K(IPBH) or K(SBBH). Potassium tricyclopentoxyborohydride and potassium triphenoxyborohydride reduce norcamphor, a rigid bicyclic ketone, with good stereoselectivity, giving 96% and 93.5% *endo*-norborneol, respectively. However, they do not show high ste-

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Table IV. Stereoselective Reaction of Potassium Trialkoxyborohydrides with Cyclic Ketones in Tetrahydrofuran at 0 °C and −25 °C[a,b]

ketone	temp, °C	R in $K(RO)_3BH$				
		i-Pr	*sec*-Bu	*tert*-Bu[c]	cyclopentyl	phenyl[d]
2-methylcyclohexanone	0	91	93	62	39.5	35
	−25	91.5	93.5	71	49	
3-methylcyclohexanone	0	74	82.5	46	33.5	21
	−25	80	84	50	39.5	
4-methylcyclohexanone	0	66.5	70	33	27.5	15
	−25	69	74.5	46	28.5	
4-*tert*-butylcyclohexanone	0	53	70.5	34	23	15
	−25	54.5	74	34.5	29.5	
3,3,5-trimethylcyclohexanone	0	95.5	97.5	87.5	60.5	81
	−25	96	98	92.5	67.5	
norcamphor	0	95.5	96	96	96	93.5
	−25	97.5	97.5	96.5	96.5	

[a] A 2:1 $K(RO)_3BH$:ketone ratio was used. [b] The yields of alcohols were more than 99%, and the figures are the percentages of the less stable isomers. [c] Very slow reaction. [d] Very slow heterogeneous reaction.

reoselectivity toward monocyclic ketones.

Conclusion

The higher potassium trialkoxyborohydrides can be prepared cleanly from the corresponding trialkoxyboranes and excess potassium hydride in tetrahydrofuran, but the reaction fails in the case of unhindered trialkoxyborohydrides, such as trimethoxy- and triethoxyborohydrides, where rapid disproportionation of the product occurs.

In the case of the most hindered derivative prepared, potassium tri-*tert*-butoxyborohydride, the product proved stable toward disproportionation in THF solution, even in the absence of added potassium hydride.

Among the higher derivatives examined, potassium triisopropoxyborohydride (K(IPBH)) and potassium tri-*sec*-butoxyborohydride (K(SBBH)) show a high degree of stereoselectivity toward cyclic ketones. These trialkoxyborohydrides have definite advantages over sodium or potassium borohydride since they are soluble in common organic solvents such as THF, diethyl ether, and glymes, and their reducing characteristics are not only highly chemoselective, but also stereoselective. Furthermore, since they carry only 1 equiv of hydride per molecule, mechanistic studies are expected to be less complicated than for borohydride reagents such as sodium borohydride, which has 4 equiv of hydride per molecule, each of which reacts at different rates.

Experimental Section

Materials. Tetrahydrofuran was dried over a 4-Å molecular sieve and distilled from sodium benzophenone ketyl prior to use. Potassium hydride was purchased from Alfa and was freed from the mineral oil according to the published procedure.[11] Triisopropoxyborane and tri-*tert*-butoxyborane were either purchased from Aldrich Chemical Co. or prepared from the corresponding alcohols and borane–methyl sulfide complex. All trialkoxyboranes were distilled from a small piece of potassium metal prior to use. ^{11}B NMR spectra were recorded on a Varian FT-80, and all ^{11}B NMR chemical shifts are reported relative to $BF_3{\cdot}OEt_2$ with chemical shifts downfield from $BF_3{\cdot}OEt_2$ assigned as positive.

GC Analyses. GC analyses were carried out by using a Varian Model 1400 FID chromatograph or a Hewlett-Packard 5750 TC chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter. The alcohol products were analyzed by using a 12 ft × 0.125 in. column of 15% THEED on a 100/120 mesh Supelcoport or 10% Carbowax 20M on 100/120 mesh Supelcoport. All GC yields were determined by using a suitable internal standard and authentic mixture.

Preparation of Tri-*sec*-butoxyborane (Representative). 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 mL of 10 M borane–methyl sulfide complex (1 mol) and kept at room temperature by using a water bath. A total of 226 g (3.05 mmol) 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 δ 17.5 corresponding to tri-*sec*-butoxyborane. The trialkoxyborane was further purified by distillation from a small piece of potassium metal: bp 99–99.5 °C (29 mm); n^{20}_D 1.3941. The results for other trialkoxyboranes are summarized in Table I.

Preparation of Potassium Tri-*sec*-butoxyborohydride (K(SBBH)) under Reflux Conditions in THF. 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 60 g 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 mL). To this pure KH was added ca. 500 mL of freshly distilled THF. The suspended KH was kept at room temperature by using a water bath. A total of 172.6 g (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 δ 6.55 (J_{BH} = 119 Hz), indicating the formation of pure potassium tri-*sec*-butoxyborohydride. An aliquot of K(SBBH) solution was quenched with water, and its potassium and boron contents were measured as potassium hydroxide and boric acid.[9] Hydride concentration was estimated by measuring the number of moles of hydrogen evolved when the reagent was hydrolyzed with a mixture of THF, glycerine, and 2 N HCl. A 0.93 M concentration of boron and hydride contents was observed. Potassium content was measured as 0.95 M. Therefore, a 1.00:0.98:0.98 ratio of K:B:H was established.

General Procedure for Stereoselective Reaction. The reaction of 2-methylcyclohexanone with K(SBBH) is representative. To a 50-mL round-bottom flask fitted with a side arm and capped by a rubber septum was added a 2.2-mL solution of K(SBBH) in THF (2.0 mM in hydride). The flask was kept at 0 °C with the aid of an ice–water bath. To this was added 1.0 mL of a 2-methylcyclohexanone solution in THF (1.0 M in ketone). The reaction mixture was kept at 0 °C for 3 h (3 days at −25 °C). It was then hydrolyzed by addition of 2 mL of 2 N HCl solution. The aqueous layer was saturated with anhydrous potassium carbonate, and the organic layer was analyzed by GC. The results are summarized in Table IV.

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Registry No. K(IPBH), 42278-67-1; K(SBBH), 91266-55-6; K(TBBH), 86743-57-9; $(i\text{-PrO})_3B$, 5419-55-6; BH_3, 13283-31-3; KH, 7693-26-7; trimethoxyborane, 121-43-7; triethoxyborane, 150-46-9; tri-*sec*-butoxyborane, 22238-17-1; tri-*tert*-butoxyborane, 7397-43-5; tricyclopentoxyborane, 65144-07-2; tris(2-methylcyclohexoxy)borane, 24848-82-6; triphenoxyborane, 1095-03-0; potassium tricyclopentoxyborohydride, 91266-56-7; potassium tris(2-methylcyclohexoxy)borohydride, 91294-43-8; potassium triphenoxyborohydride, 91266-57-8; 2-methylcyclohexanone, 583-60-8; 3-methylcyclohexanone, 591-24-2; 4-methylcyclohexanone, 589-92-4; 4-*tert*-butylcyclohexanone, 98-53-3; 3,3,5-trimethylcyclohexanone, 873-94-9; norcamphor, 497-38-1; *sec*-butyl alcohol, 78-92-2; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; *tert*-butyl alcohol, 75-65-0; cyclopentanol, 96-41-3; 2-methylcyclohexanol, 583-59-5; phenol, 108-95-2.

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