Preparation and Behavior of β-Naphthoxyboron Hydride Species

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β-Naphthoxyboranes and lithium tri-β-naphthoxyborohydride were prepared and their properties were investigated by ^{11}B-NMR. The reducing power of lithium tri-β-naphthoxyborohydride is weaker than lithium borohydride.

Introduction

Standard solution of lithium aluminum hydride in ethereal solvlents readily reacts with primary, secondary, and tertiary alcohols leading to the convenient synthesis of alkoxyaluminohydrides. The addition of four moles of methyl, ethyl, or isopropyl alcohol at 25°C to ether solution of one mole lithium aluminum hydride results in the evolution of four moles of hydrogen and the precipitation of the corresponding lithium tetraalkoxyaluminates. However, the addition of four moles of t-butyl alcohol generates only three moles of hydrogen.[1]

$$LiAlH_4 + 4MeOH \rightarrow LiAl(OMe)_4 + 4H_2$$
$$LiAlH_4 + 4EtOH \rightarrow LiAl(OEt)_4 + 4H_2$$
$$LiAlH_4 + 4i\text{-}PrOH \rightarrow LiAl(OPr\text{-}i)_4 + 4H_2$$
$$LiAlH_4 + 3t\text{-}BuOH \rightarrow Li(t\text{-}BuO)_3AlH + 3H_2$$

In General, alkoxyborane and lithium alkoxyaluminohydride are prepared from the reaction of alcohols with lithium aluminum hydride or borane. For example, catechol reacts with borane to produce catecholborane.[2]

In the course of the photo-enhanced reduction of esters by metal borohydrides, a reducing agent having a chromophore itself was required and we selected naphthoxy group as a chromophore. We prepared alkoxy-borohydrides by reacting lithium borohydride with β-naphthol and β-naphthoxyboranes by reacting borane-THF with β-naphthol, since these reactions offer the most convenient routes. The nature of these reagents was investigated by ^{11}B-NMR spectroscopy.

Experimental

Materials. Sodium borohydride (95+% purity, Ventron) was used after thoroughly dried in a heated vacuum dessicator at 110°C for 3 h. Tetrahydrofuran was treated with excess sodium and benzophenone, distilled under the anhydrous nitrogen atmosphere, and stored under a slightly positive nitrogen pressure in a flask equipped with a rubber septum syringe inlet. Borane-THF was prepared by the reaction of sodium borohydride with dimethyl sulfate in THF[3]. Lithium borohydride was prepared by the reaction of sodium borohydride with lithium chloride in THF[4]. 2-Chlorophenyl cyclohexanecarboxylic ester was synthesized by esterification of the corresponding cyclohexanecarboxylic acid (m.p. 34-35°C).

Instruments. Gas chromatographic (GC) analyses of product mixture and purified samples were performed on a Varian 2800 Gas Chromatograph with a FID detector. Boron NMR spectra were recorded on a Varian FT-80A spectrometer.

Preparation of Lithium Tri-β-naphthoxyborohydride-THF Solution. 60 mmol of lithium borohydride in THF (67 m*l*), maintained under nitrogen atmosphere, was placed in a dry 100 m*l*- flask with a magnetic stirrer and a reflux condenser which was connected to a mercury bubbler. The flask was immersed in an ice bath and 180 mmol of β-naphthol (25.95 g) in THF (20 m*l*) was added over 30 min to the borohydride solution with stirring at 0°C. After completion of the addition, the reaction mixture was stirred at 25°C for an additional 1 h. The hydride concentration was determined by hydrolyzing aliquots from the supernatant with a 1:1 mixture of 4N sulfuric acid-THF mixture and measuring the hydrogen evolution.

Preparation of Di-β-naphthoxyborane-THF Solution. 30 mmol of borane in THF (30 m*l*), maintained under nitrogen, was placed in a dry 100 m*l*-flask with a magnetic stirrer and a reflux condenser which was connected to a mercury bubbler. The flask was immersed in an ice bath, and 60 mmol of β-naphthol (8.650 g) in THF (15 m*l*) was added over 30 min to the borane solution with stirring at 0°C. After completion of the addition, the reaction mixture was stirred at 25°C for an additional 1 h. The hydride concentration was determined as described for lithium tri-β-naphthoxyborohydride-THF solution.

Stabilities of Di-β-naphthoxyborane and Lithium tri-β-naphthoxyborohydride in THF. The stabilities of these reagents were studied at 0°C. Di-β-naphthoxyborane and lithium tri-β-naphthoxyborohydride in THF were cooled and maintained at 0°C. At the appropriate periods of time, each 2 m*l* of aliquot was hydrolyzed in a 1:1 mixture of 4 N sulfuric acid-THF solution and the hydride content was measured gasometrically. Solution of both di-β-naphthoxyborane and lithium tri-β-naphthoxyborohydride showed no change in

Table 1. Reaction of B-Naphthol with Lithium Borohydride and Borane in Tetrahydrofuran at Room Temperature

Boron Hydride	Time (hr)	Hydrogen evolved[a]	Hydride used[a]	Hydride consumed by reduction[a]
Lithium	0.25	2.84	2.84	0.00
borohydride[b]	1.00	3.03	3.03	0.00
	2.00	3.14	3.14	0.00
	3.00	3.24	3.24	0.00
	5.00	3.34	3.34	0.00
	6.00	3.40	3.40	0.00
Borane-THF[c]	0.50	1.81	1.81	0.00
	1.00	2.17	2.17	0.00
	4.00	2.64	2.64	0.00
	6.00	2.72	2.72	0.00
	16.00	3.00	3.00	0.00

[a]moles/mole of compound. [b]4 Equiv of β-naphthol was added to 1 equiv of lithium borohydride. [c]3 Equiv of β-naphthol was added to 1 equiv of borane-THF.

hydride content over week and no precipitation was observed indicating that these reagents are quite stable.

Results and Discussion

The reaction of β-naphthol with lithium borohydride proceeded consuming three hydrides rapidly in 1 h and evolved hydrogen, while uptake of fourth hydride was slow. The reaction of β-naphthol with borane proceeded rapidly consuming two hydrides in 1 h and evolved hydrogen, while uptake of third hydride was slow as shown in Table 1. Di-β-naphthoxyborane was prepared by reacting borane with two equimolar β-naphthol. Lithium tri-β-naphthoxyborohydride was prepared by reacting lithium borohydride with three equimolar β-naphthol.

In the reaction of lithium hydride with methyl borate, the product was not homogeneous probably due to a disproportionation to dimethoxyborohydride and tetramethoxyborate.[5]

$$2LiBH(OCH_3)_3 \rightleftharpoons LiBH_2(OCH_3)_2 + LiB(OCH_3)_4 \quad (1)$$

Lithium tri-β-naphthoxyborohydride and di-β-naphthoxyborane have the possibilities for disproportionation and this was checked by the ^{11}B-NMR spectra which were recorded relative to external $BF_3 \cdot Et_2O$.

Lithium borohydride peak appeared as a quintet at −41.5 ppm. But in the reaction of one and two equimolar β-naphthol with lithium borohydride, the large lithium borohydride peak appeared at −41.5 ppm and a small peak appeared at +3.1 ppm as a broad singlet. However, in the reaction of three equimolar β-naphthol with lithium borohydride, a large peak appeared at +3.1 ppm as a broad singlet, and lithium borohydride peak appeared only as a trace suggesting that lithium mono- and di-β-naphthoxyborohydride were not formed but lithium tri-β-naphthoxyborohydride only was formed in the reaction of β-naphthol with lithium borohydride. From a singlet peak in its ^{11}B-NMR spectra, the disproportionation possibility shown in eq. 1 could be eliminated. From the ^{11}B-NMR spectrum in which lithium borohydride

$$4Na(MeO)_3BH \rightleftharpoons NaBH_4 + 3NaB(OMe)_4 \quad (2)$$

$$4Li(RO)_3BH \rightleftharpoons LiBH_4 + 3LiB(OR)_4 \quad (3)$$

appeared only as a trace in the reaction of three equimolar β-naphthol with lithium borohydride, the possibility of disproportionation shown in eq. 3 can also be eliminated.[6] The possibility of disproportionation

$$LiAlH(OBu\text{-}t)_3 \rightleftharpoons AlH(OBu\text{-}t)_2 + LiOBu\text{-}t \quad (4)$$

$$LiBH(OR)_3 \rightleftharpoons HB(OR)_2 + LiOR \quad (5)$$

shown in eq. 4 and 5 should be examined[7]. The borane peak appeared as a quartet at −1 ppm. In the reaction of one equimolar β-naphthol with borane, a peak appeared as a broad doublet at +23.4 ppm and borane peak appeared at −1 ppm indicating that this system is a mixture of $(RO)_{3-n}BH_n$ (n = 1,2,3). In the reaction of two equimolar β-naphthol with borane to form di-β-naphthoxyborane, a peak appeared as a broad singlet at +16.5 ppm which is very different from the peak of lithium tri-β-naphthoxyborohydride. From these data, the possibility of disproportionation shown in eq. 5 to form di-β-naphthoxyborane can be eliminated. The line broadening of naphthoxyborane and lithium tri-β-naphthoxyborohydride is probably due to the high viscosity of the solution or to the large quadrupole effect of β-naphthoxyboron compounds.

Table 2. Reduction of 2-Chlorophenyl Cyclohexanecarboxylate with Various Reducing Agents in Tetrahydrofuran[a] at Room Temperature

Reaction time (hr)	Reducing agent[b]			
	Borane	Lithium borohydride	Di-β-naphthoxyborane	Lithium tri-β-naphthoxyborohydride
0.5	3.5	33.8	—	14.9
1.0	7.0	55.6[c]	0.7	27.9
3.0	9.2	69.3	4.6	53.0
6.0	12.6	71.3	16.5[c]	57.6
12.0	22.9	—	22.2	—
24.0	31.3	—	—	64.7
72.0	65.7	83.2	—	—

[a]0.3 mmole of compound was added to 1.2 mmoles of hydride in 3 ml of reaction mixture making the ratio of hydride to compound 4 and the concentration of compound was 0.1 M. [b]Yields of products were estimated by gc. [c]7.0 h reaction.

From the spectra, it is clearly established that lithium tri-β-naphthoxyborohydride is the only product formed in the reaction of three equimolar β-naphthol with lithium borohydride and lithium mono- and di-β-naphthoxyborohydride were not formed. It suggests that the electronic effect plays a major role than the steric effect in the formation of lithium β-naphthoxyborohydride species.

The rate of reduction of 2-chlorophenyl cyclohexanecarboxylate as a model compound with naphthoxyborohydride was determined as shown in Table 2. The reduction to corresponding alcohol with borane proceeded slowly, yielding 65.7% in 72 h and 9.2% in 3 h while the reduction with lithium borohydride proceeded faster yielding 83.2% in 72 h and 53.8% in 0.5 h. The reduction with di-β-naphthoxyborane proceeded slowly.

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