# Reaction of Trialkylboranes with Sodium Diethyldihydroaluminate in the Presence of 1,4-Diazabicyclo[2.2.2]octane: a Convenient, General Method for Preparation of Sodium Trialkylhydroborates

**John L. Hubbard**

*Department of Chemistry, Marshall University, Huntington, WV 25755-2520, U.S.A.*

Trialkylboranes in tetrahydrofuran solution, even those with exceptionally large steric requirements, react readily with toluene solutions of sodium diethyldihydroaluminate in the presence of 1,4-diazabicyclo[2.2.2]octane, resulting in a convenient and general preparation of sodium trialkylhydroborates.

The utility of alkali metal trialkylhydroborates as reducing agents[1] and in hydride-induced carbonylation reactions[2] depends on their availability. Recently, general methods for preparation of sodium[3] and potassium[4] trialkylhydroborates by reaction of trialkylboranes with highly reactive sodium and potassium hydrides were reported. These methods, while of considerable interest, have disadvantages due to the requirements for handling air- and water-sensitive solids and for activating the metal hydrides prior to use.

The availability of sodium diethyldihydroaluminate,†

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† Commercially available from Ethyl Corporation and marketed as a 25% solution in toluene (OMH-1 Reducing Agent), and from Aldrich in laboratory quantities.

**Table 1.** $^{11}B$ NMR spectra of the products from reaction of representative trialkylboranes with sodium diethyldihydroaluminate in the presence of DABCO.

| Trialkylborane | Chemical shift[a] (multiplicity) | $J_{B\text{-}H}$/Hz |
|---|---|---|
| Triethylborane | −12.5 (d) | 50 |
| Tri-n-butylborane | −14.8 (d)[b] | — |
| Tri-isobutylborane | −17.8 (d) | 50 |
| Tri-s-butylborane | −5.9 (d) | 60 |
| Tricyclopentylborane | −9.9 (d) | 63 |
| Tri-*exo*-2-norbornylborane | −8.6 (d) | 55 |
| Perhydro-9b-boraphenalene[c] | −10.5 (d, 1B) | 70 |
| | −11.6 (d, 1B) | 60 |
| Tris(3-methyl-2-butyl)borane[d] | −9.7 (d, 3B) | 68 |
| | −11.9 (d, 1B) | 70 |
| Tris(*trans*-2-methylcyclopentyl)borane[d] | −10.6 (s, 3B) | — |
| | −11.5 (s, 1B) | — |

[a] Chemical shifts in p.p.m. relative to $BF_3 \cdot Et_2O$ with those upfield assigned as negative. [b] A band for the trialkylhydroborate derived from di-n-butyl-s-butylborane was also observed at −12.1 p.p.m. Although apparently a doublet, the band at −14.8 p.p.m. was insufficiently resolved to allow determination of $J_{B\text{-}H}$. [c] Isomeric pair of hydroborates. IR spectra showed B–H absorption at 2030 $cm^{-1}$, identical to that of the hydroborate prepared from NaH. [d] Diastereoisomeric pair of hydroborates.

essentially a soluble form of sodium hydride, suggested the possibility that it might be used to form sodium trialkylhydroborates. Addition of a toluene solution of this reagent to tetrahydrofuran solutions of trialkylboranes produced mildly exothermic reactions. For each of the trialkylboranes examined (triethyl-, tri-n-butyl-, tri-s-butyl-, and tricyclohexyl), the $^{11}B$ NMR spectrum of the resulting clear, colourless solution showed a mixture of the corresponding dialkylhydroborate and trialkylhydroborate.

Presumably the initial reaction in the process occurs as shown in equation (1). Apparently diethylaluminium hydride then instigates a competing reaction in which an alkyl group is transferred from boron to aluminium. To prevent this secondary reaction, it was necessary to trap the diethylaluminium hydride as soon as it was formed. Such an approach is efficacious in the reaction of lithium tetrahydroaluminate with trialkylboranes (equation 2). 1,4-Diazabicyclo[2.2.2]octane (DABCO) rapidly and quantitatively precipitates aluminium hydride as the tertiary amine addition compound.[5] Accordingly, reactions of representative trialkylboranes with sodium diethyldihydroaluminate were carried out in the presence of DABCO. In each case a voluminous white precipitate, presumably the addition compound of DABCO and diethylaluminium hydride, was formed. $^{11}B$ NMR examination of the filtered solutions (Table 1) indicates clean formation of trialkylhydroborate for all examples. The fact that the $^{11}B$ NMR signals are usually doublets suggests the absence of hydride exchange and is evidence for completeness of reaction.[6]

$$NaEt_2AlH_2 + R_3B \rightarrow NaR_3BH + Et_2AlH \qquad (1)$$

$$LiAlH_4 + R_3B + DABCO \longrightarrow LiR_3BH + DABCO \cdot AlH_3 \downarrow \qquad (2)$$

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