REACTIONS OF COMPLEX METAL HYDRIDES WITH BORATE ESTERS

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INTRODUCTION

The reduction of metal halides containing metals from Groups II A and B, III A, IV A and B and V A and B by treatment with lithium aluminum hydride, ($LiAlH_4$), is a general reaction which has been known for some time[1]. Conspicuous by their absence from the literature are references concerning the reduction of metal alkoxides [$M(OR)_3$] with complex metal hydrides. It is only recently that reports have appeared involving the reduction of a boron alkoxide group with $LiAlH_4$. Hawthorne[2] has reported the reduction of diethyl benzeneboronate with $LiAlH_4$ in pyridine to form pyridine-phenylborane and Kollonitsch[3] in one sentence mentioned the reaction of $LiAlH_4$ with a borate ester to form lithium borohydride ($LiBH_4$) and the corresponding aluminum alkoxide.

$$C_6H_5B(OC_2H_5)_2 + LiAlH_4 \xrightarrow{\text{pyridine}} C_6H_5BH_2\cdot\text{pyridine} \tag{1}$$

$$LiAlH_4 + B(OR)_3 \longrightarrow LiBH_4 + Al(OR)_3 \tag{2}$$

Recently we reported the direct synthesis of $LiAlH_4$ and $NaAlH_4$ from the elements[4,5]. Having available this convenient and economic source of reducing power, we set out to study further the versatility of these reducing agents. Having found little mention in the literature concerning the reduction of borate esters with complex metal hydrides, a systematic approach was taken to study this reaction.

RESULTS AND DISCUSSION

Reaction of sodium borohydride with borate esters

Sodium borohydride ($NaBH_4$) was combined separately with both methyl borate [$B(OCH_3)_3$] and phenyl borate [$B(OC_6H_5)_3$] in diethyl ether, tetrahydrofuran, and diglyme solvent in an attempt to prepare diborane. In diglyme solvent reaction temperatures as high as 200° were explored. In no case was there any evidence of reaction. However, when triethylamine was used as a solvent in the reaction of $NaBH_4$ with $B(OC_6H_5)_3$, triethylamine-borane was formed in 73 % yield.

$$3NaBH_4 + 4B(OC_6H_5)_3 \longrightarrow 4BH_3\cdot NR_3 + 3NaB(OC_6H_5)_4 \tag{3}$$

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The amine-borane is soluble in the amine solvent, whereas the by-product, sodium tetraphenoxyborate [$NaB(OC_6H_5)_4$], is insoluble. In all the experiments reported herein the triethylamine-borane was determined quantitatively by infrared analysis using the standard technique of comparing the sample absorption with reference standards. The by-product $NaB(OC_6H_5)_4$ was identified by elemental and infrared analyses.

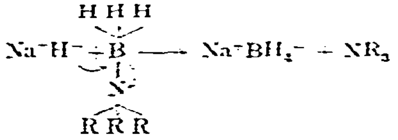
The formation of triethylamine-borane from $B(OC_6H_5)_3$ and $NaBH_4$ in triethylamine solvent is somewhat the reverse of the type reaction reported by Köster[6]. He reported that the reaction of sodium hydride, sodium methoxide or sodium trimethoxyborohydride with an amine-borane produced $NaBH_4$.

$$NaH + BH_3 \cdot NR_3 \longrightarrow NaBH_4 + NR_3 \qquad (4)$$

$$3NaOCH_3 + 4BH_3 \cdot NR_3 \longrightarrow 3NaBH_4 + B(OCH_3)_3 + 4NR_3 \qquad (5)$$

$$NaB(OCH_3)_3H + BH_3 \cdot NR_3 \longrightarrow NaBH_4 + B(OCH_3)_3 + NR_3 \qquad (6)$$

Thus he concludes that the bonding of the borane (BH_3) to the tertiary amine is weaker than the bonding to the metal hydride. This is undoubtedly correct in that a hydride ion, being a stronger base, should be capable of displacing a tertiary amine in a coordinately bonded complex.



$$Na^+H^- + \overset{H\,H\,H}{B} \cdot \underset{R\,R\,R}{N} \longrightarrow Na^+BH_4^- + NR_3 \qquad (7)$$

A similar type mechanism can be postulated for the reaction of $NaOCH_3$ or $NaB(OCH_3)_3H$ with triethylamine-borane using, when necessary, the principle of disproportionation to arrive at the desired products.

The reaction which we report (3) and the reactions reported by Köster (4, 5, and 6) are similar to reactions reported earlier by Schlesinger and Brown et al.[7].

$$2NaH + B_2H_6 \longrightarrow 2NaBH_4 \qquad (8)$$

$$3NaOCH_3 + 2B_2H_6 \longrightarrow 3NaBH_4 + B(OCH_3)_3 \qquad (9)$$

$$3NaB(OCH_3)_4 + 2B_2H_6 \longrightarrow 3NaBH_4 + 4B(OCH_3)_3 \qquad (10)$$

The only difference in the Schlesinger-Brown reactions and the ones reported by Köster is the use of diborane rather than amine-borane. The reactions reported by Köster were run at temperatures in excess of 100° whereas the reactions reported by Schlesinger and Brown involving diborane were run at room temperature or below. Since amine-boranes, in general, exhibit some dissociation (to diborane) above 100° it it reasonable to assume that the amine-borane reactions are quite similar to the reactions using diborane.

Schlesinger and Brown *et al.* have described the reaction of diborane and

$NaB(OCH_3)_4$ as involving the displacement of the weaker acid, $B(OCH_3)_3$, by the stronger acid, BH_3. Since this reaction takes place readily at −80°, it would seem, at least in this case, more reasonable to assume this mode of reaction rather than that of nucleophilic attack of an alkoxide ion produced from $NaB(OCH_3)_4$ at such a low temperature.

The fact that we have observed reaction between $B(OC_6H_5)_3$ and $NaBH_4$ in triethylamine solvent to form triethylamine-borane and $NaB(OC_6H_5)_4$ indicates, according to the above discussion, that this is an equilibrium reaction, and that probably equilibrium reactions are involved in some of the reactions, (6) (10), reported by Köster and by Schlesinger.

$$3NaBH_4 + 4B(OC_6H_5)_3 + 4NEt_3 \rightleftharpoons 4BH_3NEt_3 + 3NaB(OC_6H_5)_4 \qquad (11)$$

Reactions involving methyl borate, (6) (10), might be expected to lie on the $NaBH_4$ side since methyl borate would not be expected to displace BH_3 from $NaBH_4$. However, in reactions involving $B(OC_6H_5)_3$, an appreciable equilibrium might be expected due to the more acidic nature of $B(OC_6H_5)_3$ as compared to $B(OCH_3)_3$. Thus in reactions with $B(OC_6H_5)_3$, it should be possible to shift the equilibrium of a reaction such as (11) to the left or right by suitably adjusting the conditions for reaction. Removal of the triethylamine at a reaction temperature in excess of 100° would, of course, favor the formation of $NaBH_4$, whereas running the reaction in a large excess of triethylamine would favor the formation of the amine-borane. By the same reasoning, shifting the equilibrium in reactions such as (10), in order to favor diborane formation would be difficult when methyl borate is used, but should be possible to some extent when phenyl borate is employed.

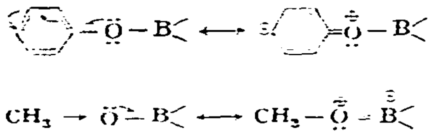
When $NaBH_4$ was allowed to react with $B(OC_6H_5)_3$ in dimethylaniline, dimethylaniline-borane was formed in only 9% yield. The lower yield with the weaker base is consistent with the trend shown in the reduction of $B(OC_6H_5)_3$ with aluminum and hydrogen in the presence of the same amines[8]. In the latter case, while, triethylamine-borane was produced in 94% yield, dimethylaniline-borane was

$$B(OC_6H_5)_3 + Al + 3/2H_2 \xrightarrow{NR_3} BH_3 \cdot NR_3 + Al(C_6H_5)_3 \qquad (12)$$

produced in only 60% yield under the same conditions. This effect is undoubtedly due to the higher heat of formation of the amine-borane that incorporates the more basic amine.

In order to further illustrate the importance of basicity of the solvent, $NaBH_4$ and $B(OC_6H_5)_3$ were allowed to react in 1-hexene as a solvent. In comparison with triethylamine, 1-hexene might be considered a weak base by virtue of its available π-electrons. Both triethylamine and 1-hexene react with diborane through nucleophilic attack at the boron atom resulting in boron–hydrogen bridge bond exchange (described earlier[9]). Thus, triethylamine-borane is produced in one case and trihexylborane in the other. Although $NaBH_4$ did react with $B(OC_6H_5)_3$ in triethylamine, trihexylborane was not formed when 1-hexene was used as the solvent. If diborane had been formed *in situ*, trihexylborane would have been produced irreversibly. Thus some minimum order of basicity is indicated for the success of this reaction.

It is interesting that the reaction of $NaBH_4$ with $B(OCH_3)_3$ in triethylamine produced no amine-borane, whereas with $B(OC_6H_5)_3$ the amine-borane was produced in 73% yield. Once again this finding is consistent with the results reported for Al–H_2 reduction of borate esters. In this case $B(OC_6H_5)_3$ in triethylamine reacted to form the amine-borane in 94% yield, whereas the same reaction using $B(OCH_3)_3$ produced $< 1\%$ yield. The most probable explanation for the large difference in reactivity between $B(OC_6H_5)_3$ is based on the comparative acidities of the boron atoms involved. Whereas $B(OC_6H_5)_3$ incurs increased acidity by resonance stabilization of structures produced when electrons from the oxygen atom are shifted to the benzene ring, the opposite is true of $B(OCH_3)_3$, *i.e.*, the oxygen electrons due to the proximity of the methyl group are pushed closer to the vacant *p*-orbital of the boron atom and hence some overlapping probably takes place, producing a less reactive boron site. Evidence for decreased acidity in $B(OCH_3)_3$ as arising from interaction of the vacant *p*-orbital of the boron atom with the *p*-electrons of the oxygen atom has been reported by Colclough *et al.*[10]. These workers observed some restriction of rotation about the B–O bond in $B(OCH_3)_3$ and shortening of the same bond due to partial double bond formation.



Reaction of lithium aluminum hydride with borate esters

Although $NaBH_4$ was unreactive toward $B(OCH_3)_3$, and reacted with $B(OC_6H_5)_3$ only in the presence of triethylamine at elevated temperatures, $LiAlH_4$ reacted with both methyl and phenyl borate even in ether solvents at room temperature. In these reactions the $LiAlH_4$ was added to the borate ester in diethyl ether at room temperature. The reactions were very rapid and exothermic, producing white solid precipitates. The precipitates consisted of the lithium tetraalkoxyaluminate by-product, with the boron product remaining in solution as lithium borohydride, amine-borane, trialkylborane or diborane (depending on whether tetrahydrofuran, amine, olefin or ether was used as the solvent). When diborane was produced in diethyl ether solvent, it was determined quantitatively by scrubbing the gas evolved from the reactor through triethylamine and measuring the intensity of absorption of the B–H stretching frequencies (4.2 and 4.4 μ).

When $LiAlH_4$ was reacted with $B(OC_6H_5)_3$ in diethyl ether at room temperature, diborane was produced in 47% yield. The by-product lithium tetraphenoxyaluminate was isolated and identified.

$$3LiAlH_4 + 4B(OC_6H_5)_3 \longrightarrow 2B_2H_6 + 3LiAl(OC_6H_5)_4 \qquad (13)$$

The major side reaction produced $LiBH_4$, probably through the reaction of diborane with $LiAlH_4$.

$$LiAlH_4 + 1/2B_2H_6 \longrightarrow LiBH_4 + AlH_3 \qquad (14)$$

Thus the $LiAlH_4$ should be added to the $B(OC_6H_5)_3$ rather than the reverse to minimize this side reaction. The $LiBH_4$ by-product (13) probably can react further by absorbing diborane to form $LiBH_4 \cdot BH_3$. This result is indicated since triethylamine-borane was formed equivalent to an additional diborane yield of 16 % when triethylamine was added to the reaction mixture after complete diborane removal.

$$LiBH_4 + 1/2B_2H_6 \longrightarrow LiBH_4 \cdot BH_3 \xrightarrow{N(C_2H_5)_3} LiBH_4 + BH_3 \cdot N(C_2H_5)_3 \qquad (15)$$

The AlH_3 produced in (14) probably can react further with $B(OC_6H_5)_3$ to produce more diborane and aluminum phenoxide, $Al(OC_6H_5)_3$. Infrared analysis has detected what appears to be $Al(OC_6H_5)_3$ in some of the reaction products. $Al(OC_6H_5)_3$ is difficult to distinguish quantitatively from $LiAl(OC_6H_5)_4$. Hence, reversal of the mode of addition of $LiAlH_4$ to $B(OC_6H_5)_3$ would result in consumption of diborane by both $LiAlH_4$ and by-product $LiBH_4$ to form $LiBH_4$, $LiBH_4 \cdot BH_3$ and $Al(OC_6H_5)_3$ as by-products.

When triethylamine was substituted for diethyl ether as the reaction solvent, triethylamine-borane was formed in 77 % yield. The white solid precipitate formed during the reaction was identified as $LiAl(OC_6H_5)_4$. The reaction filtrate was subjected to infrared analysis in order to determine the amount of triethylamine-borane present. The yield of amine-borane was higher than the yield of diborane when diethyl ether was used as the solvent probably due to the increased stability of triethylamine-borane toward $LiAlH_4$ and $LiBH_4$ as compared with diborane. Although diborane will react readily with $LiAlH_4$ at room temperature to produce $LiBH_4$, we have found that triethylamine-borane reacts very little with $LiAlH_4$ under the same conditions. Therefore, using triethylamine as a solvent is fairly effective in complexing the diborane *in situ* before it can react appreciably with the $LiAlH_4$. Also, as just mentioned, it is probable that some of the diborane liberated in the diethyl ether reaction is complexed with the $LiBH_4$ by-product as $LiBH_4 \cdot BH_3$ and is therefore not isolated as free diborane.

When $LiAlH_4$ was reacted with $B(OCH_3)_3$ in diethyl ether, no diborane was liberated from the reaction mixture. Instead, the major products were $LiBH_4$ and $LiAl(OCH_3)_4$. The actual formation of diborane in the reaction was established by adding triethylamine to the reaction mixture after the reaction was complete and identifying the triethylamine borane formed. Once again, the diborane was probably held in solution by the $LiBH_4$ as LiB_2H_7. According to previous reasoning, some $Al(OCH_3)_3$ should also have been produced; however, infrared analysis was inadequate in providing a quantitative measure of the amount of $Al(OCH_3)_3$ in the presence of $LiAl(OCH_3)_4$ due to the similarity in spectra. The *in situ* formation of diborane in this reaction was further indicated by using triethylamine as a solvent and isolating the product as the amine-borane. In this case triethylamine-borane was formed in 68 % yield. The lack of formation of free diborane when $B(OCH_3)_3$ was reacted with $LiAlH_4$ is not completely understood, since $B(OC_6H_5)_3$ in the same reaction will release diborane readily. It is probable that $B(OC_6H_5)_3$ is reduced much more rapidly to diborane than is $B(OCH_3)_3$, and thus the product is quickly removed from the reaction mixture before complete reaction with the $LiAlH_4$ or absorption by $LiBH_4$. The reaction of $LiAlH_4$ with $B(OCH_3)_3$ should be slower than the corresponding reaction with $B(OC_6H_5)_3$, possibly involving stepwise reduction.

When the desired product was diborane, the reaction was normally run by adding the $LiAlH_4$ to the borate ester. In this manner the $LiAlH_4$ was never in excess in the reaction mixture and thus the diborane or amine-borane was at best in competition with the borate ester for the reaction with $LiAlH_4$. On the other hand, if the mode of addition was reversed, the complex borohydride was obtained almost exclusively in some cases. For example, when $B(OC_6H_5)_3$ was added to $NaAlH_4$ in tetrahydrofuran, $NaBH_4$ was formed in high yield.

$$NaAlH_4 + B(OC_6H_5)_3 \longrightarrow NaBH_4 + Al(OC_6H_5)_3 \qquad (16)$$

The $NaBH_4$ was identified by infrared and elemental analyses. The reaction of $LiAlH_4$ with a borate ester to form $LiBH_4$ was recently reported by Kollonitsch[3]; however, no details were given. Unfortunately, the reaction of $NaAlH_4$ with $B(OCH_3)_3$ using the inverse mode of addition produced results that were not as clear-cut as the corresponding reaction with $B(OC_6H_5)_3$. It is possible that reactions of the type discussed by Kollonitsch, involving reaction of diborane with $Al(OR)_3$ or AlH_3 with $B(OR)_3$, were taking place, resulting in a variety of products which were not easily separable.

$$2B_2H_6 + 4Al(OR)_3 \longrightarrow AlH_3(BH_3)_3 \cdot 3Al(OR)_3 + B(OR)_3 \qquad (17)$$

$$4AlH_3 + 3B(OR)_3 \longrightarrow AlH_2(BH_3)_3 \cdot Al(OR)_3 \qquad (18)$$

Although these complicating reactions take place with the metal alkoxides, such is not the case with the metal phenoxides. For example, Kollonitsch has shown that aluminum hydride reacts with phenyl borate in a straightforward manner unlike the

$$2AlH_3 + 2B(OC_6H_5)_3 \longrightarrow B_2H_6 + 2Al(OC_6H_5)_3 \qquad (19)$$

reaction which takes place with methyl borate. This fact points out once again the unusual difference in reactivity between methyl borate and phenyl borate and accounts for the much higher yields of diborane formed from the reaction of $LiAlH_4$ with phenyl borate as compared to the same reaction with methyl borate.

Since diborane will react with olefins in diethyl ether at room temperature[11], it was decided that an olefin could be used in this reaction, just as the amine, to capture the diborane *in situ*. Although $NaBH_4$ would not react with $B(OC_6H_5)_3$ in 1-hexene at temperatures as high as 180°, $LiAlH_4$ reacted with $B(OC_6H_5)_3$ in the presence of 1-hexene at room temperature to produce trihexylborane in 47% yield (distilled yield). No effort was made to optimize the conditions and isolation procedure of this reaction in order to determine the maximum yield of trialkylborane obtainable.

Although we found little exchange between $LiAlH_4$ and triethylamine-borane, $NaAlH_4$ reacted quantitatively with triethylamine-borane in tetrahydrofuran to form $NaBH_4$ and triethylamine-alane.

$$NaAlH_4 + BH_3 \cdot N(C_2H_5)_3 \xrightarrow{THF} NaBH_4 + AlH_3 \cdot N(C_2H_5)_3 \qquad (20)$$

The $NaBH_4$ precipitated as a white solid, whereas the amine-alane remained in solution and was readily identified by infrared analysis of the filtrate. Thus when $NaAlH_4$ reacted with a borate ester in amine solvent, at least some of the $NaBH_4$ by-product could have been formed by the above reaction.

In summary, the reaction of complex aluminohydrides and borohydrides with certain borate esters can be employed to prepare complex borohydrides, diborane, amine-boranes or trialkylborane in reasonably good yields. Apparently the mode of addition and nature of the complex metal hydride and borate ester are important factors in determining the products.

EXPERIMENTAL

Materials

The $LiAlH_4$ and $NaBH_4$ were obtained from Metal Hydrides Inc. The $NaAlH_4$ was prepared by the method previously described[4,5]. Solutions of the complex metal hydrides in diethyl ether, tetrahydrofuran and diglyme were prepared by stirring the complex metal hydrides in the appropriate solvent for several hours followed by filtration. Solutions were prepared between 1–2 *M*.

Tetrahydrofuran, diglyme, triethylamine and dimethylaniline used as solvents in this work were purified by distillation over $NaAlH_4$. The tetrahydrofuran and triethylamine were distilled at atmospheric pressure whereas the diglyme and dimethylaniline were distilled at reduced pressure so that the distillation temperature was kept below 100° (~ 10–20 mm). Diethyl ether was purified by distillation over $LiAlH_4$. 1-Hexene was dried over anhydrous $MgSO_4$ and purified by distillation (b.p. 63.5°).

Methyl borate was obtained from Metal Hydrides Inc. and used without further purification. Phenyl borate was prepared according to the procedure of Lappert[12] and purified by distillation through a 3 foot glass helix packed column (b.p. 178° at 0.5 mm).

Reaction of sodium borohydride with phenyl borate

A. In triethylamine solvent. To 2.8 g (0.074 mole) of sodium borohydride in a 250 ml Magne-Dashe autoclave was added 28.0 g (0.097 mole) of phenyl borate dissolved in 100 ml of triethylamine. Approximately 0.2 g of aluminum chloride was added as catalyst. The reaction mixture was heated for 20 h at 200°, then cooled and filtered. The solid product was recrystallized from tetrahydrofuran–hexane by cooling to —60°. Filtration at —60° produced a colorless crystalline solid. A small portion of this solid was dissolved in tetrahydrofuran and subjected to infrared analysis. The spectrum was identical to the spectrum obtained from an authentic sample of sodium tetraphenoxyborate obtained from the reaction of sodium borohydride with phenol. The original reaction filtrate was diluted to 250 ml with triethylamine and then subjected to infrared analysis. It contained 8.1 g of triethylamine-borane, representing a yield of 73 %. The quantitative determination of triethylamine-borane was made by measuring the absorption of the reaction filtrate at 4.2 and 4.4 μ in a standard volume of triethylamine and calculating the yield from a previously constructed absorption *vs.* concentration curve.

B. In N,N-dimethylaniline solvent. To 3.5 g (0.0925 mole) of sodium borohydride was added 34.5 g (0.119 mole) of phenyl borate dissolved in 100 ml of N,N-dimethylaniline. The resulting mixture was heated at 180° for 14 h. A trace of aluminum chloride was used as catalyst. The reaction mixture was filtered and the filtrate diluted to 250 ml with N,N-dimethylaniline. Infrared analysis showed a yield of 1.4 g of N,N-dimethylaniline-borane, indicating a conversion of 8.6 %.

C. In 1-hexene solvent. To 1.5 g (0.0661 mole) of sodium borohydride was added 24.4 g (0.0843 mole) of phenyl borate dissolved in 100 ml of 1-hexene. The resulting mixture was heated at 180° for 12 h. A trace of aluminum chloride was used as catalyst. The product mixture was filtered, uncovering a white solid. Infrared analysis showed this solid to be mostly phenyl borate. Distillation of the filtrate followed by infrared analysis of the distillate showed the products to be a mixture of 1-hexene and *cis*- and *trans*-2-hexene; no trihexylborane was indicated.

Reaction of sodium borohydride with methyl borate

To 5.7 g (0.151 mole) of sodium borohydride was added 20.8 g (0.200 mole) of methyl borate dissolved in 100 ml of triethylamine. The resulting mixture was heated to 180° for 14 h. A trace of aluminum chloride was used as catalyst. The reaction mixture was then filtered and the filtrate subjected to infrared analysis. No triethylamine-borane was detected.

Reaction of lithium aluminum hydride with borate esters

A. Phenyl borate in triethylamine. To 28.5 g (0.0984 mole) of phenyl borate in 100 ml of triethylamine was added, over a half hour period, 3.2 g (0.0842 mole) of lithium aluminum hydride in 200 ml of diethyl ether. The reaction was very exothermic and the temperature rose from room temperature to 60°. The reaction was over quickly, producing a heavy white precipitate. The white solid was filtered, washed with diethyl ether, dried and analyzed. (Found: Al, 6.41; Li, 1.60; C_6H_5OH, 86.5. $C_{24}H_{20}AlLiO_4$ calcd.: Al, 6.65; Li, 1.72; C_6H_5OH, 91.6 %.) The infrared spectrum of the solid product was consistent with that of an authentic sample of lithium tetraphenoxyaluminate. The yield of triethylamine-borane was determined by infrared analysis of the filtrate. The intensities of the B–H stretching bands at 4.2 and 4.4 μ were measured and compared to a standard chart of concentration *vs.* per cent absorption. The yield was 77 %. The infrared spectrum indicated a small amount of $LiBH_4$ present (B–H stretch, 4.5 μ). Some boron compound was indicated in the solid product, since 0.54 % boron was detected.

The reaction described above was repeated. Following the addition of the reactants, the reaction mixture was heated to 140° for 4 h. The yield of triethylamine-borane was essentially the same (74 %).

B. Phenyl borate in diethyl ether. To 31.6 g (0.109 mole) of phenyl borate dissolved in 100 ml of diethyl ether was added 3.54 g (0.0934 mole) of lithium aluminum hydride dissolved in 150 ml of diethyl ether. The reaction was exothermic for about the first quarter of the addition, during which time a white solid precipitated. The solid precipitate did not appear to increase in amount after one-fourth of the lithium aluminum hydride had been added. A gas which evolved throughout the addition was scrubbed through triethylamine. The mixture was then refluxed for 5 h while maintaining a slow nitrogen purge on the system. The white solid product was filtered, washed thoroughly with diethyl ether, and dried. Infrared analysis of the solid product showed almost entirely lithium tetraphenoxyaluminate except for some $LiBH_4$ and what appeared to be LiB_2H_7. The triethylamine scrubber showed 5.8 g of triethylamine-borane by infrared analysis, indicating a diborane yield of 47 %.

To the reaction filtrate, after solids removal, was added 30 ml of triethylamine.

Infrared analysis of the resulting clear liquid showed the presence of 2.0 g of triethylamine-borane with approximately an equal amount of lithium borohydride. The triethylamine borane present in the reaction filtrate represented an additional yield of 16 % of reduction product.

C. Phenyl borate in 1-hexene. To 2.43 g (0.0639 mole) of lithium aluminum hydride dissolved in 130 ml of diethyl ether and 50 ml of 1-hexene was added 23.6 g (0.0816 mole) of phenyl borate dissolved in 100 ml of 1-hexene. The addition was made at —5 to —20°. A white solid precipitated during the addition. When the reaction mixture was allowed to warm to room temperature, no gas or heat was evolved. The solid product was washed thoroughly with ether, filtered, dried and subjected to infrared analysis. The spectrum was compatible with that of lithium tetraphenoxyaluminate. The ether and 1-hexene solvent of the reaction filtrate were removed under vacuum at room temperature. The approximately 30 ml of solid liquid residue was distilled under vacuum, producing a clear liquid, b.p. 133° at 1.8 mm. The liquid (10.1 g) was identified but its boiling point and infrared spectrum as tri-*n*-hexylborane contaminated with a considerable amount of dihexylborane, $(C_6H_{13})_2BH$[8]. The B–H–B bridge band at 6.38 μ indicated about 40% dihexylborane present. The yield of distilled trihexylborane contaminated with dihexylborane was 46.6 % based on boron utilization. Distillation of the product at a lower pressure would undoubtedly lessen the dialkylborane contamination.

D. Methyl borate in triethylamine. To 20.8 g (0.20 mole) of methyl borate dissolved in 80 ml of triethylamine was added 5.7 g (0.15 mole) of lithium aluminum hydride dissolved in 125 ml of diethyl ether. The reaction was begun at room temperature; however, it was very exothermic for the first half of the addition. A copious white solid precipitated during the reaction and a small amount of gas (not diborane) was evolved throughout the addition. The white solid was filtered, dried and analyzed. The analysis indicated gross contamination with boron-containing compounds. The solids were then washed thoroughly with diethyl ether. The ether wash showed 4.6 g of triethylamine-borane and approximately 1.0 g of lithium borohydride by infrared analysis. The ether-washed solid when dried weighed 23.7 g [22.8 g theory for $LiAl(OCH_3)_4$]. An infrared spectrum of the solid product was consistent with that of an authentic sample of lithium tetramethoxyaluminate; however, the spectrum also showed some lithium borohydride still present.

The original reaction filtrate was subjected to infrared analysis and found to contain 10.9 of triethylamine-borane, with no lithium borohydride indicated. The yield of triethylamine-borane based on the reaction filtrate and the ether wash of the solids (10.9 g + 4.6 g) was 68 %.

E. Methyl borate in diethyl ether. To 10.9 g (0.105 mole) of methyl borate dissolved in 100 ml of diethyl ether was added 2.98 g (0.0786 mole) of lithium aluminum hydride dissolved in 150 ml of diethyl ether. Gas was evolved and the temperature rose throughout the reaction. The gas was scrubbed through 100 ml of triethylamine. The solid which precipitated during the reaction was filtered, dried (wt. 10.9 g) and subjected to infrared analysis. The analysis showed lithium tetramethoxy aluminate with a considerable amount of lithium borohydride present. Infrared analysis of the reaction filtrate showed a large amount of lithium borohydride present, but no diborane. To the reaction filtrate was then added 30 ml of triethylamine. The resulting clear liquid showed 1.0 g of triethylamine-borane in addition to a substantial quantity of lithium borohydride. Infrared analysis of the triethylamine scrubber showed that no triethylamine-borane was present.

Reaction of sodium aluminum hydride with phenyl borate

To 20.7 g (0.0714 mole) of phenyl borate dissolved in 80 ml of diglyme was added slowly 2.9 g (0.0537 mole) of sodium aluminum hydride dissolved in 135 ml of diglyme. The reaction was exothermic throughout and a gas was liberated during the reaction. The gas was scrubbed through triethylamine and showed 1.8 g triethylamine-borane by infrared analysis, indicating a 22 % yield of diborane. To the reaction mixture was added 30 ml of triethylamine. The top reaction mixture layer contained 0.40 g of triethylamine-borane and the lower layer 0.23 g of triethylamine-borane. No B–H band for sodium borohydride was observed.

Inverse addition. To a solution of 5.4 g (0.1 mole) of sodium aluminum hydride in 200 ml of tetrahydrofuran was added 28.9 g (0.1 mole) of phenyl borate dissolved in 100 ml of tetrahydrofuran. The reaction mixture was stirred for several hours and then the white solid precipitate was filtered and dried (3.3 g). Infrared spectrum of the solid product was consistent with that for sodium borohydride with a small amount of an Al–H impurity. Although the elemental analyses indicated impure $NaBH_4$, the Na/B/H/Al ratio was 1.06/1.00/4.90/0.14, indicating the presence of sodium borohydride with possibly aluminum hydride as an impurity.

Reaction of sodium aluminum hydride with triethylamine-borane

To 25 ml (0.17 mole) of triethylamine-borane in 75 ml of tetrahydrofuran was added 11.0 g (0.194 mole) of sodium aluminum hydride (95 %) dissolved in 100 ml of tetrahydrofuran. No reaction was apparent at room temperature. The resulting clear solution was refluxed for 24 h, during which time a white solid precipitated. The solid was filtered and dried (wt. 5.9 g). The infrared spectrum of a diglyme solution indicated 98 % sodium borohydride. The infrared spectrum of the filtrate was identical to the spectrum of triethylamine-alane prepared from lithium aluminum hydride and aluminum chloride in triethylamine-ether solvent.

SUMMARY

The reaction of sodium borohydride, sodium aluminum hydride and lithium aluminum hydride with methyl borate and phenyl borate is reported. Sodium borohydride does not react with methyl borate or phenyl borate in ether solvents up to 200°; however, in tertiary amine solvent sodium borohydride does react with phenyl borate at elevated temperatures. Triethylamine-borane and dimethylaniline-borane have been prepared in this manner. In amine solvents, under the same conditions, methyl borate does not react.

Lithium aluminum hydride and sodium aluminum hydride, on the other hand, react rapidly with both methyl borate and phenyl borate at room temperature in both ether and amine solvent. Diborane and lithium tetraphenoxyaluminate [$LiAl(OC_6H_5)_4$] are formed as the major products from lithium aluminum hydride reaction with phenyl borate. If the mode of addition is reversed (borate added to hydride), no diborane is formed and lithium borohydride is the major product from normal addition. In triethylamine solvent, triethylamine-borane is formed in good yield from either methyl borate or phenyl borate reaction with lithium aluminum hydride. When an olefin is used as the solvent in conjunction with diethyl ether, the corresponding trialkylborane is formed. Similar reactions with sodium aluminum hydride are also discussed.

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