Improved Procedures for the Generation of Diborane from Sodium Borohydride and Boron Trifluoride

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Improved procedures for the generation of diborane by the reaction of $NaBH_4$ in triglyme or tetraglyme with the BF_3 adducts of di-*n*-butyl ether, *tert*-butyl methyl ether, monoglyme, dioxane, and tetrahydropyran were developed. In these systems, generation of diborane requires 2−4 h at 25 °C (faster reactions take place at 50 °C). The byproduct $NaBF_4$ precipitates from the reaction mixture at 25 °C as the reaction proceeds. The high-boiling glyme can be conveniently separated from the lower boiling carrier ethers by simple distillation of the latter. On the other hand, diborane was generated very slowly or not generated using the addition of each of six boron trifluoride−etherates (di-*n*-butyl ether, *tert*-butyl methyl ether, tetrahydrofuran, tetrahydropyran, dioxane, and monoglyme) to suspensions of sodium borohydride in the corresponding ether. However, diborane was generated rapidly and quantitatively by the addition of $NaBH_4$ in triglyme (or tetraglyme) to the BF_3 adduct of triglyme (or tetraglyme) at room temperature. No solid precipitation occurs during the reaction, making it convenient for large-scale applications. The pure solvent triglyme (or tetraglyme) can be easily recovered and recycled by either crystallizing or precipitating $NaBF_4$ from the generation flask. New procedures for the generation of diborane were also developed by the reaction of $NaBF_4$ with $NaBH_4$ in triglyme (or tetraglyme) in the presence of Lewis acids such as $AlCl_3$ and BCl_3.

Introduction

Diborane is a versatile reagent with a multitude of applications in organic and inorganic syntheses.[1−5] In recent years, a growing number of syntheses of new organic molecules have involved the use of either diborane or organoborane derivatives as reagents in research laboratories. However, owing to the pyrophoric nature of diborane, its large-scale applications are comparatively smaller because great care must be taken during such utilization in large-scale applications.[6] Diborane is a gas with a boiling point of −92.5 °C, and it is commercially supplied in cylinders that are packaged in dry ice for shipment. Accordingly, it is not suitable for shipment to distant destinations. On the other hand, the utility of diborane is highly unique and irreplaceable because of the chemo- and regioselectivities it exhibits in its synthetic applications.[6−8] Accordingly, simultaneous preparation and utilization of diborane circumvent these problems.

For many years the preferred procedure for the generation of diborane from sodium borohydride has been the treatment of sodium borohydride in diglyme with boron trifluoride−ethyl etherate.[2]

$$3NaBH_4 + 4(C_2H_5)_2O{:}BF_3 \xrightarrow[25\ °C]{\text{diglyme}} 2B_2H_6\uparrow + 3NaBF_4 + 4(C_2H_5)_2O \quad (1)$$

Sodium borohydride is essentially insoluble in ether solvents such as diethyl ether, di-*n*-butyl ether, *tert*-butyl methyl ether, tetrahydrofuran, tetrahydropyran, and dioxane.[9] Also, sodium borohydride is only partially soluble in monoglyme but is readily soluble in diglyme. The solubility of sodium borohydride in diglyme varies greatly with temperature (Figure 1). The solubility is 2.9 M at 40 °C but drops to 0.88 M at 20 °C and to 0.70 M at 60 °C.[10] This makes it necessary to control carefully the temperature of the diglyme−$NaBH_4$ mixture as the reaction is proceeding. The considerable solubility of $NaBF_4$ in diglyme also creates a problem for the ready recycle of the diglyme. Finally, the use of $F_3B{:}OEt_2$ liberates volatile diethyl ether (bp 35 °C) so that appreciable quantities of diethyl ether are carried over in the stream of diborane generated.

Also, diborane reacts instantly with sodium borohydride dissolved in the glyme solvents to form $NaBH_4{\cdot}BH_3$. This means that the addition of boron trifluoride−etherate to the sodium borohydride in the glyme solvent does not evolve diborane until after the $NaBH_4$ has been fully converted to $NaBH_4{\cdot}BH_3$.[2,11]

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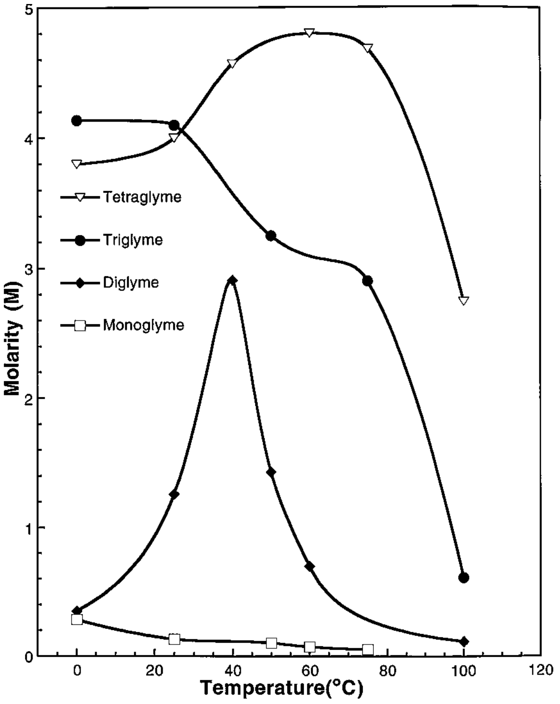

Figure 1. Solubility of $NaBH_4$ in glymes at various temperatures.

$$7NaBH_4 + 4R_2O{:}BF_3 \rightarrow 4NaBH_4{\cdot}BH_3 + 3NaBF_4 + 4R_2O \quad (2)$$

This is followed by the reaction of $BF_3{:}OR_2$ with $NaBH_4{\cdot}BH_3$, which liberates the diborane.

$$6NaBH_4{\cdot}BH_3 + 8R_2O{:}BF_3 \rightarrow 7B_2H_6\uparrow + 6NaBF_4 + 8R_2O \quad (3)$$

With the increasing use of diborane and diborane-derived reagents in synthetic organic chemistry, it appeared desirable to reexamine the current procedure in order to ascertain whether improved procedures could be developed. Also, it is desirable to develop procedures that could be carried out on a large scale. Accordingly, we undertook a systematic study of the generation of diborane in the hope of circumventing these problems.

Experimental Section

All manipulations and reactions with air-sensitive compounds were carried out in an atmosphere of dry nitrogen. The special techniques employed in handling air-sensitive material is described elsewhere.[2] All glassware was dried overnight in an oven, assembled hot, and cooled to ambient temperature in a stream of nitrogen. ^{11}B, ^{1}H, and ^{13}C NMR spectra were recorded on a Varian Gemini 300 MHz instrument. The ^{11}B NMR chemical shifts, δ, are in ppm relative to $BF_3{:}OEt_2$. All anhydrous solvents used are commercial samples and used as obtained. $NaBH_4$, $BF_3{:}OEt_2$, di-*n*-butyl ether:BF_3, and *tert*-butyl methyl ether: BF_3 were supplied by the Aldrich Chemical Co. and purified by distillation under reduced pressure over a small quantity of CaH_2. Hydride analysis studies were carried out using hydrolysis to hydrogen followed by measurement of the hydrogen evolved with a gasimeter.[14]

Solubility of Sodium Borohydride in Glymes. Solubility studies of sodium borohydride in various glymes, such as mono-, di-, tri-, and tetraglyme, at various temperatures were carried out. The following procedure for triglyme at 25 °C is representative.

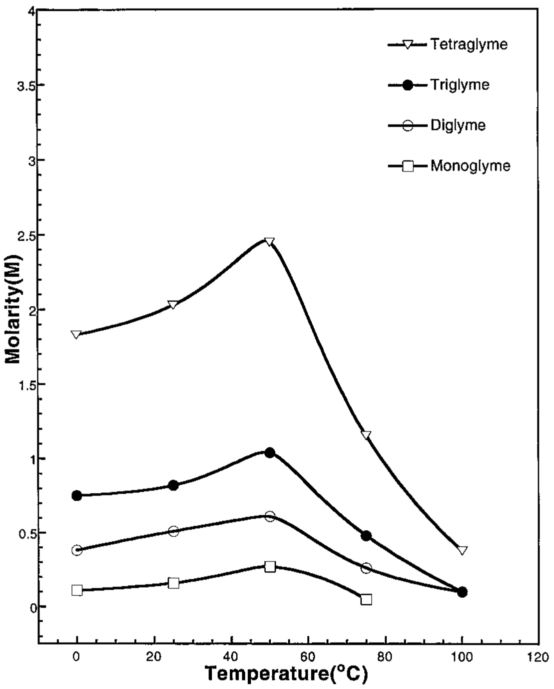

Figure 2. Solubility of $NaBF_4$ in glymes at various temperatures.

An oven-dried RB flask, provided with a septum inlet and a stirring bar, was charged with sodium borohydride (5.00 g) under nitrogen, and dry triglyme (5.0 mL) was added under nitrogen using a double-ended needle. The contents were maintained for 5 h at 25 °C with stirring. The solution was allowed to settle or was centrifuged. The clear solution was analyzed for active hydride by hydrolysis of an aliquot.[14] The solution was found to be 4.10 M in $NaBH_4$. The solubility of $NaBH_4$ in the various glymes changes with temperature, and the results are presented in Figure 1.

Solubility of Sodium Tetrafluoroborate in Glymes. Solubility studies of sodium tetrafluoroborate in various glymes, such as mono-, di-, tri-, and tetraglyme, at various temperatures were carried out. The following procedure for triglyme at 25 °C is representative.

An oven-dried centrifuge tube, provided with a stirring bar and closed with a septum, was charged with sodium tetrafluoroborate (2.00 g). Into the tube, dry triglyme (4.7 mL) at 25 °C was added with stirring. The contents were stirred further for 5 h and centrifuged to get a clear solution. The clear solution of sodium tetrafluoroborate in triglyme was transferred into a dry centrifuge tube under nitrogen. Then dry dichloromethane (5.0 mL) was added to precipitate residual sodium tetrafluoroborate completely. The resulting mixture was centrifuged, and the supernatant solution (a mixture of triglyme and dichloromethane) was removed by decantation. The precipitate was dried under vacuum (0.41 g), and the molarity of the solution at 25 °C was established as 0.82 M in $NaBF_4$. The solubilities of $NaBF_4$ in the various glymes change with temperature, and the results are presented in Figure 2.

Preparation of the BF_3 Adducts of Various Glymes and Ethers. Preparation of the BF_3−dioxane adduct is representative. Into a 50 mL RB flask provided with septum inlet and stirring bar, 2.2 mL of dioxane (25 mmol) was introduced and 2.53 mL of $BF_3{:}OEt_2$ (20 mmol) was added at room temperature. The contents were further stirred for 30 min, and the flask was connected to a water aspirator through protection tubes containing anhydrous $CaCl_2$ and blue silica gel. The volatile diethyl ether was removed under reduced pressure from the reaction flask and was collected in a cold trap (2.0 mL, 96%). The adduct thus obtained was a liquid at room temperature and crystallizes at 10 °C. The adduct showed a sharp signal at +0.5 ppm in ^{11}B NMR. The solution is 7.20 M in BF_3 and is stable at room temperature. The solution develops a dark color on standing but remains essentially pure as observed by ^{11}B NMR and diborane generation experiments.

Generation of Diborane. General Procedure. The reaction setups and procedures used for diborane generation are the same for all

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experiments. In the initial exploratory experiments on diborane generation, reactions were carried out on a 20 mmol scale. Selected procedures were tested on a 0.3 mol scale, and in one case the reaction was carried out on a 2.00 mol scale. No difficulty was encountered with the large-scale preparations. The following procedure using triglyme is representative of the exploratory experiments and represents a preferred procedure.

An oven-dried apparatus was assembled in a hood as follows. A 50 mL RB flask (generation flask) was provided with a pressure-equalizing funnel and a stirring bar. The top of the generation flask was connected to a trap via a safety valve, consisting of a T-tube immersed in a mercury pool containing acetone over mercury (to destroy escaping diborane), connected to the apparatus via a three-way stopcock. The outlet of the trap was connected to a coarse-sintered-glass dispersion tube. A 50 mL flask fitted with a sidearm was connected to a second mercury bubbler containing acetone. The system was cooled under a flow of nitrogen, and the generation flask was charged with the BF_3−triglymate (10.0 mL, 4.00 M, 40 mmol). The reaction flask is cooled by immersion in an ice−salt bath while maintaining the flow of nitrogen. Into the first trap was placed sodium borohydride in triglyme (2.0 mL, 2.00 M) to remove traces of boron trifluoride or other volatile acids in the diborane stream. A solution of $NaBH_4$ in triglyme (15.0 mL, 2.00 M, 30 mmol) was placed in the pressure-equalizing funnel and added slowly to the generation flask for 1 h at room temperature. (It could also be added with a hypodermic syringe.) The diborane gas, generated rapidly, was bubbled into tetrahydrofuran (20.0 mL) contained in the absorption flask through a coarse-sintered-glass dispersion tube at ice−salt temperature. The contents of the generation flask were further stirred for 30 min at room temperature. The completion of diborane generation was confirmed by ^{11}B NMR, which showed the absence of peaks due to BF_3−triglymate and $NaBH_4$ in triglyme, and the formation of a new peak assigned to $NaBF_4$ at −1.5 ppm. The amount of diborane generated was estimated by the standard hydride analysis involving hydrolysis of an aliquot. The adduct THF:BH_3, was 1.97 M in BH_3, indicating an essentially quantitative generation of diborane.

After the generation of diborane was complete, the generation flask was kept undisturbed at room temperature overnight. Colorless crystals of the solvated $NaBF_4$ (largely a relatively unstable 1:1 solvate that melts at 58−60 °C) separated. The generation flask was heated to 100 °C to precipitate unsolvated $NaBF_4$, and the solvated triglyme was removed by filtration at 100 °C, providing 2.90 g (93% yield) of white crystalline $NaBF_4$. The filtrate triglyme was essentially pure by ^{1}H NMR, ^{13}C NMR data, and comparison of the data with that of an authentic sample. It can be further purified by distillation under reduced pressure. In that case a small amount of dissolved $NaBF_4$ (∼4%) is recovered. The $NaBF_4$ from the solution was precipitated rapidly by the addition of a few $NaBF_4$ crystals obtained in earlier runs. Alternatively, $NaBF_4$ can be separated from the triglyme by heating the solution to 100 °C, recovering by filtration the $NaBF_4$ precipitated under these conditions, or precipitating the $NaBF_4$ by the addition of 2.00 equiv (by volume) of dichloromethane, followed by filtration. In the last case, the higher boiling triglyme can be readily recovered by removal of the volatile dichloromethane by simple distillation.

Generation of Diborane Using $NaBH_4$ in Triglyme and BF_3−*tert*-Butyl Methyl Etherate. An oven-dried apparatus was assembled in a hood as mentioned earlier. The generation flask was charged with the BF_3−*tert*-butyl methyl etherate (93.60 g, 600 mmol). A solution of $NaBH_4$ in triglyme (225.0 mL, 2.00 M, 450 mmol) was placed in the pressure-equalizing funnel, was added slowly into the generation flask for 2−3 h at room temperature. The diborane gas generated was bubbled into tetrahydrofuran (300.0 mL) contained in the absorption flask through a coarse-sintered-glass dispersion tube at ice−salt temperature. The contents of the generation flask were further stirred for 3 h at room temperature. The completion of diborane generation was confirmed by ^{11}B NMR, which showed the absence of peaks due to BF_3−triglymate and $NaBH_4$ in triglyme, and the formation of a new peak assigned to $NaBF_4$ at −1.5 ppm. The amount of diborane generated was estimated by the standard hydride analysis using hydrolysis of an aliquot. The adduct, THF:BH_3, was 1.95 M in BH_3, indicating an essentially quantitative generation of diborane. Precipitation of unsolvated $NaBF_4$ was observed even during the generation of diborane. The precipitation was made quantitative after the generation of diborane is complete, by the addition of 1−2 equiv (by volume) *tert*-butyl methyl ether followed by filtration under reduced pressure, providing unsolvated $NaBF_4$ in a 93% yield (45.50 g). From the filtrate, low-boiling *tert*-butyl methyl ether is easily separated from triglyme by distillation.

Generation of Diborane Using $NaBH_4$ in Triglyme and BF_3−Monoglymate. An oven-dried apparatus was assembled in a hood as mentioned earlier. The generation flask was charged with the BF_3−monoglymate (82.2 mL, 7.30 M, 600 mmol). A solution of $NaBH_4$ in triglyme (225.0 mL, 2.00 M, 450 mmol) placed in the pressure-equalizing funnel was added slowly into the generation flask for 2−3 h at room temperature. The diborane gas generated was bubbled into tetrahydrofuran (300.0 mL) contained in the absorption flask through a coarse-sintered-glass dispersion tube at ice−salt temperature. The contents of the generation flask were further stirred for 2 h at room temperature. The completion of diborane generation was confirmed by ^{11}B NMR, which showed the absence of peaks due to BF_3−triglymate and $NaBH_4$ in triglyme, and the formation of a new peak assigned to $NaBF_4$ at −1.3 ppm. The amount of diborane generated was estimated by the standard hydride analysis using hydrolysis of an aliquot. The adduct THF:BH_3, was 1.95 M in BH_3, indicating an essentially quantitative generation of diborane. The solution in the generation flask remained clear during the reaction and no precipitation of $NaBF_4$ was observed. Monoglyme was distilled out under reduced pressure, and $NaBF_4$ was separated from triglyme, as mentioned earlier, in a 94% (46.40 g) yield.

Generation of Diborane Using $NaBH_4$ in Triglyme and BF_3−Triglymate. An oven-dried apparatus was assembled in a hood as mentioned earlier. The generation flask was charged with the BF_3−triglymate (150.0 mL, 4.00 M, 600 mmol). A solution of $NaBH_4$ in triglyme (225.0 mL, 2.00 M, 450 mmol) placed in the pressure-equalizing funnel was added slowly into the generation flask for 2−3 h at room temperature. The diborane gas generated immediately was bubbled into tetrahydrofuran (300.0 mL) contained in the absorption flask through a coarse-sintered-glass dispersion tube at ice−salt temperature. The contents of the generation flask were further stirred for 1 h at room temperature. The completion of diborane generation was confirmed by ^{11}B NMR, which showed the absence of peaks due to BF_3−triglymate and $NaBH_4$ in triglyme, and the formation of a new peak assigned to $NaBF_4$ at −1.3 ppm. The amount of diborane generated was estimated by the standard hydride analysis using hydrolysis of an aliquot. The adduct THF:BH_3, was 1.96 M in BH_3, indicating an essentially quantitative generation of diborane. The solution in the generation flask remained clear throughout the reaction, and no precipitation of $NaBF_4$ was observed. $NaBF_4$ was separated from triglyme as mentioned earlier in a 94% (46.50 g) yield.

Generation of Diborane Using $NaBH_4$ in Tetraglyme and BF_3−Tetraglymate. An oven-dried apparatus was assembled in a hood as mentioned earlier. The generation flask was charged with the BF_3−tetraglymate (150.0 mL, 4.00 M, 600 mmol). A solution of $NaBH_4$ in tetraglyme (150.0 mL, 3.00 M, 450 mmol) placed in the pressure-equalizing funnel was added slowly into the generation flask for 2−3 h at room temperature. The diborane gas generated immediately was bubbled into tetrahydrofuran (300.0 mL) contained in the absorption flask through a coarse-sintered-glass dispersion tube at ice−salt temperature. The contents of the generation flask were further stirred for 1 h at room temperature. The completion of diborane generation was confirmed by ^{11}B NMR, which showed the absence of peaks due to BF_3−tetraglymate and $NaBH_4$ in tetraglyme, and the formation of a new peak assigned to $NaBF_4$ at −1.5 ppm. The amount of diborane generated was estimated by the standard hydride analysis using hydrolysis of an aliquot. The adduct THF:BH_3 was 1.96 M in BH_3, indicating an essentially quantitative generation of diborane. The solution in the generation flask remained clear throughout the diborane generation, and no precipitation of $NaBF_4$ was observed. $NaBF_4$ was separated from tetraglyme as mentioned earlier in 94% (46.50 g) yield.

Recovery of $NaBF_4$ from Glymes. The solubility of $NaBF_4$ in triglyme and tetraglyme is high at room temperature. In the diborane generation experiments using $NaBH_4$ in triglyme or tetraglyme and BF_3 adducts of ethers such as *tert*-butyl methyl ether, di-*n*-butyl ether, tetrahydropyran, monoglyme, and dioxane, addition of further amounts of the corresponding ether (BF_3-carrying ether) after the diborane generation is complete, precipitates unsolvated $NaBF_4$ from the glyme−ether mixture. In the diborane generation experiments using $NaBH_4$ in triglyme or tetraglyme and BF_3 adducts of the same glyme, unsolvated $NaBF_4$ from glyme was obtained by heating the generation flask to 100−120 °C after the diborane generation is complete. Fortunately, addition of volatile solvents such as dichloromethane, *n*-pentane, *n*-hexane, *tert*-butyl methyl ether, dioxane, and diethyl ether to the glyme−$NaBF_4$ mixture also precipitates unsolvated $NaBF_4$ at room temperature. The precipitation of unsolvated $NaBF_4$ from triglyme is more efficient using dichloromethane and *n*-pentane. However, in the case of tetraglyme, *n*-pentane is not effective because of miscibility problems. The procedure followed for the separation of unsolvated $NaBF_4$ from glyme is same for all the experiments, and the following procedure used for the separation of $NaBF_4$ from triglyme is representative.

The usual diborane generation was carried out using slow addition of $NaBH_4$ in triglyme (15.0 mL, 2.00 M, 30 mmol) to BF_3 in triglyme (10.0 mL, 4.00 M, 40 mmol) at room temperature. The diborane generated was recovered and measured by the usual methods. Into the resulting reaction mixture in the generation flask, dichloromethane (25.0 mL) was added. The white precipitate formed was separated by filtration under an inert atmosphere, and the filtrate was again treated with dichloromethane (20.0 mL). This resulted in further precipitation of $NaBF_4$ from the filtrate, which was separated as mentioned earlier. The combined precipitate was washed with dichloromethane (5.0 mL) to remove traces of triglyme and was dried under reduced pressure to yield $NaBF_4$ in 92% yield (2.85 g). The $NaBF_4$ thus obtained did not melt up to 300 °C (solvated $NaBF_4$ in triglyme melts at 58−60 °C), indicating the formation of unsolvated $NaBF_4$. Simple distillation of the combined filtrate gave dichloromethane-free triglyme. The residual triglyme contains up to 5% of solvated $NaBF_4$, which can be separated by distillation under reduced pressure or recycled as such for the process.

Generation of Diborane Using $NaBH_4$ in Triglyme (or Tetraglyme) and BF_3 in Triglyme (or Tetraglyme) in the Presence of $AlCl_3$. The procedures followed using triglyme or tetraglyme are the same, and the procedure followed for triglyme is representative. An oven-dried apparatus was assembled in a hood as mentioned earlier. The generation flask was charged with the BF_3 in triglyme (10.0 mL, 4.00 M, 40 mmol). A solution of $NaBH_4$ in triglyme (15.0 mL, 2.00 M, 30 mmol) placed in the pressure-equalizing funnel was added slowly to the generation flask for 2−3 h at room temperature. The diborane gas generated was immediately bubbled into tetrahydrofuran (80.0 mL) contained in the absorption flask through a coarse-sintered-glass dispersion tube at ice−salt temperature. The completion of diborane generation was confirmed by ^{11}B NMR, which showed the absence of peaks due to BF_3−triglymate and $NaBH_4$ in triglyme, and the formation of a new peak assigned to $NaBF_4$ at −1.2 ppm. Into the generation flask was introduced $AlCl_3$ (2.66 g, 20 mmol) in triglyme (10.0 mL) using a double-ended needle. (Caution! $AlCl_3$ and triglyme must be mixed at 0 °C). The contents were further stirred for 2 h at room temperature. Into the generation flask further amounts of $NaBH_4$ (45.0 mL, 2.00 M, 90 mmol) were introduced in portions using a pressure-equalizing funnel for 3 h at room temperature. The contents were further stirred for another 3 h at room temperature. The amount of diborane generated was estimated by the standard hydride analysis using hydrolysis of an aliquot. The adduct THF:BH_3 was 1.88 M in BH_3, indicating a 94% yield of diborane.

Generation of Diborane Using $NaBH_4$ in Triglyme (or Tetraglyme) and $NaBF_4$ in Triglyme (or Tetraglyme) in the Presence of $AlCl_3$. The procedures followed using triglyme or tetraglyme are the same. The procedure followed for tetraglyme is representative. An oven-dried apparatus was assembled in a hood as mentioned earlier. The generation flask was charged with the $NaBF_4$ (1.65 g, 15 mmol) and $AlCl_3$ (2.66 g, 20 mmol) at 0 °C. Tetraglyme (15.0 mL) was added slowly with stirring at 0 °C, and the contents were further stirred at room temperature for 2 h. Into the pressure-equalizing funnel was placed $NaBH_4$ in tetraglyme (15.0 mL, 3.00 M, 45 mmol), and this was added slowly to the generation flask for 2−3 h at room temperature. The diborane gas generated was bubbled into tetrahydrofuran (30.0 mL) contained in the absorption flask through a coarse-sintered-glass dispersion tube at ice−salt temperature. The completion of diborane generation was confirmed by ^{11}B NMR, which showed the absence of the peak due to $NaBH_4$. The ^{11}B NMR also showed the presence of trace amounts of $NaBF_4$ (−1.2 ppm) and $NaBH_4$:BH_3 (−24.5 ppm), which persisted even after 24 h, indicating a very slow reaction toward the end. The amount of diborane generated was estimated by the standard hydride analysis using hydrolysis of an aliquot. The adduct THF:BH_3 was 1.80 M in BH_3, indicating a 90% yield of diborane.

Generation of Diborane Using $NaBH_4$ in Triglyme (or Tetraglyme) and BF_3 in Triglyme (or Tetraglyme) with Regeneration of the BF_3 Adduct of Triglyme (or Tetraglyme) with BCl_3. The procedures followed using triglyme or tetraglyme are the same, and the procedure followed for triglyme is representative. An oven-dried apparatus was assembled in a hood as mentioned earlier. The generation flask was charged with the BF_3 in triglyme (5.0 mL, 4.00 M, 20 mmol). A solution of $NaBH_4$ in triglyme (7.5 mL, 2.00 M, 15 mmol) placed in the pressure-equalizing funnel was added slowly to the generation flask for 1 h at room temperature. The diborane gas generated was immediately bubbled into tetrahydrofuran (40.0 mL) contained in the absorption flask through a coarse-sintered-glass dispersion tube at ice−salt temperature. The completion of diborane generation was confirmed by ^{11}B NMR, which showed the absence of peaks due to BF_3−triglymate and $NaBH_4$ in triglyme, and the formation of a new peak assigned to $NaBF_4$ at −1.0 ppm. Into the generation flask was introduced BCl_3 in triglyme (2.5 mL, 2.00 M, 5 mmol) using a double-ended needle. The contents were further stirred for 1 h at room temperature, by which time ^{11}B NMR showed the complete formation of BF_3−triglymate (+0.2 ppm). Into the generation flask a further amount of $NaBH_4$ (7.5 mL, 2.00 M, 15 mmol) was introduced slowly for 1 h at room temperature. Diborane gas was generated rapidly and quantitatively, further confirming the complete regeneration of BF_3−triglymate. The total amount of diborane generated after the second cycle was estimated by the standard hydride analysis using hydrolysis of an aliquot. The adduct THF:BH_3 was 0.98 M in BH_3, indicating a 98% yield of diborane. The $NaBF_4$ thus obtained can be again converted to BF_3−triglymate by the addition of stoichiometric amounts of BCl_3 in triglyme.

Results and Discussion

To minimize the volatility of the ether used for the boron trifluoride−etherate, we avoided diethyl ether and tested the less volatile ethers, *tert*-butyl methyl ether, di-*n*-butyl ether, tetrahydrofuran, tetrahydropyran, monoglyme, and dioxane, as the boron trifluoride−etherate to be introduced into the reaction flask.

To avoid possible problems arising from the formation of a mixture of solvents, the reactions of sodium borohydride in triglyme (or tetraglyme) with the BF_3−triglymate (or −tetraglymate) were also carried out. These two reactions proceed rapidly, providing an essentially quantitative yield of pure diborane with easy recovery of sodium tetrafluoroborate and pure triglyme (or tetraglyme) for recycling.

The following systems were examined: (1) the addition of each of the six boron trifluoride−etherates to suspensions of sodium borohydride in the corresponding ether; (2) the addition of a solution of sodium borohydride in diglyme, triglyme, or tetraglyme to each of the boron trifluoride adducts of various ethers such as *tert*-butyl methyl ether, di-*n*-butyl ether, tetrahydrofuran, tetrahydropyran, monoglyme, and dioxane; (3) the addition of a solution of sodium borohydride in diglyme, triglyme, or tetraglyme to the boron trifluoride adduct of the same glyme; (4) a detailed examination of the sodium borohydride in the triglyme (or tetraglyme) system added to boron trifluoride−triglymate (or −tetraglymate); (5) a detailed examination of the sodium borohydride in the triglyme (or tetraglyme) system added to boron trifluoride−triglymate (or −tetraglymate) with regeneration of BF_3 from the $NaBF_4$ formed.

Sodium borohydride is essentially insoluble in ether solvents such as diethyl ether, di-*n*-butyl ether, *tert*-butyl methyl ether, tetrahydrofuran, tetrahydropyran, and dioxane. Consequently, with one exception (tetrahydrofuran), the boron trifluoride−etherates either do not react or react very slowly with suspensions of sodium borohydride in these ethers. In the case of suspensions of sodium borohydride in tetrahydrofuran, reaction occurs with the addition of boron trifluoride−tetrahydrofuranate, but diborane is not liberated as a gas. Instead, it combines with tetrahydrofuran to form the adduct $THF{:}BH_3$.[9]

Since diborane reacts instantly with sodium borohydride dissolved in the glyme solvents to form $NaBH_4{\cdot}BH_3$, this means that the addition of boron trifluoride−etherate to the sodium borohydride in the glyme solvent does not produce diborane until after the $NaBH_4$ has been fully converted to $NaBH_4{\cdot}BH_3$.[2,11] Consequently, it is preferable to add the solution of $NaBH_4$ in glyme to the boron trifluoride in the same glyme in the generating flask to maintain a smooth flow of diborane during the addition of the sodium borohydride solution.

The low solubility of sodium borohydride in monoglyme means that this procedure would require the use of large amounts of monoglyme to achieve clear solutions. Also, the solubility of sodium borohydride in diglyme is temperature-dependent, so it is necessary to maintain the addition vessel at a temperature of 40 °C. This is not easy for diglyme solutions in a dropping funnel. For that reason, generations using monoglyme and diglyme have been preferably carried out by adding the boron trifluoride adducts of the above-mentioned ethers to a suspension of sodium borohydride in monoglyme or to a solution of sodium borohydride in diglyme. In monoglyme, generation of diborane is slow and incomplete as observed by ^{11}B NMR, which showed the presence of appreciable amounts of both starting materials even after 12 h at room temperature. This slow reaction may be attributed to the low solubility of $NaBH_4$ in monoglyme. The generation of diborane from sodium borohydride in diglyme proceeds rapidly to completion with each of the five BF_3:ether adducts examined. However, diborane is generated only after the addition of the first 43% of the BF_3 adducts, as mentioned above.

The higher solubility of $NaBH_4$ in triglyme and tetraglyme makes these solutions more convenient for the generation of diborane. Figure 1 illustrates the variation in the solubility of the $NaBH_4$ in the different glymes at various temperatures. Experiments were carried out by the slow addition of a 2.0 M solution of $NaBH_4$ in triglyme to the theoretical quantity of the BF_3 adducts of the above-mentioned five ethers at room temperature. The generation of diborane gas was quantitative and complete in 2−4 h. The evolved diborane gas was collected by bubbling it into a weakly binding borane carrier Lewis base such as tetrahydrofuran, hindered tertiary amines, or dialkyl sulfides. The completion of diborane generation is also confirmed by ^{11}B NMR, which showed the absence of peaks due to starting materials, with the formation of a new peak assigned to $NaBF_4$ (−1.5 ppm, singlet). The $NaBF_4$ thus formed during the reaction is not completely soluble in the triglyme−ether mixtures and precipitates partially from the solution. The precipitation can be made quantitative by the addition of additional volatile material, such as diethyl ether, dichloromethane, *tert*-butyl methyl ether, dioxane, *n*-pentane, or *n*-hexane. The precipitates thus obtained are free of triglyme and do not melt up to 300 °C, indicating the formation of unsolvated $NaBF_4$. From the filtrate, the higher boiling triglyme can be easily recovered by removal of the more volatile component by fractional distillation.

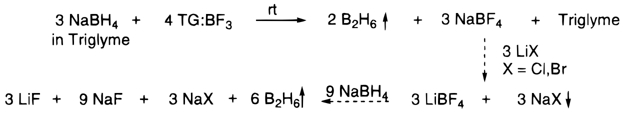
In another set of experiments, diborane generation was carried out by the addition of solutions of $NaBH_4$ in diglyme, triglyme, and tetraglyme to the boron trifluoride adducts of the same glyme to avoid formation of such mixtures of solvents. Also, the precipitation of $NaBF_4$ from the reaction mixture may pose problems in hindering stirring of the reaction mixture for large-scale preparation. On the other hand, $NaBF_4$ possesses reasonable solubilities in triglyme and tetraglyme at room temperature (see Figure 2). Accordingly, boron trifluoride adducts of diglyme, triglyme, and tetraglyme were prepared by the addition of $BF_3{:}OEt_2$ to a glyme, removing the less volatile diethyl ether under reduced pressure or by distillation. These adducts thus obtained get colored quickly but exhibit no detectable change in the ^{11}B NMR spectrum or in their effectiveness in the reaction.

Diborane generation experiments were carried out by the addition of $NaBH_4$ in a glyme to the BF_3 adduct of the same glyme at room temperature. Diborane gas was generated rapidly and quantitatively. The reaction is complete in 1 h, and the ^{11}B NMR examination of the reaction mixture revealed no dissolved diborane in the glyme. The byproduct, $NaBF_4$, possesses only a moderate solubility in diglyme. As a result, precipitation of $NaBF_4$ is observed after the addition is complete. However, in triglyme and tetraglyme, $NaBF_4$ is more soluble (see Figure 2). As a result, no precipitation of $NaBF_4$ is observed. Interestingly, $NaBF_4$ crystallized from triglyme when the generation flask was kept undisturbed overnight. The precipitate appears to be a 1:1 compound of $NaBF_4$ and triglyme of low stability, which melts at 58−60 °C. Raising the temperature results in the precipitation of unsolvated $NaBF_4$. Thus, heating the generation flask to 100 °C and filtration of $NaBF_4$ at that temperature provides $NaBF_4$ in 94% yield and free triglyme is easily recovered. The recovered triglyme contains up to 3% of $NaBF_4$, which can be recycled as such or can be further purified by distillation of the triglyme under reduced pressure. More simply, bringing the generation flask to 100 °C after the generation of diborane is complete gives a white precipitate of unsolvated $NaBF_4$ that can be separated from the triglyme, as mentioned earlier. Also, with both triglyme and tetraglyme, the precipitation of unsolvated $NaBF_4$ can be achieved without heating by adding dichloromethane (1−2 equiv by volume) to the generation flask, following completion of the generation of diborane. Filtration (or centrifugation) provides white crystalline $NaBF_4$ in essentially quantitative yields. The dried precipitates are free of glyme and do not melt below 300 °C ($NaBF_4{\cdot}TG$ melts at 58−60 °C), indicating the formation of unsolvated $NaBF_4$. The volatile dichloromethane can be readily pumped-off or distilled to obtain the pure glyme.

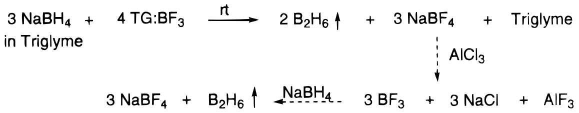
Encouraged by these observations, a detailed study was carried out using solutions of various concentrations of $NaBH_4$ in triglyme and of the BF_3 adduct of triglyme. In all the cases, the generation of diborane is rapid and quantitative and the triglyme is readily recycled. To use equal volumes of $NaBH_4$ and BF_3 adduct solutions, solutions of 3 M $NaBH_4$ in triglyme and 4 M BF_3 in triglyme were utilized for diborane generation.

$$\underset{\substack{\text{in triglyme}\\(3\text{ M, 1 equiv})}}{3NaBH_4} + \underset{(4\text{ M, 1 equiv})}{4\text{ triglyme}{:}BF_3} \xrightarrow{25\ ^\circ C} 2B_2H_6\uparrow + 3NaBF_4 + \text{triglyme} \quad (4)$$

Scheme 1



Scheme 2



Here also, diborane is generated rapidly and quantitatively. Bringing the reaction mixture to 100 °C after the diborane generation is complete precipitates the unsolvated $NaBF_4$. Filtration at that temperature provides unsolvated $NaBF_4$ in 93% yield.

Similar experiments with tetraglyme also give diborane rapidly and quantitatively. However, in this case $NaBF_4$ does not crystallize out from the solution. It can be precipitated either by heating the solution to 100 °C and filtering the hot mixture or by the addition of 1−2 equiv (by volume) of dichloromethane to the tetraglyme solution following completion of the generation of diborane.

Generation of Diborane From $NaBF_4$ and $NaBH_4$ in Glymes. In the above-mentioned studies, $NaBF_4$ in glyme is the only byproduct besides diborane. In most of the ethers and glymes such as monoglyme and diglyme, $NaBF_4$ is not soluble and precipitates even during the generation of diborane. However, in triglyme and tetraglyme $NaBF_4$ possesses considerable solubility (see Figure 2). It occurred to us that the greater solubility of $NaBF_4$ in triglyme and tetraglyme might facilitate further reaction with $NaBH_4$, as indicated in the following.

$$NaBF_4 + 3NaBH_4 \rightarrow 2B_2H_6 + 4NaF \tag{5}$$

Accordingly, diborane generation experiments were continued by the addition of further amounts of $NaBH_4$ in triglyme or tetraglyme to the $NaBF_4$ in triglyme or tetraglyme, formed after initial diborane generation at room temperature. Under these conditions, the diborane generation was found to be slow and incomplete even after 48 h. Increasing the reaction temperature to 50 °C made the diborane generation faster; however, the reaction remains incomplete, as observed by ^{11}B NMR. Further increasing the temperature to 90 °C, improved the yield of diborane (up to 70%); however, at this temperature additional signals in ^{11}B NMR (at −29.4 ppm) were observed, indicating undesired side reactions.

It is documented in the literature that similar reactions with $LiBH_4$ proceed smoothly to give LiF, as indicated in the following equation.[12,13]

$$3LiBH_4 + BF_3 \rightarrow 2B_2H_6 + 3LiF \tag{6}$$

The $LiBF_4$ formed after the initial reaction further reacts with $LiBH_4$ to give diborane and LiF. Accordingly, diborane generation reactions using $NaBH_4$ and BF_3 were carried out in the presence of LiCl and LiBr at various temperatures (Scheme 1). However, no significant improvement in diborane yield was noted under these conditions. Then we turned our attention to the use of the less expensive $AlCl_3$ in place of LiX because it is a better Lewis acid and might facilitate the formation of BF_3, which could further react with $NaBH_4$ to yield diborane. Accordingly, $AlCl_3$ was added to the $NaBF_4$ formed after initial diborane generation is complete (Scheme 2). Fortunately, $NaBH_4$ reacts completely, as observed by ^{11}B NMR, and diborane gas is generated quantitatively.

To establish the stoichiometry of the reaction of $NaBF_4$ with $AlCl_3$, three sets of reactions were carried out using 1, 2, and 3 equiv of $NaBF_4$ for 1.0 equiv of $AlCl_3$:

$$NaBF_4 + AlCl_3 \rightarrow BF_3 + NaCl + AlFCl_2 \tag{7}$$

$$2NaBF_4 + AlCl_3 \rightarrow 2BF_3 + 2NaCl + AlF_2Cl \tag{8}$$

$$3NaBF_4 + AlCl_3 \rightarrow 3BF_3 + 3NaCl + AlF_3 \tag{9}$$

The boron trifluoride thus formed reacts with a stoichiometric amount of $NaBH_4$ and the diborane generated measured by the usual methods. In all three cases, the $NaBH_4$ reacted completely, as observed by ^{11}B NMR, and the diborane was generated in good yields, indicating that all three chlorides in $AlCl_3$ are reactive. Thus, the stoichiometry of the reaction was established as 3:1 for $NaBF_4$ to $AlCl_3$.

$$3NaBF_4 + AlCl_3 \rightarrow 3BF_3 + 3NaCl + AlF_3 \tag{10}$$

During these studies, it was observed that the 1:1 mixture of $NaBF_4$ and $AlCl_3$ reacts with more than the stoichiometric amounts of $NaBH_4$, indicating the formation of more than 1.0 equiv of BF_3. This is only possible when the $NaBF_4$ formed after the second cycle of borane generation reacts further with excess $AlCl_3$ present in the reaction mixture to generate additional amounts of BF_3. Thus, to make complete use of $NaBF_4$ formed using 1 equiv of BF_3 during the diborane generation, the following stoichiometry must be followed.

$$3NaBH_4 + BF_3 + AlCl_3 \rightarrow 2B_2H_6\uparrow + 3NaCl + AlF_3 \tag{11}$$

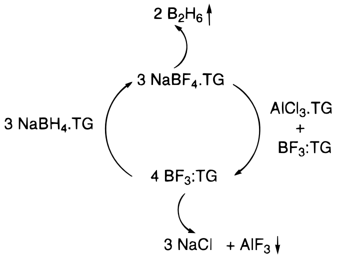
Accordingly, the following reaction was carried out in the standard diborane generation setup at room temperature. Initially, diborane generation was carried out by the slow addition of $NaBH_4$ (15 mmol) to BF_3 in triglyme (20 mmol). The diborane generated (10 mmol) was bubbled into a weakly binding Lewis base and measured by the usual methods. To the resulting solution in the generation flask, $AlCl_3$ (20 mmol) in triglyme was added followed by slow addition of $NaBH_4$ in triglyme in portions (for 3 h to avoid the formation of $NaBH_4 \cdot BH_3$ if $NaBH_4$ is present in excess at a given concentration). The solution was further stirred at room temperature. The diborane generation was complete in 6 h, as observed by ^{11}B NMR, which showed the absence of the peak due to $NaBH_4$. The ^{11}B NMR also showed the presence of trace amounts of $NaBF_4$ (−1.0 ppm) and $NaBH_4 \cdot BH_3$ (−24.5 ppm) as the reaction becomes slow as it nears completion. The overall yield of diborane is 94%.

To examine whether a similar reaction can be carried out using commercially available $NaBF_4$, $AlCl_3$ and $NaBF_4$ were dissolved in triglyme, and $NaBH_4$ in triglyme was added.

$$9NaBH_4 + 3NaBF_4 + 4AlCl_3 \rightarrow 6\,B_2H_6\uparrow + 12NaCl + 4AlF_3 \tag{12}$$

The reaction proceeded smoothly, and the diborane was generated in 90% yield. Here also, $NaBH_4$ must be added in portions to avoid the formation of $NaBH_4 \cdot BH_3$. The ^{11}B NMR examination of the reaction mixture showed the absence of starting $NaBH_4$ and the presence of small amounts of $NaBF_4$ (−0.96 ppm) and $NaBH_4 \cdot BH_3$ (−24.5 ppm). Similar results were obtained for reactions in tetraglyme.

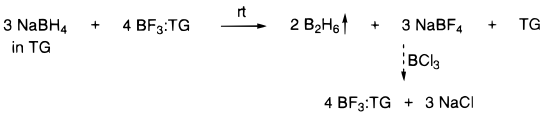
Scheme 3



Also, by the controlled addition of stoichiometric amounts of $AlCl_3$·TG, BF_3:TG, and $NaBH_4$·TG to $NaBF_4$·TG, the following cyclic process for the generation of diborane can be achieved, converting all chemicals to diborane and simple inorganic salts (Scheme 3).

Diborane generations were also carried out using $NaBF_4$ and $NaBH_4$ in triglyme or tetraglyme in the presence of several other Lewis acids such as $FeCl_3$, $ZnCl_2$, $CoCl_2$, $MgCl_2$, and $SnCl_4$. Attempted diborane generation experiments using $NaBF_4$, $FeCl_3$, and $NaBH_4$ in triglyme gave only triglyme-cleaved products. However, in reactions using anhydrous $CoCl_2$, diborane was liberated rapidly in about 70% yield, whereas in reactions using $SnCl_4$ it was liberated slowly and the reaction was not complete even after 24 h, as observed by ^{11}B NMR studies. Using the other Lewis acids, no appreciable amount of diborane was generated.

Development of a Cyclic Process in Which All Chemicals Are Converted to Diborane and Simple Inorganic Salts. In the above experiments using $AlCl_3$, the reaction becomes very slow toward the end and is only 90−94% complete even after 48 h, making it less convenient for the recovery of triglyme. In a bid to avoid the use of $AlCl_3$ and to provide an even more efficient generation of diborane the following alternative was tested.


(13)

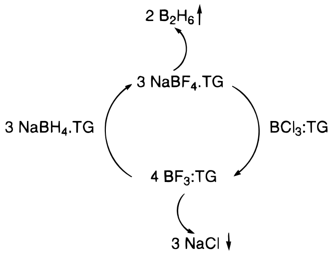
$$3\,NaBH_4 \text{ in TG} + 4\,BF_3{:}TG \xrightarrow{rt} 2\,B_2H_6\uparrow + \underset{\underset{4\,BF_3{:}TG\ +\ 3\,NaCl}{\downarrow BCl_3}}{3\,NaBF_4} + TG \quad (13)$$

Accordingly, BCl_3 in triglyme was prepared in two ways: (1) addition of BCl_3 in dichloromethane to triglyme and a pumping-off of volatile dichloromethane under reduced pressure; (2) addition of triglyme to $Et_2O{:}BCl_3$ adduct and a pumping-off of volatile diethyl ether under reduced pressure. The BCl_3:TG adduct thus obtained is stable for 2−3 h at room temperature. However, standing at room temperature for 24 h gave triglyme-cleaved product. Fortunately, the adduct is stable for 6−8 h at 0 °C. Interestingly, the adduct BCl_3:TG is readily transformed to BF_3:TG by stoichiometric amounts of $NaBF_4$, so no attack on the triglyme occurs.

$$BCl_3{:}TG + 3NaBF_4 \xrightarrow{0\ ^\circ C \text{ or rt}} 4BF_3{:}TG + 3NaCl \quad (14)$$

Thus, regeneration of BF_3:TG was carried out by the addition of BCl_3:TG (5 mmol) to $NaBF_4$ in TG (15 mmol) formed after the usual diborane generation using $NaBH_4$ (15 mmol) and BF_3 (20 mmol) in triglyme at room temperature. The ^{11}B NMR examination of the reaction mixture after 1 h showed a peak corresponding to BF_3:TG at +0.2 ppm, and the peak at −0.9 due to $NaBF_4$ disappeared. Addition of $NaBH_4$ in TG (15 mmol) to the flask gave diborane rapidly and quantitatively. The ^{11}B NMR examination of the resulting mixture showed only a peak due to $NaBF_4$ in TG (at −1.0 ppm). This can again be converted into BF_3:TG using the earlier procedure, providing an elegant cyclic process for the generation of diborane with excellent economy of chemicals used (Scheme 4).

Scheme 4



Similar reactions were also carried out using tetraglyme as solvent. Here also, diborane was generated rapidly and quantitatively and generation can readily be made cyclic with the addition of stoichiometric amounts of BCl_3−tetraglymate and $NaBH_4$ in tetraglyme in each cycle.

Conclusions

Diborane can be generated rapidly and quantitatively by the addition of $NaBH_4$ in triglyme (or tetraglyme) to the BF_3 adduct of triglyme (or tetraglyme) at room temperature. No solid precipitation occurs during the reaction, making it convenient for large-scale applications. The pure solvent, triglyme or tetraglyme, can be easily recovered and recycled either by crystallizing or by precipitating $NaBF_4$ from the generation flask. Diborane can also be generated quantitatively by the addition of $NaBH_4$ in triglyme or tetraglyme to the BF_3 adducts of di-*n*-butyl ether, *tert*-butyl methyl ether, monoglyme, dioxane, and tetrahydropyran. In these systems, generation of diborane is slower and requires 2−4 h at 25 °C (faster reactions take place at 50 °C). Also, $NaBF_4$ precipitates from the reaction mixture at 25 °C as the reaction proceeds. The high-boiling glyme can be conveniently separated from the lower boiling carrier ethers by simple distillation of the latter. Diborane was generated very slowly or not generated using the addition of each of six boron trifluoride−etherates to suspensions of sodium borohydride in the corresponding ether. Economic and elegant cyclic processes for the generation of diborane were developed by the regeneration of BF_3:TG from the byproduct $NaBF_4$ using $AlCl_3$ or BCl_3. The following are the preferred procedures.

(1) Generation of diborane using $NaBH_4$ in triglyme with BF_3−*tert*-butyl methyl etherate or BF_3−dioxanate, BF_3−monoglymate. The advantage is that the presence of the ether, *tert*-butyl methyl ether, dioxane, and monoglyme facilitates the precipitation of unsolvated $NaBF_4$ from the triglyme.

(2) Generation of diborane using $NaBH_4$ in triglyme (or tetraglyme) with BF_3−triglymate (or −tetraglymate) followed by raising the temperature to 100 °C after the B_2H_6 has evolved. The advantage is that the $NaBF_4$ is precipitated in unsolvated form.

(3) Generation of diborane in triglyme or tetraglyme by treating $NaBH_4$ in these solvents, with BF_3 in the corresponding solvent. This generates the diborane essentially quantitatively. In the second stage, $AlCl_3$ in the same solvent is added to regenerate BF_3 from the $NaBF_4$.

(4) Generation of diborane in a single-stage process in triglyme or tetraglyme by adding $NaBH_4$ slowly to $NaBF_4$ in the presence of dissolved $AlCl_3$.

(5) Generation of diborane in triglyme or tetraglyme by treating $NaBH_4$ in these solvents, with BF_3 in the corresponding solvent. This generates the diborane essentially quantitatively.

In the second stage, BCl_3 in the same solvent is added to regenerate BF_3 from the $NaBF_4$.

These improved procedures, which are free of significant disadvantages associated with the currently used procedure, offer major advantages for the generation of diborane.

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