

AN IMPROVED METHOD FOR THE PREPARATION OF SOLUTIONS OF DIBORANE

Arne Brändström, Ulf Junggren and Bo Lamm

Chemical Research Laboratory, AB Hässle, Fack, S-431 20 Mölndal 1, Sweden

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Diborane is a highly useful reagent in preparative organic chemistry (1). The standard method for the preparation of this compound is based on the reaction of sodium boranate with a Lewis acid such as boron trifluoride in a carefully dried ethereal solvent such as diglyme or tetrahydrofuran. Unfortunately these solvents are difficult to dry and to recover; they also have a high tendency to form peroxides (2).

Solvents of this type can, however, be replaced by the excellent solvent methylene chloride if a tetraalkylammonium boranate is substituted for sodium boranate.

We have reported (3) that methylene chloride solutions of tetraalkylammonium boranates are readily available by extracting with methylene chloride aqueous solutions of sodium boranate and a tetraalkylammonium sulphate (or other not easily extracted tetraalkylammonium salts). From these solutions the tetraalkylammonium boranate can be obtained in crystalline form by drying with potassium carbonate and evaporating the solvent. The yield is practically quantitative.

The tetraalkylammonium boranates are reported to have a low reactivity as reducing agents (4), which is easily demonstrated by the fact that they can be recrystallised from ethyl acetate or even acetone if the operation is rapidly performed. An anhydrous solution of tetraalkylammonium boranate in methylene chloride, however, readily gives diborane on addition of alkyl halide e.g. methyl iodide, ethyl bromide or even 1,2-dichloroethane. The diborane solution thus obtained can be used for all the usual reductions and hydroboration reactions.

The by-product of these procedures, a tetraalkylammonium halide, can be readily removed and recovered from the reaction products, since the properties of this type of compound can be varied to a large extent by proper choice of the tetraalkylammonium and halide ions. For

example tetrabutylammonium iodide greatly prefers methylene chloride to water, whereas the opposite is true for tetrapropylammonium chloride. Most tetraalkylammonium salts are more-over insoluble in ether, although readily soluble in methylene chloride; this property can also be used in the work-up procedure. The tetraalkylammonium chlorides thus recovered can be used directly for the preparation of a new portion of tetraalkylammonium boranate, whilst the bromides and iodides are readily transformed into chloride or sulphate, e.g. by means of a simple anion exchange reaction (3).

The synthesis of tetraalkylammonium boranate, one synthetic procedure and different work-up procedures are described below to illustrate the applicability of this preparation of diborane. Some further results are presented in Tables 1-3.

Preparation of a tetraalkylammonium boranate.

One mole of a tetraalkylammonium hydrogen sulphate is dissolved or suspended in 200 ml water. 250 ml 5 M NaOH is added and the mixture cooled to room temperature. A solution of 1.1 mole NaBH_4 dissolved in 100 ml water is then added and the mixture extracted with 500 ml methylene chloride (upper phase). The layers are separated and the aqueous layer is extracted with 250 ml methylene chloride (lower phase). The methylene chloride layers (usually containing some precipitated Na_2SO_4) are combined and dried with anhydrous K_2CO_3 . The methylene chloride solution contains the theoretical amount of tetraalkylammonium boranate, provided that the quarternary ammonium ion has a total number of 12 or more carbon atoms.

If the solid salt is required the methylene chloride is removed at room temperature and reduced pressure. The residue is then recrystallized from ethyl acetate

For the preparation of diborane the solution can, however, be used directly if the last traces of water are removed as an azeotrope by evaporating about 250 ml of the methylene chloride at reduced pressure. The solution should be used within a few hours.

Table 1 Generation of diborane with various acids in situ.
Reduction of benzonitrile to benzylamine.

Acid	BF ₃	H ₂ SO ₄	HCl	(CH ₃ O) ₂ SO ₂	RX
Yield %	-	25	50	50	95

Table 2 Reaction of diborane with organic compounds containing a carbonyl group.

Substrate	equiv. QBH ₄	alkyl halide	Product	Yield %
Methyl 4-nitrobenzoate	1.5	A	4-Nitrobenzyl alcohol ^{a)}	80
Ethyl (4-benzyloxyphenyl) acetate	1.5	A	2-(4'-Benzyloxyphenyl) ^{a)} ethanol	87
Benzoic acid	1	B	Benzyl alcohol	98
3-Nitrobenzoic acid	1	B	3-Nitrobenzyl alcohol	90
4-Chlorobenzoic acid	1	B	4-Chlorobenzyl alcohol ^{a)}	98
4-Chlorobenzaldehyde	1	B	4-Chlorobenzyl alcohol ^{a)}	94
4-Methoxyphenylacetic acid	1.5	C	2-(4'-Methoxyphenyl) ethanol ^{b)}	90

A = methyl iodide

B = ethyl bromide

C = 1,2-dichloroethane

a) recrystallized

b) distilled at 90-95°C/0.035 mmHg

Table 3 Hydroboration with diborane generated in situ.

Substrate	equiv. QBH ₄	alkyl halide	Product	Yield %
Cyclohexene	0.5	B	Cyclohexanol	98
Phenyl allyl ether	0.5	B	Alcohol ^{a)}	96

a) 3-Phenoxy 1-propanol was separated from 3-phenoxy 2-propanol by fractionation in vacuum to give a yield of 70 %.

Product soluble in water. Reduction of a nitrile.

In a dry 500 ml flask equipped with a stirrer, reflux condenser, dropping funnel and an inlet tube for dry argon, 25.7 g (0.1 mole) tetrabutylammonium boranate and 18.5 g (0.1 mole) benzonitrile were dissolved in 100 ml methylene chloride (dried over P_2O_5). The flask was chilled in an ice bath and 28.4 g (0.2 mole) methyl iodide was added carefully to avoid excessive evolution of methane. The solution was then stirred for half an hour at room temperature. Excess hydride was destroyed by addition of 25 ml ethanol and the mixture hydrolysed by introducing hydrogen chloride. The solution was then extracted with 2 x 100 ml water. The acidic aqueous layer were combined and made alkaline with NaOH. The benzylamine was extracted with ether. The solution was dried over Na_2SO_4 and the solvent evaporated. The residue was pure benzylamine. Yield 95 %.

The work-up procedure can be changed in several respects depending on the properties of the tetraalkylammonium halide received as by-product. When the product is insoluble in water the excess of hydride is destroyed with water and the solution made alkaline with NaOH. The organic layer is then treated in different ways as indicated on top of the second page. For a large scale (up to 50 mole) preparation, 1,2-dichloroethane is preferably used as the halide and the tetrabutylammonium chloride directly removed by repeated extractions with water. In the hydroboration of an olefine to an alcohol the organoborane is oxidized by the addition of 30 % hydrogen peroxide to the alkaline two-phase system, similar to the procedure described by Zweifel and Brown (5).

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