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Crown-ether-catalysed synthesis of amine borane and amine trideuterioborane adducts from $NaBH_4$–$NaBD_4$ in ether

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Abstract

Amine borane and amine trideuterioborane adducts have been obtained in good yield by the crown-ether-catalysed reaction of $R_3N \cdot HCl$ with $NaBH_4$ and $NaBD_4$ in ether. The absence of isotopic exchange in the reaction with $NaBD_4$ is demonstrated by IR and ^{11}B and ^{2}H nuclear magnetic resonance spectra of $Me_3N \cdot BD_3$.

Key words: Boron; Hydride; Amine

1. Introduction

Amine boranes have wide application in organic chemistry as selective reduction and hydroborating agents [1]. The most used method of synthesis of amine boranes is based on the reaction of $NaBH_4$ with the appropriate amine hydrochloride in various aprotic solvents.

It is well known that $NaBH_4$ is insoluble in diethyl ether, and so amine boranes could not be prepared in this solvent by this method [2]. Only the ether-soluble $LiBH_4$ can be used in diethyl ether for preparing $Me_3N \cdot BH_3$ from $Me_3N \cdot HCl$ [3]. Since it is known that reduction by $NaBH_4$ can be catalysed by crown ethers in hydrocarbon solvents [4], we attempted to use crown ethers to promote the formation of amine boranes by this reaction in ether.

We found that the reaction of $NaBH_4$ with $Me_3N \cdot HCl$ in boiling ether catalysed by 18-crown-6 afforded $Me_3N \cdot BH_3$ with a good yield:

$$Me_3N \cdot HCl + NaBH_4 \xrightarrow[\text{ether}]{\text{18-crown-6}} Me_3N \cdot BH_3$$

Under the same conditions, other amine boranes were prepared from the corresponding amine hydrochlorides (Table 1). The physical constants of the amine boranes were identical with those published previously [5].

We also attempted to apply this reaction to the synthesis of amine trideuterioboranes. The preparation of $Me_3N \cdot BD_3$ was first reported in 1963 [6] and was achieved by isotopic exchange of $Me_3N \cdot BH_3$ with deuterium in acidic D_2O. We have recently reported hydrogen–deuterium exchange reactions brought about by polymeric membranes and cation exchange resins [7]. We found that the reaction of $NaBD_4$ with $Me_3N \cdot HCl$ in ether at reflux is catalysed by 18-crown-6, affording $Me_3N \cdot BD_3$, as follows:

$$NaBD_4 + Me_3N \cdot HCl \xrightarrow[\text{ether}]{\text{18-crown-6}} Me_3N \cdot BD_3$$

No isotopic exchange occurred in this reaction, as shown by the IR and ^{11}B and ^{2}H nuclear magnetic resonance (NMR) spectra of the product. The IR spectra of a solution of $Me_3N \cdot BD_3$ in CCl_4 showed the gradual disappearance of the 2360 cm^{-1} B–H bond (Fig. 1(a)) and the appearance of a strong broad line at a frequency of 1783 cm^{-1} (Fig. 1(b)) characteristic of the boron–deuterium bond. ^{11}B NMR showed a multiplet of -8.92 ppm (broad, $\Delta\nu_0^{1/2} = 70$ Hz, $CDCl_3$) (Fig. 2) and ^{2}H NMR showed one of -1.699 ppm (broad, $\Delta\nu_0^{1/2} = 15.4$ Hz, $CDCl_3$) (Fig. 3).

Several other amine hydrochlorides, including trimethylamine, pyridine, morpholine, *N*-methylmor-

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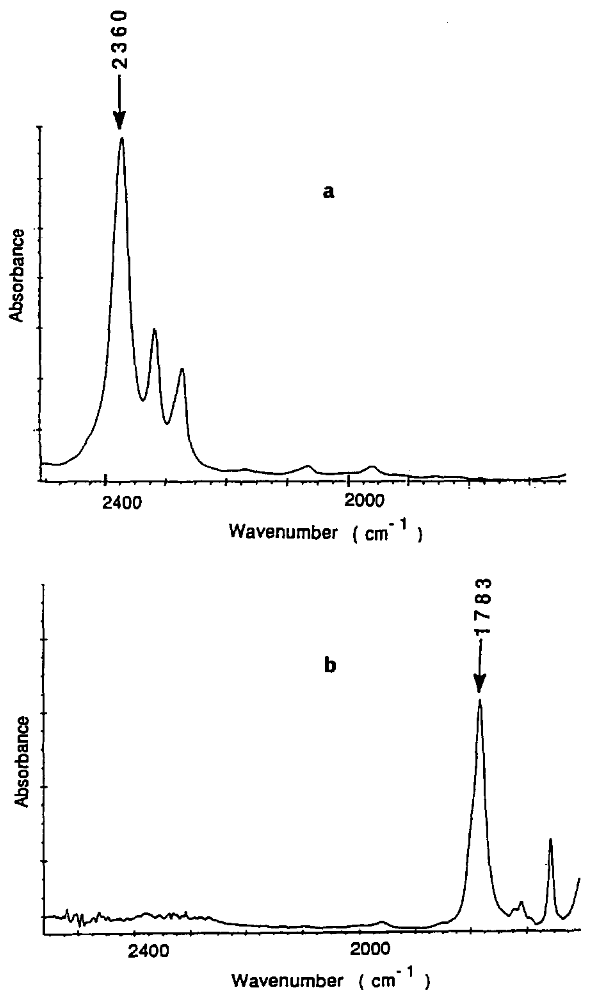


Fig. 1. IR spectra of (a) trimethylamine borane and (b) trimethylamine trideuterioborane in CCl_4.

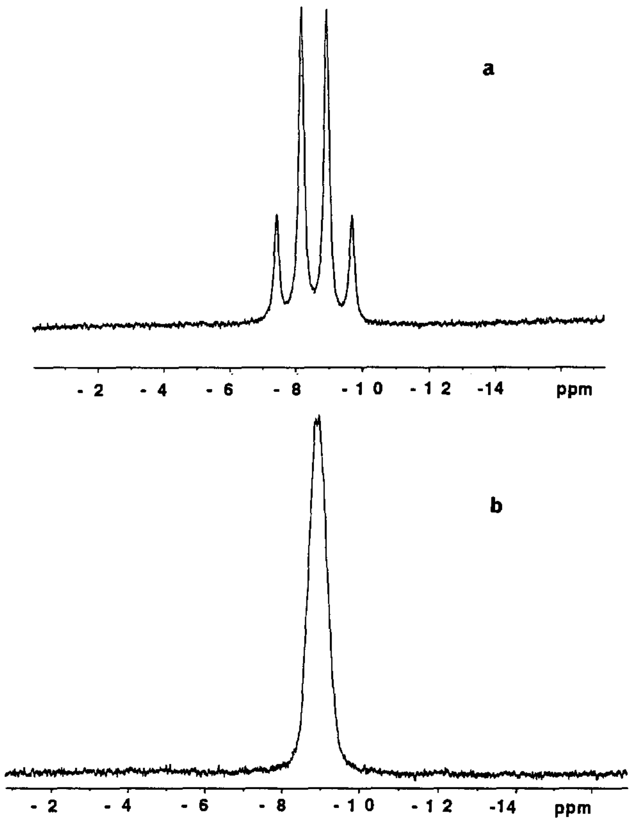
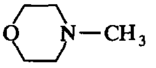
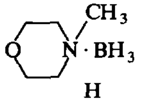
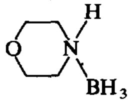
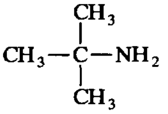
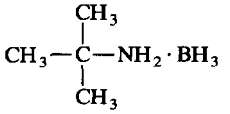


Fig. 2. ^{11}B NMR spectra of (a) trimethylamine borane and (b) trimethylamine trideuterioborane in $CDCl_3$.

pholine and isobutylamine were converted into the corresponding amine borane complexes with fair to good yields after crystallization. Thus this new approach provides a convenient method for synthesizing

TABLE 1. Melting points and yields for selected amine boranes syntheses

Amine	Amineborane	Yield [a] (%)	M.p. [b] (°C)
Me_3N	$Me_3N \cdot BH_3$	80	94
C_5H_5N	$C_5H_5N \cdot BH_3$	63	-
		75	44–45 (Et_2O)
		50	97 (Et_2O)
 $CH_3-C(CH_3)_2-NH_2$	 $CH_3-C(CH_3)_2-NH_2 \cdot BH_3$	70	97–99 (Et_2O-hexane)

[a] No attempt was made to optimize yields. [b] With solvent used for recrystallization.

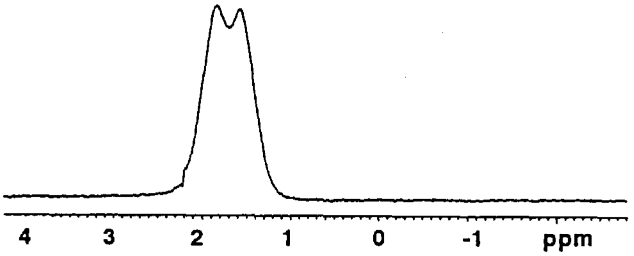


Fig. 3. ^{2}H NMR spectra of trimethylamine trideuterioborane in $CDCl_3$.

amine borane and amine trideuterioborane adducts from the readily available sodiumborohydride or sodiumborodeuteride and the relevant amine hydrochlorides.

2. Experimental details

NMR spectra were recorded on a Bruker AMX400 spectrometer. A Nicolet 510 Fouier transform IR spectrometer was used to record IR spectra in the range 4000–400 cm^{-1}. For the IR spectra of solutions a standard NaCl cell was used. Melting points were determined for samples in a capillary tube. The ether was distilled over $LiAlH_4$ under Ar prior to use.

2.1. Trimethylamine borane

A mixture of $NaBH_4$ (0.558 g, 14.7 mmol), $Me_3N \cdot HCl$ (1.0 g, 10.4 mmol) and 18-crown-6 (0.1 g, 0.38 mmol) in ether (40 ml) was refluxed under Ar for 5 h. The mixture was allowed to cool, and then the ether was evaporated and the residue sublimed under vacuum to give 0.61 g (80%) of $Me_3N \cdot BH_3$ (melting point (m.p.), 94°C).

2.2. Trimethylamine trideuterioborane

A mixture of $NaBD_4$ (0.426 g, 10 mmol), $Me_3N \cdot HCl$ (1.04 g, 11 mmol) and 18-crown-6 (0.1 g, 0.38 mmol) in ether (40 ml) was refluxed under Ar for 5 h. The work-up, as above, culminated in two sublimations under vacuum, giving 0.45 g (61%) of $Me_3N \cdot BD_3$ (m.p., 94°C).

Acknowledgments

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