Chemistry of Amine-Boranes. XI.\textsuperscript{1)} A Convenient Synthesis of Dimethylamine-Borane

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Dimethylamine-borane was synthesized in good yield from sodium borohydride and dimethylamine hydrochloride by using dimethoxyethane as a solvent.

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Amine-boranes are useful reagents which have many important laboratory and industrial applications.\textsuperscript{2)} In particular, dimethylamine-borane (DMAB) has been used widely as a reducing agent in chemical plating.\textsuperscript{3)} Commercially available DMAB is prepared by the reaction of diborane with dimethylamine at low temperature.\textsuperscript{2a)} DMAB is also prepared by other methods, such as reaction of lithium borohydride (LBH) with dimethylamine hydrochloride in ether,\textsuperscript{2b,4)} displacement of tetrahydrofuran (THF) with dimethylamine from THF-borane,\textsuperscript{2b)} or reaction of sodium borohydride (SBH) and dimethylamine in the presence of iodine.\textsuperscript{5)} We wished to prepare DMAB through a more convenient method.

It is generally accepted that ordinary amine-boranes can be prepared by the reaction of LBH with an amine hydrochloride in ether. The synthesis of pyridine-borane is exceptional, and can be successfully carried out by the reaction of SBH (instead of LBH) and pyridine hydrochloride in pyridine,\textsuperscript{6)} probably because both SBH and pyridine hydrochloride are comparatively soluble in pyridine. We have investigated the preparation of DMAB with SBH and dimethylamine hydrochloride by seeking a proper solvent. Many solvents were tested and the results were as follows: 1) DMAB was obtained in moderate but practically unsatisfactory yields in THF or dioxane. 2) Dimethylformamide (DMF) dissolves SBH and dimethylamine hydrochloride fairly well and DMAB was obtained in good yield; however, chromatography on a short silica gel column was needed to remove DMF completely. 3) Dimethoxyethane (DME) was revealed to be the best solvent not only for dissolving the reagents, but also because it could be easily removed by evaporation. Accordingly DMAB was obtained in good yield through a simple procedure.

Some secondary amine-boranes such as morpholine-borane or diethylamine-borane were also synthesized by using the combination of SBH, the amine hydrochloride and DME in yields of 71\% and 55\%, respectively. However, it is interesting to note that trimethylamine-borane could not be synthesized at all by the same procedure.

Experimental

All melting points are uncorrected. SBH was purchased from Morton Thiokol Ltd., Japan, Ventron Division. DMAB—SBH (925 mg, 25 mmol) was added in small portions to a suspension of dimethylamine hydrochloride (2.24 g, 27.5 mmol) in DME (40 ml) under stirring. After 1 h, the reaction mixture was filtered and the filtrate was evaporated \textit{in vacuo} to afford crude DMAB, mp 33°C (1.24 g, yield 84\%), which was recrystallized from dichloromethane–hexane to give pure DMAB,\textsuperscript{7)} mp 36°C (lit.\textsuperscript{5)} 36°C).
References and Notes


4) H. Nöth and H. Beyer, *Chem. Ber.*, 93, 931 (1960). It was claimed in the literature that SBH is also effective for the synthesis of amine-boranes; however, no experimental details were given. According to ref. 2b, LBH is used because it is more soluble in organic solvents than the other alkali metal borohydrides.


7) This was identified by mixed melting point determination with an authentic sample purchased from Morton Thiokol Ltd., Japan, Ventron Division.