

SYNTHESIS OF ALKYLAMINE BORANES

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ABSTRACT

The reaction of mercaptomethyleiminium salts with sodium borohydride is used to synthesize alkylamine boranes in moderate to good yields. This will enhance the use of borane derivatives in organic syntheses.

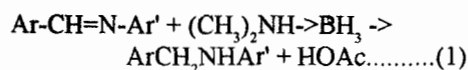
INTRODUCTION

The reactions of mercaptomethyleiminium salts with various nucleophiles have been investigated by various authors^{1,2}. In this paper, that of the borohydride ion is reported as a new synthetic route to alkylamine boranes.

The reaction of boranes with double bonds is well-known³.

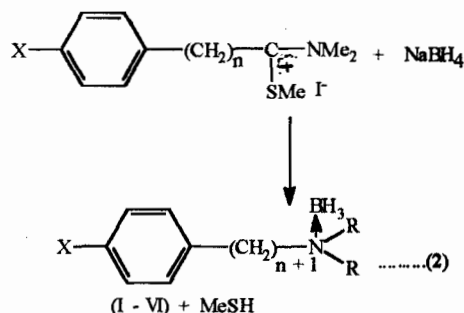
There is difficulty in preparing borane as a pure stable compound^{4,5}. Commonly it dimerises to give diborane, B₂H₆. Borane is produced commercially in the form of its complexes with tetrahydrofuran (THF), dimethylsulphide (Me₂S) or tertiary amines.

Dimethylamineborane⁶, (CH₃)₂NH→BH₃ has been used to reduce a number of Schiff bases in the presence of various functional groups such as chloro-, nitro-, methoxy-, ethoxycarbonyl-, sulphonamido-, and carboxy groups to their respective secondary amines. Reductions are usually done in glacial acetic acid, giving high yields ranging 80-97%. The other functional groups are unaffected under the reaction condition, Eqn. 1.



N,N-Dimethylbenzylamine borane⁷ has been prepared but by reacting the amine with diborane in tetrahydrofuran. Diborane is a poisonous, spontaneously inflammable gas which is difficult to handle. Sodium borohydride is, however, a readily available reagent which can be used to generate the alkylamine boranes, (Equation 2).

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I&II, X=H; III, X=Cl; IV&V, X=-NMe₂; VI, X=OMe.

I-IV&VI, R=Me; V, R=-morpholino.

I&III-VI, n=0; II, n=1.

We report here a facile synthesis of aminoborane derivatives that are stable solids at room temperature.

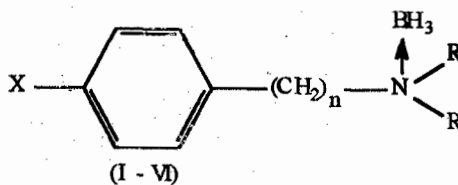
EXPERIMENTAL

NMR spectra were run with a Varian T-60 spectrometer using CDCl₃ as solvent and TMS as internal standard. Perkin Elmer 700 instrument was used for i.r. spectra run as nujol mulls. All melting points (uncorrected) were taken with the Kofler hot stage microscope. Elemental analyses were carried out at the Scandinavian Microanalytical Laboratories. Solvents were purified by standard methods.

Typical procedure

NN-Dimethylbenzylamine borane (X-H, Equation 2) Sodium borohydride (11.25g, 0.3m) was dissolved in water (25ml) and cooled in ice-salt-water mixture. Thiobenzdimethylamide methiodide (X=H, Equation 2, 6.14g, 0.02m) was added in small portions over 10-15 mins. whilst stirring magnetically. Frothing occurred and there was strong smell of methanethiol.

Table 1: Aminoboranes



ANALYSIS*							
	YIELD (%)	M.P. (°C)	%C	%H	%N	I.R. SPECTRA (NUJOL) cm ⁻¹	N.M.R. SPECTRA (δ-values)
I ^b	89	93-5	72.5 (72.6)	10.7 (10.8)	9.3 (9.4)	2925vs, 2400vs, 2325m, 2290s, 1170vs, 1005s, 800m, 750s, 700s	2.50(6H,s, -NMe ₂) 3.95(2H,s, -CH ₂ -) 7.40(5H,s, aromatic)
II	89	60	73.7 (73.7)	11.1 (11.1)	8.6 (8.6)	2950vs, 24400, 2330w, 2300m, 1190vs, 880m, 700s	2.65(6H,s, -NMe ₂) 3.0(4H,s, -CH ₂ -) 7.25(4H,s, aromatic)
III	60	89-90	58.9 (58.9)	8.1 (8.2)	7.6 (7.5)	2950vs, 2448s, 2350w, 2300m, 1180vs, 1025m, 865m, 845m, 800w	2.46(6H,s, -NMe ₂) 3.87(2H,s, -CH ₂ -) 7.38(4H,s, aromatic)
IV	47	147-8	68.6 (68.8)	11.0 (10.9)	14.8 (14.6)	3050vs, 2520s, 2450w, 2410m, 1680s, 1595s, 1510m, 1218s, 880m	2.40(6H,s, -NMe ₂ aliphatic) 2.98(6H,s, -NMe ₂ aromatic) 3.86(2H,s, -CH ₂ -) 6.90(4H,q, aromatic)
V	91	132-3	66.5 (66.7)	9.7 (9.8)	12.0 (12.0)	2925vs, 2400s, 2300w, 1610s, 1520s, 1190w, 1160w, 1110s, 800s	3.55(8H,m, morpholino) 3.35(2H,s, -CH ₂ -) 3.82(6H,s, NMe ₂) 7.15(4H,q, aromatic)
VI	96	79-80	67.0 (67.1)	10.0 (10.1)	7.9 (7.8)	3050vs, 2525s, 2450w, 2420m, 1678m, 1580s, 1520s, 1320s, 1240, 1100s, 880m	2.90(6H,s, NMe ₂) 3.65(5H,m, -OMe & - CH ₂ -) 6.85(4H,q, aromatic)

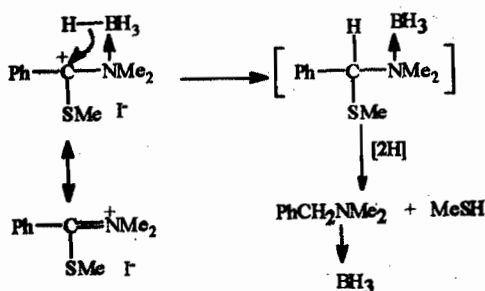
*FOUND VALUES ABOVE, REQUIRED VALUES IN BRACKETS.

After stirring for 1h, the mixture was allowed to stand for another 2h, and the solid produced was filtered off, washed and dried (2.70g). Crystallisation from petroleum ether (bp 60-80°C) gives colourless plates.

In every case investigated, a liquid by-product was obtained after filtering off the solid. For example, when 4-chlorothiobenzodimethylamide methiodide (X = Cl, Equation 2) was used, a yellow oil was obtained by extraction with diethyl ether. A colourless distillate characterised as NN-dimethyl-4-chlorobenzylamine, bp 90-92°C, (lit⁹90-90.5°C) was obtained by simple distillation.

RESULTS AND DISCUSSION

The reduction mechanism may involve the co-ordination of boron to the nitrogen atom of the salt, followed by a four-centred intramolecular hydride transfer mechanism from boron to carbon.



An intermolecular hydride transfer from borohydride ion may further explain the formation of borane which could either coordinate to the nitrogen atom or dimerise to give diborane.

The free amine was always obtained despite the use of excess sodium borohydride. This may suggest a competition between hydroboration and dimerisation of borane to give diborane.

This may not be surprising since the conditions for reductions with diborane do not exactly parallel those with sodium borohydride. The latter is a nucleophile and reacts by addition of hydrogen atom to the more positive end of a polarised multiple bond. Diborane, however, is a Lewis acid and only attacks electron-rich centres.

The nmr spectra (60MHz) show no protons attached to boron. The presence of a BH₃ group could only be confirmed by i.r. spectroscopy and by elemental analysis (Table 1).

Boranes have characteristic absorptions between 2290-2530cm⁻¹ ascribed to B-H vibrations.

Boron itself (¹¹B) with spin 3/2 should be detectable on higher resolution instruments. The special problems with this and other nuclei arise due to low signal strengths, low isotopic abundance of the particular magnetic nucleus, a nuclear electric quadrupole moment which may cause excessive signal broadening and an unfavourably long spin-lattice relaxation time⁹. The coupling between proton and boron J_{B-H} is found to vary between 80-90 Hz.

CONCLUSION

The aminoboranes prepared by our method tend to have long shelf lives and could be a ready source of the -BH₃ moiety when it is required in organic synthesis.

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accepted 24/10/96

received 26/3/96

