Exchange Reactions of Trimethylamine–Iodoborane (1/1) with Halide and Pseudohalide Anions

By **Peter J. Bratt, Michael P. Brown,*** and **Kenneth R. Seddon,** Donnan Laboratories, Liverpool University, Liverpool L69 3BX

Exchange reactions (i) (X = Cl, Br, F, CN, NCS, NCO, or BH_3CN) of Me_3N,BH_2I give high yields in tetrahydrofuran. Monoglyme and acetonitrile are less suitable solvents. The new compounds $Me_3N,BH_2(NCS)$ and

$$Me_3N,BH_2I + MX \longrightarrow Me_3N,BH_2X + MI \qquad (i)$$

$Me_3N,BH_2(NCO)$ have been isolated and characterised. A convenient two-stage preparation of $Me_3N,BH_2(CN)$ (78% yield) from Me_3N,BH_3 *via in situ* formation of Me_3N,BH_2I is described. The compounds Me_3N,BH_2X (X = Cl or Br) and Me_3N,BHX_2 (X = Br or I) do not appear to undergo similar exchange reactions.

DESPITE recent interest in the chemistry of trimethylamine-monohalogenoboranes [1-6] and their reactions with amine ligands,[7,8] their exchange reactions have remained unstudied. The present work was undertaken subsequent to an investigation of the reactions of Me_3N,BH_2I in liquid ammonia,[4] in which it was found that exchange of I for CN occurred when this compound was treated with NaCN. However, although a trace of $Me_3N,BH_2(CN)$ was obtained, the main product in liquid ammonia was $H_3N,BH_2(CN)$. This result suggested that it was worth investigating the use of more weakly basic organic solvents, which will not replace the trimethylamine ligand, for halide exchange and this paper describes studies in tetrahydrofuran, monoglyme, and acetonitrile.

---

[1] H. Nöth and H. Beyer, *Chem. Ber.*, 1960, **93**, 2251.

[2] M. P. Brown, R. W. Heseltine, P. A. Smith, and P. J. Walker, *J. Chem. Soc.* (*A*), 1970, 410.

[3] P. J. Bratt, K. R. Seddon, and I. A. Steer, *Inorg. Chim. Acta*, in the press.

[4] P. J. Bratt and M. P. Brown, unpublished work.

[5] S. Ratajzak, *Bull. Soc. chim. France*, 1960, 487.

[6] J. E. Douglass, *J. Org. Chem.*, 1966, **31**, 962.

[7] D. L. Reznicek and N. E. Miller, *Inorg. Chem.*, 1972, **11**, 858.

[8] G. E. Ryschkewitsch and K. Zutshi, *Inorg. Chem.*, 1970, **9**, 411.

RESULTS AND DISCUSSION

Reactions in Tetrahydrofuran.—This solvent gave the most favourable results and in fact Me_3N,BH_2I was found to react at room temperature with MX [X = F, Cl, Br, CN, NCS, NCO, or $BH_3(CN)$]. In all cases, except for X = F, the expected products Me_3N,BH_2X were obtained in high yield as shown in the Table. The reaction of lithium fluoride yielded a 2 : 1 mixture of Me_3N,BH_3 and Me_3N,BF_3. This is consistent with initial formation of Me_3N,BH_2F, which then disproportionates as in equation (1). Although Me_3N,BH_2F was

$$3Me_3N,BH_2F \longrightarrow 2Me_3N,BH_3 + Me_3N,BF_3 \quad (1)$$

recently prepared by VanPaasschen and Geanangel[9] from Me_3N,BH_3 and HF in benzene, Nöth and Beyer[10] previously suggested that Me_3N,BH_2F may be unstable in other solvents, especially ethers, and our experiments tend to confirm this. We observed no reaction between Me_3N,BH_2I and LiF in benzene.

Halide-exchange reactions at room temperature

Reactants (A)	(B)	Solvent	Mole ratio (A : B)	Time of reaction/h	Product	Yield (%, based on A)
a	LiBr	*b*	1 : 2	10	Me_3N,BH_2Br	77
a	LiCl	*b*	1 : 2	12	Me_3N,BH_2Cl	64
a	LiF	*b*	1 : 1	18	Me_3N,BH_3 Me_3N,BF_3	66 33
a	NaCN	*b*	1 : 1	48	$Me_3N,BH_2(CN)$	84
a	$Na[BH_3(CN)]$	*b*	1 : 1	20	$Me_3N,BH_2{\cdot}NC{\cdot}BH_3$	73
a	$Me_3N,BH_2(CN)$	*b*	1 : 1	16	No reaction	
a	KSCN	*b*	1 : 1	8	$Me_3N,BH_2(NCS)$	50
a	NaNCO	*b*	1 : 1	20	$Me_3N,BH_2(NCO)$	49
a	LiBr	*c*	1 : 3	10	Me_3N,BH_2Br	52
a	NaCN	*c*	1 : 1	6	$Me_3N,BH_2(CN)$	23
a	LiBr	*d*	1 : 1	10	Me_3N,BH_2Br $[(Me_3N)(MeCN)BH_2]I$	20
a	LiBr	*d*	1 : 10	60	Me_3N,BH_2Br $[(Me_3N)(MeCN)BH_2]I$	20
e	LiBr	*d*	1 : 2	25	No reaction	
f	LiBr	*d*	1 : 2	12	No reaction	
f	LiF	*d*	1 : 2	12	No reaction	
e	LiF	*d*	1 : 2	120	No reaction	
a	LiF	*d*	1 : 2	3	100% Reaction	*g*
a	NaCN	*d*	1 : 1	3	100% Reaction	*g*

[a] Me_3N,BH_2I. [b] thf. [c] Monoglyme. [d] MeCN. [e] $[(Me_3N)(MeCN)BH_2]I$. [f] Me_3N,BH_2Br. [g] Involatile intractable mixture.

The reaction between Me_3N,BH_2I and NaCN proved to be a convenient high-yield route (84%) to $Me_3N,BH_2(CN)$. The convenience of this method was further improved by forming Me_3N,BH_2I *in situ* by the addition of iodine to Me_3N,BH_3 and by using tetrahydrofuran (thf) as solvent throughout. An overall yield of 78% was obtained. This compound was previously prepared[11] by a low-yield reaction between $Na[BH_3(CN)]$ and Me_3N in acidified thf. Reaction between Me_3N,BH_2I and $Na[BH_3(CN)]$ gave $Me_3N,BH_2{\cdot}NC{\cdot}BH_3$ in 73% yield in contrast to its previously reported preparation[7] in only 10% yield as a by-product in the preparation of $[Me_3N{\cdot}BH_2{\cdot}CN{\cdot}BH_2{\cdot}NMe_3]PF_6$.

In the compound $Me_3N,BH_2(NCS)$ there is the possibility of linkage isomerism. The related ammonia complex[12] $H_3N,BH_2(NCS)$ has been shown by a recent structural determination[13] to be an isothiocyanatoborane and to contain an approximately linear BNCS grouping. Comparison of the i.r. spectrum of $Me_3N,BH_2(NCS)$ with that[12] of $H_3N,BH_2(NCS)$ and other isothiocyanates of boron[14] did not unfortunately lead to any definite conclusions, as the ν(CS) region was obscured by trimethylamine bands. By analogy, however, it seems most probable that $Me_3N,BH_2(NCS)$ is an isothiocyanate.

The behaviour of Me_3N,BH_2I in thf was in marked contrast to that of the other trimethylamine–halogenoborane complexes. We observed no reaction between Me_3N,BH_2Br and LiX (X = Cl or F), Me_3N,BH_2Cl and LiF, Me_3N,BHI_2 and LiX (X = Cl or Br), $Me_3N,BHBr_2$ and LiCl, and finally Me_3N,BBr_3 and LiCl, under a variety of reaction conditions. In view of the relative weakness of the boron–iodine bond, it is not surprising that the monoiodo-compound reacted whilst the monobromo- and monochloro-compounds did not. The fact that the di-iodo-derivative Me_3N,BHI_2 was unreactive is however unexpected and we are unable to offer any explanation of this.

Reactions in Monoglyme.—Exchange occurred when Me_3N,BH_2I was treated with LiBr and NaCN (see Table) but the yields were relatively low. These could not be improved by changing the reaction conditions and so investigations with this solvent were curtailed.

Reactions in Acetonitrile.—Halide exchange was observed between lithium bromide and Me_3N,BH_2I but the product Me_3N,BH_2Br was formed only in 20% yield. The major product of this reaction was $[(Me_3N)(MeCN)BH_2]I$ formed by solvent substitution. The % yield of

---

[9] J. M. VanPaasschen and R. A. Geanangel, *J. Amer. Chem. Soc.*, 1972, **94**, 2680.

[10] H. Nöth and H. Beyer, *Chem. Ber.*, 1960, **93**, 2251.

[11] S. S. Uppal and H. C. Kelly, *Chem. Comm.*, 1970, 1619.

[12] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1961, **83**, 2471.

[13] D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, 1973, **12**, 2920.

[14] M. F. Lappert and H. Pyszora, *J. Chem. Soc.* (*A*), 1967, 854.

Me_3N,BH_2Br was not affected by changing the mole ratio of $LiBr:Me_3N,BH_2I$, or by changing the reaction time. Further experiments showed that both Me_3N,BH_2Br and $[(Me_3N)(MeCN)BH_2]I$ were unchanged in the presence of LiBr and MeCN, and from these we conclude that the two reactions are competitive and not consecutive. Reactions of Me_3N,BH_2I and NaCN and LiF both yielded involatile and intractable mixtures, from which no pure reaction product could be isolated.

EXPERIMENTAL

The trimethylamine–monohalogenoboranes, Me_3N,BH_2X, and trimethylamine–dihalogenoboranes, Me_3N,BHX_2, were prepared as described elsewhere [2] and resublimed before use. Alkali-metal halides and pseudohalides were dried by heating *in vacuo*. Sodium cyanotrihydroborate (ex Aldrich) was used without further purification. Solvents were dried, acetonitrile and benzene over molecular sieves, tetrahydrofuran (thf) and monoglyme over calcium hydride, and distilled.

I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer. Analyses for C, H, and N were carried out at the Microanalytical Laboratory at Liverpool University. Boron was estimated by titration as the boric acid–mannitol complex, and halogens were determined gravimetrically as silver(I) halide.

Reactions of Me_3N,BH_2I.—The essential details of the reactions are summarised in the Table and some typical reactions are described in detail below.

Preparation of trimethylamine–isothiocyanatoborane (1/1) *in tetrahydrofuran.* A mixture of Me_3N,BH_2I (3·1 g) and potassium thiocyanate (1·8 g) in thf (25 cm^3) was stirred for 8 h. The solvent was then removed *in vacuo* and the residue extracted with benzene. The benzene was removed *in vacuo* and the crude product purified by recrystallation from ethanol at −70 °C to yield the pure *compound* (1·6 g), m.p. 73—74 °C [Found: C, 36·8; H, 8·4; B, 8·4; N, 20·9. $Me_3N,BH_2(NCS)$ requires C, 36·9; H, 8·5; N, 8·5; N, 21·5%]. The mass spectrum showed a molecular ion. I.r. spectrum: $\nu(BH_2)_{asym}$ 2 433; $\nu(BH_2)_{sym}$ 2 358 and 2 370; ν(B–N) 703 and 715; and ν(CN) 2 160 cm^{-1}.

Preparation of trimethylamine–isocyanatoborane (1/1) *in tetrahydrofuran.* A mixture of Me_3N,BH_2I (2·0 g) and sodium cyanate (0·74 g) in thf (25 cm^3) was stirred for 20 h. The solvent was then removed *in vacuo* and the residue extracted with benzene. Benzene was removed *in vacuo* and the crude product recrystallised from 1,2-dichloroethane–n-pentane to give the pure *compound* (0·5 g), m.p. 71—72 °C [Found: C, 42·0; H, 9·6; B, 9·5; N, 24·2. $Me_3N,BH_2(NCO)$ requires C, 42·1; H, 9·7; B, 9·7; N, 24·6%].

Preparation of trimethylamine–μ-cyano-diborane(6) (1/1) *in tetrahydrofuran.* A mixture of Me_3N,BH_2I (0·54 g) and $Na[BH_3(CN)]$ (0·18 g) in thf (25 cm^3) was stirred for 20 h. The solvent was then removed *in vacuo* and the residue recrystallised from 1,2-dichloroethane–n-pentane to yield the pure compound (0·22 g), m.p. 128 °C (lit.,[7] 126—128 °C) (Found: C, 43·0; H, 12·3; B, 19·5; N, 24·5. $Me_3N,BH_2{\cdot}NC{\cdot}BH_3$ requires C, 42·9; H, 12·5; B, 19·7; N, 25·0%).

Reaction with NaCN *in monoglyme.* A mixture of Me_3N,BH_2I (1·39 g) and NaCN (0·42 g) in monoglyme (30 cm^3) was stirred for 6 h. The solvent was removed *in vacuo* and the residue extracted with benzene (20 cm^3). Benzene was removed *in vacuo* and the product purified by sublimation at 50 °C (m.p. 64 °C; yield 23%) and identified as Me_3N,BH_2CN by comparison of its m.p. and i.r. spectrum with those in the literature.[11]

Reaction with LiBr *in acetonitrile.* A mixture of Me_3N,BH_2I (1·02 g) and LiBr (0·54 g) in acetonitrile (25 cm^3) was stirred for 10 h at room temperature. The solvent was then removed *in vacuo* and the white residue was heated to 50 °C. A white sublimate (0·24 g) was obtained (m.p. 69—70 °C) and was identified as Me_3N,BH_2Br by comparison of its m.p. and i.r. spectrum with those in the literature.[2,10] The involatile residue was a mixture of lithium halide and $[(Me_3N)(MeCN)BH_2]I$ (identified by its i.r. spectrum [8]).

Preparation of trimethylamine–cyanoborane (1/1) *from trimethylamine–borane.* A solution of iodine (1·73 g) in thf (15 cm^3) was added dropwise to a solution of Me_3N,BH_3 (0·96 g) in thf (15 cm^3), under an atmosphere of dry dinitrogen. When dihydrogen evolution had ceased (*ca.* 1 h), sodium cyanide (0·74 g) was added to the reaction mixture, and the mixture was stirred at room temperature for 2 d. Solvent was then removed *in vacuo*, and the residue was extracted with benzene. Benzene was removed *in vacuo* and the crude product purified by vacuum sublimation at 50 °C to give the pure compound (0·99 g), m.p. 63 °C (lit.,[11] 63 °C) (Found: C, 48·8; H, 11·2; B, 11·2; N, 27·8. Me_3N,BH_2CN requires C, 49·0; H, 11·2; B, 11·2; N, 28·6%). The mass spectrum showed a molecular ion. I.r. spectrum: $\nu(BH_2)_{asym}$ 2 422 and 2 428; $\nu(BH_2)_{sym}$ 2 328; ν(BN) 711 and 723; and ν(CN) 2 195 cm^{-1}.

We thank the S.R.C. for the award of a maintenance grant (to P. J. B.) and I.C.I. for the award of a research fellowship (to K. R. S.).

[4/763 *Received, 17th April*, 1974]