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Preliminary communication

The reaction of *N*-chlorodimethylamine with tributylborane and with dibutyl(dimethylamino)borane

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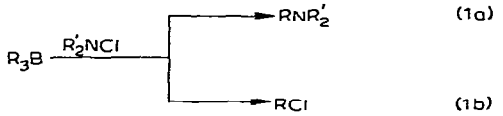
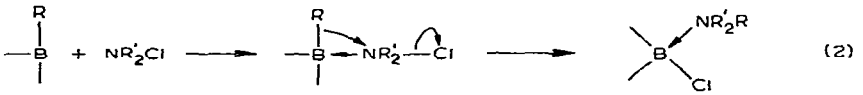
Trialkylboranes have been reported to show a dichotomy of behaviour in their reactions with *N*-chloroamines. In aqueous alkaline tetrahydrofuran, chloramine itself reacts to give the appropriate primary alkylamine in about 60% yield based on organoborane (eqn. 1a, R′=H)[1], whereas *N*-chlorodiethylamine or *N*-chloropiperidine under the same conditions gives the alkyl chloride in 30–50% yield [eqn. 1b, R′=Et or $R'_2=(CH_2)_5$][2].



(1a)

(1b)

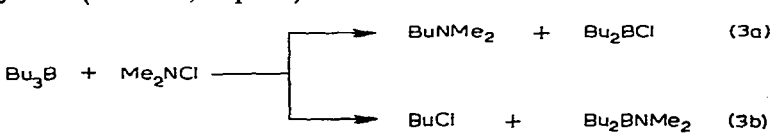
There is stereochemical evidence that reaction (1a) involves a polar 1,2-rearrangement (eqn. 2)[1].



(2)

Our recent demonstration that dimethylamino radicals will bring about bimolecular homolytic aminodealkylation at a boron centre[3], suggested that reaction (1b) might proceed by a radical chain mechanism. We have therefore investigated the reaction of *N*-chlorodimethylamine with tributylborane and with dibutyl(dimethylamino)borane. The reactants in chlorobenzene, in the absence or presence of galvinoxyl as a potential free radical scavenger, were mixed at −15° then kept at 35°. The course of each reaction was followed by NMR spectroscopy, and the products were isolated and characterised by comparison with authentic samples. The preparative reactions were carried out in isopentane solvent. The results are summarised in Table 1.

The results show that tributylborane reacts with 1 molar equivalent of *N*-chlorodimethylamine by concurrent polar (eqn. 2, R=Bu, R′=Me) and free radical processes to give butyldimethylamine and dibutylchloroborane (eqn. 3a) and butyl chloride and dibutyl(dimethylamino)borane (eqn. 3b) respectively, in approximately equal yields (Table 1, expt. 1).



(3a)

(3b)

TABLE 1

PRODUCTS OF THE REACTION OF Bu_3B AND OF Bu_2BNMe_2 WITH Me_2NCl

Expt.	Reactants (mol. equiv.)			Time (h)	Products (mol. equiv.)		
	Bu_3B	Me_2NCl	Galvinoxyl		BuCl	$Bu_nB(NMe_2)_{3-n}$	Bu_2BCl $NBuMe_2$
1	1	1	0	0.17	0.50	0.48[a]	0.5
2	1	1	0.02	0.17	0	0	1.0
3	1	2	0	0.17	0.90	[b]	0.55
				24	1.42	1.32[c]	[d]
4	1	2	0.01	24	0	0	[d]
5	1	3	0	0.17	0.91	[b]	0.53
				24	2.36	2.32[c]	[d]
6	1	3	0.01	48	0	0	[d]
	Bu_2BNMe_2	Me_2NCl	Galvinoxyl		BuCl	$Bu_nB(NMe_2)_{3-n}$	Bu_nBCl_{3-n} $NBuMe_2$[e]
7	1	1	0	24	0.96	0.91[e,f]	0
8	1	1	0.01	7	0	0	0
				36[g]	0.94	0.90[e,f]	0
9	1	2	0	7	0.99	0.97[e]	0
				24	1.82	1.72[e,h]	0

[a] $n=2$. [b] The NMR spectrum of the products was complex, indicating that side reactions were occurring, for example[4], $Me_2NBu + Me_2NCl \rightarrow Me_2N^+(Bu)NMe_2Cl^-$, and because of this quantitative determination was not possible. [c] $n=0-2$. [d] Butyldimethylamine was probably present, but because of its variable state of complexation, no yield could be determined. [e] $n=0-1$. [f] Predominantly butylbis(dimethylamino)-borane. [g] The colour of the galvinoxyl had faded before reaction took place. [h] Predominantly tris-(dimethylamino)borane.

The homolytic reaction is a long chain which can be inhibited by a trace of galvinoxyl (expts. 2, 4, and 6) so that the polar reaction can proceed in isolation, when the products of reaction (3a) are formed in essentially quantitative yield (expt. 2). The aminoborane will then not react further by the polar process, as shown by the absence of any reaction during 7 hours in the presence of galvinoxyl (expt. 8).

The homolytic reaction involves the propagation steps shown in eqns. (4) and (5).

$$Me_2N\cdot + BBu_3 \longrightarrow Me_2NBBu_2 + Bu\cdot \quad (4)$$

$$Bu\cdot + ClNMe_2 \longrightarrow BuCl + \cdot NMe_2 \quad (5)$$

Reaction (4) is rapid and has been studied in isolation by the irradiation by ultraviolet light of a mixture of tetramethyltetrazene and tributylborane in an ESR cavity, when the spectrum of the butyl radical can be observed[3]. Reaction (5) would be exothermic by about 18 kcal/mole, and would also be expected to be fast; a similar step is involved in the addition of certain *N*-halo compounds to olefins. (For a recent review see ref. 5.)

Subsequent aminodealkylation of the dibutyl(dimethylamino)borane then takes place relatively slowly by a similar homolytic mechanism (expt. 7) to give

successively butylbis(dimethylamino)borane (expts. 7 and 8) and the tris(dimethylamino)borane (expt. 9).

Reactions of this type, under conditions of inhibition, may be useful for converting olefins R(−H), via hydroboration, into the corresponding tertiary amines, RNR'_2, and the dialkylchloroboranes, R_2BCl, which can be used *in situ* for preparing further organoboron compounds. The homolytic process is unlikely to be used as a route to the alkyl chlorides, RCl, because the concurrent polar reaction cannot be suppressed, and reactions of *N*-haloamides, which appear to have relatively little polar component[6], will probably be preferred.

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