Reactions between Alkylaminobis(trifluoromethyl)phosphines and Boron Trihalides

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The reaction between alkylaminobis(trifluoromethyl)phosphines, $RNH{\cdot}P(CF_3)_2$, and boron trihalides is complex and the products depend on the reaction conditions and on the nature of both the alkyl group and the boron trihalide. At low temperatures 1 : 1 adducts are formed but at room temperature the predominant reaction is cleavage of the N–P bond to give halogenobis(trifluoromethyl)phosphines, $(CF_3)_2PX$, and alkylaminoboron–halogen compounds:

At −78°: $RNH{\cdot}P(CF_3)_2 + BX_3 = RNH{\cdot}P(CF_3)_2,BX_3$

At 25°: $RNH{\cdot}P(CF_3)_2 + BX_3 = (CF_3)_2PX + RNH{\cdot}BX_2$

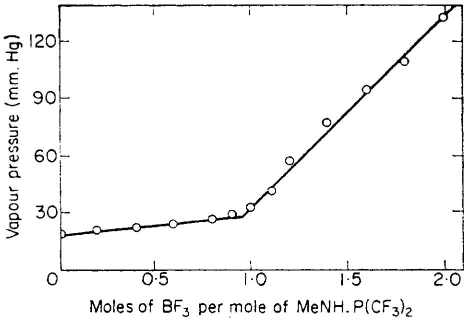
where R = Bu^t and X = F or Cl. When R = Me or Et the aminoboron product of the second reaction disproportionates into a boron trihalide adduct and the corresponding borazine:

$$2RNH{\cdot}BX_2 = RNH_2,BX_3 + \tfrac{1}{3}(RNBX)_3$$

A second reaction sequence results in elimination of hydrogen chloride and the formation of the new alkylbis(trifluoromethyl)phosphinylaminoboron dichlorides $(CF_3)_2PN(R)BCl_2$ where R = Me or Bu^t. These compounds are unstable liquids and have been characterised by analysis, molecular weight, and infrared spectra, and by proton, boron-11, and phosphorus-31 n.m.r. spectra. The methyl compound is dimeric and the t-butyl compound monomeric, and possible structures are discussed.

THE steric and electronic nature of substituents on nitrogen and boron affect both the rate and the extent of dimerisation of aminoboron dihalides of the type R_2NBX_2 (R = alkyl or H, X = halogen).[1-3] Electronegative substituents on nitrogen (R = CF_3) accelerate the dimerisation to such an extent that the precursor adducts R_2NH,BX_3 and the monomeric species R_2NBX_2 are not observed or have only a transient existence.[4] Accordingly the reaction of boron trihalides with alkylaminobis(trifluoromethyl)phosphines, $RNH{\cdot}P(CF_3)_2$, has been studied in the expectation that the resulting aminoboron dihalides and the intermediate adducts would be stable. Compounds of the type $RNH{\cdot}P(CF_3)_2$ have previously been reported for R = H, Me, and Ph,[5] and the new homologues with R = Et and Bu^t have now also been prepared in order to investigate steric factors in the reactions being studied.

Preliminary vapour-pressure studies at −78° (see Figure) indicated that 1 : 1 adducts of the alkylaminobis(trifluoromethyl)phosphines (R = Me, Et, Bu^t, and Ph with boron trifluoride and R = Me, Et, and Bu^t for boron trichloride) exist as colourless liquids. The adducts decomposed above −50° and physical data for them were not obtained; for this reason the site of coordination (N or P) was not established with certainty though indications from the subsequent chemical reactions will be discussed shortly.



At room temperature the predominant reaction of boron trihalides with alkylaminobis(trifluoromethyl)phosphines was one involving cleavage (1) of the P–N bond. Yields of $(CF_3)_2PX$ as compared with those expected from equation (1) ranged from nearly 100%

$$RNH{\cdot}P(CF_3)_2 + BX_3 = (CF_3)_2PX + [RNH{\cdot}BX_2] \quad (1)$$

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[1] O. C. Musgrave, *J. Chem. Soc.*, 1956, 4305.

[2] A. J. Banister, N. N. Greenwood, B. P. Straughan, and J. Walker, *J. Chem. Soc.*, 1964, 995.

[3] N. N. Greenwood, K. A. Hooton, and J. Walker, *J. Chem. Soc.* (*A*), 1966, 21.

[4] N. N. Greenwood and K. A. Hooton, *J. Chem. Soc.* (*A*), 1966, 751.

[5] G. S. Harris, *J. Chem. Soc.*, 1958, 512.

when X = F to 50% when R = Me and X = Cl. The only alkylaminoboron dihalide isolated was $Bu^tNH{\cdot}BF_2$ as disproportionation (2) of the lower homologues readily

$$2RNH{\cdot}BX_2 = RNH_2,BX_3 + \tfrac{1}{3}(RNBX)_3 \qquad (2)$$

occurs.[3] It is significant that the yield of RNH_2,BCl_3 was greater than expected from the simple disproportionation and this is discussed later.

When X = Cl a concurrent reaction (3) occurred with elimination of hydrogen chloride to give the desired

$$RNH{\cdot}P(CF_3)_2,BCl_3 = HCl + (CF_3)_2PN(R)BCl_2 \qquad (3)$$

alkylbis(trifluoromethyl)phosphinylaminoboron dihalides in small yield. Methylbis(trifluoromethyl)phosphinylaminoboron dichloride was isolated as a colourless volatile liquid soluble without decomposition in most non-polar organic solvents. Slow decomposition (4) (rapid

$$(CF_3)_2PN(Me)BCl_2 = (CF_3)_2PCl + \tfrac{1}{3}(MeNBCl)_3 \qquad (4)$$

if the compound was heated) to $(CF_3)_2PCl$ and the substituted borazine $(MeNBCl)_3$ occurred even *in vacuo*. Molecular-weight determinations and n.m.r. spectra established that the compound was a dimer; it is thus one of the very few examples of a dimeric substituted aminoboron dihalide which is not a solid at room temperature.

The corresponding t-butyl compound is considered to be monomeric. It was not possible to isolate an analytically pure sample owing to extensive decomposition and evidence for its existence as a monomer rests primarily on the ^{11}B n.m.r. spectrum, the liquid isolated giving a broad resonance at 31·5 p.p.m. down-field from external trimethyl borate. This value is lower than that for boron trichloride itself and for most trico-ordinate boron–chlorine compounds,[6] but it is in the position expected for a trico-ordinate boron compound containing a strongly deshielding group such as $(CF_3)_2P$. By contrast, dimeric aminoboron dichlorides and trico-ordinate boron–chlorine compounds usually show ^{11}B resonance near +7·0 and −15 p.p.m., respectively.

Another species, identified in the mass spectra of the volatile products from the reaction of boron trichloride with methylaminobis(trifluoromethyl)phosphine, was $MeN[P(CF_3)_2]_2$. This has recently been prepared by the elimination of hydrogen chloride from $(CF_3)_2PCl$ and $MeNH{\cdot}P(CF_3)_2$;[7] it is probably formed in reaction (5).

$$(CF_3)_2PCl + MeNH{\cdot}P(CF_3)_2 + MeNH_2,BCl_3 = MeN[P(CF_3)_2]_2 + MeNH_3^+BCl_4^- \qquad (5)$$

Hydrogen chloride was not detected in any of the systems investigated and examination of the solid products from the reactions revealed the presence of the ionic complexes $RNH_3^+BCl_4^-$. It is likely that the nascent hydrogen halide is removed as in reactions (6) and (7). Reaction (6) explains why the yield of RNH_2,BCl_3 was greater than expected from equation (1).

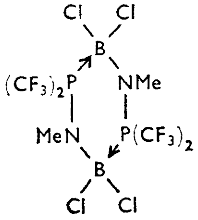
$$RNH{\cdot}BCl_2 + HCl = RNH_2,BCl_3 \qquad (6)$$

$$RNH_2,BCl_3 + HCl = RNH_3^+BCl_4^- \qquad (7)$$

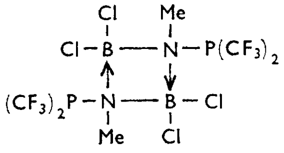
Analogous alkylbis(trifluoromethyl)phosphinylaminoboron difluorides were not found, presumably owing to the difficulty in eliminating hydrogen fluoride.

DISCUSSION

The alkylbis(trifluoromethyl)phosphinylaminoboron dihalides described above are the first metal or metalloidal derivatives of aminobis(trifluoromethyl)phosphines to be reported. Little is known of the physical and chemical properties of the aminobis(trifluoromethyl)phosphines themselves. It is significant that the methyl compound $(CF_3)_2PN(Me)BCl_2$ is dimeric as this reinforces the view that strongly electronegative substituents on nitrogen favour rapid dimerisation of aminoboron dihalides.[4] Molecular models show that the t-butyl compound cannot dimerise because of considerable steric interference from the CF_3 groups. Presumably the instability of the t-butyl, as compared with the methyl, derivative reflects the lack of association in this molecule. Two structures, (I) and (II) can be considered for the methyl compound. Structure (II) is strongly suggested by the ^{11}B and ^{31}P n.m.r. spectra since neither resonance showed any indication of ^{11}B–^{31}P spin–spin coupling (J_{B-P} is 64 c./sec. in H_3B,PMe_3)[8] while the ^{11}B resonance is broad owing to quadrupole relaxation by nitrogen. Further, the P–N stretching frequency at 809 cm.$^{-1}$ in $MeNH{\cdot}P(CF_3)_2$[9] is shifted to lower frequencies (775 cm.$^{-1}$) as expected with decreased P–N π bonding, whereas in the monomeric t-butyl analogue it is essentially unaltered. Considerable electron delocalisation with consequent slight shifts to higher frequencies would be expected for structure (I).



(I)



(II)

Because the 1 : 1 adducts $RNH{\cdot}P(CF_3)_2,BX_3$ were unstable there is insufficient evidence to decide with certainty whether the boron trihalide is co-ordinated to the phosphorus or nitrogen. However the subsequent reaction patterns of these adducts and their derivatives together with the fact that ^{11}B–^{31}P spin–spin coupling was not observed in the n.m.r. spectra of

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[6] N. N. Greenwood and J. Walker, unpublished observations.

[7] A. B. Burg and J. Heners, *J. Amer. Chem. Soc.*, 1965, **87**, 3092.

[8] H. Nöth and H. Vahrenkamp, *Chem. Ber.*, 1966, **99**, 1049.

[9] N. N. Greenwood, B. H. Robinson, and B. P. Straughan, following Paper.

$Bu^tNH{\cdot}P(CF_3)_2,BF_3$ or the dihalides suggest *N*-co-ordination. This is at first surprising as previously reported boron derivatives of alkyl P–N compounds are known to be *P*-co-ordinated.[10,11] Further it has been suggested that the π component of the P–N bond which involves the nitrogen lone pair will be of greater importance in perfluorophosphines.[12] On the other hand the availability of the phosphorus lone pair when $R = CF_3$ will be considerably reduced compared with that when R is an electropositive group such as CH_3, and this outweighs any increase in the π component;[9] that is, the $(CF_3)_2P$ group is an acceptor of electron density rather than a donor.

The donor properties of the nitrogen in these trifluoromethyl compounds and the high energy of formation of amine–boron trihalide adducts is undoubtedly the reason for the low stability and the ready cleavage of the P–N bond. Cleavage by boron trihalides in certain alkyl P–N and Si–N compounds has been noted,[11,13,14] but cleavage was not so easy as with the trifluoromethyl compounds, nor were aminophosphine–boron trihalide adducts detected. The analogous $RNH{\cdot}P(CH_3)_2$ compounds are unknown except for $R = Bu^t$.

It is interesting that Burg and Heners[7] found that boron trihalides would not react with $NH[P(CF_3)_2]_2$ or with $N[P(CF_3)_2]_3$ up to 100°. This can be attributed to the larger π component of the P–N bond in these two molecules. Also the absence of any redistribution by fluorine, common in reactions involving CF_3 groups and in the reaction of boron trihalides with bis(trifluoromethyl)amines,[4] is noteworthy.

EXPERIMENTAL

All manipulations and preparations were carried out in conventional vacuum apparatus with dry, oxygen-free materials.

Boron trifluoride and trichloride were distilled before use. The alkylaminobis(trifluoromethyl)phosphines were prepared by Harris's method[5] from iodobis(trifluoromethyl)phosphine and the appropriate amine and were purified by repeated trap-to-trap distillation. *Ethylaminobis(trifluoromethyl)phosphine* (Found: N, 6·9%; *M*, 213. $C_4H_6F_6NP$ requires N, 6·55%; *M*, 213) and *t-butylaminobis(trifluoromethyl)phosphine*, a colourless liquid (Found: P, 13·0; N, 5·7%; *M*, 238. $C_6H_{10}F_6NP$ requires P, 13·2; N, 5·8%; *M*, 241) are new; their n.m.r. and infrared spectra are discussed elsewhere.[9]

Adducts of Boron Trifluoride and Alkylaminobis(trifluoromethyl)phosphines at Low Temperature.—Boron trifluoride (0·1 mmole) was condensed on the alkylaminobis(trifluoromethyl)phosphine (0·9 mmole) contained in a tube connected to a manometer. The mixture was allowed to come to equilibrium at −78° (−50° for the t-butyl derivative) and the vapour pressure of the resulting colourless liquid recorded. This procedure was repeated until approximately 3 mmoles of boron trifluoride had been added. The resulting vapour pressure–composition graph showed a sharp break at 1 : 1 boron trifluoride–aminophosphine for the methyl, ethyl, phenyl, and t-butyl derivatives (see Figure for typical results) with no evidence of higher stoicheiometries. The volatile materials were removed and shown to contain excess of boron trifluoride only.

Adducts of Boron Trichloride and Alkylaminobis(trifluoromethyl)phosphines at Low Temperatures.—A known amount of boron trichloride (*ca.* 3 mmoles) was placed in a bulb (capacity 144·5 ml.) connected to a manometer and the initial pressure recorded. Aliquot portions from this bulb were condensed on the alkylaminobis(trifluoromethyl)phosphine ($R = Me$, Et, and Bu^t) (1·0 mmole) the mixture brought to −78°, excess of boron trichloride returned to the bulb, and the final pressure recorded. A plot of pressure against number of mmoles of boron trichloride added gave a discontinuity compatible with the formation of a 1 : 1 adduct in each case.

Reaction of Boron Trifluoride with Methylaminobis(trifluoromethyl)phosphine.—Boron trifluoride (0·167 g., 2·45 mmoles) and methylaminobis(trifluoromethyl)phosphine (0·49 g., 2·45 mmoles) were condensed into a reaction vessel and the mixture warmed slowly. At −30° a vigorous reaction occurred with formation of a white solid. The gaseous products and volatile liquids were removed and fractionated to give mainly fluorobis(trifluoromethyl)phosphine (0·44 g., 2·36 mmoles) [Found: *M*(gas phase), 189. Calc. for C_2F_7P: *M*, 189]. The main infrared bands were ν(C–F): 1220, 1178, 1115; ν(P–F): 856; and ν(CF_3 deformation): 745 cm.$^{-1}$.

A small quantity (10 mg.) of an unstable colourless liquid, b. p. 80°, was obtained but attempts to identify it by mass spectrometry failed. However, as 1 mmole decomposed to give 1 mmole of $(CF_3)_2PF$ it may have been the 1 : 1 adduct. Another fraction, an oil with bands at 710 and 720 cm.$^{-1}$, was probably the borazine.

The residual white powder was methylamine–boron trifluoride (95 mg., 0·95 mmole) (Found: C, 12·2; H, 6·0. Calc. for CH_5BF_3N: C, 12·1; H, 5·55%). The infrared spectrum was identical with that of an authentic sample as was the 10-line proton n.m.r. spectrum, $\delta = 6{\cdot}81$ p.p.m. (down-field from tetramethylsilane).[3]

Reaction of Boron Trichloride with Methylaminobis(trifluoromethyl)phosphine.—(*a*) Boron trichloride (0·7 g., 6·03 mmoles) was condensed on methylaminobis(trifluoromethyl)phosphine (1·2 g., 6·03 mmoles) and the mixture allowed to warm slowly from −78°. At *ca.* −50° a vigorous exothermic reaction occurred with the formation of a white solid. The volatile materials were collected and crudely fractionated at 0°; mass spectrography of a representative sample of the fraction of b. p. <0° showed that the predominant species was chlorobis(trifluoromethyl)phosphine, *m*/*e* 204 (^{35}Cl), 206 (^{37}Cl). Other compounds identified [*m*/*e* and the relative intensity of parent peak with respect to $(CF_3)_2P^{35}Cl$ as 100%] were: $(CF_3)_3P$, 238(3); $(CF_3)_2PH$, 170(5); and $MeN[(P(CF_3)_2]_2$, 369(10). Hydrogen chloride was not detected.

Fractionation of the total sample of volatile materials through traps at 0, −20, −60, −78, and −196° gave: (1) chlorobis(trifluoromethyl)phosphine (0·635 g., 3·1 mmoles) [Found: *M*(gas phase), 205. Calc. for

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[10] C. E. Nordman, *Acta Cryst.*, 1960, **13**, 535.

[11] H. Nöth and H. J. Vetter, *Chem. Ber.*, 1963, **96**, 1298.

[12] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872; A. B. Burg and G. Brendel, *J. Amer. Chem. Soc.*, 1958, **80**, 3198.

[13] R. R. Holmes and R. P. Wagner, *J. Amer. Chem. Soc.*, 1962, **84**, 359.

[14] E. W. Abel, D. A. Armitage, R. P. Bush, and G. R. Willey, *J. Chem. Soc.*, 1965, 62.

$(CF_3)_2PCl$: *M*, 205·5], principal bands in the infrared spectrum ν(C–F): 1214, 1166, 1124; ν(CF_3 deformation): 750(PQR) cm.$^{-1}$ (cf. ref. 15), and (2) *methylbis(trifluoromethyl)phosphinylaminoboron dichloride* (0·53 g., 1·9 mmoles) as a colourless volatile liquid, b. p. *ca.* 90° [Found: B, 4·1; Cl, 24·9; N, 5·6; P, 10·8%; *M*(gas phase), 570. $C_3H_3BCl_2F_6NP$ requires B, 3·9; Cl, 25·35; N, 5·0; P, 11·1%; *M*(dimer), 560]. The principal bands in the infrared spectrum (cm.$^{-1}$) with some tentative assignments were: 2980m (νC–H); 1510m; 1465s (νCH_3 deformation); 1280m; [1220vs, 1180vs, 1142vs, 1083m (νC–F)]; 960m (ν asym. B–Cl); 936m (ν sym. B–Cl); 775m (νP–N); 752s (νCF_3 deformation); and 723w. ^{1}H n.m.r.: $\delta = 3·05$ p.p.m. (down-field from tetramethylsilane) singlet; ^{11}B n.m.r.: $\delta = 20$ p.p.m. (down-field from trimethyl borate), singlet, weakened and very broad; ^{31}P n.m.r.: $\delta = 62$ p.p.m. (up-field from P_4O_6) septet, $J(19_F–31_P) = 90$ c./sec.

A sample of methylbis(trifluoromethyl)phosphinylaminoboron dichloride (0·12 g., 0·43 mmole) was heated to 50°. The products were $(CF_3)_2PCl$ (0·086 g., 0·42 mmole) and an oil (0·01 g.) which had an infrared spectrum identical with that of an authentic sample of the substituted borazine $(MeNBCl)_3$.

The residual white solid (0·4 g.) from the reaction of boron trichloride with methylaminobis(trifluoromethyl)phosphine contained no fluorine. Recrystallisation of this solid from dichloromethane gave methylamine–boron trichloride, 0·28 g., m. p. 128° (decomp.) (lit.,[16] 125—127°), and methylammonium tetrachloroborate, 0·11 g., m. p. 149° (lit.,[17] 150—152°).

(*b*) Reaction (*a*) was carried out in the presence of mercury or with excess of boron trichloride but there was no significant change in products or relative yields. In the presence of triethylamine a higher yield of $MeN[P(CF_3)_2]_2$ was obtained and different solid boron compounds, but smaller yields of $(CF_3)_2PN(Me)BCl_2$.

Reaction between Boron Trifluoride and t-Butylaminobis(trifluoromethyl)phosphine.—(*a*) Boron trifluoride (0·27 g., 3·94 mmoles) was condensed on a sample of t-butylaminobis(trifluoromethyl)phosphine (0·95 g., 3·94 mmoles) and the mixture brought to room temperature. After an induction period of *ca.* 3 min., during which a homogeneous liquid was present, a white solid precipitated. The volatile products were removed and fractionated to give: (1) fluorobis(trifluoromethyl)phosphine (0·7 g., 3·75 mmoles) [Found: *M*, 187. Calc. for $(CF_3)_2PF$: *M*, 188]; (2) an unstable volatile liquid (0·03 g.) which decomposed on standing or distillation *in vacuo* to give $(CF_3)_2PF$ and $Bu^tNH{\cdot}BF_2$ (m. p. 140°, lit.,[3] 140—141°; identical infrared spectrum with an authentic sample) and it is therefore considered to be t-butylbis(trifluoromethyl)phosphinylamine–boron trifluoride. The infrared spectrum was compatible with this formulation, *viz.*, 3280 cm.$^{-1}$ (νN–H), and a broad band with some structure 1250—950 cm.$^{-1}$ (νC–F and νB–F), 842 cm.$^{-1}$ (νP–N).

The residual white solid (0·2 g.) from the above reaction was t-butylamine–boron trifluoride, m. p. 129° (lit.,[3] 129—131°); ^{11}B n.m.r.: $\delta = 18·1$ p.p.m. (up-field from trimethylborate), $J_{B-F} = 15·0$ c./sec. A small quantity of an oil was also found which probably contained the borazine.

(*b*) t-Butylaminobis(trifluoromethyl)phosphine and boron trifluoride (slight excess) in dichloromethane were sealed in a heavy-walled n.m.r. tube and the reaction at room temperature followed by ^{11}B n.m.r. The initial resonance due to BF_3 (+8·6 p.p.m. from trimethyl borate) rapidly decreased in intensity with a corresponding increase in a new broad signal at 13·0 p.p.m. The latter can reasonably be ascribed to t-butylbis(trifluoromethyl)phosphinylamine–boron trifluoride. However after a few minutes an additional peak at 18·1 p.p.m. due to Bu^tNH_2,BF_3 appeared while the signal at 13·0 p.p.m. decreased in intensity.

Reaction between t-Butylaminobis(trifluoromethyl)phosphine and Boron Trichloride.—Boron trichloride (0·295 g., 2·49 mmoles) was condensed on t-butylaminobis(trifluoromethyl)phosphine (0·60 g., 2·49 mmoles) in a reaction bulb and the mixture brought to room temperature. A mild reaction occurred at about 0° to give a colourless liquid and white solid. The volatile materials were removed and fractionated to give (1) chlorobis(trifluoromethyl)phosphine (0·30 g., 1·5 mmoles) [Found: *M*, 204. Calc. for $(CF_3)_2PCl$: *M*, 205·5], and (2) *t-butylbis(trifluoromethyl)phosphinylaminoboron dichloride* (0·25 g., 0·79 mmole) as an unstable colourless volatile liquid, b. p. 60° (Found: B, 2·4; N, 4·9; Cl, 21·4%; *M*, 310. $C_6H_9BCl_2F_6NP$ requires B, 3·35; N, 4·7; Cl, 22·05%; *M*, 322). The main infrared bands were at 2910 (νC–H); 1400, 1365 (ν Bu^t deformation); 1260; [1214, 1178, 1140, 1085 (νC–F)]; 998; 956 (νB–Cl); 930 (νB–Cl); 880; 835 (νP–N); 810; 750 cm.$^{-1}$ (νCF_3 deformation). ^{1}H n.m.r.: $\delta = 5·4$ p.p.m. (down-field from tetramethylsilane); ^{11}B n.m.r.: $\delta = 31·5$ p.p.m. (down-field from trimethyl borate). Distillation of a sample (0·09 g., 0·28 mmole) of this liquid *in vacuo* gave 0·062 g. (0·3 mmole) of $(CF_3)_2PCl$ and 0·01 g. of an oil. Similar decomposition occurred rapidly on standing even *in vacuo.*

The residual solid (0·25 g.) from the initial reaction was recrystallised from dichloromethane to yield t-butylamine–boron trichloride (0·17 g.), m. p. 106° (lit.,[16] 110°), and t-butylammonium tetrachloroborate (0·06 g.), m. p. 165° (lit.,[17] 162—167°). No hydrogen chloride was detected in the mass spectra of the volatile materials from the initial reaction.

Physical Measurements.—The ^{1}H and ^{19}F n.m.r. spectra at 60 Mc./sec. and the ^{11}B and ^{31}P n.m.r. spectra at 20 Mc./sec. were recorded on an A.E.I. RS2 spectrometer; low-temperature measurements were carried out with a nitrogen-cooled probe. Mass spectra were measured on an A.E.I. MS9 or MS2 mass spectrometer.

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