90. *Reactions of Halogenobistrifluoromethylphosphines with Amines and Ammonia; and their Behaviour with Phosphine and Hydrogen Sulphide.*[1]

By G. S. HARRIS.

An investigation of the reactions of chlorobistrifluoromethylphosphine with ammonia, methylamine, dimethylamine, and aniline has led to the isolation of four new phosphorus–nitrogen compounds, $(CF_3)_2P \cdot NH_2$, $(CF_3)_2P \cdot NHMe$, $(CF_3)_2P \cdot NMe_2$, and $(CF_3)_2P \cdot NHPh$. The properties and reactions of these compounds have been studied and their infrared spectra recorded.

Halogenobistrifluoromethylphosphines with phosphine and hydrogen sulphide did not give rise to any new compounds.

INTERACTION of phosphorus and trifluoroiodomethane at 200—220° yields tristrifluoromethylphosphine, iodobistrifluoromethylphosphine, and di-iodotrifluoromethylphosphine, together with phosphorus iodides.[2] Interest in the iodotrifluoromethylphosphines has, till now, been confined to determination of their simple physical properties and their use in the preparation of the series of compounds in which the iodine atoms are replaced by other halogens or pseudo-halogens;[2] also, a detailed study of their hydrolysis has been made in connection with the preparation of trifluoromethylphosphorus oxy-acids.[3,4] Recently, Mahler and Burg[5] have used di-iodotrifluoromethylphosphine as starting material for the preparation of the compound $(CF_3 \cdot P)_4$. Comparison of the properties and

[1] Preliminary publication, Harris, *Proc. Chem. Soc.*, 1957, 118.
[2] Bennett, Eméleus, and Haszeldine, *J.*, 1953, 1565.
[3] *Idem, J.*, 1954, 3598.
[4] *Idem, J.*, 1954, 3896.
[5] Mahler and Burg, *J. Amer. Chem. Soc.*, 1957, **79**, 251.

reactions of these halogenotrifluoromethylphosphines with those of other organohalogeno-phosphines and simple phosphorus trihalides would seem to be a useful study and the work described in this paper represents the results of the first stages of such an investigation.

Numerous products have been obtained by reaction of halogenophosphines with amines;[6] but frequently they are not those to be expected if the interaction simply involved elimination of hydrogen halide. Iminophosphines are often formed and usually the reactions result in a mixture of products. Reaction of ammonia with halogeno-phosphines does not appear to have been reported and no aminophosphines of the type $R_2P \cdot NH_2$ have been described. Phosphorus trihalides, on the other hand, are said to react with liquid ammonia to yield triaminophosphine which loses ammonia on warming to 0° with the formation of condensed phosphorus–nitrogen products.[7]

Dihalogenophosphines and phosphine have been shown to interact by the elimination of hydrogen chloride,[8] giving a product of uncertain structure and, similarly, hydrogen sulphide reacts in a complex manner with dihalogenophosphines to give a mixture of phosphorus thio-acids.[9]

It was thought of interest to study analogous reactions involving halogenotrifluoro-methylphosphines to discover the effect of the strongly electronegative trifluoromethyl groups on the course of the reactions and on the nature and stability of the products. This communication describes the results of an investigation of some reactions of chloro- and iodo-bistrifluoromethylphosphine.

Chlorobistrifluoromethylphosphine and ammonia in the vapour phase produce good yields of aminobistrifluoromethylphosphine and ammonium chloride, according to the equation:

$$(CF_3)_2PCl + 2NH_3 \longrightarrow (CF_3)_2P \cdot NH_2 + NH_4Cl \quad \ldots \ldots \quad (I)$$
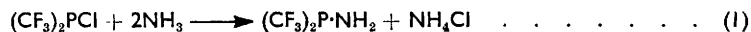
and the same products are obtained in the liquid phase.

It was not possible, by increasing the ratio of halogenophosphine to ammonia in the vapour-phase reaction, to obtain a compound with more than one hydrogen atom of ammonia replaced by the $(CF_3)_2P-$ group. This is not unexpected if the first stage of the reaction [equation (1)] involves the intermediate (A) which loses hydrogen chloride to give $(CF_3)_2P \cdot NH_2$. This molecule does not react with more $(CF_3)_2PCl$ since the strong electron-attracting influence of the trifluoromethyl groups diminishes the availability of electrons on the nitrogen atom for donation to the phosphorus of another chlorobistri-fluoromethylphosphine molecule, so that the intermediate complex (B) is not formed.

It seems likely that the nitrogen lone pair in aminobistrifluoromethylphosphine will take part in π-bonding with the 3d-orbital of the phosphorus atom; that is, a d_π–p_π bond [10] is probably formed which could account for the unusual stability of the molecule. Mahler and Burg [5] have suggested that the stability of the four-membered phosphorus ring in $(CF_3 \cdot P)_4$ is due to a similar type of " extra-bonding."

An alternative but less satisfactory method for preparing aminobistrifluoromethyl-phosphine is by the interaction of tristrifluoromethylphosphine and liquid ammonia at about —70°, when the main reaction taking place is the slow ammonolysis:

$$(CF_3)_3P + NH_3 \longrightarrow (CF_3)_2P \cdot NH_2 + CHF_3$$

[6] See Kosolapoff, " Organophosphorus Compounds," Wiley, New York, 1950, p. 300, for a list of compounds.

[7] Hugot, *Compt. rend.*, 1905, **141**, 1235.

[8] Michaelis, *Ber.*, 1875, **8**, 499.

[9] Kosolapoff, *op. cit.*

[10] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, **332**.

From the reaction mixture a material of low volatility was also isolated, possibly a product of further ammonolysis of the CF_3–P bond in aminobistrifluoromethylphosphine. It is noteworthy that tristrifluoromethylphosphine is not hydrolysed by water, even at 100°.[2]

Aminobistrifluoromethylphosphine is not obtained when iodobistrifluoromethylphosphine and sodamide are allowed to interact: $(CF_3)_2PI + NaNH_2 \not\longrightarrow (CF_3)_2P \cdot NH_2 + NaI$. This contrasts with the behaviour of phosphorus halides, which react readily with sodamide.[11]

The vapour-phase reactions of chlorobistrifluoromethylphosphine with methylamine and dimethylamine follow a similar course to (1) above, yielding methylaminobistrifluoromethylphosphine, $(CF_3)_2P \cdot NHMe$, and dimethylaminobistrifluoromethylphosphine, $(CF_3)_2P \cdot NMe_2$, respectively. Phenylaminobistrifluoromethylphosphine, $(CF_3)_2P \cdot NHPh$, has been obtained by the reaction of aniline and chlorobistrifluoromethylphosphine in the liquid phase.

When iodobistrifluoromethylphosphine and phosphine are mixed in the gas phase (at *ca.* 300 mm. and 20°) crystals of phosphonium iodide and phosphorus di-iodide are slowly deposited and the iodophosphine is reduced to bistrifluoromethylphosphine. The same reaction appears to occur in the liquid phase and no evidence was obtained for the formation of a compound containing a P–P link.

Chlorobistrifluoromethylphosphine and hydrogen sulphide do not react in the vapour (at 15 mm. and 25°) or liquid phase.

Dihalogenotrifluoromethylphosphines react readily with ammonia and amines; the products are being investigated.
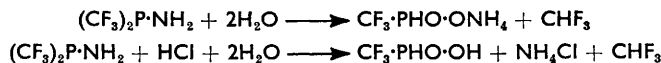
The four aminotrifluoromethylphosphines obtained are colourless liquids. Their melting points ($\pm 0.5°$) were determined directly, and boiling points have been obtained by extrapolation of the vapour pressure–temperature graphs which are straight lines expressible by the general formula $\log_{10} p_{mm.} = AT^{-1} + B$ (see Table).

| Compound	M. p.	B. p.	A	B	Latent heat of vaporn. (cal. mole^{-1})	Trouton's constant
$(CF_3)_2P \cdot NH_2$	−87.6°	67.1°	−1872	8.398	8565	25.20
$(CF_3)_2P \cdot NHMe$	−46.5	73.2	−1890	8.336	8650	24.98
$(CF_3)_2P \cdot NMe_2$	−81.5	83.2	−1698	7.651	7771	21.80
$(CF_3)_2P \cdot NHPh$	+ 1.7	182.1	−2183	7.658	9991	21.96

Aminobistrifluoromethylphosphine is considerably less volatile than tristrifluoromethylphosphine (b. p. 17°) and chlorobistrifluoromethylphosphine (b. p. 21°), and the abnormally high values of Trouton's constant for this compound and methylaminobistrifluoromethylphosphine suggest that association is present in the liquid phase, due to hydrogen bonding.

Aminobistrifluoromethylphosphine is unaffected by the action of heat *in vacuo* (in a Pyrex glass tube) up to 250°, but above this temperature decomposition begins and among the products identified are fluoroform, phosphorus fluorides, nitrogen, hydrogen cyanide (and silicon tetrafluoride).

The aminophosphines described are all unstable to hydrolytic agents and these bring about rupture of the P–N bond as well as one or both of the P–C bonds. Aminobistrifluoromethylphosphine is hydrolysed by water and dilute acid at 20°, liberating 1 mol. of fluoroform:

$$(CF_3)_2P \cdot NH_2 + 2H_2O \longrightarrow CF_3 \cdot PHO \cdot ONH_4 + CHF_3$$

$$(CF_3)_2P \cdot NH_2 + HCl + 2H_2O \longrightarrow CF_3 \cdot PHO \cdot OH + NH_4Cl + CHF_3$$

Alkaline hydrolysis at 20° removes the two trifluoromethyl groups quantitatively as fluoroform and the amino-group as ammonia:

$$(CF_3)_2P \cdot NH_2 + 2NaOH + H_2O \longrightarrow Na_2HPO_3 + NH_3 + 2CHF_3$$
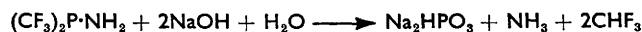
[11] Winter, *J. Amer. Chem. Soc.*, 1904, **26**, 1484.

The other aminophosphines of the series undergo similar alkaline hydrolysis at 80—100°, but their reaction with water at 20° is not quantitative except in the case of phenylaminobistrifluoromethylphosphine which reacts like aminobistrifluoromethylphosphine, giving 1 mol. of fluoroform.

Hydrogen chloride reacts with aminobistrifluoromethylphosphine through attack on the phosphorus–nitrogen bond, to give chlorobistrifluoromethylphosphine and ammonium chloride:

$$(CF_3)_2P \cdot NH_2 + 2HCl \longrightarrow (CF_3)_2PCl + NH_4Cl$$
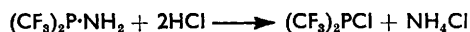
and the reaction of aminobistrifluoromethylphosphine with chlorine also results in breakage of the phosphorus–nitrogen link; but it is more complex and yields ammonium chloride and a slightly volatile liquid which is probably a mixture of the addition compound $(CF_3)_2P \cdot NH_2, Cl_2$ and bistrifluoromethylphosphorus trichloride, $(CF_3)_2PCl_3$; a trace of chlorotrifluoromethane is also produced.

The composition of the molecule $(CF_3)_2P \cdot NH_2$ suggests that the hydrogen atoms attached to nitrogen may be acidic [compare the behaviour of sulphamide which forms a silver salt $(Ag \cdot NH)_2SO_2$]. However, attempts to prepare the salt $(CF_3)_2P \cdot NHM$ (M = Ag, Na) were not successful and the only evidence for acidic character of the hydrogens is that solutions of aminobistrifluoromethylphosphine in pyridine are better electrolytes than the pure solvent $(\kappa_{solv.} = 1 \cdot 07 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$; $\kappa_{soln.} = 5 \cdot 6 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$; $\Lambda_m = 0 \cdot 03$ ohm^{-1} cm.^{2} mole^{-1}) and this might conceivably be due to the presence in the solution of $[(CF_3)_2P \cdot NH^-][C_5H_5 \cdot NH^+]$ ion-pairs. In the same connection it was found that dimethylaminobistrifluoromethylphosphine did not form a quaternary salt with methyl iodide and this seems to indicate the absence of basic character of the nitrogen atom in these compounds.

The infrared absorption spectra of the aminophosphines, $(CF_3)_2P \cdot NH_2$, $(CF_3)_2P \cdot NHMe$, $(CF_3)_2P \cdot NMe_2$, and $(CF_3)_2P \cdot NHPh$, are useful for characterisation (cf. p. 519). The nitrogen–hydrogen stretching vibrations lie in the region 3350—3490 cm.$^{-1}$, and the NH_2 deformation is represented by one band at 1569 cm.$^{-1}$. Carbon–fluorine stretching lies between 1210 and 1100 cm.$^{-1}$ and there are three strong maxima in each case [cf. Bennett, Eméleus, and Haszeldine [2] who report that trifluoromethylphosphorus derivatives of the type $(CF_3)_2PX$ (X = I, CN) have three main maxima in this region]. Each compound has one band in the region 730—750 cm.$^{-1}$ and this is probably a trifluoromethyl deformation frequency.[2,4] The absorption bands due to the N-alkyl and N-aryl groups in these compounds are at the usual frequencies. It is not possible to assign with certainty absorption due to phosphorus–nitrogen stretching in the spectra of these compounds (Corbridge [12] gives 750—680 cm.$^{-1}$ as the region for phosphorus–nitrogen stretching). In the simplest member of the series, aminobistrifluoromethylphosphine, two strong bands appear between the carbon–fluorine stretching absorption (1115 cm.$^{-1}$) and the trifluoromethyl deformation frequency (736 cm.$^{-1}$), whereas in the compounds $(CF_3)_2PX$ (X = Cl, I) only one band is present. The additional maximum in the case of the aminophosphine could possibly be due to phosphorus–nitrogen stretching, moved to a higher frequency on account of partial double bonding, but on the other hand P–NH_2 vibration is also likely to have an absorption band in this region.

EXPERIMENTAL

Since it was undesirable for the compounds to come into contact with moisture or oxygen, extensive use was made of high-vacuum technique and where this was inconvenient the materials were handled in a nitrogen-filled dry-box containing phosphoric oxide. B. p.s were determined from the vapour-pressure data, and m. p.s were found by using a modification of the Stock type of plunger apparatus. The molecular weights of volatile liquids were

[12] Corbridge, *J. Appl. Chem.*, 1956, **6**, 456.

determined by Regnault's method. Carbon, hydrogen, and nitrogen percentages were obtained by microcombustion and trifluoromethyl groups as fluoroform liberated on hydrolysis by dilute sodium hydroxide solution.

Materials.—Good commercial chemicals used were purified and dried. The halogenotrifluoromethylphosphines were prepared by the method of Bennett, Eméleus, and Haszeldine,[2] and standard methods were used for the preparation of the other chemicals.

Reactions of Chlorobistrifluoromethylphosphine with Ammonia and Amines.—With the exception of the reaction of aniline, these were carried out in the vapour phase in a cylindrical glass vessel (capacity *ca.* 700 ml.) which had a cold-finger appendage at each end and a manometer for following pressure changes, and was connected with a general-purpose vacuum-system. The halogenotrifluoromethylphosphine was condensed in one of the cold fingers and the amine in the other, and these traps were then allowed to warm to temperatures at which the respective vapour pressures were equal (usually *ca.* 10 mm.). When the reaction was complete the volatile products were removed to the vacuum-system and fractionated before identification. The solid products were removed mechanically after breaking the reaction vessel. The reaction between aniline and chlorobistrifluoromethylphosphine was carried out in the liquid phase in a sealed tube.

(a) *Reaction with ammonia.* Chlorobistrifluoromethylphosphine (8·93 mmoles) and ammonia (17·86 mmoles) at 5 mm. gave ammonium chloride and a volatile liquid which, after fractional condensation to remove traces of the reactants, gave tensimetrically pure *aminobistrifluoromethylphosphine* (1·59 g., 96%) [Found: C, 14·1; H, 1·7; N, 7·7; CF_3, 71·9 (as fluoroform); NH_2, 8·65% (as ammonia); *M*, 186·1. $C_2F_6H_2NP$ requires C, 13·0; H, 1·1; N, 7·58; CF_3, 73·6; NH_2, 8·65%; *M*, 185·0].

(b) *Reaction with methylamine.* Chlorobistrifluoromethylphosphine (6·12 mmoles) and methylamine (12·24 mmoles) at 10 mm. in the vapour phase gave methylamine hydrochloride and *methylaminobistrifluoromethylphosphine* (1·16 g., 95%) [Found: C, 18·2; H, 1·8; N, 7·1; CF_3, 67·3% (as fluoroform); *M*, 200·5. $C_3F_6H_4NP$ requires C, 18·1; H, 2·0; N, 7·0; CF_3, 69·3%; *M*, 199·1].

(c) *Reaction with dimethylamine.* Chlorobistrifluoromethylphosphine (5·5 mmoles) and dimethylamine (11·0 mmoles) at 10 mm. in the vapour phase gave dimethylamine hydrochloride and *dimethylaminobistrifluoromethylphosphine* (0·82 g., 70%) [Found: C, 22·7; H, 2·6; N, 6·6; CF_3, 61·6% (as fluoroform); *M*, 216·5. $C_4F_6H_6NP$ requires C, 22·6; H, 2·8; N, 6·6; CF_3, 64·8%; *M*, 213·1].

(d) *Reaction with aniline.* Aniline (3·63 mmoles) and chlorobistrifluoromethylphosphine (2·01 mmoles) were condensed into a constricted tube which was sealed and allowed to warm to 0°. A vigorous reaction took place, to form aniline hydrochloride and *phenylaminobistrifluoromethylphosphine* (0·3 g., 65%) [Found: C, 36·6; H, 2·5; N, 5·5; CF_3, 51·5% (as fluoroform). $C_8F_6H_6NP$ requires C, 36·8; H, 2·3; N, 5·4; CF_3, 52·9%]. This compound has a pleasant aromatic odour, unlike that of aniline or the chlorophosphine.

Reaction of Tristrifluoromethylphosphine with Ammonia.—Purified tristrifluoromethylphosphine (5·98 mmoles) and ammonia (5·98 mmoles) were mixed in the vapour phase at 22° and 157 mm. The volume of the mixture was equal to the sum of the volumes of the components and apart from the formation of a small trace of white solid (probably ammonium iodide formed by ammonia reacting with a trace of iodophosphines still present in the tristrifluoromethylphosphine) no apparent change occurred. However, liquefying the vapours (−70°) for 30 min. and re-warming the mixture to room temperature afforded a less volatile liquid and the pressure had decreased. Repetition of this procedure resulted in an increase in the amount of the less volatile liquid. The volatile contents of the reaction vessel were fractionally condensed several times and in addition to ammonia and tristrifluoromethylphosphine the following were separated: fluoroform (1·72 mmoles) (Found: *M*, 69·0. Calc. for CHF_3: *M*, 70·0), aminobistrifluoromethylphosphine (0·54 mmole) (Found: *M*, 173. The infrared spectrum of this material indicated that it contained a trace of ammonia), and an involatile liquid of unknown structure.

Reaction between Iodobistrifluoromethylphosphine and Sodamide.—Iodobistrifluoromethylphosphine (1·42 mmoles) and sodamide (2·7 mmoles) were sealed together in a tube and set aside for 24 hr. at room temperature. Examination of the vapour in the tube showed it to be unchanged iodobistrifluoromethylphosphine (1·34 mmoles, 94·5%) (Found: *M*, 292·5. Calc. for C_2F_6IP: *M*, 296·0).

Reaction of Iodobistrifluoromethylphosphine with Phosphine.—Iodobistrifluoromethylphosphine (3·49 mmoles) was mixed with phosphine (6·98 mmoles) in the vapour phase. In 12 hr. at 20° the pressure fell from 276 mm. to 187 mm., and the wall of the reaction vessel was coated with a reddish-brown deposit (phosphorus) and some large white transparent crystals (phosphonium iodide). Repeated fractional distillation of the volatile contents of the vessel gave unchanged phosphine (0·145 g., 61·4%) (Found: M, 34·5. Calc. for PH_3: M, 34·0), iodobistrifluoromethylphosphine (0·07 g., 6·8%) (Found: M, 285·5), and bistrifluoromethylphosphine (0·43 g., 73%) (Found: C, 13·9; H, 0·7%; M, 168·5. Calc. for C_2F_6HP: C, 14·1; H, 0·59%; M, 170). The identity of this material was confirmed by its infrared spectrum. During the separation of these compounds by fractional condensation an orange-red solid was deposited in the traps and this probably consists mainly of phosphorus di-iodide (Found: I, 87·3. Calc. for P_2I_4: I, 89·1%) formed when phosphine and iodobistrifluoromethylphosphine are present together in the liquid state during the distillation.

Treatment of Chlorobistrifluoromethylphosphine with Hydrogen Sulphide.—Hydrogen sulphide (2·95 mmoles) and chlorobistrifluoromethylphosphine (2·95 mmoles) did not react when mixed in the vapour phase at 20° for 12 hr., or in the liquid phase at −76° for several hours. The mixture was fractionated, giving unchanged hydrogen sulphide (0·096 g., 95%) (Found: M, 37·9. Calc. for H_2S: M, 34·1), and chlorobistrifluoromethylphosphine (0·575 g., 95·3%) (Found: M, 205. Calc. for C_2ClF_6P: M, 204·5) of known infrared spectrum.

Properties of the Aminobistrifluoromethylphosphines.—The aminobistrifluoromethylphosphines are colourless liquids (see Table). They appear to be readily oxidised by air (aminobistrifluoromethylphosphine is spontaneously inflammable), but can be kept unchanged indefinitely (as is indicated by the constancy of vapour pressures and molecular weights) in a sealed Pyrex tube at 0°. There is no reaction with mercury.

Vapour-pressure determination. Except in the case of the involatile phenylaminobistrifluoromethylphosphine, vapour pressures were determined from room temperature down to a temperature at which the vapour pressure of the liquid was *ca.* 1 mm. Pressures were obtained from a wide-bore mercury manometer in a system which incorporated a Pyrex-glass spiral-gauge null-meter. The thermostat bath consisted of a Dewar flask containing a suitable stirred liquid (usually acetone); cooling was achieved by adding small pieces of solid carbon dioxide and the bath was warmed by the addition of suitable quantities of the liquid. Fairly efficient temperature-control was obtained by this procedure and vapour pressures at ascending and descending temperatures were coincident. A pentane thermometer was used for low-temperature measurement. The vapour pressure of phenylaminobistrifluoromethylphosphine was measured in the range 24—145° by means of a mercury isteniscope.

Action of Heat on Aminobistrifluoromethylphosphine.—Known weights of aminobistrifluoromethylphosphine were heated in sealed Carius tubes at 78°, 180°, 218°, 250°, 300°, and 370° severally for 48 hr. From the tubes heated to $\not> 250°$ the compound was recovered almost quantitatively (>90%). After 48 hr. at 300° only 75% of the aminophosphine was recovered, and among the volatile decomposition products (identified by their infrared spectra) were fluoroform, phosphorus fluorides, and silicon tetrafluoride (presumably from attack on the glass by hydrogen fluoride). At 370° aminobistrifluoromethylphosphine was decomposed completely and there was a deposit of carbon. The volatile products contained nitrogen which was removed at a Töpler pump, and the condensable material was resolved into a very volatile and a less volatile portion by fractional condensation. By means of their infrared spectra the former was shown to consist of a mixture of fluoroform, phosphorus fluorides and silicon tetrafluoride, and the latter identified as hydrogen cyanide (Found: M, 28·6. Calc. for HCN: M, 27·0).

Hydrolysis of Aminobistrifluoromethylphosphines.—(1) *Aminobistrifluoromethylphosphine.* (*a*) Water. The aminophosphine (7·39 mmoles) was sealed in a Carius tube with distilled water (7 ml.) and left for 48 hr. at 20°. The volatile products were fractionated, yielding fluoroform (7·41 mmoles) (Found: M, 70·4). The aqueous hydrolysate reduced warm mercuric chloride solution. Freeze-drying of the solution recovered from the Carius tube gave a very hygroscopic white solid which, from its infrared spectrum, appeared to be ammonium trifluoromethylphosphonite, $CF_3 \cdot PHO \cdot ONH_4$, and not the possible alternative, trifluoromethylphosphonamidous acid, $CF_3 \cdot P(NH_2) \cdot OH$.

(*b*) Acid. Aminobistrifluoromethylphosphine (9·76 mmoles) and N-hydrochloric acid (10 ml.) were sealed in a Carius tube and kept for 14 days at 20°. Fractionation of the volatile products

gave fluoroform (9·67 mmoles) (Found: M, 69·9). The ammonium ion content of the hydrolysate was estimated by semi-micro Kjeldahl analysis: [13] the total amount of ammonia liberated was 9·74 mmoles. The solution left in the Carius tube reduced warm aqueous mercuric chloride. After oxidation of this solution by boiling (30%) aqueous hydrogen peroxide, neutralisation with dilute potassium hydroxide solution, then freeze-drying, gave a white solid whose infrared spectrum indicated the presence of potassium trifluoromethylphosphonate, $CF_3 \cdot PO(OK)_2$.

(*c*) *Alkali.* The aminophosphine (1·134 mmoles) and 10% sodium hydroxide solution (10 ml.) were sealed in a Carius tube and left at 20° for 14 days. The volatile products were shaken with N-hydrochloric acid (25 ml.) to dissolve liberated ammonia. The remainder of the volatile hydrolysis product was fractionated and shown to be fluoroform (2·19 mmoles) (Found: M, 69·4). The ammonia produced by hydrolysis was estimated as before (1·067 mmoles). A portion of the original hydrolysate was freeze-dried and sodium phosphite was identified in the solid residue by means of its infrared spectrum.

(2) *Methylaminobistrifluoromethylphosphine.* (*a*) *Water.* The aminophosphine (0·538 mmole) was distilled into a hydrolysis bulb containing distilled water (8 ml.) and the reaction allowed to proceed for 48 hr. at 20°. The bulb was then opened to the vacuum-system and fractionation of the volatile products yielded fluoroform (0·468 mmole) (Found: M, 69·5).

(*b*) *Alkali.* Methylaminobistrifluoromethylphosphine (0·913 mmole), sealed in a Carius tube with 10% sodium hydroxide solution (8 ml.) and left for 24 hr. at room temperature, gave volatile materials which were distilled into a bulb containing N-hydrochloric acid (25 ml.). This was shaken to absorb any amine (NH_2Me) present in the vapour phase, and then the remaining volatile materials was fractionated. This yielded fluoroform (1·88 mmole) (Found: M, 69·6). The solution left in the Carius tube reduced mercuric chloride in the cold.

(3) *Dimethylaminobistrifluoromethylphosphine.* (*a*) *Water.* Dimethylaminobistrifluoromethylphosphine (0·826 mmole) and distilled water (8 ml.) were sealed in a hydrolysis bulb and left at room temperature, but the aminophosphine did not dissolve completely. However, partial hydrolysis had occurred since fractionation of the volatile materials yielded fluoroform (0·123 mmole) (Found: M, 70·0).

(*b*) *Alkali.* The aminophosphine (0·982 mmole) and 10% sodium hydroxide solution (7 ml.) were sealed in a Carius tube: at room temperature two liquid phases were present. Hence the tube was heated at 88—94° for 48 hr. at the end of which no insoluble material remained. The volatile products were shaken in a bulb containing N-hydrochloric acid to remove amine and/or ammonia vapour, then fractionated, yielding fluoroform (1·866 mmoles) (Found: M, 70·2). The aqueous hydrolysate contained a component which reduced mercuric chloride.

(4) *Phenylaminobistrifluoromethylphosphine.* (*a*) *Water.* The aminophosphine (0·128 mmole) and distilled water (3 ml.) were allowed to react in a sealed tube at room temperature for 2 weeks. The compound dissolved in the water and the volatile product of hydrolysis was fluoroform (0·134 mmole) (Found: M, 74·0), isolated after fractionation. The solution left in the tube was acidic and reduced mercuric chloride on warming.

(*b*) *Alkali.* Phenylaminobistrifluoromethylphosphine (0·423 mmole) was hydrolysed by 10% sodium hydroxide solution (5 ml.) in a sealed Carius tube heated to 120° for 48 hr. At the end of this period the alkali contained oily globules (aniline), and fluoroform (0·823 mmole) (Found: M, 70·5) was obtained as the only volatile product of hydrolysis. The solution left in the tube had an odour of aniline and reduced mercuric chloride in the cold.

Reaction of Aminobistrifluoromethylphosphine with Hydrogen Chloride.—Aminobistrifluoromethylphosphine (0·62 mmole) and excess of hydrogen chloride were sealed together in a tube, and at −64° a vigorous reaction occurred, one product of which was ammonium chloride. The volatile contents of the tube were fractionated and, after removal of the excess of hydrogen chloride, chlorobistrifluoromethylphosphine (0·52 mmole) (Found: M, 200) was obtained.

Reaction of Aminobistrifluoromethylphosphine with Chlorine.—Chlorine (10·3 mmoles) and aminobistrifluoromethylphosphine (2·0 mmoles) were allowed to interact in a sealed tube at −78° but no reaction appeared to occur at this temperature and the tube was allowed slowly to warm to 20°. During this, effervescence occurred and a white solid was produced. This was identified as ammonium chloride by its infrared spectrum. The liquid was fractionated

[13] Belcher and Godbert, " Semi-micro Quantitative Organic Analysis," Longmans, Green & Co London, 1954, p. 89.

several times and split into a very volatile fraction, a middle fraction which was mainly chlorine, and a fraction of low volatility. The very volatile fraction was sealed in a tube containing 10% sodium hydroxide solution, shaken for some time, and fractionated, giving only a small amount of very volatile material which, from its infrared spectrum, appeared to be chlorotrifluoromethane. The involatile fraction had an estimated molecular weight of 236 and chlorine analysis gave 24·6% (by precipitation as silver chloride after hydrolysis). The material gave ammonia when boiled with dilute alkali. A white solid (presumably ammonium chloride) was slowly formed in the liquid. From this evidence it is not possible to assign a structure to this substance, but it is probably a mixture of bistrifluoromethylphosphorus trichloride, $(CF_3)_2PCl_3$ (which is formed when chlorobistrifluoromethylphosphine reacts with chlorine), and an addition compound of chlorine and aminobistrifluoromethylphosphine, $[(CF_3)_2P \cdot NH_2, Cl_2]$, which slowly decomposes at room temperature.

Attempted Preparation of a Salt of Aminobistrifluoromethyl Phosphine.—(a) *Silver salt.* Equimolar quantities (0·69 mmole) of silver nitrate and aminobistrifluoromethylphosphine were dissolved in pyridine (1·2 ml.). The solution, originally colourless, became yellow and then orange-brown; no solid could be crystallised and removal of the solvent under vacuum left an involatile viscid liquid whose infrared spectrum indicated the presence of pyridine as well as a $(CF_3)_2P$-component.

(b) *Sodium salt.* Aminobistrifluoromethylphosphine (1·75 mmoles) and sodamide (1·38 mmoles) were allowed to react in a sealed tube at room temperature. Effervescence occurred and in place of the mobile aminophosphine, a gelatinous substance was formed. The volatile products were fractionated, yielding fluoroform (0·69 mmole) (Found: M, 69·1) and unchanged aminobistrifluoromethylphosphine (0·33 mmole) (identified by its infrared spectrum) together with a trace of ammonia. The residue is presumably some kind of phosphorus–nitrogen polymer; its infrared spectrum suggests the presence of trifluoromethyl groups.

Conductance Measurements.—These were made with a small cell (capacity *ca.* 1·5 ml.) with smooth platinum electrodes (cell constant, 0·8233 cm.$^{-1}$). Solutions were prepared by weight and introduced into the cell by distillation in the vacuum-system. Resistances were measured at 25° by the Wheatstone bridge circuit described by Haszeldine and Woolf.[14]

Infrared Spectra.—The spectra were measured on a Perkin-Elmer Model 21 Spectrometer with rock-salt optics. The compounds were studied in the vapour state (in a 100 mm. cell) with the exception of phenylaminobistrifluoromethylphosphine, which was examined as a liquid film. In the following list the figures are in cm.$^{-1}$ and the letters have their usual meaning.

$(CF_3)_2P \cdot NH_2$: 3490s, 3380s, 3100w, 2520w, 2360w, 2260m, 1954w, 1898w, 1856w, 1760w, 1675w, 1569s, 1366m, 1282s, 1207s, 1160s, 1115s, 976s, 888s, 736s, 675m.

$(CF_3)_2P \cdot NHMe$: 3400m, 3430s, 2930w, 2830m, 2260m, 1897w, 1675w, 1566w, 1487m, 1464m, 1440m, 1394s, 1280m, 1206s, 1157s, 1112s, 998w, 807s, 732m.

$(CF_3)_2P \cdot NMe_2$: 3030w, 2980s, 2910s, 2870s, 2810s, 2380w, 2300m, 2250m, 1990w, 1890w, 1687m, 1625w, 1487s, 1467s, 1385m, 1298s, 1200s, 1155s, 1112s, 1069s, 1000s, 880w, 805w, 742m, 690s.

$(CF_3)_2P \cdot NHPh$: 3375m, 3350m, 3045m, 2260w, 1940w, 1845w, 1705w, 1605s, 1503s, 1477m, 1390m, 1380m, 1335w, 1282s, 1238s, 1200s, 1148s, 1103s, 1032m, 1000w, 920s, 793m, 748s, 688s.

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[14] Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544.