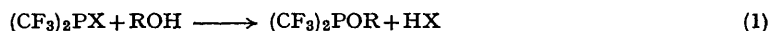


1110. *Some Bistrifluoromethylphosphino-derivatives of Sulphur.*

By R. G. CAVELL and H. J. EMELÉUS.

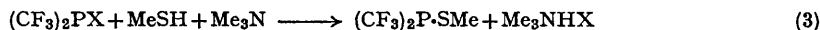
The preparations and properties of bistrifluoromethyl(methylthio)phosphine, bistrifluoromethyl(mercapto)phosphine, and di(bistrifluoromethylphosphino) sulphide are described. All the compounds are derivatives of trivalent phosphorus. Bistrifluoromethyl(methylthio)phosphine did not react with hydrogen halides. The di(phosphino) sulphide reacts slightly with hydrogen bromide to give bistrifluoromethyl(mercapto)phosphine and bistrifluoromethylbromophosphine. The mercaptophosphine formed a salt with trimethylamine, and reacted with mercuric chloride to give bistrifluoromethylchlorophosphine. The mercaptophosphine reacted with bistrifluoromethylchlorophosphine to eliminate hydrogen chloride and form the di(phosphino) sulphide.

ALCOHOLS¹ and amines² react readily with bistrifluoromethylhalogenophosphines to eliminate hydrogen halide (in the latter case as the amine salt) and form the appropriate trifluoromethyl phosphorus ester or amide:



In contrast, ethanethiol did not react with bistrifluoromethylchlorophosphine at room temperature, but, on heating, moderate yields (23%) of bistrifluoromethyl(ethylthio)phosphine were obtained.³ Hydrogen sulphide did not react with the chlorophosphine, and phosphine itself reduced bistrifluoromethylidophosphine to bistrifluoromethylphosphine, $(\text{CF}_3)_2\text{PH}$.²

We have now found that bistrifluoromethyl(methylthio)phosphine can be prepared in nearly quantitative yield from the rapid reaction of bistrifluoromethylhalogenophosphines with methanethiol, using a stoichiometric amount of trimethylamine to take up the hydrogen halide eliminated:



This result suggests that the mercaptolysis of bistrifluoromethylhalogenophosphines, and probably also the alcoholysis, is an equilibrium where the former system favours the reactants and the latter favours the products. Formation of the amine salt thus displaces the equilibrium in the mercaptolysis to yield the (methylthio)phosphine almost quantitatively. That removal of hydrogen halide as the amine salt is not necessary to obtain high yields of phosphorus ester is reasonable since approximate bond energies, such as those given by Cottrell,⁴ indicate a gain in bond energy of about 25 kcal./mole for the reaction of bistrifluoromethylchlorophosphine with alcohols but a small loss in bond energy on reaction of the chlorophosphine with thiols.

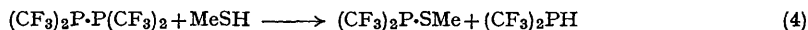
¹ H. J. Emeléus and J. D. Smith, *J.*, 1959, 375.

² G. S. Harris, *J.*, 1958, 512.

³ G. S. Harris, Ph.D. Thesis, Cambridge, 1958.

⁴ T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd edn., Butterworths, London, 1958.

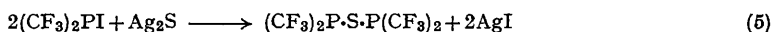
Methanethiol also reacted with tetrakis(trifluoromethyl)diphosphine according to the equation:



but in contrast to the analogous reaction between the diphosphine and methanol, which is quantitative,⁵ the cleavage of the phosphorus–phosphorus bond by methanethiol was not complete even with heating to 100°. The difficulty of separating reactants and products makes this reaction a poor preparative route to bistrifluoromethyl(methylthio)phosphine. Approximate bond-energy⁴ calculations again indicate a much greater gain in bond energy (and thus in facility of reaction, other things being equal) on reaction of the diphosphine with alcohol than with thiol.

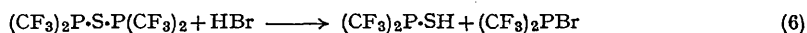
Bistrifluoromethyl(methylthio)phosphine is a clear colourless liquid, boiling at 89°, which has the foul odour typical of the thiophosphines prepared in this study. The heat of vaporization of 8810 cal./mole gave a Trouton constant of 24, indicating little if any association in the liquid. The nuclear magnetic resonance (n.m.r.) data (Table 1) are consistent with the formulation of the compound as a derivative of trivalent phosphorus with the structure $(\text{CF}_3)_2\text{P}\cdot\text{SMe}$, rather than the quinquevalent structural isomer. These data are discussed more fully later. The compound liberates all of the trifluoromethyl groups as fluoroform on alkaline hydrolysis, a property typical of derivatives of trivalent phosphorus which do not have P–P bonds.⁶ Bistrifluoromethyl(methylthio)phosphine did not react with hydrogen chloride or bromide up to 60°, even though the preparative reactions would suggest that the thiophosphine would readily react with hydrogen halides to regenerate halogenophosphine and thiol. It may be, however, that the strong electron-withdrawing power of the trifluoromethyl group reduces the basicity of the thiophosphine so that much more vigorous conditions than those employed would be necessary to induce attack by an acidic reagent. The non-basic character of bistrifluoromethyl(methoxy)phosphine supports this interpretation.⁵

Bistrifluoromethyliodophosphine reacted readily with silver sulphide at room temperature, to form di(bistrifluoromethylphosphino) sulphide:



The di(phosphino) sulphide is a clear, colourless liquid with a foul odour. It was thermally stable up to 150°. It melted at –35° and boiled at 104·7°. The heat of vaporization was 10,080 cal./mole, corresponding to a Trouton constant of 26·6. Alkaline hydrolysis liberated four moles of fluoroform per mole of compound, indicating that the structure contains neither quinquevalent phosphorus nor a phosphorus–phosphorus bond.⁶ The phosphorus-31 n.m.r. spectrum showed only one rather complex absorption at -27 ± 2 p.p.m. relative to phosphoric acid, thus indicating that the two phosphorus atoms are equivalent. Thus, both the chemical and physical evidence favours the sulphide structure, $(\text{CF}_3)_2\text{P}\cdot\text{S}\cdot\text{P}(\text{CF}_3)_2$, rather than the isomeric structure with non-equivalent phosphorus atoms, $(\text{CF}_3)_2\text{P}\cdot\text{PS}(\text{CF}_3)_2$.

Hydrogen bromide reacted with di(bistrifluoromethylphosphino) sulphide to yield bistrifluoromethyl(mercapto)phosphine:



but, in contrast to the quantitative cleavage of the analogous oxide, $(\text{CF}_3)_2\text{P}\cdot\text{O}\cdot\text{P}(\text{CF}_3)_2$, by hydrogen halides,⁵ the reaction with the sulphide was not complete even after prolonged heating at 150°.

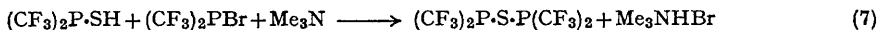
Although hydrogen sulphide alone did not react with bistrifluoromethylchlorophosphine,³ in the presence of trimethylamine immediate reaction occurred between hydrogen sulphide and bistrifluoromethylbromophosphine, forming a 50% yield of bistrifluoromethyl(mercapto)phosphine. The other product was di(bistrifluoromethylphosphino) sulphide,

⁵ J. E. Griffiths and A. B. Burg, *J. Amer. Chem. Soc.*, 1962, **84**, 3442.

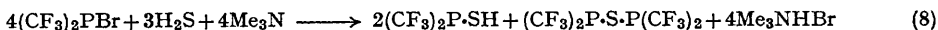
⁶ F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J.*, 1954, 3896.

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presumably formed by subsequent condensation of the mercaptophosphine with bromophosphine in the presence of amine:



The overall reaction is represented by the equation:



The condensation of bistrifluoromethylchlorophosphine and bistrifluoromethyl(mercapto)phosphine to give hydrogen halide and di(bistrifluoromethylphosphino) sulphide was subsequently found to proceed, although not quantitatively, in the absence of amine, thus verifying the suggestion that reaction (7) is responsible for the formation of the di(phosphino) sulphide.

Bistrifluoromethyl(mercapto)phosphine is a clear, colourless liquid boiling at 59.0°. The heat of vaporization of 7340 cal./mole gave a normal Trouton constant of 22.1, indicating little, if any, hydrogen-bonding in the liquid phase. Indeed, the observed boiling points for the series $(\text{CF}_3)_2\text{P}\cdot\text{SR}$ for $\text{R} = \text{H}, \text{Me},$ and Et (115.3°)³ exhibit a linear relationship with the formula weight. A similar relationship exists for the boiling points of the analogous ester series $(\text{CF}_3)_2\text{P}\cdot\text{OR}$ only if R is an alkyl group; the boiling point of $(\text{CF}_3)_2\text{P}\cdot\text{OH}$ is actually 6° greater than that of $(\text{CF}_3)_2\text{P}\cdot\text{OME}$, and this anomaly has been explained in terms of hydrogen-bonding.⁵ The lack of hydrogen-bonding in bistrifluoromethyl(mercapto)phosphine in contrast to the strong hydrogen-bonding effects in $(\text{CF}_3)_2\text{P}\cdot\text{OH}$ is not unexpected in view of the behaviour of the parent hydrides, H_2O and H_2S .⁷

The n.m.r. spectra of bistrifluoromethyl(mercapto)phosphine support the formulation of the compound as a derivative of trivalent phosphorus, rather than the quinquevalent isomer with H bonded directly to phosphorus. In the latter case the coupling constant (J_{PH}) would be expected to be similar to that observed in $\text{R}_2\text{P}(\text{:S})\text{H}$ compounds, *i.e.*, about 450 c./sec.,⁸ rather than the observed value of 22.6 c./sec. which is in better agreement with that found for P-X-H couplings.^{9,10} The P-H coupling constant is similar to that observed in $(\text{CF}_3)_2\text{P}\cdot\text{SMe}$ (15.5 c./sec.), and it seems that the additional bond separating the coupled nuclei has little effect. The proton and fluorine chemical shifts are very similar in both $(\text{CF}_3)_2\text{P}\cdot\text{SH}$ and $(\text{CF}_3)_2\text{P}\cdot\text{SMe}$; the similarity of fluorine chemical shifts indicates the similarity in electronic effects of SH and SMe groups.

The phosphorus-fluorine coupling constants in both $(\text{CF}_3)_2\text{P}\cdot\text{SH}$ and $(\text{CF}_3)_2\text{P}\cdot\text{SMe}$ are similar, 77.4 and 77.8 c./sec., respectively, values which are well within the range of (J_{PCF_3}) values observed for trivalent bistrifluoromethylphosphorus derivatives¹¹ and well below the range generally observed for quinquevalent trifluoromethylphosphoranes,^{11,12} thus further supporting the formulation of these compounds as phosphine derivatives. The n.m.r. data are summarized in Table I.

Further evidence for the PSH structure is also provided by the infrared spectrum, since a medium-intensity absorption was observed at 2600 cm^{-1} , in the region expected for S-H stretching vibrations. Two peaks at 868 and 838 cm^{-1} were assigned to S-H bending modes. Since the presence of P-H could not be excluded on the infrared evidence because the P-H stretch region is masked by the CF stretch overtones at 2300 cm^{-1} , the deuterio-compound, $(\text{CF}_3)_2\text{P}\cdot\text{SD}$, was prepared. The spectrum in the 2300 cm^{-1} region was unchanged on deuteration, thus confirming the identity of this band as CF overtones rather than P-H stretch; no bands appeared near 1600 cm^{-1} , the expected region for P-D . The SH band at 2600 cm^{-1} disappeared on deuteration, and a new band at 1800 cm^{-1} appeared, which is in the region expected for S-D . The bands at 868 and 838 cm^{-1} are shifted on deuteration to 645 and 620 cm^{-1} , thus confirming their assignment as S-H bending modes.

⁷ L. Pauling, "The Nature of the Chemical Bond," 3rd edn., Cornell, Ithaca, 1960.

⁸ G. Peters, *J. Amer. Chem. Soc.*, 1960, **82**, 4751.

⁹ J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, 1964, **20**, 449.

¹⁰ N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Amer. Chem. Soc.*, 1956, **78**, 3557.

¹¹ K. J. Packer, *J.*, 1963, 960.

¹² R. G. Cavell, and H. J. Emeléus, *J.* 1964, 5896.

TABLE 1.
Nuclear magnetic resonance data for bistrifluoromethylthiophosphines.

	(CF ₃) ₂ P-SH	(CF ₃) ₂ P-SMe
Chemical shifts		
¹⁹ F (p.p.m. vs. CCl ₃ F)*	59.6	56.7
¹ H (τ)†	7.95	7.61
³¹ P (p.p.m. vs. 85% H ₃ PO ₄)*	—	-37.1
Coupling constants (c./sec.)		
<i>J</i> _{PH} (from ¹ H spectra)	22.6	15.5
(from ³¹ P spectra)	—	15.6
<i>J</i> _{PCF₃} (from ¹⁹ F spectra)	77.4	77.8
(from ³¹ P spectra)	—	78

* Positive values indicate resonances to high field of the standard. † τ scale; SiMe₄ taken as τ = 10.0.

The infrared spectra for all the compounds prepared in this study are given in Table 2, along with tentative assignments. All are very similar and all show the expected three strong bands in the CF stretch region. It was not possible to identify a P-S mode because of the strong absorptions arising from the (CF₃)₂P unit in the 600—450 cm.⁻¹ region where P-S is to be expected.¹³

TABLE 2.
Infrared spectra of (CF₃)₂P-SR compounds.

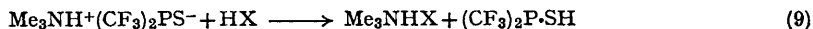
R = H	D	CH ₃	(CF ₃) ₂ P	Assignment*
		2980w 2910m 2820w		} CH, ν
2600w 2580sh 2290m 1920vw 1880vw	2290m 1880m	2250mw	2260w	2 ν (CF)
		1435m 1325m		c SD, ν(+vw c?)
1280vw 1200vs 1175vs 1138vs	1290m 1200vs 1175vs 1135vs	1195vs 1170vs 1135vs	1275m 1200vs 1170vs 1140vs 1135sh	} CH ₃ , δ _a c
1030w	1030w	1030w 945m	1030w	c CH ₃ , ρ
868ms 838m 753s 725w			875w	?
				} SH, δ
	750s 725sh 645m 620w	750ms 730sh	750m 720sh	CF ₃ , δ _e PC, ν(?)
				} SD, δ
558w	560s	560m	578w 557m 545w 508s	} CF ₃ , δ _a
523s 510sh 460sh 440s, br	523s 440s, vbr	525m 450s	460m 445s	

* c = combination, ν = stretch, δ = deformation, ρ = rocking, e = symmetric, a = antisymmetric.

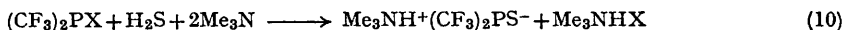
Bistrifluoromethyl(mercapto)phosphine formed an equimolar complex with trimethylamine analogous to that observed for (CF₃)₂P-OH.⁵ The complex may be reasonably formulated as the ammonium salt, Me₃NH⁺(CF₃)₂PS⁻, although the infrared evidence is by no means conclusive. Hydrogen halides displaced the mercaptophosphine, which can be

¹³ R. A. McIvor, G. A. Grant, and C. E. Hubley, *Canad. J. Chem.*, 1956, **34**, 1611.

easily recovered, in contrast to $(\text{CF}_3)_2\text{P}\cdot\text{OH}$,⁵ because of the lack of hydrogen-bonding, from the salt to form the ammonium halide:



This property was used to obtain higher conversion of bistrifluoromethylhalogenophosphine into the mercaptophosphine, for if an equimolar mixture of bistrifluoromethylhalogenophosphine and hydrogen sulphide was treated with a two-fold ratio of trimethylamine, the appropriate ammonium salts were immediately formed:



Hydrogen halide reacted with this mixed salt according to equation (9), to yield the mercaptophosphine in 85% yield, as opposed to 50% obtained with equimolar amounts of all these reagents as described earlier. The higher yield of mercaptophosphine in the presence of excess of amine is probably due to the salt formation blocking the condensation of mercaptophosphine with unreacted halogenophosphine (equation 7).

Bistrifluoromethyl(mercapto)phosphine reacted with mercuric chloride to yield bistrifluoromethylchlorophosphine and presumably mercuric sulphide, rather than the mercurial $(\text{CF}_3)_2\text{P}\cdot\text{S}\cdot\text{HgCl}$.

EXPERIMENTAL

All reactions were done in sealed tubes and standard vacuum techniques were used throughout. Bistrifluoromethyliodophosphine was obtained from the reaction of trifluoromethyl iodide with phosphorus.¹⁴ The corresponding chlorophosphine and bromophosphine were obtained from the reaction of bistrifluoromethyliodophosphine with the mercuric halide,¹⁵ and were characterized by comparison of their properties with those published.^{14,16,19} Other reagents were purified by vacuum-fractionation before use.

Deuterium sulphide was prepared from the reaction of deuterium oxide (99.85%; Norsk-Hydro) with a mixture of calcium sulphide (British Drug Houses) and phosphorus pentoxide. Since the equimolar complex of trimethylamine with D_2S was required for subsequent reaction, the crude deuterium sulphide was purified by forming the trimethylamine complex with an intentional deficiency of trimethylamine and fractionating the complex through a -78° bath, a procedure which effectively removed COS and CO_2 , impurities which cannot be fractionally distilled from D_2S . The "molecular weight" of the $\text{D}_2\text{S}\cdot\text{Me}_3\text{N}$ complex was 48 (Calc., 47.5). A small portion was also treated with deuterium chloride to give deuterotrimethylammonium chloride and deuterium sulphide (Found: M , 36.2. Calc. for D_2S : M , 36.0).

Infrared spectra were measured on Perkin-Elmer Infracord spectrometers with NaCl or KBr optics, usually on vapours contained in a 10-cm. cell with KBr windows. N.m.r. spectra were measured with a Varian Associates V4300A spectrometer with a 12-in. electromagnet and a Varian V4356 field-homogeneity control unit. Spectra were calibrated by means of the normal side-band technique, using a Muirhead-Wigan D695A decade oscillator to generate the side bands. Phosphorus-31 spectra were measured at 16.2 Mc./sec. in 10-cm. tubes without spinning. The standard, 85% phosphoric acid, was contained in large (2-mm.) capillaries in the sample tubes. Fluorine and proton spectra were measured at 40 Mc./sec. in 5-mm. tubes which were spun during the measurement. Trichlorofluoromethane was used as the internal ^{19}F standard and solvent. A small amount of cyclohexane or chloroform was also added to the sample for the proton standard.

The Reaction of Bistrifluoromethylchlorophosphine with Methanethiol.—Equimolar quantities of bistrifluoromethylchlorophosphine (1.98 g., 8.0 mmoles) and methanethiol (0.40 g., 8.3 mmoles) were recovered unchanged after 1 hr. at room temperature. Addition of an equimolar amount of trimethylamine (0.49 g., 8.3 mmoles) to the above mixture resulted in immediate reaction at room temperature, to form a white solid. The volatile materials were fractionated and a small amount (0.037 g.) of a mixture of unreacted trimethylamine and methanethiol was collected. The majority of the volatile product was collected at -78° and identified as *bistrifluoromethyl(methylthio)phosphine* [Found: CF_3 (as CF_3H), 62.9; P, 14.15%; M , 216. $\text{C}_3\text{F}_6\text{H}_3\text{P}$ requires CF_3 ,

¹⁴ F. W. Bennett, H. J. Emel us, and R. N. Haszeldine, *J.*, 1953, 1565.

¹⁵ A. B. Burg and J. F. Nixon, *J. Amer. Chem. Soc.*, 1964, **86**, 356.

¹⁶ A. B. Burg and J. E. Griffiths, *J. Amer. Chem. Soc.*, 1960, **82**, 3514.

63.9; P, 14.35%; M, 216] (7.85 mmoles, 98%). The white solid residue remaining in the reaction tube contained 8.2 mmoles of halide, slightly more than the expected yield of 8.0 mmoles. Bistrifluoromethyl(methylthio)phosphine liberated 99% of its trifluoromethyl groups as fluoroform on hydrolysis in normal alkali at 100°. The vapour pressure was measured from 0.3 to 48° in a mercury microtensimeter with both ascending and descending temperatures. The values obey the linear equation: $\log_{10} p$ (mm.) = $8.195 - 1925/T$.

t (°C)	1.6	7.0	14.9	25.8	35.0	40.0	48.3	31.0	19.8	0.3
p (mm.) .	15.59	20.93	32.71	56.60	88.44	107.5	159.8	77.75	43.98	15.15

The Reaction of Bistrifluoromethyl(methylthio)phosphine with Hydrogen Bromide and Hydrogen Chloride.—Bistrifluoromethyl(methylthio)phosphine (0.191 g., 0.87 mmole) was treated with hydrogen bromide (0.18 g., 2.2 mmoles) at 60° in a sealed tube for 5 hr. Fractionation of the volatiles yielded unreacted hydrogen bromide (0.17 g., 2.08 mmoles) and bistrifluoromethyl(methylthio)phosphine (0.18 g., 0.83 mmole). A similar reaction of the methylthiophosphine with hydrogen chloride also yielded almost complete recovery of the unchanged reagents after 3 days at room temperature and 8 hr. at 60°.

The Reaction of Tetrakis(trifluoromethyl)diphosphine with Methanethiol.—Tetrakis(trifluoromethyl)diphosphine (0.76 g., 2.25 mmoles), prepared from bistrifluoromethyliodophosphine and mercury,¹⁴ was heated to 50° in a sealed tube for 8 hr. with methanethiol (0.17 g., 3.59 mmoles). Fractionation of the volatile products led to the recovery of unreacted tetrakis(trifluoromethyl)diphosphine (0.63 g., 1.86 mmoles), identified by its molecular weight (Found: M, 332. Calc. for $C_4F_{12}P_2$: M, 338). A more volatile fraction, collected at -78°, contained a mixture of tetrakis(trifluoromethyl)diphosphine and bistrifluoromethyl(methylthio)phosphine, and the most volatile fraction, collected at -196°, was a mixture of methanethiol and bistrifluoromethylphosphine, the latter identified by its characteristic infrared absorptions¹⁷ at 2350 (P-H stretch) and 810 and 860 cm^{-1} (PH bend). Heating of the mixture to 100° for an additional 15 hr. did not lead to appreciable further reaction.

The Reaction of Bistrifluoromethyliodophosphine with Silver Sulphide.—Bistrifluoromethyliodophosphine (3.14 g., 10.6 mmoles) was sealed with silver sulphide (2 g.) and heated to 50° for 5 hr. Fractionation of the volatile products in the vacuum system yielded, in the least volatile fraction, collected at -45°, *di(bistrifluoromethylphosphino) sulphide*, $(CF_3)_2P \cdot S \cdot P(CF_3)_2$ [Found: CF_3 (as CF_3H), 74.0; P, 16.85%; M, 374. $C_4F_{12}P_2S$ requires CF_3 , 74.6; P, 16.75%; M, 370] (4.35 mmoles, 82%). About 1 mmole of more volatile material, collected at -196°, was identified as bistrifluoromethylchlorophosphine by molecular weight (Found: M, 208. Calc. for C_2ClF_6P : M, 204) and infrared. The recovery of bistrifluoromethylphosphino-groups in both products was 97% of the amount taken. Di(bistrifluoromethylphosphino) sulphide liberated 99.6% of its trifluoromethyl groups as fluoroform on hydrolysis in normal alkali for 10 hr. at 60°. It was also quantitatively recovered unchanged after heating to 150° for 36 hr. in a glass tube. Its vapour pressure was measured from 0° to 62° in an all-glass, spiral-gauge microtensimeter at both ascending and descending temperatures. The results obey the linear equation: $\log_{10} p$ (mm.) = $8.708 - 2202/T$.

t (°C) . .	0.4	7.6	15.6	22.3	30.45	36.6	49.8	55.3	61.8	39.7	22.6	0.6
p (mm.)	4.55	7.55	12.49	18.89	30.06	40.62	79.85	101.09	133.76	49.96	20.75	5.09

The Reaction of Di(bistrifluoromethylphosphino) Sulphide with Hydrogen Bromide.—The sulphide (0.27 g., 0.7 mmole) was treated with hydrogen bromide (0.086 g., 1.06 mmoles) in a sealed tube for 10 hr. at 100°. Separation of the volatile products yielded, in the most volatile fraction, collected at -196°, unchanged hydrogen bromide (0.073 g., 0.90 mmole) identified by its molecular weight (Found: M, 80.9. Calc. for HBr: M, 80.9), and in the least volatile fraction, collected at -63°, unchanged diphosphino sulphide (0.22 g., 0.61 mmole) identified by molecular weight (Found: M, 362) and vapour pressure (Found: 5 mm./0°). The fraction of intermediate volatility, collected at -126°, had M 216 and was identified as a difficultly separable mixture of bistrifluoromethylbromophosphine (M, 249) and *bistrifluoromethyl(mercapto)phosphine* (M, 202), the latter being identified by its characteristic infrared S-H absorption at 2600 cm^{-1} . Heating the above mixture at 150° for a further 48 hr. did not alter significantly the proportions of product and reactant.

The Preparation of Bistrifluoromethyl(mercapto)phosphine.—(a) Approximately equimolar

¹⁷ F. W. Bennett, H. J. Emel us, and R. N. Haszeldine, *J.*, 1954, 3896.

amounts of bistrifluoromethylbromophosphine (2.17 g., 8.7 mmoles), hydrogen sulphide (0.29 g., 8.5 mmoles), and trimethylamine (0.50 g., 8.5 mmoles) were combined in a sealed tube. On warming to room temperature a vigorous reaction occurred, to form copious quantities of white solid. Fractionation of the volatile products yielded di(bistrifluoromethylphosphino) sulphide (0.79 g., 2.14 mmoles) and slightly impure bistrifluoromethyl(mercapto)phosphine (0.87 g., 4.3 mmoles) identified by its molecular weight (Found: M , 206. Calc. for C_2F_6HPS : M , 202) and infrared spectrum. The very volatile material collected at -196° was identified by molecular weight (Found: M , 35.3. Calc. for H_2S : M , 34.0) as unreacted hydrogen sulphide (0.08 g., 2.3 mmoles) contaminated, according to the infrared spectrum, by a trace of bistrifluoromethylphosphine. The solid residues which remained in the reaction tube contained 8.7 mmoles of bromide, in exact agreement with the amount of bromophosphine taken.

(b) In a second experiment, bistrifluoromethylbromophosphine (1.19 g., 4.98 mmoles) was treated with a large excess (22.5 mmoles) of an equimolar mixture of trimethylamine and hydrogen sulphide in a sealed tube. On warming to room temperature, immediate reaction to form an involatile white solid occurred. Separation of the volatile products yielded hydrogen sulphide (0.17 g., 5.0 mmoles) identified by its molecular weight (Found: M , 33. Calc. for H_2S : M , 34) and unreacted 1:1 trimethylamine–hydrogen sulphide mixture (1.065 g., 11.4 mmoles) identified by its “molecular weight” of 45.6, in reasonably good agreement with the value of 46.5 expected for the “molecular weight” of a completely dissociated equimolar mixture of trimethylamine and hydrogen sulphide. The overall stoichiometry is represented by equation (10).

Anhydrous hydrogen bromide (0.50 g., 6.1 mmoles) reacted with the solid residues forming a volatile liquid, identified as bistrifluoromethyl(mercapto)phosphine by infrared spectroscopy, molecular weight, and analysis [Found: CF_3 (as CF_3H), 67.5; P, 15.2%; M , 202. Calc. for C_2F_6HPS : CF_3 , 68.35; P, 15.85%; M , 202] (0.81 g., 4.0 mmoles; 82% of the initial amount of bistrifluoromethylbromophosphine taken). The more volatile fraction, collected at -196° , was hydrogen sulphide (0.86 g., 1.65 mmoles), contaminated, according to the infrared spectrum, by a trace of silicon tetrafluoride. A very small amount (0.2 mmoles) of impure di(bistrifluoromethylphosphino) sulphide was collected in the less volatile fraction. The solid residues remaining in the reaction tube contained 11.15 mmoles of bromide, in fair agreement with the expected amount of 10.9 mmoles contributed by 4.8 mmoles of $(CF_3)_2PBr$ and 6.1 mmoles of hydrogen bromide.

The Properties of Bistrifluoromethyl(mercapto)phosphine.—(a) *Hydrolysis.* Hydrolysis of bistrifluoromethyl(mercapto)phosphine in *n*-alkali at 60–70° for 3 days liberated 99% of the trifluoromethyl groups as fluoroform.

(b) *Vapour pressure.* The vapour pressure of bistrifluoromethyl(mercapto)phosphine was measured from -4° to 31° in an all-glass spiral-gauge microtensimeter with both ascending and descending temperatures. The results obey the linear equation: $\log_{10} p$ (mm.) = $7.712 - 1604/T$.

t ($^\circ C$)	-4.4	0.6	7.0	10.4	25.9	31.0	25.0	21.1	16.1	0.85
p (mm.)	55.89	70.46	95.77	113.08	224.16	263.65	215.25	184.78	149.15	71.69

(c) *The reaction with trimethylamine.* Bistrifluoromethyl(mercapto)phosphine (0.24 g., 1.18 mmoles) was combined with trimethylamine (0.113 g., 1.91 mmoles) in a sealed tube. On warming to room temperature a white solid formed immediately. The volatile material was removed and identified as trimethylamine (0.032 g., 0.54 mmole) by molecular weight (Found: M , 59.8. Calc. for C_3H_9N : M , 59.0). The amount of amine consumed is therefore 1.37 mmoles, corresponding to an amine/ $(CF_3)_2P-SH$ ratio of 1.16/1.

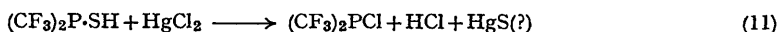
Dry hydrogen chloride (0.050 g., 1.37 mmoles) was added to the solid residues. Immediate reaction to form a volatile liquid along with a white solid occurred on warming to room temperature, which was identified as bistrifluoromethyl(mercapto)phosphine (1.07 mmoles) by molecular weight (Found: M , 200) and infrared spectrum. The solid residue remaining in the reaction tube contained 1.21 mmoles of chloride ion, in fair agreement with the expected amount of 1.18 mmoles.

A second sample of the bistrifluoromethyl(mercapto)phosphine–trimethylamine adduct was prepared for infrared measurements. The following peaks were observed in the mullied samples. The bands marked (*) are also observed in the spectrum of trimethylammonium chloride:¹⁸ 2995* m , 2600* m , br, 2450* m , 1480* m , 1240* m , 1180s, 1165* sh , 1125vs, 1070s, 1020m, 986* m , 830m, 810* sh , 735m, 590s, 551m, 536w, 430–450m, br.

¹⁸ W. Kyanston, B. E. Larcombe, and H. S. Turner, *J.*, 1960, 1772.

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(d) *The reaction with mercuric chloride.* Bistrifluoromethyl(mercapto)phosphine (0.264 g., 1.31 mmoles) was added to resublimed and carefully dried mercuric chloride (1 g.). After a few minutes at room temperature, the mercuric chloride assumed a bright yellow colour. Separation of the volatile products after 3 hr. at room temperature yielded hydrogen chloride (0.014 g., 0.39 mmole) identified by infrared and molecular-weight measurements (Found: M , 38.5). The less volatile fractions contained unreacted bistrifluoromethyl(mercapto)phosphine (0.218 g., 1.08 mmoles), identified by molecular weight (Found: M , 202), infrared spectroscopy, and vapour pressure (71 mm./0°), and a trace (0.1 mmole) of di(bistrifluoromethylphosphino) sulphide. All the volatile materials, with the exception of the hydrogen chloride, were returned to the reaction tube. After several weeks at room temperature, the yellow solid mercuric chloride had changed to a grey colour. Fractionation of the volatile products yielded a fraction of molecular weight 42 which was shown by infrared spectroscopy to be a mixture of hydrogen chloride, silicon tetrafluoride, and fluoroform. Titration of the chloride in the fraction indicated the presence of 0.78 mmole of hydrogen chloride, to give a total yield of hydrogen chloride in the reaction of 1.17 mmoles. The less volatile material was identified as slightly impure bistrifluoromethylchlorophosphine (0.233 g., 1.14 mmoles) by infrared spectroscopy, molecular weight (Found: M , 202. Calc. for C_2ClF_6P : M , 204.5), and vapour pressure (Found: 315 mm./0°; lit.,¹⁹ 297 mm./0°). Yields of hydrogen chloride and bistrifluoromethylchlorophosphine are consistent with the conversion of 88% of the bistrifluoromethyl(mercapto)phosphine according to the reaction:



The grey solid residues were not investigated.

(e) *The reaction with bistrifluoromethylchlorophosphine.* Bistrifluoromethyl(mercapto)phosphine (0.228 g., 1.13 mmoles) and bistrifluoromethylchlorophosphine (0.257 g., 1.26 mmoles) were allowed to react for 9 days at room temperature in a sealed tube. Separation of the volatile products by vacuum-fractionation led to the collection (at -63°) of di(bistrifluoromethylphosphino) sulphide (0.266 g., 0.70 mmole), identified by molecular weight (Found: M , 356) and vapour pressure (Found: 5.3 mm./0°). A mixture (0.06 g.) of bistrifluoromethyl(mercapto)phosphine and the diphosphino sulphide (M , 268) was collected at -78°, and a mixture (0.127 g.) of bistrifluoromethylchlorophosphine (M , 103) and hydrogen chloride was collected at -126°. The most volatile fraction contained 0.0223 g. of material with a molecular weight of 40, which contained mainly hydrogen chloride. The difficulty of separating all of the components by vacuum-fractionation did not permit a quantitative conclusion to be obtained.

The Preparation of Bistrifluoromethyl(deuterio)phosphine. To an equimolar mixture of trimethylamine and deuterium sulphide (0.579 g., 6.1 mmoles) was added an equimolar amount of bistrifluoromethylchlorophosphine (1.266 g., 6.2 mmoles). Immediate reaction occurred on warming the reagents to room temperature. Fractionation of the volatile products after 3 hr. at room temperature led to the isolation of a small amount (0.2 mmole) of di(bistrifluoromethylphosphino) sulphide, identified by its vapour pressure (Found: 4.5 mm./0°), which was collected at -63°. The majority of the volatile products, collected at -96°, was identified as *bistrifluoromethyl(deuterio)phosphine*, $(CF_3)_2P\cdot SD$, by molecular weight (Found: M , 202, 204. C_2F_6DPS requires M , 203) and by the infrared spectrum which shows no absorption at 2600 cm^{-1} (S-H) but an absorption at 1880 cm^{-1} in the expected region for S-D (5.25 mmoles, 85% of the chlorophosphine taken).

A small amount (0.15 mmole) of unreacted bistrifluoromethylchlorophosphine was collected at -136° and identified by molecular weight (Found: M , 205. Calc. for C_2ClF_6P : M , 204.5) and by infrared spectroscopy which confirmed the absence of S-D compound. Deuterium sulphide (0.6 mmole), identified by molecular weight (Found: M , 37. Calc. for D_2S : M , 36), was collected at -196°. The solid residues remaining in the reaction tube contained 6.0 mmoles of chloride, in good agreement with the expected value of 6.1 mmoles.

One of us (R. G. C.) is indebted to the National Research Council of Canada for the award of a N.A.T.O. Postdoctoral Science Fellowship.

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[Received, September 8th, 1964.]

¹⁹ K. J. Packer, Ph.D. Thesis, Cambridge, 1962.