Organometallic and Organometalloidal Fluorine Compounds. Part XI. The Hydrolysis of Trifluoromethylphosphorus Compounds.*

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Trifluoromethyl compounds of phosphorus are rarely stable to aqueous or alkaline hydrolysis, and usually yield fluoroform or a mixture of fluoroform and fluoride; examples of the three types are given. Aqueous hydrolysis of $(CF_3)_2PX$ (X = Cl or I) is stepwise, giving first the unstable $(CF_3)_2P{\cdot}OH$ which decomposes to $CF_3{\cdot}P(OH)_2$ and fluoroform. The hydrolysis of $(CF_3)_3P$ is base-initiated; one equivalent of base liberates two equivalents of fluoroform, since the $(CF_3)_2P{\cdot}ONa$ first formed decomposes slowly in the neutral solution to yield sodium trifluoromethylphosphonite and fluoroform. Trifluoromethylphosphonous acid is monobasic, and yields fluoroform in strongly alkaline solution. The reaction of three equivalents of base with di-iodotrifluoromethylphosphine yields sodium trifluoromethylphosphonite quantitatively; addition of a fourth equivalent liberates fluoroform.

The alkaline hydrolysis of tetrakistrifluoromethyldiphosphine is shown to proceed *via* P–P fission. Bistrifluoromethylphosphine decomposes in alkaline solution to give fluoroform, fluoride, and carbonate, and an unidentified trifluoromethylphosphorus acid. The synthesis of mono- and bistrifluoromethylphosphine is described, and their infra-red spectra are presented and discussed. Trifluoromethylphosphonic acid shows extreme stability to hydrolysis.

One of the more interesting properties of certain of the trifluoromethyl compounds of phosphorus described in Parts VII and X (*J.*, 1952, 1565; 1954, 3598) is their ready and quantitative liberation of fluoroform on hydrolysis with aqueous alkali. This behaviour, however, is not shown by all trifluoromethylphosphorus compounds, and the present communication is concerned mainly with the apparently anomalous compounds and with studies on the hydrolysis reactions of phosphorus compounds by water or aqueous alkali.

Three types of behaviour with aqueous alkali can be distinguished: (*a*) hydrolysis yielding fluoroform quantitatively, (*b*) hydrolysis yielding both fluoride and fluoroform, (*c*) marked resistance to hydrolysis.

Compounds which yield only Fluoroform.—Into this class fall the majority of the trifluoromethylphosphorus compounds studied: $(CF_3)_3P$, $(CF_3)_2PX$ (X = I, CN, or Cl), $CF_3{\cdot}PX_2$ (X = I or Cl), $CF_3{\cdot}P(OH)_2$.

The hydrolysis of the compounds of type $CF_3{\cdot}PX_2$ by water alone proceeds as expected: halide ion is liberated, trifluoromethylphosphonous acid, $CF_3{\cdot}P(OH)_2$, is formed, and the solution becomes homogeneous. The hydrolysis of iodobistrifluoromethylphosphine by water occurs in two stages: the reactants are initially immiscible, but as the iodo-compound (the lower layer) disappears evolution of fluoroform occurs from the upper aqueous layer, *i.e.*,

$$(CF_3)_2PI + H_2O \longrightarrow (CF_3)_2P{\cdot}OH + HI$$

$$(CF_3)_2P{\cdot}OH + H_2O \longrightarrow CF_3{\cdot}P(OH)_2 + CHF_3$$

Chlorobistrifluoromethylphosphine similarly yields trifluoromethylphosphonous acid and one equivalent of fluoroform when hydrolysed by water. The phosphonous acid is monobasic and stable to water, but liberates fluoroform quantitatively in alkaline solution.

The stepwise liberation of fluoroform from the compounds $(CF_3)_2PX$ led to a closer investigation of the hydrolysis of tristrifluoromethylphosphine, which liberates fluoroform quantitatively when treated with an excess of aqueous base. Tri-alkyl- and -aryl-phosphines are stable to hydrolysis under most conditions, and the fluoro-compound resembles

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* Part X, *J.*, 1954, 3598. Part IX (*J.*, 1954, 881) was incorrectly called Part VIII.

more closely the esters of phosphorous acid in this respect. Thus triphenyl phosphite is hydrolysed by water to phenol and phosphorous acid, 2-chloroethyl diphenyl phosphite yields 2-chloroethanol and phenol, and diethyl and dipropyl phosphites undergo stepwise hydrolysis with water or very dilute alkali (Noack, *Annalen*, 1883, **218**, 85; Kabachnik, *Bull. Acad. Sci. U.R.S.S.*, 1947, 631; *Chem. Abs.*, 1948, **42**, 5845; Miłobendzki and Sachnowski, *Chem. Polski*, 1917, **15**, 48; *J.*, 1918, **114**, I, 478; Nylen, *Svensk Kem. Tidskr.*, 1937, **49**, 29, 79). Tristrichloromethylphosphine has recently been reported to hydrolyse to chloroform and phosphite (Yakubovich and Ginsburg, *Doklady Akad. Nauk U.S.S.R.*, 1952, **82**, 273; *Chem. Abs.*, 1953, **47**, 2685), and there is some evidence that phosphorus trichloride undergoes stepwise hydrolysis (Mitchell, *J.*, 1925, **127**, 336; Voigt, *Compt. rend.*, 1951, **232**, 2442). In general, the attachment of negative groups to phosphorus favours rapid hydrolysis.

The hydrolysis of tristrifluoromethylphosphine is base-initiated since, although the compound is stable to water at 100°, addition to a mixture of tristrifluoromethylphosphine and water at 20° of sufficient alkali to liberate theoretically one equivalent of fluoroform actually liberates two equivalents. The reaction occurs in two stages. The first,

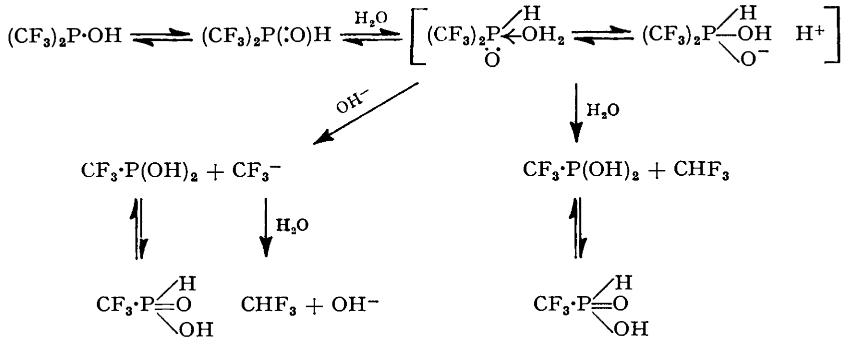
$$(CF_3)_3P + OH^- \longrightarrow (CF_3)_2P{\cdot}O^- + CHF_3$$

is rapid, and is followed by the slow liberation of fluoroform from the now neutral solution :

$$(CF_3)_2P{\cdot}O^- + H_2O \longrightarrow CF_3{\cdot}P(OH){\cdot}O^- + CHF_3$$

The final solution is still neutral with weak reducing properties, and on evaporation to dryness yields sodium trifluoromethylphosphonite (see Part X, *loc. cit.*). The hydrolysis of phosphorus oxyfluoride by water also proceeds stepwise, and in dilute alkaline solution the reaction practically ceases after conversion into the acid HPO_2F_2 (Lange, *Ber.*, 1929, **62**, 786).

The decomposition of bistrifluoromethylphosphinous acid in aqueous or alkaline solution presumably involves the initial co-ordination of a water molecule or attack by a hydroxide ion, followed by rearrangement and decomposition :



The decomposition of bistrifluoromethylphosphinous acid is acid-catalysed, since, when it is prepared in presence of hydriodic acid by the aqueous hydrolysis of iodobistrifluoromethylphosphine, liberation of the equivalent of fluoroform is much more rapid than from the neutral solution obtained from tristrifluoromethylphosphine as described above. The hydrolysis of di*iso*propyl phosphorofluoridate similarly shows acid and base catalysis (Kilpatrick and Kilpatrick, *J. Phys. Chem.*, 1949, **53**, 1388).

Trifluoromethylphosphonous acid is also formed by the aqueous hydrolysis of diiodotrifluoromethylphosphine. Three equivalents of aqueous sodium hydroxide can be added to the last compound without liberation of fluoroform, *i.e.*,

$$CF_3{\cdot}PI_2 + 3NaOH \longrightarrow 2NaI + CF_3{\cdot}P(OH)(ONa) \rightleftharpoons CF_3{\cdot}PH(:O)(ONa)$$

and the infra-red spectrum of the solid obtained on evaporation of the aqueous solution is the same as that of the solid obtained from tristrifluoromethylphosphine and 1 equiv. of aqueous sodium hydroxide. Addition of a fourth equivalent of aqueous base liberates fluoroform quantitatively, just as the reaction of tristrifluoromethylphosphine with two equivalents of aqueous base liberates almost the theoretical amount of fluoroform :

$$CF_3{\cdot}PH(:O){\cdot}O^- + OH^- \longrightarrow CHF_3 + HPO_3^{2-}$$

Fluoroform is also liberated from trifluoromethylphosphonous acid merely by heating its aqueous solution at 100° : $CF_3{\cdot}P(OH)_2 \xrightarrow{H_2O} CHF_3 + H_3PO_3$.

The evaporation by freeze-drying of concentrated solutions of trifluoromethylphosphonous acid prepared by the aqueous hydrolysis of di-iodotrifluoromethylphosphine causes the acid to undergo reaction to give a solid dibasic phosphorus acid and trifluoromethylphosphine (see p. 3903). This reaction does not occur when more dilute solutions are evaporated, and the volatile trifluoromethylphosphonous and hydriodic acids evaporate, leaving no residue.

Compounds which liberate both Fluoride and Fluoroform.—The first trifluoromethyl derivative of a metalloid which was observed to yield both fluoride and fluoroform on hydrolysis by aqueous base was tetrakistrifluoromethyldiphosphine (Part VII, *loc. cit.*). This unusual reaction has been studied further, and its course is now clear. Alkaline hydrolysis (10% sodium hydroxide) yields 75% of the total trifluoromethyl content as fluoroform, *i.e.*, one mole of the diphosphine yields three moles of fluoroform. The solution from the alkaline hydrolysis contains fluoride ion representing 9% of the original trifluoromethyl content; neutralisation of this solution and evaporation to dryness yields a solid whose infra-red spectrum shows strong bands at 8·85 (broad), 9·2 (sharp side band), and 10·2 μ (sharp) revealing the presence of a trifluoromethyl group. The covalent fluorine content of the solid trifluoromethyl compound (probably disodium trifluoromethylphosphonate) accounts for a further 13% of the fluorine in the tetrakistrifluoromethyldiphosphine. The weight balance for fluorine is thus CHF_3 75%, F^- 9%, CF_3–P compound 13%.

The mechanism suggested for this hydrolysis of tetrakistrifluoromethyldiphosphine involves hydrolytic fission of the P–P bond :

$$(CF_3)_2P{\cdot}P(CF_3)_2 \xrightarrow{H_2O} (CF_3)_2PH + (CF_3)_2P{\cdot}OH$$

and since the decomposition of bistrifluoromethylphosphinous acid in basic solution gives two mols. of fluoroform (see above), it follows that the unidentified trifluoromethylphosphorus acid and the fluoride ion must arise by alkaline hydrolysis of bistrifluorophosphine. The last compound was therefore synthesised to test the validity of the mechanism.

Bistrifluoromethylphosphine is best prepared by the reduction by hydrogen of iodobistrifluoromethylphosphine in the presence of Raney nickel [$(CF_3)_2PI \longrightarrow (CF_3)_2PH$]; replacement of halogen by hydrogen in substituted halogeno-phosphines by catalytic hydrogenation has not been reported hitherto. The phosphine (b. p. 1°) appears to form a compound with the nickel, since it is removed from it only by pumping and heating. Reaction of tetrakistrifluoromethyldiphosphine with hydrogen and Raney nickel also gives bistrifluoromethylphosphine, but in smaller yield. Attempts to prepare the phosphine by lithium aluminium hydride reduction of iodobistrifluoromethylphosphine (cf. the successful preparation of bis- and mono-trifluoromethylarsine, Part VI, *J.*, 1953, 1551), or by a photochemical reaction between the iodo-compound and hydrogen [$(CF_3)_2PI \longrightarrow (CF_3)_2P{\cdot} \xrightarrow{H_2} (CF_3)_2PH$] were unsuccessful.

Trifluoromethylphosphine was prepared in low yield by the lithium aluminium hydride reduction of di-iodotrifluoromethylphosphine, but the use of Raney nickel and hydrogen failed to yield the phosphine. This failure may be attributed to compound formation with the nickel, since there was no evidence of unchanged di-iodo-compound, or of etching of the glass reaction vessel, and volatile products were not obtained on strong heating.

An alternative explanation is the formation of polymeric material by reaction of the trifluoromethylphosphine formed initially with unchanged di-iodo-compound :

$$CF_3{\cdot}PH_2 + CF_3{\cdot}PI_2 \longrightarrow CF_3{\cdot}P{:}P{\cdot}CF_3 + 2HI$$

$$n\text{-}CF_3{\cdot}PH_2 + n\text{-}CF_3{\cdot}PI_2 \longrightarrow H{\cdot}\underset{CF_3}{P}\text{—}\underset{CF_3}{P}\text{—}\underset{CF_3}{P}\cdots\underset{CF_3}{P}I + 2HI$$

Reaction of di-iodotrifluoromethylphosphine with anhydrous hydrazine or with zinc and hydrochloric acid (cf. preparation of trifluoromethylarsine, Part VI, *loc. cit.*) also failed to yield trifluoromethylphosphine. The most convenient method for the preparation of the last compound is, however, by hydrolysis of di-iodotrifluoromethylphosphine in highly concentrated aqueous solution, followed by freeze-drying of the solution; trifluoromethylphosphine (b. p. —26·5°) is liberated during the last process :

$$CF_3{\cdot}PI_2 \longrightarrow CF_3{\cdot}P(OH)_2 \longrightarrow CF_3{\cdot}PH_2$$

Bistrifluoromethylphosphine and trifluoromethylphosphine are spontaneously inflammable. Unlike dimethylphosphine, bistrifluoromethylphosphine forms no solid addition compounds with methyl iodide, carbon disulphide, silver iodide, or chloroplatinic acid. When heated with iodine the trifluoromethyl compound reacts quantitatively to give an equimolar mixture of trifluoroiodomethane and fluoroform.

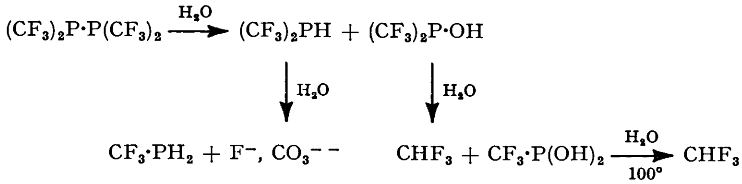
The infra-red spectra of the trifluoromethylphosphines show strong absorption bands at 8—9 μ ascribed to C–F stretching vibrations. Since phosphorus is much heavier than hydrogen, it is to be expected that the movement in a P–H bond is largely that of the hydrogen atom, *i.e.*, the P–H stretching vibration should be fairly constant and substantially independent of the other groups attached to the phosphorus atom. In accord with this, the P–H stretching vibrations in trifluoromethylphosphine (C.S. No. 134) and bistrifluoromethylphosphine (C.S. No. 133) appear as strong bands at 4·31 and 4·30 μ, readily distinguished from the weaker C–F overtone bands which also appear in the 4·2—4·3 μ region. The infra-red spectrum of phosphine shows a triplet centred on 4·32 μ (4·17, 4·32, 4·44 μ) which is in good agreement with the P–H vibration assigned at 4·29 μ from the Raman spectrum (Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853). The P–H bending vibration in phosphine is at 8·92, 10·09 μ, but since this vibration is much more sensitive to the nature of the other substituents on the phosphorus atom, there is a marked shift in the trifluoromethylphosphines; the triplet at 11·90, 12·04, 12·17 μ in trifluoromethylphosphine, and the 12·35 or possibly the 11·70 μ band in bistrifluoromethylphosphine are ascribed to this vibration. A band appears at 13·3—13·6 μ in the spectra of all the trifluoromethyl compounds so far studied, as is shown in the annexed Table, and by analogy with other trifluoromethyl compounds is assigned to a trifluoromethyl deformation frequency, although the $P\text{–}C_{\text{aliph.}}$ stretching vibration has been noted in this region for compounds which do not contain fluorine.

$(CF_3)_2PH$	13·27, 13·35, 13·43	$CF_3{\cdot}PH_2$	13·34, 13·47, 13·65	$CF_3{\cdot}PO(ONa)_2$	13·6
$(CF_3)_2PI$	13·34, 13·40	$CF_3{\cdot}PI_2$	13·55	$CF_3{\cdot}PO(OH)(ONa)$	13·5
$(CF_3)_2PCl$	13·25, 13·32	$CF_3{\cdot}PCl_2$	13·30, 13·34	$(CF_3)_4P_2$	13·37
$(CF_3)_2P{\cdot}CN$	13·24, 13·34	$CF_3{\cdot}P(OH)(ONa)$	13·6	$(CF_3)_3P$	13·25, 13·73

When hydrolysed with aqueous alkali under precisely the same conditions as used for tetrakistrifluoromethyldiphosphine, bistrifluoromethylphosphine yields 50% of its trifluoromethyl content as fluoroform, and 18% is present in the residual solution as fluoride and carbonate. Evaporation of the hydrolysate to dryness gives a solid whose infra-red spectrum is identical with that of the solid obtained from the diphosphine, and the covalent fluorine content of the solid is equivalent to 28% of the fluorine content of the bistrifluoromethylphosphine. Thus by the postulated mechanism for the hydrolysis of tetrakistrifluoromethyldiphosphine, 1 mole of the diphosphine would be expected to give 2 moles of fluoroform from $(CF_3)_2P{\cdot}OH$, and 1 mole of fluoroform from $(CF_3)_2PH$, a total of 3 moles, as is actually found. The fluoride ion and the trifluoromethyl phosphorus acid formed during the hydrolysis of the diphosphine would be expected to be equivalent to 9% and

14% respectively of the fluorine content of the diphosphine, and the favourable agreement of these figures with the experimental values of 9 and 13% (see above) is strong support for the postulated mechanism.

The theory is strengthened by the isolation of bistrifluoromethylphosphine when tetrakistrifluoromethyldiphosphine is hydrolysed by water or dilute hydrochloric acid at 100°; fluoroform (2 mols.) is also produced. Trifluoromethylphosphonous acid, which is formed from bistrifluoromethylphosphinous acid at room temperature by loss of fluoroform, reacts with water at 100° to give fluoroform quantitatively; bistrifluoromethylphosphine, however, is only partly decomposed, to give trifluoromethylphosphine (1 mol.), fluoride, and carbon dioxide, and no fluoroform :



$$\begin{tikzcd}
(CF_3)_2P{\cdot}P(CF_3)_2 \arrow[r, "H_2O"] & (CF_3)_2PH \arrow[d, "H_2O"] & + & (CF_3)_2P{\cdot}OH \arrow[d, "H_2O"] & \\
& CF_3{\cdot}PH_2 + F^-, CO_3^{--} & & CHF_3 + CF_3{\cdot}P(OH)_2 \arrow[r, "H_2O", "100^\circ"'] & CHF_3
\end{tikzcd}$$

This accounts for the liberation of 3 mols. of fluoroform when tetrakistrifluoromethyldiphosphine is treated with aqueous alkali, and of only 2 mols. when heated with water.

The bonding of hydrogen to elements such as arsenic, phosphorus, nitrogen, oxygen, or sulphur which also carry a trifluoromethyl group thus reduces the stability of the normally extremely stable trifluoromethyl group to such an extent that the group readily decomposes into fluoride and carbonate.

Trifluoromethylphosphine also decomposes readily by aqueous alkali, to give 65—70% of the theoretical amount of fluoride ion.

Compounds which do not liberate Fluoride or Fluoroform.—Only one trifluoromethylphosphorus compound has so far shown marked resistance to hydrolysis, *viz.*, trifluoromethylphosphonic acid. This compound, which can be prepared by oxidative hydrolysis of the compounds $(CF_3)_2PX$ or $CF_3{\cdot}PX_2$ (X = I or Cl) (see Part X), has now been obtained quantitatively by an alternative route involving oxidation of trifluoromethylphosphine with 30% nitric acid. Trifluoromethylphosphonic acid is extremely stable, and fails to react with concentrated sulphuric acid at 140° or with 10% sodium hydroxide at 100°; a very slow hydrolysis occurs in alkaline solution at 150°. In this respect trifluoromethylphosphonic acid resembles more the alkyl- and aryl-phosphorus compounds, where the breaking of the P–C bond during hydrolysis is rare.

It should perhaps be emphasised finally that the C–Z bond in a compound CF_3–Z is usually very resistant to hydrolytic attack {*e.g.*, CF_3I, $CF_3{\cdot}CO_2H$, $(CF_3)_3N$, $CF_3{\cdot}SF_5$, $CF_3{\cdot}[CF_2]_n{\cdot}CF_3$, $(CF_3)_2S$}, and in only relatively few cases does the C–Z bond break with liberation of the CF_3 group as fluoroform [$CF_3{\cdot}CO{\cdot}CF_3$, $CF_3{\cdot}CHO$, $CF_3{\cdot}COPh$, $(CF_3)_3As$, $(CF_3)_2AsX$ (X = I, CN, Cl, SCN, Br, or F), $CF_3{\cdot}AsX_2$ (X = I, Cl, or Br), $(CF_3)_3AsX_2$ (X = F or Cl), $(CF_3)_2AsO{\cdot}OH$], or decomposition of the CF_3 group to fluoride and carbonate [$CF_3{\cdot}OF$, $(CF_3)_4As_2$, $(CF_3)_2NH$, $(CF_3)_2O_2$, $CF_3{\cdot}SH$, $(CF_3)_2AsH$].

EXPERIMENTAL

The general techniques used have been described earlier in this series. Reactions were carried out in sealed Pyrex tubes or in conventional ground-glass apparatus. Oxygen was carefully excluded at all times. The products were identified tensimetrically and by molecular-weight determination, and identity was confirmed by examination of infra-red spectra. The reactants and products were manipulated in a vacuum system where practicable, since handling losses are then negligible. For preparation of starting materials see Part VII (*loc. cit.*).

Bistrifluoromethylphosphine.—(a) *From iodobistrifluoromethylphosphine.* (i) With Raney nickel and hydrogen. Pressures of hydrogen of less than 1 atm. have been used, in tubes or flasks of 50—1000 ml. capacity. The Raney nickel catalyst (2 g.; prepared in the usual way) as a slurry in ethanol was poured into the vessel, which was then evacuated to remove the ethanol (30 hr.). A known weight of iodobistrifluoromethylphosphine was then added and the vessel was filled with almost 1 atm. of hydrogen and sealed. After being heated at 100° (4—20 hr.) the vessel was cooled by liquid nitrogen and opened, and the excess of hydrogen removed by pumping. Pumping was continued whilst the flask was heated at 150° (1 hr.). The combined volatile products were then fractionated *in vacuo*. In one experiment the final heating was effected by use of a naked flame instead of an oil-bath, but this brought about a vigorous exothermic reaction with incandescence, and the yield dropped appreciably.

In a typical reaction, iodobistrifluoromethylphosphine (0·562 g.) in a 50 ml. tube with 600 mm. pressure of hydrogen at 110° (16 hr.) gave *bistrifluoromethylphosphine* (65%), b. p. 1° (isoteniscope) (Found: 66·1%; *M*, 170. C_2HF_6P requires F, 67·0%; *M*, 170).

Catalytic reduction of the iodo-compound can be detected at room temperature, but is inconveniently slow. At 100°, some hydrogen fluoride is liberated, since there is appreciable etching of the apparatus; small amounts of phosphine and fluoroform are also formed.

(ii) With lithium aluminium hydride. In a single experiment, iodobistrifluoromethylphosphine (0·896 g.) in sodium-dried dibutyl ether (10 ml.) was added dropwise to lithium aluminium hydride (0·080 g.) in dibutyl ether (10 ml.). The mixture was heated at 70° (6 hr.) with stirring, but after the cautious addition of water, fractionation of the volatile products *in vacuo* failed to yield bistrifluoromethylphosphine.

(iii) By photochemical reaction with hydrogen. Since iodobistrifluoromethylphosphine readily liberates iodine on irradiation, its photochemical reaction with hydrogen was investigated; iodobistrifluoromethylphosphine (0·729 g.) was sealed in a 100-ml. Pyrex tube with dry hydrogen at 47 cm. pressure. Iodine crystals had appeared after 16 hours' irradiation, but slowly disappeared when the light was turned off. The products obtained after 3 months' irradiation were iodobistrifluoromethylphosphine (0·612 g., 84%), a small quantity of di-iodotrifluoromethylphosphine, and only a trace (0·005 g.) of more volatile material.

(b) *From tetrakistrifluoromethylphosphine.* The diphosphine (0·484 g.) was sealed with hydrogen (650 mm. pressure) in a 500-ml. bulb which was then heated at 65—75° (10 hr.). Fractionation of the products *in vacuo* gave bistrifluoromethylphosphine (0·135 g., 28%) (Found: *M*, 167), identified by means of its vapour pressure and its infra-red spectrum.

A single attempt to convert tetrakistrifluoromethyldiphosphine into bistrifluoromethylphosphine by reaction with zinc and hydrochloric acid was unsuccessful.

The formation of bistrifluoromethylphosphine during the aqueous hydrolysis of the diphosphine is considered below.

Properties of Bistrifluoromethylphosphine.—The compound is unchanged after 3 days at 210—215°. Its constitution follows from an experiment in which bistrifluoromethylphosphine (0·1221 g.) and an excess of dry iodine were heated at 280° (2 days) to give fluoroform (0·0518 g., 51%) and trifluoroiodomethane (0·139 g., 49·5%), identified tensimetrically and by their molecular weights and spectra.

Bistrifluoromethylphosphine does not form a solid addition compound when mixed at room temperature with methyl iodide, carbon disulphide, silver iodide, or chloroplatinic acid.

Trifluoromethylphosphine.—(a) *From di-iodotrifluoromethylphosphine.* (i) By use of lithium aluminium hydride. A solution of di-iodotrifluoromethylphosphine (2·02 g.) in butyl ether (15 ml.) was added dropwise to lithium aluminium hydride (0·19 g.) in butyl ether (10 ml.). There was no reaction in the cold, but at 70° effervescence occurred; after reaction at this temperature for 6 hr. water was added and the volatile products were removed by pumping. Fractionation of these products gave *trifluoromethylphosphine* (0·035 g., 6%), b. p. (isoteniscope) −25·5° (Found: F, 55·6%; *M*, 102. CH_2F_3P requires F, 55·9%; *M*, 102), and a mixture (0·11 g.) of phosphine and trifluoromethylphosphine which could not be separated by distillation.

A similar reaction with lithium aluminium hydride (0·34 g.) in ethyl ether (20 ml.) and di-iodotrifluoromethylphosphine (1·54 g.) in ethyl ether (10 ml.) was more vigorous, and no heating was necessary. The volatile products present after the addition of water were fractionated to give trifluoromethylphosphine (0·035 g., 8%) (Found: *M*, 102), identified by means of its infra-red spectrum.

Lithium aluminium hydride reacted violently with di-iodotrifluoromethylphosphine in absence of a solvent, to give a bright yellow solid, but trifluoromethylphosphine was not formed. The colour indicates a stable complex, since fluoroform was not a reaction product.

(ii) By use of hydrogen and Raney nickel. In an experiment typical of several unsuccessful attempts to prepare trifluoromethylphosphine in an analogous manner to that used for bistrifluoromethylphosphine, di-iodotrifluoromethylphosphine (1·90 g.), Raney nickel (3 g.), and hydrogen (at 600 mm. in a 500-ml. flask) were heated at 65° for 30 min. Distillation of the volatile condensable products gave small unidentified fractions, but no trifluoromethylphosphine. Strong heating *in vacuo* of the residual Raney nickel gave an unidentified non-inflammable liquid, but no trifluoromethylphosphine.

(iii) By hydrolysis. This forms the most convenient synthesis of the phosphine. See p. 3903.

Oxidation of Trifluoromethylphosphine.—The phosphine (0·143 g.) was sealed *in vacuo* with 4·1N-nitric acid (2 ml.) and shaken (12 hr.). Concentrated nitric acid (2 ml.) was then added, and the resealed tube was again shaken (12 hr.). Evaporation of the solution to dryness by freeze-drying (2 days) and vacuum sublimation of the residue gave trifluoromethylphosphonic acid (0·21 g., 96%; 0·17 g., 82% when resublimed). The disodium salt of the acid had an infra-red spectrum identical with that of the salt prepared from the acid made by alternative routes (Part X, *loc. cit.*).

Hydrolysis Reactions.—(a) *Tristrifluoromethylphosphine.* (i) With an excess of alkali. Tristrifluoromethylphosphine (0·392 g.), sealed *in vacuo* with sodium hydroxide (1 g.) and water (15 ml.), underwent immediate reaction, and after 48 hr. yielded fluoroform (0·338 g., 98%).

(ii) With 1 equiv. of alkali. Tristrifluoromethylphosphine (0·655 g., 2·75 mmoles) was sealed in a tube with sodium hydroxide (24 ml. of 0·1146N; 2·75 mmoles) and shaken vigorously at room temperature (1 hr.). Fractionation gave unchanged tristrifluoromethylphosphine (0·055 g., 8%) and fluoroform [0·177 g., 33% based on $P(CF_3)_3$ comsumed]. One trifluoromethyl group has thus been lost from the missing tristrifluoromethylphosphine, and the aqueous solution contains $(CF_3)_2P{\cdot}ONa$ at this stage.

The reaction tube was resealed and shaken for a further 2 days. A further quantity of fluoroform (0·173 g., 33%) had then been produced. Thus the initial rapid loss of one trifluoromethyl group as fluoroform is followed by a slower loss of a second group as fluoroform. The residual aqueous solution contained sodium trifluoromethylphosphonite, since on treatment with an excess of aqueous sodium hydroxide the final equivalent of fluoroform (0·173 g., 33%) was evolved.

In a further experiment tristrifluoromethylphosphine (0·226 g., 0·95 mmole) and aqueous sodium hydroxide (8·26 ml. of 0·1146N; 0·95 mmole) were shaken at 20° for 84 hr. to give unchanged tristrifluoromethylphosphine (0·022 g., 9%) and fluoroform (0·123 g., 68%). The residual solution was evaporated to dryness and the infra-red spectrum of the residual white solid (0·125 g.) showed it to be sodium trifluoromethylphosphonite.

(b) *Iodobistrifluoromethylphosphine.* (i) With water. Iodobistrifluoromethylphosphine (0·484 g.), shaken with water (2 ml.) for 7 hr. at 20°, gave fluoroform (0·114 g., 48%). The iodo-compound initially formed a lower layer with the water, and as the lower layer disappeared gas was evolved from the aqueous layer. Evaporation of the residual aqueous solution at $20°/10^{-2}$ mm. left no residue. The aqueous condensate liberated fluoroform quantitatively when treated with an excess of aqueous alkali.

(ii) With acid. Iodobistrifluoromethylphosphine (0·537 g.) underwent an immediate effervescence with N-hydrochloric acid (15 ml.), and after 5 days at 20° had yielded fluoroform (0·120 g., 47%).

(iii) With alkali. The iodo-compound (0·188 g.), shaken with an excess of 10% sodium hydroxide solution (15 ml.) for 24 hr., gave fluoroform (0·088 g., 99%).

(c) *Di-iodotrifluoromethylphosphine.* (i) With alkali. Reaction of an excess of aqueous sodium hydroxide (10 ml.; 10%) with di-iodotrifluoromethylphosphine (0·385 g.) yielded fluoroform (0·076 g., 100%).

(ii) Stepwise hydrolysis by alkali. The aqueous hydrolysis of di-iodotrifluoromethylphosphine yields an acid solution which can be treated with up to three successive equivalents of aqueous alkali before evolution of fluoroform occurs. This was shown as follows: Di-iodotrifluoromethylphosphine (0·718 g., 2·03 mmoles) was placed in an evacuated, 500-ml., two-necked flask, one neck of which was sealed with a rubber cap through which could be pushed a hypodermic needle; the second neck was connected to a trap cooled in liquid oxygen to collect volatile products. Water (2 ml.) was added and the flask was set aside until hydrolysis of the iodo-compound was complete, as indicated by the disappearance of the yellow lower layer. One equivalent of 0·496N-sodium hydroxide (4·15 ml., 2·05 mmoles) was then added *via* the hypodermic needle; no fluoroform was evolved. A second equivalent of sodium hydroxide was then added, and again there was no evolution of fluoroform. Addition of a third equivalent of sodium hydroxide, diluted by water (5 ml.), caused slight evolution of fluoroform (0·018 g., 12%). A 15-ml. portion of the solution was then evaporated to dryness to give a white solid (0·511 g.), shown to contain sodium trifluoromethylphosphonite by means of its infra-red spectrum.

In a further experiment di-iodotrifluoromethylphosphine (0·708 g., 2 mmoles) was hydrolysed by water (1 ml.). 0·29 Equiv. more than the theoretical 3 equiv. of sodium hydroxide was then added (13·24 ml. of 0·496N-sodium hydroxide, 6·58 mmoles). Fluoroform in an amount corresponding to the excess of base added was liberated (0·042 g., 0·6 mmole, 30%). Addition of a large excess of aqueous alkali at this stage liberated the rest of the trifluoromethyl groups as fluoroform. The stepwise hydrolysis thus shows that aqueous hydrolysis of the di-iodo-compound yields trifluoromethylphosphonous acid and 2 mols. of hydrogen iodide.

(iii) With limited amounts of water to produce trifluoromethylphosphine. Di-iodotrifluoromethylphosphine (5·34 g., 0·0151 mole) and water (1—2 ml.) were allowed to react at 20° until hydrolysis was complete (3 hr.) as indicated by the merging of two layers. The solution was then evaporated to dryness by freeze-drying (14 days) and the evolved water and gases were condensed in a trap cooled by liquid oxygen. The residue from the freeze-drying procedure was a white solid (1·42 g.), initially believed to be a new acid of empirical formula $CF_3{\cdot}P(OH)_2,H_2O$ (see Part VII), but subsequently shown (Paul, unpublished observations) to be trifluoromethylphosphonic acid. The condensate collected in the liquid-oxygen trap consisted of water, hydrogen iodide, and trifluoromethylphosphine (0·363 g., 24%) (Found : *M*, 103), identified by means of its infra-red spectrum.

(d) *Chlorobistrifluoromethylphosphine.* (i) With water. The compound (0·467 g.), shaken with water (2 ml.), underwent immediate reaction, and after 3 hr. the volatile product was examined and shown to be fluoroform (0·157 g., 49%).

(ii) With alkali. The chloro-compound (0·160 g.) reacted vigorously with an excess of aqueous sodium hydroxide (10 ml. of 10%) to give fluoroform (0·109 g., 67%) after 3 days.

(e) *Dichlorotrifluoromethylphosphine.* (i) With water. The chloro-compound (0·233 g.) underwent a vigorous reaction with water (1 ml.) at room temperature and the two layers soon became homogeneous. When evaporated to dryness at 20°/10^{-2} mm., the aqueous solution left no residue; treatment of the condensate (collected in a trap cooled by liquid oxygen) with an excess of 10% aqueous sodium hydroxide yielded fluoroform (0·092 g., 90%).

In a second experiment dichlorotrifluoromethylphosphine (0·233 g.) was sealed with water (2 ml.), then allowed to warm to room temperature. There was an immediate exothermic reaction, but gas was not evolved. The mixture was frozen, an excess of aqueous sodium hydroxide (6 ml. of 10%) was added, and the tube resealed. There was an immediate evolution of gas at room temperature, and fractionation, etc., showed this gas to be fluoroform (0·092 g., 96%). These experiments show that dichlorotrifluoromethylphosphine is hydrolysed to trifluoromethylphosphonous acid which is volatile in water vapour and unstable to base.

(ii) With alkali. Reaction of dichlorotrifluoromethylphosphine (0·215 g.) with an excess of aqueous sodium hydroxide (10 ml. of 5%) at 20° gave fluoroform (0·088 g., 99%).

(f) *Cyanobistrifluoromethylphosphine.* Hydrolysis of this compound (0·105 g.) with an excess of aqueous sodium hydroxide (10 ml. of 10%) at 20° (4 days) yielded fluoroform (0·074 g., 99%).

(g) *Bistrifluoromethylphosphine.* (i) By water. There is no reaction with water at room temperature. The phosphine (0·184 g.) and water (5 ml.), heated *in vacuo* at 110—130° (50 hr.), gave carbon dioxide, unchanged bistrifluoromethylphosphine (26%), and trifluoromethylphosphine (0·065 g., 39%). The volatile products were identified by their infra-red spectra. The aqueous solutions contained fluoride (36%).

(ii) By aqueous alkali. Bistrifluoromethylphosphine (0·2266 g.) and aqueous sodium hydroxide (0·5 g. in 10 ml. of water) liberated a gas at room temperature. After 2 weeks, fractionation of the volatile products gave fluoroform (0·0948 g., 51%) (Found : *M*, 70). The aqueous solution contained fluoride (0·027 g., 17·8%) as shown by distillation as fluorosilicic acid and titration with thorium nitrate.

The experiment was repeated with bistrifluoromethylphosphine (0·1968 g.), sodium hydroxide (0·75 g.), and water (10 ml.). The products were fluoroform (0·0813 g., 50%), fluoride (0·0233 g., 17·7%, by titration), and a trifluoromethylphosphorus acid. The last compound was detected by neutralisation of an aliquot of the solution followed by freeze-drying. The infra-red spectrum of the residual solid revealed the presence of a trifluoromethyl group; the solid was fused with sodium at 550—600° (4 hr.), and the total fluoride obtained was equivalent to 46% of the bistrifluoromethylphosphine. The covalent fluorine in the solid (*i.e.*, as trifluoromethylphosphorus acid) was thus 28·3%, and the weight balance for fluorine is 96%.

(h) *Trifluoromethylphosphine.* In a single experiment, trifluoromethylphosphine (0·106 g.) was sealed with aqueous sodium hydroxide (0·5 g. in 5 ml. of water), and the reaction tube was set aside for 7 days. Fluoride (72%) was formed, and after neutralisation of the solution, evaporation to dryness gave a white solid whose infra-red spectrum suggested the presence of an unidentified compound containing covalent fluorine.

(i) *Attempted hydrolysis of trifluoromethylphosphonic acid.* The acid (0·204 g.), sealed in a Carius tube with 10% sodium hydroxide (15 ml.), and heated at 150° (10 hr.), yielded no fluoroform; fluoride (0·009 g., 12·5%) had been liberated and was estimated by the thorium nitrate method.

Trifluoromethylphosphonic acid (0·036 g.) was mixed with concentrated sulphuric acid (50 ml. of 50%) and heated to 135—140°. Steam was then passed through the mixture, and the condensed distillate was analysed for fluoride; none was detected. Since only a small amount (0·05 ml.) of 0·5N-sodium hydroxide was required to neutralise the distillate, it follows that trifluoromethylphosphonic acid is not volatile in steam.

(j) *Reactions of trifluoromethylphosphonous acid.* (i) When heated in acid solution. A solution of this acid, prepared by the reaction of iodobistrifluoromethylphosphine (0·537 g.) with an excess of N-hydrochloric acid at room temperature, was heated to 100° for 16 hr. to give fluoroform (0·125 g., 49%). In a second experiment, a solution of the acid, prepared by the reaction of iodobistrifluoromethylphosphine (0·182 g.) with water, was heated at 100° for 12 hr. to give fluoroform (0·043 g., 50%).

(ii) With aqueous alkali. When a solution of trifluoromethylphosphonous acid, prepared by the reaction of di-iodotrifluoromethylphosphine (0·71 g., 0·002 mole) with an excess of water, was treated with an excess of aqueous sodium hydroxide, a quantitative evolution of fluoroform was found.

(iii) With two equivalents of alkali. Tristrifluoromethylphosphine (0·172 g., 0·72 mmole), shaken with aqueous sodium hydroxide (12·57 ml. of 0·1146N; 1·44 mmoles) for 84 hr., gave fluoroform (0·137 g., 91%) and not more than a trace of unchanged tristrifluoromethylphosphine.

(k) *Hydrolysis of tetrakistrifluoromethyldiphosphine.* This compound was prepared as described earlier (*J.*, 1953, 1565).

(i) By water. The diphosphine (0·209 g., 0·62 mmole) failed to react with water (10 ml.) during 36 hr. at 20°. Fluoroform (0·089 g., 1·3 mmoles, 51%) (Found: *M*, 70) and bistrifluoromethylphosphine (0·064 g., 0·4 mmole, 32%), b. p. 1° (Found: *M*, 170. Calc. for C_2HF_6P: *M*, 170), were formed by reaction at 100° for 24 hr., and were identified spectroscopically.

(ii) By acid. The diphosphine (0·566 g., 1·7 mmoles) and 1·25N-hydrochloric acid (25 ml.) failed to react at 20°, and after 24 hr. at 100° two layers were still present. The liquid phase became homogeneous after a further 12 hr. at 100°. Fractionation of the volatile products gave fluoroform (0·224 g., 48%) (Found: *M*, 70) and bistrifluoromethylphosphine (0·232 g., 41%) (Found: *M*, 169).

(iii) By alkali. Tetrakistrifluoromethyldiphosphine (0·508 g.), sealed *in vacuo* with 10% aqueous sodium hydroxide (10 ml.), underwent vigorous reaction (5 min.) with evolution of gas. The reaction tube was set aside (10 days) with intermittent shaking, and fractionation of the volatile products then gave fluoroform (0·310 g., 75%) (Found: *M*, 70). Determination of the fluoride in one-fifth of the solution showed that fluoride (0·031 g., 9%) had been produced. A neutralised portion (60% of original) of the residual liquid was evaporated to dryness by freeze-drying to give a white solid (1·220 g.). The infra-red spectrum of the solid showed it to contain C–F bonds. A portion of the solid (0·823 g.) was fused with sodium at 600° (3 hr.) and the ionic fluoride was then determined to be 0·0762 g., *i.e.*, 22%. Since 9% was present as ionic fluorine before sodium fusion, 13% must have been present as covalent fluorine in the unknown trifluoromethylphosphorus acid. Alkaline hydrolysis of tetrakistrifluoromethyldiphosphine thus yields fluoroform (75%), fluoride (9%), and a trifluoromethylphosphorus acid (13%).

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