PHOSPHORUS-FLUORINE CHEMISTRY—I FLUORIDES OF PHOSPHONIC AND PHOSPHINIC ACIDS

R. SCHMUTZLER

E. I. du Pont de Nemours & Company, Experimental Station Laboratory Explosives Department, Wilmington, Delaware

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Abstract—Reaction of methyldichlorophosphine with potassium fluorosulphinate led to the formation of the phosphonic acid fluorides, CH_3POF_2 and CH_3PSF_2 , by addition of the elements of sulfur dioxide to the trivalent phosphorus, no fluorophosphine, CH_3PF_2 , being observed. Dimethylmonochlorophosphine, in the same fashion, was converted into the phosphinic fluorides, $(CH_3)_2POF$ and $(CH_3)_2PSF$. Chloromethyldichlorophosphine, under similar conditions, gave a small amount of the spontaneously inflammable fluorophosphine, $ClCH_2PF_2$, while the principal product corresponded to $ClCH_2PCl_2 \cdot ClCH_2POF_2$.

The synthesis of a number of phosphonic and phosphinic fluorides of the composition RPOF₂, RPSF₂, R₂POF and R₂PSF (R = aliphatic or aromatic) by metathetical reactions is described. Certain phosphonic and phosphinic fluorides were isolated as by-products of the facile partial hydrolysis of the corresponding fluorophosphoranes, RPF₄ and R₂PF₃, respectively.

¹⁹F nuclear magnetic resonance spectra of substituted aromatic fluorophosphoranes and phosphonic fluorides, whose synthesis is based on dichlorophosphines, revealed that aromatic dichlorophosphination under FRIEDEL-CRAFTS conditions invariably leads to mixtures of isomers (p and m). The preparative separation of the tolylphosphonic fluoride isomer mixture by vapour phase chromatography is described.

Some infra-red data on phosphonic and phosphinic fluorides are presented.

IN 1955 a novel fluorinating agent, potassium fluorosulphinate KSO_2F , was introduced into synthetic chemistry.^(1a-b) The new reagent permitted the convenient preparation of a variety of fluorine compounds already known as well as providing a route to novel fluorine compounds (cf. References 1a-d; 2a-g).

One of the uses of potassium fluorosulphinate was its application in the fluorination of phosphorus-chlorine bonds, e.g. for the preparation of phosphorus trifluoride, phosphorus oxyfluoride, phosphorus thiotrifluoride (cf. References 1a-b; 3), the phosphonitrilic fluorides (cf. References 2a; 2c; 2e-g), ester derivatives of pentavalent phosphorus,^(1d,3) fluorophosphine complexes of zerovalent nickel⁽⁴⁾ and certain fluorides of phosphonic acids.^(3,4)

In the course of systematic studies on the scope and limitations of fluorinations with potassium fluorosulphinate, its behaviour towards chlorophosphines, RPCl₂ and

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R₂PCl, was investigated. It was expected that the previously unknown fluorophosphines, RPF₂ and R₂PF, might be obtained, which were deemed to be of interest as novel ligands in co-ordination chemistry.

A vigorous reaction occurred when phenyldichlorophosphine was reacted with potassium fluorosulphinate, both in the presence and absence of a solvent. Instead of being the expected fluorophosphine the product was identified as a constant boiling mixture of the phosphonic fluorides, C₆H₅POF₂ and C₆H₅PSF₂, which could not be separated by distillation. That the product mixture consisted of the phosphonic acid fluorides was demonstrated by the independent synthesis of both compounds.^(3,4)

A similar redox reaction was also encountered when methyldichlorophosphine was reacted with potassium fluorosulphinate, the pure phosphonic fluorides CH₃POF₂^(5,7a,b,f) and CH₃PSF₂^(3,6,7e,k,m) being readily isolable in this case, due to a remarkably high difference in boiling points (b.p. CH₃POF₂, 98-99°; b.p. CH₃PSF₂, 59-60°). Apparently the P=O compound is considerably associated, compared with the P-S derivative, a known property of certain organophosphorus compounds containing P-O and P-S bonds, respectively.⁽⁸⁾

There was no indication for the formation of the fluorophosphine $(CH_3)_2PF$, when dimethylmonochlorophosphine was fluorinated with potassium fluorosulphinate, and the same type of redox reaction as above occurred. The phosphinic fluorides, (CH₃)₂POF and (CH₃)₂PSF, were the sole reaction products, identified by vapour phase chromatographic separation of the reaction mixture and comparison with the independently prepared authentic compounds. In a preliminary communication,^(1a) dimethylmonofluorophosphine was mentioned as a product of the reaction of the chlorophosphine with potassium fluorosulphinate, in the absence of physical or experimental data.

The elements of sulphur dioxide which is generally formed on fluorinations with potassium fluorosulphinate, according to

 $R-X + KSO_2F \rightarrow R-F + KX + SO_2$ (X = halogen),

add to the trivalent phosphorus as follows:

 $3CH_3PCl_2 + 6KSO_2F \rightarrow 2CH_3POF_2 + CH_3PSF_2 + 6KCl + 5SO_2;$

$$3(CH_3)_2PCl + 3KSO_2F \rightarrow 2(CH_3)_2POF + (CH_3)_2PSF + 3KCl + 2SO_2$$

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A particularly interesting observation was made in the reaction of chloromethyldichlorophosphine, $ClCH_2PCl_2$, with potassium fluorosulphinate. With antimony trifluoride, chloromethyldichlorophosphine was converted smoothly into the spontaneously flammable fluorophosphine, $ClCH_2PF_2$ (10) while a variety of other chlorophosphines were invariably converted to fluorophosphoranes, R_nPF_{5-n} (cf. below). With potassium fluorosulphinate as a fluorinating agent, small amounts of the fluorophosphine, $ClCH_2PF_2$, and of the phosphonothioic difluoride, $ClCH_2PSF_2$ were formed, while the bulk of the product, b.p. 119°, had the composition

ClCH₂PCl₂·ClCH₂POF₂

(cf. b.p. $ClCH_2PCl_2 = 129^\circ$; b.p. $ClCH_2POF_2 = 128^\circ$). The same 1:1 product was obtained on combination of equimolar amounts of the pure components, no noticeable heat of reaction being observed. The refractive index of the 1:1 product was found to be almost linearly related to the indices of the pure components, suggesting a relatively weak molecular interaction.

A comparison of the ¹⁹F nuclear magnetic resonance spectrum (at 56.4 mc/s) of pure chloromethylphosphonic difluoride and of its 1:1 product with chloromethyldichlorophosphine showed a doublet, P—F coupling constant J = 1140 c/s, at the same position in both products, again favouring the formulation of the 1:1 product as a mere azeotrope.

The infra-red spectrum appeared essentially as superimposed from the pure components, except for the P=O absorption in chloromethylphosphonic difluoride, which was raised by ca. 20 cm^{-1} . The product may be regarded as an azeotrope, especially in view of its boiling point being slightly lower than the boiling points of the individual pure components. On the gas chromatography column the product was readily separated into its components, and no peaks besides pure chloromethyldichlorophosphine and chloromethylphosphonic difluoride were detected. The exact 1:1 composition of the product, however, is noteworthy. A study on the interaction between chloromethylphosphonic difluoride and certain other trivalent phosphorus compounds in view of the above observations may be of interest.

Further attempts to prepare fluorophosphines by conventional fluorination methods either failed or led to similar redox reactions. It must be concluded, therefore, that fluorophosphines are strongly reducing compounds, and, in fact, the first representatives of this new class of compounds^(9,10) were found to be highly reactive, flammable materials. Fluorophosphines co-ordinated to a zerovalent transition metal, e.g. nickel, could readily be obtained by fluorination of nickel-chlorophosphine complexes with potassium fluorosulphinate.⁽⁴⁾ The fluorination of chlorophosphines, R_nPCl_{3-n} , with Group V fluorides usually led to fluorophosphoranes, R_nPF_{5-n} in excellent yield, instead of the expected derivatives of trivalent phosphorus, R_nPF_{3-n} , where n = 1 or $2^{(7m,10)}$.

An extensive study of organophosphorus-fluorine compounds⁽¹⁰⁾ led to the preparation of a number of phosphonic and phosphinic acid fluorides, $RP(X)F_2$ and $R_2P(X)F$ (R = organic group; X = O, S), whose synthesis and properties are discussed below. Phosphonic and phosphinic fluorides represent a new class of compounds, and a few

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representative examples have been described only recently, almost simultaneously by several different workers.^(3-6,7a-m) Usually the synthesis was by fluorination of the corresponding chlorides with hydrogen fluoride, alkali fluorides in polar solvents like tetramethylene sulphone or acetonitrile, potassium fluorosulphinate, potassium bi-fluoride, zinc fluoride, benzoyl fluoride, sodium hexafluorosilicate, etc.

In the present work, some of the above mentioned fluorinating agents were also employed. In addition, advantage was taken from the strongly reducing properties of fluorophosphines, which permitted a simple synthesis of phosphonic fluorides: dichlorophosphines were reacted with alkali fluorides in a polar solvent like acetonitrile in the presence of air and a catalyst, e.g.

The combination of antimony trifluoride with catalytic amounts of antimony pentachloride was used in a few instances (e.g. chloromethyl groups bonded to phosphorus in phosphonic chlorides). No attack on the carbon-chlorine bond was noted while the phosphorus-chlorine bond was readily fluorinated.

Phosphonic and phosphinic fluorides were frequently obtained on the preparation of the corresponding fluorophosphoranes, RPF_4 and R_2PF_3 ,⁽¹⁰⁾ particularly if moisture was not rigorously excluded. Due to the marked difference in reactivity of fluorine atoms in RPF_4 (and R_2PF_3) compounds, it was also possible to effect their partial hydrolysis under controlled conditions (temperature below 0°) with an equimolar amount of water, preferably in a solvent, e.g.

$$\operatorname{RPF}_4 + \operatorname{H}_2O \xrightarrow{\leq 0^\circ} \operatorname{RPOF}_2 + 2\operatorname{HF} \rightarrow (\xrightarrow{\operatorname{excess} \operatorname{H}_2O} \operatorname{RPO}(\operatorname{OH})_2)$$

It was also found in certain instances that on prolonged storage in glass fluorophosphoranes were converted to the corresponding phosphonic fluorides, e.g.

$$C_2H_5PF_4 \rightarrow C_2H_5POF_2$$

Phosphonic and phosphinic acid fluorides are relatively easy to handle, as compared with the corresponding fluorophosphoranes, the latter being far more sensitive towards hydrolysis. Compounds of the type RPSF₂ are more stable towards hydrolysis than RPOF_2 compounds, while $\operatorname{R}_2 P(X)F$ compounds (X = O or S) are generally more stable than $RP(X)F_2$. Some of the compounds possessed an unpleasant odour, which may be partially due to small amounts of impurities since highly purified compounds, particularly RPOF₂ and R₂POF, were found to be almost odourless. Characteristic is the smell of certain compounds containing the --PSF₂ group, some of them also fuming slightly in the atmosphere. Preliminary screening on possible biological properties of phosphonothioic diffuorides revealed activity of a lower order as compared with phosphinothioic monofluorides, R₂PSF^(7g) or phosphonamidothioic difluorides, RP(S)(NR₂)F^(6,7e,k) the latter being readily obtained upon interaction of secondary amines with phosphonothioic difluorides. These novel types of compounds are distinguished by their high insecticidal activity. Useful insecticides of the composition $R \cdot C_6 H_4 P(X)(OR')F$ (X = O or S) have been obtained via the phosphonic difluorides.^(11a) An independent synthesis of the same type of compounds has been described simultaneously.^(11b)

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Except for the above mentioned examples, little is known about the chemistry of phosphonic or phosphinic fluorides. It has been demonstrated that RPOF₂ intermediates are useful in the synthesis of unsymmetrical phosphinic acids via the GRIGNARD reaction.⁽⁵⁾ In a similar manner, phosphonic fluorides were employed as convenient intermediates in the synthesis of tertiary phosphine oxides, which are of current interest with respect to their application as high-temperature stable fluids.⁽¹²⁾ The electronegativity of the fluorine apparently facilitated the nucleophilic attack on the phosphorus atom in the Grignard reaction, where the corresponding chloro compounds failed to react in a defined manner. Phenylphosphonic difluoride was the starting material for an interesting synthesis of the tetrafluorophosphorane, $C_{e}H_{5}PF_{4}$, by fluorination of the P=O group with sulphur tetrafluoride.⁽¹³⁾

In connection with the present work, some interesting information was obtained on the orientation of phosphorus in the extensively explored and widely applied process of aromatic dichlorophosphination.

A standard method for the preparation of aromatic dichlorophosphines consists in the reaction of aromatic hydrocarbons with phosphorus trichloride/aluminium chloride, i.e. under Friedel-Crafts conditions, first introduced by MICHAELIS almost seventy years ago:^(14a,b)

$$\mathbf{R} \cdot \mathbf{C}_{6}\mathbf{H}_{5} + \mathbf{PCl}_{3} \xrightarrow{\mathrm{AlCl}_{3}} \mathbf{R} \cdot \mathbf{C}_{6}\mathbf{H}_{4} \cdot \mathbf{PCl}_{2} + \mathbf{HCl}$$

Although MICHAELIS considered the possibility of isomers in this reaction, little attention has been given to this question, since, and until recently the procedure was described to give essentially the para-isomers (cf. 15-21, for example).

KOSOLAPOFF⁽¹⁸⁾ assumed the presence of ortho and para-isomers in a phosphonate synthesis based on the corresponding aromatic dichlorophosphine, and reported later the formation of o, m, and p-isomer in the dichlorophosphination of toluene.⁽²²⁾ Some criticism of the classical Friedel-Crafts method has also been offered by ERLENMEYER^(23,24), who reported for the first time an unambiguous synthesis of o- and *p*-tolyldichlorophosphine. It is obvious that boiling points and refractive indices of the isomeric compounds show only little difference, and usually the reaction products of the Friedel-Crafts synthesis were regarded and used as p-substituted dichlorophosphines.

Recent work of MUETTERTIES^(25a,b), however, showed that dichloroborination of

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aromatic hydrocarbons under similar conditions as the dichlorophosphination invariably led to mixtures of m- and p-isomers (a m:p-ratio between 1:1, 5 and 1:5 being observed), whereas the o-isomer seems to be less favoured from sterical reasons. The isomer ratio was readily established by perhydrolysis of the dichloroborane mixture with subsequent IR identification of the corresponding substituted phenols:



A similar approach for dichlorophosphines is difficult due to the great stability of the carbon-phosphorus bond.

Fluorine (¹⁹F) nuclear magnetic resonance spectra of several substituted aromatic fluorophosphoranes were taken of tolyl-, chlorophenyl-, methoxyphenyl- and isopropylphenyl-tetrafluorophosphorane,⁽²⁶⁾ whose synthesis⁽¹⁰⁾ is based on the corresponding dichlorophosphines. In every case, the presence of at least two different species, presumably aromatic isomers, was revealed. The ¹⁹F nuclear magnetic resonance spectrum of the aryl-tetrafluorophosphoranes was found to consist of a single resonance split into a doublet by ³¹P, these data being consistent with a tetragonal pyramid structure with the aryl group at the apical position. The data can also be interpreted, however, in terms of a trigonal bipyramidal structure, and an intramolecular exchange process may be responsible for the NMR-spectroscopical equivalence of the fluorine atoms in fluorophosphoranes.

For the isomer mixture of the tolyl tetrafluorophosphoranes a P—F coupling constant of 960 c/s and an isomer ratio of ca. 2:1 was found. The corresponding data for tolylphosphonic difluoride, which was prepared from the same tolyldichlorophosphine, are 1099 c/s and ca. 2:1, respectively. Similarly, on gas chromatography analysis of the tolyltetrafluorophosphorane two peaks in an approximate ratio between 2:1 and 3:1 were observed. A preparative separation by gas chromatography in order to establish the identity of the isomers was then carried out on the tolylphosphonic difluorides since the highly reactive tetrafluorophosphoranes presented some handling difficulties. The reliability of the gas chromatography method was checked by running authentic samples of phenyltetrafluorophosphorane (1 peak), phenylphosphonic difluoride (1 peak), and isopropyl phenyltetrafluorophosphorane (2 components). It was impossible to analyse the original tolyldichlorophosphine under a variety of conditions without sizeable decomposition. It can, however, be safely assumed that the isomer distribution found in tolyltetrafluorophosphorane and

⁽²⁶⁾ E. L. MUETTERTIES, R. SCHMUTZLER and W. MAHLER. Submitted for publication.

tolylphosphonic difluoride also represents the composition of the starting tolyldichlorophosphine. Both analytical and preparative gas chromatography on the tolylphosphonic difluoride mixture showed an isomer ratio close to 2:1 (p:m, as will be demonstrated below). One of the separated isomers (p) was found to be solid at room temperature, while the other pure component was liquid. Both separated products were hydrolysed to give the corresponding phosphonic acids which were shown to be identical with authentic products, as summarized below. Hydrolysis of the original tolyltetrafluorophosphorane gave a mixture of isomeric phosphonic acids, melting over a range.



The results described do not rigorously exclude the presence of *ortho* compound but strongly support the presence of only two isomers in tolyldichlorophosphine, as ⁽²⁷⁾ A. BURGER and N. D. DAWSON, J. Org. Chem. 16, 1250 (1951) reported m.p. 188^{.5}-190°.

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obtained by the Friedel-Crafts method. A comparison of the refractive indices of pure o- and p-tolyldichlorophosphine^(23,24) with the value for the isomer mixture again indicates that the impurity of the p-isomer is m rather than o.

BALDWIN et al.⁽²⁹⁾ recently reported similar observations on the formation of isomers in the aromatic dichlorophosphination, using a different approach to establish the isomer ratio. Ethylphenyldichlorophosphine, for instance, was found to contain p- and m-isomer in a ratio 1.63:1, similar to tolyldichlorophosphine, as described above.

Infrared spectra of phosphonic and phosphinic fluorides

No observations on the infra-red spectra of phosphonic or phosphinic fluorides have been reported so far. In the course of the present work some data on the spectra of



compounds, where X and Y may represent F and Z = an organic group, or X = F and Y and Z = organic groups, were obtained and are summarized in Tables 1-4. For P=O compounds, an empirical relation between the electronegativity of the substituents in XYZP=O and the position of the P=O stretching frequency was given by BELL *et al.*⁽³⁰⁾

$$\lambda(\mu) = \frac{39.96 - \Sigma x}{3.995} \tag{A}$$

where $\lambda(\mu) =$ phosphoryl absorption wavelength

 $\Sigma x =$ sum of the phosphoryl absorption shift constants, derived from Pauling electronegativities.

Supported by data obtained on numerous different types of XYZP-O molecules with various substituents X, Y and Z, it was concluded that the effects of substituents upon the position of the P=O stretching frequency are constant and additive. It was therefore deduced that for this correlation the band-shifts observed are determined mainly by the electrical effect of the substituents upon the force constant rather than by mass effects. The results now obtained on numerous compounds of the types $RPOF_2$ and R_2POF (R = organic group) are in good agreement in most instances with the values calculated using Equation (A) and the phosphoryl absorption shift constants, as given by BELL et al.⁽³⁰⁾ Where available, data on the corresponding chloro compounds, RPOCl₂ and R₂POCl, are also included. The shift of the P=O absorption towards higher wave numbers, according to an increased double bond character, on substitution of chlorine by the more electronegative fluorine is obvious. P-F stretching frequencies also included in the table are derived from a comparison of RPOF₂ and R₂POF compounds with either the corresponding chloro compounds RPOCl₂ and R₂POCl, or with the chlorophosphines, RPCl₂ and R₂PCl, respectively. ⁽²⁹⁾ R. A. BALDWIN, K. A. SMITHEMAN and R. A. WASHBURN, J. Org. Chem. 26, 3547 (1961). (80) J. V. BELL, J. HEISLER, H. TANNENBAUM and J. GOLDENSON, J. Amer. Chem. Soc. 76, 5185 (1954).

TABLE 1. -PHOSPHONIC AND PHOSPHINIC FLUORIDES

						Analyses								
			Denting	30.14	Delling and of	, С Н Р			F	.				
Formula	Method	Reactants	Conditions	rield (%)	Refractive index	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Reference
CH ₃ POF ₂	A	cf. (A) Experimental	2070°/0-8 hr 70°/2 hr	88	$98-99^{\circ}$ $n_{\rm D}^{\rm S5} = 1.3170$							38-0	38.3	5, 7a, b, f
CICH ₂ POF ₂	С	CICH ₂ POCl ₂ (VICTOR) 0.2 mole 60 g KSO ₂ F (technical grade) in 100 ml <i>o</i> -dichlorobenzene	130°/2 hr	41	129.5-130 (a) $n_D^{25} = 1.3720$					23.0	22·2	28.3	27-9	7h, 12
	D	ClCH ₂ POCl ₂ 0·3 mole SbF ₃ 0·35 mole SbCl ₃ 1 g	60-80°/1·5 hr	85	$127-128^{\circ}$ $n_{\rm D}^{25} = 1.3721$							28.3	28-2	
	E	CICH,POCi_02 mole C6H5COF-0.5 mole	145°/3 hr	84	$127.5-128^{\circ}$ $n_{\rm D}^{25} = 1.3774$	8-9	8.8	1-5	1.5			28.3	28-0	
C ₂ H ₅ POF ₂	G	SbCl ₈ —1 g cf. (G)	cf. (b)	cf. (b)	53°/100 mm	21.2	21-3	4-4	4.6			33-3	32.7	7ь
n-C ₄ H ₉ POF ₂	G	cf. (G)	cf . (f)	cf. (f)	$n_{\rm D}^{20} = 1.3365$ $60-61^{\circ}/55 {\rm mm}$ $n_{\rm D}^{20} = 1.3700$	33-8	33-6	6.4	6.2					7Ь
C_6H_6 ·CH—CH·POF ₂	н	C ₈ H ₅ ·CHCH·POCl ₂ 0·12 mole KHF ₂ 0·26 mole in 75 ml benzene	80°/12 hr	31	$n_{\rm D} = 1.5300$ $67.5^{\circ}/0.1 \mathrm{mm}$ $n_{\rm D}^{22} = 1.5290$	51-0	50-9	3.8	3.6	16-5	16.6	20-2	19-8	-
H POF	с	C ₈ H ₁₁ POCl ₈ =0 1 mole 30 g KSO ₈ F in 60 ml benzene	80°/6 hr	46	$60-61^{\circ}/6 \text{ mm}$ $n_{\rm D}^{21} = 1.4138$	42·9	43-1	6-6	6.9	18-4	18-0	22.6	22.5	. –
C ₈ H ₃ POF ₂	В	$C_6H_8PCl_8=0.5$ mole NaF=1.5 mole Sb_8O_8=1 g in 130 ml CH_2CN	80°/10 hr	20-40	$77^{\circ}/15 \text{ mm}$ $n_{\rm D}^{\rm 45} = 1.4645$ (d)									4, 7d, 1, h ç
	С	C₀H₃POCl₂—0.2 mole 75 g KSO₂F in 120 ml benzene	80°/2·5 hr	95	$69^{\circ}/10 \text{ mm}$ $n_{\mathrm{D}}^{20} = 1.4669$					19-2	19-3	23.5	23-3	
$CH_{8} \cdot C_{8}H_{4}POF_{8} \ (m, p)$	в	$CH_3 \cdot C_6H_4PCl_2$ —0·1 mole (40) NaF—0·3 mole	80°/10 hr	54	$80-81^{\circ}/8 \text{ mm}$ $n_{\rm B}^{26-8} = 1.4850$							21-6	20·8 (e)	7d
	с	Sb_2O_3 0.5 g in 60 ml CH ₃ CN CH ₃ ·C ₆ H ₄ POCl ₂ 0.1 mole	80°/3 hr	68	97-5°/19 mm					17.6	17.5	21.6	21.5	
	F	$CH_3 C_8H_4POCl_3-0.2$ mole NaF0.6 mole in 80 ml	120–140°/3 hr	73	$n_{\rm D} = 1.4710$ 83-84-5°/8 mm $n_{\rm D}^{\rm ss} = 1.4710$							21-6	21-9	
$(CH_3)_2CH \cdot C_5H_4POF_2 (m, p)$	G	cf. (f)	cf. (G)		118–119°/19 mm	52-9	53·0	5.4	5.6	15-1	14.8	18-6	18.6	
Cl [.] C ₆ H ₄ POF ₂	G	$Cl \cdot C_8 H_4 PF_4 = 0.0206 \text{ mole}$	0°-25°/0·7 hr	50	$n_{\rm D}^{\rm ac} = 1.4701$ 73-75°/7 mm $n^{24.8} = 1.5056$							19-3	19-0	7d
(CH ₃) ₂ POF	С	(CH _a) ₂ POCl—015 mole KSO ₂ F techn. 40 g in 100 ml	80°/5 hr	77·1 %	$n_{\rm D} = 1.3030$ 69–70°/20 mm $n_{\rm D}^{23\cdot8} = 1.3940$	25.0	24.9	6-3	6.6			19-8	19-9	7c
(n-C4H2)3POF	G	cf. (f)	ef. (f)	cf. (f)	$118^{\circ}/9 \text{ mm}$ $n^{25} = 1.4650$	53-3	53·0	10-1	10-2	17·2	16-7	10-6	10.5	-
(CH _a)(C _e H ₅)POF	G	cf. (f)	cf. (f)	cf. (f)	$101-102 \cdot 5^{\circ}/4 \text{ mm}$ $n_{27}^{27} = 1.5436$	53·2	53·1	5.1	4.9			12.0	12.0	-
$(C_6H_3)_2POF$	С	(C ₈ H ₈) ₂ POCl (VICTOR)-0.25 mole 40 g KSO ₈ F in 120 ml benzene	80°/10 hr	60	$157^{\circ}/1.4 \text{ mm}$ $n_{\rm P}^{\rm sc} = 1.5730$	65·4	65-4	4.6	4.5	14.1	13-8	8.6	9.0	_
CH ₃ PSF ₂	А	cf. (A)	2070°/0·8 hr 70°/2 hr	88	59–60°							32.8	31.6	3;6; 7e.k.m
CICH ₂ PSF ₃	с	CICH ₂ PSCl ₂ (VICTOR)-0-2 mole 73 g KSO ₂ F in 120 ml c-di- chlorobenzene	100°/2 hr	65	$93.5-94^{\circ}$ $n_{\rm D}^{22} = 1.4433$	8-0	8.1	1.3	1.1					_
	D	ClCH ₂ PSCl ₂ -0·15 mole SbF ₂ -0·13 mole	60°/1-5 hr 100°/1 hr	92	93-5-94°	8-0	7·8	1-3	1.1	20.6	20-4	25-2	24.7	
C ₂ H ₆ PSF ₅	E	C ₂ H ₃ PSCl ₂ -0·1 mole NaF-0·15 mole in 70 ml	100140°/2 hr	89	90° (g)					23-8	24-1	29-2	28.9	6, 7e, k, m
	F	$C_{g}H_{s}PSCl_{g}=0.1$ mole $C_{g}H_{s}COF=0.25$ mole 1 g SbCl ₅	100°/3 hr	ca, 70	91–93°							29-2	28.6	
i-C ₈ H ₁₅ PSF ₂	с	$i-C_8H_{16}PSCl_2$ (h)—0·1 mole 37 g KSO ₉ F in 100 ml benzene	80°/4 hr	50	$83-84^{\circ}/12 \text{ mm}$ $n_{\rm P}^{25} = 1.4530$					14-6	14-6	17-9	18-3	-
C ₆ H ₅ ·CH==CH·PSF ₂	С	C ₈ H ₅ ·CH-CH·PSCl ₂ (h)-0.05 mole 43 g KSO ₂ F in 70 ml benzene	80°/6 hr	51	$63-65^{\circ}/0.8 \text{ mm}$ $n_{\rm D}^{25} = 1.5575$	47-0	47 ·4	3.5	3.7	15-2	15-3	18-6	18-3	-
(CH ₃) ₂ PSF	С	(CH ₃) ₂ PSCl (i)—0·2 mole 43 g KSO ₂ F in 150 ml benzene	80°/3 hr	53	$63.5-64.5^{\circ}/25 \text{ mm}$ $n_{D}^{23.9} = 1.4875$					27.6	27.1	16-9	16-5	7g
$(C_{g}H_{\delta})_{g}PSF$	н	(C ₈ H ₅) ₂ PSCI (k)0·1 mole KHF ₂ 0·26 mole	80°/12 hr	61	$168-172^{\circ}/1.5 \text{ mm}$ $n_{\rm D}^{30} = 1.6250$	61-0	60-8	4-3	4.0	13-1	13-2	8-0	7•5	

(a) The reported b.p. 112-13? (7b) is to low (C. W. TuLLOCK, personal communication);
 (b) This product was isolated in 80% yield on redistillation of a sample of C₂H₂PF₄ (b.p. 33)? after 6 no. storage in glass;
 (c) The b.p. 83-5° as given in (7b) should probably read 183-5°;
 (d) Identification by IR spectrum and refractive index (4c);
 (e) The product contained a small amount of impurity which could not be removed on distillation, IR comparison with the product obtained according to (C) or (F) showed identify;
 (f) Phosphonic and phosphinic fluorides were isolated as by-products on the proparation of the corresponding fluorephosphones; (10), (CH₂)CH₂CH₄H₇ = hc⁻¹H₂FP₄;
 (CH₃)C₄CH₃)FF₈, (ac, H₃)FF₈, respectively;
 (H) isolar-91-91, as given in (7m), is in lock agreement;
 (h) E. N. Watsu, T. M. Beck, and W. H. Woopstock, J. Amer. Chem. Soc., 77, 929 (1955);

(i) (CH₂),PSCI was isolated as the principal product on the preparation of (CH₄),PCI from [ICH₂),PSC] and C,H,PCI, according to the directions of G, W, PARSMALI, (33) and was characterized as identical with the previously described compound: 1. P. KOMKOV, K. W. KARAWANOV, and S. Z. IVIN, J. Gen. Chem. USSR. (Engl. Transl.) **28**, 2902 (1989). (CH₄),PSCI was also prepared by R. Collun and G. SCHRADRE, Ger. Pat. 1054(43) (April 1995). [10 Farthendhaften Bayer A G] and by L. MALER, Chem. Ber. **94**, 3051 (1961). The latter author boilated (CH₄),PSCI on reacting [ICH₄),PSC, With (CH₄),PSCI (instead of C, CH₄),PSCI (instead

Compound	vP==O (cm ⁻¹) found	νP=O cm ⁻¹ calc. from Eqn. (A)	νP—F (cn	a ⁻¹) found	Remarks
CH ₃ POF ₂	1334 vs		930 vs	887 vs	Dura
CICH ₂ POF ₂	1332 vs	1333	930 vs	916 vs	liquid
C ₂ H ₅ POF ₂	1328 vs		906 vs	880 vs	-
n-C4H9POF2	1333 vs		ca. 900 vs	885 vs (bd)	In benzene
	1332 vs	1349	896 vs	870 vs	Pure liquid
C ₆ H ₅ CH—CH·POF ₂	1321 vs	[1333]	ca. 900 (vs,	bd)	
C ₅ H ₅ POF ₂	1335 vs	1349	905 vs	875 vs	In benzene
ClC ₆ H ₄ POF ₂	1337 vs	1342	912 s	868 vs	Dune liquid
$\begin{array}{c} CH_3 \cdot C_6 H_4 \cdot POF_2 \\ (CH_3)_2 CH \cdot C_6 H_4 \cdot POF_2 \end{array}$	1330 vs 1336 vs	1349	902 vs 904 vs	878 vs 877 vs	
For comparison: POF ₃	1415 s ⁽³⁴⁾	1430			Gas

TABLE 2.—CHARACTERISTIC INFRA-RED ABSORPTIONS OF RPOF₂ COMPOUNDS

Table 3.—P==O stretching frequencies in $RPOCl_2$ compounds

Compound	$\nu P = O$ cm ⁻¹ found	vP=O calc. from Eqn. (A)	Lit. reference
CH ₃ POCl ₂	1270		35
CICH ₂ POCl ₂	ca. 1275 vs	1250	
C ₂ H ₅ POCl ₂	1273 vs		36
C ₆ H ₅ POCl ₂	1275 vs	1266	
For comparison: POCl ₃	1292	1290	37

ABLE 4.—CHARACTERISTIC INI	RA-RED ABSORPTIONS	OF R ₂ POI	- COMPOUNDS
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	vP=O	$\nu P = O$ (cm ⁻¹) calc. using	vP—F
Compound	(cm ⁻¹) found	Eqn. (A)	(cm ⁻¹) found
(CH ₃) ₂ POF	1250	1250	808 vs
(n-C ₄ H ₂) ₂ POF	1260 s	1250	819 vs
(CH _s)(C ₆ H ₅)POF	1258 s	1266	807, [786] vs
(C ₆ H ₅) ₂ POF	1256 s	1282	835 vs
-f (CII) DOCL D	0 1000	1 () (E	

cf. $(C_6H_6)_2$ POC1: ν P=O = 1233 cm⁻¹ (s) (Found) 1242 cm⁻¹ (Calc.)

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Far more uncertainty exists about the infra-red spectra of P-S compounds, and it has been stated that no useful correlation between the nature of the group attached to the phosphorus and the P-S stretching frequency can be made.^(31,32) The intensity (81) L. J. BELLAMY, The Infra-red Spectra of Complex Molecules p. 311 ff. Methuen, London (1958). (32) D. E. C. CORBRIDGE, J. Appl. Chem. (London) 6, 456 (1956). (33) F. N. HOOGE and P. J. CHRISTEN, Rec. Trav. Chim. 77, 911 (1958).

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of the P—S absorption was found to be very variable, and some P—S compounds did not show any absorption to be assigned to P—S. HOOGE and CHRISTEN⁽³³⁾ reported some semiquantitative considerations on the infra-red spectra of P—S compounds. In view of the small differences of electronegativities between P and S, implying only a small amount of ionic character of the P—S bond, as compared with P—O, electronegative substituents may be expected to have only little influence on the position of the P—S stretching frequency. The assignments for P—S stretching frequencies made in the present work were obtained by comparison of the spectra of P—S compounds with the corresponding sulphur-free compounds, but most of the data are only tentative and quite uncertain.

R ₂ 1 SI ⁺ COMFOUNDS				
Compound	$\nu P = S (cm^{-1})$ found	νP—F (cm ⁻¹)		
CH ₃ PSF ₂	?	856 vs 845 vs		
CICH ₂ PSF ₂	659 vs (?)	916 vs 888 vs		
C ₂ H ₅ PSF ₂	?	ca. 870 vs (bd)		
i-C ₈ H ₁₅ PSF ₂	ca. 680 vs (?)	882 vs 856 vs		
C ₆ H ₅ CH=CH·PSF ₂	?	905 vs 873 vs		
C ₆ H ₅ PSF ₂	?	895 vs 870 vs		
(CH ₃) ₂ PSF	756 vs	794 s (?)		
(C ₆ H ₅) ₂ PSF	738 vs (?)	827 vs		

TABLE 5a.—P—S AND P—F INFRA-RED ABSORPTIONS IN $RPSF_2$ and R_2PSF compounds

TABLE 5b.—P==S INFRA-RED ABSORPTION IN RPSCl₂ and R₂PSCl compounds

Compound	<i>ν</i> P =S (cm ⁻¹)	Lit. reference
CH.PSCl.	664*	36
C ₂ H ₅ PSCl ₂	Triplet at 680, 665, 640	36
i-C ₈ H ₁₅ PSCl ₂	ca. 680 vs, bd (?)	
C ₆ H ₅ PSCl ₂	745 s	37
(C ₆ H ₅) ₂ PSCl	735 vs (?)†	

* Comparison of the infra-red spectra of CH₃PCl₂ and CH₃PSCl₂ shows clearly one strong new band at 780 cm⁻¹ in the latter. Assignment to the P—S stretch however, is doubtful,^(33,36) and assuming ν P—S at 665 cm⁻¹ seems to be more justified. † (C₆H₅)₂PCl absorbs at 745 cm⁻¹ but the intensity of the 735 cm⁻¹ band in (C₆H₅)₂PSCl is greatly increased as compared with (C₆H₅)₂PCl, possibly due to the new P—S absorption.

EXPERIMENTAL

A. Reaction of chlorophosphines with potassium fluorosulphinate

The reaction of phenyldichlorophosphine with potassium fluorosulphinate has been described in a previous paper.⁽⁴⁾

Interaction of methyldichlorophosphine with potassium fluorosulphinate. One hundred and twenty grammes of Technical grade (ca. 35 per cent) potassium fluorosulphinate (Ozark Mahoning Co.) was suspended in 100 ml abs, decalin under nitrogen. An exothermic reaction started immediately

⁽³⁴⁾ H. S. GUTOWSKY and A. D. LIEHR, J. Chem. Phys. 20, 1652 (1952).

(35) J. QUINCHON, M. LESECH and E. GRYSZKIEWICZ-TROCHIMOWSKI, Bull. Soc. Chim. France 169 (1962).

(36) E. M. POPOV, T. A. MASTRYUKOVA, N. P. RODIONOVA, and M. I. KABACHNIK, J. Gen. Chem. USSR (Eng. Transl.) 29, 1967 (1959).

⁽³⁷⁾ L. W. DAASCH and D. C. SMITH, U.S. Naval Research Laboratory Report No. 3657 (1950).

on the dropwise addition of 35 g (0.3 mole) methyldichlorophosphine, and reflux of a low boiling material was observed. When the addition of the chlorophosphine was completed (50 min) the mixture was heated for 2 hr at 70° inner temperature. Distillation at atmospheric pressure gave 27.9 g (88.2 per cent) of CH₃PSF₂/CH₃POF₂, b.p. 57–99°.

On redistillation (10 in. helix-packed column) 4.9 g CH₃PSF₂ (b.p. 59–60°,* after fractionation, in agreement with Reference 3), and 13.2 g CH₃POF₂, b.p. 98–99°; $n_D^{25} = 1.3170$, was obtained.†

Reaction of dimethylmonodichlorophosphine with potessium fluorosulphinate. This reaction was solutide. This reaction was studied in essentially the same way as described above for methyldichlorophosphine. The starting chlorophosphine was prepared according to the directions of PARSHALL⁽³⁸⁾ with the modification that the crude mixture of dimethylchlorophosphine-dimethylphosphinothioic chloride was redistilled, over tributylphosphine. The yield of dimethylchlorophosphine could thus readily be doubled.

Dimethylchlorophosphine, 19.3 g (0.2 mole), was distilled into a dropping funnel attached to a 200 ml three-necked flask fitted with a reflux condenser and a mechanical stirrer in which 50 g technical potassium fluorosulphinate had been suspended in 100 ml benzene under strict exclusion of air and moisture. A strongly exothermic reaction occurred on the dropwise addition of the chlorophosphine to the stirred suspension. After the addition was completed the mixture was refluxed for 5 hr. The cooled mixture was filtered under nitrogen at atmospheric pressure and the volatile products were distilled off over a Vigreux column. Boiling point and refractive index of the distillate confirmed its identity as virtually pure benzene. A compound $(CH_3)_2PF$ would be expected to have a boiling point of approximately $40-50^{\circ}$ (b.p. $(CH_3)_2PCl = 75^{\circ}$). Several samples of the distillate were also analysed by gas chromatography,‡ and found to contain only negligible impurities, which did not show up in the infra-red spectrum.

The higher boiling residue was then distilled in a vacuum over a 4 in. Vigreux column to give a total of 12.5 g = 61.5 per cent of a colourless liquid, b.p. $60-72^{\circ}/20 \text{ mm}$. Two cuts, having the following refractive indices were taken:

(1)
$$n_{\rm D}^{24 \cdot 2} = 1.4590$$
 (2) $n_{\rm D}^{24 \cdot 4} = 1.4216$

By comparison with the refractive indices of the pure components $((CH_3)_2POF: n_D^{23\cdot 6} = 1.3940;$ $(CH_3)_2PSF: n_D^{23\cdot 9} = 1.4875$) the molar ratio $(CH_3)_2POF/(CH_3)_2PSF$ was found to be ca. 7:3 in the first cut and ca. 3:7 in the second. This result is in good agreement with the ratio derived from the VPC data obtained for cut 2: at 77° (40 cm³/min., 20 per cent silicon grease on 60–80 super support) 1 peak at 4.7 min = $(CH_3)_2POF$, 1 peak at 5.3 min = $(CH_3)_2PSF$; approximate ratio ca. 3:7. No by-products were detected by VPC. Identification of the components was by comparison with authentic $(CH_3)_2POF$ and $(CH_3)_2PSF$. The change in composition of cut (1) and (2) is also reflected in the infra-red spectra: the P==O stretching frequency at 1250 cm⁻¹ is much stronger in cut (1) than in cut (2), in accordance with the decreasing $(CH_3)_2POF$ content in the latter.

Reaction of chloromethyldichlorophosphine with potassium fluorosulphinate. There was no immediate exothermic reaction when 45.5 g (0.3 mole) chloromethyldichlorophosphine⁽³⁹⁾ was added dropwise to a suspension of 110 g technical potassium fluorosulphinate in 130 ml *o*-dichlorobenzene under nitrogen. Slight reflux of a lower boiling product was noted when the mixture was stirred at gradually increasing temperature up to 110° (2 hr). Distillation at atmospheric pressure gave first 5.5 g of a spontaneously flammable liquid, b.p. 33-40° (ClCH₂PF₂, c.f. 10). Only 0.3 g of ClCH₂PSF₂, b.p. 87-94°; $n_D^{25} = 1.4430$ (identified by b.p. and refractive index) was then isolated. The higher boiling products were recovered under vacuum (ca. 50 mm) and redistilled at atmospheric pressure at 119°; $n_D^{26} = 1.4520$ (cf. ClCH₂POF₂: $n_D^{25} = 1.3720$; ClCH₂POF₂: $n_D^{25} = 1.52.82$). Found: C, 8.4; H, 1.6; P, 21.8; F, 13.4. Calc. for ClCH₂PCl₂ · ClCH₂POF₂(285.8): C, 8.4; H, 1.4; P, 21.7; F, 13.3%).

Direct combination of chloromethyl dichlorophosphine with chloromethylphosphonic difluoride. No exothermic reaction occurred when 11.5 g (0.076 mole) chloromethyldichlorophosphine was added dropwise to 10.0 g (0.076 mole) chloromethylphosphonic difluoride. Distillation of the mixture at atmospheric pressure (under nitrogen protection) gave 21.0 g (97 per cent) of a colourless liquid, b.p. $119-120^{\circ}$; $n_D^{26.5} = 1.4470$. Boiling point and refractive index remained unchanged on redistillation over a 10 in. helix-packed column. Physical data and analysis confirmed that the product

* The b.p. 84° for CH₃PSF₂, as reported by SCHRADER^(6,7e,k) must be corrected (G. SCHRADER, personal communication); a difference of only 14° (84° vs. 98°) between the b.p. of CH₃PSF₂ and C₂H₅PSF₂ would be unlikely. In the meantime in another paper^(7m) a b.p. of 61–62° was reported.

[†] DAWSON and KENNARD⁽⁵⁾ reported for CH₃POF₂ b.p. 98–99°; $n_D^{25} = 1.3148$, while RAZUMOV and coworkers ^(7b) presumably had an impure product, reporting $n_D^{20} = 1.3277$.

[‡] The author is indebted to Mr. C. R. TALLEY for the gas chromatography work described herein. ⁽³⁸⁾ G. W. PARSHALL, J. Inorg. Nucl. Chem. 12, 372 (1960).

(39) E. UHING, K. RATTENBURY and A. D. F. TOY, J. Amer. Chem. Soc. 83, 2299 (1961).

was the same as above. Found: C, 8.6; H, 1.8; P, 22.0; F, 13.7; Cl, 49.1. Calc. for ClCH₂PCl₂· ClCH₂POF₂(285.8): C, 8.4; H, 1.4; P, 21.7; F, 13.3; Cl, 49.6%).

Infra-red spectra. The infra-red spectra were recorded on the pure components chloromethyldichlorophosphine and chloromethylphosphonic difluoride, and on the 1:1 products obtained upon interaction of $ClCH_2PCl_2$ with $KSO_2F(A)$ and on direct combination of $ClCH_2PCl_2$ with $ClCH_2POF_2$ (B), respectively.

The spectra of the 1:1 products appear essentially as a superposition of the spectra of the pure components, except for a strong absorption in product A at 1719 cm⁻¹, which cannot be explained, but may be due to an unknown impurity. The considerable shift of the P=O stretching frequency (1332 vs. 1352 cm⁻¹) indicates that this bond is involved in the interaction with the chlorophosphine while most of the other absorptions are virtually unchanged.

Gas chromatography on ClCH₂PCl₂ ClCH₂POF₂. ClCH₂POF₂ was clearly separated into two pure components (104° ; 60 cm³ carrier gas/min; 6 ft silicon oil column, 20 per cent on 60-80 super support); retention times 2.2 and 6.3 min., respectively. Comparison with authentic samples showed the 2.2 min. peak to be chloromethylphosphonic diffuoride, while the 6.3 min. peak was due to chloromethyldichlorophosphine.

ClCH ₂ PCl ₂	CICH ₂ POF ₂	CICH ₂ PCl ₂ ·CICH ₂ POF ₂	ClCH ₂ PCl ₂ ·ClCH ₂ POF ₂	
	1	(A)	(B)	
2980 m	2990 m	2990 s	2990 s	J.C. II
		2930 s	2930 s	PC-H
		1719 vs		
1388 vs	1395 m	1388 s	1388 s	$\delta C - H$
	1332 vs	1352 vs	1352 vs	vP==O
1286 vs		1276 m*	1280 vw	
	1232 m	1230 s	1229 s	
		1188 m	1187 m	
	1138 w	1134 m	1132 m	
	930 vs	930 vs	930 vs	
	916 vs	917 vs	917 vs	}v₽—r
	899 s	901 s	901 s	,
810 vs		813 s	813 s	
	795 m	796 s	• 796 s	
775 m		775 w	775 w	
746 s		746 s	746 s	
	712 sh	713 s	713 s	
	704 s	704 s	704 s	
682 vs		683 s	683 s)vC-Cl

* Position of band shifts with dilution with a solvent, e.g. benzene

B. Reaction of phenyldichlorophosphine with sodium fluoride/oxygen in acetonitrile in the presence of a catalyst

Only trace amounts of phenylphosphonic diffuoride were detected when air was bubbled through the stirred suspension of sodium fluoride in acetonitrile-phenyldichlorophosphine for 16 hr at 80°, and most of the dichlorophosphine was recovered unchanged. The reaction was more efficient when antimony trioxide or antimony pentachloride was added as a catalyst.

In a typical experiment, 63 g (1.5 mole) sodium fluoride +1 g antimony trioxide was suspended in a mixture of 89.5 g (0.5 mole) phenyldichlorophosphine and 130 ml acetonitrile, and air was bubbled through the suspension with stirring at reflux for 10 hr. After removal of the solids by filtration, 55 g of distillate, b.p. 40-84°/19 mm; $n_D^{s5} = 1.4740$ was obtained, no unreacted C₆H₈PCI₈ was found. On redistillation, 20 g of a product, b.p. 37-40°/18 mm (129-130°/760 mm); $n_D^{s5} = 1.4812$ was isolated, but not identified, while 22 g of the desired pure phenylphosphonic diffuoride, b.p. 77°/15 mm; $n_D^{s5} = 1.4645$ was further obtained. Identification of phenylphosphonic diffuoride was by boiling point, refractive index and infra-red spectrum.⁽⁴⁾ In another run, the amount of the lower boiling by-product was substantially lower. Antimony pentachloride was found to have catalytic properties similar to antimony trioxide.

C. The fluorination of phosphonic or phosphinic chlorides with potassium fluorosulphinate

The fluorination was conducted by suspending excess potassium fluorosulphinate(technical product of Ozark Mahoning Co.) in benzene, and dropwise addition of the compound to be fluorinated to the stirred suspension, the reaction being exothermic in some cases. The reaction mixtures were stirred until the evolution of sulphur dioxide had ceased (2-10 hr), and the products were isolated by vacuum distillation after removal of the solids by filtration and distillation of the solvent.

D. Fluorination with antimony trifluoride

These reactions were carried out in a three-necked flask fitted with a reflux condenser, thermometer, and a solid addition funnel, the latter containing a slight excess of antimony trifluoride. The P—Cl compound, together with a few drops of antimony pentachloride, was placed into the flask under nitrogen. An exothermic reaction occurred when the antimony trifluoride was gradually added, a temperature of ca. $50-60^{\circ}$ being maintained. Stirring at this temperature was continued for 1-2 hr and the product was isolated by distillation.

In the specific examples investigated the addition of antimony pentachloride could probably have been omitted since a fluorination of the C—Cl bond did not occur, and P—Cl compounds normally react with antimony trifluoride in the absence of a catalyst.

E. Benzoylfluoride as a fluorinating agent

This compound^(7h) was used in slight excess in combination with small amounts of antimony pentachloride as a catalyst. The P—Cl compound was added to the benzoyl fluoride with stirring, and a temperature of $100-150^{\circ}$ was maintained for ca. 3 hr. The fluorination products were isolated by distillation.

F. Fluorinations with sodium fluoride in tetramethylene sulphone (TMSO)

These reactions were carried out according to the directions of TULLOCK and COFFMAN^(7h) by the dropwise addition of the P—Cl compound to excess oven-dried sodium fluoride, suspended in TMSO, with stirring. The reaction mixtures were stirred at elevated temperature for the period indicated, and the fluorides were isolated by distillation, followed by careful fractionation.

G. Controlled hydrolysis of fluorophosphoranes

A typical example is as follows: chlorophenyltetrafluorophosphorane^(7d,10) was dissolved in a small amount of tetrahydrofurane and the exact equimolar amount of water was gradually added at or below 0° (cooling with ice-salt). After the exothermic reaction had subsided the mixture was allowed to warm up to room temperature, and stirring was continued for 0.5–1 hr. After removal of the solvent the phosphonic fluoride was isolated by distillation *in vacuo*.

Other phosphonic or phosphinic fluorides were isolated as by-products on the preparation of the corresponding fluorophosphoranes, while ethylphosphonic diffuoride, for example, was obtained on redistillation of a sample of ethyl tetrafluorophosphorane (b.p. 32-33°), which was stored in a glass vial over a prolonged period (ca. 6 months).

H. Fluorination with potassium bifluoride

The P-Cl compound was stirred with an excess of the fluorinating agent in refluxing benzene.

Remarks on the aromatic dichlorophosphination

a. *Preparations*. In the preparation of aromatic dichlorophosphines the procedure of BUCHNER and LOCKHART⁽²⁰⁾ was followed. Boiling points and refractive indices were found in agreement with the reported data. It may be noted that on the preparation of isopropyl-phenyldichlorophosphine some dealkylation occurred, phenyldichlorophosphine being among the products identified. A similar observation has been made in the preparation of ethylphenyldichlorophosphine.⁽²⁹⁾

The tolyldichlorophosphine more closely investigated had b.p. $99^{\circ}/5$ mm; $n_D^{20} = 1.5901$; $n_D^{25} = 1.5880$; $n_D^{27} = 1.5871$. The yield was between 65-70 per cent. A slight difference in composition of the isomer mixture as reflected by a small change in refractive index on different preparations under essentially identical conditions was noted. The lack of homogeniety of the product thus obtained was also indicated by comparison of its refractive index with the data for authentic *o*- and *p*-tolyldichlorophosphine:^(23,24) o, $n_D^{20} = 1.598$; $p, n_D^{20} = 1.591$, the impurity in the *p*-compound probably being the *m*- rather than the *o*-isomer, since the latter has a refractive index higher than pure *para*).

The preparation of aryl tetrafluorophosphoranes will be described elsewhere.⁽¹⁰⁾ B.p. $CH_3 \cdot C_6 H_4 \cdot PF_4 = 44^{\circ}/4$ mm. Tolylphosphonic dichloride was made from the tolyldichlorophosphine isomer mixture according to the directions of $Toy^{(40)}$, b.p. $161-164^{\circ}/18$ mm; $n_{25}^{25} = 1.5546$ (reported: $n_{25}^{25} = 1.5542$). Fluorophosphoranes and phosphonic fluorides were hydrolysed by repeated evaporation with excess water on a steam-bath. The mixture of the isomeric tolylphosphonic acids and the ⁽⁴⁰⁾ A. D. F. Toy, J. Amer. Chem. Soc. **70**, 186 (1948).

pure *p*-isomer were recrystallized from water, while the hydrolysis product from *m*-tolylphosphonic difluoride was dried over phosphorus pentoxide at $45^{\circ}/0.1$ mm for 24 hr. after evaporation to dryness. The gummy solid thus obtained was dissolved in a small volume of benzene, decolorized with charcoal and recrystallized from 1:1 benzene-hexane to give white crystals.

b. Vapour phase chromatography. A Perkin Elmer Model 154 Analytical Gas Chromatograph (10 ft \times 1/4 in. column) was used for the analytical work:

 $C_6H_5PF_4$: at 156° (40 cm³ carrier gas (helium) per min), 1 peak at 14.5 min.

 $C_6H_5POF_2$: at 152° (40 cm³ carrier gas/min), 1 peak at ca. 19.6 min, in accordance with a b.p. of ca. 185° vs. 135° for $C_6H_5PF_4$.

 CH_3 : C_6H_4 : PF₄: at 155° (40 cm³ carrier gas/min), 2 peaks (approximate ratio 2:1-3:1) at 12 and 14.5 min, respectively.

 $CH_3 \cdot C_6H_4 \cdot POF_2$: at 168° (40 cm³ carrier gas/min), 2 peaks (approximate ratio 2:1-3:1) at 24.2 and 31.1 min, respectively.

 $(CH_3)_2CH C_6H_4 POF_2$: at 156° (40 cm³ carrier gas/min), 2 peaks (apporximate ratio 2:1-3:1) at 45 and 48 min, respectively. The isomer mixture has b.p. 118-119°/19 mm.

All runs were carried out on a diisodecyl phthalate column. The tolyldichlorophosphine was run at 175° on a di-isodecyl phthalate column and at 202° on a silicon oil column DC 200. The material could not be eluted under these conditions and some chemical change seemed to occur.

The preparative separation of the tolylphosphonic fluoride isomers was carried out on a gas chromatograph Autochrome 200 (Potomac Instruments Co., Springfield, Va). with a silicon oil (20 per cent on fire brick) column, 14 ft \times 1 in., temperature 154°C, flow rate of carrier gas ca. 600 cm³/min. Retention times of 95 min (m) and 110 min (p) were observed. The identification of the separated compounds (purity checked by analytical VPC) is described above.