Reaction of Xenon Difluoride. Part II. Oxidative-fluorination of Phosphorus and Iodine Compounds and Cleavage of Silicon–Sulfur and Silicon–Nitrogen Bonds[1]

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Reaction of alkyl(aryl)phosphines with xenon difluoride gives alkyl(aryl)hydridofluorophosphoranes which were characterized by proton and fluorine n.m.r. spectroscopy. With phenylchlorophosphines, substitution of chlorine by fluorine accompanied oxidative-fluorination to give phenylfluorophosphoranes, $(C_6H_5)_nPF_{5-n}$. With *tert*-butylchlorophosphines, chlorination of the *tert*-butyl group accompanied oxidative-fluorination, and a mixture of products was obtained. Reaction of xenon difluoride with methyl iodide gives methyliodine(III) difluoride, characterized by proton and fluorine n.m.r. spectroscopy.

Silicon–sulfur and silicon–nitrogen bonds are cleaved by xenon difluoride and an intermediate containing a xenon–nitrogen bond is postulated.

Reaction of xenon difluoride with hexafluoroacetone, perfluoropinacol, or disodium perfluoropinacolate failed to give stable xenon esters.

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La réaction des alkyl(aryl)phosphines avec le difluorure de xénon conduit aux alkyl(aryl)-hydridofluorophosphoranes que l'on a caractérisé par spectroscopie r.m.n. du proton et du fluor. Avec les phénylchlorophosphines, une substitution du chlore par du fluor accompagne la fluoration oxydative pour fournir des phénylfluorophosphoranes, $(C_6H_5)_nPF_{5-n}$. Avec les *tert*-butylchlorophosphines, une chloration du groupement *tert*-butyle accompagne la fluoration oxydative et on obtient un mélange de produits. La réaction du difluorure de xénon avec l'iodure de méthyle fournit le méthyl difluorure d'iode(III) que l'on a caractérisé par spectroscopie r.m.n. du fluor et du proton.

Les liens Si—S et Si—N sont coupés par le difluorure de xénon et on fait l'hypothèse qu'il y a formation d'un intermédiaire contenant un lien Xe—N.

La réaction du difluorure de xénon avec l'hexafluoroacétone, le perfluoropinacol ou le perfluoropinacolate de sodium ne donne pas d'esters stables du xenon.

[Traduit par le journal]

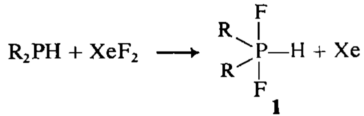
The reactions of xenon difluoride with a variety of main group compounds were investigated with the aim of comparing the reactivity and fluorinating ability of XeF_2 to the more common fluorinating agents of groups VA to VIIA. Previously we described some reactions of XeF_2 with organosilicon compounds (1) and with $(C_6H_5)_2PC(OH)(CF_3)_2$ (2), while other workers have reported the reactions with organic compounds, including aromatics (3), olefins (4), acetylenes (5), and acids (6). XeF_2 is known to react with chlorides of various metals (7), and the oxidation of zinc tetraphenylporphyrin has been reported (8). Adducts of XeF_2 with metal fluorides have been studied in some detail and recent review articles are available (9).

Results and Discussion

XeF_2 and Phosphines

The previous finding that XeF_2 did not attack silicon–hydrogen bonds (1) suggested that oxidative-fluorination of phosphines might occur without destruction of the P—H bond. This was confirmed for reactions of XeF_2 with dialkyl(aryl)phosphines and monoalkylphosphines (eqs. 1 and 2).

[1]



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a R = C_6H_5
b R = CH_2CH_2CN

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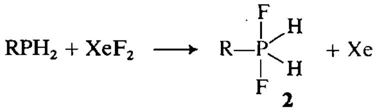
[1] Taken in part from the doctoral dissertation of J. A. Gibson, University of Manitoba, 1973. Presented in part at the 6th International Symposium on Fluorine Chemistry, Durham, England, July 18–23, 1971, and at the 55th Canadian Chemical Conference, Quebec City, June 4–7, 1972.

TABLE 1. Proton and fluorine n.m.r. chemical shifts and coupling constants of some alkyl(aryl)hydridofluorophosphoranes

	Chemical shifts (p.p.m.)*		Coupling constants, J (Hz)				
Compound	H_e	F_a	H_eP	H_ePF_a	H_ePCH	F_aP	F_aPCH
1*a* $(C_6H_5)_2PHF_2$	−6.45	+51.7	773.4	110	—	612	—
1*b* $(NCCH_2CH_2)_2PHF_2$	−6.92	+61.2	757.7	100.5	3.5	595	6.5
2*a* $NCCH_2CH_2PH_2F_2$	−6.94	+60.5	743.0	89	3.8	556	6.0
2*b* $C_6H_{11}PH_2F_2$	−6.75	+65.2	714	92	br	567	br

*Proton and fluorine chemical shifts relative to internal TMS and external $CFCl_3$. Compounds were dissolved in 1:2 (v/v) mixture of $CDCl_3$ and CD_3CN and spectra recorded at ambient probe temperatures.

[2]


$$RPH_2 + XeF_2 \longrightarrow R{-}PH_2F_2\ (\mathbf{2}) + Xe$$

a $R = CH_2CH_2CN$
b $R = C_6H_{11}$

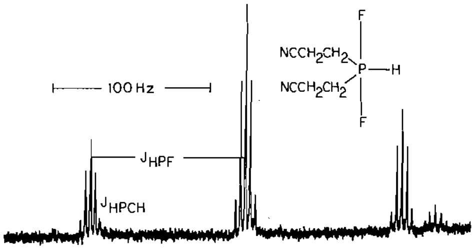


FIG. 1. Proton n.m.r. spectrum of $(NCCH_2CH_2)_2$-PHF_2 showing low field half of symmetrical doublet (P—H coupling). Chemical shifts and coupling constants are found in Table 1.

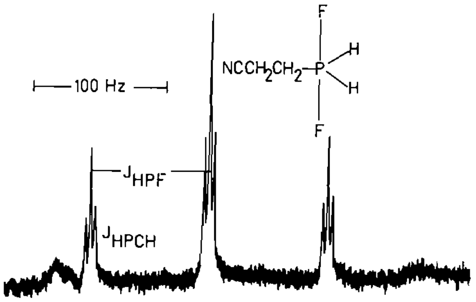


FIG. 2. Proton n.m.r. spectrum of $NCCH_2CH_2PH_2$-F_2 showing low field half of symmetrical doublet (P—H coupling). Chemical shifts and coupling constants are found in Table 1.

Reactions were carried out in acetonitrile solution in standard n.m.r. tubes under anhydrous conditions at −35 to −15 °C and the products were formed in yields of at least 90%. Xenon gas was removed and identified by mass spectrometry and the products were characterized by proton and fluorine n.m.r. The n.m.r. data are consistent with trigonal bipyramidal geometry in which fluorines occupy axial positions and alkyl(aryl) and hydrogen substituents occupy equatorial positions.

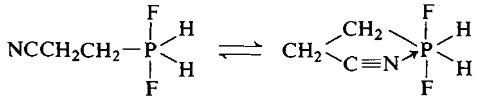
The chemical shifts and coupling constants of products **1** and **2** are summarized in Table 1 and typical proton n.m.r. spectra of **1***b* and **2***a* are shown in Figs. 1 and 2. The n.m.r. spectra are well resolved at room temperature thus indicating that intermolecular fluorine or hydrogen exchange is extremely slow on the n.m.r. time scale. Only the cyclohexyldihydridofluorophosphorane **2***b* showed somewhat broadened lines in the n.m.r. spectrum, hence J_{F_aPCH} and J_{H_ePCH} could not be estimated, but this broadening could be due to conformational equilibrium of the cyclohexyl ring.

The n.m.r. spectra were recorded in acetonitrile solution and, since it is known that acetonitrile forms a 1:1 complex with phosphorus pentafluoride (10), it is possible that products **1** and **2** interact with solvent CH_3CN in a typical Lewis acid–base manner (eq. 3) involving five and six

[3] $RPH_2F_2 + CH_3CN \rightleftharpoons RPH_2F_2{:}NCCH_3$

coordinate structures. In order to examine this possibility the preparation of $NCCH_2CH_2PH_2$-F_2 **2***a* was carried out in CH_2Cl_2 solution. The n.m.r. spectrum in CH_2Cl_2 gave a chemical shift of F_a = 58.7 p.p.m. and $J_{H_ePF_a}$ = 89 Hz, J_{H_ePCH} = 3.8 Hz, and J_{F_aP} = 566 Hz. These values are reasonably close to those observed in acetonitrile solution and therefore the equilibrium of [3], if it is rapid, must be essentially to the left and the data of Table 1 refer to five coordinate molecules.

Rapid intramolecular Lewis acid–base reaction is also possible, but the equilibrium of [4] must lie essentially to the left, since the chemical shifts and coupling constants of **1***a* and **2***b*, where no cyano substituent is present, are very similar to those of **1***b* and **2***a*.

[4]


The reaction of XeF_2 with phosphines represents a convenient synthesis of mono- and dihydridofluorophosphoranes, although other synthetic routes are known, such as addition of alcohols, thiols, or amines to fluorophosphines (11), reaction of fluorophosphoranes with trimethylstannane or trimethylsilane (12), and reaction of KHF_2 with chlorophosphines or HF with alkylphosphines and phosphorous acids (13).

Reaction of chlorophosphines with XeF_2 was studied since it was of interest to establish whether oxidative-fluorination would occur without affecting the P—Cl bond. In the case of organosilicon chlorides, XeF_2 invariably converted Si—Cl to Si—F bonds (1).

The reaction of chlorophenylphosphines with XeF_2 gave fluorophenylphosphoranes, as well as Xe and Cl_2. Intermediate chlorofluorophenylphosphoranes were not identified and the relative ease of oxidative-fluorination *vs.* chlorine substitution could not be studied. Since one of the end products of reactions 5 and 6 is Cl_2, there is the further possibility that fluorophenylphosphoranes are formed as a result of oxidative-chlorination followed by fluorination. The reaction with triphenylphosphine was therefore carried out, as Cl_2 is not produced in this reaction, and oxidative-fluorination occurred under conditions very similar to those of $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$; hence it is reasonable to assume that XeF_2 is the effective oxidizing reagent in reactions 5–7.

$$[5] \qquad C_6H_5PCl_2 \xrightarrow{XeF_2} C_6H_5PF_4$$

$$[6] \qquad (C_6H_5)_2PCl \xrightarrow{XeF_2} (C_6H_5)_2PF_3$$

$$[7] \qquad (C_6H_5)_3P \xrightarrow{XeF_2} (C_6H_5)_3PF_2$$

When the reaction was extended to *tert*-butylchlorophosphines, oxidative-fluorination was again observed but, at the same time, extensive chlorination of the *tert*-butyl group occurred and the products were not characterized. Chlorination of alkyl groups was observed previously during reactions of $(CH_3)_2SiCl_2$ and $C_6H_5(CH_3)_2SiCl$ where $CH_3(CH_2Cl)SiF_2$ and $C_6H_5(CH_3)(CH_2Cl)SiF$ were formed in about 25% yield (1).

XeF_2 and Iodine Compounds[2]

The syntheses of perfluoroalkyliodine(III and V) fluorides involve the use of powerful fluorinating agents such as F_2, BrF_3, and ClF_3 (14–19) and these would not be applicable to the syntheses of alkyliodine fluorides owing to destructive fluorination of alkyl groups. Since XeF_2 oxidizes phosphorus(III) compounds without attacking alkyl or aryl groups (unless a P—Cl bond is present), it seemed reasonable that oxidation of iodine compounds might also be accomplished under mild conditions.

The reaction of XeF_2 with an excess of methyl iodide proceeded smoothly for 20 min, in the absence of solvent at room temperature, in essentially quantitative yield; no reaction was observed below −40 °C.

$$XeF_2 + CH_3I \rightarrow CH_3IF_2 + Xe$$

The proton and fluorine n.m.r. spectra of CH_3IF_2, dissolved in excess methyl iodide, gave a triplet at −4.23 p.p.m. (external TMS) and a quartet at +176.4 p.p.m. (external $CFCl_3$) with $J_{HCIF} = 7$ Hz (Fig. 3). The fluorine chemical shift is close to that of CF_3IF_2 (+172.7 p.p.m. (15)) and other iodine(III) fluorides, such as $CF_3IF_2 \cdot$pyridine (+174.6 (17), $SF_5(CF_2)_2IF_2$ (+175.6 (16)), and IF_3 (+165 (18)).

CH_3IF_2 was found to be surprisingly stable in solution, 50% remaining after 4 h at 20 °C, suggesting that the product is at least as stable as CF_3IF_2 (14, 15). Excess of methyl iodide may be removed *in vacuo* from the involatile product. The product reacts slowly with glass and rapidly with mercury, while decomposition at room temperature gives iodine and oily material.

The reaction of XeF_2 with isopropyl iodide was also carried out; however, the reaction was extremely rapid at 0 °C and iodine was one of the end products. Fluorine n.m.r. confirmed the disappearance of XeF_2 but failed to detect the desired isopropyliodine(III) difluoride.

Reaction of XeF_2 with excess phenyl iodide proceeded at 0 °C to give a product with a fluorine chemical shift of +170.4 p.p.m. (half-height width 4 Hz). The chemical shift is characteristic of iodine(III) fluorides and is assigned to $C_6H_5IF_2$. The product is fairly stable, 80% remaining after standing at 5 °C for 12 h. During this time another peak appeared at +173.8 p.p.m., half-height width 18 Hz, which may be

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[2] The synthesis of methyliodine(III) difluoride has been reported in a preliminary account (40).

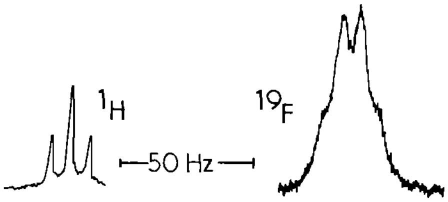

FIG. 3. Proton and fluorine n.m.r. spectra of CH_3IF_2. See text for chemical shifts and coupling constants.

assigned to partially fluorinated phenyliodide(III) difluoride, $C_6H_xF_yIF_2$, since the chemical shift is that of an iodine(III) fluoride while the half-height width is consistent with coupling to *ortho* fluorines ($J_{\mathrm{FICF}} = 26$ Hz for $C_6F_5IF_4$ (19)).

The stability of $C_6H_5IF_2$ may be compared with $C_6F_5IF_2$ which decomposes rapidly above -5 °C (20). It is interesting that both CH_3IF_2 and $C_6H_5IF_2$ are found to be at least as stable as their perfluoro analogs, however, this 'stability' probably reflects the influence of impurities, since any synthesis involving XeF_2 probably introduces fewer impurities than reagents such as F_2 or ClF_3 and catalyzed decompositions are less likely.

Reaction of XeF_2 with I_2 in acetonitrile solution occurred very slowly and the iodine color was discharged over a period of 24 h at 20 °C. This slow reaction is probably due to the introduction of HF, as a result of decomposition of XeF_2/CH_3CN solution (1, 39), since it has been shown that I_2 is rapidly oxidized by XeF_2 in CH_3CN if an acid such as HF is introduced (21). It was also observed that reaction with I_2 could be speeded up by adding $(CH_3)_3SiF$ to the solution, and the iodine color was now discharged within 5 min. In separate experiments it was shown that $(CH_3)_3SiF$ does not react with XeF_2 or with I_2, therefore, $(CH_3)_3SiF$ must be a sufficiently strong Lewis acid to catalyze oxidation of I_2 in the manner of HF, BrF_3, and SO_2 (21, 22).

XeF_2 and Organosilicon Compounds

Reactions of Si—S, Si—N, and Si—O compounds with, for example, fluorides of phosphorus (23), sulfur (24), or iodine (25) have been widely used to prepare substituted derivatives of these elements. We therefore studied the reactions of Si—S and Si—N compounds (Si—O bonds are unreactive towards XeF_2 (1)) with the aim of preparing Xe—S or Xe—N compounds or, failing that, to gain evidence of their formation as intermediates.

The reaction of XeF_2 with *tert*-butylthiotrimethylsilane in acetonitrile solution proceeded smoothly to give di-*tert*-butyldisulfide in high

$$XeF_2 + (CH_3)_3SiSC(CH_3)_3 \rightarrow (CH_3)_3CSSC(CH_3)_3 + (CH_3)_3SiF + Xe$$

yield, along with minor amounts of $(CH_3)_3CSSSC(CH_3)_3$ and $(CH_3)_3CSH$. Xenon and $(CH_3)_3SiF$ were recovered quantitatively.

In the absence of solvent, the reaction was more complex, most probably due to the rapidity of the reaction and inadequate cooling, and the products were S_8, $(CH_3)_3CS_nC(CH_3)_3$ where $n = 2$–7, and $(CH_3)_3CF$, as well as the expected Xe and $(CH_3)_3SiF$.

The reactions of XeF_2 with silicon–nitrogen compounds such as $[(CH_3)_3Si]_2NH$ and $(CH_3)_3SiNR_2$ where R = CH_3, C_2H_5, $(CH_3)_2CH$ were studied extensively but few firm conclusions can be made at this time, partly because of the hazardous nature of these reactions (see Experimental section).

Despite difficulties, it was possible to show that reaction

$$XeF_2 + 2(CH_3)_3SiNR_2 \rightarrow 2(CH_3)_3SiF + Xe + R_2N(?)$$

gave quantitative yield of xenon and always more than 90% $(CH_3)_3SiF$. The fate of the dialkylamino fragment was investigated as described in greater detail in the Experimental section. All reactions produced dialkylamines with yields in the order $(CH_3)_2NH < (C_2H_5)_2NH < [(CH_3)_2CH]_2NH$. Presumably, $R_2N\cdot$ radicals are formed in solution, followed by hydrogen abstraction from solvent acetonitrile or reagents. Nitrogen-containing radicals are known to react with CH_3CN (26) and a g.c./m.s. study of products from reaction of $(CH_3)_3SiN(CH_3)_2$ showed a g.c. peak with ions *m/e* 84, 83, 58, 44, 42 assigned to $(CH_3)_2NCH_2CN$.

Oily, polymeric material was formed in all reactions with Si—N compounds, in some cases molecular weights greater than 750 were confirmed by mass spectrometry. Polymerization via dialkylamino, *e.g.*

$$(CH_3)_2N\cdot \rightarrow CH_3N{=}CH_2 \rightarrow \text{polymer}$$

radicals has been suggested in the literature (27).

The original goal of preparing Xe—N or Xe—S compounds was not realized, however, the production of $R_2N\cdot$ and $RS\cdot$ radicals is consistent with homolytic bond fission of intermediates such as F—Xe—NR_2 or F—Xe—SR. The reaction of $(CH_3)_3SiN(CH_3)_2$ with XeF_2 gave further evidence of an intermediate, since it was observed that reaction at −25 to −30 °C produced a white solid, before the onset of violent reaction, and it is tentatively suggested that the solid is $FXeN(CH_3)_2$. LeBlond and DesMarteau have reported very recently the synthesis of a stable Xe—N compound $FXeN(SO_2F)_2$ which decomposes at 70 °C to give $[N(SO_2F)_2]_2$, Xe, and XeF_2 (28).

Attempts to prepare xenon–nitrogen compounds[3] by reaction of XeF_2 and $(CH_3)_3SiN{=}C(CF_3)_2$ gave only Xe, $(CH_3)_3SiF$, and $(CF_3)_2C{=}NH$, while reaction with $(CF_3)_2C{=}NLi$ gave Xe, $(CF_3)_2C{=}NH$, and LiF.

Impurities and Fluorine Exchange

Previously we showed that H_2O and HF impurities are invariably present in solutions containing reactive fluorides and that n.m.r. spectroscopy may conveniently monitor the presence of these impurities (29). In the case of the less reactive $(CH_3)_3SiF$, hydrolysis and fluorine exchange are catalyzed by dialkylamines (30).

The elimination of trace amounts of impurities was also one of the recurring experimental problems encountered in this work. Since reactions were carried out with XeF_2/CH_3CN solutions, which decompose at room temperature in Pyrex glassware (1, 39), it appears likely that HF and H_2O, along with other impurities, were present in reaction mixtures. Decomposition of hydridofluorophosphoranes and methyliodine(III) difluoride was catalyzed by impurities and it is not known to what extent the isolation of new xenon derivatives may have been prevented by impurities.

In some reactions, n.m.r. spectroscopy confirmed the presence of H_2O and HF impurities. For example, $(CH_3)_3SiF$ and dialkylamines were produced in reactions of XeF_2 and silicon–nitrogen compounds (*vide supra*) and the proton n.m.r. spectrum of $(CH_3)_3SiF$ in some samples showed a single peak rather than the expected doublet. This collapse of the doublet is due to the dialkylamine catalyzed hydrolysis of $(CH_3)_3SiF$

$$(CH_3)_3SiF + H_2O \rightleftharpoons (CH_3)_3SiOH + HF$$

as reported previously (30). No evidence was found of fluorine exchange between XeF_2 and $(CH_3)_3SiF$, as the chemical shift and coupling constant of unreacted XeF_2 showed no change in these solutions.

XeF_2 and Hexafluoroacetone, Perfluoropinacol, and Disodium Perfluoropinacolate

No reaction was detected between hexafluoroacetone and XeF_2, either in acetonitrile as solvent, without solvent, or in the presence of CsF. Some $(CF_3)_2CFOH$ was produced slowly when reaction was carried out in acetonitrile, but this may be explained as the product of HF addition to $(CF_3)_2CO$. Perfluoropinacol was also resistant to attack by XeF_2.

Reaction of XeF_2 with $OC(CF_3)_2C(CF_3)_2O^{2-}$ $2Na^+$ failed to give a stable xenon heterocyclic derivative, the products being NaF, Xe, $(CF_3)_2CO$, and $HOC(CF_3)_2C(CF_3)_2OH$. Perhaps the desired intermediate was formed, which then oxidized to $(CF_3)_2CO$ or reacted with trace amounts of HF or H_2O to liberate perfluoropinacol, but this could not be established.

Experimental

CAUTION: Reaction of XeF_2 with silicon–nitrogen compounds may lead to explosions. Furthermore, the production of Cl_2 or Cl from reaction of XeF_2 with chlorides of P, Si, Ge, etc., may lead to potentially hazardous chlorinations. All reactions involving XeF_2 were carried out behind ⅜ in. acrylic plastic safety shields within a fume cupboard.

General

XeF_2 was prepared photochemically (31) or obtained commercially (PCR, Gainesville) and dissolved in dried (P_2O_5) and distilled CH_3CN to give approximately 0.5 *M* solutions. These solutions were standardized by reacting aliquots with mercury and weighing xenon gas produced. $(CH_3)_3SiN(CH_3)_2$ was prepared by treating $(CH_3)_3SiCl$ with a 2:1 excess of dimethylamine in xylene (32) and distilling the product. $(CH_3)_3SiN[CH(CH_3)_2]_2$ was prepared in a similar manner. $(CH_3)_3SiN(C_2H_5)_2$ (PCR) and methyl iodide (Eastman) were redistilled prior to use. $(CH_3)_3SiSC(CH_3)_3$ was kindly supplied by O. C. Vaidya and checked to be free of *tert*-butylthiol. Hexamethyldisilazane (Alfa), organochlorosilanes (PCR), $(CH_3)_3GeBr$ (Alfa), organophosphines (Aldrich), chloro-*tert*-butylphosphines (Strem), and di-*tert*-butyldisulfide (PCR) were used without further purification.

Fluorine and proton nuclear magnetic resonance spectra were recorded on Varian A-56/60A and HA100D spectrometers. Chemical shifts are relative to TMS and $CFCl_3$, positive shifts indicating high field shifts. Mass spectra were obtained on a Finnigan 1015 quadrupole mass spectrometer coupled to a Varian 1700 gas chromatograph. Electron spin resonance experiments were carried out on a Varian E-3 e.p.r. instrument. Elemental analyses were performed by Alfred Bernhardt, West Germany.

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[3] A. F. Janzen and S. N. Kay. Unpublished results.

XeF$_2$ and Triphenylphosphine

$(C_6H_5)_3P$ (0.052 g, 0.20 mmol) in CH_3CN (0.3 ml) was added to XeF_2 (0.12 mmol) in CH_3CN (0.3 ml) at −10 °C. Reaction occurred on warming to room temperature, complete within 4 min, to give $(C_6H_5)_3PF_2$ (94%), identified by fluorine n.m.r. (33).

XeF$_2$ and Diphenylphosphine

$(C_6H_5)_2PH$ (0.14 g, 0.75 mmol) was syringed onto XeF_2 (0.64 mmol) in CH_3CN (0.2 ml) at −196 °C. Reaction occurred at −25 °C to give $(C_6H_5)_2PHF_2$, identified by proton and fluorine n.m.r. (Table 1).

A violent reaction occurred when a chloroform solution of $(C_6H_5)_2PH$ was added to solid XeF_2 at room temperature.

XeF$_2$ and Bis(2-cyanoethyl)phosphine

$(NCCH_2CH_2)_2PH$ (0.12 g, 0.85 mmol) in CD_3CN was syringed onto XeF_2 (0.82 mmol) in CD_3CN (0.4 ml) at −196 °C. All operations were carried out in a dry box. Reaction occurred at −20 °C and was complete within 5 min to give $(NCCH_2CH_2)_2PHF_2$, identified by proton and fluorine n.m.r. (Table 1 and Fig. 1). The clear solution turned yellow and a solid formed after several days at room temperature.

XeF$_2$ and (2-Cyanoethyl)phosphine

$NCCH_2CH_2PH_2$ (0.1 g, 1.2 mmol) was syringed onto XeF_2 (0.87 mmol) in CD_3CN (0.4 ml) at −196 °C. All operations were carried out in a dry box. Reaction occurred at −35 °C and was complete within 5 min to give $NCCH_2CH_2PH_2F_2$, identified by proton and fluorine n.m.r. (Table 1 and Fig. 2). The clear solution turned yellow and a solid formed after several days at room temperature.

The reaction was repeated on the same scale in CH_2Cl_2 solvent. Reaction occurred at −15 °C and required 30 min for completion to give $NCCH_2CH_2PH_2F_2$. Decomposition to a white solid occurred within 1 day.

XeF$_2$ and Cyclohexylphosphine

$C_6H_{11}PH_2$ (0.10 g, 0.86 mmol) was syringed onto XeF_2 (0.83 mmol) in CD_3CN (0.4 ml) at −196 °C in a dry box. Reaction occurred at −20 °C to give $C_6H_{11}PH_2F_2$, identified by proton and fluorine n.m.r. (Table 1). The product decomposed after several days at room temperature to give a yellow solid.

XeF$_2$ and Diphenylchlorophosphine

$(C_6H_5)_2PCl$ (0.022 g, 0.10 mmol) was added to XeF_2 (0.15 mmol) in CH_3CN (0.3 ml) at −10 °C. Reaction occurred on warming to room temperature, complete within 4 min, to give $(C_6H_5)_2PF_3$, identified by fluorine n.m.r. (33).

XeF$_2$ and Phenyldichlorophosphine

$C_6H_5PCl_2$ (0.012 g, 0.07 mmol) was condensed into a solution of XeF_2 (0.15 mmol) in CH_3CN (0.3 ml) at −196 °C. On warming to 0 °C, a vigorous reaction occurred, complete within 1 min, to give $C_6H_5PF_4$, identified by fluorine n.m.r. (33).

XeF$_2$ and Di-tert-butylchlorophosphine and tert-Butyldichlorophosphine

$[(CH_3)_3C]_2PCl$ (0.11 g, 0.61 mmol) was added in aliquots of 10 μl to XeF_2 (0.59 mmol) in CH_3CN (0.2 ml) at −20 °C. Reaction occurred immediately on addition of $[(CH_3)_3C]_2PCl$ to give a pale yellow–green solution and a mixture of products which were not fully characterized but assumed to be partially chlorinated alkylfluorophosphoranes, since the mass spectrum revealed fragments containing three chlorine atoms (isotopic ratio) and the proton n.m.r. showed complex peaks in the *tert*-butyl region, while the fluorine n.m.r. showed a sharp doublet (J_{FP} = 726 Hz) at +71.6 p.p.m. (external $CFCl_3$) and a broad doublet (J_{FP} = 1030 Hz) at +56.8 p.p.m.

When the reaction was repeated in cyclohexene solution, the products again showed complex peaks in the *tert*-butyl region, but a fluorine signal was not observed.

Similar results were obtained for the reaction of XeF_2 with $(CH_3)_3CPCl_2$.

XeF$_2$ and Methyl Iodide

Solid XeF_2 (0.6 mmol) was added to excess methyl iodide (1.5 g) at −196 °C and the solution slowly warmed to room temperature. No reaction was observed below −40 °C; however, at room temperature the reaction proceeds smoothly for 20 min to give an essentially quantitative yield of CH_3IF_2, as monitored by fluorine n.m.r. Excess of methyl iodide may be removed *in vacuo* from the involatile product; however, attempts to purify the product were unsuccessful.

CH_3IF_2 could also be prepared by reaction of XeF_2 (0.20 mmol) in CH_3CN (0.4 ml) with excess methyl iodide at +20 °C. The reaction was slower, requiring 100 min for 75% reaction, while decomposition appeared to be faster and was complete after several hours.

XeF$_2$ and Phenyl Iodide and Isopropyl Iodide

Reaction of XeF_2 (0.1 g, 0.6 mmol) with excess phenyl iodide (1.9 g) was carried out at 0 °C. The fluorine n.m.r. spectrum of the product showed a single peak (half-height width 4 Hz) at +170.4 p.p.m. assigned to $C_6H_5IF_2$. After 12 h at 5 °C a second peak appeared at +173.8 p.p.m. (half-height width 18 Hz) of relative intensity 18%, which may be assigned to *ortho*-fluorinated $C_6H_4FIF_2$ or $C_6H_3F_2IF_2$.

The reaction of XeF_2 with excess isopropyl iodide at 0 °C was extremely rapid and appeared to give iodine as the major product. Fluorine n.m.r. examination failed to detect any iodine(III) difluoride product.

XeF$_2$ and Iodine

A few crystals of iodine were dissolved in a solution of XeF_2 (0.12 mmol) in CH_3CN (0.4 ml). The color of the iodine was discharged slowly over a period of 24 h at 20 °C.

In a similar experiment, a few crystals of iodine were dissolved in a solution of XeF_2 (0.11 mmol) in CH_3CN (0.4 ml) but this time dried $(CH_3)_3SiF$ was slowly bubbled into the solution. The iodine color was now replaced by a milky brown coloration which in turn faded to give a colorless solution. The reaction took 3–5 min for completion.

Reaction of XeF$_2$ with tert-Butylthiotrimethylsilane

In Solvent Acetonitrile

$(CH_3)_3SiSC(CH_3)_3$ (0.28 g, 1.73 mmol) was added to XeF_2 (0.83 mmol) in CH_3CN (0.3 ml) at −196 °C. The reaction mixture was allowed to warm to −7 °C in an ice–salt bath and reaction was complete within 7–9 min, resulting in a pale solution. Products were separated by trap-to-trap distillation and identified by n.m.r. and mass spectrometry by comparison with authentic samples. Products (and yields) were Xe (100%), $(CH_3)_3SiF$ (100%), $(CH_3)_3CSSC(CH_3)_3$ (85%), $(CH_3)_3CSSSC(CH_3)_3$ (7%), and $(CH_3)_3CSH$ (7%).

Without Solvent

XeF_2 (0.83 mmol) was weighed into a U-tube, cooled to −196 °C, and $(CH_3)_3SiSC(CH_3)_3$ (0.25 g, 1.54 mmol) was added. On warming to about −30 °C, a rapid exothermic reaction occurred, complete within 1 min, and the final temperature of the mixture was +60 °C. Volatile products were removed and identified as Xe (100%), $(CH_3)_3SiF$ (86%), and $(CH_3)_3CF$ (12%). The residue consisted of a solid identified as S_8 (0.12 g), and a yellow oil which was soluble in $CHCl_3$. The oil showed no fluorine peaks in the n.m.r. but the proton n.m.r. showed at least six singlet peaks in the *tert*-butyl region. By comparison with authentic samples, it was possible to identify $(CH_3)_3CSSC(CH_3)_3$ (12%) and $(CH_3)_3CSSSC(CH_3)_3$ (3%). The remaining *tert*-butyl peaks in the n.m.r. spectrum are assigned to $(CH_3)_3CS_nC(CH_3)_3$ where $n = 4–7$, since mass spectral examination of the oil confirmed the presence of compounds with $n = 2–7$. After three weeks at room temperature, S_8 precipitated from the oil and the yield of $(CH_3)_3CSSC(CH_3)_3$ and $(CH_3)_3CSSSC(CH_3)_3$ increased.

Reaction of XeF_2 with Dimethylaminotrimethylsilane

Without Solvent

Reactions of XeF_2 and $(CH_3)_3SiN(CH_3)_2$ in the absence of solvent were found to be explosive and the following behavior was typical: a mixture of XeF_2 and $(CH_3)_3SiN(CH_3)_2$ appeared stable from −196 to −35 °C. No reaction was apparent on standing at −35 °C for 10 h. At −30 to −25 °C, XeF_2 was observed to react and a white solid formed, followed shortly by a loud detonation which completely destroyed the glass reaction tube. Explosions occurred on two other occasions. When the reaction was attempted in $CFCl_3$, in which XeF_2 is insoluble, a detonation occurred on warming the mixture to approximately −15 °C, shortly after the formation of a white solid had been observed. A similar detonation occurred when a saturated solution of XeF_2 in CH_3CN was used.

Using adequate safety precautions, $(CH_3)_3SiN(CH_3)_2$ (0.35 g, 3.0 mmol) was condensed onto solid XeF_2 (1.65 mmol) at −196 °C and the reaction monitored by changes in pressure. By alternately warming the reaction mixture to −22 °C to initiate reaction, and rapidly cooling to −196 °C, the reaction could be moderated. When pressure build-up ceased, the reaction was assumed complete and all volatile products were removed and identified as Xe (100%), $(CH_3)_3SiF$ (86%), and $(CH_3)_2NH$ (17%). A liquid residue showed a variety of peaks in the dimethylamino region. One of these peaks, at −2.21 p.p.m., is tentatively assigned to $(CH_3)_2NN(CH_3)_2$ (20%) on the basis of the n.m.r. of an authentic sample (kindly supplied by H. D. Gesser) and the m.p. of its methyl iodide derivative 207–211 °C (lit. (34) 222–223 °C). Removal of liquid products under reduced pressure left behind an oil (0.04 g) which analyzed as C, 33.07%; H, 9.17%; N, 19.17%; F, 38.91%. The high fluorine content of the oil and the carbon to nitrogen to hydrogen ratio of 2.01:1.00:6.65 suggests that the oil consists of a mixture of ionic $(CH_3)_2NH_2F$, $(CH_3)_2NH_2HF_2$, and polymeric $(C_2H_6N)_n$.

In Solvent Acetonitrile

Reactions in CH_3CN solution were carried out many times. Typically, $(CH_3)_3SiN(CH_3)_2$ (0.049 g, 0.42 mmol) was condensed onto a solution of XeF_2 (0.20 mmol) in CH_3CN (0.3 ml) at −196 °C. As reactants warmed to above −20 °C a brisk exothermic reaction occurred, complete within 1–2 min. The color of the resulting solution depended on the effectiveness of the cooling of the mixture during reaction. Pale brown solutions could be obtained by maintaining the temperature between −20 and −15 °C, while over-heating resulted in very dark solutions and larger quantities of oily, intractable material. Separation of volatile products gave Xe and $(CH_3)_3SiF$ in quantitative yield and $(CH_3)_2NH$ in 20–30% yield.

Attempts to identify products remaining in CH_3CN solution were unsuccessful, partly because the reactions were carried out on a small scale for safety reasons. Nuclear magnetic resonance showed at least 12 singlet peaks in the dimethylamino region −1.25 to −3.25 p.p.m., their relative intensities varying from reaction to reaction and some products appeared unstable with time. Combined gas chromatography – mass spectrometry using columns Chromasorb 103 and 8% FFAP on Chromasorb 45 showed at least 20 compounds, most of their fragmentation patterns suggesting products containing some or more of the groupings $(CH_3)_2N$, CH_2CN, and CH_3NCH_2. One g.c. peak showed ions *m/e* 84, 83, 58, 44, 42 which may be assigned to $(CH_3)_2NCH_2CN$ and its fragments. Other products could not be assigned with certainty.

Removal of all volatile components from reaction mixture left behind an oily material.

An electron spin resonance study was undertaken to see if free radicals could be detected. $(CH_3)_3SiN(CH_3)_2$ (0.025 g, 0.21 mmol) was allowed to react with XeF_2 (0.10 mmol) in CH_3CN (0.3 ml) at −10 °C in a silica tube. At the onset of a vigorous reaction, the solution was rapidly cooled to −196 °C and the e.s.r. spectrum recorded. A very poorly resolved but nevertheless reproducible spectrum was obtained, with splitting of 28 G, in agreement with that reported for the $(CH_3)_2N$ radical (35). If the reaction was allowed to go to completion, no e.s.r. signal was observed. Starting materials were checked to be free of e.s.r. signals.

Reaction of XeF_2 with Diethylaminotrimethylsilane

In a typical reaction, $(CH_3)_3SiN(C_2H_5)_2$ (0.049 g, 0.34 mmol) was added to a solution of XeF_2 (0.16 mmol) in CH_3CN (0.5 ml) at −10 °C. A brisk reaction occurred, complete within 1–2 min, to give a brown solution. Products were Xe (100%), $(CH_3)_3SiF$ (90%), diethylamine, and an oily residue. The yield of diethylamine was variable, but generally accounted for 70–80% of available diethylamino groups. In an e.s.r. experiment similar to that above, no free radicals could be detected.

The reaction was repeated many times in baked out glassware, silylated glassware, Teflon tubes, monel reactor, and polypropylene container, all giving essentially similar results.

Reaction of XeF_2 with Diisopropylaminotrimethylsilane

In a typical reaction, $(CH_3)_3SiN[CH(CH_3)_2]_2$ (0.074 g, 0.42 mmol) was added to XeF_2 (0.20 mmol) in CH_3CN (0.4 ml) at -10 °C. On warming to room temperature the solution turned brown and reaction was complete within 5 min to give Xe (100%), $(CH_3)_3SiF$ (90%), $[(CH_3)_2CH]_2NH$ (80–90%), and an oily residue.

Electron spin resonance experiments proved misleading, since a well resolved signal was observed at room temperature, but this signal was also observed in a sample of unreacted $(CH_3)_3SiN[CH(CH_3)_2]_2$ and may be attributed to a trace of $[(CH_3)_2CH]_2NO$ (36), present in the starting material.

Reaction of XeF_2 with Hexamethyldisilazane

$[(CH_3)_3Si]_2NH$ (0.52 g, 3.3 mmol) was condensed onto XeF_2 (3.2 mmol) in CH_3CN (8 ml) at -196 °C and reaction monitored by changes in pressure. Reaction occurred slowly at room temperature and was complete after 30 min to give Xe (100%), $(CH_3)_3SiF$ (95%), a small amount of noncondensable gas (at -196 °C) assumed to be nitrogen, and an oily residue.

The oil contained organic polymeric material since the mass spectrum showed peaks up to *m*/*e* 750, with a complex fragmentation pattern dominated by loss of 14 mass units (loss of CH_2 or N). Washing the oily residue with CH_3CN and drying under vacuum gave a pale brown solid (0.03 g) which analyzed as C, 7.55%, H, 5.55%; N, 22.56%; F, 30.30%. The ratio H:N:F of 3.42:1.00:0.99 suggests the solid is mainly NH_4F. Its i.r. spectrum showed broad N—H bands and the solid was soluble in water and partly soluble in acetone.

Monitoring the Reaction of XeF_2 with Organosilicon Chlorides

The production of Cl_2 from reaction of XeF_2 with organosilicon chlorides (1) was confirmed in this study as follows: a u.v. cell with two chambers, each of 4.375 mm path length, was stoppered with a drilled (to permit escape of Xe) Teflon stopper. One chamber contained XeF_2 (0.33 mmol) in CH_3CN, the other $(CH_3)_3SiCl$ (0.074 g, 0.68 mmol) in CH_3CN. The cell was cooled to 0 °C and reaction initiated by quickly inverting cells. The u.v. spectrum was scanned every 20–30 s and an increase in absorption at 315–320 nm (37) confirmed the production of Cl_2. Repeating the experiment with a 20:1 molar ratio of $(CH_3)_3SiCl$ to XeF_2 suppressed the build-up of Cl_2. Evidently, chlorination of excess $(CH_3)_3SiCl$ gave $(CH_2Cl)(CH_3)_2SiCl$. Chloromethyl derivatives gave characteristic downfield shifts of the CH_2Cl protons, -3.06 p.p.m. for $CH_2Cl(CH_3)_2SiCl$ and -2.98 p.p.m. for $CH_2Cl(CH_3)_2SiF$.

To verify the n.m.r. spectra of chloromethyl derivatives, $CH_2Cl(CH_3)SiF_2$ was prepared from a commercial sample of $(CH_3)_2SiF_2$ (1.97 g, 20.5 mmol) and Cl_2 (1.12 g, 15.8 mmol) in a sealed Pyrex tube exposed to sunlight for 3 days. Fluorine n.m.r. of the product gave a quartet of triplets at $+138.2$ p.p.m. $J_{F-CH_3} = 6$ Hz, $J_{F-CH_2Cl} = 4$ Hz. Proton n.m.r. showed a triplet (CH_3) at -0.56 p.p.m. and a triplet (CH_2Cl) at -2.91 p.p.m., with intensity ratio 3:2, consistent with the product $CH_2Cl(CH_3)SiF_2$.

Reaction of organochlorosilanes could also be monitored by fluorine n.m.r., for example reaction of XeF_2 with $(CH_3)_3SiCl$ in CH_3CN occurred at a moderate rate at 0 °C, and the decrease of XeF_2 and increase of $(CH_3)_3SiF$ concentration could be followed conveniently. However, accurate rate studies were not carried out.

Reaction of XeF_2 and Trimethylgermanium Bromide

$(CH_3)_3GeBr$ (0.079 g, 0.40 mmol) was added to XeF_2 (0.25 mmol) in CH_3CN (0.4 ml). Reaction occurred at 25 °C and was complete within 10 min to give Xe and $(CH_3)_3GeF$ in quantitative yield, and bromine. The color of the solution was reddish brown and the presence of Br_2 was confirmed by adding olefins which discharged the color. $(CH_3)_3GeF$ was identified by mass spectrometry and fluorine n.m.r., dectet at $+186.5$ p.p.m., $J_{FH} = 7$ Hz, and proton n.m.r., doublet at -0.6 p.p.m.

XeF_2 and Hexafluoroacetone

Hexafluoroacetone (0.10 g, 0.60 mmol) was condensed onto XeF_2 (0.15 mmol) in CH_3CN (0.3 ml) at -196 °C and contents sealed in an n.m.r. tube. Fluorine n.m.r. showed no initial reaction, however, after 3 weeks at room temperature, all XeF_2 was consumed and the solution now contained $(CF_3)_2CFOH$, identified by fluorine n.m.r., doublet ($J_{FF} = 2$ Hz) at $+82.8$ p.p.m. and septet at $+125.8$ p.p.m.

In attempts to prepare a fluoroxy derivative, $(CF_3)_2CFOF$, hexafluoroacetone and XeF_2 without solvent were kept at room temperature for 5 days; in another experiment CsF was added as a catalyst, but no evidence of the desired product was found.

XeF_2 and Disodium Perfluoropinacolate

Disodium perfluoropinacolate, $OC(CF_3)_2C(CF_3)_2O^{2-}$ $2Na^+$ was prepared in THF (38). In separate experiments it was found that solutions of XeF_2 in THF were unstable, hence it was necessary to replace THF by CH_3CN by removing THF under vacuum and adding CH_3CN and repeating procedure several times.

In a typical experiment XeF_2 (0.35 mmol) was added to a solution of $OC(CF_3)_2C(CF_3)_2O^{2-}$ $2Na^+$ (0.32 mmol) in CH_3CN (0.5 ml), prepared as described above, at -196 °C and the reaction monitored by pressure changes. At -20 °C, the original pale brown solution turned yellow to greenish-yellow and finally colorless, and a white solid formed. Volatile products were identified as $(CF_3)_2CO$ and $HOC(CF_3)_2C(CF_3)_2OH$. The solid was identified as sodium fluoride by X-ray powder pattern; very faint lines indicated that the powder contained some Na_2SiF_6.

Perfluoropinacol was found to be resistant to attack by XeF_2.

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