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Fluorophosphorus Azides

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Mixed phosphorus chloride fluorides undergo ready reaction with sodium azide to provide an excellent route to new azide-containing compounds, including F_2PN_3, $F_2P(O)N_3$, $FP(O)(N_3)_2$, and $FP(S)(N_3)_2$. In addition, the previously reported $F_2P(S)N_3$ is easily prepared by this method. F_2PN_3 has particularly limited stability.

Azidobis(trifluoromethyl)phosphine, which is modestly stable at 0° and decomposes slowly at 20°, was prepared some years ago by reaction of chlorobis(trifluoromethyl)phosphine with lithium azide.[1] At 50°, slow decomposition occurs to give phosphonitriles, $((CF_3)_2PN)_x$. Difluorothiophosphoryl azide results from μ-oxo-bis(thiophosphoryl difluoride) with sodium azide.[2] Apparently this compound is stable and can be handled without difficulty. Although a number of organophosphorus azides are known and found to be fairly stable, there appear to be no others which also contain fluorine or a fluorine-containing species as a ligand.

In our synthesis, new azides result from phosphorus(III) and phosphorus(V) chloride fluorides and sodium azide

$$F_{3-x}P(E)Cl_x + x NaN_3 \xrightarrow{\text{solvent}} F_{3-x}P(E)(N_3)_x + x NaCl$$
$$x = 1, 2;\ E = O, S$$
$$x = 1;\ E = \text{absent}$$

or hydrazoic acid displaces hydrofluoric acid from a monoazide.

$$F_2P(O)N_3 + HN_3 \xrightarrow{60°} FP(O)(N_3)_2 + HF$$

The role played by the solvent in the former reactions is an important one in some cases, but one which is not clearly understood. In other instances, *e.g.*, with $F_2P(O)Cl$, reaction occurs to give a 76% yield of the monoazide without solvent. Mass spectra are particularly useful in confirming these mono- and diazides since a molecule ion is observed in every case.

Experimental Section

General Methods.—A standard Pyrex vacuum system equipped with a Heise-Bourdon tube gauge was used in all reactions. Purification of the azides was obtained either through trap-to-trap fractionation or by fractional codistillation.[3] Molecular weights were determined by the method of Regnault. Infrared spectra were recorded with either a Perkin-Elmer Model 621 or a Perkin-Elmer Model 457 spectrophotometer at 15 Torr in a cell of 5-cm path length with KBr windows. A Hitachi Perkin-Elmer Model RMU-6E spectrometer operating at an ionization potential of 70 eV at 25° was used to record mass spectra. Low-resonance ^{19}F nuclear magnetic resonance spectra were obtained at 94.1 MHz with a Varian HA-100 spectrometer. The ^{31}P nuclear magnetic resonance spectra were recorded at 40.5 MHz on the latter instrument. For fluorine, trichlorofluoromethane was the internal reference in 25% solutions. For phosphorus, the external reference was 85% phosphoric acid. In addition, the diazides were diluted to give 50% solutions in acetonitrile, while the monoazides were run neat.

Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrometer on samples at pressures less than 1 Torr in a 10-cm quartz cell. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Reagents.—Chlorodifluorophosphine[4] and $F_2P(O)Cl$[5] were prepared by methods described in the literature. Sodium azide, obtained from K & K Laboratories, was purified by dissolving the salt in water, acidifying to litmus with HCl, and precipitating the azide with acetone. After the salt was filtered, washed, and dried at 100°, it appeared to be free of hydrolysis products and reacted cleanly with the phosphorus halides. Hydrazoic acid was obtained in 80% yield from the reaction of gaseous HCl with sodium azide at 25° for 24 hr.

Both $FP(S)Cl_2$ and $F_2P(S)Cl$ were prepared in relatively high yields by modifying the method for PSF_3.[6] Fluorination of $SPCl_3$ with NaF at 140° for 0.5 hr with sulfolane as solvent gives average yields of 30, 50, and 20% for the mono-, di-, and trifluoride, respectively. These products are easily separated with traps at −91, −120, and −183°. Purity was checked by comparison with published infrared spectra.[7]

Caution. Although we experienced minimal difficulties in handling these azides, they should be treated as potentially hazardous materials and prepared in less than 10-mmol amounts (much less than this for PF_2N_3).

General Preparative Procedure for Phosphorus(III) and Phosphorus(V) Azides.—Essentially the same method can be employed in the preparation of all of the new azides, although the success of the reaction seems to depend largely upon the presence of and type of solvent. In general, the appropriate P(III) or P(V) compound is condensed onto sodium azide which has been carefully dried after recrystallization.

(a) **Azidodifluorophosphine, F_2PN_3.**—Difluorochlorophosphine (5 mmol), condensed onto sodium azide (1 g) in 1 ml of toluene and allowed to react for 2 hr at 25°, gives azidodifluorophosphine (4 mmol). The product is purified by trap-to-trap fractionation and is retained in a trap at −120° after passing −78°. (If no solvent is used, a very minor amount of F_2PN_3 forms with the major products, phosphorus trifluoride and nitrogen. When CH_3CN is used as a solvent, reaction takes place immediately on warming to 25° and produces nitrogen and PF_3 quantitatively. Despite the low thermal stability of F_2PN_3, in the synthesis involving toluene, the reaction mixture can remain at 25° for more than 24 hr without a trace of decomposition.) Care must be taken to maintain anhydrous conditions, since the hydrolysis product, HN_3, can be separated from the F_2PN_3 only with great difficulty. The experimentally determined molecular weight is 109.8 (111.0 theory).

(b) **Difluorothiophosphoryl Azide and Fluorothiophosphoryl Diazide, $F_2P(S)N_3$ and $FP(S)(N_3)_2$.**—Difluorothiophosphoryl chloride or fluorothiophosphoryl dichloride (10 mmol) is condensed onto a sodium azide (1 g)–acetonitrile (1 ml) slurry at −183°. The reaction is completed on warming to 25° and after trap-to-trap purification either of the azides is obtained in greater than 80% yield. No reaction occurs without acetonitrile. $F_2P(S)N_3$ passes a trap at −63° and stops at −91°. $FP(S)(N_3)_2$ is stopped at −41° after passing a trap at −23°. $F_2P(S)N_3$ has been well characterized after having been prepared from $(F_2P(S))_2O + NaN_3$.[7]

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TABLE I

INFRARED SPECTRA, CM^{-1}

F_2PN_3	$F_2P(O)N_3$	$FP(O)(N_3)_2$	$F_2P(S)N_3$	$FP(S)(N_3)_2$	
2140 s	2175 s	2195 vs	2195 vs	2175 vs	ν_{N_3}
	1365 s	1330 vs			$\nu_{P=O}$
1260 s	1265 s	1270 vs, br	1280 s	1262 s	ν_{N_3}
1230					
855 s	950 sh	910 s	955 vs	925 m	$\nu_{P-F}{}^{sym}$
835 s, br	907 s, br		930 sh		$\nu_{P-F}{}^{asym}$
740 s	777 m	805 s	825 s	825 m	ν_{P-N}
		760 w		775 m	
613 s	600 m	610 m	660 vw		
		570 w	575 mw	605 vw	
	430 m	430 s	415 mw	480 vvw	
		418 sh			

TABLE II

MASS SPECTRA

		Relative abundance				
m/e	Species	F_2PN_3	F_2P-$(O)N_3$	F_2P-$(S)N_3$	$FP(O)$-$(N_3)_2$	$FP(S)$-$(N_3)_2$
31	P	55.9	20	3.6	7.5	
42	N_3	16.2	44	4.5	37.6	40.5
50	PF	55			36.9	
63	PS			6.3		
64	FPN	51.7				
66	FPO		100			
69	F_2P	100	22	100		
77	SPN					100
80	FP(O)N				34.2	
82	FPS			3.6		
83	F_2PN	75.7				
85	F_2PO		60			
92	FPN_3	66.7			17.1	77.4
99	$F_2P(O)N$		68			
101	F_2PS			17.1		
108	$FP(O)N_3$		32			
111	F_2PN_3	27.9				
115	$F_2P(S)N$			2.7		
122	$FP(O)N_4$				43.8	
124	$FP(S)N_3$			1.8		9.5
127	$F_2P(O)N_3$		79			
131	$P(O)(N_3)_2$				2.1	
133	$P(S)N_5$					7.1
134	$FP(N_3)_2$					4.8
138	$FP(S)N_4$					1.2
143	$F_2P(S)N_3$			89.1		
150	$F_2P(O)(N_3)_2$				100	
166	$(F_2PN)_2$	1.8				57.1
	$FP(S)(N_3)_2$					

TABLE III

^{19}F AND ^{31}P NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	^{19}F (ϕ*)	^{31}P, ppm	J_{P-F}, Hz
F_2PN_3	57.5	. . .	1280
$F_2P(O)N_3$	73.5	15.3 tr	1042
$FP(O)(N_3)_2$	60.3	12.6 d	1020
$F_2P(S)N_3$	42.9[2]	−56.3 tr	1140
$FP(S)(N_3)_2$	38.8	−65.6 d	1102

(c) **Difluorophosphoryl Azide, $F_2P(O)N_3$.**—Difluorophosphoryl chloride (10 mmol) is condensed onto dry, recrystallized sodium azide (1 g) and warmed to and allowed to remain at 25° for 24 hr. Yields of greater than 76% were isolated from the trap at −78° having passed a trap at −20°. Acetonitrile is not useful as a solvent in this case since it cannot be separated easily from the product. The molecular weight is 127.3 (127.0 theory). *Anal.* Calcd for $F_2P(O)N_3$: F, 29.90; P, 24.40; N, 33.10. Found: F, 29.10; P, 23.80; N, 33.20.

Because of the possible hazardous nature of these compounds, vapor pressure data were obtained for only one compound, $F_2P(O)N_3$ (P_{Torr}, °K): 14.0, 256.7; 24.0, 265.2; 39.5, 273.2; 105.0, 290.7; 126.6, 293.5; 156.5, 298.2; 179.0, 301.5; 208.6, 304.0; 235.3, 307.0; 301.5, 312.5; 310.0, 313.2; 355.0, 316.0; 399.5, 319.0; 411.0, 370.5; 460.0, 321.3; 600.0, 329.0; 659.5, 331.3; 761.5, 335.2; 801.0, 336.2. The boiling point is 62°. From the Clausius–Clapeyron equation, $\Delta H_{vap} = 6.9$ kcal/mol and the Trouton constant is 20.6 eu. The vapor pressure–temperature relationship is given by the equation $\log P_{Torr} = 8.56 - (1902/T°K)$.

(d) **Fluorophosphoryl Diazide, $FP(O)(N_3)_2$.**—This compound may be prepared by either of two methods. (1) Difluorophosphoryl chloride (10 mmol) is condensed onto 1 g of sodium azide which has been exposed to the atmosphere and thus contains hydrolysis products and allowed to remain at 25° for 24 hr. Fluorophosphoryl diazide results in greater than 60% yield. (2) An excess of hydrazoic acid (4 mmol) is condensed with difluorophosphoryl azide (1 mmol) and held at 60° for 1 hr; 93% of the latter compound was consumed and a 46% yield of the diazide was obtained. In addition, an unidentified white solid coated the walls of the vessel. Infrared spectra indicate the presence of bands attributable to N–H, N_3, P=O, and P–F stretching frequencies. The fluorophosphoryl diazide is isolated in a trap at −30° after having passed a trap at −12°. *Anal.* Calcd for $FP(O)(N_3)_2$: F, 12.66; P, 20.66; N, 56.00. Found: F, 12.70; P, 20.80; N, 56.01.

Infrared, mass, and nmr spectra of these azides are recorded in Tables I, II, and III, respectively.

Results and Discussion

All of the new azides are colorless liquids at 25° and freeze to a glass when cooled. They are extremely sensitive to small amounts of water (*e.g.*, moist air) and hydrolyze to yield hydrazoic, hydrofluoric, and various phosphoric acids with the exception of F_2PN_3 which gives μ-oxo-bis(difluorophosphine) as the only phosphorus-containing product. The hydrolysis products were identified by comparing their infrared spectra with published data. The phosphorus(V) azides are thermally stable to at least 100° but, upon decomposition, the major products are phosphorus trifluoride, phosphoryl fluoride (or thiophosphoryl fluoride), and nitrogen.

Azidodifluorophosphine is unstable thermally and photolytically and has on occasion exploded spontaneously at 25°. In all cases, the decomposition products are nitrogen, phosphorus trifluoride, and various cyclic phosphonitrilic polymers of the type $(F_2PN)_x$ ($x \leq 6$). These polymers were separated by fractional codistillation and identified by comparison of their mass and infrared spectra with those reported in the literature.[8–10] Azidodifluorophosphine is explosively sensitive to sudden changes in pressure, *e.g.*, expansion into a vacuum or a sudden surge when boiling. Fluorothiophosphoryl diazide has exploded at −183° which may be due to transformation from a glass-like material to a crystalline substance at that temperature. However, traces of hydrazoic acid may have been responsible for the observed explosions.

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The ^{19}F and ^{31}P nmr data are recorded in Table III. The ^{19}F spectra consist of simple doublets centered in the ϕ^* 39–74 range with J_{P-F} varying between 1020 and 1140 Hz for phosphorus(V) azides and J_{P-F} is 1280 Hz for F_2PN_3. The ^{31}P spectra are well-resolved triplets or doublets depending on the presence of two or one fluorine atom(s). It should be noted that for both ^{19}F and ^{31}P chemical shifts the diazides and thiophosphoryl compounds resonate at lower field than monoazides and phosphoryl compounds, respectively. Spin–spin coupling interactions also decrease with number of azide groups. This would suggest greater electron delocalization from the phosphorus and fluorine atoms into the d orbitals of sulfur or π system of the azide moiety. No ^{31}P nmr data are available for F_2PN_3 because, despite prerun checking for thermal stability, the compound detonated destroying the phosphorus probe.

The covalent nature of these azides is demonstrated by the occurence of two bands in their ultraviolet spectra similar to those of typical alkyl azides.[11,12] However, because of inductive effects of the fluorophosphoryl or fluorothiophosphoryl groups, there is a marked shift to higher energies. Our values agree well with those reported by Ruff[13] for FSO_2N_3 (199, 249 nm) and $CF_3SO_2N_3$ (195, 238 nm). These bands arise from $\pi_y \rightarrow \pi_x^*$ and $sp_x \rightarrow \pi_y^*$ transitions with the latter occurring at higher energy. Both transitions involve charge transfer from electron pairs largely localized on the nitrogen atom bonded to the phosphorus into antibonding π orbitals on the other two nitrogen atoms.[11]

Mass spectral data (Table II) are particularly helpful in confirming the existence of these five new azides since all fragment at 70 eV to give a molecular ion with an intensity of at least 28% base, *e.g.*, F_2PN_3, 28%; $F_2P(O)N_3$, 79%; $F_2P(S)N_3$, 89%; $FP(O)(N_3)_2$, 100%; and $FP(S)(N_3)_2$, 57%. In the case of F_2PN_3, a fragment at *m/e* 166 is very likely attributable to $(F_2PN)_2$ although this species is not observed when the parent compound is decomposed either thermally or photolytically. As would be expected, the heavier fragments are due primarily to loss of nitrogen or fluorine. Comparison of the fragmentation pattern for $F_2P(S)N_3$ found in this work with that reported at 100 eV[2] shows very good agreement.

Some band assignments in the infrared spectra (Table I) can be made. However, because of the disagreement in the literature regarding assignment of $\nu_{P=S}$, we have not attempted at this time to unequivocally make these assignments, and work is continuing in this area. $\nu_{P=N}$ should be regarded as entirely tentative.

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Bis(hexafluoroisopropylidenimino) Disulfide, Chloro(hexafluoroisopropylidenimino)sulfur(II), and Some Derivatives

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Hexafluoroisopropylideniminolithium reacts with disulfur dichloride to give bis(hexafluoroisopropylidenimino) disulfide which undergoes two different types of reactions with chlorine to yield bis(2-chlorohexafluoroisopropylimino)sulfur(IV) and chloro(hexafluoroisopropylidenimino)sulfur(II). The latter gives new sulfur(II) compounds with reactants that contain active hydrogen or with silver salts. $(CF_3)_2C{=}NSCl$ is readily converted to $(CF_3)_2CF{=}NSF_2$ by fluorinating agents.

The lithium salt of hexafluoroisopropylidenimine has been shown to react with compounds that contain labile halogens (Cl, F) to introduce the hexafluoroisopropylidenimine moiety intact.[2-5] The compounds formed are most often slightly volatile, yellow liquids or sublimable solids. In this work, advantage has been taken of the high reactivity of $LiN{=}C(CF_3)_2$ with disulfur dichloride to prepare bis(hexafluoroisopropylidenimino) disulfide in good yield. The reactions of this disulfide are somewhat more complicated than those of the simpler, saturated fluorinated alkyl disulfides in that the former has three reactive sites. Just as thermally induced chlorination of CF_3SSCF_3 leads to CF_3SCl, so heating chlorine with $((CF_3)_2C{=}N)_2S_2$ gives $(CF_3)_2C{=}NSCl$. However, when the latter mixture is photolyzed through quartz, elemental sulfur is formed accompanied by double bond shifts and chlorination to give bis(2-chlorohexafluoroisopropylimino)sulfur(IV), $(CF_3)_2CClN{=}S{=}NCCl(CF_3)_2$. Although Seel has fluorinated Cl_3SCl stepwise to CF_3SF with KF at 150°[6] or with HgF_2 solely to CF_3SF and its dimer at 130°,[7] and CF_3SSCF_3 is readily fluorinated to CF_3SF_3 with

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