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# 2-Hydroperfluoropropyl Azide—a Versatile Reagent for the Oxidative Fluorination of Organic Compounds of Trivalent Phosphorus

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## ABSTRACT

*2-Hydroperfluoropropyl azide $CF_3CHFCF_2N_3$, **1**, an inexpensive, readily available, and stable (easy to store) compound, is suggested as an effective fluorinating reagent for different classes of trivalent organophosphorus compounds in accordance with the general scheme $R_3P \rightarrow R_3PF_2$. Generally, the reactions are performed without solvent, the highly volatile $CF_3CHFCN$ being the main by-product. The fluorination is usually an exothermic process, but slight heating is necessary in the case of alkyldifluorophosphites. The unusual Arbuzov rearrangement, accompanied by isomerization of an isobutyl or neopentyl group into a tert-group, $ROPF_2 \rightarrow t\text{-}R'POF_2$, under the action of a catalytic amount of **1**, was observed.*

## *INTRODUCTION*

Two generally used procedures for the fluorination of organophosphorus compounds are the following. First, the nucleophilic displacement of a halide ion (or another good leaving group) bonded to the phosphorus atom by a fluoride ion [1]. Another well-known procedure is the oxidative addition of fluorine to organophosphorus P(III) molecules. There exists a large variety of reagents which will affect the following transformation P(III) → P(V). Among them, α-fluoroamines [2], $SF_4$ [3], $CCl_4$ in the presence of $Et_3N \cdot 3HF$ [4], $SbF_3$ [5], $SOF_2$ [6], $COF_2$ [7], and $XeF_2$ [8] should be mentioned. All these reagents have some limitations, such as cost ($XeF_2$), safety problems ($COF_2$), reaction scope ($SbF_3$), or the pronounced acidic character of the reagent which prevents its use for the fluorination of sensitive compounds ($CCl_4/Et_3N \cdot 3HF$, $SF_4$ and $SOF_2$).

Recently, we have found that 2-hydroperfluoropropyl azide, **1**, can perform the oxidative fluorination of many P(III) compounds [9a]. This azide was first prepared by Knunyants and Bykhovskaya [10] and appeared to be a very stable and easily stored compound. However, only a few properties of the azide **1**, mainly photochemical and thermochemical, were investigated [11]. The goal of the present article is to demonstrate that azide **1** may be employed as a convenient versatile reagent for the oxidative fluorination of most types of P(III)-organic compounds.

## *RESULTS*

### *Reaction with Alkyl Phosphites*

Interaction of azide **1** with trialkyl phosphites or their analogs containing at least one P–OR bond proceeds smoothly in the absence of solvent to yield

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the corresponding difluorophosphoranes, or products of their further transformations (Equations 1–3).

$$\underset{\mathbf{2}}{(CF_3CH_2O)_3P} \xrightarrow[-N_2,\ -CF_3CHFCN]{1,\ rt} \underset{\mathbf{5}}{(CF_3CH_2O)_3PF_2} \quad (1)$$

$$\underset{\mathbf{3}}{(MeO)_3P} \xrightarrow[-N_2,\ -CF_3CHFCN]{1,\ rt} (MeO)_2P(O)F + [MeF] \quad (2)$$
$$\mathbf{6}$$

$$\underset{\mathbf{4}}{(Et_2N)_2POMe} \xrightarrow[-N_2,\ -CF_3CHFCN]{1,\ rt} (Et_2N)_2P(O)F + [MeF] \quad (3)$$
$$\mathbf{7}$$

The reactions are slightly exothermic, products **5–7** being isolated in moderate to high yields. In addition to the desired products **5–7**, the reaction mixture contains $CF_3CHFCN$, a highly volatile compound (bp 34–35°C) which can be easily removed by distillation. In the case of amide **4**, the reaction mixture showed two signals in the $^{31}P$ NMR spectrum: at $\delta$ 15.5, $[(Et_2N)_2POF]$, and at $\delta$ −64.5, (t, $J$ = 720 Hz). The latter signal, which disappears after distillation, was attributed to $(Et_2N)_2(MeO)PF_2$. The fluorination of **3** gives compound **6** and apparently proceeds *via* initial formation of the unstable difluorophosphorane, $(MeO)_3PF_2$.

The fluorination of silylated esters and amides of alkyl phosphoric acid was unsuccessful: these reactions were not selective and gave complex mixtures.

### *Fluorination of Halophosphites and Phosphines*

Methyldifluorophosphine, **8**, reacts with azide **1** to give the unstable monophosphazene **9** which decomposes on storage or upon distillation, yielding methyltetrafluorophosphorane, **10** (4).

$$\underset{\mathbf{8}}{CH_3PF_2} + \underset{\mathbf{1}}{CF_3CHFCF_2N_3} \xrightarrow{n} \underset{\mathbf{9}}{CH_3PF_2{=}N\text{-}CF_2CHFCF_3}$$

$$\rightarrow \underset{\mathbf{10}}{CH_3PF_4} + CF_3CHFCN \quad (4)$$

Diethyl fluorophosphite, **11**, is converted (5) into the phosphonium salt **13** which apparently arises from the labile trifluorophosphorane **12**. The rapid transformation (Equation 5) of **12** → **13** has been previously described [12].

$$\underset{\mathbf{11}}{(EtO)_2PF} + \mathbf{1} \rightarrow \left[\underset{\mathbf{12}}{(EtO)_2PF_3}\right] \rightarrow \underset{\mathbf{13}}{(EtO)_4P^+PF_6^-} \quad (5)$$

In contrast to the fluoride **11**, the corresponding chloride **14**, in its reaction with **1**, yields only ethyl difluorophosphate, **16**. The difluorochlorophosphorane **15** is likely an intermediate product in this process (6).

$$\underset{\mathbf{14}}{(EtO)_2PCl} + \mathbf{1} \rightarrow \left[(EtO)_2PClF_2\ \mathbf{15}\right] \xrightarrow{-EtCl} \underset{\mathbf{16}}{EtOP(O)F_2} \quad (6)$$

Unusual results were obtained when azide **1** was allowed to react with the alkyl difluorophosphites **17** (7). The principal result is the Arbuzov type of rearrangement with the formation of the alkylphosphonic difluorides **18**.

$$ROPF_2 \xrightarrow[60–80\ °C;\ 8–40\ h]{CF_3CHFCF_2N_3} R'P(O)F_2 \quad (7)$$

| | |
|---|---|
| **17a** R = Me | **18a** R′ = Me |
| **17b** R = *i*-Bu | **18b** R′ = *t*-Bu |
| **17c** R = $Me_3CCH_2$ | **18c** R′ = $EtMe_2C$ |
| **17d** R = BuEtCHCH$_2$ | **18d** R′ = BuEtMeC |
| **17e** R = cyclo-$C_6H_{11}CH_2$ | **18e** R′ = 1-methylcyclohexyl |
| **17f** R = $MeOCH_2CH_2$ | |
| **17g** R = $EtMeCHCH_2$ | |

These reactions are catalyzed by azide **1**, and the product yields do not depend on the amount of **1**: an azide to phosphite ratio of either 1:1 or 1:10 gave the same results. In a control experiment, the phosphite **17b** was heated without azide **1** and not even traces of the rearranged product **18b** could be detected. Hence, a specific catalytic role of azide **1** is indicated.

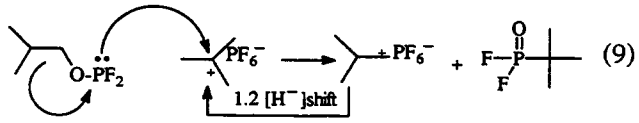
$^{31}P$ NMR spectra of the reaction mixtures show that the phosphonic difluoride content exceeds 90%; small amounts of $ROP(O)F_2$ and $PF_6^-$ anion were also detected. The reaction of **1** with propyl and isopropyl difluorophosphites (1:1 molar ratio) is unselective: complex mixtures of five to seven substances were obtained in each case.

An intriguing feature of these reactions is the rearrangement of the phosphites **17b,c,d,e,g** bearing isobutyl or neopentyl groups into tertiary and alkyl phosphonic difluorides **18b,c,d** and **e**.

We propose the following rationalization of these processes. The first step has to be the fluorination of the phosphite with subsequent disproportionation of the resulting tetrafluorophosphorane to give an equimolar mixture of alkyl hexafluorophosphate and alkyl difluorophosphate. Indeed, such a disproportionation for the case where R = Me has been documented in the literature [13].

$$ROPF_2 + 1 \rightarrow ROPF_4 \rightarrow R'^+PF_6^- + ROP(O)F_2 \quad (8)$$

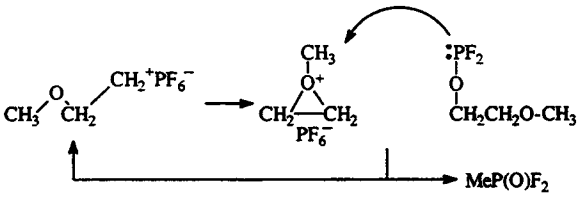
During this step, a true catalyst, namely, an alkyl hexafluorophosphate, is formed (Equation 8) and the isomerization of a primary into a stable tertiary alkyl group occurs readily in this ionic complex. The second step is the catalyzed Arbuzov rearrangement. The process is catalyzed by alkyl cation and accompanied by the catalyst recovery. Equation (9) for the *i*-Bu → *t*-Bu case illustrates these transformations:



(9)

This sequence explains both the catalytic character of the reaction and the isomerization of the alkyl group into a stable tertiary alkyl group. While rare examples of the Arbuzov rearrangement of compounds containing a F–P(III) bond under the action of methyl iodide or an acyl halide are known [14], to the best of our knowledge, this is the first well-established example of the Arbuzov rearrangement of alkyl difluorophosphites. Furthermore, this reaction can be used for the large scale preparations of phosphonic difluorides with tertiary alkyl groups which are difficult to obtain by other ways.

Another surprising result is the exclusive formation of $MeP(O)F_2$, **18a**, in the case of the reaction of (β-methoxyethyl) difluorophosphite, **17f**, instead of the expected $MeOCH_2CH_2P(O)F_2$. This result may be explained by the assumption that the intermediate methoxyethyl cation is transformed into the corresponding oxonium species and that nucleophilic attack by P(III) occurs at the $CH_3$ group but not at the $CH_2$-group of an intermediate oxonium salt, as shown in Equation 10.



(10)

## *Fluorination of Hydrophosphoryl Compounds*

Reaction of the dialkyl phosphites **19a–c** with the azide **1** proceeds smoothly in the presence of triethylamine to give the corresponding dialkyl fluorophosphates **20a–c** in good yields (11).

$$(RO)_2P(O)H + CF_3CHFCF_2N_3 \xrightarrow[-HF]{Et_3N} (RO)_2P(O)F \quad (11)$$

**19a** R = $C_2H_5$ **20a** R = $C_2H_5$
**19b** R = *n*-$C_3H_7$ **20b** R = *n*-$C_3H_7$
**19c** R = *i*-$C_3H_7$ **20c** R = *i*-$C_3H_7$

Diphenylphosphinous acid, **21**, is fluorinated by azide **1** even in the absence of a base, but the reaction is not as simple as in the case of dialkyl phosphites (12). Indeed, we detected the expected product **22** in the mixture along with the trifluorophosphorane **23** as well as amide **24** (12).

$$\underset{\mathbf{21}}{Ph_2P(O)H} + \underset{\mathbf{1}}{CF_3CHFCF_2N_3} \xrightarrow{-N_2}$$

$$\underset{\mathbf{22}}{Ph_2P(O)F} + \underset{\mathbf{23}}{Ph_2PF_3} + \underset{\mathbf{24}}{CF_3CHFC(O)NH_2} \quad (12)$$

Tetrafluoropropionitrile, $CF_3CHFCN$, might serve as the dehydrating agent, as indicated in Equation 13.

$$P\text{-}OH + HF + CF_3CHFCN \rightarrow P\text{-}F + CF_3CHFC(O)NH_2 \quad (13)$$

## *Fluorination of Aminophosphines and Fluoraminophosphines*

Interaction of azide **1** with triamidophosphines **25a–b** initially gave the corresponding unstable phosphazides **26a–b** which eliminate nitrogen on storage or upon distillation to give difluorophosphoranes **27a–b** (14).

$$(R_2N)_3P + CF_3CHFCF_2N_3 \rightarrow (R_2N)_3P{=}NN{=}NCF_2CHFCF_3 \xrightarrow[-CF_3CHFCN]{-N_2} (R_2N)_3PF_2 \quad (14)$$

**25a** R = $CH_3$ **26a** R = $CH_3$ **27a** R = $CH_3$
**25b** R = $C_2H_5$ **26b** R = $C_2H_5$ **27b** R = $C_2H_5$

The isolation of the phosphazides **26a–b** is a rare case of direct proof of the intermediacy of this type of compound in the Staudinger reaction. A comparison of these reactions with the one for compound **4** (Equation 3) reveals the crucial influence of the alkoxy substituents on the course of the reaction.

For the reaction of azide **1** with (dimethylamino)difluorophosphine, **28**, a more complex mixture was obtained (Equation 15) in which products **29–31** were identified.

$$\underset{\mathbf{28}}{Me_2NPF_2} + CF_3CHFCF_2N_3 \xrightarrow{-N_2} \underset{\mathbf{29}}{Me_2NPF_2{=}NCF_2CHFCF_3} \rightarrow \quad (15)$$

$$Me_2NPF_3{-}N{=}CF{-}CHFCF_3 + Me_2N^+{=}C{-}N{=}\tilde{P}{=}N{-}C{=}N^+Me_2 \; PF_6^-$$
**30** **31**

The structures of **29** and **30** were identified by $^{31}P$ NMR, and the structure of **31** was confirmed by X-ray diffraction [15].

## *DISCUSSION*

The data presented previously convincingly demonstrate that 2-H-perfluoropropyl azide, **1**, is a versatile, easily used reagent which fluorinates a variety of organophosphorus (III) compounds under mild conditions. The general mechanism of this fluorination may be represented by the sequence of steps i–iv in Equation 16.

$$R_3P + N_3CF_2CHFCF_3 \xrightarrow{i} R_3P{=}N{-}N{=}N{-}CF_2CHFCF_3 \xrightarrow[-N_2]{ii} R_3P{=}N{-}CF_2CHFCF_3 \xrightarrow{iii} R_3PF{-}N{=}CF{-}CHFCF_3 \xrightarrow{iv} R_3PF_2 + CF_3CHFCN \quad (16)$$

This sequence includes the well-known Staudinger reaction (stages i and ii). However, both step iii, the sigmatropic transfer of a fluorine atom to phosphorus in α-fluorophosphazenes, as well as step iv are rather uncommon. Moreover, the rearrangement of these phosphazenes could not be predicted *a priori* from literature data. Indeed, there are at least two articles describing examples of relatively stable compounds of this class. For instance, N-perfluoroalkenylphosphazenes of type $R_3P{=}N{-}CF{=}C(R')CF_3$, where R′ = F and $CF_3$, undergo thermal decomposition to give $R_3PF_2$ only at 150°C [16]. Moreover, N-trifluoromethylphosphazenes, $R_3P{=}N{-}CF_3$, are so stable that they can be distilled [17].

On the other hand, the fluorine atom in the F–C–N < moiety is known to be very labile toward nucleophilic displacement, and this chemical behavior of fluoramines was rationalized in terms of the nonbonded resonance $>N{-}C(R_2){-}F \leftrightarrow >N^+ = CR_2\ F^-$[18]. Moreover, this feature was used to design the specific fluorinating reagents (e.g., the so-called Yarovenko reagent, $R_2N{-}CF_2CHFCl$ [19], and the Ishikawa reagent, $R_2N{-}CF{=}CF{-}CF_3$ + $R_2N{-}CF_2{-}CHFCF_3$ [20]). These reagents smoothly convert alcohols and even carbonyl compounds into the corresponding fluorinated derivatives in accordance with Equations 17 and 18.

$$ROH + {-}CF_2{-}NR'_2 \rightarrow R{-}F + {-}C(O){-}NR'_2 + HF \quad (17)$$

$$R_2C{=}O + {-}CF_2{-}NR'_2 \rightarrow R_2CF_2 + {-}C(O)NR'_2 \quad (18)$$

The analogous α-fluoramine fragment, P=N–C–F, is present in the phosphazenes formed in the reaction of azide **1** with P(III) compounds. The fluorination in this case seems to be a consecutive two-step process which includes as the first step (iii) the nucleophilic attack at the P=N bond by the fluoride ion. The driving force for this 1,3-sigmatropic shift is the formation of the very strong P–F bond as well as perhaps the N=C vs. P=N bond. Second, step iv is the nucleophilic attack at the P=N bond by the fluoride ion with elimination of a nitrile. Here, the driving forces are the formation of the strong P–F and C≡N bonds. Thus, the azide **1** plays a triple role: (a) it oxidizes P(III) to P(V); (b) it serves as a source of fluoride anion; and (c) it forms a highly nucleofugic nitrile leaving group. To the best of our knowledge, only one slightly analogous example of the transformation of 1-azido-1,1,2,2,4,4,4-heptafluorobutanone-3 into the nitrile of perfluoroacetoacetic acid is documented to date in the literature [21].

## EXPERIMENTAL

$^1H$, $^{13}C$, $^{19}F$, and $^{31}P$ NMR spectra were recorded on a Bruker CXP-200 spectrometer. Chemical shifts are reported in δ units relative to external TMS, $CF_3COOH$, and 85% $H_3PO_4$, respectively. Mass spectra were recorded on a Finnigan GC\MS-4021 spectrometer.

*2-Hydroperfluoropropyl azide,* **1.** This compound was prepared by a modified procedure [10]. Sodium azide (100 g) was placed into a three-necked flask (equipped with a mechanical stirrer, gas inlet tube, and Liebig condenser) and was suspended in 1.5 L of dry methylcellosolve. The mixture was heated to 65°C, and a strong flow of perfluoropropene, $C_3F_6$, was passed into the mixture. The crude azide **1** was distilled off and purified by fractionation using a 50 cm Vigreux column. Yield 134 g (45%). Bp 51–53°C. Ref. [10]: bp 51°C.

**Caution: This procedure has been innocuous to date, and the azide seems to be stable. The usual cautions are nevertheless strongly recommended.**

*Tris(trifluoroethoxy)difluorophosphorane,* **5.** Tris(trifluoroethyl)phosphite, **3**, 28 g (10 mmol) was added dropwise to 1.93 g (10 mmol) of azide **1** (the temperature must be less than 30°C). After the end of the gas evolution, the volatile products were distilled off at room temperature *in vacuo* ($1 \cdot 10^{-2}$ mm) and collected in a trap cooled by liquid nitrogen. The residue was distilled to give 1.97 g (68%) of phosphorane **5**, bp 58–63°C/10 mm. $^{31}P$ NMR ($CDCl_3$): −77.1 (t, $J_{P\text{-}F}$ = 749 Hz); $^{19}F$ NMR ($CDCl_3$): 0.4 (s, 9F), 19 (d, $J_{P\text{-}F}$ = 747 Hz, 2F). Ref. [19]: $^{31}P$ NMR: −77.3, $J_{P\text{-}F}$ = 747 Hz.

The 2-hydroperfluoropropionitrile (bp 39–42°C) collected in the trap was purified by distillation. $^1H$ NMR ($CDCl_3$): 5.44 (dq, $^2J_{H\text{-}F}$ = 44.6 Hz, $^3J_{H\text{-}F}$ = 5 Hz). $^{19}F$ NMR ($CDCl_3$): −126.7, −1.6 ($J_{F\text{-}F}$ = 15 Hz). $^{13}C$ NMR ($CDCl_3$): 75.54 ($^1J_{C\text{-}F}$ = 200 Hz, $^2J_{C\text{-}F}$ = 42 Hz), 109.31 ($^2J_{C\text{-}F}$ = 29 Hz, $^3J_{C\text{-}F}$ = 2 Hz), 118.99 ($^1J_{C\text{-}F}$ = 282 Hz, $^2J_{C\text{-}F}$ = 26 Hz). IR($cm^{-1}$): 2264 (C≡N). Ref. [23]: bp 40–41°C. The retention time of this sample (GLC SE-30, XE-60) agrees with that of a sample prepared by the published procedure [23].

*Dimethylfluorophosphate,* **6.** Dimethylfluorophosphate was obtained analogously (1.34 g, 67%) from 1.99 g (16 mmol)) of trimethyl phosphite and 3.1 g (16 mmol) of azide **1**. Bp 60–65°C/15 mm. $^{31}P$ NMR ($CDCl_3$): −6 (d, $J_{P\text{-}F}$ = 970 Hz). Ref. [24]: bp 149°C/760 mm.

*Bis(diethylamino)fluorophosphate,* **7.** Bis(diethylamino)fluorophosphate was obtained analogously from 1.31 g (6.4 mmol) of amidoester **4** and 1.23 g (6.4 mmol) of azide **1** (41% yield). Bp 58–63°C/0.1 mm. $^{31}P$ NMR ($CDCl_3$): −15.5 (d, $J_{P\text{-}F}$ = 949 Hz). Ref. [25]: bp 124–125°C/20 mm.

*Fluorination of Methyldifluorophosphine,* **8.** A two-necked flask equipped with a gas-inlet tube and a Dry Ice reflux condenser was charged with 6 g (0.031 mol) of azide **1** under an atmosphere of thoroughly purified argon. A slow stream of phosphine **8** (3.5 g, 0.04 mol) was passed through the azide cooled with a water bath (15–18°C). In 0.5 hours, the $^{31}P$ NMR spectrum showed that the re-

action mixture contained almost pure phosphazene **9** (21.65 ttd, $^1J_{P\text{-}F}$ = 1120 Hz, $^3J_{P\text{-}F}$ = 32.4 Hz, $^4J_{P\text{-}F}$ = 7.5 Hz) and traces of $MeP(O)F_2$ ($^{31}P$ NMR data, see later). In a week, the reaction mixture contained no phosphazene **9** but instead contained $MePF_4$, **10** (−28.8 quintet, $J_{P\text{-}F}$ = 970 Hz. Ref. [26]: $^{31}P$ NMR: −29.6, $J_{P\text{-}F}$ = 965 Hz), and 3–5% of $MeP(O)F_2$, probably as a result of phosphorane hydrolysis.

*Fluorination of Diethyl Fluorophosphite,* **11.** A vigorous reaction between azide **1** (0.97 g, 5 mmol) and phosphite **11** (0.7 g, 5 mmol) afforded the phosphonium salt **13** as the single product in quantitative yield. $^{31}P$ NMR ($CDCl_3$): 0.96 (s, 1P), −143 (septet, 1P, $J_{P\text{-}F}$ = 710 Hz). Ref. [27]: $^{31}P$ NMR: −5, s, −1.47, (septet, $J_{P\text{-}F}$ = 700 Hz).

*Ethyl Difluorophosphate,* **16.** Ethyl Difluorophosphate was obtained in 84% yield (1.5 g) from 2.15 g (13.7 mmol) of diethyl chlorophosphite **14** and 2.65 g (13.7 mmol) of azide **1** without solvent. Bp 82–85°C. $^{31}P$ NMR ($CDCl_3$): −19.5 (t, $J_{P\text{-}F}$ = 1008 Hz). Ref. [27]: $^{31}P$ NMR: −20.9, $J_{P\text{-}F}$ = 1015 Hz.

*Fluorination of Methyl Difluorophosphite,* **17a.** 3 g (30 mmol) of **17a** was condensed into an evacuated glass ampoule charged with 0.58 g (3 mmol) of azide **1**. The ampoule was sealed and kept at room temperature for 48 hours. Distillation of the reaction mixture afforded 2.55 g (85%) of methylphosphonic difluoride **18a**. Bp 96–98°C. $^{31}P$ NMR ($CDCl_3$): 25.6 (t, $J_{P\text{-}F}$ = 1104 Hz). $^{19}F$ NMR ($CDCl_3$): 15.8 (d, $J_{F\text{-}P}$ = 1096 Hz). $^1H$ NMR ($CDCl_3$): 1.93 (dt, $J_{H\text{-}P}$ = 19.6 Hz, $J_{H\text{-}F}$ = 6 Hz). Ref. [27]: $^{31}P$ NMR: 27.4, $J_{P\text{-}F}$ = 1093 Hz.

*Fluorination of Isobutyl Difluorophosphite,* **17b.** 4 g (28 mmol) of phosphite **17b** and 0.54 g (2.8 mmol) of azide **1** were heated for 8 hours at 70°C in a steel bomb. The $^{31}P$ NMR of the reaction mixture contains three signals ascribed to *t*-$BuP(O)F_2$, **18b**, (92%), *i*-$BuOP(O)F_2$ (8%; −19.23 ppm, tt, $J_{P\text{-}F}$ = 1008 Hz, $J_{P\text{-}H}$ = 8 Hz), and traces of $PF_6^-$ anion (−143 ppm, septet, $J_{P\text{-}F}$ = 710 Hz). Tert-Butylphosphonic difluoride, **18b**, was isolated by distillation in 67% yield (2.68 g), bp 117–119°C. $^{31}P$ NMR($CDCl_3$): +31.7(t of decets, $J_{P\text{-}F}$ = 1172 Hz, $J_{P\text{-}H}$ = 19.5 Hz). $^1H$ NMR($CDCl_3$): 1.3 (dt, $J_{P\text{-}H}$ = 19.6 Hz, $J_{H\text{-}F}$ = 1 Hz). Ref. [28]: bp 97°C/100 mm. $^{31}P$ NMR: 31.3, $J_{P\text{-}F}$ = 1169 Hz, $J_{P\text{-}H}$ = 19 Hz. An analogous result was obtained when **17b** and **1** were employed in 1:1 molar ratio.

*Fluorination of Neopentyl Difluorophosphite,* **17c.** 4.68 g (30 mmol) of **17c** and 0.58 g (3 mmol) of azide **1** were heated at 80°C for 12 hours. tert-Pentylphosphonic difluoride, **18c**, was isolated by distillation (1.96 g, 42% yield), bp 62–65°C/15 mm. $^{31}P$ NMR ($CDCl_3$): 31.5 (t of nonets, $J_{P\text{-}F}$ = 1179 Hz, $J_{P\text{-}H}$ = 19.5 Hz). $^1H$ NMR ($CDCl_3$): 0.97 (t, $J_{H\text{-}H}$ = 7 Hz 3H), 1.25 (d, $J_{H\text{-}P}$ = 19 Hz 6H), 1.62 (m, 2H). Mass spectrum (70 ev): 157 $(M + 1)^+$, 128 $(M\text{-}C_2H_4)^+$. Anal. calcd for $C_5H_{11}F_2OP$: C, 38.47; H, 7.1. Found: C, 38.65; H, 6.91.

*Fluorination of 1-(2-Ethyl)hexyl Difluorophosphite,* **17d.** 46.17 g (233 mmol) of **17d** and 4.44 g (23 mmol) of azide **1** were heated for 8 hours at 60°C in a steel bomb. The bomb was cooled to room temperature and opened, and an additional 2.7 g (14 mmol) of azide **1** was added, with heating continued for 8 hours at 60°C. 1-(1-Methyl-1-ethyl)pentylphosphonic difluoride, **18d**, was obtained in 69% yield (31.69 g). Bp 72–74°C/12 mm. $^{31}P$ NMR ($CDCl_3$): 31.8 (t, $J_{P\text{-}F}$ = 1182 Hz). $^1H$ NMR ($CDCl_3$): 0.70 (t, $J_{H\text{-}H}$ = 7 Hz, 3H), 0.78 (t, $J_{H\text{-}H}$ = 7 Hz, 3H), 1.08 (d, $J_{H\text{-}P}$ = 20 Hz), 1.12 (m, 4H), 2.5 (m, 4H). Mass spectrum (70 ev): 199 $(M + 1)^+$, 198 $(M^+)$, 142 $(M\text{-}C_4H_8)^+$, 127 $(F_2PO\text{-}CH\text{-}C_2H_5)^+$. Anal. calcd for $C_8H_{17}F_2OP$: F, 19.17. Found: F, 19.22. Reactions of the phosphonic difluoride **18d** with either $CH_3OH/CH_3ONa$ or $C_2H_5ONa$ (2–4 hours reflux and usual workup) gave either 1-(1-methyl-1-ethyl-pentyl) dimethylphosphonate (bp 124°C/13 mm; anal. calcd for $C_{10}H_{23}O_3P$: P, 12.40; found: P, 12.58) or (1-methyl-1-ethylpentyl-1) diethyl phosphonate (bp 128°C/13 mm; anal. calcd for $C_{12}H_{27}O_3P$: C, 54.05; H, 10.36; found: C, 54.10; H, 9.91), respectively.

*Fluorination of Cyclohexylmethyl Difluorophosphite,* **17e.** 5.46 g (30 mmol) of phosphite **17e** and 0.58 g (3 mmol) of azide **1** were heated in a steel tube at 70°C for 12 hours. Distillation afforded 3.93 g of 1-methylcyclohexylphosphonic difluoride, **18e** (72%). Bp 64–66°C/10 mm. $^{31}P$ NMR ($CDCl_3$): 30.4 (t, $J_{P\text{-}F}$ = 1180 Hz). $^1H$ NMR ($CDCl_3$): 0.95 (d, $J_{H\text{-}P}$ = 20 Hz 3H), 1–1.4 (m, 8H), 1.55 (m, 2H). $^{13}C$ NMR ($CDCl_3$): 17.53 (d, $^2J_{C\text{-}P}$ = 3.4 Hz), 19.15 (d, $^3J_{C\text{-}P}$ = 10.6 Hz), 23.88 (d, $^4J_{C\text{-}P}$ = 1 Hz) 29.79 (d, $^2J_{C\text{-}P}$ = 2.9 Hz), 33.5 (dt, $^1J_{C\text{-}P}$ = 135.5 Hz, $^2J_{C\text{-}F}$ = 13.5 Hz). Mass spectrum (70 ev): 183 $(M + 1)^+$, 97 $(C_7H_{13})^+$. Anal. calcd for $C_7H_{13}F_2OP$: C, 46.16; F, 20.86. Found: C, 46.19; F, 20.35. Reaction of the difluoride **18e** with $C_2H_5OH/C_2H_5ONa$ (reflux 2–4 hours and usual workup) gave 1-methylcyclohexyl diethyl phosphonate (bp 128–130°C/13 mm; anal. calcd for $C_{11}H_{23}O_3P$: C, 56.4; H 9.9; P, 13.22; found: C, 56.83; H, 9.87; P, 12.58).

*Fluorination of 2-methoxyethyl difluorophosphite,* **17f.** 1.9 g (13 mmol) of **17f** and 0.25 g (1.3 mmol) of azide **1** were kept at room temperature for 2 weeks. Distillation afforded 1.23 g (93%) of methylphosphonic difluoride, **18a**. Bp 95–98°C (NMR data, see earlier).

*Fluorination of 1-(2-methyl)butyl difluorophosphite,* **17g.** A mixture of 23 g (150 mmol) of phosphite **17g** and 0.96 g (15 mmol) of azide **1** was heated

in a steel bomb at 60°C for 24 hours. The bomb was opened, 0.96 g (15 mmol) of additional azide **1** was added, and heating was continued for another 16 hours. Distillation afforded 7.29 g (31.7%) of phosphonic difluoride **18c**. Bp 58–60°C/10 mm (NMR data of **18c**, see earlier).

*Fluorination of Dialkyl Phosphites* **19a–c.** 20 mmol of azide **1** was added to a solution of 20 mmol of the appropriate dialkyl phosphite in 2 mL of dried triethylamine. After the completion of a vigorous reaction, the dialkyl fluorophosphates **20a–c** were isolated by distillation.

**20a** (R = Et): bp 57–60°C/10 mm (75%). $^{31}$P NMR ($CDCl_3$): −8 (d, $J_{P\text{-}F}$ = 967 Hz). Ref. [27]: $^{31}$P NMR: −9.2, $J_{P\text{-}F}$ = 963 Hz.

**20b** (R = Pr): bp 79–82°C/10 mm (72%). $^{31}$P NMR ($CDCl_3$): −8.2 (d, $J_{P\text{-}F}$ = 972 Hz). Ref. [27]: $^{31}$P NMR: −8.5, $J_{P\text{-}F}$ = 965 Hz.

**20c** (R = *i*-Pr): bp 59–64°C/10 mm (70%). $^{31}$P NMR ($CDCl_3$): −10.2 (d, $J_{P\text{-}F}$ = 966 Hz). Ref. [27]: $^{31}$P NMR: −4.5, $J_{P\text{-}F}$ = 963 Hz.

*Fluorination of Diphenylphosphinous Acid,* **21.** 3.86 g (20 mmol) of azide **1** was added dropwise to 4.04 g (20 mmol) of **21** in 5 mL of dry $CHCl_3$. Nitrogen evolution ceased after 3–4 hours. The $^{31}$P NMR of the reaction mixture showed 70–75% of **22** (δ 42, d, $J_{P\text{-}F}$ = 1019 Hz; Ref. [26]; $^{31}$P NMR: δ 40, $J_{P\text{-}F}$ = 1020 Hz) and 25–30 of **23** [−33.8, dt, $J_{P\text{-}F}$ = 972 Hz(e), 836 Hz(a); Ref. [26]; $^{31}$P NMR: −34.8, $J_{P\text{-}F}$ = 968 Hz(e), 830 Hz(a)]. Distillation afforded 2.32 g (58%) of **22**, bp 100–120°C/$10^{-5}$ mm. The amide **24** was collected in a $N_2$-cooled trap. Mp 179–182°C (from benzene). $^1$H NMR ($CDCl_3$): 5.03 (dq, $^2J_{H\text{-}F}$ = 46 Hz, $^3J_{H\text{-}F}$ = 6.8 Hz 1H), 6.63 (m, 1H), 6.90 (m, 1H). $^{19}$F NMR ($CDCl_3$): −123.3 (m, 1F), 1.1 (m, $J_{F\text{-}F}$ = 11 Hz, 3F). $^{13}$C NMR ($CDCl_3$): 85.25 (dq, $^1J_{C\text{-}F}$ = 203 Hz, $^2J_{C\text{-}F}$ = 34 Hz), 120.41 (m, $^1J_{C\text{-}F}$ = 282 Hz, $^2J_{C\text{-}F}$ = 25 Hz), 163.85 (d, $^2J_{C\text{-}F}$ = 20 Hz). IR ($cm^{-1}$): 1725 (C = 0), 1585 (N–H). Mass spectrum (70 ev): 146 (M + 1)$^+$, 145 ($M^+$), 101 ($CF_3CHF^+$). Anal. calcd for $C_3H_3F_4NO$: H, 2.08; N, 9.65. Found: H, 2.09; N, 9.56.

*Reaction of Hexamethyltriamidophosphine,* **25a,** *with Azide* **1.** 4.54 g (24 mmol) of azide **1** was added dropwise to a solution of 3.83 (24 mmol) of **25a** in 5 mL of dry $Et_2O$ and kept at 25°C. A white crystalline solid formed slowly, and no gas evolution could be detected (gas burette). After 24 hours, the residue was filtered off, washed with ether and hexane, and dried in vacuo resulting in 3.63 g (43%) of pure **26a**. $^{31}$P NMR ($CDCl_3$): δ 43.4. $^{19}$F NMR ($CDCl_3$) 3.5 (m, 3F), −14.8 (m, 2F), −134.8 (m, 1F). Mass spectrum (70 ev): 357 (M + 1)$^+$, 356 ($M^+$). Anal. calcd for $C_9H_{19}F_6N_6P$: C, 30.34; H, 5.38. Found: C, 30.42; H, 5.46. The compound is rather unstable and liquifies on slight heating or during 3–4 days at room temperature affording the difluorophosphorane **27a**. $^{31}$P NMR ($CDCl_3$): −64 (t, $J_{P\text{-}F}$ = 699 Hz). Ref. [29]: $^{31}$P NMR: −65.7.

*Reaction of Hexaethyltriaminophosphine,* **25b** *with Azide* **1.** 3.27 g (1.32 mmol) of phosphite **25b** and 2.55 g (1.32 mmol) of azide **1** were kept for 12 hours at 15–18°C. No gas evolution occurred. Volatile impurities were pumped off at room temperature. The $^{31}$P NMR spectrum of the reaction mixture contained only one singlet at δ 42.6, which was attributed to the phosphazide **26b**. An attempt to distill the compound in vacuo ($10^{-5}$ mm) was unsuccessful and gave only decomposition products (the volatile products were nitrogen and $CF_3CHFCN$). $(Et_2N)_3PF_2$, **27b**, (1.82 g, 49%) was isolated as a result. $^{31}$P NMR ($CDCl_3$): −58.4 (t, $J_{P\text{-}F}$ = 700 Hz); bp 68–72°C/0.03 mm. Ref. [30]: $^{31}$P NMR: −58.8, $J_{P\text{-}F}$ = 696 Hz.

*Fluorination of Dimethylaminodifluorophosphine,* **28.** 10 g (52 mmol) of azide **1** were added dropwise to 5.96 g (52 mmol) of **28** at 10–15°C. A smooth gas evolution was observed. After 4 hours, the $^{31}$P NMR spectrum of the reaction mixture contained the signals of the starting $Me_2NPF_2$ and of **29** (δ −4, ttd, $^1J_{P\text{-}F}$ = 1010 Hz, $^3J_{P\text{-}F}$ = 23.4 Hz, $^4J_{P\text{-}F}$ = 7.8 Hz). White crystals of **31** appeared at this time. After 24 hours, the crystals were filtered off, washed with ether, and dried (for X-ray structure analysis data for **31**, see Ref. [15]. The supernatant liquid contained no starting **28**, the main components being **29** and compound **30** [$^{31}$P NMR ($CDCl_3$): −65.5 (dtdd, $J$ = 891, 766, 59 and 6.5 Hz)]. This liquid slowly converts into crystals of **31** during a period of 1 month.

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