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Fluoroalkoxy-derivatives of trivalent phosphorus: synthesis and reactivity

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Abstract. The review surveys and gives a systematic account of the electronic structures, syntheses, and chemical properties of fluoroalkyl derivatives of trivalent phosphorus (phosphites, thiophosphites, and amidophophites). The methods of preparation and reactivities of fluoroalkyl phosphites are compared with those of unsubstituted phosphites. The bibliography includes 420 references.

I. Introduction

Derivatives of trivalent phosphorus are of key importance in the synthesis of a wide variety of organophosphorus compounds with different coordinations at the phosphorus atom and exhibit in most cases pronounced nucleophilic properties. This is associated with the accessibility of the lone pair (LP) of the phosphorus atom in the above derivatives and with the ease of their conversion into compounds with a phosphoryl group.

Various aspects of the influence of alkyl-, alkoxy-, amido-, etc. substituents on the reactivity of trivalent phosphorus compounds have been described in fair detail in the literature, but there have been no surveys of the influence of fluorine atoms, although a number of questions, concerning, for example, the electronic structures of fluorinated derivatives of P(III), have been discussed in monographs.[1–3]

A systematic description of the syntheses and chemical properties of fluoro-alkoxy-derivatives of trivalent phosphorus and the identification and possible explanation of their characteristic features compared with the unsubstituted analogues are the subject of the present review.

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II. The influence of fluorine-containing substituents on the properties of the P(III) atom. Photoelectron spectroscopic and electrochemical data

The introduction of a fluorine atom into trivalent phosphorus compounds almost always alters the properties of the derivatives obtained compared with their nonfluorinated analogues, although as a rule the fluorine atom in such derivatives is not a reaction centre or a leaving group. In order to give a systematic account of data concerning the influence of fluorine on the properties of the P(III) atom, it is useful to examine four conventional groups of compounds containing P and F atoms: (1) compounds with a P–F bond; (2) compounds containing the P–C–F fragment (the F atom occupies the α-position relative to the P atom — these are usually CF_3 derivatives); (3) compounds containing the P–E–C–F fragment, where E = C, O, S, Se, N, etc. (the F atom occupies the β-position relative to the P atom); (4) compounds with the P–E–C–C–F fragment (the F atom occupies the γ position relative to the P atom). The available information about the reactivities of the first two groups of compounds have been surveyed.[4–9] The chemistry of the compounds belonging to the third group, in which E = S, Se, or Te, has been scarcely investigated. Among the compounds with E = C, the pentafluorophenyl derivatives have been most thoroughly investigated.[10] In compounds with P–E–C–C–F fragments, the fluorine and phosphorus atoms are separated by four bonds and the inductive effect of the fluorine atom on phosphorus in them should be minimal. Nevertheless, experimental data indicate an appreciable influence of the fluorine atoms on the phosphorus centre in such compounds.

According to X-ray photoelectron spectroscopic data, the replacement of a hydrogen atom by fluorine in an organic compound leads to profound perturbations of the electronic core of the molecule as far as the 1*s* level of carbon. The binding energy of the electrons of the carbon atom $E(C1s)$ in the CF_nH_{4-n} molecule then increases by ~2.7 eV for each fluorine atom introduced.[1] On passing from ethane to trifluoroethane ($C_\beta H_3-CF_3$), an additive increase in the binding energy for the β-carbon $E(C_\beta 1s)$ is also observed, although to a lesser extent than in methane (from 290.7 to 292.1 eV).

The additivity breaks down when an oxygen atom is introduced at the β-carbon atom. Thus, on passing from ethanol to trifluoroethanol, $E(C_\beta 1s)$ changes by only 0.3 eV (from 292.5 to 292.8 eV), while on replacement of one hydrogen atom in

$C_\alpha F_3 C_\beta H_3$ by OH groups, $E(C_\alpha 1s)$ does not change [$E(C_\alpha 1s)$ = 297.8 eV]. It follows from these data that the manifestation of the inductive effect for $C_3 1s$ on passing from ethane to trifluoroethane is almost five times greater (Δ = 1.4 eV) than on passing from ethanol to trifluoroethanol (Δ = 0.3 eV). This phenomenon is classified as the β-effect of the fluorine atom.[11]

Calculations [12] yield a negative charge on the carbon atom in the β-position relative to fluorine. Thus in ethane the charge on the carbon atom is zero, while in CF_3CH_3 we have q^{C_α} = 0.60–0.72 e and q^{C_β} = (−0.09)–(−0.11) e, i.e. the presence of the fluorine atom increases the electron density on the β-carbon atom and diminishes it on the C_α atom. The consequences of the β-effect of the F atom are particularly strikingly manifested, as will be seen below, in the case of fluorinated alkoxy-derivatives of P(III). In order to explain it, the concepts of hyperconjugation,[11,13–15] antibonding orbitals,[16,17] and the perfluoro-effect [11] have been resorted to.

According to Davis et al.[12] and Bock et al.,[18] the effect can be accounted for by the fact that the strong acceptance of electronic charge by fluorine via the system of σ-bonds is accompanied by the reverse polarisation of the π-electron system or the σ* orbitals. Overall, if the charges on the carbon atoms of ethane are zero, the substitution of a hydrogen atom by fluorine leads to the appearance of an effective positive charge of 0.24 e at the α-carbon atom and of a negative charge of −0.03 e at the β-atom; the charge on the fluorine atom is −0.23 e. These features are fully retained for ethene and benzene.[1]

By virtue of its small size (the van der Waals radius of fluorine is 0.14 nm), close to that of the hydrogen atom (0.12 nm), the fluorine atom is capable of substituting all the hydrogen atoms in linear molecules. When all the valences of the carbon atom in the carbon chain are saturated by fluorine atoms, the carbon skeleton passes from the zigzag to the helical shape, whereupon the electronegative fluorine atoms fully protect the carbon skeleton against attack by nucleophiles.[19,20] The helix exhibits a 180° twist for each 13 carbon atoms. In a weakened form, this effect is probably manifested also in fluoroalkyl phosphites, particularly those with long fluorinated carbon chains.

In order to estimate the quantitative influence of fluorine on various properties of the molecule, photoelectron spectroscopy (PES) has been widely used together with X-ray spectroscopy.[21–23] A characteristic feature of the photoelectron spectra of organofluorine compounds is the absence of narrow (without a vibrational structure) bands, typical for ionisation with participation of nonbonding MOs, although formally the molecules contain a large number of fluorine lone pairs (n_F), whereas such narrow bands are observed for the chloro- and bromo-derivatives. The broad bands present in the spectra of organofluorine compounds, frequently with vibronic structures, indicate that in the organofluorine compounds there are no true n_F orbitals. The photoelectron spectra of fluoroalkanes, fluoroalkenes, and fluoromethyl derivatives of nitrogen subgroup elements, i.e. simple and planar molecules, almost fully reproduce the photoelectron spectra of hydrocarbon analogues, although they are displaced towards higher ionisation potentials (IP). However, the effect of the perfluoroalkyl substituent, postulated [24] and defined as a shift towards higher IP (without changes in the sequence, energy differences, and symmetry type of the MO for the n and σ MO of the central atom) when alkyl groups are replaced by perfluoroalkyl groups, is not a general rule for fluorinated molecules, because it requires a correspondence between the nature of the MO and the energies and symmetries of the fluorinated and hydrocarbon analogues. This is possible only subject to the condition of the complete localisation of the orbitals n_F on the fluorine atoms, which in its turn conflicts with the nature of the photoelectron spectra.

The ionisation potential of the molecule is a measure of the difference between the energies of formation of the molecule and the molecular ion (radical-cation). The replacement of a hydrogen atom by an alkyl group with electron-donating properties leads to the stabilisation of the radical-cation, while the replacement by a fluorine atom or a fluorinated alkyl (σ-acceptors) results in destabilisation. The σ-acceptor effect of the CF_3 group is then intensified by its weak π-acceptor effect, while the effect of the F atom is weakened by the donor influence.[3]

The complex nature of the effect of the CF_3 group has been demonstrated recently.[25] Thus, when a F atom is replaced by the CF_3 group in fluoroalkenes, the π levels of the molecule are strongly stabilised with some destabilisation of the σ levels. For example, on passing from $CF_2=CF_2$ to $(CF_3)_2C=C(CF_3)_2$, the π-type HOMO energy diminishes by 3.8 eV, while the LUMO (π*) energy decreases by 2.1 eV. Under these conditions, the occupied π- and σ- type MO approach one another. The CF_3 group induces a marked alternation of the charge (the appearance of a negative charge on the β-carbon atom and of a positive charge on the α-carbon atom). Thus the overall effect of the CF_3 group in perfluoroalkene is electron-donating (M-acceptor, σ-donor). Evidently, the electronic effects of the CF_3 group on the F atom can change depending on the nature of the fragment to which they are attached. Thus, using the LCAO-MO SCF methods supplemented by the optimisation of the geometrical parameters, it has been shown that the $C_\alpha - C_\beta$ distance decreases with increase in the number of CF_3 groups at the α-atoms of the carbanions $CF_3CH_2^-$, $(CF_3)_2CF^-$, and $(CF_3)_3C^-$, which indicates the existence of negative hyperconjugation at the fluoroalkyl substituents.[26]

In simple, planar molecules, the substitution of hydrogen by fluorine leads to a more pronounced stabilisation of the σ MO than the π MO. The preferential σ-stabilisation on fluoro-substitution is called the perfluoro-effect. The ranges of the π-electron IP then overlap markedly and the composition of the fluorinated derivatives changes qualitatively compared with that of the nonfluorinated analogues.[27]

The photoelectron spectra of fluorinated alcohols have a complex form with broad overlapping bands.[28–30] Overall, they are subject to the effect of the perfluoroalkyl group, i.e. they have the same band sequence as in the spectra of the usual alcohols which has undergone an almost parallel shift into the region of higher potentials; furthermore, quantum-chemical calculations [28,29,31] yield the same sequence of the MO. The highest occupied molecular orbital of alkanols and their fluoro-derivatives is not a pure n_0 orbital. The contributions of the 2p AO LP of oxygen to the HOMO in the series CH_3CH_2OH, CH_2FCH_2OH, $(CF_3)_3COH$ are 43%, 41%, and 27% respectively. This suggests that the n_0 orbitals, like the n_F orbitals, are not fully localised on oxygen and fluorine.

In trifluoroethanol, the CF_3 group is separated from the oxygen atom by the CH_2 unit, which weakens both the σ_I-effect and the conjugation effect.

Extremely interesting data have been obtained in the study of fluorinated alcohols by the ^{17}O and ^{13}C NMR methods.[32] It was found that the influence of fluorine in the β- and γ-positions ($F_\beta - C - O$, $F_\gamma - C - C - O$) is manifested much more strikingly in the ^{17}O NMR spectra than in the ^{13}C NMR spectra. Bearing in mind that the quantity $\delta_O(\delta_C)$ is linearly related to the charge on the corresponding atom and hence to the electron density,[33] one may reach certain conclusions about its distribution. The fluorine atoms in the β-position relative to the oxygen (and carbon) atom exert a powerful deshielding effect ($\Delta_O = 36 \pm 5$ ppm) on the oxygen atom (the β-effect), whereas the F_γ atoms exert a weak shielding effect ($\Delta_O = 10 \pm 3$ ppm). The above effects may be accounted for by the different manifestations of the effect due to the field of the fluorine atom.[34]

The vertical IP for fluorine-containing phosphites have been determined.[35–37] It was shown that the replacement of hydrogen atoms by fluorine increases significantly IP_1, which largely corresponds to ionisation with participation of the n_p orbital. Thus the IP_1 for the phosphites **2** and **4** exceed the IP_1 for the phosphites **1** and **3** by 1.33–1.37 eV (Table 1). Finally, the IP_1 for tris(hexafluoroisopropyl) phosphite **5** is greater than IP_1 for phosphorus trichloride by 0.29 eV, i.e. the electron-accepting

Table 1. Photoelectron spectroscopic data for certain P(III) derivatives.

Compound	$IP_1(n_P)$ / eV	$IP_2(n_O)$ / eV	Ref.
$(CH_3CH_2O)_3P$ (1)	9.0	10.3	38, 39
$(CF_3CH_2O)_3P$ (2)	10.37	11.71	35
$(CH_3CH_2CH_2O)_3P$ (3)	8.85	10.18	37
$(CHF_2CF_2CH_2O)_3P$ (4)	10.18	11.07	36
$[(CF_3)_2CHO]_3P$ (5)	10.81	11.94	37
PCl_3	10.52	–	40
PBr_3	9.35	–	40

effect of the hexafluoroisopropyl substituent exceeds that of the chlorine atom. Overall, the photoelectron spectra of the fluorinated phosphites resemble those of the usual phosphites, but they are displaced towards higher ionisation potentials, i.e. the perfluoroalkyl effect rule holds in this case, since the sequence and symmetry of the MO (n_P, n_O, σ_{CC}) are retained.

It has been shown[40] that the IP_1 in the PX_3 series increase in proportion to the IP_1 of the functional hydrides HX (the fluorinated phosphites **2**, **4**, and **5** are not an exception). The relation between $IP(PX_3)$ and IP(HX) is linked to the parallel manifestation of the inductive effect of the substituent X and the mixing of the orbitals l_P and n_X.[40] Thus the contribution of the 3*p* AO LP of phosphorus to the HOMO increases in the sequence $C_6F_5P(NEt_2)_2 < C_6F_5P(NCS)_2 < C_6F_5P(OMe)_2$ in conformity with the increase in the $IP_1(HX)$: $HNEt_2$ (8.15) < HNC (9.94) < HOMe (10.96).[41] The $IP(n_P)$ for the phosphites **2**, **4**, and **5** exceed those for the phosphonites enumerated, like the $IP(n_O)$ of fluorinated alcohols, so that the contribution of the phosphorus 3*p* AO to the HOMO increases, with an overall increase in $IP(n_P)$, on passing from the phosphites $P(OR)_3$ and the phosphonites $C_6F_5PX_2$ to the fluorinated phosphites **2**, **4**, and **5** and $P(OC_6F_5)_3$. Under these conditions, the n_P orbital to which the 3_p AO of phosphorus contributes significantly (from 75% to 87% according to different estimates),[40] is also capable of $n_P - \sigma^*_{C-O}$ conjugation.

The electron-accepting nature of the C–O σ*-bond increases as a result of the introduction of the fluorinated substituent at the carbon atom. In the usual compounds, the $n_P - \sigma^*_{C-O}$ interaction in the P(III)–O–C fragment is weak, since the excitation is localised mainly on the carbon atom.[42,43] In fluorinated phosphites, such interaction is apparently more effective; here there is a partial delocalisation of the n_P electrons to the C–O σ-bond. An appreciable delocalisation of the n_P electrons has been noted for the compound $P(OC_6F_5)_3$, which has been investigated by X-ray emission spectroscopy (PK_β).[41]

The enhancement of the electron-accepting properties of the OR_F substituents via the σ_I mechanism is accompanied by an increase in the electrophilicity of the P–O σ*-bonds, the electron deficiency occurring predominantly on the phosphorus atom, because it is less electronegative than oxygen. Bearing in mind the electronic interaction occurring in the $O-CH_2-CF_3$ fragment and enhancing the electron-accepting properties of the orbital σ^*_{CO}, one may postulate that the conjugation of the P–O σ*-bond and the n_O electrons, characteristic of the usual P(III) compounds, is unlikely in compounds with this fragment.

Thus, by virtue of the strong electron-accepting effect of the fluoroalkoxy-groups, a significant electron density deficiency arises on the phosphorus atom, which imparts electrophilic properties to the latter. Hence one should expect a greater reactivity of R_F phosphites in reactions with nucleophiles compared with R_H phosphites.

One of the consequences of the replacement of the H atoms by F atoms in phosphites is the strengthening of the C–O bond, i.e. an increase in its energy. This change in the bond energy may be explained on the basis of the orbital model of $n_O - \sigma^*_{C-C}$ hyperconjugation.[16,42,43] The introduction of fluorine atoms lowers the energy of the σ^*_{C-C} orbital, which is localised predominantly on the terminal carbon atom of the $C-CF_3$ fragment and increases the effectiveness of its interaction with n_O.

The transfer of electron density from the oxygen atom to the fluorinated alkyl group is possible both via the σ_I mechanism and via a mechanism involving $n_O - \sigma^*_{C-C}$ and $\sigma_{C-O} - \sigma^*_{C-F}$ conjugation. Furthermore, the substituent $CF_3(R_F)$ exhibits a π-acceptor effect,[3] which may occur via the mechanism involving the hyperconjugation of the antibonding MO of the CF_3 group localised on the carbon atom with the π-type MO of the CH_2 fragment. All this strengthens the C–C and C–O bonds, i.e. stabilises the σ levels and enhances the electron-accepting properties of the alkoxy-fragment OR_F.

The photoelectron spectra of cyclic phosphites containing electron-accepting substituents $(CF_3)_2CH$ have been investigated.[37] The results are presented in Table 2.

The first two potentials, IP_1 and IP_2, in the photoelectron spectra of benzodioxaphospholanes **6–9** and the salicyl derivatives **13** and **14** correspond to the ionisation of two π orbitals of the benzene ring, $a_2(\pi)$ and $b_1(\pi)$, perturbed by the effective interaction with the antisymmetric (n^-_O) and symmetrical (n^+_O) combinations of the group orbitals of oxygen. Under these conditions, the $a_2(\pi) - n^+_O$ orbital is the HOMO.

The ionisation potential IP_3 of the benzophospholanes **6–9** corresponds to the ionisation of the n_P orbital. exceeding the $IP_1(n_P)$ for the analogous phospholanes **10–12** by 0.35 –0.6 eV. The reason for the increase in $IP_3(n_P)$ in the benzophospholanes **6–9** is the effective interaction. The replacement of one oxygen atom in compounds **6** and **7** by an ester group (compounds **13** and **14**) leads to an appreciable increase in the energies of the $a_2(\pi)$ and $b_1(\pi)$ orbitals, but at the same time facilitates the ionisation of the n_P orbital. This is consistent with the M effect of the C(O)O group.

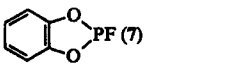
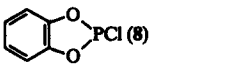
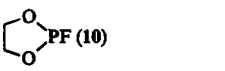
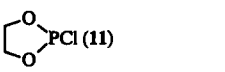
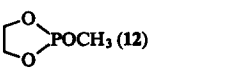
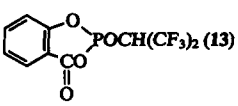
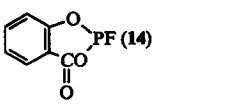
Naturally the $n^+_O - a^*_2(\pi)$ and $n^+_O - b^*_1(\pi)$ conjugation is just as effective as the $n^+_O - \pi$ interaction. The $n_O - \pi^*$ conjugation shifts electron density from the oxygen atom to the ring.

It follows from the foregoing that cyclic benzodioxaphospholanes and unsubstituted dioxaphospholanes contain an extremely electrophilic phosphorus atom, the positive charge on which is comparable to that for acyclic fluorinated phosphites (the ionisation potentials of such compounds are very high). If weak electron-accepting substituents, such as NR_2, OMe, or $OSiMe_3$ are present at the phosphorus atom in the phospholane, then the σ^*_{PO} orbitals, localised mainly on the phosphorus atom, behave as acceptors in the $\sigma^*_{PO} - n_X$ conjugation,[44] the electrophilicity of the σ^*_{PO} orbitals of the cyclic fragment increasing after the introduction of the benzene ring owing to $n_O - \pi^*$ conjugation. On the other hand, if there are strong π-acceptor substituents, for example OC_6F_5, $OCH(CF_3)_2$, or OCH_2CF_3, at the phosphorus atom, then the nature of the electronic interactions of the cyclic fragment with the exocyclic substituent changes. In this case, the electrophilicity of the σ^*_{PO} orbital weakens, and the $n_O - \sigma^*_{PX}$ interactions are intensified, which diminishes somewhat, in its turn, the $n_O - \pi^*$ conjugation. Thus the $IP_1(\pi_1)$ and $IP_2(\pi_2)$ for compounds **6** and **7** increase by ~0.45 and ~0.30 eV compared with the corresponding ionisation potentials of compound **9** (Table 2).

The photoelectron spectroscopic data for fluorinated phosphites examined above show that the $IP_3(n_P)$ for these compounds are higher by 1.3–2 eV compared with the ionisation potentials of the unsubstituted phosphites, which should undoubtedly be reflected in the electrochemical properties of fluoroalkyl phosphites. The study of the electrochemical behaviour of fluoroalkyl phosphites[37,45–47] has shown that acyclic derivatives are not oxidised in the accessible range of potentials (for example, compounds **2**, **4**, and **5**), which is fully consistent with photoelectron spectroscopic data. Table 2 presents also the half-wave oxidation potentials ($E_{1/2}$/V) of some of the fluorinated P(III) derivatives investigated. They were obtained by the voltammetric method at a platinum electrode in acetonitrile (25 °C).[47]

The value of $E_{1/2}$ quoted[48,49] for tris(tetrafluoropropyl) phosphite **4** (0.85 eV) is erroneous and has not been reproduced.

Table 2. Photoelectron spectroscopic data for certain cyclic phosphites (IP/eV).[37]

Compound	$IP_1(\pi_1)$ $a^2(\pi)-n_O^+$	$IP_2(\pi_2)$ $b_1(\pi)-n_O^-$	$IP_3(n_P)$	$E_{1/2}$/V
 POCH(CF$_3$)$_2$ (6)	8.89	9.58	10.75	1.59, 2.03
 PF (7)	8.90	9.53	11.11	1.58, 1.85
 PCl (8)	8.86	9.57	10.55 ($n_P-n_O-n_{Cl}$)	–
 POCH$_3$ (9)	8.45	9.26	10.33	1.29, 1.99
 PF (10)	10.74(n_P)	11.19(n_O)	12.51(σ_{CC})	–
 PCl (11)	10.20(n_P)[48]	–	–	–
 POCH$_3$ (12)	9.55(n_P)[48]	–	–	–
 POCH(CF$_3$)$_2$ (13)	9.42(π_1)	9.80(π_2)	10.30 ($n_P+n'_O$)	2.34
 PF (14)	9.54	10.04	10.43	–

This is understandable because the value of $E_{1/2}$ determined by the above workers[48,49] is actually lower than $E_{1/2} = 1.68$ V for P(OEt)$_3$.[50] One-electron and (according to cyclic voltammetric data) irreversible waves were observed on the voltammograms for fluoroalkyl phosphites derived from catechol and salicylic acid. The reaction centre in these compounds is the benzene ring and an electron is abstracted from the HOMO which is the $a_2(\pi)-n_O^*$ orbital.

The calculated number of electrons for cyclic fluoroalkyl phosphites is less than integral values, which may be associated with the interaction of the radical-cation formed with the initial phosphite.This leads to the formation of dimeric species, for example in the case of bis(trifluoroethyl) phenylphosphonite.[51]

The shift of the potential $E_{1/2}$ to the negative region for compound **13** and its analogues[47] is associated with the presence of the electron-accepting substituent C(O)O in the ring, which agrees with the higher ionisation potential of the $a_2(\pi)$ orbital.

Thus electrochemical oxidation, photoelectron spectroscopic, NMR spectroscopic, and calculated data clearly indicate that the phosphorus in fluorinated cyclic and acyclic phosphites has a very high IP(n_P), carries an appreciable effective positive charge, and exhibits (together with nucleophilic properties) pronounced electrophilic properties. As a result of the characteristic features of the electronic interactions in the fluoroalkoxy-group, it is difficult to split off R_F from phosphonium centres compared with the splitting off of R_H. For this reason, one should expect the ready elimination of this group in the corresponding nucleophilic reactions, i.e. the easier cleavage of the P–OR$_F$ bond compared with the P–OR$_H$ bond. The easier elimination of the CF_3CH_2O group compared with CH_3CH_2O has been noted[52] in relation to the aminolysis of the esters $RCOOCH_2CF_3$. In this sense, the chemistry of fluoroalkyl phosphites resembles that of P(III) halides, which is known to reduce largely to nucleophilic substitution reactions at the phosphorus atom. Furthermore, the chemistry of fluoroalkyl phosphites is significantly richer and is not restricted solely to the nucleophilic reactions indicated above. The difference in the behaviour of fluoroalkyl phosphites and P(III) halides, having similar IP(n_P), may be due to the difference in the hybridisation of the phosphorus lone pairs, which has predominantly *s* character in the case of phosphorus halides and is distinguished by a significant contribution of *p* character in the case of trialkyl phopshites.[2,40] Finally, the formation of products with a phosphoryl group from fluorinated phosphites should be more convenient than their formation from unsubstituted phosphites.

III. Synthesis of fluoroalkoxy-derivatives of P(III)

1. Reactions of P(III) halides with fluorine-containing alcohols

Various methods of synthesis of P(III) derivatives containing fluorinated substituents have been developed: reactions involving phosphorylation of fluorinated alcohols by P(III) acid halides and amides, alcoholysis and transamination reactions, interaction of P(III) derivatives with hexafluoroacetone, etc.

The interaction of P(III) halides with fluorinated alcohols is one of the most frequently employed approaches to the synthesis of fluoroalkyl phosphites. As we have already noted, fluorinated alcohols are relatively weak nucleophiles. They are less basic than the usual alcohols.[31] Being fairly acidic ($pK \approx 4-12$),[53,54] R_F-alcohols react with difficulty with P(III) chlorides, in contrast to R_H-alcohols. They are unusually inert in reactions proceeding via the intermediate formation of carbonium ions, which indicates a strong interaction of the oxygen lone pair with the fluoroalkyl fragment (the 'mesomeric' nature of the bonds).[55] Quantum-chemical calculations,[31] carried out for CF_3CH_2OH, $CF_3CH_2O^-$, $(CF_3)_2CHOH$, and $(CF_3)_2CHO^-$, indicate shortening of the C–O bond in fluoroalcohol anions (compared with

R_H-alcohols) and a corresponding increase in the length of the C–F and C–C bonds and an increase in the effective negative charge on the CF_3 and $(CF_3)_2CH$ fragments, which is interpreted as the manifestation of the field effect.[31] The nucleophilicity of $P(OR_F)_3$ differs little from that of PX_3 (X = Cl, Br). This probably explains the inertness of fluoroalkyl phosphites when acted upon by hydrogen halides so that in the synthesis of R_F phosphites from PX_3 there is no need to employ bases in order to bind the HX.

Phosphites based on fluorinated alcohols — tris(2-fluoroethyl) phosphite and tris(2,2,2-trifluoroethyl) phosphite — were first obtained from PCl_3.[56,57] It was noted that, in the interaction of PCl_3 with linear R_F-alcohols, mainly trialkyl phosphites are formed together with a small amount of R_F-dialkyl chlorophosphites.[57–59] Further studies[60–62] demonstrated that the result depends on the ratio of the initial compounds, the reaction conditions, and the catalyst. At 80 °C and for the ratio $PCl_3 : R_FOH$ = 1:1, it is possible to isolate dichlorophosphites, the yield of trialkyl phosphites increasing with increase in temperature. The latter are formed almost quantitatively if the initial alcohol is employed in (2–3)-fold excess. We have frequently noted that the acid phosphite $(R_FO)_2PHO$ is frequently formed as a side product, i.e. the reaction of fluoroalkyl phosphites with PCl_3 does nevertheless occur to a slight extent (up to 10%–15%). It becomes the main reaction in the case of 2-fluoroethanol, which affords bis(2-fluoroethyl) phosphites in a high yield on treatment with PCl_3.[63] The addition of a catalyst (pyridine) accelerates the reaction significantly and improves the yield of the trialkyl phosphite:[60,61]

$$PCl_3 + R_FOH \xrightarrow[\leqslant 80\ ^\circ C,\ 1:1]{} R_FOPCl_2 + HCl$$
$$\xrightarrow[>80\ ^\circ C,\ 1:3]{} R_FOPCl_2 + (R_FO)_3P + HCl$$
$$\xrightarrow[Py,\ 80\ ^\circ C,\ 1:3]{} (R_FO)_3P + 3HCl$$

$R_F = CHF_2(CF_2)_nCH_2$, n = 1, 3, 5.

The catalytic role of pyridine is seen in relation to the synthesis of tris(hexafluoroisopropyl) phosphite **5**: at 25 °C, hexafluoroisopropyl alcohol does not react with PCl_3 (1 : 1), on prolonged heating the phosphite **5** is formed in 70% yield,[64] while in the presence of pyridine the reaction ends after 2 h and the yield of the phosphite **5** is almost quantitative.[65] Tertiary alcohols such as $(CF_3)_2MeCOH$, do not react with PCl_3 even at 90 °C,[64] whereas the alcohols R_FMe_2COH [R_F = CF_3, CHF_2CF_2, $CHF_2(CF_2)_3$], taken in an appropriate amount, interact with PCl_3 in the presence of pyridine as catalyst, affording high yields of the dichloro- and monochloro-phosphites $Cl_{3-n}P(OCMe_2R_F)_n$ (n = 1, 2).[66] Pentafluorophenol reacts with PCl_3 on heating to form (depending on the initial reactant ratio) predominantly $C_6F_5OPCl_2$ or a mixture of $(C_6F_5O)_2PCl$ and $P(OC_6F_5)_3$, all three compounds being separated by distillation.[67]

Numerous studies (see, for example, Refs 57 and 68–73) have been made of the interaction of PBr_3 with fluorinated alcohols, but their results are contradictory. On the whole, PBr_3 reacts more readily with fluoro-alcohols than PCl_3, but the reaction proceeds via several paths. For the ratio $PBr_3 : R_FOH$ = 1 : 3, fluorine-containing trialkyl phosphites are formed in high yields.[57,73] Attempts to obtain bromo- and dibromo-phosphites were unsuccessful. The preparation of the dibromophosphite $CHF_2(CF_2)_3CH_2OPBr_2$ has been reported in only one study.[72] In the case of trifluoroethanol and the fluoroalkanols $CH_2F(CH_2)_nOH$ (n = 1, 2, 5, 7), an appreciable amount of the fluoroalkyl bromide is produced.[68–71] Such results are associated both with the greater tendency of P(III) bromides to disproportionate compared with the chlorides and with the more effective dealkylation of fluoroalkyl phosphites by HBr. Tris(fluoroalkyl) phosphites, dialkyl chlorophosphites, chlorophosphonites, and chlorophosphinites, their fluorinated analogues, asymmetric fluoroalkyl phosphites, and amidophosphite have been obtained in high yields by Arbuzov's method via alkoxides.[58,64,74] These reactions proceed smoothly and, depending on the initial reactant ratio, lead to mono-, bis-, or tris-(fluoroalkyl) phosphites. However, here too dismutation occurs in certain cases, particularly in the synthesis of fluoroalkyl phosphites with linear groups.

Lithium alkoxides are usually employed in the synthesis of fluoroalkyl phosphites.[64,74–88] Sometimes (see, for example, San et al.[74]) lithium alkoxide is obtained beforehand from R_FLi [R_F = $CF_2CF_2OCF(CF_3)_2$] and hexafluoroacetone.

$$R_FLi + (CF_3)_2C{=}O \longrightarrow R_FC(CF_3)_2OLi \xrightarrow[MeCN,\ (CF_2Cl)_2]{PCl_3}$$
$$\longrightarrow [R_FC(CF_3)_2O]_3P.$$
94%

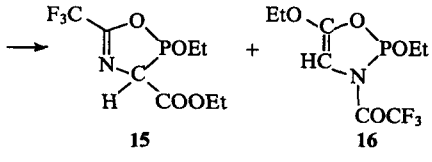
Bis(fluoroalkyl) chlorophosphites show a much greater tendency to disproportionate than dialkyl chlorophosphites. Nevertheless they have been obtained in a number of studies from PCl_3 and the corresponding alcohols both in the presence[59,89,90] and absence[58,59,66] of a base. Other approaches to the synthesis of bis(fluoroalkyl) chlorophosphites have also been proposed: the exchange reactions of $P(OCH_2CF_3)_3$ with BCl_3 and PCl_3,[58] as well as the exchange reactions of PX_3 with lithium R_F-alkoxides.[76,89]

Fluoroalkyl difluorophosphites and bis(fluoroalkyl) fluorophosphites are obtained by the reactions of PF_3 with R_F-alcohols or R_FOLi and R_FONa[77,78,82,91] by fluorinating bis(fluoroalkyl) chlorophosphites and fluoroalkyl dichlorophosphites with SbF_3.[81,92,93] The synthesis of the phosphite containing mobile halogen atoms $[(Pr^iO)_2POCCl(CCl_3)CF(CF_3)(SO_2F)]$ described by Eleev et al.,[94] gives rise to doubts owing to the presence of extremely reactive fragments in this compound.

Table 3 presents acyclic P(III) compounds obtained by phosphorylating fluorinated alcohols or their alkoxides by P(III) halides; it also lists cyclic phosphites containing an exocyclic fluoroalkoxy-substituent, as well as compounds obtained from fluorinated diols and their lithium derivatives.[53,54,56–165]

An extremely interesting example of phosphorylation leading to the isomeric azaphospholines **15** and **16** has been described.[166] On heating, 1,3,5-oxazaphospholine **15** (δ_P = 166 ppm) is converted into 1,3,2-oxazaphospholine **16** (δ_P = 112 ppm)

$$CF_3CNHCH_2COOEt + Cl_2POEt \xrightarrow[-Et_3N\cdot HCl]{NEt_3}$$



15 **16**

Phosphorylation of the potassium and silver salts of 2,3,4,5-tetrakis(trifluoromethylthio)pyrrole (HetM) by treatment with PCl_3, $PhPCl_2$, Ph_2PCl, PI_3, and PBr_3 afforded fluorinated heterocyclic amidophosphites:[167] Het_2PCl, $PHet_3$, Het_2POEt, Het_nPPh_{3-n} (n = 1, 2, 3). The chemistry of these compounds has been surveyed by Weiss.[168]

Another interesting type of fluorinated P(III) amides comprises phosphorylated derivatives of hexafluoroacetone imine **17**.[169]

$$(CF_3)_2C{=}NLi + F_nPCl_{3-n} \longrightarrow F_nP[N{=}C(CF_3)_2]_{3-n}$$

17

n = 1, 2, 3.

Table 3. Acyclic and cyclic fluoroalkyl phosphites.

Compound	R_F	R (or NR_2)	R′ (or X)	Ref.
$(R_FO)_3P$	CF_3CH_2	–	–	57, 58, 95
	$CHF_2(CF_2)_nCH_2$ (n = 1, 3, 5)	–	–	58–61, 73
	CH_2FCH_2	–	–	56
	$CF_3CF_2CH_2$	–	–	59
	$CF_3(CF_2)_2CH_2$	–	–	59
	$C_6F_{13}CH_2CH_2$	–	–	75
	$(CF_3)_2CH$	–	–	64, 65, 76, 77, 88, 96
	CF_3MeCH	–	–	64
	$(CF_3)_2CMe$	–	–	64
	CF_3CMe_2	–	–	64
	$(CF_3)_2C(CN)$	–	–	78, 79
	$(CF_3)_2CFO(CF_2)_2C(CF_3)_2$	–	–	74
	$(ClCF_2)_2C(CN)$	–	–	80
	$C_6F_5CH_2$	–	–	97
	C_6F_5	–	–	67, 92, 98
$(R_FO)_2PCl$	CF_3CH_2	–	–	58, 99
	$CHF_2CF_2CH_2$	–	–	58, 59, 89, 90
	$CF_3CF_2CH_2$	–	–	59, 100
	$CF_3(CF_2)_2CH_2$	–	–	59, 100
	$(CF_3)_2CH$	–	–	64, 76, 81
	$CHF_2CF_2CMe_2$	–	–	66
	$(CF_3)_2CMe$	–	–	64
	CF_3CMe_2	–	–	64
	C_6F_5	–	–	67
R_FOPCl_2	$CHF_2(CF_2)_nCH_2$ (n = 1, 3, 5)	–	–	58, 60–62
	CF_3CH_2	–	–	64
	$(CF_3)_2CH$	–	–	64
	$(CF_3)_2CMe$	–	–	64
	CF_3CMe_2	–	–	64
	$CHF_2(CF_2)_3CMe_2$	–	–	66
	CF_3CEt_2	–	–	66
	$CHF_2CF_2CMe_2$	–	–	67
	C_6F_5	–	–	67
	$MeOOCC(CF_3)_2$	–	–	79
	$Cl_2POCH_2(CF_2)_nCH_2$ (n = 2, 3)	–	–	101
	$(CF_3)_2CHCH_2$	–	–	102
$(R_FO)_2PF$	$(CF_3)_2CH$	–	–	81
	$(CF_3)_2C(CN)$	–	–	78
	C_6F_5	–	–	103
R_FOPF_2	CF_3CH_2	–	–	91
	$(CF_3)_2CH$	–	–	77, 103, 104
	$CHF_2(CF_2)_3CH_2$	–	–	92
	$CHF_2CF_2CH_2$	–	–	93
	$(CF_3)_2C(CN)$	–	–	82
	C_6F_5	–	–	103
	$(CF_3)_2CH$	–	–	104
	$(CF_3)_2Cl$	–	–	104
	$(CF_3)_2CBr$	–	–	104
R_FOPBr_2	$CH_2F(CF_2)_3CH_2$	–	–	73, 92
$R_FOP(OR)_2$	CH_2FCH_2	Et	–	63
	$CHF_2CF_2CH_2$	Et	–	105
	$FSO_2CF(CF_3)CCl(CCl_3)$	Pr^i	–	94
	$C_4F_9C{\equiv}CCH_2$	Et	–	106
	$C_4F_9C{\equiv}CCHMe$	Et^i	–	106
	$EtOOCCH{=}CCF_3$	Et	–	107
	$MeC(O)CH{=}CCF_3$	Et	–	108
	$Bu^tC(O)CH{=}CCF_3$	Et	–	108
	$PhN{=}CCF_3$	Et	–	109
	$(CF_3)_2CH$	Ph	–	110
	$CHF_2(CF_2)_3CH(NHCOOEt)$	Et	–	111

Table 3 (continued).

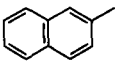
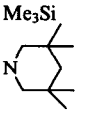
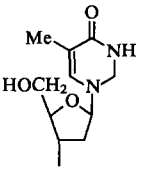
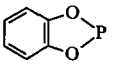
Compound	R_F	R (or NR_2)	R′ (or X)	Ref.
$R_FOP(OR)(OR')$	$CHF_2CF_2CH_2$	4-(4-$PhNHC_6H_4$)C_6H_4		112
$(R_FO)_2POR$	CH_2FCH_2	Et	–	63
	$CHF_2CF_2CH_2$	Et	–	113
	$EtOOCCH=CCF_3$	Et	–	108
	$(CF_3)_2CH$	Pr^i	–	88, 114
	$(CF_3)_2CH$	Ph	–	110
$(R_FO)_2PNR_2$	$C_2F_5CH_2$	Et	–	100, 115
	$C_2F_5CH_2$	H	–	100
	CF_3CH_2	Me_3Si	–	83
	$CHF_2CF_2CH_2$	Me_3Si	–	116
	$CHF_2CF_2CH_2$	N=C=O	–	89, 117
	$CHF_2CF_2CH_2$	N=C(Ph)OMe	–	89, 117
	$CHF_2CF_2CH_2$	N=C(Ph)OEt	–	89, 117
	$C_3F_7CH_2$	Et	–	100
	$C_3F_7CH_2$	H	–	100
	$(CF_3)_2CH$	H	–	84
	$(CF_3)_2CH$	NHMe	–	84
	$(CF_3)_2CH$	$NHBu^t$	–	84
	$(CF_3)_2CH$	Me	–	118
	$(CF_3)_2CH$	Et	–	118
	$(CF_3)_2CH$	Me_3Si	–	118
	$(CF_3)_2CH$		–	118
$(R_FO)(R'O)PNR_2$	$(CF_3)_2CHCH_2$	Pr^i		102
	$Et_2N(EtO)POCH_2(CF_2)_3CH_2$	Et	Et	100, 119
$(RO)_2PN(R_F)_2$	3-$CF_3C_6H_4$	Et	–	120
$(RO)_2PNR_FR'$	3-$CF_3C_6H_4$	Et		120
$(R_FO)P(Cl)NR_2$	$(CF_3)_2CHCH_2$	Pr^i	–	102
$(R_FO)P(NR_2)_2$	$EtOOCCH=C(CF_3)$	Et	–	108
	$(CF_3)_2CH$	Pr^i	–	121
	$CHF_2(CF_2)_3CH(NHCOOEt)$	Et	–	111
$(R_FO)PRX$	$(CF_3)_2CH$	Me	$(CF_3)_2CHO$	87, 122
	CF_3CH_2	Me	CF_3CH_2O	105,123
	$CHF_2(CF_2)_nCH_2$ ($n=1, 3$)	Me	$CHF_2(CF_2)_nCH_2O$ ($n=1, 3$)	124
	$C_2F_5CH_2$	CF_3	NEt_2	115
	CF_3CH_2	CF_3	CF_3CH_2O	125
	$CHF_2(CF_2)_nCH_2$ ($n=1, 3$)	CF_3	$CHF_2(CF_2)_nCH_2O$ ($n=1, 3$)	126
	$CHF_2(CF_2)_nCH_2$ ($n=1, 3$)	C_2F_5	$CHF_2(CF_2)_nCH_2O$ ($n=1, 3$)	126
	$C_2F_5CH_2$	CF_3	NH_2, NEt_2, Cl	100, 115
	$C_2F_5CH_2$	C_2F_5	NH_2, NEt_2, Cl	100, 115
	$C_2F_5CH_2$	C_3F_7	NH_2, NEt_2, Cl	100, 115
	$C_3F_7CH_2$	CF_3	NH_2, NEt_2, Cl	100, 115
	$C_3F_7CH_2$	C_2F_5	NH_2, NEt_2, Cl	100, 115
	$C_3F_7CH_2$	C_3F_7	NH_2, NEt_2, Cl	100, 115
	CF_3CH_2	Et	CF_3CH_2O	125
	CF_3CH_2	CCl_3	CF_3CH_2O	125
	$CHF_2CF_2CH_2$	Et	$CHF_2CF_2CH_2O$	105
	$CHF_2(CF_2)_5CH_2$	Et	$CHF_2(CF_2)_5CH_2O$	105
	$CHF_2(CF_2)_3CH_2$	Et	$CHF_2(CF_2)_3CH_2O$	124
	$(CF_3)_2CH$	Et	$(CF_3)_2CHO$	86

Table 3 (continued).

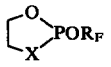
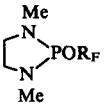
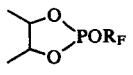
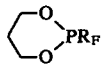
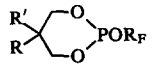
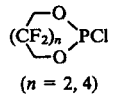
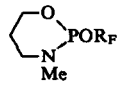
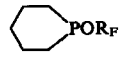
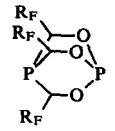
Compound	R_F	R (or NR_2)	R′ (or X)	Ref.
$(R_FO)PRX$	$C_4F_9CH_2$	$CH_2=CH$	$C_4F_9CH_2O$	127
	$C_4F_9CH_2$	CH_2ClCH_2	$C_4F_9CH_2O$	127
	$CHF_2(CF_2)_2CH_2$	$CH_2=CH$	$CHF_2(CF_2)_2CH_2O$	127
	$CHF_2(CF_2)_2CH_2$	CH_2ClCH_2	$CHF_2(CF_2)_2CH_2O$	127
	$CHF_2CF_2CH_2$	$EtOCH=CH$	$CHF_2CF_2CH_2O$	128
	CF_3CH_2	Ph	F	129
	$(CF_3)_2CH$	Ph	F	87, 129, 130
	$C_3F_7CH_2CH_2$	Ph	$C_3F_7CH_2CH_2O$	131
	CF_3CH_2	Ph	CF_3CH_2O	95, 105, 123, 132, 133
	$CHF_2CF_2CH_2$	Ph	$CHF_2CF_2CH_2O$	105
	$(CF_3)_2CH$	Ph	$(CF_3)_2CHO$	81, 87, 96
	$(CF_3)_2CH$	Bu^t	F	81, 130
	$(CF_3)_2CH$	Bu^t	Cl	81
	$(CF_3)_2CH$	Bu^t	Me	130
	$(CF_3)_2CH$	C_6F_5	$(CF_3)_2CHO$	81
	$(CF_3)_2CH$	Me	Me	87, 122
	$(CF_3)_2CH$	CF_3	CF_3	81, 87
	$(CF_3)_2CH$	Et	Et	86
	$(CF_3)_2C(CN)$	CF_3	CF_3	134
	$(CF_3)_2CH$	Ph	Ph	96, 135
	$CHF_2CF_2CH_2$	Ph	Ph	136
	CF_3CH_2	–	O	137, 140
	CF_3CH_2	–	S	137, 140
	CF_3CH_2	–	NMe	137, 140
	$(CF_3)_2CH$	–	O	96, 135
	$(CF_3)_2CH$	–	S	96, 135
	$(CF_3)_2CH$	–	NMe	96, 135
	$CHF_2CF_2CH_2$	–	O	138, 139
	$EtOOCCH=CCF_3$	–	O	107, 108
	CF_3CH_2	–	–	137, 140
	$(CF_3)_2CH$	–	–	137, 140
	$CHF_2CF_2CH_2$	–	–	138, 139
	$CHF_2CF_2CH_2O$	–	–	138
	CF_3CH_2O	–	–	141
	$(CF_3)_2CHO$	–	–	141
	C_3F_7	–	–	119
	$(CF_3)_2CH$	Bu^t	H	141–143
	$(CF_3)_2CH$	Ph	H	143
	$(CF_3)_2CH$	Me	Me	141, 142
 (n = 2, 4)	–	–	–	101
	CF_3CH_2	–	–	144
	CF_3CH_2	–	–	145
	$(CF_3)_2CH$	–	–	145
	CF_3	–	–	146
	CHF_2CF_2	–	–	146
	$CHF_2(CF_2)_3$	–	–	146

Table 3 (continued).

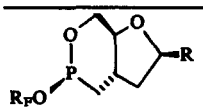
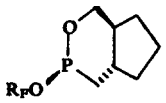
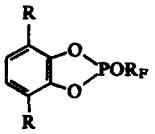
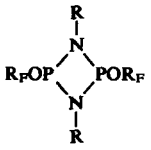
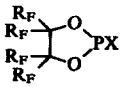
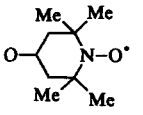
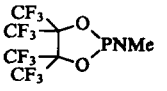
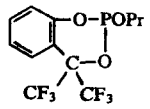
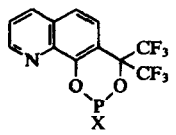
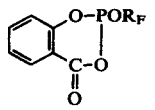
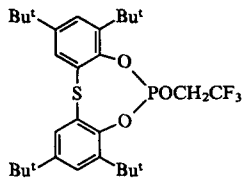
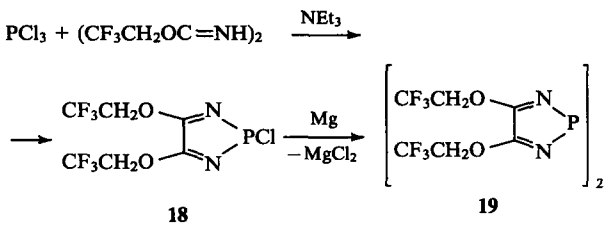
Compound	R_F	R (or NR_2)	R′ (or X)	Ref.
	$(CF_3)_2CH$	H	–	143, 147
	$(CF_3)_2CH$	Thymin-1-yl	–	143, 147
	$(CF_3)_2CH$	–	–	143
	$(CF_3)_2CH$	H	–	148
	CF_3CH_2	H	–	37
	$CHF_2CF_2CH_2$	H	–	138
	$CHF_2(CF_2)_3CH_2$	H	–	148
	$CHF_2(CF_2)_3CH_2$	H	–	149
	C_6F_5	H	–	148, 149
	CF_3CH_2	Bu^t	–	150
	CF_3CH_2	Bu^t	–	151–153
	$CF_3C(O)$	Bu^t		151–153
	$(CF_3)_2CH$	Bu^t		151–153
	$-CH_2(CF_2)_nCH_2-$ ($n=2, 3$)	Bu^t		153
	CF_3	–	NEt_2	154, 155
	CF_3	–	OEt	154
	CF_3	–	NH_2	155, 156
	CF_3	–	NMe_2	155
	CF_3	–	NHBu^t	155
	CF_3	–	$NH(SiMe_3)$	155
	CF_3	–	$N(SiMe_3)_2$	155
	CF_3	–	F	157–159
	CF_3	–	Cl	158
	CF_3	–	Br	158
	CF_3	–	$(CF_3)_2CHO$	157, 160
	CF_3	–	Me_3SiO	160
	CF_3	–	CF_3COO	160
	CF_3	–	I	160
	CF_3	–	H	160
	CF_3	–		161
	CF_3	–		162
	–	–	–	163
	–	–	EtO	164
	–	–	Et_2N	164
	$(CF_3)_2CH$	–	–	37, 103
	$CHF_2CF_2CH_2$	–	–	165
	$CHF_2(CF_2)_3CH_2$	–	–	103
	C_6F_5	–	–	165

Table 3 (continued).

Compound	R_F	R (or NR_2)	R′ (or X)	Ref.
	–	–	–	150

The 1,3,2-diazaphospholines **18** and **19**, containing trifluoroethyl groups, have been obtained from PCl_3 and $(CF_3CH_2OC=NH)_2$.[170]



18 **19**

2. Transesterification, transamination, alcoholysis, and acidolysis

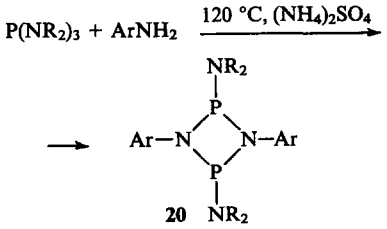
Certain R_F phosphites and amidophosphites have been obtained by the transesterification of phosphites with trifluoroethanol.[171] Transesterification proceeds more readily in the case of P(III) derivatives with 'acid' residues, whereas the transesterification of $P(OMe)_3$ is difficult.[171]

There are few examples of the alcoholysis of P(III) amides by R_F-alcohols.[113, 143, 144, 172, 173] Bearing in mind that fluorinated alcohols are extremely acid reagents, one may expect that alcoholysis with their participation would be facilitated by virtue of protophilic cooperation.[172] Indeed, the alcoholysis of amides by R_F-alcohols proceeds under comparatively mild conditions[113, 173] and, depending on the ratio of the P(III) amide and $R_F(OH)$, leads to full phosphites and mono- and di-amidophosphites, i.e. $P(OR_F)_3$ $Et_2NP(OR_F)_2$, and $(Et_2N)_2POR_F$, where $R_F = CHF_2(CF_2)_3CH_2$ or $CHF_2(CF_2)_{11}CH_2$ and also to cyclic phosphites, for example to 1,3,2-dioxaphosphorinane with the exocyclic substituent $OCH_2C_3F_7$.[172]

The alcoholysis of cyclic amides by hexafluoroisopropyl alcohol also takes place under mild conditions at 20 °C in CH_2Cl_2.[143, 147]

The interaction of trifluoropropanol with *o*-phenylene trifluoroacetyl phosphite affords a high yield of the corresponding full phosphite.[174]

The transamination reaction has been used[175] to obtain fluorinated diazadiphosphetidines **20**.



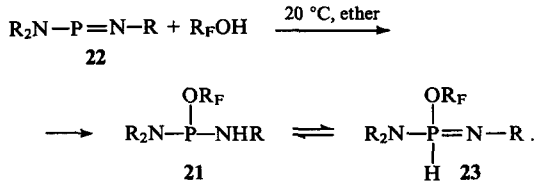
20

R = Et, Me; Ar = 2-$CF_3C_6H_4$, 2,4-$F_2C_6H_3$, 2-CF_3-4-ClC_6H_3, 2-Me-3-FC_6H_3.

Examples of the acidolysis of the amides $(R_FO)_2PNEt_2$ and $(R_FO)(R'_F)PNEt_2$ ($R_F = C_2F_5$, C_3F_7; $R' = CF_3$, C_3F_7) by HCl in order to obtain the corresponding R_F chlorophosphites are available in only one communication.[100]

3. Reactions involving the addition of dicoordinate phosphorus to alcohols

The R_F phosphites **21** have been synthesised from dicoordinate phosphorus compounds $R_2N-P=NR$ **22**.[176]



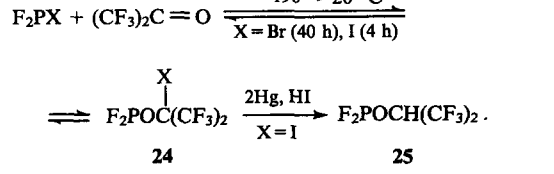
22 **21** **23**

R = Me_3Si, Bu^t.

The diamidophosphite **21** is in equilibrium with the amide **23**, the stability of which increases by virtue of the presence of the electron-accepting group R_FO.

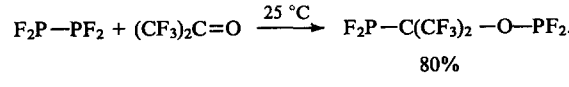
4. Reactions of P(III) derivatives with hexafluoroacetone

The reactions of P(III) derivatives with hexafluoroacetone are extremely diverse. The products of these reactions are usually compounds with the phosphorane structure. The reactions of hexafluoroacetone with chloro-, bromo-, and pyro-phosphites, as well as acyl phosphites, in which the final products are P(III) derivatives, are therefore of special interest. The insertion of hexafluoroacetone in a P–Hal bond without change in the coordination at the phosphorus atom was first described in 1967.[104] The phosphite **24** (X = I) formed in this reaction was reduced to compound **25**.



24 **25**

It was later shown that hexafluoroacetone may also be inserted in the P–P bond of tetrafluorodiphosphine.[177]

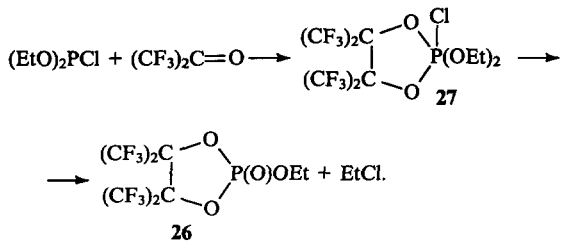


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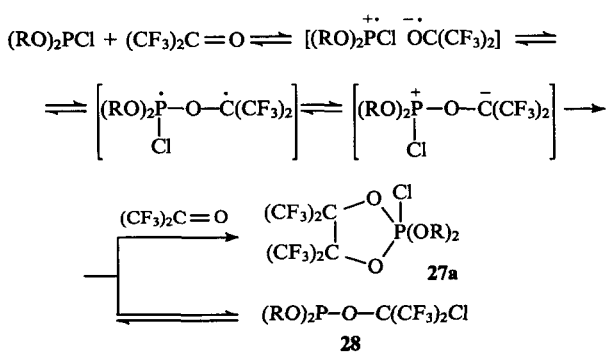
A whole range of compounds are formed in the reactions of the diphosphines Me_2PPMe_2 and $Me(Bu^t)PPMe(Bu^t)$ with hexafluoroacetone owing to the instability of the phosphinites $R_2PC(CF_3)_2OPR_2$ formed initially.[178]

The reactions of phosphines containing a P–H bond with hexafluoroacetone have been examined in reviews.[179, 180]

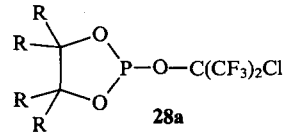
The interaction of chlorophosphites with $(CF_3)_2CO$ was first described by Knunyants and coworkers,[181] who obtained σ^4-dioxaphospholane **26**.



Later the reactions of dialkyl chlorophosphites with $(CF_3)_2C=O$ were investigated in greater detail.[182,183] It was shown that at −40 °C the insertion products **28** are formed almost quantitatively, whereas on raising the temperature to 20 °C a mixture of products **26**–**28** is formed.

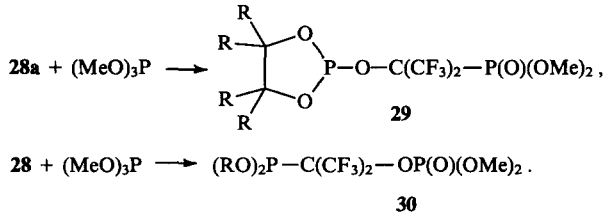


It has been suggested that the first reaction step involves one-electron transfer from the phosphite to the ketone, i.e. a radical mechanism operates.† When cyclic chlorophosphites are made to react with hexafluoroacetone, only the insertion products **28a**, which are more stable than the phosphites **28**, are obtained.



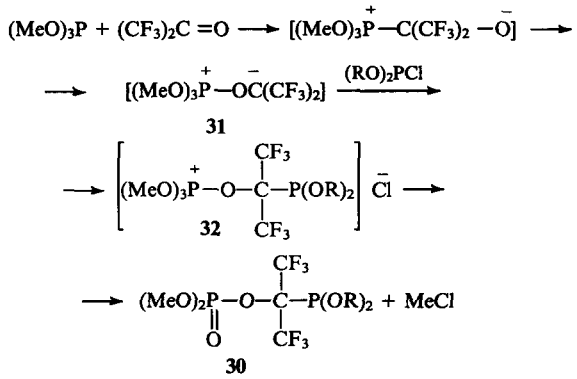
R = H, Me.

The authors of the studies quoted, suggest that the phosphites **28** enter into the Arbuzov reaction with trimethyl phosphite, forming compound **29**, whereas the phosphites **28** afford compounds **30**.

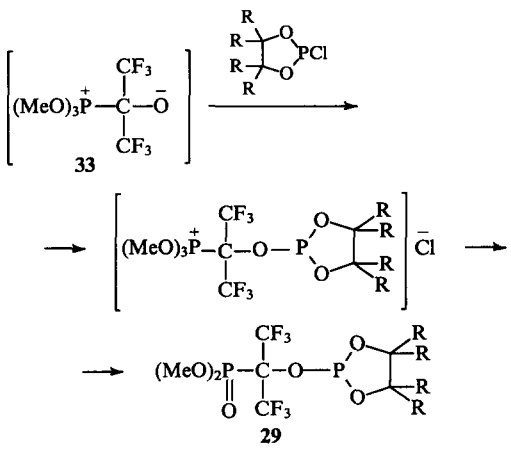


We believe that the product **30** cannot be obtained from the phosphite **28**. Careful analysis of the experimental part of the study of Heine and Roschenthaler [182] confirms our view. Apparently the first reaction stage is the interaction of hexafluoroacetone with the more nucleophilic trimethyl phosphite. The resulting dipolar ion P^+OC^- **31** reacts as a C-nucleophile with $(RO)_2PCl$, affording the salt **32**. The elimination of MeCl from the latter leads to the phosphonite **30**.

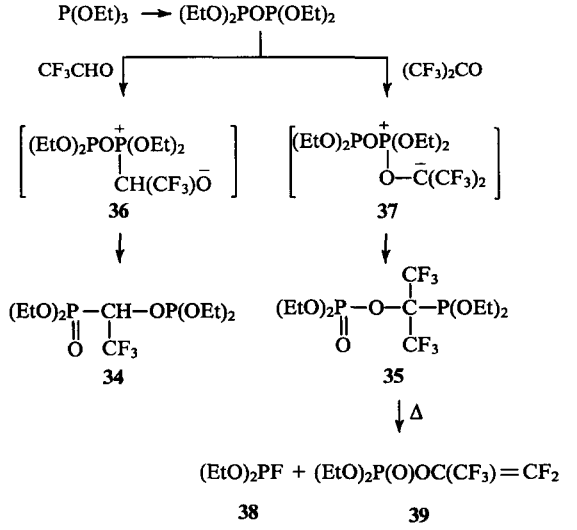
† The proposed mechanism was taken from data presented in Professor Roschenthaler's lecture delivered in Tallin in 1989. More detailed data have not been published.



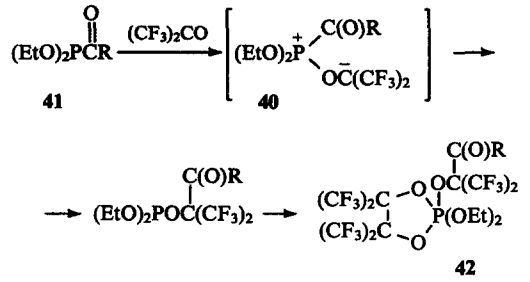
Bearing in mind the greater electrophilicity of cyclic chlorophosphites compared with the acyclic ones, it is logical to assume that they have sufficient time to 'capture' the dipolar ion P^+CO^-:



The treatment of the mechanism of the formation of compounds **29** and **30** presented here has been confirmed, from our point of view, by results [184] which show that hexafluoroacetone and fluoral react with triethyl phosphite to form compounds **34** and **35** with different types of substitution at the phosphorus atom, because the $P(OEt)_2$ group migrates in different dipolar ions **36** and **37**. Thermolysis of compound **35** leads to the fluorophosphite **30** and the vinyl phosphate **39**.

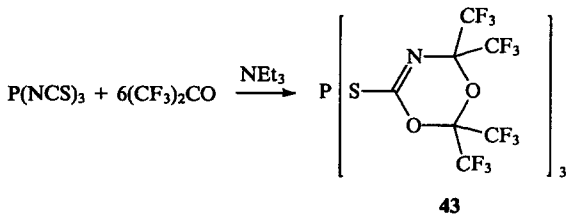


The reaction of the acyl phosphonite $(EtO)_2PC(O)R$ (R = Pr^i, Bu^t, OMe) with hexafluoroacetone apparently proceeds via the same path.[185] If hexafluoro acetone is taken in exess, the σ^5-1,3,2-dioxaphospholane **42** is formed.

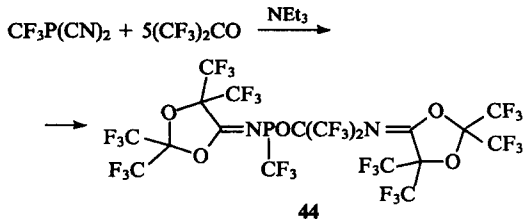


41 40 42

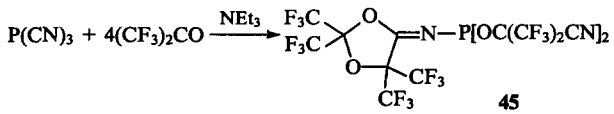
The complex phosphites **43–45**, incorporating heterocyclic fragments, have been obtained from hexafluoroacetone and phosphines containing the N=C=S and C≡N groups.[186–188] It was noted that the interaction of the above reactants entails the isomerisation of the isothiocyanate group to the thiocyanate group and of the nitrile group to the isonitrile group. The structure of compound **43** (δ_P = 89.3 ppm) has been demonstrated by X-ray diffraction.[188] The hexafluoroacetone dimer reacts similarly with $P(CN)_3$.[189]



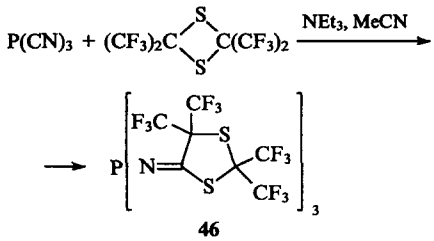
43



44



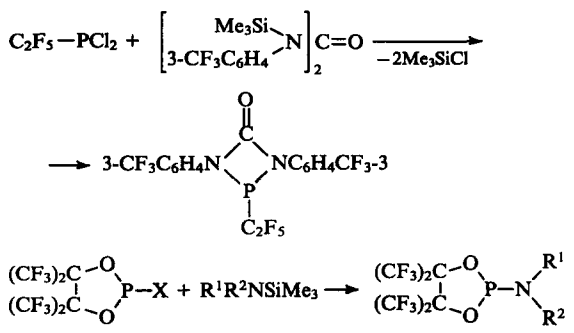
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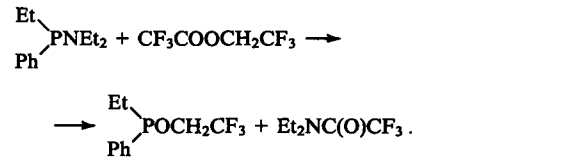
46

5. Other approaches to the synthesis of fluoroalkoxyfluoroalkyamino-derivatives of P(III)

Amido- and amino-phosphites are obtained by the interaction of silylated amides and amines with P(III) chlorides:[155, 188, 190]



The reactions of aminophosphines with R_F-esters of perfluorocarboxylic acids proceed with retention of configuration at the phosphorus atom.[191]



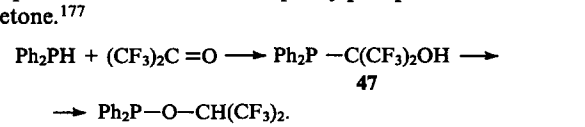
The interaction of phosphorus trichloride with perfluoro-*tert*-butyl hypochlorite is accompanied by the formation of tris(perfluoro-*tert*-butyl) phosphite.[192]

$$(CF_3)_3C-O-Cl + PCl_3 \rightarrow P[O-C(CF_3)_3]_3 + Cl_2,$$

The chlorine liberated does not then react with the phosphine. Attempts to employ this approach in order to obtain $P(OCF_3)_3$ from CF_3OCl and PCl_3 proved unsuccessful, since in this case CF_3OCl behaves as a fluorinating agent, being converted into the very stable COF_2.[192]

The compounds $(CF_3O)_3PO$, $(CF_3O)P(O)Cl$, and $(CF_3O)P(O)Cl_2$ have been detected among the reaction products by mass spectrometry. It was not possible to detect any kind of P(III) derivatives.

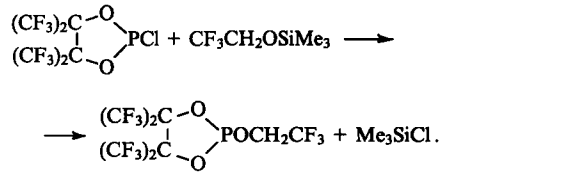
Apart from the reactions listed above, the rearrangement PCO → POC in the series of α-hydroxyphosphines is also used to obtain fluorinated phosphines. This reaction was first described in 1974 for (1-hydroxyperfluoroisopropyl)diphenylphosphine **47** — the product of the reaction of diphenylphosphine with hexafluoroacetone.[177]



47

It was found that the rearrangement of the phosphine **47** is effectively catalysed by tertiary phosphines and that the higher the nucleophilicity of the phosphine the faster the rearrangement. The possibility of the occurrence of this reaction for the products of the reaction of bis(*tert*-butyl)phosphine and *tert*-butylmethylphosphine with hexafluoroacetone has been indicated,[193] but more detailed information has not been published.

It has been suggested [160] that $CF_3CH_2OSiMe_3$ be used for the synthesis of fluoroalkyl phosphites. The corresponding phospholane was obtained in a high yield.



6. Bis(fluoroalkyl) phosphites

The classical method of synthesis of dialkyl phosphites — the reaction of P(III) chloride with alcohols — cannot be extended to fluorine-containing dialkyl phosphites. The only exception is the reaction of P(III) chlorides with FCH_2CH_2OH.[63] The synthesis of phosphites containing a large number of fluorine atoms by this method is impossible because of the difficulty of splitting off the fluorinated alkyl group. Indirect approaches to the synthesis of bis(fluoroalkyl) phosphites by the reaction of R_FOH with PCl_3 were therefore developed. Thus bis(fluoroalkyl) phosphites have been obtained by the reaction of PCl_3 with R_FOH in the presence of methanol [194] or *tert*-butyl alcohol.

$$PCl_3 \xrightarrow[-RCl]{ROH,\ CH_2Cl_2} [Cl_2PHO] \xrightarrow{R_FOH,\ CH_2Cl_2} (R_FO)_2PHO$$

R = Me, Bu^t; R_F = $HCF_2(CF_2)_nCH_2$ (n = 1, 3, 5),[194] CF_3CH_2,[195-198] $CF_3CF_2CH_2$,[198] $CF_3CH_2CH_2$,[198] $(CF_3)_2CH$.[199-201]

(The latter reaction is carried out either in methylene chloride [195-201] or in the absence of a solvent.[197])

It has been shown recently [202] that bis(fluoroalkyl) phosphites can be readily obtained from PCl_3 and R_FOH in the presence of water by a method proposed by Mandel'baum et al.[203]

$$PCl_3 + H_2O \longrightarrow [Cl_2PHO] \xrightarrow{2R_FOH} (R_FO)_2PHO$$

R_F = $CHF_2(CF_2)_nCH_2$ (n = 1, 3), CF_3CH_2, $(CF_3)_2CH$.

In the synthesis of bis(hexafluoroisopropyl) phosphite, it is essential to avoid an excess of the fluorinated alcohol, because the latter forms readily a fairly stable adduct — $[(CF_3)_2CHO]_2PHO \cdot HOCH(CF_3)_2$.[202]

It has been suggested [204,205] that bis(fluoroalkyl) phosphites and alkyl fluoroalkyl phosphites be obtained by the transesterification of alkyl phosphites in the presence of H_3PO_4 at 110–160 °C.

$$(RO)_2PHO + R_FOH \longrightarrow (RO)(R_FO)PHO$$

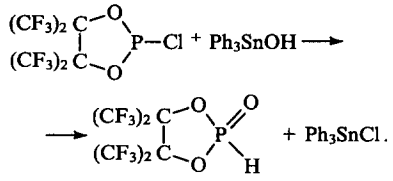
R = Me, Et; R_F = $CHF_2(CF_2)_5CH_2$;

$$(RO)_2PHO + 2R_FOH \longrightarrow (R_FO)_2PHO$$

R = Me, Et; R_F = $CF_3CF_2O(CF_2CF_2O)_2CF_2CH_2$.

The asymmetric phosphite $(R_FO)(EtO)PHO$ has been recently obtained by the interaction of tetrafluoropropyl dichlorophosphite (R_F = $CHF_2CF_2CH_2$) with two equivalents of ethanol.[206]

The interaction of $P[OCH_2(CF_2)_nCHF_2]_3$ (n = 1, 3, 5) with CF_3COOH [62] and H_3PO_4 [207] also leads to bis(fluoroalkyl) phosphites in satisfactory yields. Perfluoropinacol phosphite **48** has been obtained by the reaction of the corresponding chloride with Ph_3SnOH;[160] despite the presence of the strong electron acceptor in the molecule, this compound exists in the P(IV) oxo-form:

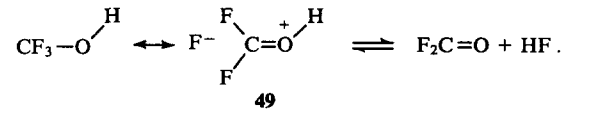


48

7. Perfluoroalkyl phosphites, thiophosphites, and amidophosphites as well as related compounds

a. Perfluoroalkyl phosphites

All the fluoroalkyl-containing phosphites and their derivatives examined above contain a fluorine atom in the γ-position relative to the P(III) atom. We did not find in the literature a single example where the $POCF_3$ or $POCF_2$ fragment was present in the P(III) derivative, although attempts to obtain such compounds were undertaken.[192,208,209] The analogous boron derivative $B(OCF_3)_3$ was synthesised, but it was stable only at temperatures below −20 °C.[210] The higher stability of $B(OCF_3)_3$ compared with $P(OCF_3)_3$ is associated with the electron-accepting nature of the boron atom, which diminishes the extent of the $n_O - \sigma^*_{CF}$ conjugation as a result of the competing $\pi_B - n_O$ interaction. Fluoro-alcohols containing a F atom in the α-position relative to the OH group are unstable and readily eliminate HF, which is associated with the formation of thermodynamically stable acyl fluorides. Thus the alcohol CF_3OH decomposes at 20 °C.

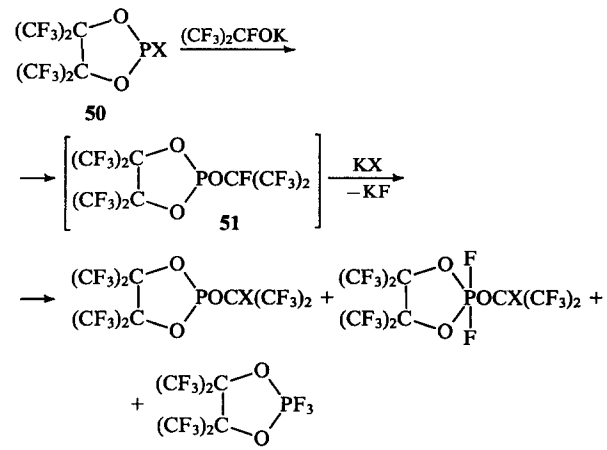


49

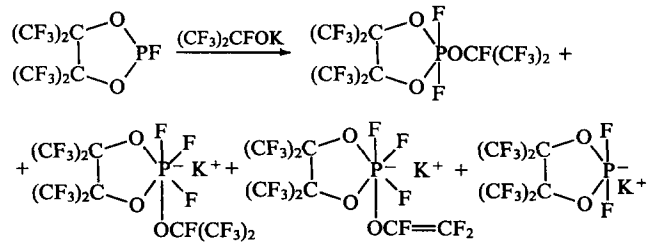
The contribution of the mesomeric form **49** to the CF_3OH structure is very large owing to the extremely effective $n_O - \sigma^*_{CO}$ conjugation.[211] The introduction of a P(III) atom would have led to an even greater destabilisation of the CF_3-O-P system owing to the additional shift of electron density from the phosphorus atom via the $n_P - \sigma^*_{CO}$ conjugation mechanism; on the other hand, under these conditions the formation of products with a P–F bond is thermodynamically favourable because this bond is one of the strongest.

In terms of its electronic effects the OCF_3 group is close to SCF_3 and Cl,[212] but it is a stronger σ-acceptor. The introduction of strong acceptors at the oxygen atom stabilises the CF_3O extremely effectively. Thus the compounds CF_3OF, CF_3OOF, CF_3OOCF_3, $CF_2(OF)_2$, and CF_3OOOCF_3 are stable.[213,214]

Bohlen and Roschenthaler [209] investigated the reactions of perfluoropinacol halophosphites **50** with the salts $(CF_3)_2CFOM$ [M = K, Cs $Si(Me_2N)_3$] in order to obtain the perfluoroalkyl phosphites **51** containing a F atom in the β-position relative to the P atom. It was found that the latter are extremely unstable and readily exchange the fluorine atom for X on treatment with the salts KX (X = Cl, Br).



The formation of a whole range of fluorination products has been observed for perfluoropinacol fluorophosphite **50** (X = F):



Bohlen and Roschenthaler [209] attribute this to radical processes occurring in the $\underline{OC(CF_3)_2C(CF_3)_2OPF}$ + $(CF_3)_2CFO^-$ system.

The perfluoroalkylperoxyphosphines $CF_3OOP(CF_3)_2$ and $(CF_3OO)_2PCF_3$ have been postulated [215] as intermediate species in the oxidation of $P(CF_3)_3$ by oxygen, but they were not detected by spectroscopic methods.

b. Perfluoroalkyl thiophosphites and selenophosphites

In contrast to perfluoroalkyl phosphites, their fluorinated thio- and seleno-analogues are more stable. The derivatives **52**–**54** were obtained for the first time in 1960 [216] from the compounds $Hg(SCF_3)_2$ and PCl_3 by exchange reactions:

$$PCl_3 \xrightarrow{Hg(SCF_3)_2,\ 20\ ^\circ C} CF_3SHgCl + Cl_2PSCF_3 \quad \mathbf{52}$$

$$PCl_3 \xrightarrow{2Hg(SCF_3)_2,\ 20\ ^\circ C,\ 40\ h} 2CF_3SHgCl + ClP(SCF_3)_2 \quad \mathbf{53}$$

$$PCl_3 \xrightarrow{3Hg(SCF_3)_2,\ 50\ ^\circ C,\ 72\ h} 3CF_3SHgCl + P(SCF_3)_3 \quad \mathbf{54}$$

The products **52–54** are liquids, which are separated by distillation at the usual pressure. A quartet (δ_P = 194.4 ppm, $^3J_{PF}$ = 24 Hz), a septet (δ_P = 143 ppm, $^3J_{PF}$ = 22 Hz), and a decet (δ_P = 85 ppm, $^3J_{PF}$ = 20 Hz) correspond to them respectively in the ^{31}P NMR spectra.[217]

$CF_3SP(CF_3)_2$,[218,219] $CF_3SeP(CF_3)_2$,[218] CF_3SPF_2,[220] CF_3SePF_2,[221] $PhP(SeCF_3)_2$,[222] $(CF_3Se)_2P-P(SeCF_3)_2$,[222] $P(SeCF_3)_3$,[222] and $PhP(SCF_3)_2$[223] were synthesised similarly. The initial compounds employed were the corresponding phosphorus iodides. $Hg(SeCF_3)_2$ was used to synthesise the selenides. In the ^{31}P NMR spectrum, a decet with δ_P = 65 ppm ($^3J_{PF}$ = 14.9 Hz) corresponds to the selenophosphite $P(SeCF_3)_3$.[220] This compound is unstable, its decomposition resulting in the segregation of $CF_3SeSeCF_3$ and the formation of a polymer. The ^{19}F and ^{31}P NMR spectra of the selenophosphinite $(CF_3)_2PSCF_3$ have also been described.[224]

Subsequently several approaches were developed for the synthesis of fluorinated thio- and seleno-phosphites. Thus it has been suggested that the reaction of polyphosphines with CF_3SSCF_3[225,226] and $CF_3SeSeCF_3$[222] be used for the synthesis of CF_3E derivatives of P(III), in which E = S or Se.

$$(CF_3P)_4 + 4(CF_3S)_2 \xrightarrow{200\ ^\circ C} (CF_3S)_2PCF_3,$$

$$[(CF_3)_2P]_2 + (CF_3S)_2 \xrightarrow{\Delta} (CF_3)_2PSCF_3,$$

$$(PhP)_5 + 5(CF_3Se)_2 \xrightarrow{40\ ^\circ C,\ 10\ days} 5PhP(SeCF_3)_2.$$

Fluorinated thiophosphines have been obtained by the reaction of R_FSCl with white phosphorus.[217]

$$P_4 + CF_3SCl \xrightarrow{CS_2,\ 48\ h,\ -80 \rightarrow 20\ ^\circ C} (CF_3S)_nPCl_{3-n}$$

n = 1–3.

The synthesis of an organoboron derivative of thiophosphine has been described.[225,226]

$$(CF_3S)_2PCF_3 + LiB_5H_8 \xrightarrow{-45\ ^\circ C,\ ether} CF_3SP(CF_3)B_5H_8.$$

The reaction of trifluoromethanesulfenyl chloride with methyl dichlorothiophosphite involves the substituent CH_3S.[227]

$$CF_3SCl + CH_3SPCl_2 \xrightarrow{-70 \rightarrow 20\ ^\circ C,\ 7\ h} CF_3SCH_2SPCl_2 + HCl.$$

The interaction of PCl_5 with $Pb(SC_6F_5)_2$ constitutes yet another unusual approach to the synthesis of thiophosphites. Tris(pentafluorophenyl) thiophosphite **55** has been obtained by this procedure.[97,228] The phosphorane **56** formed initially in this reaction is extremely unstable and decomposes to the thiophosphite **55** and a disulfide.

$$(C_6F_5S)_2Pb + PCl_5 \xrightarrow[-PbCl_2]{0-20\ ^\circ C,\ hexane} [(C_6F_5S)_5P] \rightarrow (C_6F_5S)_3P + (C_6F_5S)_2.$$

56 **55**

The chemistry of the CF_3E derivatives of P(III) has been only slightly developed. The reactions with S_8,[219,223,229] EtOH,[216] and $CF_nCl_{3-n}SCl$ (n = 1, 2, 3)[217] and the oxidation of the phosphite **54**[229] have been studied. The complexes of perfluoroalkyl-substituted phosphites $(CF_3)_2PECF_3$ (E = S, Se) with molybdenum and manganese carbonyls have been synthesised.[230,231]

c. Perfluoroalkyl amidophosphites

Perfluoroalkylaminophosphines **57** (n = 1, 2, 3) have been obtained by the exchange reactions of tris(trifluoromethyl)phosphine with $[(CF_3)_2N]_2O$.[232–234]

$$(CF_3)_3P + (CF_3)_2NON(CF_3)_2 \rightarrow (CF_3)_nP[N(CF_3)_2]_{3-n} + [(CF_3)_2NOCF_3].$$

57

The interaction of the stable bis(trifluoromethyl)nitroxyl radical with E(III) (E = P, As, Sb) derivatives has been investigated.[235–239] P(III) compounds were obtained only when phosphorus hydrides,[235] iodides,[236,237] and cyanides[238] were used as the initial compounds. It is suggested that the reactions proceed via a radical mechanism.

$$CF_3PI_2 + 2(CF_3)_2NO^\bullet \rightarrow CF_3P[ON(CF_3)_2]_2 + I_2,$$

$$(CF_3)_2PI + (CF_3)_2NO^\bullet \rightarrow (CF_3)_2PON(CF_3)_2 \rightarrow (CF_3)_2P(O)N(CF_3)_2,$$

$$PhP(CN)_2 + (CF_3)_2NO^\bullet \rightarrow Ph(NC)PON(CF_3)_2,$$

$$Ph_2PCN + (CF_3)_2NO^\bullet \rightarrow Ph_2PON(CF_3)_2.$$

The amidophosphite $(Me_2N)_2PON(CF_3)_2$ can be obtained from hexamethylphosphorous triamide and bis(trifluoromethyl)nitroxyl.[240]

$$(Me_2N)_3P + (CF_3)_2NO^\bullet \rightarrow (Me_2N)_2PON(CF_3)_2 + [(CF_3)_2NONMe_2].$$

The analogous arsenic and antimony compounds are more stable than the phosphorus compounds.[239,241]

Other perfluoroalkyl and nitrogen derivatives, for example $(CF_3)_2NONO$ and CF_3NO, are not only inserted into the CF_3-P bond but also oxidise the compounds formed to P(V) derivatives.[241–243] Bis(trifluoromethyl)phosphine adds to CF_3NO with retention of the coordination at the phosphorus atom, forming the amidophosphine $(CF_3)_2PN(OH)CF_3$.[243]

IV. Reactions of fluoroalkyl phosphites

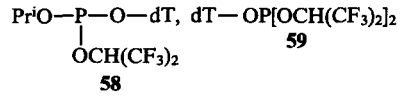
As a result of the presence of the fluorinated substituent R_F, fluoroalkyl phosphites and related compounds (phosphonites, phosphinites, etc.) exhibit a reduced reactivity in nucleophilic reactions and an enhanced reactivity in electrophilic reactions compared with alkyl phosphites. The characteristic features of the chemical behaviour of the R_F-derivatives of P(III) are caused by the difficulty of cleaving the $O-R_F$ bond owing to the strong electron-accepting properties of polyfluorinated groups. The inertness of the polyfluorinated radicals derived from the fluoroalkanols $CHF_2(CF_2)_nCH_2OH$ (n = 1, 3)[244] in reactions involving the formation of polyfluoroalkylcarbenium ions[60,245] provides grounds for the hope that stable phosphoranes may be obtained from them. The chemistry of the latter has been developed vigorously precisely as a result of the introduction of fluorinated substituents at the phosphorus atom.[246–248]

1. Reactions of fluoroalkyl phosphites with retention of the coordination the phosphorus atom

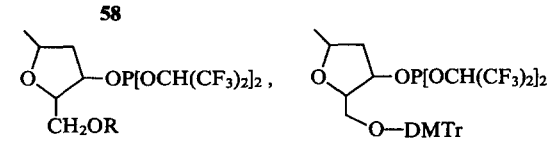
Reactions involving nucleophilic substitution at the phosphorus atom, which behaves as an electrophilic centre, must take first place among the reactions involving retention of the coordination at the phosphorus(III) atom. Such reactions are extremely characteristic of R_F-phosphites. They include alcoholysis, trans-

esterification, disproportionation or dismutation, as well as reactions involving insertion into multiple bonds without change in the coordination state of the phosphorus atom. Attention was first turned to the ease of the alcoholysis of R_F-alkyl phosphites by more basic alcohols in the studies of Fokin and coworkers.[60,62] Thus the reaction of tris(tetrafluoropropyl) phosphite with MeI, in which MeOH was used as the catalyst, has been described.[62] In the presence of an excess of methanol and under comparatively mild conditions, the complete transesterification of tris(tetrafluoropropyl) phosphite is observed.[62]

Dimethyl 1-hydroxymethylphosphonate interacts readily with tris(tetrafluoropropyl) phosphite, forming the phosphite $(MeO)_2P(O)CH_2OP(OCH_2CF_2CHF_2)_2$.[113] Tris- and bis-(fluoroalkyl) phosphites proved to be exceptionally mild phosphorylating agents in the synthesis of oligonucleotides.[88,114,249-256] It has been suggested that tris(hexafluoroisopropyl) phosphite be used as the most convenient reagent for the synthesis of DNA oligomers by the phosphite method. Various type **58–61** phosphites are obtained initially from the deoxyribonucleoside phosphite.



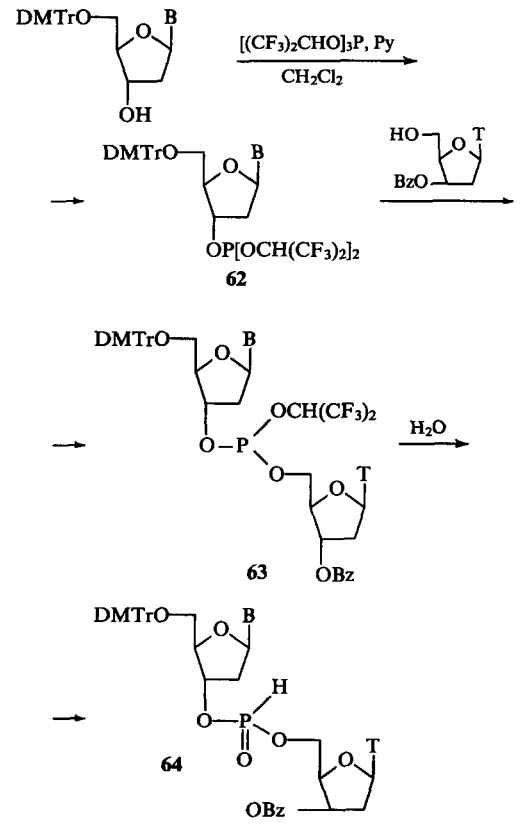
58 **59**



60 **61**

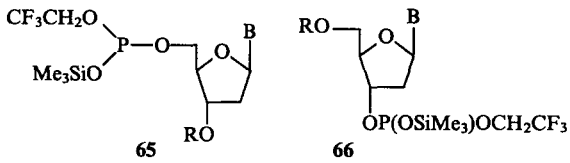
dT = 5′-*O*-dimethoxytrityldeoxyribonucleosid-3′-yl,
DMTr = dimethyoxytrityl.

A mild synthesis of oligodeoxyribonucleotides employing the phosphites **62–64** as key intermediates has been described.[114]



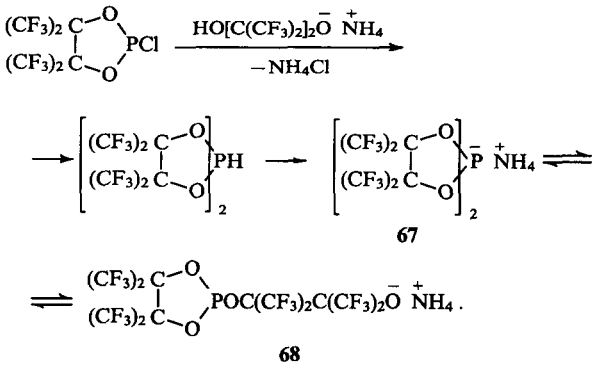
B = T, BzA, BzC, or Bu^{i}G (T = thymine, BzA = benzoyladenine, BzC = benzoylcytosine, Bu^{i}G = isobutyrylguanine).

The ready hydrolysis of phosphites or the reactions with nucleosides are used in the synthesis of *H*-phosphonatonucleotides and oligonucleotides. Data on the phosphorylation of oligonucleotides by certain fluorinated P(III) derivatives can be found in a recently published review.[257] It has also been suggested that bis(hexafluoroisopropyl) phosphite,[199,201] bis(trifluoroethyl) phosphite,[195,196,198,258,259] and bis(trifluoroethyl) trimethylsilyl phosphite[260-263] be used for the phosphorylation of oligonucleotides and natural and common alcohols. The P(III) derivatives **65** and **66** are formed initially in the phosphorylation of nucleosides by bis(trifluoroethyl) trimethylsilyl phosphite.[260]



65 **66**

The nucleophilic substitution reactions of a series of phosphites containing the perfluoropinacol fragment have been investigated.[264,265] The electrophilicity of the phosphorus atom in these systems is so high that it was possible to obtain the relatively stable bicyclic phosphoranide intermediate **67**.

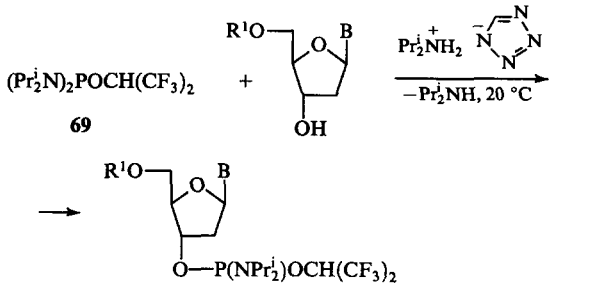


67

68

In solution, compound **67** is in equilibrium with compound **68**.

The reactions involving the phosphorylation of the alcohols by R_F phosphites proceed under very mild conditions (20 °C). Thus the reaction of the amidophosphite $(Pr^i_2N)_2POCH(CF_3)_2$ **69** with deoxyribonucleosides takes place selectively with formation of diisopropylamine.[121]



R^1 = DMTr; B = T, BzA, BzC, Bu^{i}G.

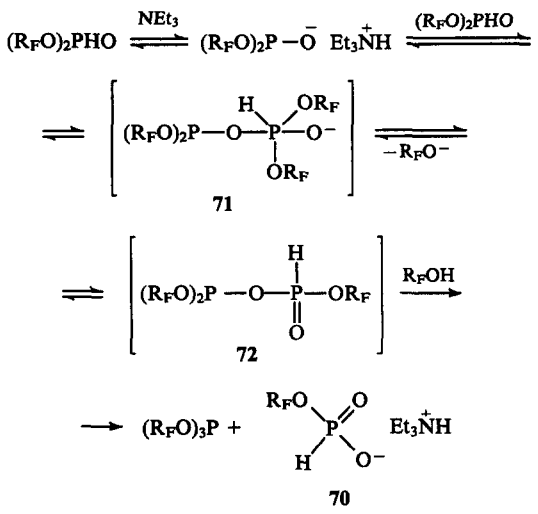
In certain studies, bases such as pyridine have been used as catalysts of the phosphorylation by R_F phosphites,[199-201] while triethylamine has been used as the catalyst for reactions involving the addition of bis(fluoroalkyl) phosphites to carbonyl compounds such as CF_3CHO, $CF_2ClCOCFCl_2$, $(ClCF_2)_2C=O$, $(CF_3)_2C=O$,[266] and $PhC(O)CHCl_2$[267] and the alkylation of such phosphites by halogen-containing crown-ethers.[268,269] In the alkylation of bis(trifluoroethyl) phosphite by functionally substituted alkyl bromides, sodium hydride is added to the reaction mixture.[270] In many cases, the reaction is carried out for a long time at a high temperature (80–140 °C).

Fluorine-free dialkyl phosphites are known to be capable of undergoing self-alkylation at the phosphorus atom with formation of phosphonates on treatment with alkali metal alkoxides.[271] It has been shown that an anionic-chain mechanism operates in the special case of the Arbuzov reaction.[272]

It has been claimed[273] that dialkyl phosphites form salts with amines such as NEt_3, $HNEt_2$, aniline, triethanolamine, toluidines, etc. In order to test this claim, we prepared mixtures of $(EtO)_2PHO$, $(PrO)_2PHO$, $(Pr^iO)_2PHO$, and $(BuO)_2PHO$ with NEt_3.[103] However, no changes were observed in the ^{31}P NMR spectra of these phosphites after the addition of NEt_3. Bearing in mind that the amines employed in the above study[273] are significantly weaker bases than NEt_3, one may doubt the validity of the results of this study. Only diphenyl phosphite,[274-276] methyl trichloromethylphosphonite,[277] and *S,S*-dialkyl dithiophosphites[278] are symmetrised to the corresponding full phosphites on treatment with bases.

On treatment with triethylamine, bis(fluoroalkyl) phosphites are readily converted into tris(fluoroalkyl) phosphites even at 20 °C (Scheme 1).[202,279] This results in the formation of the mono(fluoroalkyl) phosphite salts **70**. In contrast to dialkyl phosphites, monoalkyl phosphites readily form salts with bases,[280,281] which is used for the separation of the former from

Scheme 1

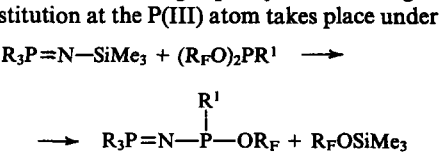


R_F = $(CF_3)_2CH$, CF_3CH_2, $CHF_2CF_2CH_2$, $CHF_2(CF_2)_3CH_2$.

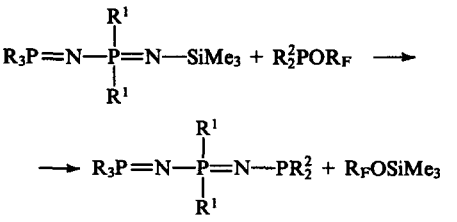
the latter.

In terms of their reactivities in the reaction presented in Sheme 1, bis(fluoroalkyl) phosphites can be arranged in the following order:[202] $[(CF_3)_2CHO]_2PHO \gg (CF_3CH_2O)_2PHO > [H(CF_2)_nCH_2O]_2PHO$. Evidently, this reactivity series does not agree in any way with the mechanism of the alkylation[279] of bis(fluoroalkyl) phosphite anions $(R_FO)_2PO^-$, which are relatively weak nucleophiles, by the initial bis(fluoroalkyl) phosphite. The latter does not exhibit an alkylating capacity in any of the known reactions. Diethyl and dipropyl phosphites, which are stronger alkylating agents compared with fluorodialkyl phosphites, also do not alkylate The corresponding phosphite anions, whereas the reaction with diphenyl phosphite takes place readily. Apparently, the dialkyl phosphite first attacks the phosphorus atom of the initial phosphite, the electrophilicity of which is enhanced by the electron-accepting substituents. The reaction is accompanied by the formation of the phosphorane intermediate **71**. Compound **72** with the P–O–P fragment, formed as a result of the abstraction of the R_F-O^- anion, decomposes, affording the salt **70** and a phosphite.

R_F-Derivatives of P(III) have been introduced into reactions with the compounds $R_3P=NSiMe_3$ and $R_3P=N.PR^1_2(=NSiMe_3)$ containing the $SiMe_3$ group.[123,282,283] By virtue of the effective leaving capacity of the OR_F groups, nucleophilic substitution at the P(III) atom takes place under mild conditions.

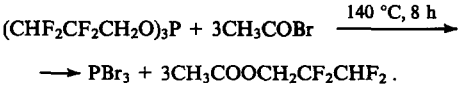


R = Me, Me_2N; R_F = CF_3CH_2; R^1 = Me, Ph, CF_3CH_2O;



R = Me, Me_2N; R^1 = NMe_2, CF_3CH_2O; R^2 = Ph, CF_3CH_2O.

The disproportionation reactions of the R_F-derivatives of P(III) proceed more readily than those of the usual phosphites.[60,62,98] Thus octafluoropentyl dibromophosphite has been obtained by the disproportionation of tris(octafluoropentyl) phosphite in the presence of PBr_3 in acetonitrile.[284] Exchange and symmetrisation occur in the interaction of $CHF_2CF_2CH_2OPCl_2$ with piperylene and epoxyethane.[60,62] The reaction of tris(tetrafluoropropyl) phosphite with acetyl bromide also leads to the formation of exchange products, in contrast to R_H phosphites.[285]



2. The reactions of fluoroalkoxy-derivatives of P(III) involving an increase in the coordination number of the phosphorus atom

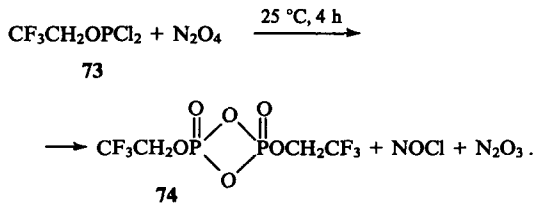
In most of the reactions involving P(III) derivatives, the phosphorus atom behaves as a nucleophile, which is associated with the accessibility of its electron pair and with its tendency to expand its valence shell. The P(III) → P(IV) transition is a reaction extremely characteristic of the usual R_H derivatives of P(III).

The introduction of electron-accepting R_FO groups at the P(III) atom contributes its characteristic features to the course of many reactions. As already mentioned, the ionisation potential of the phosphorus lone pair is appreciably higher in the R_FO derivatives of P(III), while the R_F-O bond has a 'mesomeric' character, as a result of which it is strengthened and is much more difficult to break, particularly if carbenium ions are formed in the reactions.

a. Oxidation reactions

Atmospheric oxygen does not oxidise fluoroalkoxy-derivatives of P(III) under the usual conditions.[286] Thus, bis(trifluoroethyl) trichloromethylphosphonite is oxidised by oxygen only under UV radiation.[105]

Stronger oxidants — N_2O_4,[60-62,64,101,180,286] SO_3,[73] Bu^tCOOH,[287] DMSO,[86] O_3,[288,289] and EtOOEt[290,291] — have been used to oxidise R_F derivatives of P(III). In the case of ozone, relatively stable ozonides were obtained.[288,289] The oxidation of the chloride **73** by an excess of N_2O_4, leading to 1,3-dioxa-2,4-diphosphetane **74**, proceeds in an unusual manner.[64]



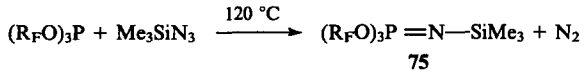
73 **74**

Sulfur adds to tris- and bis-(fluoroalkyl) phosphites with much greater difficulty than to the corresponding alkyl phosphites. The reaction takes place only after prolonged heating in dioxane[61,62,164,292] or pyridine.[293] Only one reaction involving the addition of selenium to a phosphite, leading to the selenophosphate $CF_3CH_2OP(Se)(OCH_2)_2$, has been described in the literature.[294]

2-Nitro-1,1,3,4,4-pentachlorobuta-1,3-diene, which has electrophilic properties and contains fairly mobile terminal chlorine atoms, reacts fairly readily with fluoroalkyl phosphites, but, in contrast to other types of nucleophiles (for example, amines), only its nitro-group is involved. This results in the oxidation of phosphites to phosphates in high yields.[295] The rate of reaction increases with increasing nucleophilicity of the phosphite.

b. The Staudinger reaction

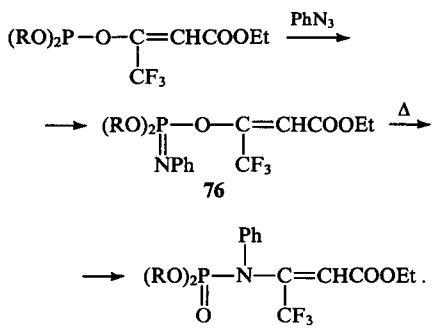
Fluoroalkoxy-derivatives of P(III) enter into the Staudinger reaction with greater difficulty than the R_H analogues, the type **75** iminophosphoranes formed are stable and do not undergo imide–amide rearrangement.[296–301]



75

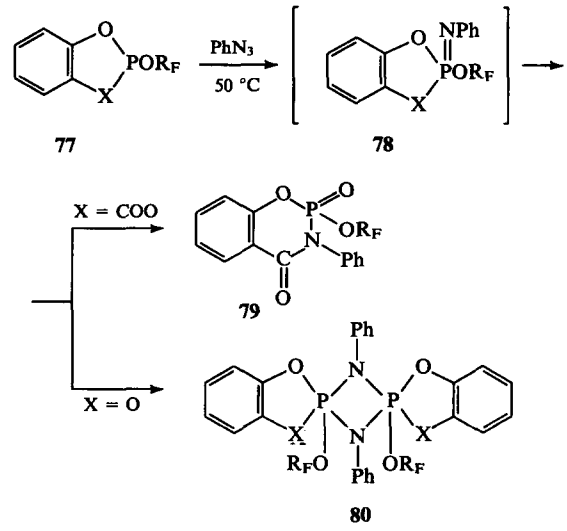
$R_F = CF_3CH_2$.

This course of the reaction becomes understandable in the light of data obtained recently on the imide–amide rearrangement,[302] which proceeds via an intermolecular chain mechanism with the intermediate formation of carbonium ions. Thus the rearrangement of the iminophosphorane **76** takes place on heating.[107,108]



76

It was found that the result of the Staudinger reaction for the cyclic fluoroalkyl phosphites **77** — derivatives of salicylic acid — depends significantly on the nature of the exocyclic substituent R_F at the phosphorus atom.[103,303] If $R_F = C_6F_5$, then the intermediate iminophosphorane **78** readily undergoes the imide–amide rearrangement, affording σ^4-1,3,2-oxazaphosphorinane **79**, but, if $R_F = CF_3CH_2$ or $CHF_2(CF_2)_nCH_2$ (n = 1, 3), then the intermediate **78** is almost fully converted into the diazadiphosphetidine **80**. When catechol derivatives are used, only the diazadiphosphetidines **80** are formed.



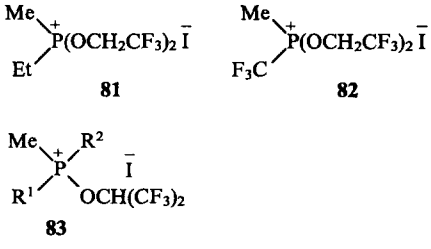
77 **78** **79** **80**

X = O, COO; $R_F = CF_3CH_2$, $CHF_2(CF_2)_nCH_2$ (n = 1, 3), C_6F_5.

c. The Arbuzov reaction and its nonclassical variants

Tris(perfluoroalkyl) phosphites do not isomerise even at 250 °C.[60,62] The Arbuzov reaction of tris(tetrafluoropropyl) phosphite with MeI (1 : 1 ratio) takes place at 220 °C in a stainless steel test tube,[60,62,304] whilst the iodide $CHF_2CF_2CH_2I$ does not react with the above phosphite.[62] The kinetics of such reactions have been investigated[305] and it has been shown that the rate-determining stage is nucleophilic attack on the P(III) atom. The decrease in the nucleophilicity of the latter is apparently more important for the Arbuzov reaction than the enhancement of the electrophilicity of the C_α atom in the R_FCH_2O group, which favours elimination via an S_N2 mechanism. It is of interest to note that, in the reaction of the phosphite $(EtO)_2POCH_2CH_2F$ with EtI, a mixture of the phosphonates $(EtO)_2P(O)Et$ and $(EtO)(CH_2FCH_2O)P(O)Et$ is formed, whereas the reaction with MeI affords only the phosphonate $(EtO)(CH_2FCH_2O)P(O)Me$.[63] The reaction temperature decreases after the addition of MeOH,[304] which is associated with the fact that, not the initial phosphite, but the transesterification product interacts with RI.

In the presence of two alkyl substituents at the P(III) atom, its fluoro alkoxy-derivatives form the quasi-phosphonium salts **81**–**83** with MeI.[122,125,177,178,306]



81 **82**

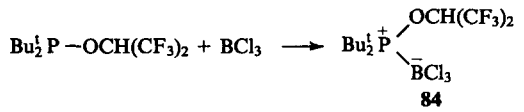
83

R^1, R^2 = Me, Et, Ph, Bu^t.

These salts do not decompose up to 100–140 °C, which is due, according to the authors, to the electron-accepting influence of the CF_3 groups on the α-carbon atom.

However, it is known that electron-accepting substituents accelerate the substitution reaction via an S_N2 mechanism,[307] so that, for example, the stability of compound **83** may be associated either with the effective shielding of the C_α atom in the hexafluoroisopropyl group or with the fact that the elimination stage has significant features of an S_N1 process.[308]

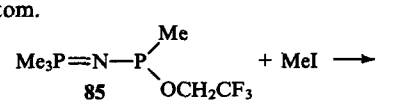
The preparation of the salt **84**, stable up to 150 °C, has been reported.[306]



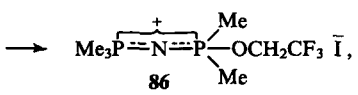
84

For the salt **84**, the exchange processes do not occur even at 100–150 °C.

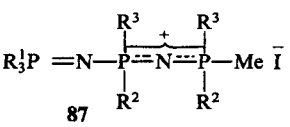
The stable quasi-phosphonium salt **86** has been obtained by the interaction of MeI with the imine **85**.[125,306] The authors believe that the stability of the salt **86** and its analogues **87** is due to the delocalisation of the positive charge on the phosphorus atom.



85



86

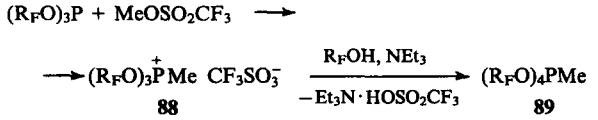


87

$R^1 = Me_2N$, $R^2 = CF_3CH_2O$ *or* Ph, $R^3 = CF_3CH_2O$.

In the quasi-phosphonium salts examined above, an electron-donating amide or alkyl group was always present together with the fluorinated substituent at the phosphorus atom, stabilising the positive charge on the latter.

It has been shown[309] that tris(fluoroalkyl) phosphites are capable of forming the quasi-phosphonium salts **88** with methyl triflate.

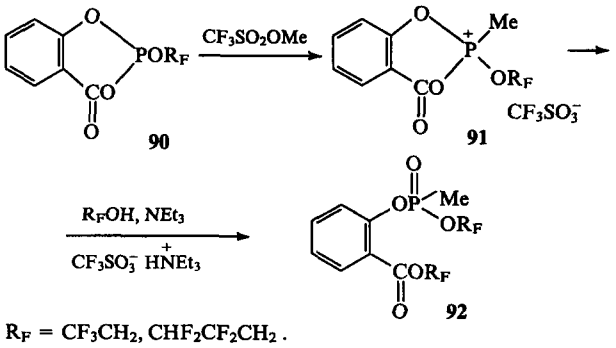


88 **89**

$R_F = CF_3CH_2$, $CHF_2CF_2CH_2$, $CHF_2(CF_2)_3CH_2$.

The latter are converted into the phosphoranes **89** in a high yield. The interaction of R_F phosphites is much slower than that of R_H-phosphites.[310–312] The phosphite **5** with $R_F = (CF_3)_2CH$ reacts at 120–150 °C,[103] while the phosphites **2** and **4** with $R_F = CF_3CH_2$ and $CHF_2(CF_2)_nCH_2$ (n = 1, 3) react at 20 °C. The salts **88** formed have significantly weaker alkylating properties than R_H-phosphonium triflates. This follows from the inertness of tris(fluoroalkyl) phosphites in relation to fluoroalkylphosphonium triflates. Even in the presence of 50 mass % of the triflates **88** in the reaction mixture, the latter do not react with the initial phosphites, whereas R_H phosphites react via a cationic chain mechanism at an exceptionally high rate.[310–312] Another significant difference between the R_F-quasi-phosphonium salts and the R_H-salts is the ability to react with R_F-alcohols at the phosphorus atom, i.e. to phosphorylate alcohols, whereas R_H-phosphonium triflates alkylate alcohols.[313]

In contrast to acyclic fluoroalkyl phosphites, the cyclic phosphites **90** — derivatives of salicylic acid — react more slowly with methyl triflate. This has been established[37,103] in a study of the competing reaction of the phosphites **4** and **90** ($R_F = CHF_2CF_2CH_2$) with $MeOSO_2CF_3$ by the ^{31}P NMR method. The stability of the cyclic salts **91** was found to be lower than that of the acyclic analogues **88**.

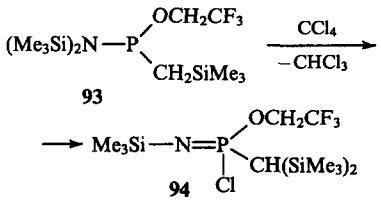


90 **91** **92**

$R_F = CF_3CH_2$, $CHF_2CF_2CH_2$.

The salts **91** behave in this reaction merely as acylating agents, forming the phosphonate **92** in the reaction with tetrafluoropropanol.

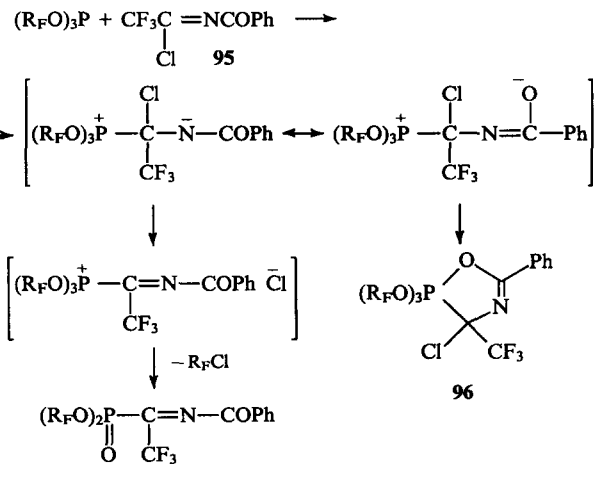
The reactions of carbon tetrachloride with fluoroalkyl phosphonites[105,314] take place after prolonged heating in CH_3CN, while those with tris(fluoroalkyl) phosphites do not occur at all. The interaction of the silyl amidophosphonite **93** with CCl_4 leads to the PCl-iminophosphine **94**.[315]



93 **94**

It has been noted that the elimination of $CHCl_3$ in this reaction is promoted by nonpolar solvents and by the absence of steric shielding of the protons of the CH_2Si fragment in compound **93**.

The interaction of *N*-benzoyltrifluoroacetimidoyl chloride **95** with tris(tetrafluoropropyl) phosphite proceeds with formation of σ^5-1,4,2-oxazaphospholine **96** (δ_P = −41.7 ppm) and the phosphonate **97**.[316]



95 **96** **97**

$R_F = CHF_2CF_2CH_2$.

Striking differences between cyclic and acyclic fluoroalkyl phosphites, on the one hand, and the corresponding unsubstituted phosphites, on the other, have been observed in the reactions of these compounds with the halogens, which lead, depending on the structure of the P(III) derivative, to different products —

halophosphates **98**, *P*-haloimines **99**, and the phosphoranes **100** and **101**.[57,64,65,76,77,83,87,96,98,284,317–319]

$$(R_FO)_3P + X_2 \longrightarrow \underset{\mathbf{98}}{(R_FO)_2P(O)X} + R_FX$$

X = Cl, Br; R_F = CF_3CH_2, CF_3CMe_2, $(CF_3)_2CMe$, CF_3MeCH, $CHF_2CF_2CH_2$, $CHF_2(CF_2)_3CH_2$;[57,284,315]

$$(R_FO)_2PHO + X_2 \longrightarrow \underset{\mathbf{98}}{(R_FO)_2P(O)X} + HX$$

R_F = CF_3CMe_2,[64] $CHF_2CF_2CH_2$;[284]

$$(Me_3Si)_2NP(OCH_2CF_3)_2 + Br_2 \longrightarrow Me_3Si{-}N{=}P(OCH_2CF_3)_2Br + Me_3SiBr;$$

99 [83]

$$(R_FO)_3P + X_2 \longrightarrow \underset{\mathbf{100}}{(R_FO)_3PX_2}$$

R_F = $(CF_3)_2CH$[65,76,77,96,317]; C_6F_5;[98,316]

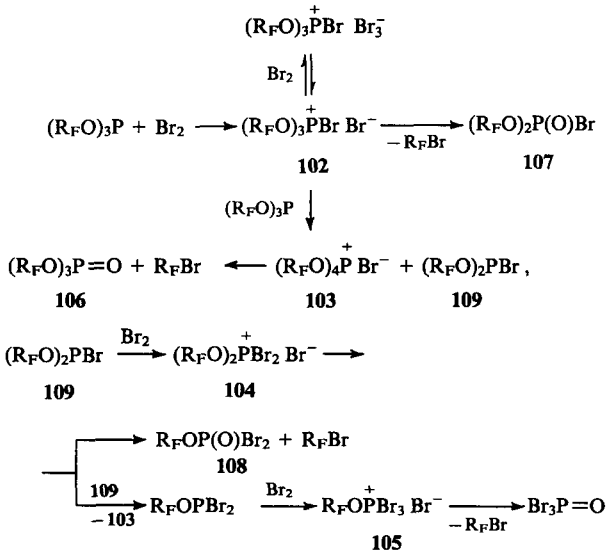
$$RP[OCH(CF_3)_2]_2 + Cl_2 \longrightarrow \underset{\mathbf{101}}{RP[OCH(CF_3)_2]_2Cl_2}.$$

[87]

It is noteworthy that the compounds containing the $CH(CF_3)_2$ substituent react with the halogens to form the stable phosphoranes **100** and **101**.

The interaction of tris(tetrafluoropropyl) phosphite with bromine has been investigated by the dynamic ^{31}P NMR method (Scheme 2).[284] As in the case of triethyl phosphites,[320,321] this results in the formation of the quasi-phosphonium intermediate **102**. A further three quasi-phosphonium salts **103–105** were detected in the reaction mixture, and, depending on the ratios of the reactants and the order in which they were mixed, different phosphates **106–108** and the bromophosphite **109** were obtained.[284]

Scheme 2



R_F = $CHF_2CF_2CH_2$.

Despite the presence of electron-accepting substituents destabilising the phosphonium centre, the stability of the bromide **102** is higher than that of its close analogue $(EtO)_3P^+$ Br Br^- **110**. In this case, it is impossible to explain the greater stability of the fluorinated salt by the increase in the fraction of the phosphorane formed in the possible phosphonium ⇄ phosphorane equilibrium because, according to ^{31} P NMR spectroscopic data, the chemical shifts, which are very sensitive to the position of equilibrium between phosphonium salts and phosphoranes, are virtually identical for the two salts **102** and **110** (δ_P = 13–15 ppm).‡ This effect is apparently due to the fact that substitution at the C_α atom has certain features characteristic of an S_Ni process. Only in this case would fluorinated radicals reduce the rate of cleavage.

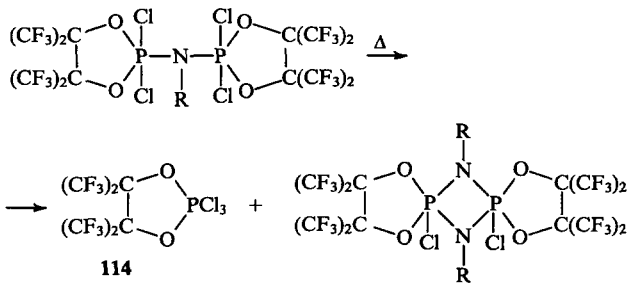
Another specific difference in the behaviour of the salts **102** and **110** is the ability of the former to enter into disproportionation reactions with the initial phosphites.

The tricyclic phosphites **111** also afford the phosphoranes **112**.[48,49]

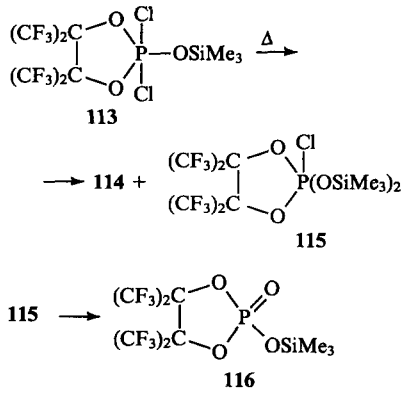
$$\underset{\mathbf{111}}{P[CHR_F{-}O]_3P} + X_2 \longrightarrow \underset{\mathbf{112}}{P[CHR_F{-}O]_3PX_2}$$

X = Cl, Br; R_F = CF_3, CHF_2CF_2, $CHF_2(CF_2)_3$.

The stability of the phosphoranes increases significantly if a perfluoropinacol fragment is introduced at the phosphorus atom.[155,157,158,160,162] It effectively stabilises the bipyramidal phosphorus structure.[162,319,322] The stabilisation effect is so strong that it is actually possible to obtain halophosphoranes with substituents such as CH_2Ph,[157] NH_2, $NHBu^t$, $N(SiMe_3)_2$, NMe_2, and $OSiMe_3$.[155,160] The thermolysis of these compounds proceeds in an extremely unusual manner:



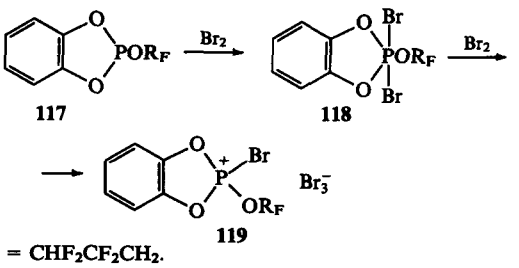
R = Me, Bu^t.



In the case of compound **113**, the latter initially disproportionates to the phosphoranes **114** and **115** after which the phosphorane **115** is converted into the phosphate **116**.[160]

The catechol derivative **117** reacts with bromine to form the relatively stable phosphorane **118**, its stability being significantly higher than that of the bis(ethoxy)derivative,[320] which readily decomposes to the phosphate via the Arbuzov reaction. In an excess of bromine, the phosphorane **118** forms the quasi-phosphonium salt **119**. When the phosphorane **118** is allowed to stand (at 20 °C), it disproportionates with formation of P(III) and P(V) derivatives.[323]

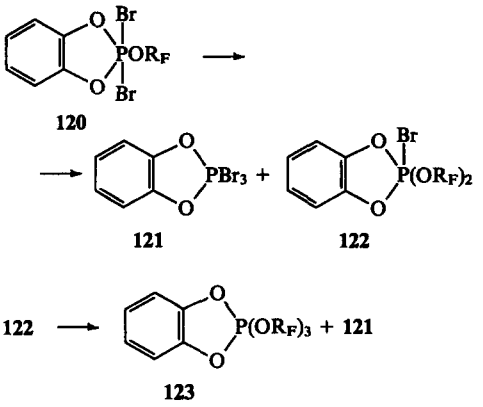
‡ The value δ_P = 2 ppm quoted[48] for compound **102** is erroneous.



117 118 119

$R_F = CHF_2CF_2CH_2$.

The hexafluoroisopropyl derivative **120** disproportionates to the phosphoranes **121** and **122**, the latter being subsequently converted into a mixture of the phosphoranes **121** and **123**.[324]

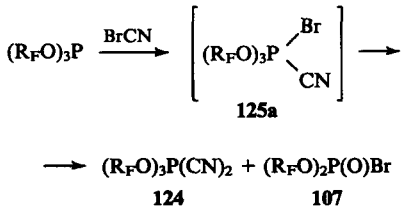


120 121 122 123

$R_F = (CF_3)_2CH$.

The fluorination of acyclic fluoroalkyl phosphites by fluorine,[132] the azide $CF_3CHFCF_2N_3$,[325] or perfluoroepoxypropane[326] leads to difluorophosphoranes. The reaction of bis(tetrafluoropropyl) phosphite with the perfluoroepoxypropane dimer and trimer proceeds with the preferential formation of the tetrafluoropropyl ester of monofluorophosphorous acid and bis(tetrafluoropropyl) fluorophosphate.[327]

Bromocyanogen reacts slowly with R_F-alkyl phosphites, forming the dicyanophosphoranes **124** and the bromophosphates **107**,[328,329] whereas only phosphates are obtained from the R_H phosphites.[330] It has been suggested that the process proceeds via the intermediate **125a**.

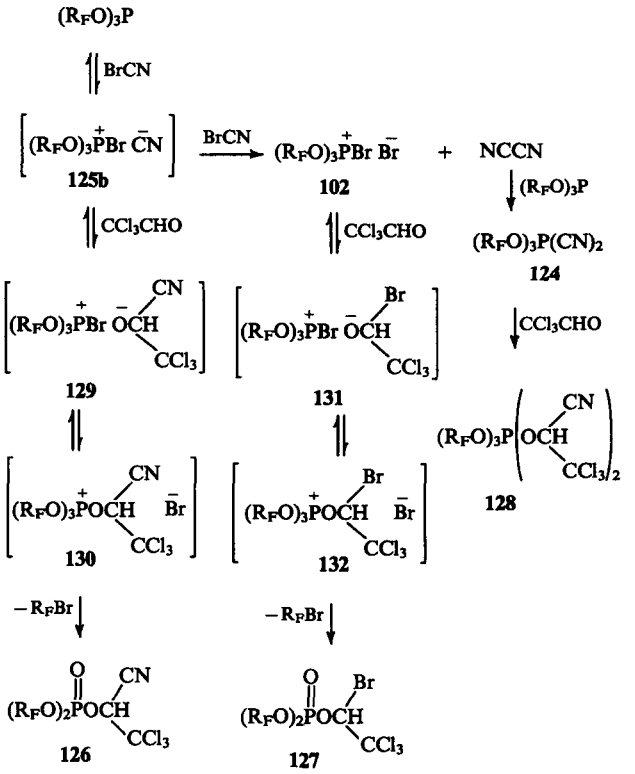


125a

124 107

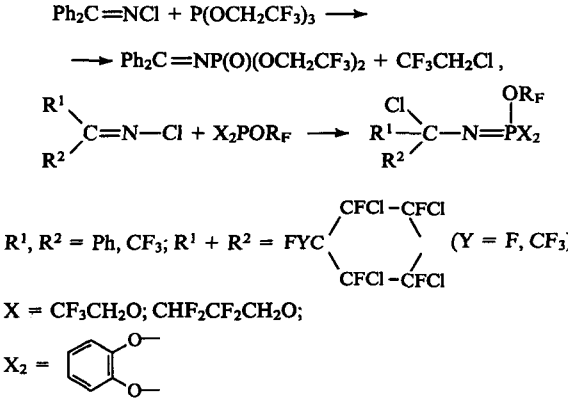
$R_F = CHF_2CF_2CH_2$, $CHF_2(CF_2)_3CH_2$.

The nature of the intermediate (**125a** or **125b**) was established when the above reaction was carried out in the presence of a third reagent — chloral.[331] The phosphates **126** and **127** and the phosphorane **128** were obtained in this case, indicating the initial appearance of the quasi-phosphonium intermediate **125b**, which may react with the initial bromocyanogen. The interaction of the intermediates **124**, **125b**, and **102** with chloral leads to the final compounds **126**–**128**. The formation of the phosphates **126** and **127** includes the initial appearance of the salts **129** and **131** and their subsequent conversion via ligand exchange into the phosphonium salts **130** and **132**.



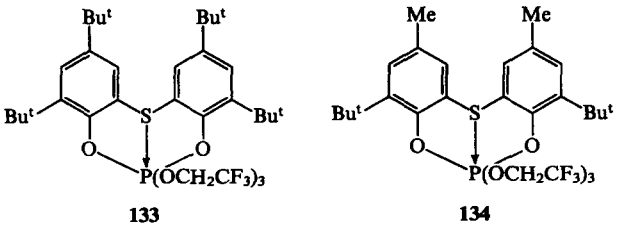
125b 102 124 129 131 128 130 132 126 127

It has been shown[329,332,333] *that N-chloroamines react with* R_F-alkyl phosphites to form iminophosphines, but the intermediate monochlorophosphoranes were not detected.

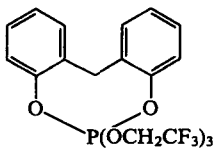


$X = CF_3CH_2O$; $CHF_2CF_2CH_2O$;

An interesting approach to the synthesis of fluoroalkoxyphosphoranes has been proposed.[334–337] It consists in the successive treatment of tris(trifluoroethyl) phosphite with diisopropylchloroamine and bisphenol, the role of a base being assumed by the amine produced during the reaction. The eight-membered heterocyclic compounds **133**–**135** were obtained in this way.



133 134

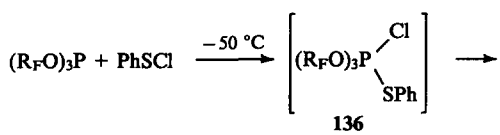


135

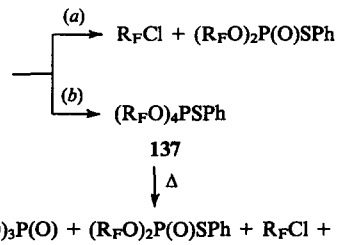
The structure of compound **134** was demonstrated by X-ray diffraction. The determination of the conformations of these phosphoranes was important for the understanding of the interaction of phosphates with the active sites of enzymes in the presence of sulfur-containing aminoacids.[338]

The interaction of P(III) derivatives with the halogens and sulfur(II, IV, VI) halides has many features in common and represents a nonclassical variant of the Arbuzov reaction.[330, 339] In contrast to the halogens, sulfur halides have two different centres (the sulfur and halogen atoms), which are readily polarisable and are accessible to nucleophilic attack by the P(III) atom.[339]

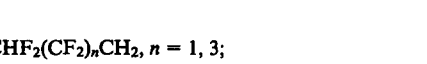
Considerable attention has been devoted in the literature (see, for example, Refs 148 and 340–345) to the reactions of sulfur(II, IV, VI) chlorides with R_F-derivatives of P(III). Thus benzenesulfenyl chloride interacts with R_F-phosphites to form mixtures of compounds.[342]



136



137

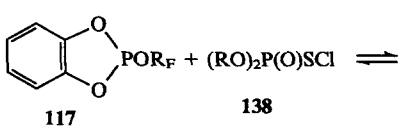


$R_F = CHF_2(CF_2)_nCH_2$, $n = 1, 3$;

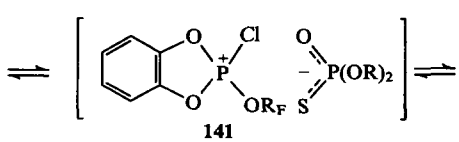
(*a*) 20 °C; (*b*) −50 °C, R_FOH, NEt_3.

The intermediate **136** was not detected, but its presence was deduced from the formation of the unstable monothiophosphorane **137** as a result of the treatment of the reaction mass with a mixture of the corresponding alcohol and triethylamine at −50 °C.

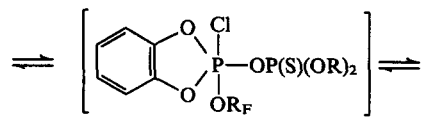
The interaction of acyclic and cyclic fluoroalkyl phosphites with dialkyl phosphonosulfenyl chlorides **138** is accompanied by the deoxygenation of the latter.[103, 148, 344, 345] The catechol derivatives **117** also react similarly with compounds **138** [148, 344, 345] with the preferential formation of the phosphate **139** and the chlorothiophosphate **140**.



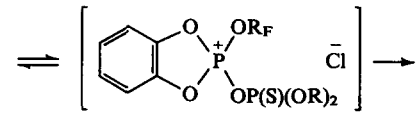
117 138



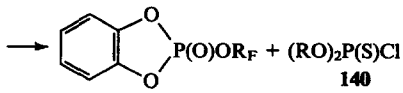
141



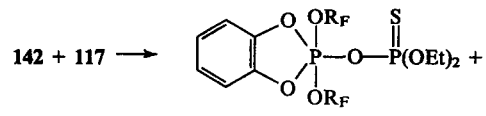
142



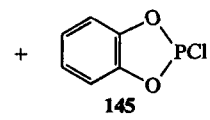
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139 140



144

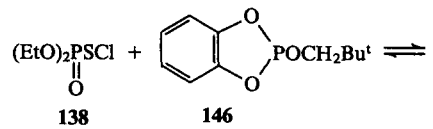


145

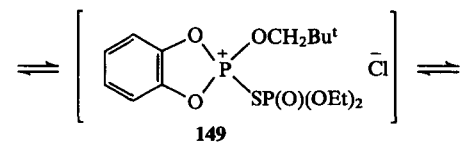
R = Me, Et, Pr; $R_F = CHF_2CF_2CH_2$, CF_3CH_2, $CHF_2(CF_2)_3CH_2$.

The reaction probably begins with halogenophilic attack on the phosphorus atom and the formation of the quasi-phosphonium salt **141**, which is in equilibrium with the phosphorane **142**. The latter is converted via the salt **143** into the main products **139** and **140**. The formation of small amounts of the phosphorylated phosphoranes **144** and of the *o*-phenylene phosphite **145** during the disproportionation process, which has been investigated in detail in relation to the reactions of the phosphites **117** with bromine, also constitutes evidence in support of the formation of the chlorophosphorane **142**.[323]

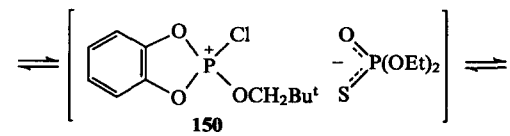
The mechanism of the reaction of the neopentyl *o*-phenylene phosphite **146** with the sulfenyl chloride **138** (R = Et), which also leads mainly to the phosphates **140** (R = Et) and **147**, has been recently investigated by dynamic ^{31}P NMR (from 100 °C).[346] The authors were able to detect the intermediate **148**, which is analogous to the phosphorane **142** postulated above. On this basis, it was concluded that the sulfur atom in compound **138** is initially attacked with subsequent two-step ligand exchange.



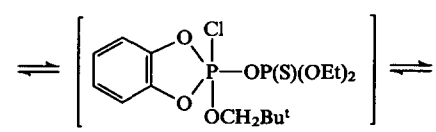
138 146



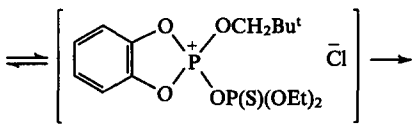
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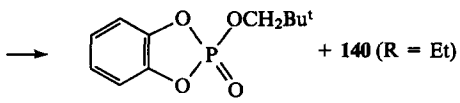
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148



151



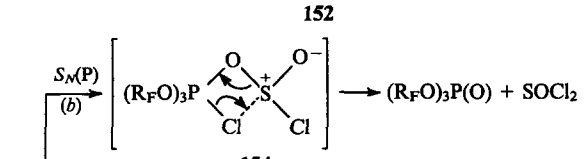
147

However, despite such a low reaction temperature, the intermediates **149–151** were not detected. In our view, the data presented in no way disprove the halogenophilic deoxygenation mechanism and cannot serve as proof that the sulfur atom is attacked. The high rates of the reactions of the sulfenyl chloride **138** with both the usual and fluorinated phosphites may indicate orbital control in these reactions or initial one-electron transfer from the phosphorus atom to the σ^*_{S-Cl}.

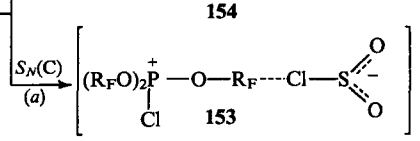
In the reactions of sulfuryl chloride with fluoroalkyl phosphites, the formation of chlorophosphates is accompanied by oxidation to phosphates.[344] It has been suggested that the chlorophosphonium salt **152** formed initially enters into nucleophilic substitution reactions either at a carbon atom [path (*a*), intermediate **153**] or at the phosphorus atom [path (*b*), intermediate **154**].

$$(R_FO)_3P + SO_2Cl_2 \longrightarrow [(R_FO)_3\overset{+}{P}Cl\ ClSO_2^-] \longrightarrow$$

152



154

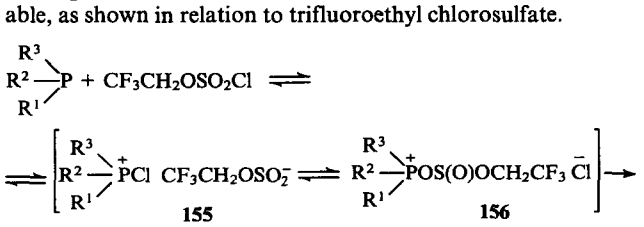


153

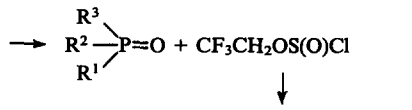
$$(R_FO)_2P(O)Cl + SO_2 + R_FCl$$

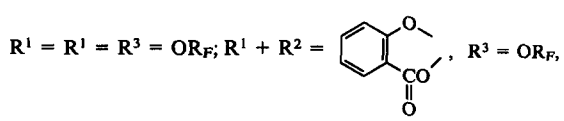
$R_F = CHF_2(CF_2)_nCH_2$ (n = 1, 3, 5).

It has been noted[344] that the high electronegativity of the R_FO [$R_F = CHF_2(CF_2)_nCH_2$] group hinders the elimination of R_F in the reaction with SO_2Cl_2 and promotes the formation of oxidation products. However, if the elimination stage were bimolecular, as described above, then the electron-accepting substituent R_F would be split off easily. It has to be assumed that the formation of the P = O bond in the given reaction must take place before the attack by the Cl^- ion on R_F, i.e. the process should possess features of an S_N1 mechanism of fission of an alkyl group, which is naturally hindered by electron-accepting substituents such as fluorine atoms. It is doubtful if the intermediate **154** has the character of a phosphorane. Monochlorophosphoranes have been obtained only for $R_F = CH(CF_3)_2$[341] and in all the remaining cases only quasi-phosphonium salts are formed from acyclic fluoroalkyl phosphites. Ligand exchange in the salt **152** and nucleophilic attack on the sulfur atom are therefore more probable, as shown in relation to trifluoroethyl chlorosulfate.



155 156





where R_F = CF_3CH_2, $CHF_2CF_2CH_2$, $CHF_2(CF_2)_3CH_2$, $(CF_3)_2CH$, C_6F_5.

The reactivity of trifluoroethyl chlorosulfate towards fluoroalkyl phosphite is lower than that of sulfuryl chloride.[103,344]

According to the authors, the reactions involve the initial formation of the chlorophosphonium salt **155** and subsequent ligand exchange with formation of the intermediate **156**, the decomposition of which leads exclusively to a phosphate (the yield is quantitative).

The fact that the first stage in the reaction of trifluoroethyl chlorosulfate with R_F-phosphites is nucleophilic attack on the chlorine atom is confirmed by the results of the reaction of trifluoroethyl chlorosulfate with the silyl phosphite **157**, which leads to a bis(fluoroalkyl) chlorophosphate.[344]

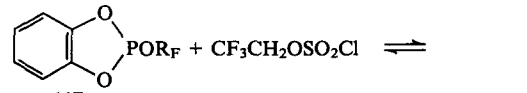
$$(R_FO)_2POSiMe_3 + CF_3CH_2OSO_2Cl \longrightarrow$$

157

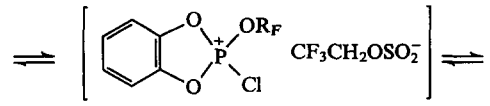
$$\longrightarrow (R_FO)_2P(O)Cl + [CF_3CH_2OS(O)OSiMe_3]$$

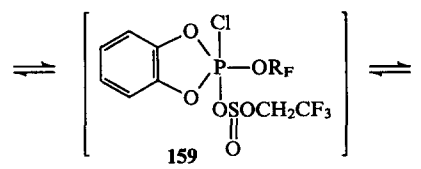
$R_F = CHF_2CF_2CH_2$.

In contrast to the reactions examined above, the interaction of trifluoroethyl chlorosulfate with fluoroalkyl *o*-phenylene phosphites **117** takes place with formation of the phosphoranes **158** and the phosphates **139**. The phosphoranes **158** are obtained as a result of ligand exchange between the initial phosphite and the intermediate chlorophosphorane **159**. However, the main path in the reaction of the latter is transition via the salt **160** to the phosphate **139**.

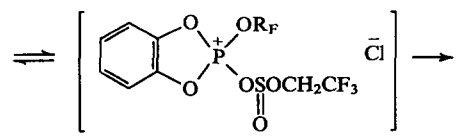


117

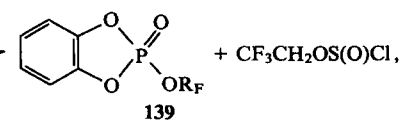




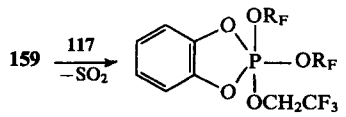
159



160

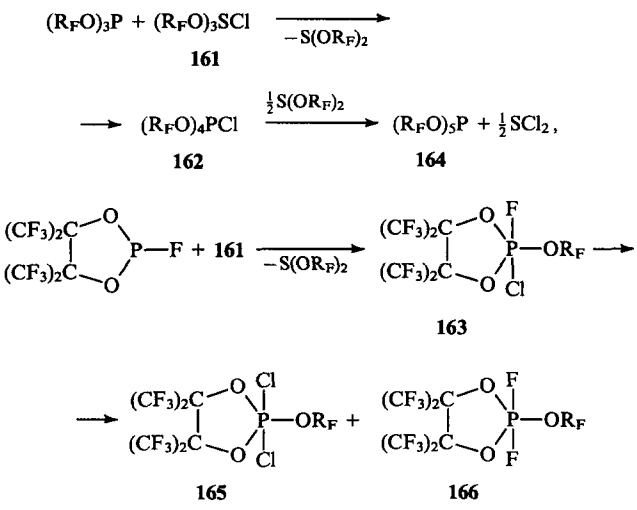


139



158

The chlorosulfurane **161** readily reacts with R_F phosphites to form the phosphoranes **162** and **163**,[340,344] which are converted into compounds **164–166** as a result of exchange reactions with the initial chloride **161** and disproportionation.



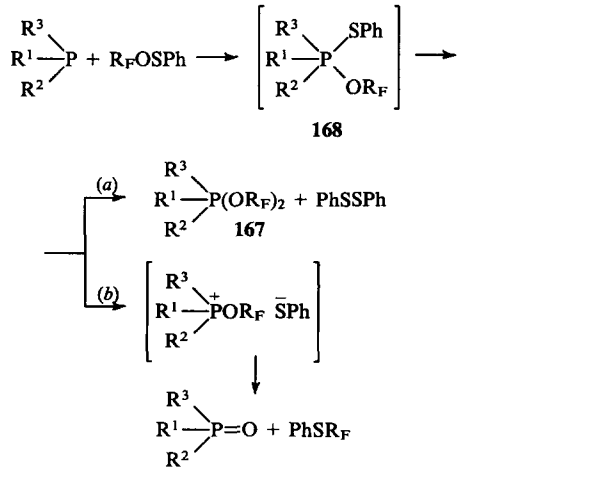
161 162 164 163 165 166

Thus the reactions of fluoroalkyl phosphites with sulfur chlorides and bromine have shown that a whole series of characteristic features, associated primarily with the low nucleophilicity of the P(III) atom and the hindrance to the elimination of the fluoroalkyl group from quasi-phosphonium intermediates, are typical of fluorinated P(III) derivatives. This leads to new reaction paths and unusual ways in which halophosphoranes and quasi-phosphonium salts are stabilised, such as transition to P(V) and P(III) compounds via exchange and disproportionation reactions.

It is known from theoretical studies and data on the stability of phosphorus(V) compounds[246,248] that electronegative groups stabilise the phosphorane molecule. As we have already noted, fluoroalkoxy-groups have electron-accepting properties and effectively stabilise phosphorane structures and this is the reason why much attention has been devoted in the literature to the synthesis of stable phosphoranes from R_F-phosphites.

The stable phosphoranes **167** have been synthesised[95–97,135,140,150] via the reaction of R_F-phosphites with sulfenic acid esters (Scheme 3).

Scheme 3



168 167

R_F = CF_3CH_2, $(CF_3)_2CH$;

R^1	R^2	R^3
CF_3CH_2O	CF_3CH_2O	CF_3CH_2O
Ph	CF_3CH_2O	CF_3CH_2O
Ph	Ph	CF_3CH_2O
C_6F_5O	C_6F_5O	C_6F_5O
$(CF_3)_2CHO$	$(CF_3)_2CHO$	$(CF_3)_2CHO$
$(CF_3)_2CHO$	$(CF_3)_2CHO$	Ph
$(CF_3)_2CHO$	Ph	Ph
$-OCH_2CH_2O-$		$(CF_3)_2CHO$
$-SCH_2CH_2S-$		$(CF_3)_2CHO$
$-MeNCH_2CH_2NMe-$		$(CF_3)_2CHO$

It was suggested that, in the interaction of R_F-phosphites with sulfenic acid esters, the P atom is inserted in the S–O bond with formation of the alkoxythiophosphorane **168**. Such mixed phosphoranes have been obtained for $R^1 = R^2 = R^3 = CF_3CH_2O$ and $(CF_3)_2CHO$[95,96] (δ_P = 50–54 ppm). Next, the phosphorane **168** reacts via path (*a*) with yet another $PhSOR_F$ molecule, forming the pentaalkoxyphosphorane **168**. Path (*b*) operates for substituents at the phosphorus atom with more pronounced electron-donating properties.

The interaction of the hexafluoroisopropyl ester of sulfoxylic acid with fluoroalkyl phosphites results in the formation of a mixture of products.[341]

$$4(R_FO)_3P + S(OR_F)_2 \longrightarrow$$

$$\longrightarrow (R_FO)_5P + (R_FO)_3P(S) + (R_FO)_3P(O) + R_FOR_F$$

R_F = $(CF_3)_2CH$.

3. Reactions of fluoroalkoxy-derivatives of P(III) with carbonyl compounds and their aza-analogues

The reactions of fluoroalkoxy-derivatives of P(III) with carbonyl compounds have been investigated for a comparatively small number of carbonyl compounds, among which most attention has been devoted to hexafluoroacetone. This is not fortuitous, because the latter forms with various P(III) derivatives σ^5-1,3,2- or σ^5-1,4,2-dioxaphospholanes, which are of great interest in view of their stability and the possibility of studying the structures of pentacoordinate phosphorus compounds, the role of which in biochemical processes is very important.[143,347] The importance of fluoroalkoxyphosphoranes in organic synthesis has also been increasing.[348]

a. Bis(fluoroalkyl) phosphites

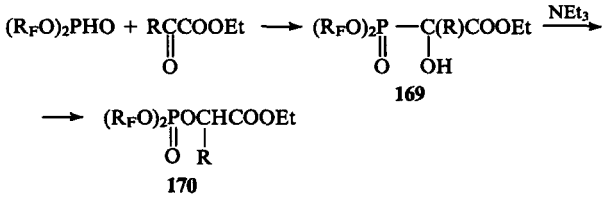
Bis(fluoroalkyl) phosphites are stronger acids than dialkyl phosphites.[47] The nucleophilicity of phosphorus in the P(III)-tautomeric form of bis(fluoroalkyl) phosphites is lower than in dialkyl phosphites.

The products of the phosphonate–phosphate rearrangement (hexafluoroisopropyl phosphates) have been obtained in the interaction of bis(fluoroalkyl) phosphites with $(CF_3)_2C{=}O$ in the presence of NEt_3.[160,266] Fluorodialkyl phosphites readily add to fluoral and chloral with formation of 1-hydroxyphosphonates,[62,208] which are converted into phosphates or vinyl phosphates on heating in the presence of NEt_3. Hexafluoroacetone *N*-benzenesulfonylimine reacts with bis(tetrafluoro-propyl) phosphite to form a stable 1-aminoalkylphosphonate.[349]

The kinetics and mechanism of the addition of bis(fluoroalkyl) phosphites to benzylideneacetone, chalcone, butyl cinnamate and *p*-methoxycinnamate, and also to a phenylglyoxylic acid ester have been investigated.[350,351] The reduced reactivity of bis(fluoroalkyl) phosphites in the Abramov and Pudovik reactions as well as certain specific features of their behaviour uncharacteristic of the usual dialkyl phosphites have been noted. For example, an excess of bis(fluoroalkyl) phosphite in the reaction of benzylideneacetone in the presence of R_FONa lowers the rate of reaction compared with the rate of reaction of

dialkyl phosphites, which the authors attribute to the formation of fairly stable hydrogen-bonded complexes between the free acid and its anion.

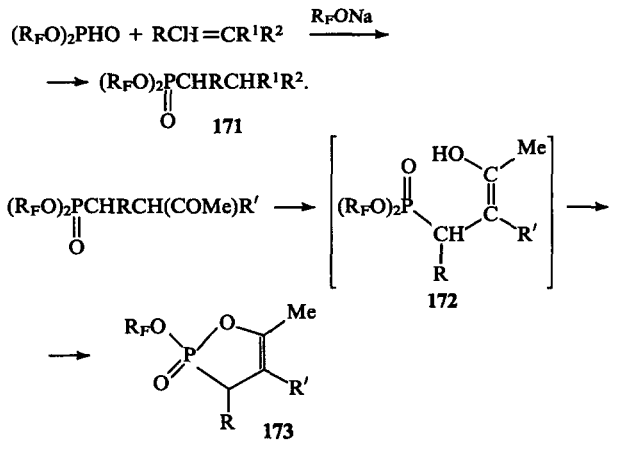
The esters of α-ketocarboxylic and mesoxalic acids react with bis(fluoroalkyl) phosphites to form the 1-hydroxyphosphonates **169**. The phosphonate obtained from ethyl pyruvate (R = Me) partly undergoes the phosphonate–phosphate rearrangement during distillation, while the analogous phosphonate synthesised from the phenylglyoxylic acid ester (R = Ph) is fully converted into the rearrangement product **170**.[99,352]



R_F = CF_3CH_2, $CHF_2CF_2CH_2$; R = Me, Ph, COOEt.

The fluoroalkyl groups at the phosphorus atom in the 1-hydroxyalkyl phosphonate obtained from bis(tetrafluoropropyl) phosphite and 2-acetoxyethyl methyl ketone promote a more ready occurrence of the phosphonate–phosphate rearrangement compared with the fluoroalkyl groups in the 1-hydroxyalkyl-phosphonate obtained from diethyl phosphite.[116]

The reactions of bis(fluoroalkyl) phosphites with ethylideneacetylacetone and ethyl acetoacetate and benzylidenemalonate are exothermic. In the presence of a catalyst, they lead to the phosphonates **171**.[353] On heating, compounds **171** cyclise (probably via the enolic form **172**) to the σ⁴-1,2-oxaphospholenes **173**.



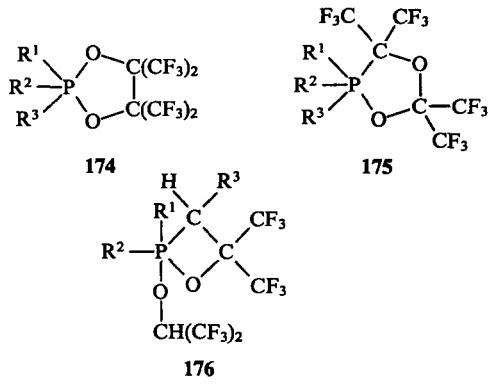
R = Me, Ph; R^1, R^2 = MeCO, COOEt; R_F = CF_3CH_2, $CHF_2CF_2CH_2$.

An analogue of the phosphonates **171**, containing OEt substituents instead of OR_F, cyclises under much more severe conditions than compounds **171**, which is associated with the greater leaving capacity of the fluoroalkoxy-group compared with the ethoxy-group. The phosphonate **171**, obtained from benzylidenemalonic ester which is incapable of enolisation, does not give rise to the phospholene **173**.

b. Fluoroalkyl phosphites, phosphonites, phosphinites, and amidophosphites

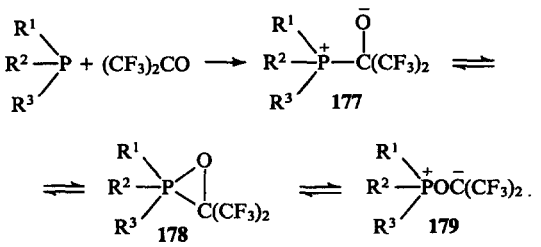
Fluoroalkyl phosphites, amidophosphites, phosphinites, and phosphonites have been allowed to react with hexafluoroacetone,[84–86,118,122,130,141,155,161,177,178,354,355] diacetyl,[161] perfluorodiacetyl,[137,140,143,144,147] carboxylic α-ketoacid esters,[351] benzoylnitrile,[90] *o*-anthraquinone,[133] diethyl mesoxalate,[356] *o*-chloranil,[357,358] halogen-containing esters of di- and trifluoroacetoacetic[356,359] and pyruvic[360] acids, 1,1-dichloroacetophenone,[266] pentafluorophenylbromoacetophenone,[361] dimethyl trichloroacetylphosphonate,[90] fluorinated aldehydes,[49,208] and chloral and bromal.[362,363]

Hexafluoroacetone reacts with fluorinated P(III) derivatives to form phospholanes of three types: σ⁵-1,3,2- and σ-1,4,2-dioxaphospholanes **174**[85,86,118,122,130,141,142,161,177,178,355] and **175**[14,86] respectively, as well as σ⁵-1,2-oxaphosphetanes **176**.[84,86,122,130,155,177,178,354] In the case of fluoroalkyl phosphites, mainly the σ⁵-1,3,2-dioxaphospholanes **174** are formed.

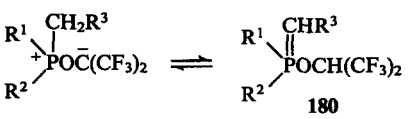


R^1, R^2, R^3 = Ph, Et, Me, RO, $(CF_3)_2CHO$.

It has been suggested that P(III) initially attacks the carbon atom of the carbonyl group with formation of the dipolar ion **177**, which is converted into the zwitterion **179** via the phosphorane **178**.



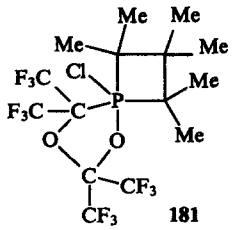
If one of the substituents at the P atom contains protons at the α-carbon atom, such a proton may be transferred to the carbanionic centre of the dipolar ion **179** with formation of the ylide **180**.



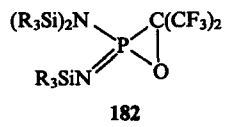
The addition of a second acetone molecule to the intermediates **177**, **179**, and **180** leads to the final reaction products **174–176**. The intermediates **177–179** were not detected by any methods.

It is noteworthy that analysis of the available data on the reactions of P(III) derivatives with hexafluoroacetone, in which σ⁵-1,4,2-dioxaphospholanes are formed,[86,122,181,364–369] does not reveal the causes of the formation of the latter and the factors promoting the appearance of 1,3,2-dioxaphospholanes. 1,4,2-Dioxaphospholanes have been obtained from cyclic and acyclic P(III) derivatives containing both electron-donating (NR_2) and electron-accepting [F, $OCH(CF_3)_2$] substituents, as well as bulky groups. A particularly effective example is quoted in a study[366] in which the synthesis of the phosphorane **181** is described.

The structure of compound **182** is interesting as a model of the intermediate **178** containing a three-membered ring.[370]

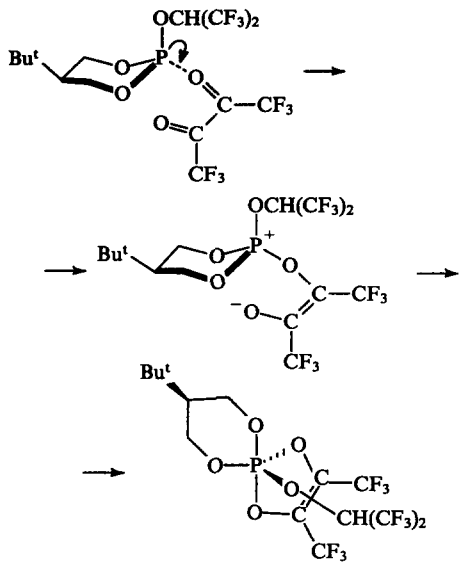


181

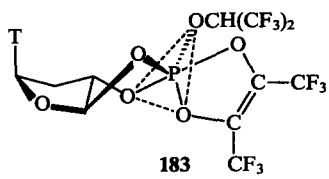


182

The reactions of cyclic fluoroalkyl phosphites with perfluorodiacetyl have been investigated [143, 144, 147] and it has been shown that they proceed stereospecifically — with retention of configuration at the phosphorus atom. The authors believe that this is a consequence of the attack by P(III) on the oxygen atom.

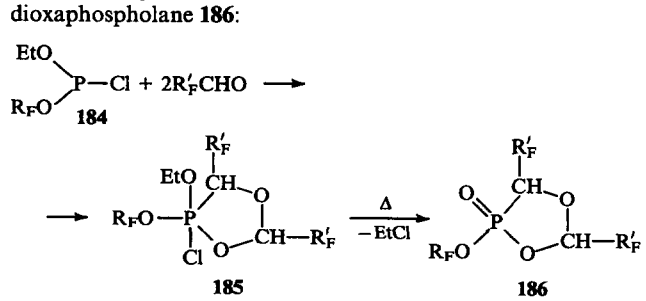


It has been suggested that the phosphorane **183** be used as a phosphorus-containing model of the P(V)-intermediate cyclic nucleotide for enzymic reactions. It has been shown by NMR (500 MHz) that the phosphorinane ring exists predominantly in the twist-conformation.



183

Fluoral and tetrafluoropropanal react with fluoroalkyl phosphites [49, 208] and fluoroalkyl chlorophosphites [49, 136] to form σ^5-1,4,2-dioxaphospholanes. For example, the chlorophosphite **184** forms an unstable intermediate monochlorophosphorane **185** (δ_P = −40 ppm), which is readily converted into the σ^5-1,4,2-dioxaphospholane **186**:

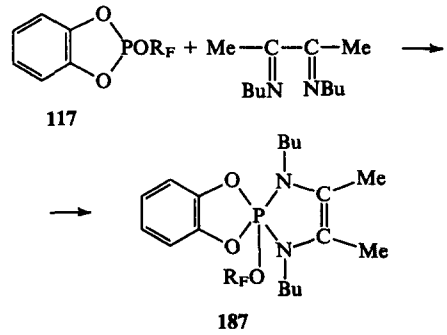


184 185 186

R_F = CF_3CH_2, R'_F = CHF_2CF_2.

Diethyl mesoxalate,[356] *o*-chloranil,[356, 357] and the ethyl ester and nitrile of phenylglyoxylic acid [352] react with fluoroalkyl phosphites to form σ^5-1,3,2-dioxaphospholanes; the reactions take place under more severe conditions than those with alkyl phosphites.

A single example of the interaction of the fluoroalkyl phosphites **117** with α-diimines [371] to form the σ^5-1,3,2-diazaphospholine **187** has been described.

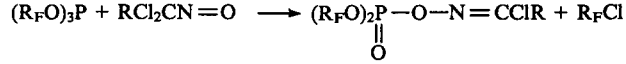


117 187

R_F = $(CF_3)_2CH$, CF_3CH_2.

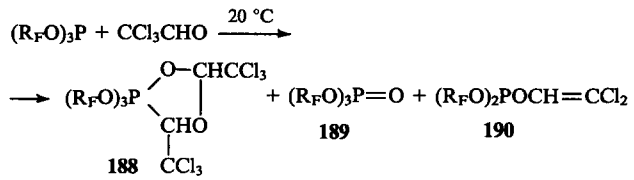
It is noteworthy that alkyl phosphites do not interact with mono- and di-imines.[372]

Carbonyl compounds containing a mobile halogen atom have been less studied in reactions with fluoroalkoxy-derivatives of P(III) — there have been only a few communications on this topic. Thus tris(tetrafluoropropyl) phosphite undergoes the Perkow reaction with chloral (in a stainless steel tube at a temperature > 200 °C),[60, 62] with halogen-containing esters of di- and trifluoroacetoacetic [358] and pyruvic [90] acids, with 1,1-dichloroacetophenone,[267] with pentafluorophenylbromoacetophenone,[361] and with dimethyl trichloroacetylphosphonate.[90] Tris(tetrafluoropropyl) phosphite also undergoes the Perkow reaction with polychloronitrosoethanes.[373]



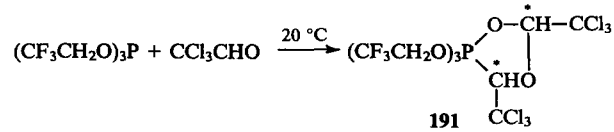
R_F = $CHF_2CF_2CH_2$, R = $ClCH_2$, Me.

A detailed reinvestigation of the reaction of tris(fluoroalkyl) phosphites with chloral showed [363] that it begins even at 20 °C and leads mainly to the σ^5-1,4,2-phosphorane **188**, the phosphate **189**, and small amounts of the vinyl phosphite **190**.



188 189 190

The fundamental results obtained in the study of the reactions of fluoroalkyl phosphites with chloral are briefly surveyed below.[103, 362, 363, 374, 375] In the first place, it was possible to demonstrate the reversibility of the formation of the phosphorane **188**, which decomposes at 100 °C into the initial compounds and is reformed at 20 °C.[360] In the case of tris(trifluoroethyl) phosphite, the corresponding phosphorane **191** was isolated in the form of one diastereoisomer;[375] the stereoselectivity of the reaction is > 90%.



191

An extremely unusual fact was noted in the reaction of the phosphite $P(OR_F)_3$ with chloral in the presence of the alcohol R_FOH: together with the phosphate **189**, the fraction of which increases, the phosphorane **188** is also produced.[103, 363] The

product of the Perkow reaction — the vinyl phosphate **192** — is formed only at 160 °C.[60,62,363] Hence it follows that fluoroalkyl phosphites react with chloral predominantly at the carbonyl group, but the dechlorination of the CCl_3 substituent also takes place to a slight extent.

$$(R_FO)_3P + CCl_3CHO \longrightarrow$$

$$\xrightarrow{R_FOH,\ 20\ ^\circ C} \mathbf{188} + \mathbf{189} + CHCl_2CHO$$

$$\xrightarrow{160\ ^\circ C} (R_FO)_2P(O)OCH{=}CCl_2 + R_FCl$$

192

Chloral proved to be an effective catalyst of the oxidation of fluoroalkyl phosphites by oxygen.[362]

$$(R_FO)_3P + CCl_3CHO \xrightarrow{O_2,\ 2\ h} (R_FO)_3P{=}O.$$

189

The initial attack on the carbon atom of the carbonyl group has been confirmed also by the results of the reaction of chloroalkyl phosphites with chloral in the presence of Lewis acids.[374] When $SbCl_5$ was used, the betaine **193** with a P–C bond, stabilised by coordination to the Lewis acid at the anionic centre, was obtained. At 20 °C, the betaine **193** is slowly converted into the quasi-phosphonium salt **194** with a P–Cl bond.

$$(R_FO)_3P + CCl_3CHO \xrightarrow{SbCl_5}$$

$$\longrightarrow (R_FO)_3\overset{+}{P}-\underset{\bar{O}SbCl_5}{\overset{CCl_3}{\underset{|}{CH}}} \longrightarrow$$

193

$$\longrightarrow (R_FO)_3\overset{+}{P}Cl\ \ Cl_2C{=}CH\bar{O}SbCl_5.$$

194

The betaine **195** (δ_P = 26 ppm), obtained by the interaction of tris(fluoroalkyl) phosphite with chloral in the presence of $BF_3 \cdot OEt_2$, undergoes various reactions on heating, one of which is intramolecular fluorination to the difluorophosphorane **196** (δ_P = −57.9 ppm, $^1J_{PF}$ = 894 Hz).[363]

$$(R_FO)_3P + CCl_3CHO \xrightarrow[-Et_2O]{BF_3 \cdot OEt_2}$$

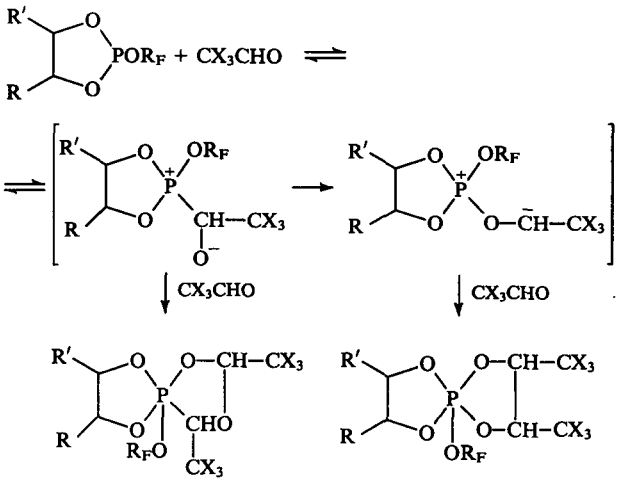
$$\longrightarrow (R_FO)_3\overset{+}{P}-\underset{\bar{O}BF_3}{\overset{CCl_3}{\underset{|}{CH}}} \longrightarrow$$

195

$$\longrightarrow (R_FO)_2\overset{F}{\underset{F}{P}}-\underset{\bar{O}B\ \ OR_F}{\overset{CCl_3}{\underset{|}{CH}}}{}^{F}$$

196

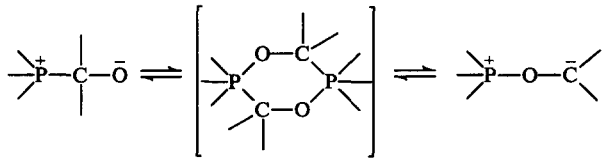
The asymmetric fluoroalkyl phosphites $(R_FO)_2POR$, containing one nonfluorinated substituent, react with chloral to form σ^5-1,4,2-phospholanes with a P–C bond [R = Et, $(EtO)_2P(O)CH_2$], which are stable at 20 °C.[113] We obtained the same result for cyclic fluoroalkyl phosphites.[138,139] The reaction with chloral led to the isolation for the first time of both σ^5-1,4,2-dioxaphospholanes **197** and σ^5-1,3,2-dioxaphospholanes **198**, the structures of which were confirmed by NMR data (δ_P = −20 to −30 ppm for compound **197** and −42 to −50 ppm for compound **198**). Bromal gives rise to 1,4,2-dioxaphospholanes **197** only.



197 **198**

R = R′ = H, Me; R = H, R′ = Me; R = α-Me, R′ = β-Me(*d,l*); $R_F = CHF_2CF_2CH_2$; X = Cl, Br.

There exist two points of view in the literature concerning the mechanism of the rearrangement $P^+-C-O^- \rightarrow P^+-O-C^-$. One of them is that of Ramirez,[376] who believes that the rearrangement proceeds via the formation of a six-membered cyclic diphosphorane, i.e. is bimolecular. This cyclic diphosphorane has been recently obtained from PhCHO and ethyl pinacol phosphite,[377] which confirmed this mechanism.



According to the second point of view, the rearrangement involves the formation of a three-membered transition state (or intermediate) on the path to the POC adduct, i.e. follows a unimolecular path.[378,379] Theoretically, one cannot rule out also the possibility of a direct electrophilic attack by P on the oxygen atom of the C=O group.[379]

When σ^5-1,3,2- and σ^5-1,4,2-dioxaphospholanes are formed simultaneously, their ratio should be affected by the dilution. When the C=O group is attacked simultaneously at the O and C atoms, the dilution of the reaction mixture should not lead to a significant change in the ratio of the phospholanes **197** and **198**. Where the rearrangement follows a bimolecular mechanism, dilution should diminish the fraction of the phospholane **198**. When the P atom attacks the C=O group at the C atom with an intramolecular rearrangement, the fraction of the phospholane **198** should increase with dilution. The experimental data obtained[139] for *d,l*-2,3-butylene tetrafluoropropyl phosphite and chloral have shown that the fraction of the phospholane **198** increases with dilution, whilst that of the isomer **197** falls, which confirms the intramolecular character of the rearrangement $P^+-C-O^- \rightarrow P^+-O-C^-$ in the case of chloral.

The results obtained in the study of the reaction of bromal with fluoroalkyl phosphites differ from those for chloral.[363,375] Bromal is much more reactive than chloral. When bromal is employed, the vinyl phosphate **199** and the phosphate **189** are formed as the main products. The dibromovinyl phosphite **200** was also detected in a small amount.

$$(R_FO)_3P + CBr_3CHO \xrightarrow{20\ ^\circ C} \longrightarrow (R_FO)_2P(O)OCH{=}CBr_2 \ (\mathbf{199}) + (R_FO)_3P{=}O \ (\mathbf{189}) + (R_FO)_2POCH{=}CBr_2 \ (\mathbf{200})$$

When this reaction is carried out in the presence of an alcohol, the phosphate **189** (yield ~97%) and the aldehyde $CHBr_2CHO$ are formed. This reaction has been proposed in the literature as a test reaction for the halogenophilic mechanism.[380,381] Under these conditions, even the use of a much less acid alcohol (propanol) affords more than 90% of the phosphate **189**.[103,363]

$$(R_FO)_3P + CBr_3CHO \longrightarrow \begin{cases} \xrightarrow[20\ ^\circ C]{R_FOH} \mathbf{189} + CHBr_2CHO + R_FBr \\ \xrightarrow[20\ ^\circ C]{PrOH} \mathbf{189} + CHBr_2CHO + PrBr \end{cases}$$

$R_F = CHF_2CF_2CH_2$.

Taking into account the difference between the reactivities of chloral and bromal and also the fact that the rate-determining stage in the Perkow reaction is the nucleophilic attack by the phosphorus atom, a halogenophilic mechanism has been proposed for the reactions of fluoroalkyl phosphites with bromal.[103,363]

The use of a third reagent (a Lewis acid) in the reaction with bromal on the whole confirms that the bromine atom is attacked, but in this case the shielding of both the carbonyl group and of the phosphorus atom by bulky substituents plays a certain role. Thus, when $SbBr_5$ is used as the Lewis acid, the quasi-phosphonium salt **201** with a P–Br bond is formed. The salt **202** is obtained similarly from the branched tris(hexafluoroisopropyl) phosphite and $SbCl_5$.[103] On the other hand, the interaction of the complex $CBr_3CHO \cdot SbCl_5$ with tris(tetrafluoropropyl) phosphite leads to the formation of the betaine **203**.[374]

$$(R_FO)_3P + CBr_3CHO \longrightarrow \begin{cases} \xrightarrow[R_F = CHF_2CF_2CH_2]{SbBr_5} (R_FO)_3\overset{+}{P}Br\ \overset{-}{Br_5Sb}OCH{=}CBr_2 \ (\mathbf{201}) \\ \xrightarrow[R_F = CH(CF_3)_2]{SbCl_5} [(CF_3)_2CHO]_3\overset{+}{P}Br\ \overset{-}{Cl_5Sb}OCH{=}CBr_2 \ (\mathbf{202}) \\ \xrightarrow[R_F = CHF_2CF_2CH_2]{SbCl_5} (R_FO)_3\overset{+}{P}{-}CH(CBr_3)\overset{-}{O}SbCl_5 \ (\mathbf{203}) \end{cases}$$

The betaine **204**, stabilised by coordination to BF_3, is converted into the difluorophosphorane **205** ($\delta_P = -77.9$ ppm, $^1J_{PF} = 729.6$ Hz) after being kept at 20 °C.

$$(R_FO)_3\overset{+}{P}{-}CH(CBr_3)\overset{-}{O}BF_3 \ (\mathbf{204}) \longrightarrow (R_FO)_3PF_2 \ (\mathbf{205})$$

$R_F = CHF_2CF_2CH_2$.

When oxygen is bubbled through a mixture of a phosphite and bromal, the oxidation product — the phosphate **189** — is formed in 100% yield.[362]

$$(R_FO)_3P + CBr_3CHO \xrightarrow[20\ ^\circ C]{O_2} (R_FO)_3P{=}O \ (\mathbf{189})$$

$R_F = CHF_2CF_2CH_2$.

This is an extremely important result, indicating the appearance of radical species during the reactions of fluoroalkyl phosphites with bromal, i.e. the occurrence of a one-electron transfer. Only in this case is there a possibility of catalysis of the reactions of phosphites with paramagnetic oxygen. A possible mechanism of the interaction of fluoroalkyl phosphites with bromal is presented below.[103]

$$(R_FO)_3P + CBr_3CHO \rightleftharpoons [(R_FO)_3\overset{+\cdot}{P}\ \overset{-\cdot}{C}Br_2CHO] \rightleftharpoons \rightleftharpoons [(R_FO)_3\overset{+}{P}Br\ \overset{-}{O}CH{=}CBr_2] \longrightarrow \begin{cases} \xrightarrow{(R_FO)_3P} \mathbf{200} + [(R_FO)_4\overset{+}{P}\ \overset{-}{Br}] \longrightarrow \mathbf{189} + R_FBr \\ \rightleftharpoons [(R_FO)_3\overset{+}{P}OCH{=}CBr_2\ \overset{-}{Br}] \longrightarrow \mathbf{199} + R_FBr \end{cases}$$

$R_F = CF_3CH_2$, $CHF_2CF_2CH_2$, $(CF_3)_2CH$.

We may note that the appearance of small amounts of vinyl phosphite as well as bromophosphites in reactions with bromine is associated with ligand exchange between the quasi-phosphonium intermediates and the initial fluoroalkyl phosphite.

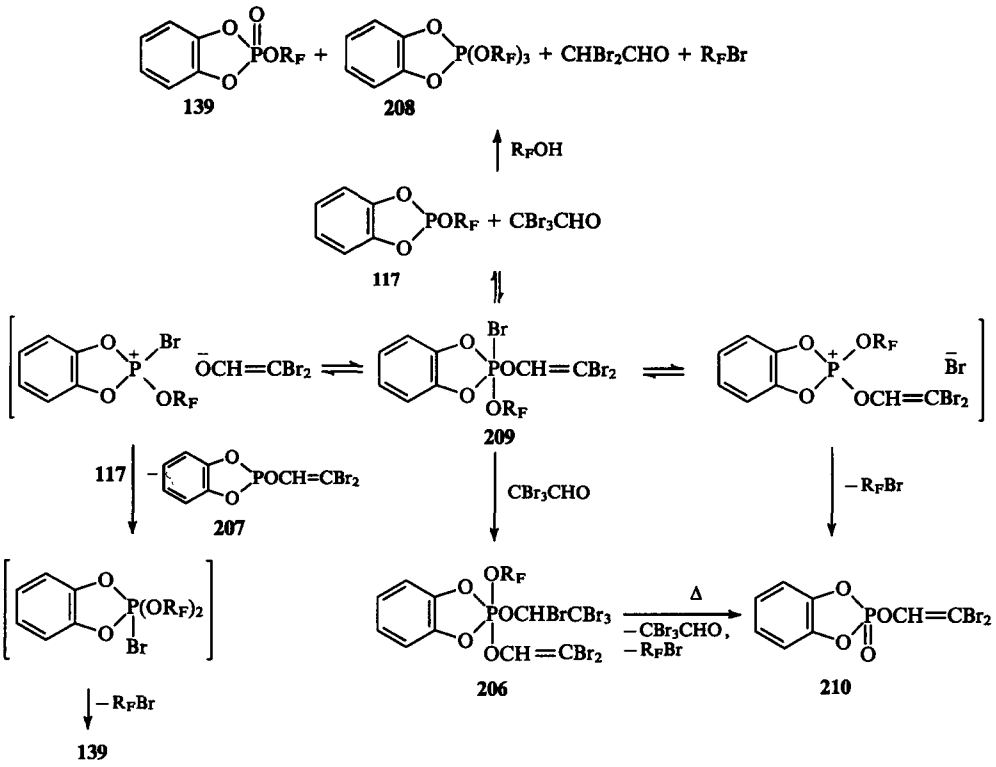
The interaction of the phosphite **117** with chloral and bromal is complex.[103,382,383] P(III) derivatives, formed on cleavage of the CCl_3 group and representing disproportionation products, were detected together with σ^5-1,3,2- and σ^5-1,4,2-dioxaphospholanes in the reaction with chloral.[383]

The replacement of chloral by bromal increases the contribution of the processes accompanied by the partial reduction of the CBr_3 group. The reaction products are the monocyclic pentaalkoxyphosphorane **206**, the phosphate **139**, and a small amount of the vinyl phosphite **207** (Scheme 4).[382] It was also possible to make the interesting observation that the above reaction is accelerated on UV irradiation.[103] These data as well as the results of the interaction of oxygen with the phosphite **117** in the presence of bromal, leading to the phosphate **139**, indicate the occurrence of one electron transfer in the reaction with bromal. The interaction of the phosphite **117** with bromal in the presence of R_FOH leads to the phosphate **139**, the phosphorane **208**, and dibromoacetaldehyde, which also confirms that the phosphorus atom attacks the bromine atom of bromal. When the last reaction is carried out in the presence of a base, the phosphorane **208** becomes the only phosphorus-containing reaction product.[382]

On heating, the phosphorane **206** decomposes to the vinyl phosphate **210**; when it is kept for a long time at room temperature in an acid medium, symmetrisation results in the formation of various phosphoranes containing both one and two catechol fragments and different acyclic substituents.

Thus the reaction of the phosphite **117** with bromal proceeds via a halogenophilic mechanism with the intermediate formation of the bromophosphorane **209**, which adds to the C=O bond of bromal, affording the phosphorane **206**. The monobromophosphorane **209** is unstable and decomposes to the vinyl phosphate **210** at 20 °C.

Scheme 4

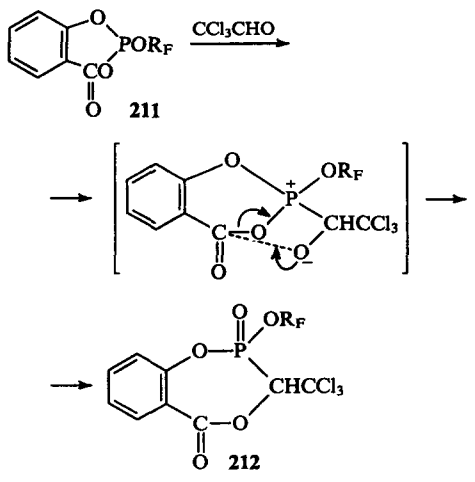


$R_F = CHF_2CF_2CH_2$.

c. 2-Fluoroalkyl-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinanes

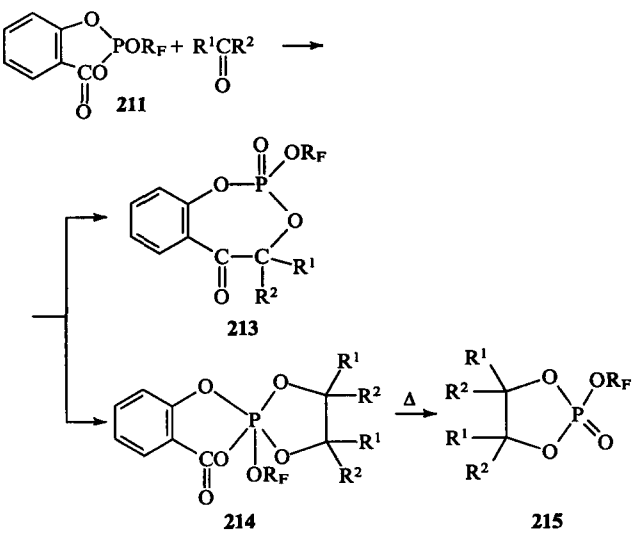
The stabilisation of the pentacoordinate phosphorus structure by the fluoroalkoxy-substituent makes it possible to obtain spirophosphoranes with an endocyclic POC(O) fragment. The phosphorylated salicylic acid derivatives (salicyl phosphites) used in this reaction are of considerable interest as reagents in the synthesis of phosphorus-containing natural products,[384] functioning as acylating and phosphorylating agents simultaneously. Fluoroalkyl salicyl phosphites have been allowed to react with hexafluoroacetone,[165,385] the esters of trifluoropyruvic,[386-388] pyruvic,[360,388] and mesoxalic acids,[356,388] chloral,[389] bromal,[359] dimethyl trichloroacetylphosphonate,[383] halogencontaining esters of di- and tri-fluoroacetoacetic acids,[358,359] α-diketones and α,β-unsaturated ketones,[390,391] and imines.[392]

Fluoroalkyl salicyl phosphites **211** react in a very unusual way with chloral and bromal, 1,4,2-dioxaphosphepanes **212** being produced in the former case with a stereoselectivity > 90%.[389]



$R_F = CF_3CH_2$, $CHF_2CF_2CH_2$, C_6F_5.

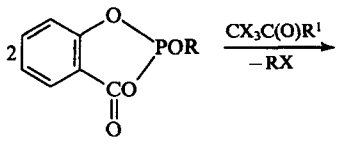
The interaction of hexafluoroacetone and ethyl pyruvate with compounds **211** affords 1,3,2-dioxaphosphepanes **213**. Methyl and diethyl trifluoropyruvates and mesoxalates react in a very unusual manner, forming σ^5-spirophosphoranes **214** at −40 °C and the products **213** at 80 °C. Compounds **214**, containing salicylic acid fragment which is readily eliminated on heating, being converted into σ^4-1,3,2-dioxaphospholanes **215**.



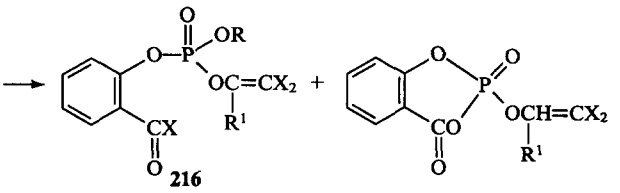
$R_F = CF_3CH_2$, $CHF_2(CF_2)_nCH_2$ (n = 1, 3);

$R^1 = R^2 = CF_3$, COOEt; $R^1 = CF_3$, R^2 = COOMe.

Bromal and dimethyl trichloroacetylphosphonate, which are more reactive than chloral, react with fluoroalkyl salicyl phosphites **122** to form the vinyl phosphates **216** — the products of the Perkow reaction, which is accompanied by 100% ring opening. The nonfluorinated salicyl phosphites **211** form both cyclic and acyclic vinyl phosphates. The latter cyclise on heating.[359,383]



211

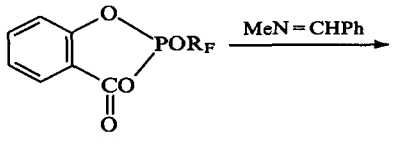


216

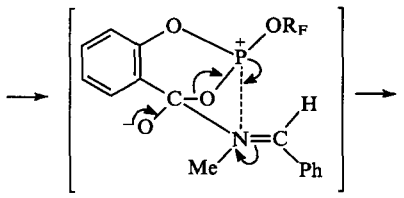
R = CF_3CH_2, $CHF_2CF_2CH_2$, Me, Bu;

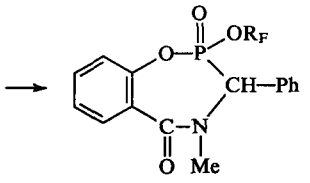
R^1 = H, X = Br; R^1 = $(MeO)_2P(O)$, X = Cl.

Fluoroalkyl salicyl phosphites **211** interact readily with imines to form 1,4,2-oxazaphosphepanes **217**.[392] It has been suggested that the imine nitrogen atom behaves as a nucleophile.



211

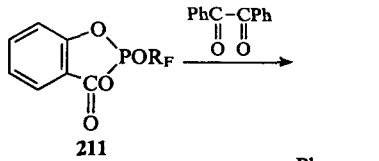




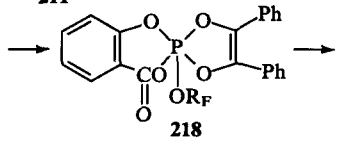
217

R_F = $(CF_3)_2CH_2$, CF_3CH_2.

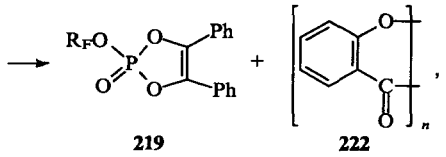
Dibenzoyl reacts with the phosphite **211** (R_F = CF_3CH_2) to form the unstable σ^5-1,3,2-dioxaphospholene **218**, which readily eliminates the salicylic acid fragment on heating and is converted into σ^4-1,3,2-dioxaphospholene **219**.[390,391]



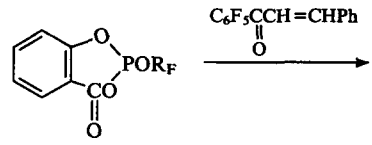
211



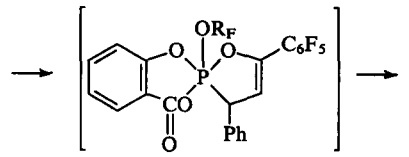
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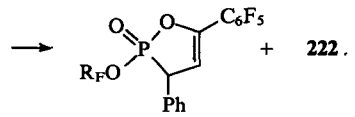
219 222



211



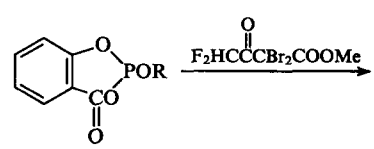
220



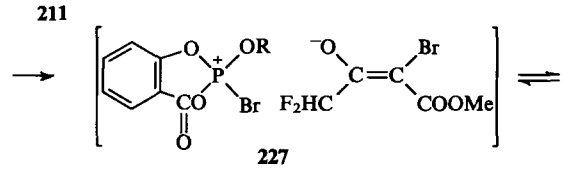
221

Despite the presence of the electron-accepting pentafluorophenyl substituent, 1-pentafluorophenyl-3-phenylprop-2-en-1-one (the *trans*-isomer) reacts with salicyl trifluoroethyl phosphite only on heating.[390,391] As in the case of dibenzoyl, the final product is a σ^4-1,2-oxaphospholene **221**, which does not contain a salicylic acid fragment. The 1,4-adduct (the phosphorane **220**) formed initially is unstable and decomposes to the phospholene **221** under the reaction conditions.

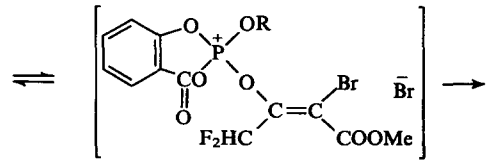
The esters of halogen-substituted acetoacetic acids undergo the Perkow reaction with the salicyl phosphites **211**, the process being accompanied by the regioselective cleavage of the anhydride fragment (in the case of fluoroalkyl salicyl phosphites) or partial elimination of the acyclic group (in the case of alkyl salicyl phosphites).[358,359] The reactions are highly stereoselective and, when a dibromo-ester is used, lead to the isomers **223** with the *trans*-disposition of the ester group and the phosphorus-containing fragment (yield more than 90%), whereas in the case of the chloro-ester they lead to the thermodynamically more stable *cis*-isomers **224** (yield 60%–80%). The phosphates **223** and **224** cyclise on heating with formation of compounds **225** and **226**. Taking into account the greater reactivity of the dibromo-ester compared with the chloro-ester, one may assume that, when the former is employed, a halogenophilic mechanism operates (the intermediate **227** is formed), whereas in the case of the chloro-ester there is attack on the carbon atom of the carbonyl group (the intermediate **238** is formed).

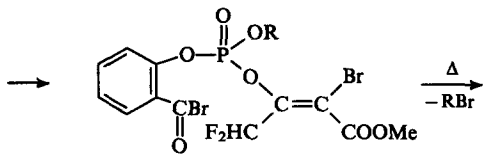


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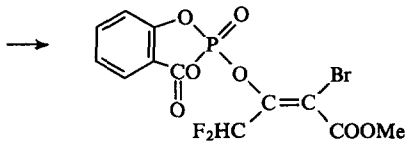


227



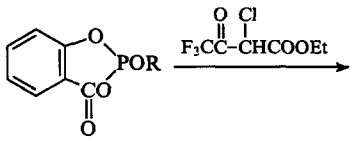


223

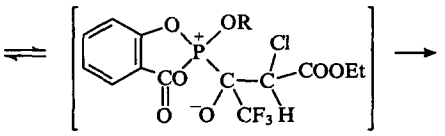


225

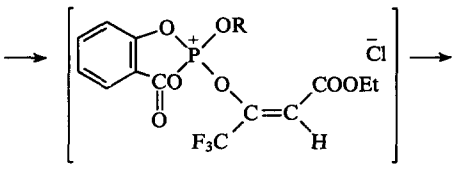
R = Et, CF_3CH_2, $CHF_2CF_2CH_2$;

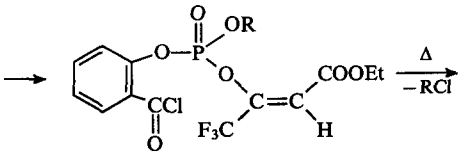


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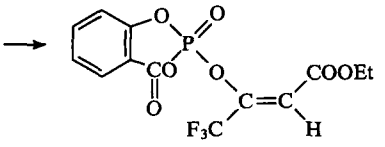


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224



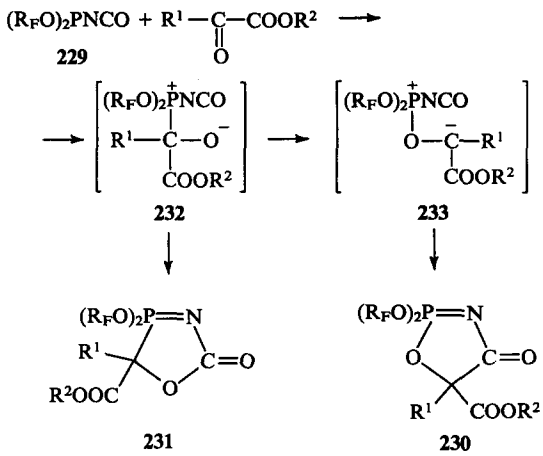
226

R = Et, CF_3CH_2, $CHF_2CF_2CH_2$.

d. Bis(fluoroalkyl) isocyanatophosphites

The introduction of fluorinated substituents into the molecules of isocyanatophosphites not only lowers the nucleophilicity of the phosphorus atom in these compounds in reactions with carbonyl compounds and their aza-analogues but also determines a whole series of specific features of the behaviour of these isocyanates: the formation of the products of the dimerisation of σ^4-1,3,2-oxazaphospholines and the complete absence of the products of the imide–amide rearrangement, cycloaddition to the P=N bond, and the formation of stable phosphoranes.[89, 90, 117, 233, 352, 393] Certain aspects of the influence of fluoroalkyl groups on the reactivity of isocyanatophosphites in reactions with carbonyl compounds have been demonstrated.[345]

Thus the formation of stable σ^4-1,3,2- and σ^4-1,3,4-oxazaphospholines and **231** is characteristic of the interaction of fluoroalkyl isocyanatophosphite **229** with phenylglyoxylic and pyruvic acid esters.[117, 361] The oxazaphospholines obtained from unsubstituted isocyanatophosphites are unstable and undergo rapidly the imide–amide rearrangement.[394, 395]



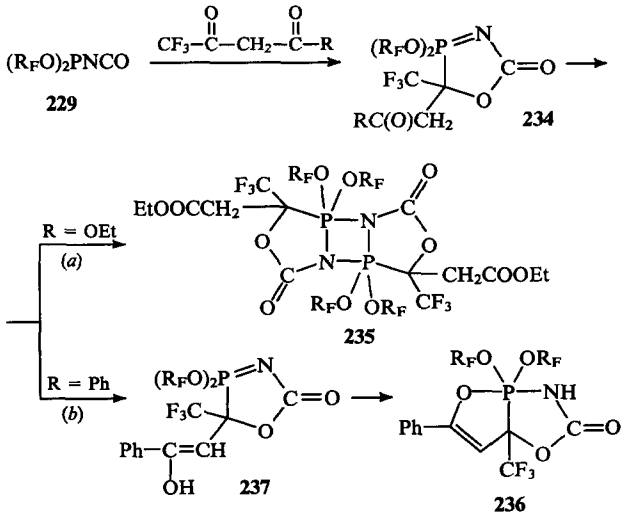
229 232 233 231 230

R_F = $CHF_2CF_2CH_2$; R^1 = Me, Ph; R^2 = Me, Et.

It has been suggested that in the case of compound **229** the phosphorus atom attacks initially the carbon atom of the carbonyl group with formation of the dipolar ion **232** which subsequently undergoes either intramolecular cyclisation with formation of the product **231** or the phosphonate–phosphate rearrangement to the dipolar ion **233** and subsequent cyclisation to the azaphospholine **230**.

The reduced reactivity of fluoroalkyl isocyanatophosphites compared with the nonfluorinated analogues in the reactions with ethyl phenylglyoxylate and dibenzoyl has been demonstrated by differential thermal analysis.[117]

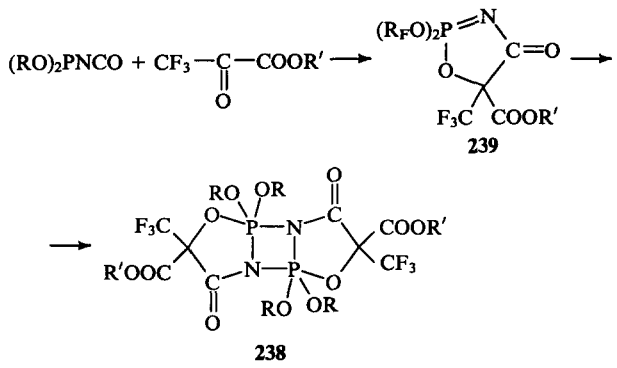
In the reactions of the isocyanatophosphite **229** with trifluoroacetoacetic ester [393, 396] and benzoyltrifluoromethylacetone,[397] the corresponding intermediate 1,3,4-oxazaphospholine **234** dimerises in the former case with formation of diphosphatricyclodecane **235** [path (*a*)], while in the latter it is converted into the bicyclooctene **236** as a result of intramolecular cyclisation via the enolic form **237** [path (*b*)].



229 234 235 237 236

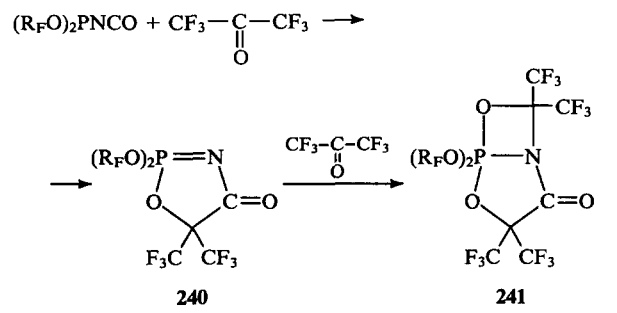
R_F = $CHF_2CF_2CH_2$.

Bis(tetrafluoropropyl) isocyanatophosphite and diphenyl isocyanatophosphite react with trifluoropyruvic acid esters to form the dimers **238** (σ^4-1,3,2-oxazaphospholines **239** are intermediates in these reactions, whereas the interaction of dimethyl isocyanatophosphite with the above esters leads to a mixture of σ^4-1,3,2- and σ^4-1,4,2oxazaphospholines.[398]



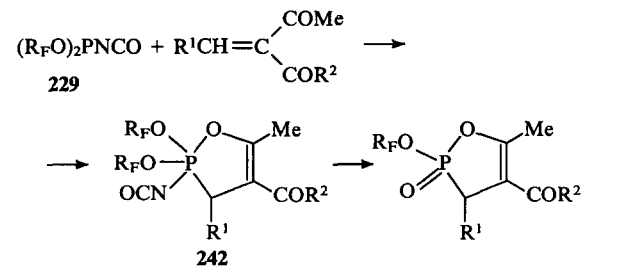
R = $CHF_2CF_2CH_2$, Ph; R′ = Me, Et.

In contrast to trifluoropyruvic acid esters, hexafluoroacetone adds to the intermediate azaphospholine **240** with formation phosphabicycloheptanes **241**.[361,398]



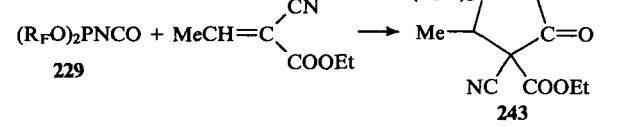
R = $CHF_2CF_2CH_2$, CF_3CH_2.

The relatively stable intermediate σ^5-1,2-oxaphospholenes **242** have been detected by ^{31}P NMR in reactions of fluoroalkyl isocyanatophosphite **229** (R_F = $CHF_2CF_2CH_2$) with alkylidene-β-dicarbonyl compounds.[399]



R^1 = Me, Ph; R^2 = Me, OEt; R_F = $CHF_2CF_2CH_2$.

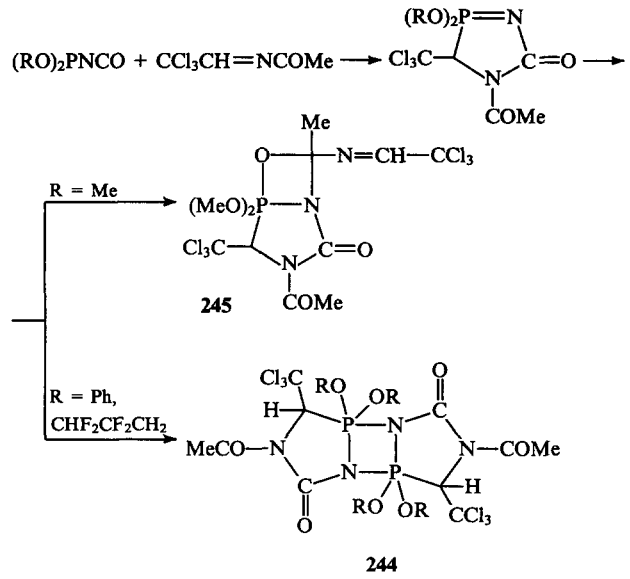
Fluorinated substituents stabilise the structure of σ^4-1,2-azaphospholine **243**, formed in the reaction of the phosphite **229** with ethylidenecyanoacetic ester.



R_F = $CHF_2CF_2CH_2$.

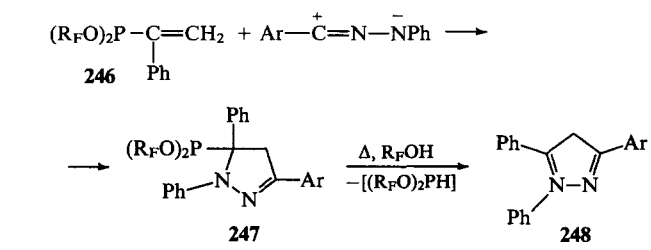
Such stabilisation is due to the high resistance of the R_F-O bond to cleavage, which occurs readily in the imide–amide rearrangement of R_H-isocyanatophosphites.

Bis(tetrafluoropropyl) and diphenyl isocyanatophosphites react with *N*-trichloroethylideneacetylamine to form substituted diphosphatricyclodecanes **244**,[400] whereas dimethyl isocyanatophosphite affords the phosphabicycloheptane **245**.



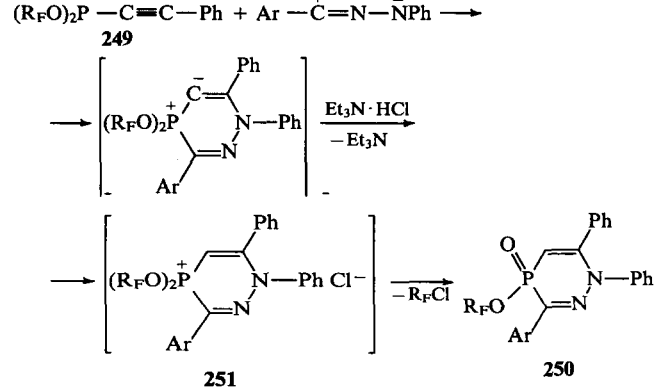
e. Fluoroalkyl-substituted alkenyl and alkynyl phosphonites

Fluoroalkyl-containing alkenyl and alkynyl phosphonites, first obtained by Erofeeva and coworkers,[401–403] have been allowed to react with nitrilimines. The reactions of the usual alkenyl phosphonites with nitrilimines proceed with participation of phosphorus as the reaction centre and lead to cyclic [3 + 3]-adducts.[404] The fluorinated phosphonite **246** undergoes [3 + 2]-cycloaddition without the incorporation of the phosphorus atom in the heterocycle. The pyrazolines **247** formed (δ_P = 187–189 ppm) are unstable and are converted on heating into pyrazole derivatives **248**.



Ar = Ph, 4-$O_2NC_6H_4$, R_F = CF_3CH_2.

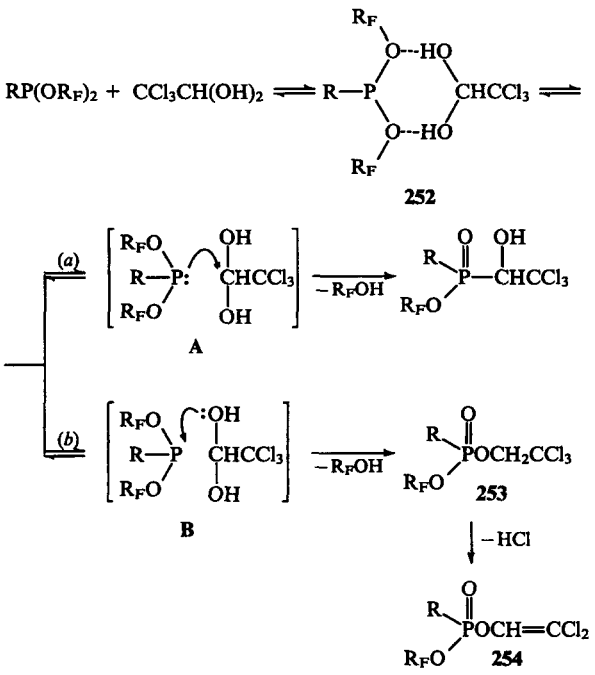
The alkynyl phosphonite **249** as well as its fluorine-free analogue undergo [3 + 3]-cycloaddition to the nitrilimine with formation of σ^4-1,2,4-diazaphosphorine derivatives **250**. It has been suggested that the reaction proceeds via the intermediate formation of the phosphonium salts **251**.[402]



R_F = CF_3CH_2.

4. Reactions of fluoroalkyl phosphites with aldehyde hydrates

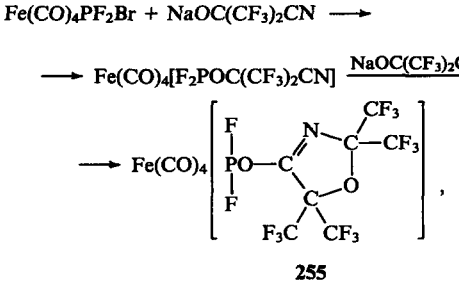
Since the reactions of fluoroalkyl phosphites with aldehyde hydrates have a number of characteristic features, they are considered in a separate section. It has been shown in a series of studies [124,405-414] that, when fluoroalkyl phosphites react with aldehyde hydrates, phosphates and α-hydroxyphosphonates are formed. For example, the hydrates $CF_3CH(OH)_2$ and $(CF_3)_2C(OH)_2$ give rise to phosphates,[405] while chloral hydrate and $H(CF_2CF_2)_nCH(OH)_2$ (n = 1, 2, 3) afford predominantly α-hydroxyphosphonates.[408,410,411] This reaction has been considered in detail in relation to chloral hydrate.[412] The authors[412] believe that the 'molecular association complex' **252** arises in the first stage, where there is either attack by the phosphorus atom on a carbon atom (**A**) or by an oxygen atom on the phosphorus atom (**B**), which lead to an α-hydroxyphosphonate and phosphate respectively.



It is noteworthy that not only the structure of the 'molecular association complex' **252** but also the path leading to the formation of the phosphate **254** [path (*b*)], presupposing the elimination of HCl from trichloroethyl phosphate **253**, give rise to doubts, since it is known that P(III) and P(V) compounds with the OCH_2CCl_3 substituent are extremely stable (for example the quasi-phosphonium salts,[46,211,415]) while the oxygen atom in the $P-O-R_F$ group is a very weak electron donor (the electron density on this atom is reduced by the electron-accepting effect of the substituent R_F).

5. Complex formation

There have been several studies [294,416-418] in which the use of fluoroalkoxy-derivatives of P(III) in the synthesis of iron and nickel complexes has been described.



$$Ni(CO)_4 + P(OCH_2CF_3)_3 \longrightarrow (CO)Ni[P(OCH_2CF_3)_3]_4,$$

$$CpFe(CO)_2I + P(OCH_2CF_3)_3 \longrightarrow CpFe[P(OCH_2CF_3)_3]I.$$

The proposed structure of complex **255** [416] was questioned [188] in view of the complexity of the IR spectra (more than seven $\nu_{C=O}$ bands), which is associated with the occurrence of side reactions and hydrolysis.

V. Conclusion

The above analysis of the reactivities and the systematic description of the syntheses and properties of fluoroalkyl derivatives of P(III) revealed, on the one hand, a whole series of characteristic features of the syntheses and chemical behaviour of fluoroalkyl phosphites, associated with the influence of fluorinated substituents on the phosphorus atom, and, on the other hand, it made it possible to obtain many new data concerning the mechanisms of known reactions, such as the interactions with the halogens, sulfur halides, halocarbonyl compounds, etc. On the whole, the introduction of fluorine atoms diminishes the nucleophilicity of the P(III) atom and lowers the rate of reaction, because in most of the cases considered nucleophilic attack by the phosphorus atom is probably the rate-determining stage of the reaction. However, the introduction of electron-accepting fluorinated substituents does not affect the rate of interaction with bromine and dialkylphosphonosulfenyl chlorides, which in our view is associated with the ready polarisability of the chlorine and bromine atoms.

The appreciable deficiency of electron density on the phosphorus atom in fluoroalkyl phosphites and the presence of a lone pair with a fairly high ionisation potential impart to these compounds the character of a biphilic reagent, capable of both nucleophilic and electrophilic attack. In certain reactions, it is actually difficult to determine the kind of species that phosphorus represents (electrophilic or nucleophilic), which from our point of view may be associated with orbital control in these reactions, where the initial step is a two-sided exchange interaction of the $n_P-\pi^*$ and σ^*-n types; here n_P is the lone pair of the phosphorus atom and σ^* is an antibonding orbital of the R_FO-P bond localised on phosphorus and constituting the LUMO, whereas π^* and n are the LUMO and the HOMO of the organic reactants.[419] The possibility of applying orbital control rules to the reactions of phosphines with alkyl halides and carbonyl compounds is discussed in a recently published communication.[420]

The study of fluoroalkyl phosphites as potential biphilic reagents in reactions with different nucleophiles and electrophiles is promising not only because there is a possibility of new varieties of the reactions and of new ways of stabilising the intermediates but also in terms of a purely practical aspect — for the very mild phosphorylation of natural alcohols and for the synthesis of new types of phosphorylating agents and phosphorus derivatives with diverse useful properties.[55]

One of the most important and interesting differences between fluoroalkyl phosphites and the R_H derivatives is the reduced rate at which the fluoroalkyl group is split off from the phosphonium centre and the stabilisation of intermediate structures of the phosphorane and phosphonium types. The increase in the stability of quasi-phosphonium compounds is due to the stability of the $O-R_F$ bond. In certain cases, the R_F-O bond is not cleaved at all, although for the R_H derivatives of P(III) the dealkylation stage takes place fairly readily and on the whole obeys the rules governing nucleophilic substitution at a carbon atom via an S_N2 mechanism (the Perkow and Arbuzov reactions and the nonclassical variants of the latter). In this sense, the weakening of the nucleophilic properties of the P(III) atom is more significant than the increase in the electrophilicity of the CH_2 carbon atom in the R_FCH_2O fragment.

The appearance of new paths in the interaction of P(III) derivatives with halogen-containing reagents is a consequence of the retardation or complete suppression of the elimination of the

fluoroalkyl group from phosphonium intermediates. These include reactions with retention of the coordination on the phosphorus atom, the disproportionation of haloquasi-phosphonium or phosphorane intermediates in the presence of the initial P(III) derivatives, and the very ready conversion of P(III) compounds into P(V) compounds. In the reactions considered, R_H derivatives of P(III) are as a rule converted into compounds with a phosphoryl group.

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