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Phosphorus-containing nucleophiles in reactions with polyfluorinated organic compounds

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Abstract. The review presents a compilation of new experimental data on the reactions of phosphorus-containing nucleophiles [triphenylphosphine, trialkylphosphines, trialkyl phosphites, phosphorus tris(diethylamide), etc.] with perfluorinated olefins and aromatic and heterocyclic compounds, leading to substances both with and without a phosphorus atom. It is shown that the interaction of phosphorus tris(diethylamide) and trialkylphosphines with organic polyfluoro-compounds and perfluoroolefins leads to the formation of phosphoranes, the decomposition of which is accompanied by the generation of aryl and alkenyl anions. The reactions of these anions with C-electrophiles and compounds containing mobile halogen atoms are examined. In addition, the pathways in the Arbuzov reaction involving a series of unsaturated perfluorinated compounds are analysed. Possible applications of these reactions in organic synthesis are demonstrated. The bibliography includes 120 references.

I. Introduction

The interest shown by investigators in the chemistry of organophosphorus compounds can be explained by their high reactivity and a unique set of properties, which make these substances valuable objects for theoretical research and impart to them practical importance.[1] However, organophosphorus compounds containing polyfluorinated alkyl and aryl substituents began to be investigated only recently. Bearing in mind the mutual influence of the fluorine and phosphorus atoms on the properties of the entire molecule, one can postulate that such compounds have many interesting properties.

The methods of synthesis of organophosphorus compounds are based on reactions involving the nucleophilic substitution of fluorine atoms in unsaturated organofluorine compounds on treatment with P-nucleophiles (compounds of trivalent phosphorus). Three types of reactions are then possible:

(1) substitution reactions without change in the valence of the phosphorus atom (one of the substituents at the phosphorus atom undergoes the usual exchange for a perfluorinated substituent);

(2) substitution reactions accompanied by the oxidation of the phosphorus atom (they lead to the formation of phosphonium salts, phosphoranes, and phosphinic and phosphonic acid esters in which the phosphorus atom is in pentacoordinate and tetracoordinate states);

(3) reactions in which compounds of tricoordinate phosphorus play the role of a synthon, the final product of such reactions being compounds with a new C–C bond and without a phosphorus atom.

Whereas the reactions of the first two types have long been known and have been thoroughly investigated for a wide range of P-nucleophiles, those of the third type are in fact characteristic of the polyfluorinated compounds. They have come to constitute one of the methods of synthetic organic chemistry used to introduce various perfluorocarbon groups into the molecule. One can now note that these procedures have a great future.

The introduction of a fluorine atom into organophosphorus compounds leads to extensive possibilities both in the synthesis of biologically active compounds and in the determination of the relation between the chemical structure and properties of compounds of this class. At the present time, the stage involving the accumulation of experimental data on the synthesis of compounds of this class may be regarded as completed and attention should now be concentrated on the study of their structures, reactivities, and reaction mechanisms. A series of experimental data on the reactions of triethyl phosphite with perfluoroisobutene and aromatic polyfluoro-compounds have been compiled in a number of reviews.[2–4] On the other hand, inadequate attention has been devoted in the literature to questions of the reactivity of other P-nucleophiles in reactions with organic polyfluoro-compounds. At the same time, the biological activity and unique properties of materials based on fluorine-containing organophosphorus compounds have created a basis for their practical use, so that systematic treatment and analysis of the accumulated extensive data are urgently required and the publication of a review on this topic should stimulate further research on these lines.

The arrangement of the data is based on the nature of the P-nucleophile because the latter actually introduces significant differences into the behaviour of perfluorinated compounds and determines the nature of the products formed.

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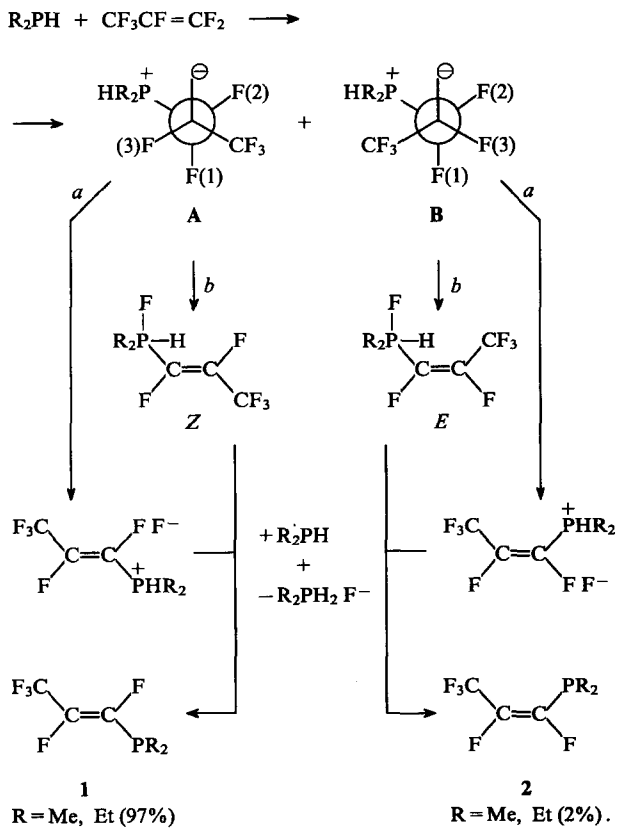
II. Reactions of phosphorus-containing nucleophiles with unsaturated perfluorinated compounds

Nucleophilic reactions of derivatives of trivalent phosphorus are some of the most important and varied in the chemistry of organophosphorus compounds. One of the most widely used is the reaction of trialkyl phosphites and dialkyl phosphonites with alkyl halides and other alkylating agents, accompanied by the formation of phosphonic and phosphinic acid esters.[5] By virtue of the high electronegativity of the fluorine atom, its introduction into an organic molecule influences significantly the charge characteristics of the carbon atom, increasing its positive charge.[3] Nucleophilic substitution reactions become characteristic of compounds of this type and the nature of the products formed depends significantly on the structure of the initial compound.

1. Reactions with trialkyl-, dialkyl-, and triphenylphosphines

Trivalent phosphorus compounds, which are highly nucleophilic, are known to react readily with substances incorporating electronegative halogen, sulphur, and oxygen atoms. In conformity with their nucleophilicity, phosphines can be arranged in the following sequence in terms of their reactivities: $PPh_3 > Ph_2POEt > PhP(OEt)_2 > P(OEt)_3$. When halogen-containing compounds are acted upon by phosphines and phosphites, compounds of two types may be formed, in which the phosphorus atom either retains its valence (new phosphines and phosphites) or its valence increases (for example, with formation of phosphoranes). We shall consider reactions occurring with retention of the valence of the phosphorus atom.

It has been shown[6,7] that hexafluoropropene reacts with dialkylphosphines R_2PH, affording perfluoropropenyl derivatives and phosphonium fluoride $R_2P^+H_2F^-$. The reaction proceeds via the intermediate formation of two 1,3-betaines as a result of the nucleophilic attack by the phosphorus atom on the C(1) atom. The intermediate **A** is more favourable on energy grounds than **B**, because the steric hindrance generated by the bulky CF_3 and PR_2H groups is smaller in the latter.



The intermediates **A** and **B** can be stabilised in two ways: either as a result of the migration of the F(1) ion (pathway *a*) in the *trans*-position with respect to the electron pair of the C(2) atom (the quasi-phosphonium ions formed are deprotonated, affording the corresponding phosphines) or as a result of the 1,2-migration of the fluorine atom to the phosphorus atom (pathway *b*) [the (*Z*)- and (*E*)-fluorophosphoranes formed in this process are subsequently dehydrofluorinated].

In the reaction of tri(*tert*-butyl)phosphine with hexafluoropropene, the fluorine atom at the C(1) atom is substituted and the phosphine **3**, isobutene, and tri(*tert*-butyl)phosphonium fluoride are formed. The last two compounds are obtained from the initial phosphine and fluorotrimethylmethane — one of the products of the reaction of the perfluoroolefin with phosphine.

In contrast to this, in the reaction of phenylphosphine with

$$CF_3CF=CF_2 + P(Bu^t)_3 \longrightarrow [CF_3CF=CF-P(Bu^t)_3]^+F^- \xrightarrow{P(Bu^t)_3} CF_3CF=CFP(Bu^t)_2 + Me_2C=CH_2 + (Bu^t)_3\overset{+}{P}HF^-.$$

3

tetrafluoroethylene, nucleophilic addition to the double bond takes place with formation of phenyltetrafluoroethylphosphine **4**.[8]

In the presence of an excess of tetrafluoroethylene, the disubstituted phosphine $PhP(CF_2CHF_2)_2$ is formed as well as compound **4**. In the presence of an inhibitor of the polymerisation of tetrafluoroethylene and for the 1 : 1 reactant ratio, the yield of compound **4** is 84%. The adduct resulting from the addition of phenylphosphine to 1,1-difluoroethylene is formed in approximately the same yield.

$$CF_2=CF_2 + PhPH_2 \xrightarrow{150^\circ C} PhPHCF_2CHF_2.$$

4

Diethylphosphine reacts with perfluorobut-2-yne at −78 °C with formation of the *trans*-isomer **5**.[9]

$$CF_3C\equiv CCF_3 + Et_2PH \longrightarrow Et_2P(CF_3)C=CHCF_3$$

5 (45%).

According to Fild et al.,[10] the reaction of CF_2Br_2 with organylbis(trimethylsilyl)phosphine $RP(SiMe_3)_2$ and diorganyl(trimethylsilyl)phosphine R_2PSiMe_3 (R = Ph, Bu^t, Me) leads to the formation of the diphosphetan **6** and R_2PCF_2Br respectively.

$$RP(SiMe_3)_2 + CF_2Br_2 \longrightarrow \text{R—P(CF}_2\text{)P—R};$$

6

$$R_2PSiMe_3 + CF_2Br_2 \longrightarrow R_2PCF_2Br.$$

The structure of compound **6** was confirmed by X-ray diffraction analysis and ^{19}F and ^{31}P NMR spectroscopy. It is suggested that the diphosphetan **6** is formed via an intermediate phosphaalkene as a result of its subsequent thermal decomposition.

The reaction of diphenyltrimethylsilylphosphine with CF_3I at 20 °C leads to the formation of diphenyltrifluoromethylphosphine in 78% yield.[11] The same compound is obtained in a satisfactory yield by the reaction of CF_3I with triphenylphosphine at 185–200 °C.[12]

Table 1. Fluorophosphoranes obtained by the reaction of tributylphosphine with perfluoroolefins.[15]

Olefin	Reaction product	Yield (%)	*E*/*Z*
$CF_3(CF_2)_2CF=CF_2$	$CF_3(CF_2)_2CF=CFPF(Bu^n)_3$	81	100 (*Z*)
$CF_3(CF_2)_4CF=CF_2$	$CF_3(CF_2)_4CF=CFPF(Bu^n)_3$	83	100 (*Z*)
$CF_3CPh=CF_2$	$CF_3CPh=CFPF(Bu^n)_3$	84	91/9
$CF_3CF_2CPh=CF_2$	$CF_3CF_2CPh=CFPF(Bu^n)_3$	87	92/8

Trimethylphosphine reacts with trifluoroiodomethane to form dimethyltrifluoromethylphosphine and tetramethylphosphonium iodide.[13, 14]

$$Me_3P + ICF_3 \longrightarrow [Me_3PCF_3]^+I^- \xrightarrow{Me_3P} Me_2PCF_3 + [Me_4P]^+I^-.$$

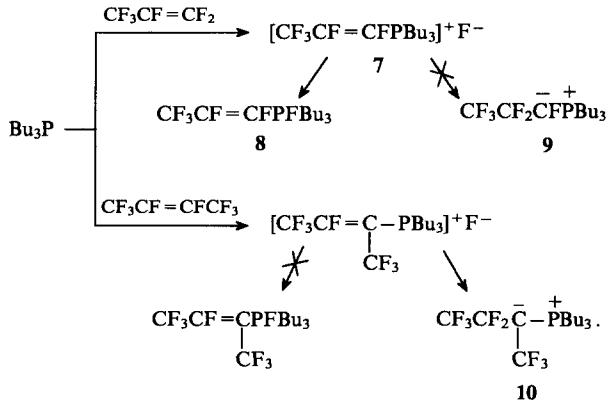
Reactions of another type, specific to perfluorinated organic compounds, involve the formation of fluorophosphoranes. Thus it has been shown[15] that tributyl- and trimethyl-perfluoropropenylfluorophosphoranes are formed in the reaction of hexafluoropropene with tributyl- and trimethylphosphines respectively.

$$CF_3CF=CF_2 + R_3P \longrightarrow CF_3CF=CFPFR_3$$

R = Me, Bu^n.

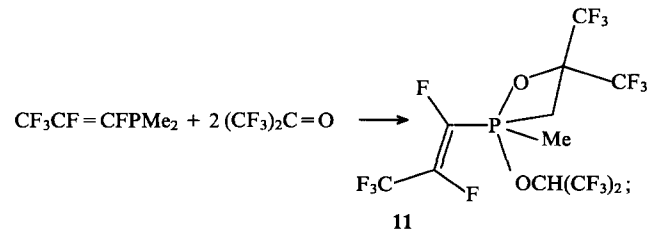
Other perfluoroalk-1-enes react similarly (Table 1), the *trans*-isomers being mainly formed (Scheme 1).

Scheme 1

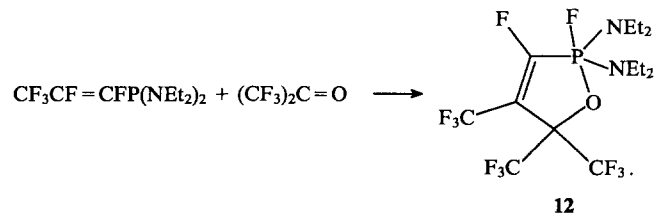


The primary step in these reactions involves the attack by the nucleophilic phosphorus atom on a carbon atom, leading to the quasi-phosphonium salt **7**, from which compound **8** is formed as a result of the 1,2-migration of the fluoride anion to the phosphorus atom. The phosphorus ylide **9** is not obtained in this reaction. On the other hand, in the case of perfluorobut-2-ene the main reaction product is believed[15] to be in fact the ylide **10** of this kind, while the corresponding phosphorane is not formed. The structure of compound **10** was confirmed by ^{31}P and ^{19}F NMR spectroscopy.

A series of phosphines react with carbonyl compounds. Thus it has been shown[6, 7] that dimethylperfluoropropenylphosphine and bis(diethylamino)perfluoropropenylphosphine react with hexafluoroacetone, affording cyclic phosphorus compounds: 1,2-oxaphosphetan **11** and 1,2-oxaphospholen **12** respectively.

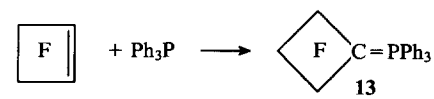


11



12

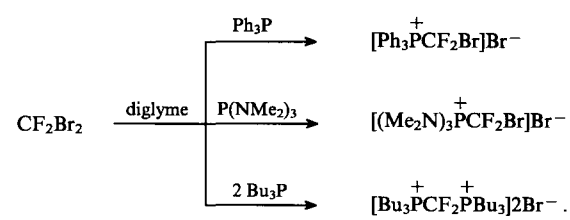
By allowing triphenylphosphine to react with perfluorocyclobutene, Stochel et al.[16] obtained, instead of a phosphorus ylide, 2,2,3,3,4,4-hexafluoro(triphenylphosphoranylidene)cyclobutane **13**, the structure of which was later confirmed by X-ray diffraction.[17]



13

Perfluorobutadiene also reacts with triphenylphosphine to form 1 : 1 adducts, which consist of relatively unstable cyclic phosphoranes.

When the polyfluoroolefin molecule contains other halogen atoms as well as those of fluorine, stable phosphonium salts are formed. For example, the reaction of dibromodifluoromethane with triphenylphosphine[18] or tris(dimethylamino)phosphine[19] affords phosphonium salts in quantitative yields. A diphosphonium salt is formed in the presence of an excess of the phosphine. The reaction is of the S_N2 type.



2. The Arbuzov reactions of perfluorinated compounds

Trialkyl phosphites induce the dehalogenation of certain vicinal dihalo-derivatives.[21]

$$(EtO)_3P + BrCF_2CFBrCl \longrightarrow CF_2=CFCl + (EtO)_2P(O)Br + EtBr.$$

Table 2. Reactions of haloperfluoroalkanes with triethyl phosphite.[20]

Initial compound	Reaction product	Yield (%)
$I(CF_2)_6CFClCF_2Cl$	$I(CF_2)_6CF=CF_2$,	23,
	$I(CF_2)_6CF=CFP(O)(OEt)_2$	50
$I(CF_2)_4CFClCF_2Cl$	$I(CF_2)_4CF=CF_2$,	38,
	$I(CF_2)_4CF=CFP(O)(OEt)_2$	46
$I(CF_2)_2CFClCF_2Cl$	$I(CF_2)_2CF=CFP(O)(OEt)_2$	43.5
$ClCF_2CFCl(CF_2)_4CFClCF_2Cl$	$(EtO)_2(O)PCF=CF(CF_2)_4CF=CFP(O)(OEt)_2$	17

When trialkyl phosphites are heated with $Cl(CF_2CFCl)_nCl$, olefins are formed.[22] Having observed this property of trialkyl phosphites, the authors suggest that the reaction proceeds via the formation of the product **14** of the usual Arbuzov rearrangement, which subsequently decomposes, affording diethyl phosphorochloridate and a polyfluoroolefin.

$$CFCl_2CF_2CFClCF_2Cl + P(OEt)_3 \longrightarrow$$

$$\longrightarrow \underset{\mathbf{14}}{CFCl_2CF_2CFClCF_2P(O)(OEt)_2} \longrightarrow$$

$$\longrightarrow CFCl_2CF_2CF=CF_2 + ClP(O)(OEt)_2.$$

It has been shown[20, 23, 24] that the reactions of triethyl phosphite with α,β-dichloro-ω-iodoperfluoroalkanes does indeed involve dehalogenation, but the products are a mixture of ω-iodoperfluoroalk-1-enes and diethyl esters of ω-iodoper-fluoroalk-1-enylphosphonic acids (Table 2).

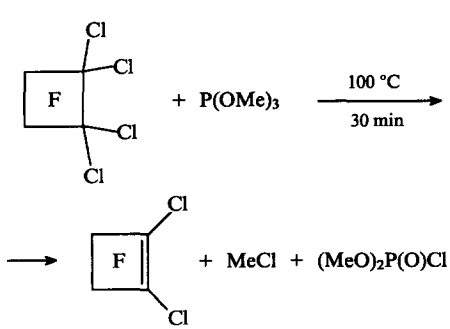
$$\underset{\substack{|\\X}}{\overset{|}{RCF-CY_2}}\ \xrightarrow[[-XCl]]{P(OEt)_3}\ [RCF=CY_2]\ \xrightarrow[-EtY]{P(OEt)_3}$$

$$\longrightarrow RCF=CYP(O)(OEt)_2$$

X = F, Y = Cl, R = $CFCl_2$;
X = Cl, Y = F, R = $I(CF_2)_2$, $I(CF_2)_4$, $I(CF_2)_6$.

Knunyants and Pervova[23] suggest a different mechanism of the dehalogenation process, consisting in the initial splitting off of two halogen atoms in vicinal positions with formation of diethyl phosphorochloridate and ω-iodoperfluoroalk-1-ene, which interacts with triethyl phosphite, affording the product of the Arbuzov rearrangement. Only in the reaction of triethyl phosphite with dichloroiodotrifluoroethane is the halogen split off without the formation of the corresponding phosphonates. Chlorotrifluoroethylene is then obtained in a quantitative yield.

The results of a study[25] in which it was shown that the dehalogenation of polyhalogenated cyclobutanes by trimethyl phosphite leads to polyfluorocyclobutenes are consistent with these ideas.



The defluorination of perfluoro-*N*-fluoropiperidine by triphenylphosphine, leading to perfluoro-1-azacyclohexene, was described previously.[26]

In the reaction of chlorofluoroalkanes with triethyl phosphite, attack by the chlorine atom on the phosphite molecule results in the intermediate formation of the phosphonium salt **16**.[27]

$$(EtO)_3P + CCl_3(CF_2)_nCl \longrightarrow$$

$$\longrightarrow \underset{\mathbf{16}}{[(EtO)_3PCl]^+[CCl_2(CF_2)_nCl]^-} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{17}}{CCl_2=CF(CF_2)_{n-1}Cl} + \underset{\mathbf{18}}{EtCCl_2(CF_2)_nCl} +$$

$$+ \underset{\mathbf{19}}{(EtO)_2P(O)CCl=CF(CF_2)_{n-1}Cl} + (EtO)_2P(O)Cl.$$

The further reaction of the salt **16** leads to the dehalogenation and alkylation products **17** and **18** respectively. Furthermore, the Arbuzov reaction with participation of the olefin **17** affords compound **19**.

Certain perfluorohaloalkanes also enter into the Arbuzov reaction. In the presence of bromine as well as fluorine atoms in the alkyl group, the Arbuzov reaction then proceeds with participation of the bromine atoms (Table 3).[28]

$$CFXY_2 + P(OR)_3 \xrightarrow[25-50\ °C,\ 24\ h]{\text{triglyme}} (RO)_2(O)PCFXY + RY.$$

On the other hand, the compounds CF_3Cl, CF_3I, and $CFCl_3$ are inert under the conditions of the Arbuzov reaction.[29, 30]

The Arbuzov reaction with participation of polyfluorinated alkyl halides can be carried out under UV irradiation. Thus the reaction of perfluoroalkyl iodides with triethyl phosphite under UV irradiation,[31] leading to diethyl perfluoroalkylphosphonate **20**, has been achieved. The reaction probably proceeds in accordance with the following mechanism:

$$CF_3I \xrightarrow{h\nu} \dot{C}F_3 + \dot{I},$$

$$\dot{C}F_3 + (EtO)_3P \longrightarrow CF_3\dot{P}(OEt)_3 \xrightarrow{CF_3I}$$

$$\longrightarrow \underset{\mathbf{21}}{[CF_3P(OEt)_3]^+I^-} + \dot{C}F_3;$$

$$[CF_3P(OEt)_3]^+I^- \longrightarrow \underset{\mathbf{20}}{CF_3P(O)(OEt)_2} + EtI.$$

Table 3. Reactions of dibromodifluoromethane and tribromofluoromethane with trialkyl phosphites $P(OR)_3$ (data of Burton and Flynn[28]).

$CFXY^2$	R	Solvent	Yield (%)
CF_2Br_2	Me	triglyme	55
	Et	diethyl ether	95
	Et	triglyme	55
	Bu^n	diethyl ether	65
	Pr^i	triglyme	42
$CFBr^3$	Et	diethyl ether	78
	Et	triglyme	60
	Pr^i	diethyl ether	22

The trifluoromethyl radical, formed on dissociation of trifluoromethyl iodide, attacks a molecule of triethyl phosphite, giving rise to a phosphoranyl radical. The latter is oxidised by trifluoromethyl iodide to the quasi-phosphonium salt **21**, which decomposes with liberation of ethyl iodide and diethyl trifluoromethylphosphonate **20**. The reaction is carried out in an excess of trifluoromethyl iodide over a period of 10 h, the yield of the phosphonate being 51%.

Pentafluoroiodobenzene reacts with triethyl phosphite at the C–I bond also only on exposure to UV radiation (350 nm), whereupon diethyl pentafluorophenylphosphonate **22** is formed.

$$C_6F_5I + (EtO)_3P \longrightarrow \underset{\mathbf{22}\ (32\%)}{C_6F_5P(O)(OEt)_2} + EtI.$$

The reaction of dichlorotrifluoroethyl hexafluoroiodopropyl ether **23** with triethyl phosphite in the presence of *tert*-butyl peroxide takes place similarly.[32] The trivalent phosphorus derivative **24** is formed initially and is then oxidised to the phosphonate **25**.

$$\underset{\mathbf{23}}{CF_2ClCFClO(CF_2)_3I} + P(OEt)_3 \xrightarrow{(Bu^tO)_2} \underset{\mathbf{24}}{CF_2ClCFClO(CF_2)_3P(OEt)_2} \xrightarrow{Bu^tOOH} \underset{\mathbf{25}}{CF_2ClCFClO(CF_2)_3P(O)(OEt)_2}.$$

It is seen from these examples that an advantage of photochemical initiation of the Arbuzov reaction is the possibility of synthesising fluorine-containing phosphonates from available reagents in one stage.

The CH_2Br group and not CF_2Br participates in the reaction of the bromo-derivative **26** with triethyl phosphite, although the positive charge on the carbon atom of the CF_2Br group is higher than that on the carbon atom of CH_2Br.[33] Under these conditions, the (*Z*)-isomer of diethyl 4-bromo-3,4,4-trifluorobut-2-enylphosphonate **27** is formed. Steric factors probably play a role in this instance.

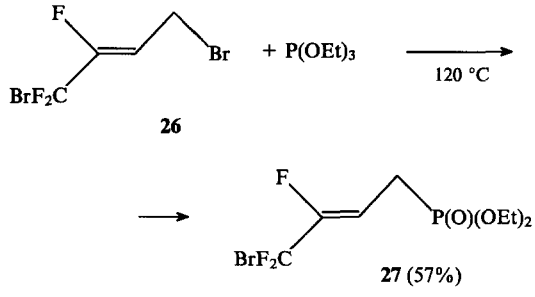


Table 4. Reactions of polyfluoroolefins with trialkyl phosphites.[36]

Fluorooelfin	Trialkyl phosphite	Reaction product	Yield (%)
$CF_2=CFCl$	$(EtO)_3P$	$CFCl=CFP(O)(OEt)_2$	10
$CF_2=CF_2$	$(Pr^iO)_3P$	$CF_2=CFP(O)(OPr^i)_2$	26
$CF_3CF=CF_2$	$(Pr^iO)_3P$	$CF_3CF=CFP(O)(OPr^i)_2$	48
$(CF_3)_2C=CF_2$	$(BuO)_3P$	$(CF_3)_2C=CFP(O)(OBu)_2$	35
$CF_3CF=CF_2$	$MeP(OPr^i)_2$	$CF_3CF=CFP(O)(OPr^i)$ | Me	51
$(CF_3)_2C=CF_2$	$(Pr^iO)_3P$	$(CF_3)_2C=CFP(O)(OPr^i)_2$	50

In contrast to perfluoroalkyl halides, perfluoroolefins react readily with trialkyl phosphites to form the esters of perfluoroalkenylphosphonic acids (Table 4).[34–36] Thus perfluoroisobutene reacts vigorously with triethyl phosphite even at −35 to 30 °C, affording the fluorophosphorane **28**, which is stable under the usual conditions. The phosphorane decomposes at 120 °C with formation of diethyl perfluoroalkenylphosphonate **29**.[37]

$$(CF_3)_2C=CF_2 + P(OEt)_3 \xrightarrow{-35\ ^\circ C} \underset{\mathbf{28}}{(CF_3)_2C=CFPF(OEt)_3} \xrightarrow{120\ ^\circ C} \underset{\mathbf{29}}{(CF_3)_2C=CFP(O)(OEt)_2}.$$

Perfluoroolefins behave similarly.[34–39]

The interaction of perfluoroolefins with triethyl phosphite takes place in two stages: the first stage of the reaction involves the formation of triethoxyperfluoroalkenylfluorophosphorane **28**, which then decomposes under more severe conditions with formation of the final products of the Arbuzov rearrangement—compound **29**. In the reaction of hexafluoropropene with triethyl phosphite, the intermediate fluorophosphorane cannot be detected, but the final product is diethyl pentafluoropropenylphosphonate.[37] The decomposition of the intermediate fluorophosphorane takes place via two pathways and leads, on the one hand, to ethyl fluoride and the full ester of perfluoroalkenylphosphonic acid and, on the other, to the fluoride of the acid ester of perfluoroalkenylphosphonic acid and diethyl ether.[37] This constitutes the specificity of the Arbuzov reaction for unsaturated perfluorinated compounds.

$$\underset{\mathbf{28}}{(CF_3)_2C=CFPF(OEt)_3} \longrightarrow \begin{cases} (CF_3)_2C=CFP(O)(OEt)_2 + EtF \\ (CF_3)_2C=CFPF(O)(OEt) + Et_2O. \end{cases}$$

The reactivity of perfluoroolefins in the reaction with triethyl phosphite diminishes in the following sequence:

$$\boxed{F} > (CF_3)_2C=CF_2 > CF_3CF=CF_2 \approx CF_2=CF_2.$$

When one fluorine atom is replaced in perfluoroethylene by another halogen atom, a fluorine and not a chlorine[36] or iodine[40] atom participates in the reaction with phosphites.

Thus the reaction of trifluoroiodoethylene with tris(isopropyl) phosphite[40] affords the *trans*-di(isopropyl) ester of phosphonic acid **30**.

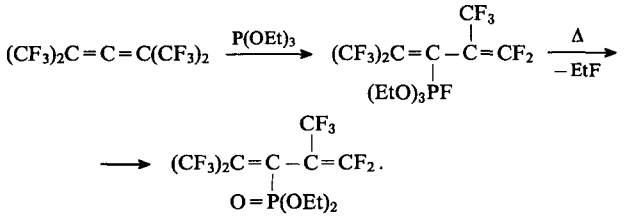
$$CF_2=CFI + (Pr^iO)_3P \longrightarrow \begin{cases} \xrightarrow[60\ h]{80^\circ C} \underset{\mathbf{30}\ (67\%)}{CFI=CFP(O)(OPr^i)_2} \\ \xrightarrow[80\ h]{100^\circ C} \underset{\mathbf{31}}{(Pr^iO)_2(O)P\diagdown C=C\diagup F \quad (F,\ P(O)(OPr^i)_2)} \end{cases}$$

However, when an excess of tri(isopropyl) phosphite is used, the iodine atom is also substituted with formation of the corresponding ester of the diphosphonic acid **31**. The reaction of trifluoroiodoethylene with other trialkyl phosphites (R = Pr^i, Et, Me) takes place similarly. We may note that in the case of bromotrifluoro- and chlorotrifluoro-ethylenes, the esters of phosphonic acids are obtained in very low yields. Thus the presence of an iodine atom at the double bond activates the fluorine atom involved in the reaction with trialkyl phosphites.

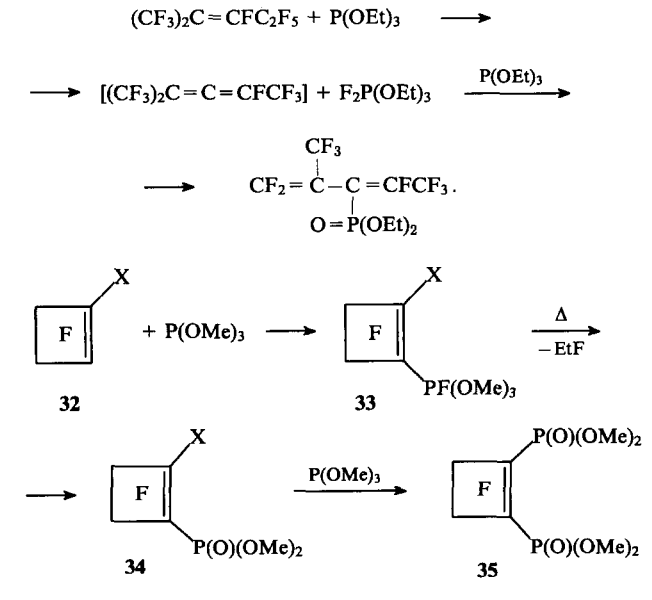
The interaction of pentafluoroazapropene $CF_3N=CF_2$ with triethyl phosphite leads to the formation of the stable trialkoxytetrafluoroazapropenylfluorophosphorane $CF_3N=CFPF(OR)_3$.[41]

The bisphosphonate $(RO)_2P(O)CF=CFP(O)(OR)_2$ **32**, where R = Et or Pr^i, is formed when tetrafluoroethylene is treated with $(RO)_2POSiMe_3$.[42]

The reaction of triethyl phosphite with allenes results in the formation of the corresponding perfluorinated 1,3-dienylphosphonic acid esters.[43] Thus the corresponding 1,3-dien-2-ylphosphonate was obtained from tetrakis(trifluoromethyl)allene and triethyl phosphite probably as a result of the occurrence of a reaction of the S_N2 type.



The synthesis of diethyl 2-trifluoromethylperfluoropenta-1,3-dien-3-yl-phosphonate from perfluoro-2-methylpent-2-ene and triethyl phosphite has been described[44] from the standpoint of the initial formation of tris(trifluoromethyl)allene as a result of the defluorination of the initial perfluoroolefin by triethyl phosphite and its subsequent reaction with the latter.



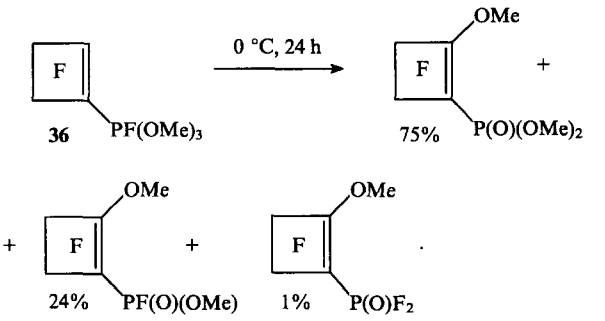
X = F, Cl, Br, I.

X	Yield of **33** (%)	Yield of **34** (%)
F	43	–
Cl	100	60
Br	100	49
I	100	45

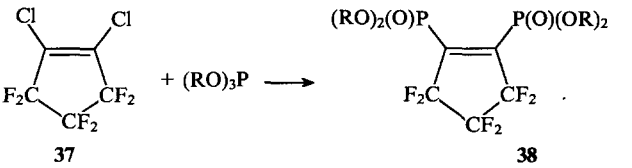
Perfluorocycloalkenes can also be introduced into the Arbuzov reaction. Thus it has been shown[45, 46] that 3,3,4,4-tetrafluoro-1-halocyclobut-1-enyl-2-(trimethoxy)fluorophosphorane is formed as a result of the exothermic reaction of 1-halopentafluorocyclobut-1-ene **32** with trimethyl phosphite.

The phosphorane **33** is stable at 0 °C for several days. Its controlled decomposition leads to dimethyl cyclobutenylphosphonate **34**. On treatment of the ester **34** with an excess of trimethyl phosphite, the tetramethyl ester of 3,3,4,4-tetrafluorocyclobutenylenediphosphonic acid **35** is formed.

On the other hand, the decomposition of 1,3,3,4,4-pentafluorocyclobutenyl-(trimethoxy)fluorophosphorane **36** leads to a mixture of tetrafluorocyclobutenes, in which the fluorine atom at the multiple bond is replaced by the methoxy-group.

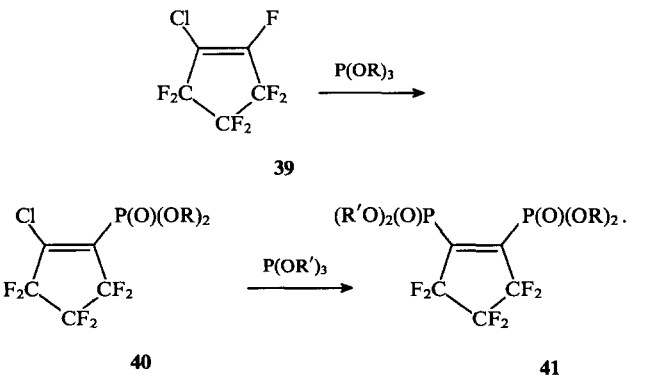


The reaction between 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene **37** and trialkyl phosphite affords tetraalkyl hexafluorocyclopentenylenediphosphonates **38**.[47]



R	Me	Et	Bu	$CH_2CH=CH_2$	Ph
Yield of **38** (%)	40	74	93	92	75

In the presence of two different halogen atoms at the double bond, for example of a chlorine and a fluorine atom, the reaction involves the C–F bond,[48] while in the presence of an excess of



R	Yield of **40** (%)	R	R′	Yield of **41** (%)
Et	33	Et	Et	50
Bu	88	Bu	Et	72.5
Me	38	CH_2CF_3	CH_2CF_3	51

trialkyl phosphite both atoms are substituted.[49] Thus the dialkyl ester of 2-chloro-3,3,4,4,5,5-hexafluorocyclopent-1-enylphosphonic acid **40** is obtained in the reaction of 1-chloro-2,3,3,4,4,5,5-heptafluorocyclopent-1-ene **39** with trialkyl phosphites, while in the presence of an excess of the phosphite the product is tetraalkyl 3,3,4,4,5,5-hexafluorocyclopent-1-en-1,2-ylenediphosphonate **41**.

It has been shown[50] that 2-chloro-1-ethylthiofluorocyclopent-1-ene is converted into diethyl 2-ethylthio-3,3,4,4,5,5-hexafluorocyclopent-1-enylphosphonate (yield 63.7%).

Arbuzov type reactions can be achieved also by treating hexafluoropropene with ethyl and isopropyl methylphosphonites.[51] The yield of the corresponding phosphinate esters **42** was 45% to 55%. The replacement of phosphites by phosphonites makes it possible to carry out the reactions under milder conditions.

$$CF_2{=}CFCF_3 + MeP(OR)_2 \xrightarrow[8-10\ h]{100-120\ ^\circ C} \underset{\textbf{42}}{MeP(O)(CF{=}CFCF_3)OR} + R{-}F$$

R = Et, Pr^i.

Knunyants et al.[52] introduced the chlorides of dialkylphosphinous, dialkylphosphorous, and *N,N,N',N'*-tetraalkylphosphorodiamidous acids into reactions with perfluoroolefins and, depending on the substituents and the reaction conditions, obtained different products of the reactions of the intermediate perfluoroisobutylfluorophosphoranes **43**, in particular the ester of perfluoroisobutenylphosphinic acid **44**.

$$(CF_3)_2C{=}CF_2 + X{-}PCl{-}Y \longrightarrow \underset{\textbf{43}}{[(CF_3)_2C{=}CFPFClXY]} \xrightarrow[X = Y = OEt]{\Delta} (CF_3)_2C{=}CFPF(O)(OEt)$$

44

X = Y = Et, EtO, Me_2N, Et_2N.

The reactivities of the chlorides of the above acids in relation to perfluoroisobutene proved to be lower than the reactivity of their full esters. Thus, whereas perfluoroisobutene reacts with triethyl phosphite at −30 °C, the acid chlorides react with the above olefin only at an elevated temperature, except for *N,N,N',N'*-tetraethylphosphorodiamidite, which reacts at room temperature. Knunyants et al.[52] derived the following reactivity series for the above reagents:

$$(Et_2N)_2PCl > (Me_2N)_2PCl > (EtO)_2PCl > Et_2PCl.$$

They explain the above decrease in reactivity by the decrease in the capacity of the substituents X for $p{-}d$ conjugation with the phosphorus atom. In the last compound, there is no $p{-}d$ conjugation.

It has been shown[6] that the reactions of the phosphites $(R^2O)_2POSiMe_3$ (R^2 = Et, $SiMe_3$) with the perfluoroolefins $R^1CF{=}CF_2$ ($R^1 = CF_3$, SF_5) give rise to fluorotrimethylsilane and the fluoroalkenylphosphonates **45** and **46** in conformity with the Arbuzov rule (Scheme 2). It is suggested that the reaction follows the pathway described above for perfluoroisobutene. In the case of $F_5SCF{=}CF_2$, the (*E*)-isomer **45** formed exclusively, whereas in the case of $F_3CCF{=}CF_2$ the product with the *cis*-configuration **46** is obtained in very small amounts, which indicates the occurrence of slight interaction between the substituents Et and $SiMe_3$, on the one hand, and the fluorine atoms of the CF_3 group, on the other.

It has been shown[53-55] that the derivatives of perfluoromethacrylic acid **47**, which is no less reactive than perfluoroisobutene, react with trialkyl phosphites to form the fluorophosphoranes **48**.

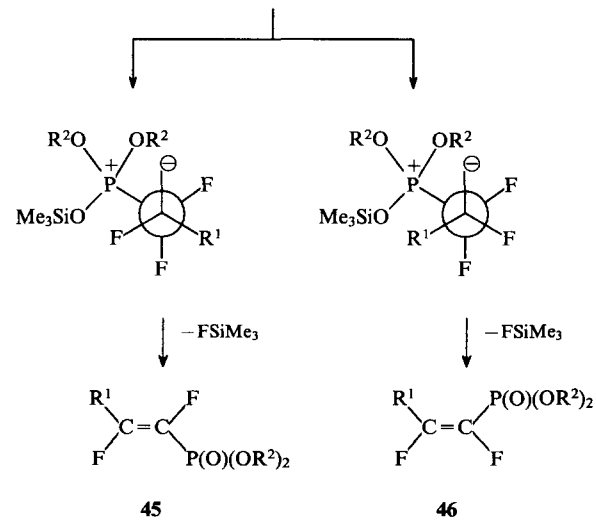
$$(RO)_3P + CF_2{=}C(CF_3){-}C(O)X \longrightarrow \underset{\textbf{48}}{(RO)_3PFCF{=}C(CF_3){-}C(O)X}$$

47

R = Me, Et; X = OMe, OEt, NMe_2.

Scheme 2

$$(R^2O)_2POSiMe_3 + R^1CF{=}CF_2$$



45 **46**

R^1	R^2	Yield of **45** (%)	Yield of **46** (%)
CF_3	Et	97	3
	$SiMe_3$	99	1
SF_5	Et	100	–
	$SiMe_3$	100	–

The phosphoranes **48** proved to be stable compounds, which decompose only on heating to 115–120 °C. They could be actually vacuum distilled without decomposition. It was then found unexpectedly that the main products of the decomposition of the phosphoranes **48** are alkyl phosphorodifluoridites **49** and the acetals of the substituted ketones **50**.

$$(RO)_3PFCF{=}C(CF_3)COOR^1 \longrightarrow$$

48

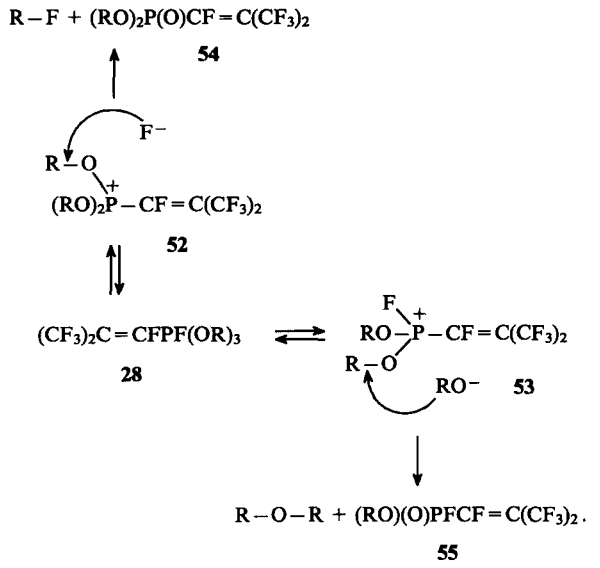
$$\longrightarrow \underset{\textbf{51}}{(RO)_2(O)P{-}CF{=}C(CF_3)COOR^1} + R{-}F$$

$$\longrightarrow \underset{\textbf{49}}{RO{-}PF_2} + \underset{\textbf{50}\ (70\%-90\%)}{(RO)_2C{=}C(CF_3)COOR^1}$$

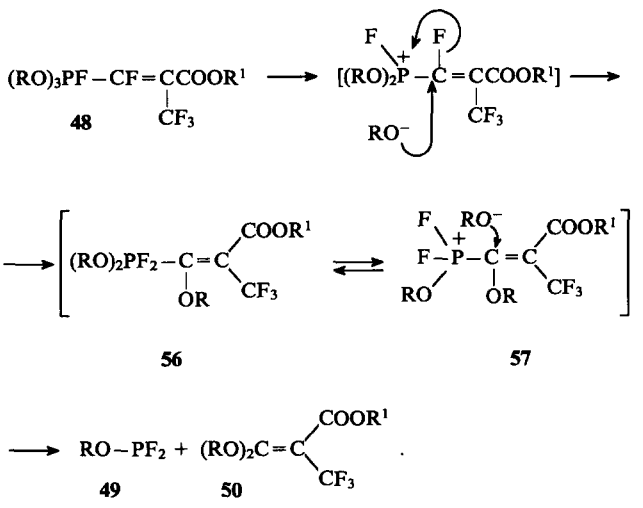
R = Me, Et; R^1 = Me, Et.

The Arbuzov reaction products **51** are not formed at all from the phosphoranes **48** or are obtained only in small amounts. On the other hand, the first stage of the decomposition of the phosphorane **28** is reversible dissociation leading to quasiphosphonium cations of type **52** or **53** and the anions F^- or RO^-. The authors explained this difference in the behaviour of the phosphoranes **28** and **48** by the much greater electrophilicity of the carbon atom of the CF group in the phosphoranes **48** compared with the phosphoranes **28**. In the decomposition of the phosphoranes **28**, the carbon atom of the alkyl group R functions as the electrophilic centre.

Attack by an alkoxide or fluoride ion on the carbon atom leads to the ester **54** or to the acid fluoride **55**.



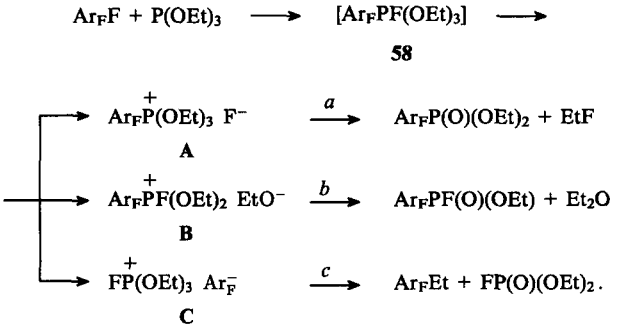
On the other hand, in the phosphoranes **48** the nucleophilic alkoxide anion attacks the β-carbon atom of the acrylic system with formation of the new phosphorane **56**. The dissociation of the latter leads to the quasi-phosphonium salt **57**, which is split into the acetal **50** and the alkyl phosphorodifluoridite **49** as a result of the attack by the alkoxide anion on the same carbon atom.



The possibility of carrying out the Arbuzov reaction with participation of aromatic polyfluoro-compounds of the type C_6F_5X (X = Cl, Br, F, H, OMe) and triethyl phosphite has been discussed.[56] Later this reaction was investigated in greater detail in relation to the interaction of pentafluorobenzonitrile, decafluorobiphenyl, and pentafluoropyridine with triethyl phosphite. The reaction takes place at 140–150 °C with formation of the diethyl esters of polyfluoroarylphosphonic acids in 25–30% yield and is accompanied by a series of side processes: triethyl phosphite, diethyl ethylphosphonate, diethyl phosphonofluoridate, and diethyl ether were detected in the reaction mixtures. An increase in temperature diminishes the yield of phosphonic acid esters. Markovskii et al.[58] determined the factors influencing the occurrence of the side reactions characteristic of compounds of the aromatic polyfluoro-series. In view of the fact that the rate of nucleophilic substitution diminishes significantly in the sequence $C_6F_5NO_2 > C_6F_5CF_3 > C_6F_5H$, a similar sequence might have been expected for the rate of the Arbuzov reaction. However, analysis of the compositions of the reaction mixtures showed that the overall yield of the phosphorylated polyfluorobenzenes increases, contrary to expectation, on passing from pentafluoronitrobenzene to pentafluorobenzene. Furthermore, compounds formed as a result of the reduction and alkylation processes were detected among the reaction products and their amount was actually found to decrease in the above series (Table 5).

This finding, which cannot be explained in terms of the S_N2 nucleophilic substitution mechanism, may indicate the influence on the Arbuzov reaction of factors specific to compounds of the aromatic polyfluoro-series. Apparently, the specific features lie in the fact that a mechanism similar to that proposed by Knunyants et al.[54] for the reaction between perfluoroisobutene and triethyl phosphite operates in the case of aromatic polyfluoro-compounds. A dominant role is assigned in this mechanism to the intermediate polyfluoroaryltriethoxyfluorophosphorane **58**, the reactions of which actually lead to the observed set of products (Scheme 3). The type of the reactions of the phosphorane **58** should be determined both by the stability of the phosphonium cations **A**, **B**, and **C** formed and by the stability of the polyfluoroaryl anion.

Scheme 3



Indeed, with increase in the stability of Ar_F^-, the yield of the alkylation (ethyltetrafluorobenzene Ar_FEt) and reduction (tetrafluorobenzenes Ar_FH) products as well as diethyl phosphorofluoridates should increase (pathway *c*), while the yield of diethyl esters of polyfluoroarylphosphonic acids should diminish (pathway *a*) (Table 5). The reduction process comes down in this instance to the reaction of the polyfluoroaryl anion with a proton from the medium. Indeed, when the reaction of triethyl phosphite with octafluorotoluene or pentafluoropyridine is carried out in the presence of methanol as a source of protons, the yields of heptafluorotoluene and 2,3,5,6-tetrafluoropyridine increase.

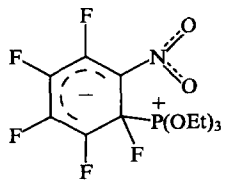
We may note that, together with 4-ethyl-2,3,5,6-tetrafluoronitrobenzene, 2-ethyl-3,4,5,6-tetrafluoronitrobenzene is formed in the reaction of triphenyl phosphite with pentafluoronitrobenzene. This is due to the *ortho*/*para* directing effect of the nitro-group in the nucleophilic substitution reaction.[59]

Table 5. The products of the Arbuzov reaction in $Ar_FF + P(OEt)_3$ reaction mixtures (data of Markovskii et al.[58]).

Ar_F	$Ar_FP(O)(OEt)_2$	$Ar_FPF(O)(OEt)$	Ar_FEt	Ar_FH
$4\text{-}NO_2C_6F_4$	2.2 [a]	0	4.2; 30.0 [a]	3.8; 44.1 [a]
$4\text{-}CF_3C_6F_4$	8.5	5.0	12.8	14.5
$4\text{-}HC_6F_4$	44.0	0	traces	2.0

[a] The product of *ortho*-sustitution relative to the NO_2 group is quoted.

The dominant yield of the product of *ortho*-substitution (Table 5) may be due to the formation of the more favourable transition complex **59** as a result of the interaction of the oxygen of the nitro-group with the phosphorus atom.



59

In addition, triethyl phosphate and the ethyl esters of (1′-ethylethoxy) (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)-phosphinic and bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)-phosphinic acids were detected among the products of the reaction of octafluorotoluene with triethyl phosphite. The authors[59] explain the formation of the phosphonous acid ester **60** as well as the appearance of the H^+ cation in the system by the following reactions of the phosphonium cation:

$$[Ar_FP(OEt)_3]^+ \longrightarrow \underset{\mathbf{60}}{Ar_FP(OEt)_2} + [OEt]^+ \longrightarrow H^+ + MeCHO.$$

Compound **60** can react in its turn both with acetaldehyde and with octafluorotoluene. The fact that, despite the presence of a 20% excess of triethyl phosphite relative to octafluorotoluene, the entire triethyl phosphite is consumed can be explained by the oxidation of triethyl phosphite with acetaldehyde to triethyl phosphate[60] and also by the rearrangement of triethyl phosphite to diethyl ethylphosphonate.

The results obtained in the reaction of octafluorotoluene and pentafluoropyridine with triethyl phosphite in the presence of Lewis acids ($FeCl_3$, $ZnCl_2$, $SnCl_4$) can serve as yet another confirmation of the formation of the polyfluoroaryl anion. A Lewis acid is known to promote the occurrence of the Arbuzov reaction by activating the carbonium centre.[61] However, octafluorotoluene and pentafluoropyridine do not enter into the Arbuzov reaction and their interaction with triethyl phosphite is unaffected by the presence of Lewis acids. Perfluorobitolyl and octafluoro-4,4′-bipyridyl are then formed as the main products together with the phosphorylation, reduction, and alkylation products. It is natural to suppose that the formation of octafluorobiphenyl derivatives is induced by the generation of polyfluoroaryl anions during the reaction and their subsequent interaction with pentafluorobenzene derivatives.

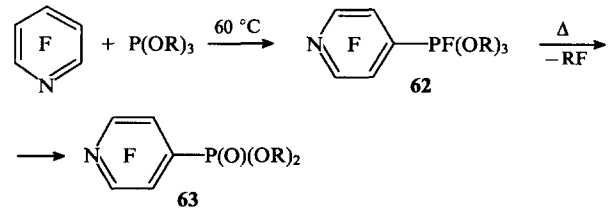
It may be that the diethyl esters of 4-trifluoromethyl-2,3,5,6-tetrafluorophenylphosphonic and 2,3,5,6-tetrafluoropyridyl-phosphonic acids can afford the activated complex **61** in their reactions with $FeCl_3$ as a consequence of the coordination of the Lewis acid to the phosphoryl oxygen atom, from which the corresponding anion Ar_F^- is generated on thermolysis.

$$\underset{\mathbf{61}}{Cl_3Fe...O{=}P(OEt)Ar_F} \longrightarrow FeCl_3 + [O{=}P(OEt)_2]^+ + Ar_F^-.$$

However, in the reaction of octafluorotoluene and pentafluoropyridine with the corresponding alkylphosphonic acid esters in the presence of $FeCl_3$ under the conditions of the Arbuzov reaction, the initial compounds are returned unchanged and 1% of a polymeric product is formed. Evidently the Lewis acids play an active role in the stage involving the postulated formation of triethoxypolyfluoroarylfluorophosphorane **58**, which is in equilibrium with quasi-phosphonium compounds containing fluoride and heptafluorotoluene or tetrafluoropyridine anions. The formation of the stable anions $FeCl_3 \cdot Ar_F^-$ and $FeCl_3F^-$ actually determines the further course of the reaction. The $FeCl_3 \cdot Ar_F^-$ anions are apparently more active nucleophiles than the $FeCl_3F^-$ anions. They enter vigorously into competing reactions with the phosphonium cation and the initial compound, forming the corresponding alkylation products.

On the other hand, the reaction of tris(trimethylsilyl) phosphite with pentafluoropyridine, pentachloropyridine, and 3-cyanotetrachloropyridine in the presence of catalytic amounts of nickel chloride leads to the formation of the corresponding phosphonates in virtually quantitative yields. The reaction takes place at 150 °C over a period of 30 min.[62] The authors[62] note that under non-catalytic conditions tris(trimethylsilyl) phosphite reacts with pentafluoropyridine more effectively than do trialkyl phosphites. The yield of the final products is 60–69%.

Boenigk and Hagele[63] were able to isolate the stable trialkoxy-(2,3,5,6-tetrafluoro-4-pyridyl)fluorophosphorane **62** (stable for several days) in the reaction of pentafluoropyridine with trialkyl phosphites (R = Et, Pr^i) at 60 °C. When the temperature is raised, the phosphorane **62** decomposes with formation of dialkyl esters of 2,3,5,6-tetrafluoro-4-pyridylphosphonic acid **63** and alkylation (4-alkyl-2,3,5,6-tetrafluoropyridine) and reduction (2,3,5,6-tetrafluoropyridine) products. On passing from triethyl phosphite to triisopropyl phosphite, an increase in the yield (up to 90%) of diisopropyl 2,3,5,6-tetrafluoro-4-pyridylphosphonate is observed.

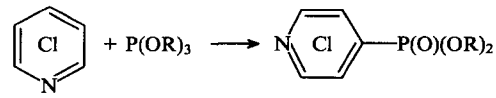


62 **63**

R = Et (50%, 80 °C, 24 h);
Pr^i (90%, 90 °C, 10 h).

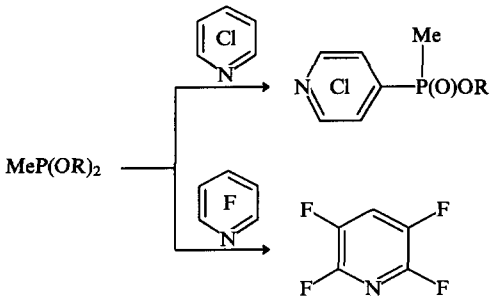
On the other hand, when trimethyl phosphite is introduced into the reaction with pentafluoropyridine, dimethyl 2,3,5,6-tetrafluoro-4-pyridylphosphonate is not formed, the reduction product 2,3,5,6,-tetrafluoropyridine and trimethyl phosphate being obtained instead.

When pentafluoropyridine is replaced by pentachloropyridine, the formation of a stable phosphorane is not observed, the dialkyl esters of 2,3,5,6-tetrachloro-4-pyridylphosphonic acid being isolated as the main products.



R = Me (45%, 120 °C, 15 h); Et (48%, 150 °C, 15 h);
Pr^i (60%, 130 °C, 16 h).

It has been shown[64] that pentachloropyridine enters into the Arbuzov reaction with dialkyl esters of methylphosphonous acid, affording the corresponding phosphinic acid ester, whereas pentafluoropyridine reacts with these esters to form the reduction product — 2,3,5,6-tetrafluropyridine.



R = Et (20%), Pr^i (14%).

Trialkyl phosphites react with the chlorides of carboxylic perfluoroacids[65] giving rise to the phosphonic acid esters **64**. However, when this reaction was carried out in the presence of LiBu–CuI at temperatures ranging from 0 °C to room temperature, diethyl perfluoroalkenylphosphonate **65** was obtained (Scheme 4).[66] A convenient method of synthesis of perfluoroalkylacetylenes, involving treatment of the ester **65** with tetrabutylphosphoramidite (TBPA), was developed on the basis of this reaction.

Scheme 4

$R_FCF_2COCl + P(OEt)_3 \longrightarrow$

$\longrightarrow [R_FCF_2C(O)P(O)(OEt)_2]$

$\downarrow$

$R_F(F)C{=}C(OP(O)(OEt)_2)P(O)(OEt)_2$ **64**

$R_F = CF_3$ (77%), C_2F_5 (74%), n-C_6F_{13} (60%)

LiBu–CuI: $R_FCF{=}CHP(O)(OEt)_2$ **65** $\xrightarrow[20\ °C]{TBPA} R_FC{\equiv}CH$.

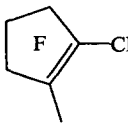
The unsaturated sulphenyl chlorides **66**, containing fluorine atoms in the carbon chain, react with triethyl phosphite via the chlorine atom with formation of the unstable intermediate **67**, the decomposition of which leads to ethyl perfluoroalkenyl sulphides **68** and diethyl phosphorochloridate.[67]

$R_FSCl + P(OEt)_3 \longrightarrow R_FS^-[Cl{-}P(OEt)_3]^+ \longrightarrow$

66 **67**

$\longrightarrow R_FSEt + (EtO)_2P(O)Cl$

68

$R_F = (CF_3)_2C{=}CF$, 

Trialkyl phosphites react with non-fluorinated sulphenyl chlorides via the sulphur atom, affording alkyl halides and phosphates.[68]

$RSCl + P(OR')_3 \longrightarrow [RS{-}P(OR')_3]^+Cl^- \longrightarrow$

$\longrightarrow RS{-}P(O)(OR')_2 + R'{-}Cl.$

Trifluoromethanesulphenyl chloride reacts with trimethyl phosphite via two pathways simultaneously, which results in the formation of the sulphide CF_3SMe and the phosphorothioate $CF_3SP(O)(OMe)_2$.

The reaction of perfluoroisobutenyl isothiocyanate **69** with triethyl phosphite leads to the formation of the diethyl ester of the phosphonic acid **70** as a result of the nucleophilic atack by the trivalent phosphorus atom on the carbon atom of the C = S bond. Under these conditions, the fluorine atoms attached to the double bond are not substituted.[69]

$(CF_3)_2C{=}CFNCS + P(OEt)_3 \longrightarrow$

69

$\longrightarrow [(CF_3)_2C{=}CF{-}N{=}C(S^-){-}P^+(OEt)_3] \longrightarrow$

$\longrightarrow (CF_3)_2C{=}CF{-}N{=}C(SEt){-}P(O)(OEt)_2.$

70

On the other hand, treatment of the thione **71** with triethyl phosphite affords the product **72**, which contains no phosphorus atom.[70]

$(CF_3)_2CH{-}C(=S){-}C_2F_5 + P(OEt)_3 \longrightarrow (CF_3)_2CH{-}C(SEt){=}CFCF_3.$

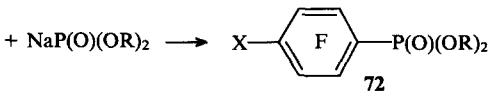
71 **72**

3. The Michaelis–Bekker reaction in the series of aromatic polyfluoro-compounds

The reactions of perfluoroolefins with dialkyl phosphites have been achieved only under radical conditions,[71] which resulted in the formation of a mixture of telomeric fluorinated alkylphosphonic acid esters of the type $H(CF_2CF_2)_nP(O)(OR)_2$ (n = 1–7). Alkyl esters of difluoromethylphosphonic acid were synthesised from chlorodifluoromethane and sodium dialkyl phosphite.[72]

$CHF_2Cl + NaOP(OR)_2 \longrightarrow (RO)_2P(O)CF_2H + NaCl.$

It has been shown[73] that pentafluorobenzene derivatives and pentafluoropyridine enter into the Michaelis–Bekker reaction with the sodium salts of dimethyl and diethyl phosphites in tetrahydrofuran and afford the corresponding esters of polyfluoroarylphosphonic acids **72** in 10–60% yields.

$C_6F_5X + NaP(O)(OR)_2 \longrightarrow$ 

72

X = NO_2, CN, CF_3, H, F, OMe;
R = Me, Et.

The low yield of the polyfluoroalkylphosphonic acid esters may be due to the interaction of the nucleophile with the phosphorus atom.[74] The Michaelis–Bekker reaction takes place similarly with pentachlorobenzene,[75] hexachlorobenzene,[76] and certain chlorine-containing heterocyclic compounds.[77] Iodobenzene interacts with the sodium salt of diethyl phosphite to form diethyl phenylphosphonate only when the reaction is carried out under irradiation.[77]

III. P-Nucleophiles as synthons in the synthesis of perfluorinated organic compounds without phosphorus atoms

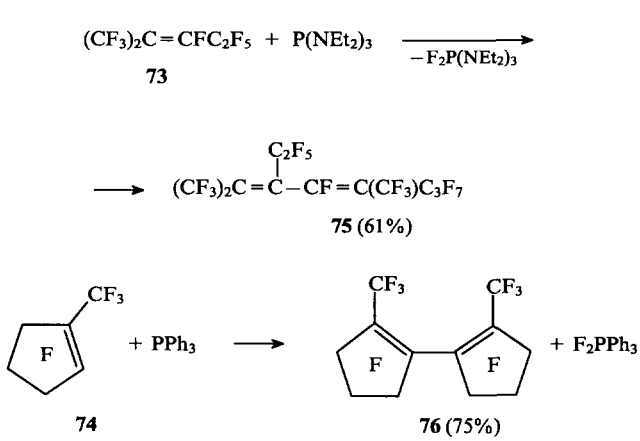
As shown above, the reactions of phosphines with perfluoroolefins and aromatic polyfluoro-compounds lead initially to the formation of fluorophosphoranes, which proved to be extremely stable in some cases. The stability of fluorophosphoranes is determined by the electronegativity of the atoms of the substituents attached to the phosphorus atom: its increase entails an increase in the stability of the phosphorane.

The cleavage of the P–X bonds in phosphoranes generates a stable phosphonium cation. Such cleavage is controlled by thermodynamic factors. Because of this, the cleavage of the P–C bond, and not P–F and P–O, is energetically more favourable.[78] The thermolysis of phosphorane accompanied by the formation of the P=O bond is even more effective.

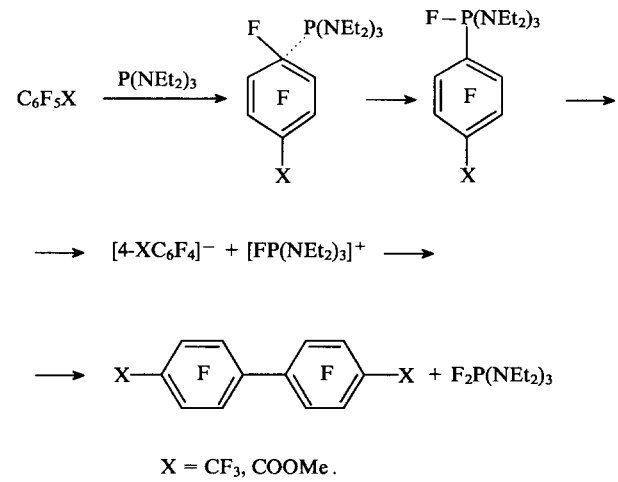
These factors suggested that the generation of carbanions, the transfer of the organic fragment in the form of an anion, and the formation of a new C–C bond may be expected for phosphoranes having a specific structure. In synthesis, the phosphorane need not necessarily be isolated beforehand. The most important factor is that a phosphorane of this kind should be formed during the reaction, whereupon the entire process can be carried out in one stage. We shall consider certain examples of reactions in which trialkylphosphines or triphenylphosphines are reactants in the synthesis of fluorophosphoranes, the subsequent interactions of which with unsaturated polyfluorinated compounds can lead to the formation of new C–C bonds. In this case, there is a possibility that the entire process can be achieved in one stage. We shall therefore consider primarily the reactions of trialkylphosphines or triphenylphosphine with organic perfluoro-compounds containing mobile fluorine atoms.

1. Reactions of organic perfluoro-compounds with trialkyl- and triphenyl-phosphines in the presence of C-electrophiles

It has been found[79] that the reactions of fluoroolefins having three perfluoroalkyl substituents with phosphines lead to the reductive dimerisation of the olefins, as a result of which conjugated dienes are formed. Thus, when perfluoro-2-methylpent-2-ene **73** is acted upon by phosphorus tris(diethylamide) or perfluoro-1-methylcyclopent-1-ene **74** is acted upon by triphenylphosphine, perfluoro-3-ethyl-2,5-dimethylocta-2,4-diene **75** and perfluoro-1-methyl-2-(2′-methylcyclopent-1′-enyl)-cyclopent-1-ene **76** are formed respectively.

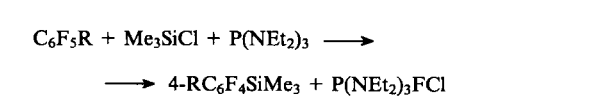


According to the data of Markovskii et al.,[80] the reaction of compounds of the type C_6F_5X with phosphorous tris-(diethylamide) results in the formation of symmetrically substituted octafluorobiphenyls, while in the reaction with pentafluoropyridine the product is octafluoro-4,4′-bipyridyl (yield 50–60%).



X = CF_3, COOMe.

Presumably, in the reactions of perfluoroalkenes or substituted perfluorobenzenes, the trivalent phosphorus atom attacks in the first stage the electrophilic carbon atom involved in the multiple bond or in the benzene ring with subsequent migration of the fluoride anion to the phosphorus atom. The resulting phosphorane is thermally unstable and decomposes, affording a phosphonium cation and a perfluoroalkenyl or pentafluorophenyl anion, which subsequently react with the initial substrates, affording the reaction products. The pentafluorophenyl anion generated in this way reacts further both with the initial aromatic polyfluoro-substrate and with other compounds having more mobile halogen atoms. For example, the addition of chlorotrimethylsilane to a mixture of octafluorotoluene and phosphorus tris(diethylamide) leads to 4-trifluoromethyltetrafluorophenyltrimethylsilane.[81] Pentafluoropyridine and 3-chlorotrifluoropyrimidine have also been introduced into this reaction.



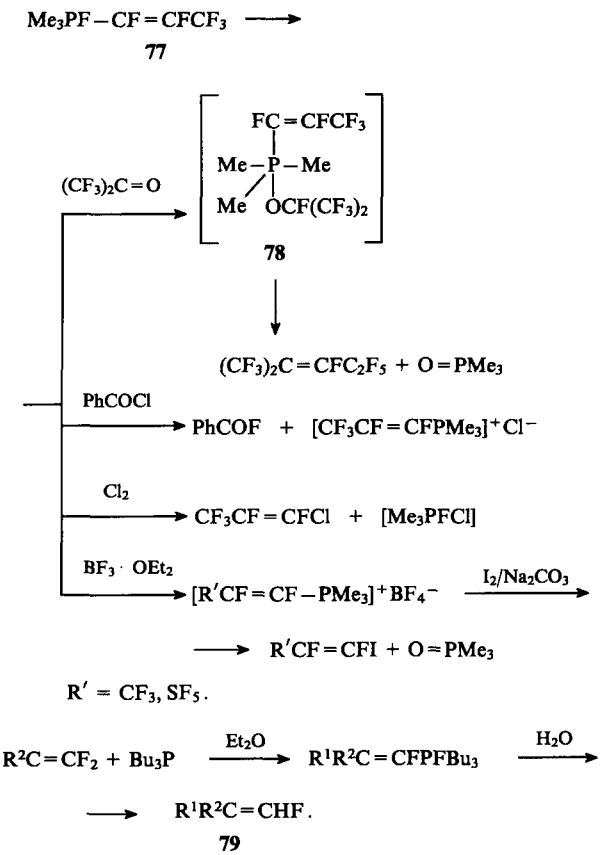
R = CF_3, CN, COOEt.

This opens a pathway to the synthesis of various polyfluoro-derivatives of Group IV–VI elements, which were previously difficult to obtain. It is particularly significant that compounds containing strong electron-accepting substituents in the benzene ring can be obtained by this method.

It has been shown[82] that the phosphorane **77**, formed in the reaction of triphenylphosphine with hexafluoropropene, reacts further with hexafluoroacetone in the presence of the fluoride ion, affording triphenylphosphine oxide and perfluoro-2-methylpent-2-ene. The authors assume that these products are obtained as a result of the decomposition of the phosphorane **78**. Scheme 5 presents other reactions of the phosphorane **77**.

Using this approach, a method has been developed for the reduction of perfluoroolefins. The first stage of this reaction involved the formation from the perfluoroolefin and tributylphosphine of a fluorophosphorane, the subsequent hydrolysis of which leads to the olefin **79**. This reaction can be regarded

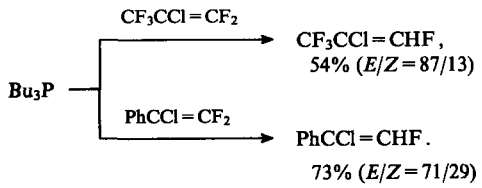
Scheme 5



R^1	R^2	*E*/*Z*	Yield of **79** (%)
CF_3	F	100(*E*)	97
$CF_3(CF_2)_2$	F	100(*E*)	72
$CF_3(CF_2)_4$	F	100(*E*)	85
Ph	CF_3	12/88	100
Ph	C_2F_5	100(*Z*)	47
4-$MeOC_6H_4$	CF_3	9/91	100

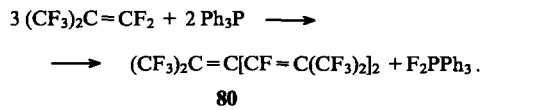
formally as substitution of a fluorine atom at the multiple bond by a hydrogen atom.[83, 84]

Since treatment of chloroperfluoroolefins with tributylphosphine involves a fluorine atom and not the chlorine atom, a fluorine atom is formally split off from the final product.



Hydrolysis of the *cis*-isomer of vinylphosphorane in moist dimethylformamide (DMF) proceeds stereoselectively. When the reaction of β,β-difluorostyrene with tributylphosphine is carried out in the presence of $BF_3.OEt_2$, the *trans*-isomer of the vinylphosphonium salt is obtained and subsequently hydrolysed. The selectivity of the formation of the (*Z*)- and (*E*)-isomer is 100%, but it diminishes after the introduction into the alkene, together with the perfluoroalkyl group, of substituents such as phenyl and *p*-methoxyphenyl.

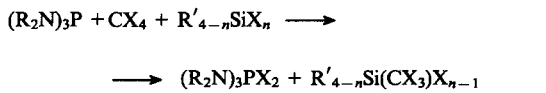
In contrast to the examples mentioned above, where triphenylphosphine behaves as a nucleophile and the final product contains a phosphorus atom, in the reaction with perfluoroisobutene it behaves as a defluorinating agent and the final product—1,1-divinylalkene **80**—does not contain a phosphorus atom.[85]



The authors suggest that the triene **80** is formed from an intermediate fluorophosphorane.

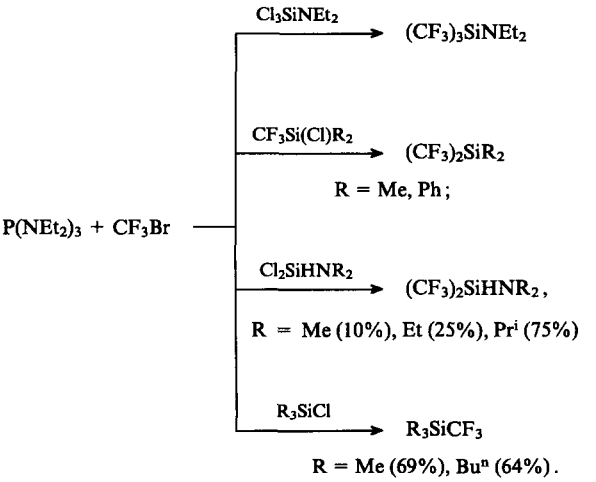
2. The use of perfluoroalkyl bromides (or bromopolyfluorobenzenes)-phosphorus tris(dialkylamide) systems as nucleophiles

If the aromatic compounds contain a halogen atom with a low mobility, for example, iodine or bromine, there is a possibility of a situation where the rate of nucleophilic substitution of such a halogen by trivalent phosphorus derivatives is very low and there is only polarisation of the C–halogen bond under the influence of the phosphorus atom. However, in this case too it is possible to make use of the nucleophilic properties of such a complex. It has been found that the phosphorous tris(diethylamide)–alkyl bromide system is a unique nucleophile. This system has found extensive applications in organic synthesis in recent years owing to the formation in the intermediate stage of the trihalomethanide ion, which is highly reactive towards proton-donating agents and electrophiles.[86, 87]



Ruppert and coworkers[88, 89] showed that bromotrifluoromethane enters into this reaction. It was later found that the $CF_3Br-P(NEt_2)_3$ system is fairly universal and can be used as the reagent for the introduction of the trifluoromethyl group. Thus it has been shown[90, 91] that this system is effective in the synthesis of various organosilicon compounds (Scheme 6).

Scheme 6



Instead of halotrimethylsilanes, it is possible to use trimethylsilyl azide, trimethyl isothiocyanate, and trimethyl isocyanate.[92, 93] A number of workers[94–99] have used the $CF_3Br-P(NEt_2)_3$ system for the trihalomethylation of organophosphorus compounds containing P–halogen bonds, while Burger et al.[100] used it for the methylation of boron compounds.

$$R_nE-X + CF_3Br + P(NEt_2)_3 \longrightarrow$$
$$\longrightarrow R_nE-CF_3 + [XP(NEt_2)_3]Br$$

E = P, Si, B.

Wakselman and Tordeux[101] used the $CF_3Br-P(NEt_2)_3$ system for the direct introduction of the trifluoromethyl group into anilines.

Bardin et al.[102] used the $C_6F_5Br-P(NEt_2)_3$ system instead of $CF_3Br-P(NEt_2)_3$. A method of synthesis of polyfluoroaryl-substituted silanes, germanes, and stannanes was developed on its basis.

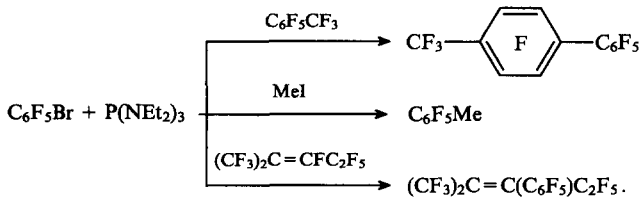
$$4\text{-}R'C_6F_4Br + P(NEt_2)_3 + R_3MX \longrightarrow$$
$$\longrightarrow 4\text{-}R'C_6F_4MR_3 + (NEt_2)_3PXBr$$

R = Me, Et; R′ = F, PrO, CF_3;
M = Si (66%), Ge (57%), Sn (50%); X = Cl, Br.

Pentachlorobenzene, bromobenzene, 3-bromo-1-trifluoromethylbenzene, and benzyl bromide do not react under these conditions. Pentafluoroiodobenzene reacts with the above system, giving rise to methyl(pentafluorophenyl)silane.

The nucleophilic phosphorus atom in the $C_6F_5Br-P(NEt_2)_3$ system attacks the bromine atom, affording a phosphonium cation and a carbanion. The subsequent reactions of these species depend on the presence of C-electrophiles. It has been shown,[102, 103] that this system is convenient for the introduction of the polyfluoroaryl fragment into aromatic polyfluoro-compounds and perfluoroolefins. Certain reactions are illustrated in Scheme 7 below.

Scheme 7

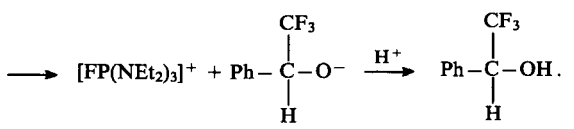


The interaction of CF_3Br with $P(NR_2)_3$ (R = Me, Et) leads to the phosphonium salt **81** in a virtually quantitative yield.[104] The structure of the latter was confirmed by NMR spectroscopic data and X-ray diffraction.

$$(R_2N)_3P + BrCF_3 \longrightarrow [CF_3P(NR_2)_3]^+Br^-.$$
81 (95%–100%)

On the other hand, in the reaction of CF_3I and $P(NEt_2)_3$ other products are formed, namely $CF_3P(NEt_2)_2$ and the salt $[P(NEt_2)_4]^+I^-$.[105] The salt **81** is stable up to the melting point. The high positive charge on the phosphorus atom in this compound promotes the reaction with the fluoride anion (arising from CsF, TASF, etc.). The fluorophosphorane **82** is formed as an intermediate in this reaction. It reacts, for example, with benzaldehyde to form the alcohol **83**.

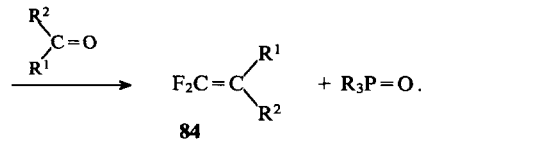
$$[CF_3P(NEt_2)_3]^+Br^- + F^- \longrightarrow [(Et_2N)_3PFCF_3] \xrightarrow{PhCHO}$$
81 **82**



83 (73%)

Phosphonium salts may react with salts of type **81** also via a different pathway. Thus, in the presence of an excess of this P-nucleophile, the corresponding ylide, having pronounced nucleophilic properties, is formed. It reacts with aldehyde and ketones, forming terminal olefins.[106]

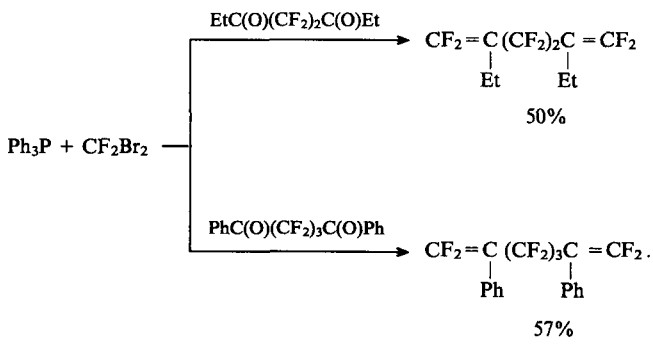
$$[R_3PCF_2Br]Br^- + R_3P \longrightarrow [R_3P-CF_2] + [R_3PBr]Br^- \longrightarrow$$



84

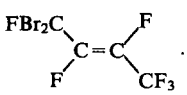
R	R^1	R^2	Yield of **84** (%)
Ph	Ph	H	65
	C_6F_5	H	20
	Ph	CF_3	85
	C_6H_{11}	CF_3	90
	Ph	C_2F_5	82
	3-BrC_6H_4	CF_3	83
NMe_2	Ph	Me	81
	Ph	Et	82
	Et	Et	75
	Me	Me	60
	Ph	CF_3	25

Polyfluorinated ketones react similarly.



The PPh_3-CFBr_3 system is capable of reacting with perfluoroolefins, substituting a fluorine atom at the double bond by the $CFBr_2$ group.[107]

$$Ph_3P + CFBr_3 + CF_3CF=CF_2 \longrightarrow$$



$P(NEt_2)_3$ may be used instead of triphenylphosphine.[108]

$$P(NEt_2)_3 + BrCF_2X + Me_3SiCl \longrightarrow$$
$$\longrightarrow Me_3SiCF_2Cl + [(Et_2N)_3PX]^+Br^-$$

X = Cl, Br, I.

The reaction of the $CF_3Br-P(NEt_2)_3$ system with benzaldehyde[109] leads to the formation of the phosphonium salt **85**, which decomposes at 140 °C, affording α-bromophenylethane and not the alcohol **83**. Owing to the ease of formation of a phosphorus compound with P=O bond, in this case the intermediate carbonium ion reacts with the bromide anion,

giving rise to the final reaction product. The reaction is general in character. Perfluoroalkyl bromides with different carbon chain lengths (from 2 to 6) have been used as reactants in it.

$$PhCHO + CF_3Br + P(NEt_2)_3 \longrightarrow$$

$$\longrightarrow \underset{\mathbf{85}\ (77\%)}{[PhCH(CF_3)OP(NEt_2)_3]^+Br^-} \xrightarrow{140\ ^\circ C}$$

$$\longrightarrow \underset{99\%}{PhCHBrCF_3} + \underset{95\%}{O{=}P(NEt_2)_3}.$$

According to the data of Kolomeitsev et al.,[110] chloro- and bromo-alkanes **86** react in the presence of $P(NEt_2)_3$ with $PhCH_2SCN$, affording the product **87** resulting from the substitution of the CN group.

$$\underset{\mathbf{86}}{PhCH_2SCN + F(CX_2)_mY} \xrightarrow[CH_2Cl_2,\ -70\ ^\circ C]{P(NEt_2)_3} \underset{\mathbf{87}}{PhCH_2S(CX_2)_mF}$$

X = Cl, F; Y = Cl, Br; m = 1–3.

The interaction of the $C_2F_5I-P(NEt_2)_3$ system with benzoyl chloride[111] in a non-polar solvent results in the formation of the product of the substitution of the chlorine atom — the corresponding ketone (yield 58%).

The reaction of the partly fluorinated aliphatic-aromatic ketones **88** with $CF_3Br-P(NEt_2)_3$ leads to the formation of the tertiary alcohol **89**.

$$\underset{\mathbf{88}}{PhCOC_2F_5 + CF_3Br + P(NEt_2)_3} \xrightarrow[-70\ ^\circ C,\ 5\ h]{H^+} \underset{\mathbf{89}\ (56\%)}{Ph-\overset{\overset{CF_3}{|}}{\underset{\underset{C_2F_5}{|}}{C}}-OH}.$$

On the other hand, in the case of benzoyl fluoride, the reaction is very slow and leads to the ultimate formation not of a tertiary alcohol but of the products of the esterification of benzoic acid by the latter. The yield of the ester is 81%.

In the presence of $P(NEt_2)_3$, polyfluoroalkyl iodides react with various aroyl chlorides to form aryl polyfluoroalkyl ketones (Table 6).[112]

$$R_FI + ArCOCl + P(NEt_2)_3 \longrightarrow ArCOR_F + ClP(NEt_2)_3.$$

The primary step in this reaction is nucleophilic attack by the phosphorus atom on the iodine atom. The subsequent nucleophilic attack by the anionoid polyfluoroalkyl group on the electrophile present in the reaction mixture affords the corresponding ketone and phosphorane.[113] The reaction between the phosphonium ylide and acetyl halide usually leads to the ylide acylation product. The Wittig reaction also occurs here. This has been used to obtain olefins from acyl halides.[114]

Table 6. Reactions of polyfluoroalkyl iodides with aroyl chlorides in the presence of phosphorus tris(diethylamide).[112]

ArCOCl	R_FI	Time/h	Yield (%)
$4\text{-}ClC_6H_4COCl$	$CF_3(CF_2)_5I$	6	41
$2,4\text{-}Cl_2C_6H_3COCl$	$CF_3(CF_2)_7I$	6	36
$4\text{-}ClC_6H_4COCl$	$Cl(CF_2)_4I$	3.5	42
PhCOCl	$Cl(CF_2)_4I$	6	43
$2,4\text{-}Cl_2C_6H_3COCl$	$Cl(CF_2)_4I$	4	43
$4\text{-}ClC_6H_4COCl$	$Cl(CF_2)_6I$	5	41
PhCOCl	$Cl(CF_2)_6I$	6	41
$2,4\text{-}Cl_2C_6H_3COCl$	$Cl(CF_2)_6I$	6.5	40

$$R_3P + CFX_3 \longrightarrow \underset{\mathbf{90}\ (90-95\%)}{[R_3\overset{+}{P}-\overset{-}{C}F-\overset{+}{P}R_3]X^-} + R_3PX_2,$$

R = Bu, Ph; X = Cl, Br

$$\mathbf{90} + R_FCOF \longrightarrow R_3\overset{+}{P}-CF-\overset{+}{P}R_3\cdot X^- \longrightarrow$$

$$\longrightarrow R_3P{=}O + \underset{\mathbf{91}}{R_3\overset{+}{P}(X^-)-C(F)=C(F)R_F} \xrightarrow{H_2O}$$

$$\longrightarrow \underset{\mathbf{92}}{H(F)C=C(F)R_F} + R_3P{=}O.$$

R_F	Yield of **91** (%)	Yield of **92** (%)
C_2F_5	80	62
Pr^n	82	52
CF_2Cl	73	50
$MeOOCCF_2$	70	20
$CF_3(CF_2)_2OCF(CF_3)$	75	49

Various alkyl halides may be used to obtain phosphorus ylides. The $PPh_3-CF_2Br_2$[106] and PPh_3-CClF_2COONa[115] systems were used to synthesise 2-phenylpentafluoropropene from $4\text{-}RC_6H_4COCF_3$.

$$4\text{-}RC_6H_4COCF_3 + Ph_3P + CClF_2COONa \longrightarrow \underset{CF_3}{\overset{4\text{-}RC_6H_4}{\diagdown}}C=CF_2$$

R = H (75.9%), Me (81.9%), OMe (90.7%), F (66.6%).

A convenient method of synthesis of 1,1-bis(trifluoromethyl)-alkenes **93** from aldehydes and 2,2-dichlorohexafluoropropane in the presence of triphenylphosphine has been developed.[116]

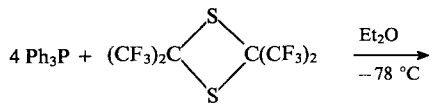
$$Cl_2C(CF_3)_2 + Ph_3P + RCHO \longrightarrow$$

$$\longrightarrow \underset{\mathbf{93}}{H(CF_3)C=C(R)CF_3} + Ph_3P{=}O + Cl_2PPh_3$$

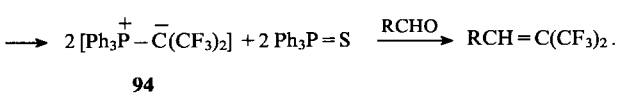
R = Et (31%), Pr (22%), $4\text{-}ClC_6H_4$ (88%), $4\text{-}MeOC_6H_4$ (27%), C_6H_{11} (4%), $Cl_2C{=}CH$ (83%), Ph (54%), $Me_2CHCHCl$ (62%).

The mechanism of this reaction is so far obscure. Two pathways have been suggested: either the carbanion reacts directly with the aldehyde or the phosphorus ylide is formed as an intermediate and then reacts with the aldehyde.

The phosphorus ylide **94** can be obtained also by the reaction of triphenylphosphine with tetrakis(trifluoromethyl)-1,3-dithietan.[117] Its subsequent interaction with aldehydes leads to the corresponding perfluoroolefins.



$$4\,Ph_3P + (CF_3)_2C\langle S\rangle C(CF_3)_2 \xrightarrow[-78\ ^\circ C]{Et_2O}$$



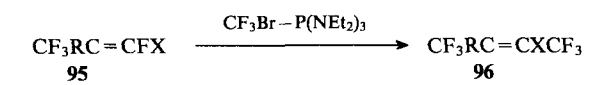
$$\longrightarrow 2\,[Ph_3\overset{+}{P}-\overset{-}{C}(CF_3)_2] + 2\,Ph_3P{=}S \xrightarrow{RCHO} RCH{=}C(CF_3)_2.$$

94

R	Ph	C_6F_5	$Me(CH_2)_5$
Yield of olefin (%)	99	100	100
R	MeCHPh	PhCH=CH	4-$MeOC_6H_4$
Yield of olefin (%)	61	60	52

The effectiveness of the PPh_3–F_3CCCl_3 system in reactions with aldehydes, which lead to the formation of trifluoromethylolefins, has been demonstrated.[118] The reaction with aromatic and α,β-unsaturated aliphatic aldehydes proceeds with a high stereoselectivity [the (*Z*)-isomers are formed exclusively], whereas the reaction with other aliphatic aldehydes affords a mixture of the (*Z*)- and (*E*)-isomers in proportions ranging from 2 : 1 to 3 : 1.

The highly reactive perfluoroolefins **95** react under mild conditions with the CF_3Br–$P(NEt_2)_3$ system, giving rise to monosubstitution products **96**.[119]



$$CF_3RC{=}CFX \xrightarrow{CF_3Br-P(NEt_2)_3} CF_3RC{=}CXCF_3$$

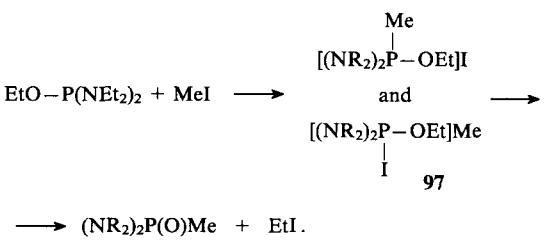
95 **96**

R = CF_3, X = F; R = F, X = C_2F_5; R = $CONEt_2$, X = F.

In the reaction of perfluoro-2-methylpent-2-ene and perfluoromethacrylamide with the above system, the products of the substitution of two fluorine atoms are formed together with the monosubstituted products (the yields are 45 and 34% respectively). The reaction with perfluoroisobutene gives rise to a mixture of isomeric perfluorodienes, whilst the reaction with octafluorotoluene affords a mixture of isomeric perfluoroxylenes in a yield of only 7%.

3. Reactions with phosphines containing P–O and P–N bonds simultaneously

In an early study, Michaelis[120] reported two stable quasi-phosphonium salts **97**, formed when methyl iodide is acted upon by alkyl *N,N,N',N'*-tetraalkylphosphorodiamidites. The salts decompose in accordance with the scheme.



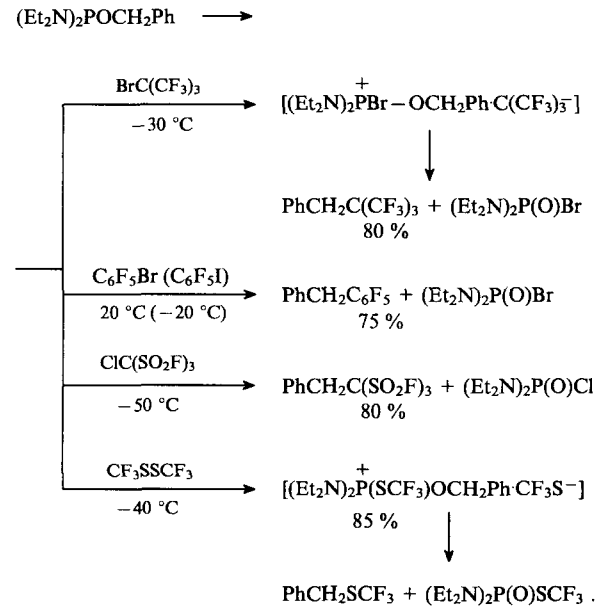
$$EtO-P(NEt_2)_2 + MeI \longrightarrow \begin{matrix} Me \\ | \\ [(NR_2)_2P-OEt]I \end{matrix} \text{ and } \begin{matrix} [(NR_2)_2P-OEt]Me \\ | \\ I \end{matrix} \longrightarrow$$

97

$$\longrightarrow (NR_2)_2P(O)Me + EtI.$$

Wakselman and Tordeux[101] developed the research based on this observation and showed that such phosphorodiamidites react exothermally with fluorine-containing electrophiles incorporating mobile groups such as Br, SCF_3, etc., forming *N,N,N',N'*-tetraethylphosphorodiamidic halides and fluorinated compounds with new C–C bonds. Thus it became possible to synthesise a series of phosphorus-containing compounds which are otherwise difficult to obtain. Some examples of these reactions are presented in Scheme 8.

Scheme 8



$(Et_2N)_2POCH_2Ph \longrightarrow$

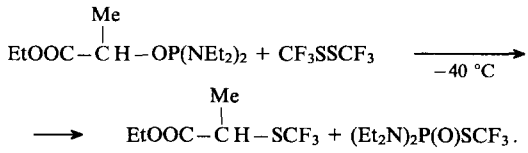
$BrC(CF_3)_3$, −30 °C → $[(Et_2N)_2PBr-OCH_2Ph\cdot C(CF_3)_3^-]$ → $PhCH_2C(CF_3)_3 + (Et_2N)_2P(O)Br$, 80 %

C_6F_5Br (C_6F_5I), 20 °C (−20 °C) → $PhCH_2C_6F_5 + (Et_2N)_2P(O)Br$, 75 %

$ClC(SO_2F)_3$, −50 °C → $PhCH_2C(SO_2F)_3 + (Et_2N)_2P(O)Cl$, 80 %

CF_3SSCF_3, −40 °C → $[(Et_2N)_2P(SCF_3)OCH_2Ph\cdot CF_3S^-]$, 85 % → $PhCH_2SCF_3 + (Et_2N)_2P(O)SCF_3$.

Instead of the benzyl residue, other groups can also be used, for example:



$$EtOOC-\underset{\displaystyle Me}{\underset{|}{C}}H-OP(NEt_2)_2 + CF_3SSCF_3 \xrightarrow[-40\ ^\circ C]{}$$

$$\longrightarrow EtOOC-\underset{\displaystyle Me}{\underset{|}{C}}H-SCF_3 + (Et_2N)_2P(O)SCF_3.$$

IV. Conclusion

The examples presented in this review show that phosphorus-containing nucleophiles play an important role not only in the synthesis of organophosphorus compounds containing perfluorinated substituents but also in reactions where they behave as synthons. This has made it possible to develop novel methods of synthesis of compounds with new C–C bonds. There is no doubt that all these features have enriched synthetic organic chemistry by a series of new approaches to the specific synthesis of interesting organic compounds. Further development of this field of chemistry and the discovery of new possibilities in the reactions of phosphorus-containing nucleophiles with unsaturated halogen-containing substances may be expected. The author does not claim to have given an exhaustive bibliographic survey in the present review, but the latter reflects fully the principal aspects of studies both in the field of methods of synthesis of organofluorine compounds and as regards the principal trends in the development of methods for the introduction of organophosphorus fragments into various molecules and also in the application of organo-phosphorus synthons in the synthesis of compounds with new carbon–carbon bonds. The author hopes that the review will be useful not only to investigators working in the field of the organic chemistry of fluorine but also to a wider range of chemists concerned with synthesis.

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