Translated from *Uspekhi Khimii*, 57, 1488-1509 (1988) U.D.C. 542.91:547.1'118'161:547.341

Fluoroalkenylphosphonates

A.A.Kadyrov and E.M.Rokhlin

In this review we survey the methods for the preparation of derivatives of fluoroalkenylphosphonic acid and their reactions. The main methods for obtaining these compounds are based on the reactions of fluoroolefins with phosphites and also on the elimination of halogens, hydrogen halides and alkyl halides from fluoroalkylphosphonates or fluorine-containing phosphorus ylides. The chemical properties of fluoroalkenylphosphonates are due to the combined effect of the fluorine atoms and the phosphonate group. Their reactions with different reagents leads to modifications of the phosphonate group, addition to the C=C bond, replacement of the vinyl halogen atom, and cleavage of the C-P bond.
The bibliography includes 96 references.

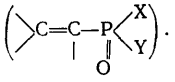
CONTENTS

I. Introduction 852
II. Methods of synthesis 852
III. Chemical properties 857

I. INTRODUCTION

Unsaturated phosphonic acids and their derivatives make up an important class of organophosphorus compounds that are of interest because of the variety of their chemical reactions and their possible practical applications.[1-4] The attention of research workers has in recent years been drawn increasingly towards fluorine-containing alkenylphosphonates. The presence in the same molecule of fluorine atoms, a C=C double bond, and $PO(OR)_2$ groups gives these compounds a unique reactivity, combining the properties of fluoroolefins and unsaturated phosphonates. There are also some examples which confirm the practical value of products derived from them. Some compounds of this type have been proposed as monomers for making cation exchange resins,[5-7] impregnating agents for textiles and paper,[8] intermediates in the synthesis of insecticides and incombustible polymers,[9] extraction agents for heavy metal ions,[10] components of toothpaste[11] and even antibiotics.[12]

The present review attempts to correlate and systematise the information on the methods of obtaining and the chemical properties of fluoroalkenylphosphonic acids and their derivatives, in particular for those compounds in which the phosphonate group is bonded directly to the α-carbon atom of the fluoroalkenyl fragment



In selecting literature data we used the automated formation search system AIPS-FTOR [AISS-FLUORINE] (VINITI) [All Union Institute of Scientific and Technical Information].

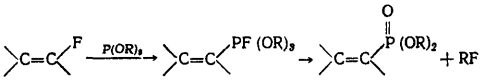
II. METHODS OF SYNTHESIS

Some methods used for obtaining fluoroalkenylphosphonates are essentially no different from those used for their nonfluorinated analogues, in this case being mainly reactions such as dehalogenation and dehydrohalogenation of haloalkylphosphonates. However, specific methods based on the unique reactions of fluoroolefins and other fluorine-containing unsaturated compounds are often used for the synthesis of fluoroalkenylphosphonates.

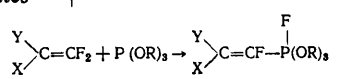
1. Substitution of Vinyl Halogen Atoms in Fluoroolefins

A reaction for "vinyl" substitution of a halogen atom that is typical for fluoroolefins and related compounds is widely used for the synthesis of fluoroalkenylphosphonates containing a C=C bond conjugated with the phosphonate group.

Trialkyl phosphites react fairly readily with polyfluoroolefins to form fluoroalkenylphosphonates:

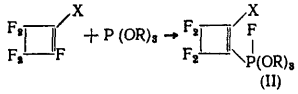


In this case trialkoxyfluorophosphoranes are likely to be formed as intermediates. Phosphoranes such as (I) and (II) are isolated from reactions of trialkyl phosphites with perfluoroisobutylene,[13] polyfluorocyclobutenes,[13,14] perfluoromethacrylates,[15-17] and difluoromethylenemalonates[17,18]†



(I)

R = Et, X = Y = CF_3 (a); R = Me, X = CF_3, Y = COOMe (b), COOEt (c); R = Et, X = CF_3, Y = COOMe (d), COOEt (e); R = Me, X = Y = COOME (f); R = Et, X = Y = COOEt (g)



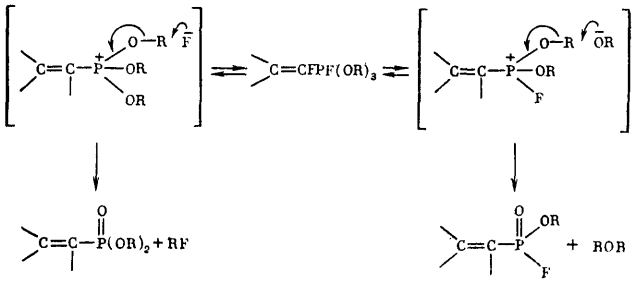
(II)

X = F, R = Me (a), Et (b); R = Me, X = Cl (c), Br (d), I (g)

Thermal decomposition of polyfluoroalkenyltrialkoxyfluorophosphoranes, which may be regarded as intermediates of an Arbuzov rearrangement, usually leads to the formation of alkyl fluorides and dialkyl polyfluoroalkenylphosphonates.[13-15] In some cases there is a different decomposition route—dialkyl ether and monoalkyl polyfluoroalkenylphosphonofluoridate are formed.[13-15] Elimination of the fluoride anion from trialkoxyfluorophosphonate is evidently

† A similar reaction of pentafluoroazapropene $CF_3N=CF_2$ leads to the formation of stable pentafluoroazapropenyltrialkoxyfluorophosphoranes $CF_3N=CFPF(OR)_3$.[19]

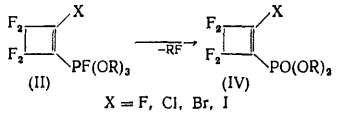
inhibited as a result of the strength of the P–F bond and the elimination of alkoxide anion starts to complete successfully with this reaction. The latter is alkylated by a quasiphosphonium cation and as a result there is a second route for formation of decomposition products—phosphonofluoridate and ether:



For example, when perfluoroisobutenyltriethoxyfluorophosphorane (Ia) is heated to 120–150 °C, ethyl fluoride, diethyl ether, and the perfluoroisobutenylphosphonic acid derivatives—the ester $(CF_3)_2C=CFPO(OEt)_2$ (III) and phosphonofluoridate $(CF_3)_2=CFPF(O)OEt$—are formed.[13]

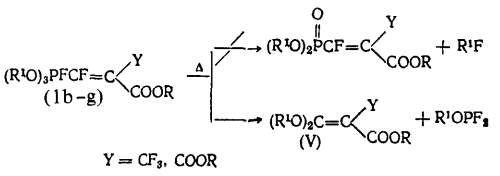
Fluorophosphorane (Ia) is converted to perfluoroisobutenyl phosphonic acid derivatives not only by thermal decomposition but also by hydrolysis. Prolonged reaction with an aqueous solution of sodium bicarbonate gives a mixture of the phosphonic acid $(CF_3)C=CFPO(OH)_2$ and its acid ester $(CF_3)_2C=CFPO(OEt)OH$.[20]

The corresponding phosphonates (IV) are obtained from polyfluorocyclobutenylphosphoranes (II) by heating:[13,14]



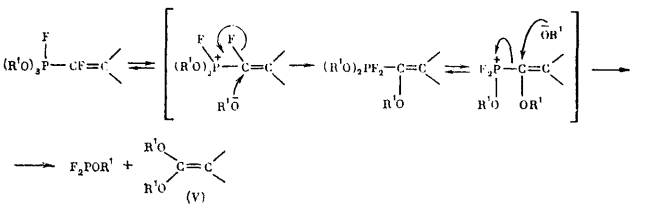
X = F, Cl, Br, I

The alkoxide anion that is formed as an intermediate on decomposition of trialkoxyfluorophosphoranes can, in addition to attacking the alkyl group, react with other electrophilic sites of the molecules, which leads to unusual decomposition of fluorophosphoranes. Thus, pyrolysis of fluorophosphoranes (Ib–g) containing carbalkoxyl groups results in the formation not of fluoroalkenylphosphonates but of acetals of substituted ketones (V) and the trivalent phosphorus compounds—alkyl phosphorodifluoridites:[15,17,18,21]

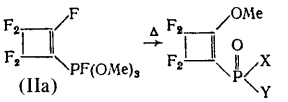


Y = CF_3, COOR

Such a marked difference is probably due to the much greater electrophilicity of the carbon atom in the CF= group in phosphoranes (Ib–g), obtained from perfluoromethacrylates or difluoromethylenemalonates compared to phosphorane (Ia) obtained from perfluoroisobutylene (cf. Ref.22). During pyrolysis it is not the alkyl group but the β-carbon atom of the "acrylic" system that is attacked by the alkoxide anion. As a result of "vinyl" substitution of the geminal fluorine atom a new phosphorane is formed, in which the fluorine atom and alkoxy group have exchanged places. This phosphorane dissociates again into an R^1O^- anion and quasiphosphonium cation; repeated attack by R^1O^- on the β-carbon atom leads to the splitting of the molecule into acetal (V) and alkyl phosphorodifluoridite

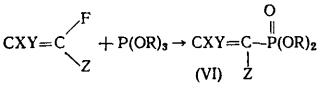


Attack by alkoxide anion on the sp^2-hybridised carbon atom leading to an exchange of substituents between these atoms and the phosphorus atoms has also been detected in the thermal decomposition of perfluorocyclobutenyltrimethoxyfluorophosphorane (IIa).[13,14] However, in this case a vinyl fluorine atom is replaced, the C–P bond does not break, and as a result 2-alkoxytetrafluorocyclobutenyl phosphonic acid derivatives are formed:



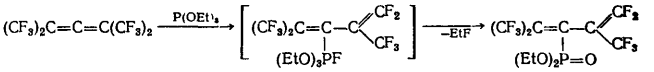
X, Y = F, OMe

In the reactions of fluoroolefins with trialkyl phosphites the fluorophosphoranes formed as intermediates have in a majority of cases not been isolated; heating of the initial compounds gives esters of polyfluoroalkenylphosphonates. Thus, the syntheses of the respective α,β-unsaturated phosphonates (VI) have been reported from tetrafluoroethylene,[20,23,24] trifluorovinyl chloride,[24] trifluorovinyl iodide,[25] perfluoropropylene,‡[23,24,26] perfluoroisobutylene,[23,24] monohydroperfluorobutylene,[27] and ethoxyperfluoroisobutylene:§[27]

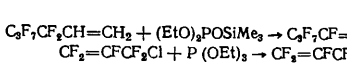


	(a)	(b)		(c)	(d)				(e)	
X=	F	F	Cl	I	CF_3	CF_3	CF_3	CF_3	CF_3	CF_3
Y=	F	F	F	F	F	F	CF_3	CF_3	CF_3	CF_3
Z=	F	F	F	F	F	F	F	F	H	OEt
R=	Et	iso-Pr	Et	iso-Pr	Et	iso-Pr	iso-Pr	Bu	Et	Et

Reaction of *tetrakis*(trifluoromethyl)allene gives the corresponding 1,3-dienyl-2-phosphonate probably by an S_N2' reaction:[28]



Nonafluorohexene[29] and perfluoroallyl chloride[30] undergo similar reactions:



Trifluorovinyl iodide reacts with $(iso\text{-}PrO)_3P$ or $(EtO)_2POSiMe_3$ to form phosphonate (VIc) or $ICF=CFPO(OEt)_2$. When phosphite is in excess, products derived from substitution of the

‡ In the reaction of perfluoropropylene with triethyl phosphite (130–140 °C), phosphonofluoridate $CF_3CF=CFPF(O)OEt$ is formed in addition to ester (VId).[13]

§ Ethoxyperfluoroisobutylene also shows alkylating properties towards triethyl phosphite.[32]

fluorine and iodide atoms are obtained—*bis*-phosphonates (VII).[25,31] *bis*-Phosphonate (VIIa) is also formed by the action of $(EtO)_2POSi.Me_3$ on tetrafluoroethylene[31]

$$(RO)_2\overset{O}{\overset{\|}{P}}CF=CF\overset{O}{\overset{\|}{P}}(OR)_2,\ R = Et\,(a),\ iso\text{-}Pr\ (b)$$
(VII)

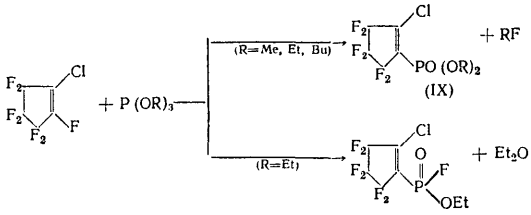
Halogen-substituted polyfluoroalkanes are sometimes used as starting materials for the preparation of polyfluoroalkenylphosphonates:[33,34]

$$RCF(X)-CY_2(Cl) \xrightarrow{P(OEt)_3\ [-XCl]} [RCF=CY_2] \xrightarrow{P(OEt)_3\ [-EtY]} RCF=CYPO(OEt)_2$$
(VIII)

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

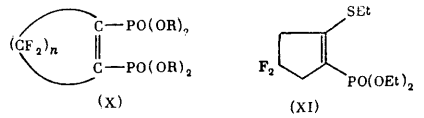
In this case fluoroolefins are evidently formed as intermediates. The formation of the fluoroolefin $CFCl_2CF_2CF=CF_2$ has been demonstrated, for example, in the reaction of 1,2,4,4-tetrachloroperfluorobutane with triethyl phosphite.[3]

1-Chloroperfluorocyclopentene reacts with trialkyl phosphites to give 2-chloroperfluorocyclopenteneylphosphonates (IX). When triethyl phosphite is used, Et_2O and phosphonofluoridate are also formed:[36]



Products from the substitution of both chlorine atoms (X) are obtained from 1,2-dichloroperfluorocycloalkenes.[10] However, reaction of dichloroperfluorocyclopentene with triisopropyl phosphite gives exclusively the monosubstitution product (IX), where R = iso-Pr. Evidently steric hindrance plays an important role in substitution of the second halogen atom.

In the reaction of 1-ethylthio-2-chloroperfluorocyclopentene with triethyl phosphite the corresponding phosphonate (XI) is obtained.

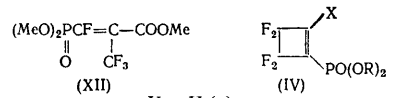


$n = 2-4$; R = Me, Et, Bu, $CH_2=CHCH_2$

Neutral phosphonites and phosphinites react with flouroolefins in a similar manner to trialkyl phosphites, giving perfluoroalkenylphosphinates and perfluoroalkenylphosphine oxides.[24,38]

Dialkyl phosphites usually react with fluoroolefins to form addition products.[39] However, in some cases "vinyl" substitution products are also formed. Thus, when perfluoromethacrylate reacts with dimethyl phosphite the unsaturated phosphonate (XII) is obtained.[15] The mechanism of this reaction is not clear. The possibility cannot be excluded that here, as in certain other cases, an addition product is initially formed, then undergoes dehydrofluorination by the action of dialkyl phosphite.

Polyfluorocyclobutenylphosphonates (IV) are formed from polyfluorocyclobutenes and dialkyl phosphites by irradiation.[39]



X = H (a), F, Cl, OR

Sodium dialkyl phosphite reacts with terminal perfluoroolefins by replacing one of the fluorine atoms in the difluoromethylene group:[8]

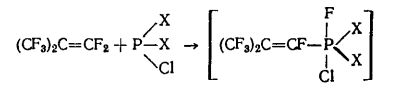
$$R_FCF=CF_2 + NaOP(OEt)_2 \rightarrow R_FCF=CFPO(OEt)_2$$
$$R_F = n\text{-}C_6F_{13},\ n\text{-}C_7F_{15}$$

The substitution of both vinyl fluorine atoms on treatment with salts of acid esters of phosphorus or methylphosphorous acids has been reported for perfluorosiobutylene,[40] in a similar manner to reactions of this fluoroolefin with certain other nucleophiles:[41]

$$(CF_3)_2C=CF_2 + NaOP(X)OR \rightarrow (CF_3)_2C=C[P(O)(X)OR]_2$$
X = RO, Me

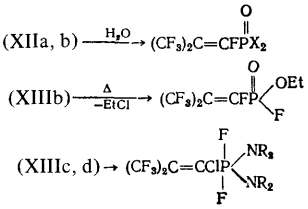
However, there is some doubt about this result since the IR spectra ($\nu_{C=C}$ at 1745 cm^{-1}) are apparently not consistent with the proposed *bis*-phosphonate and *bis*-phosphinate structures.

The vinyl fluorine atom in perfluoroisobutylene is replaced by the action of certain acid chlorides of trivalent phosphorus.[42] The intermediate formation of fluorophosphoranes (XIII) is suggested here:



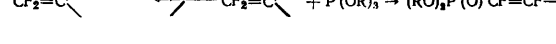
X = Et (a), OEt (b), NMe_2 (c), NEt_2 (d)

Dialkyl- and dialkoxy-fluorochlorophosphoranes (XIIIa, b) are hydrolysed with very great ease to the phosphine oxide or phosphonate respectively. For dialkoxy derivative (XIIIb) in the complete absence of moisture the reaction is accompanied by the liberation of alkyl chloride and the formation of phosphonofluoridate. Diamino derivatives (XIIIc, d) are isomerised to α-chloro-substituted difluorophosphoranes:



In this case the fluorine and chlorine atoms exchange places [the mechanism of this reaction is possibly similar to the mechanism for exchange of fluorine atoms and alkoxy groups in the thermal decomposition of trialkoxyfluorophosphoranes (Ib–g), see above].

Thus, reaction of fluoroolefins with phosphites is a general method for the synthesis of fluoroalkenylphosphonates with the olefin double bond in the α,β-position. However, in this case compounds with an internal double bond are formed since the mechanism for "vinyl" substitution in fluoroolefins usually makes these reactions unsuitable for the preparation of "terminal" fluoroalkenylphosphonates containing the $CF_2=\overset{|}{C}-P$ fragment:



An exception to this could be the reaction of trialkyl phosphites with tetrafluoroethylene, which, according to Ref.24, gives trifluorovinylphosphonates (VIa, b). However, these compounds apparently cannot be obtained from tetrafluoroethylene in satisfactory yield, since they readily react further with neutral phosphites[31] (see section III, 2e). The method used for preparing trifluorovinylphosphonates is given in section II, 3.

2. Formation of C=C Double Bond by Elimination

Like their nonfluorinated analogues[1] many fluorine-containing alkenylphosphonates are obtained by dehalogenation or dehydrohalogenation of the appropriate unsaturated halogenated derivatives. Thus, when products of the radical addition of dialkyl phosphites to dichlorodifluoroethylene or trichlorofluoroethylene are treated with zinc in alcohol, fluorine-containing vinylphosphonates are formed:[43,44]

$$CFCl{=}CX_2 + HPO(OR)_2 \rightarrow CHX_2CFClPO(OR)_2 \xrightarrow{Zn} CHX{=}CFPO(OR)_2$$
$$X = F,\ Cl;\ R = Me,\ Et,\ n\text{-}Pr$$

Dechlorination of the dichloro-substituted ester (XIV) with metallic zinc in ether gives an adduct of zinc chloride with unsaturated ester:[45]

$$ClCF_2{-}\underset{\displaystyle CF_3}{\underset{|}{C}}Cl{-}PO(OMe)_2 \xrightarrow{Zn} CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}PO(OMe)_2 \cdot ZnCl_2$$
(XIV)

Trihaloethylphosphonates (XV)¶ are fairly readily dehydrochlorinated with triethylamine or potassium *tert*-butoxide to form dihalovinylphosphonates (XVI):[46–48]

$$YCH_2\underset{\displaystyle Cl}{\underset{|}{C}}XPO(OEt)_2 \xrightarrow[-HCl]{} YCH{=}CXPO(OEt)_2$$
(XV) (XVI)
X, Y = F, Cl

Dehydrofluorination of 2,2-difluoroethylphosphonates using sodium alkoxides gives various 2-fluorovinylphosphonates:[9]

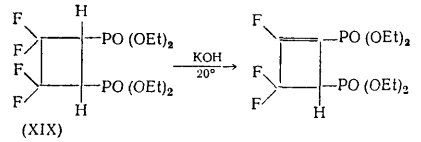
$$HCF_2CH_2PO(OR)_2 \xrightarrow[-HF]{} HCF{=}CHPO(OR)_2$$
$$R = Me,\ Et,\ C_5H_{11}$$

2-Fluorovinylmethylphosphonate is synthesised in the same manner.[9]

Unsaturated α-phosphoryloxyphosphonates (XVIII) are obtained from α-*H*-α-phosphoryloxyphosphonates (XVII):[49]

$$R_FCF_2CH\begin{matrix}OPO(OR)_2\\PO(OR)_2\end{matrix} \xrightarrow{(iso\text{-}Pr)_2NLi} R_FCF{=}C\begin{matrix}OPO(OR)_2\\PO(OR)_2\end{matrix}$$
(XVII) (XVIII)

The product (XIX) of the radical addition of diethyl phosphite to 2-monohydroperfluorocyclobutenylphosphonate is dehydrofluorinated with alkali under mild conditions:[39]



(XIX)

For the dehydrofluorination of 2,2,3,3-tetrafluorocyclobutyl phosphonate see section III, 2e.

The reaction of hexafluoroisopropylphosphonates (XX) with $Et_3N.BF_3$ adducts under mild conditions gives pentafluoroisopropenylphosphonates (XXI):[50,51]

$$(CF_3)_2C\underset{S}{\overset{S}{\diagup\diagdown}}C(CF_3)_2 \xrightarrow{P(OR)_3} (CF_3)_2C{=}P(OR)_3 \xrightarrow{HCl} (CF_3)_2CHPO(OR)_2 \rightarrow$$
(XXII) (XX)
$$\xrightarrow[-Et_3\overset{+}{N}H\ \bar{B}F_4]{Et_3N\cdot BF_3} CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}PO(OR)_2$$
(XXI)
R = Me (a), Et (b)

Apart from 1,2-elimination of halogens or hydrogen halides, fluoroalkenylphosphonates can be obtained by 1,4-elimination of alkyl fluorides from P-alkoxy-substituted fluorine-containing phosphorus ylides. When hexafluoroisopropylidenetriethyoxyphosphorane (XXIIb) is heated with a catalytic quantity of boron trifluoride etherate, ethyl fluoride, and pentafluoroisopropenylphosphonate (XXIb)† are formed:[51]

$$(CF_3)_2C{=}P(OEt)_3 \xrightarrow[Et_2O\cdot BF_3]{} CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}PO(OEt)_2 + EtF$$
(XXIIb) (XXIb)

This reaction is similar to the conversion of alkoxypolyfluoroisobutylenes $(CF_3)_2C{=}CXOR$ to perfluoromethacrylic acid derivatives

$$CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}COX$$ [21].

1,4-Elimination of alkyl fluoride evidently occurs in stages. Initially the Lewis acid (BF_3) removes a fluoride anion from the phosphorus ylide to form an unstable adduct (XXIII) containing a mesomeric cation. This adduct readily decomposes to ethyl fluoride and an adduct (XXIV) of unsaturated phosphonate with boron trifluoride. The latter is converted to the final product—free phosphonate (XXIb) by the action of another molecule of phosphorus ylide (XXIIb), which in the process again gives adduct (XXIII), and so on:[51]

$$(XXIIb) \xrightarrow{BF_3} CF_2{\cdots}\underset{\displaystyle CF_3}{\overset{+}{\underset{|}{C}}}{\cdots}P(OEt)_3\ \bar{B}F_4 \xrightarrow[-EtF]{} CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}PO(OEt)_2\cdot BF_3 \rightarrow$$
(XXIII) (XXIV)
$$\xrightarrow{(XXIIb)} CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}PO(OEt)_2 + (XXIII)$$
(XXIb)

Each stage of this scheme has been confirmed experimentally.

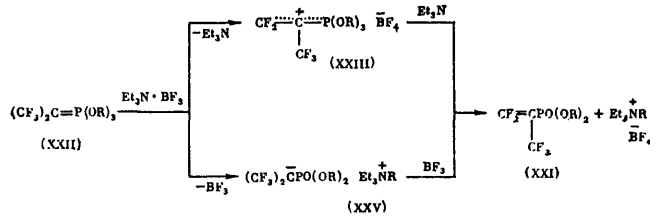
The *bis*-trimethylsilyl ester of pentafluoroisopropenylphosphonic acid (XXIc) is obtained by the direct reaction of *tris*(trimethylsilyl) phosphite with hexafluorothioacetone dimer, and also from phosphorus ylide (XXIIa) and trimethylsilyl iodide:[52]

$$(CF_3)_2C\underset{S}{\overset{S}{\diagup\diagdown}}C(CF_3)_2 \xrightarrow[-(Me_3SiO)_4PS]{(Me_3SiO)_4P} [(CF_3)_2C{=}P(OSiMe_3)_3] \xrightarrow{-Me_3SiF}$$
$$(CF_3)_2C{=}P(OMe)_3 \xrightarrow[-MeI\ -Me_3SiF]{Me_3SiI} CF_2{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}PO(OSiMe_3)_2$$
(XXIIa) (XXIb)

¶ Obtained as mixtures of stereoisomers by treatment of the olefins FCH=CHF and FCH=CHCl with phosphorus trichloride and oxygen and subsequent ethanolysis of the reaction mixture.[48]

† Under similar conditions trimethoxyphosphorane $(CF_3)_2C{=}P(OMe)_3$ (XXIIa) rearranges to the saturated phosphonate $(CF_3)_2C(Me)PO(OMe)_2$.[51]

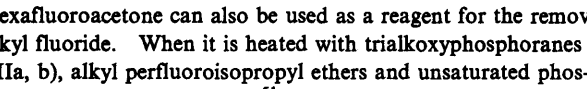
It seems that the most convenient method for obtaining pentafluoroisopropenylphosphonic acid derivatives is removal of alkyl fluoride from phosphorus ylides (XXII) with an equimolar quantity of $Et_3N.BF_3$ adduct:[51]



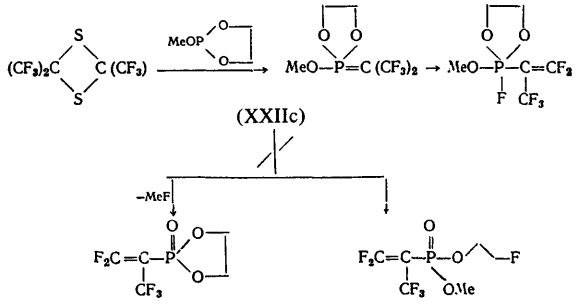
In the process tetraalkylammonium fluoroborates are formed together with phosphonates (XXI). The reaction may occur by one of two pathways. The first of them assumes an initial elimination of fluoride ion to give adduct (XXIII) followed by the transfer of alkyl to amine, the second assumes initial dealkylation followed by elimination of fluoride ion from the mesomeric carbanion of tetraalkylammonium salt (XXV).[51]

Amide $CF_2=C(CF_3)PO(NEt_2)_2$ is similarly obtained from alkoxydiaminophosphorus ylide $(CF_3)_2C=P(OEt)(NEt_2)_2$.[45]

Hexafluoroacetone can also be used as a reagent for the removal of alkyl fluoride. When it is heated with trialkoxyphosphoranes (XXIIa, b), alkyl perfluoroisopropyl ethers and unsaturated phosphonates (XXIa, b) are formed:[51]



In contrast to trialkoxyphosphorus ylides (XXIIa, b), 2-(hexafluoroisopropylidene)-2-methoxy-1,3,2$\lambda^5\sigma^4$-dioxaphospholan (XXIIc) does not eliminate alkyl fluoride but rearranges under mild conditions to 2-(pentafluoroisopropenyl)-2-fluoro-2-methoxy-1,3,2$\lambda^5\sigma^4$- dioxaphospholan:[53]

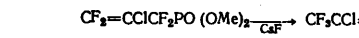


The methods based on elimination of halogens, hydrogen halides, or alkyl halides from saturated phosphonates or alkoxyphosphorus ylides have considerable potential for the preparation of fluoroalkenyl phosphonates, although they have not so far been developed to a sufficient extent. It should be emphasised that when these methods are used both "internal" and "terminal" fluoroalkenylphosphonates can be obtained.

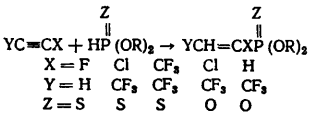
3. Other Methods

Apart from the two main synthetic methods described above, fluoroalkenylphosphonates can also be obtained by a variety of methods, which are based on the introduction of a fluorine atom, formation of a C–P bond, formation of a C=C bond by means of Wittig–Horner reactions, various rearrangements, etc.

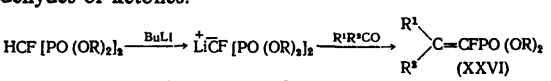
2-Chlorotetrafluoropropenylphosphonate is obtained by rearrangement of 2-chlorotetrafluoroallylphosphonate:[54]



Treatment of fluorine-containing acetylenes with acid phosphites and phosphorothioites gives the corresponding fluoroalkenylphosphonates and fluoroalkenylthiophosphonates:[55]

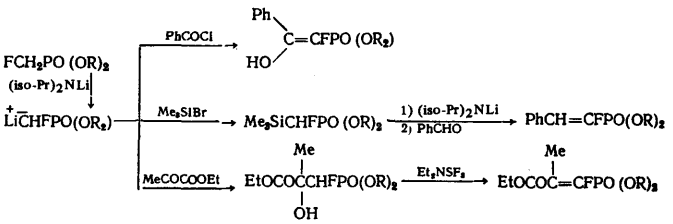


The Wittig–Horner reaction is used to obtain α-fluorovinylphosphonates (XXVI) from tetraalkyl fluoromethylene-*bis*-phosphonates and aldehydes or ketones:[56]

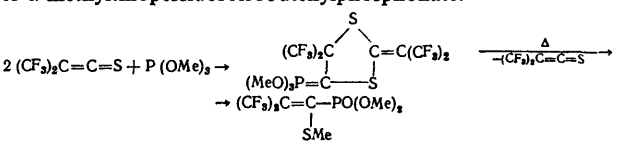


R = iso-Pr; R^1 = H, Me; R^2 = H, Me, iso-Pr, Ph, etc.

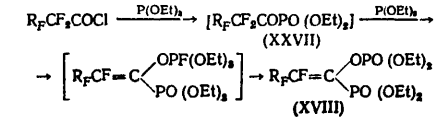
The lithium derivative obtained from dialkyl fluoromethylphosphonate is also used for the synthesis of unsaturated α-fluorophosphonates:[57]



Reaction of *bis*(trifluoromethyl)thioketen with trimethyl phosphite gives α-methylthioperfluoroisobutenylphosphonate:[58]

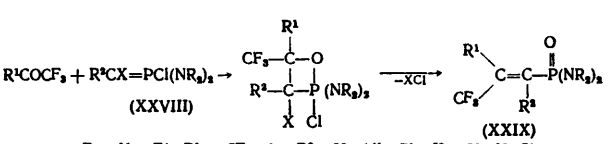


An interesting method for obtaining α-substituted fluorine-containing alkenylphosphonates (XVIII) is that based on the reaction of perfluorocarboxylic acid chlorides with triethyl phosphite:[49,59–62]



Acylphosphonate (XXVII) formed as an intermediate cannot be isolated from the reaction as it immediately undergoes a rapid reaction with another molecule of phosphite. The mobility of the phosphate group in compounds (XVIII) opens up extensive possibilities of synthesising various organofluorine compounds either containing or not containing a phosphorus atom (see below).

The reaction of chlorophosphonium ylides (XXVIII) with fluoroketones gives fluoroalkenylphosphonic acid amides (XXIX):[63–64]

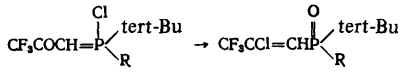


R = Me, Et; R^1 = CF_3, Ar; R^2 = H, Alk, Ph; X = H, Me_3Si

P-Chloro-substituted oxaphosphetans are formed in the process as intermediates.

Phosphinic acid amides and phosphine oxides are obtained in a similar manner.[63–66]

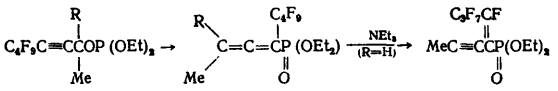
Chlorophosphonium acylmethylides undergo an interesting rearrangement:[67]



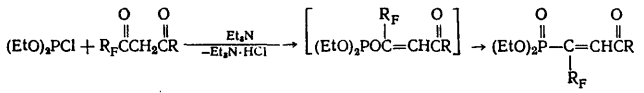
R = tert-Bu, NEt_2

The oxygen and chlorine atoms exchange places as a result of reaction.

Rearrangement of diethyl alkynyl phosphites (XXX) gives fluorine-containing allenylphosphonates; when R = H a further dehydrofluorination is possible:[68]

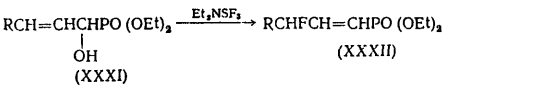


Reaction of fluorine-containing β-diketones with diethyl phosphorochloridite leads to the synthesis of α-perfluoroalkyl-γ-ketovinylphosphonates, which are probably formed by rearrangement of the corresponding phosphites:[69]



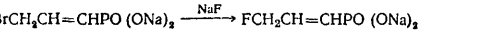
$R_F = CF_3$, C_3F_7; R = Me, tert-Bu

Monofluoroalkenylphosphonate derivatives can be obtained from unsaturated phosphonate compounds by standard reactions for the introduction of fluorine atoms. Thus, fluoroalkenylphosphonates (XXXII) are synthesised by treatment of hydroxyphosphonates (XXXI) with (N-ethylethanaminato)trifluorosulphur (DAST).[70]

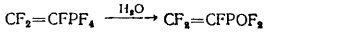


(XXXI) (XXXII)

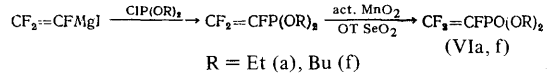
The salt of 3-fluoropropenylphosphonic acid is obtained by the replacement of a bromine atom with a fluorine atom:[71]



When $C_2F_5SiF_3$ is pyrolysed in the presence of PF_3, trifluorovinyltetrafluorophosphorane is formed, hydrolysis of which gives trifluorovinylphosphonic difluoride:[72]



Reaction of trifluorovinylmagnesium iodide with dialkyl phosphorochloridates followed by oxidation of the phosphonites formed gives trifluorovinylphosphonates (VIa, f):[31]



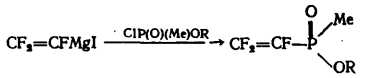
(VIa, f)

R = Et (a), Bu (f)

A similar sequence of reactions has been used previously to synthesise vinylphosphonates.[73]

The direct formation of phosphonates $RPO(OR^1)_2$ from organometallic compounds RM and dialkyl phosphorochloridates ClPO.$(OR^1)_2$ is usually complicated by side reactions.[3] It was not possible to obtain trifluorovinylphosphonate (VIa) by reaction of trifluoromagnesium iodide with diethyl phosphorochloridate.[45]

However, the preparation of trifluorovinylmethylphosphinates by reaction of trifluorovinylmagnesium iodide with alkyl methylphosphonochloridates has been reported:[40]

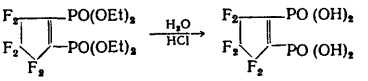


Among the methods for obtaining fluoroalkenylphosphonic acid derivatives it is also possible to include many reactions of those compounds which lead to products in which the C=C bond and $P(O)X_2$ group are retained. These reactions together with other conversions of fluoroalkenylphosphonates are examined in the next chapter.

III. CHEMICAL PROPERTIES

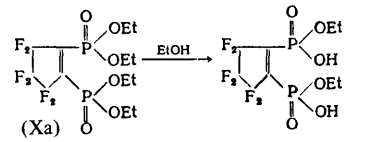
1. Modification of Phosphonate Groups

Fluorine-containing unsaturated phosphonate esters and also phosphinate esters are converted in the usual way to free acids by acid hydrolysis,[36,74–77] for example:



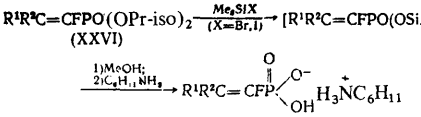
(Xa)

When *bis*-phosphonate (Xa) is boiled with ethanol, *bis*-phosphonic acid ester is formed:[74, 75]



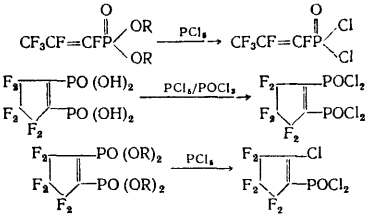
(Xa)

For the conversion of α-fluoroalkenylphosphonates (XXVI) to the corresponding acids, a reaction with trimethylsilyl halides is used followed by alcoholysis (the acids are isolated as their cyclohexylammonium salts):[56]



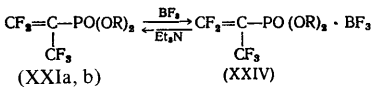
(XXVI)

Reaction of fluoroalkenylphosphonic acids or their esters with phosphorus pentachloride gives the corresponding acid chlorides.[13,36,38,74,75] In the case of *bis*-phosphonates replacement of one of the phosphonate groups by a chlorine atom also sometimes occurs:[36,74]



The chlorine atoms in fluoroalkenylphosphonic acid chlorides can be replaced with fluorine atoms in the usual way by treatment with SbF_3 [13] and replaced with hydroxy or alkoxy groups by treatment with water or alcohol.[36,74–76]

Despite the high electrophilicity of the pentafluoroisopropenyl residue, the phosphoryl group in pentafluoroisopropenylphosphonates displays its own basic properties. Esters (XXI) readily form adducts with the Lewis acids $ZnCl_2$ (see section II,2) and BF_3. When treated with triethylamine, the BF_3 adduct (XXIV) is converted to free phosphonate (XXI):[51]



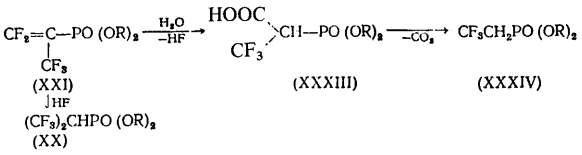
(XXIa, b) (XXIV)

2. Reactions Involving the Fluoroalkenyl Group

The electron-withdrawing effect of the phosphonate groups and fluorine atoms causes the C=C bond in fluoroalkenylphosphonates to have considerable electrophilicity. Hence they react quite readily with various nucleophiles, giving products from the substitution of the halogen atoms on the sp^2-hybridised carbon atom or addition products on the C=C bond.‡ There is considerable interest in the conversions that lead to cleavage of the C–P bond; these sometimes prove to be convenient methods for the synthesis of organofluorine compounds. Reactions with electrophiles are generally less typical for fluoroalkenylphosphonates, although there are examples of addition of halogens and hydrogen halides to the C=C bond.

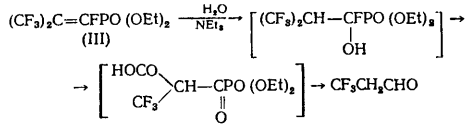
(a) Reactions with Water, Alcohols, and Amines

The highly electrophilic pentafluoroisopropenylphosphonates (XXI), the "phosphoric analogues of perfluoromethacrylates"§ readily react with water, and as a result of hydrolysis of the difluoromethylene group form unstable carboxyphosphonates (XXXIII), decarboxylation of which give trifluoroethylphosphonates (XXXIV):[80]



The reaction is complicated by the fact that the initial unsaturated phosphonate adds on liberated hydrogen fluoride to give dialkyl hexafluoroisopropylphosphonate (XX).

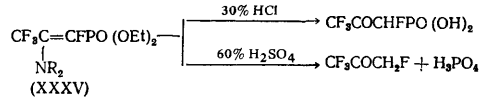
The less electrophilic perfluoroisobutenylphosphonate (III) reacts with water in the presence of triethylamine and is converted to trifluoropropionaldehyde, with the addition product of water to the multiple bond probably being formed as an intermediate:[27]



In this case the orientation for addition of water is determined by the strong electron-withdrawing action of the two trifluoromethyl groups (see below).

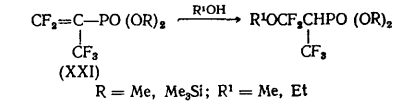
When perfluoroalkenylphosphonates are treated with aqueous alkalis, the fluorine atoms are removed as anions. By determining the quantity of fluoride anions eliminated, Knunyants, Sterlin, et al.[24] conclude that in the reaction of trifluorovinylphosphonate the C–P bond is preserved, while for pentafluoropropenyl- and perfluoroisobutenyl-phosphonates a "haloform" decomposition occurs.

In contrast to perfluoroalkenylphosphonates, enaminophosphonate (XXXV) is readily hydrolysed in acidic medium, with either ketophosphonic acid or tetrafluoroacetone being formed depending on the conditions:[27]



(XXXV)

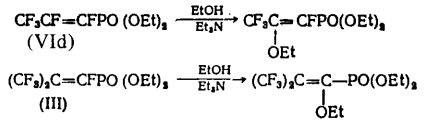
Pentafluoroisopropenylphosphonates (XXIa, c) react with alcohols under mild conditions to form addition products—α-*H*-β-alkoxypentafluoroisopropylphosphonates:[45,52,80]



On the other hand, trifluorovinylphosphonate (VIa) does not react with alcohol even after prolonged heating (~100 °C).[31]

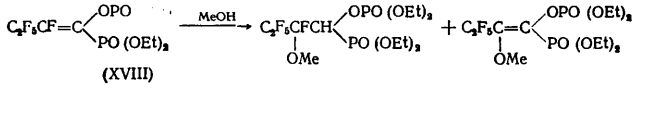
The completing reaction of pentafluoroisopropenylphosphonate (XXIa) and methyl perfluoromethacrylate has been used to demonstrate that these compounds have similar reactivity.[80]

Pentafluoropropenylphosphonate (VIa) and pentafluoroisobutenylphosphonate (III) react with ethanol in the presence of triethylamine.¶ In the first case a vinyl fluorine atom at the β-position is replaced by an alkoxy group, in the second case a fluorine atom at the α-position is replaced:[27]



Here, as in the reactions with water and secondary amines (see below) the direction of nucleophilic attack depends on the competition between the trifluoromethyl and phosphonate groups for conjunction with the C=C double bond; one CF_3 group cannot compete effectively with the $PO(OR)_2$ group, but the electron-withdrawing effect of two trifluoromethyl groups can "overcome" the effect from the $PO(OR)_2$ group.†[27]

α-Phosphoryloxy-substituted perfluoroalkenylphosphonate (XVIII) reacts with methanol to form a mixture of addition and substitution products:[59]



(XVIII)

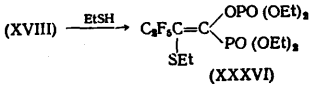
‡ Nucleophilic additions to nonfluorinated alkenylphosphonates have become widely known.[1] However, vinylphosphonates are somewhat less reactive than the analogous acrylates.[78,79]

§ See Ref.21 concerning the electrophilicity of perfluoromethacrylates.

¶ In the reaction of (III) with ethanol in the presence of EtOK, the fluorine atoms are completely eliminated as anions.[27]

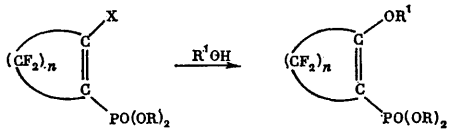
† For a similar competition between trifluoromethyl groups and carbalkoxyl groups, see Ref.81.

However, in the reaction with mercaptan only the product (XXXVI) from substitution of the vinyl fluorine atom is obtained.[59]

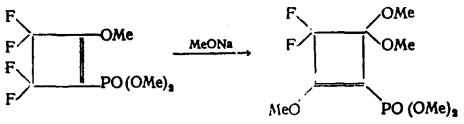


(XXXVI)

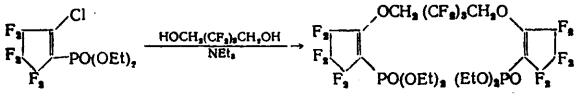
Reaction of unsaturated cyclic fluorine-containing phosphonates with alcohols leads to replacement of the vinyl halogen atoms.[14,39,82] Further substitution of the allyl fluorine atoms by alkoxy groups is also possible:[14]



$n = 2,3$; X = F, Cl, Br

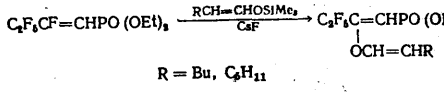


2-Chloroperfluorocyclopentenylphosphonate reacts with hexafluoropentanediol in the presence of triethylamine to form *bis*-phosphonate:[82]



In free 2-chloroperfluorocyclopentenylphosphonic acid the chlorine atom is stable towards the action of bases.[82]

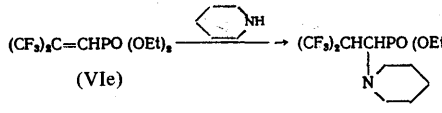
Replacement of a vinyl fluorine atom by a vinyloxy group occurs when α-*H*-perfluorobutenylphosphonate reacts with trimethylsilyl enol ethers:[83]



R = Bu, C_6H_{11}

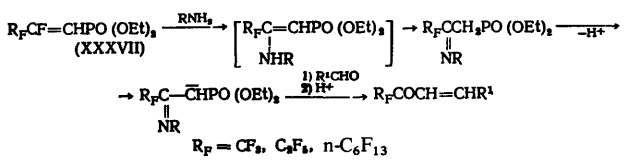
In the reactions of fluoroalkenylphosphonates with amines, depending on the structure of the initial compounds addition products are formed or substitution of the vinyl halogen atom or further conversions occur.

α-*H*-perfluoroisobutenylphosphonate (VIe) adds on a piperidine molecule to the double bond, with the nucleophile attacking the α-position:[27]



(VIe)

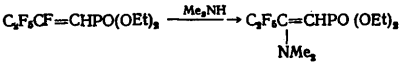
α-*H*-Perfluoroalkenylphosphonates (XXXVII) react with primary amines to form the corresponding imino derivatives evidently by substitution of the vinyl fluorine atom and subsequent rearrangement of the enaminophosphonates:[59]



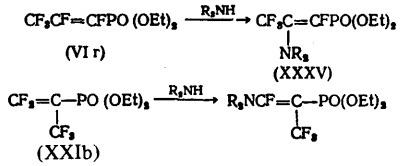
$R_F = CF_3$, C_2F_5, n-C_6F_{13}

Reaction of iminophosphonates with bases gives carbanions that can undergo the Wittig–Horner reaction with aldehydes.[59]

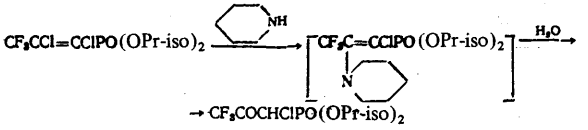
A β-Enaminophosphonate is obtained by the reaction of α-*H*-perfluorobutenylphosphonate with dimethylamine:[59,84]



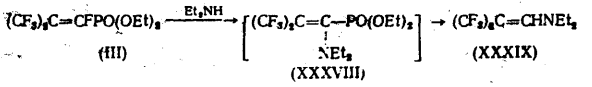
Products from the substitution of the vinyl β-halogen atoms are obtained from pentafluoropropenylphosphonate (VId)‡[38] and pentafluoroisopropenylphosphonate (XXIb):[80]



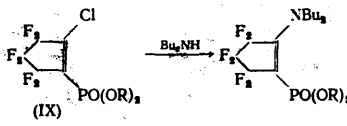
It is reported in one patent[71] that substitution of a vinyl chlorine atom occurred when 1,2-dichloro-3,3,3-trifluoropropenylphosphonate was treated with piperidine; subsequent hydrolysis gave a ketophosphonate:



Reaction of perfluoroisobutenylphosphonate (III) with diethylamine apparently leads to substitution of a vinyl fluorine atom in the α-position, but the unstable enaminophosphonate (XXXVIII) decomposes when treated with excess amine to form enamine (XXXIX):[27]



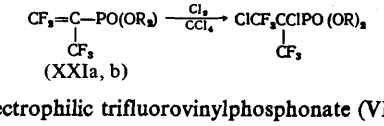
Reaction of unsaturated cyclic phosphonates (IX) with secondary amines gives the corresponding enaminophosphonates:[82]



(IX)

(b) Halogenation and Hydrohalogenation

The electrophilic addition of halogens and hydrogen halides to the C=C double bond is usually hindered when electron-withdrawing groups are introduced into an unsaturated compounds.[85,86] However, despite their high electrophilicity pentafluoroisopropenylphosphonates (XXIa, b) very readily add on chlorine in an inert solvent, and the reaction does not require base catalysis:[87]



(XXIa, b)

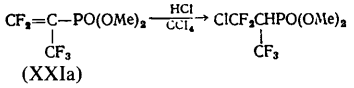
The less electrophilic trifluorovinylphosphonate (VIa) is chlorinated under these conditions much more slowly, which is demonstrated by means of a competing reaction.[31]

---

‡ Methyl(pentafluoropropenyl)phosphinate reacts in a similar way.[38]

It is suggested that the phosphonate group acts as an "internal base" which activates the halogen molecule and transfers the halogenation of the highly electrophilic unsaturated compound to a "nucleophilic pathway".[87]

For a similar reason pentafluoroisopropenylphosphonate (XXIa) readily forms an addition product with hydrogen chloride:§[87]



(XXIa)

In these reactions pentafluoroisopropenylphosphonates behave similarly to perfluoromethacrylic acid dialkylamides (cf. Ref.21).

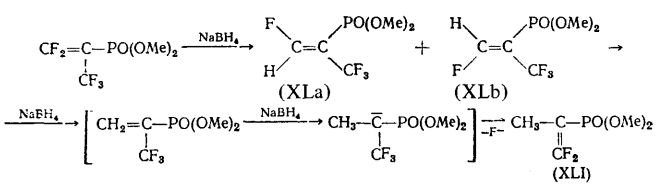
2-Chloroperfluorocyclopentenylphosphonate (IX), when R = Et, decolorises a solution of bromine, while *bis*-phosphonate (X), n = 3, R = Et, does not react with bromine.[77] When tetraallyl perfluorocyclopentenylene-*bis*-phosphonate is brominated, only the C=C bonds in the nonfluorinated allyl fragments react.[10,75]

(c) Reduction and Oxidation

The C=C double bond in fluoroalkenylphosphonate derivatives can be saturated by hydrogenation and oxidation. α-Fluorovinylphosphonates (XXVI) undergo catalytic hydrogenation to give the corresponding phosphonates:[56]

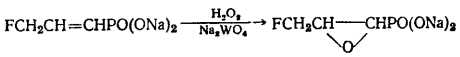
(XXVI)

Reaction of pentafluoroisopropenylphosphonate (XXIa) with sodium borohydride leads to replacement of fluorine atoms by hydrogen. The monohydro derivatives (XLa, b) and trihydro derivatives (XLI) have been identified among the reaction products:[45]



(XLa) (XLb) (XLI)

The formation of the α-oxide from 3-fluoropropenylphosphonate salt has been reported:¶[71]

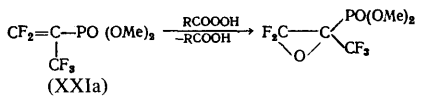


---

§ Chlorine-containing alkynylphosphonates react in a similar manner with hydrogen chloride.[88]

¶ Oxides of nonfluorinated unsaturated phosphonates can be obtained by various methods including epoxidation. Propenylphosphonic acid oxide $CH_3CH\!-\!CHPO(OH)_2$ (phosphonomycin) is an antibiotic.[91]

Pentafluoroisopropenylphosphonate (XXIa) is readily epoxidised when treated with an aromatic peroxyacid in ether:[89,90]



(XXIa)

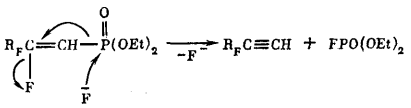
Perfluoromethacrylic acid derivatives behave in a similar manner.[21,89]

2-Chloroperfluorocyclopentenylphosphonate (IX), where R = Et, decolorises a solution of permanganate.[77]

(d) Reactions with Fluoride Ion

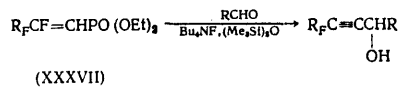
Attack by a fluoride ion can be directed on to either the phosphorus atom or an electrophilic carbon atom of a fluoroalkenylphosphonate depending on its structure.

Thus, α-*H*-perfluoroalkenylphosphonates (XXXVII) when treated with a catalytic quantity of tetrabutylammonium fluoride or caesium fluoride are converted to perfluoroalkylacetylenes:[60,83]



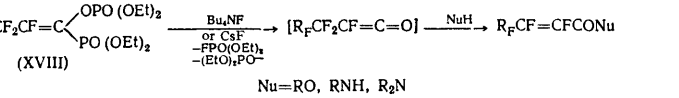
(XXXVII)

In the presence of aldehydes, ethynylcarbinols are formed:[92]



(XXXVII)

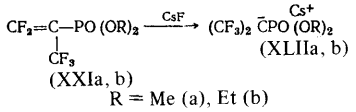
For phosphoryloxyphosphonates (XVIII) cleavage of the C–P bond is also possible. Combined treatment with fluoride anion and alcohol or amine gives α,β-unsaturated carboxylic acid derivatives, with fluorine-containing ketenes probably formed as intermediates:[93]



(XVIII)

Nu=RO, RNH, R_2N

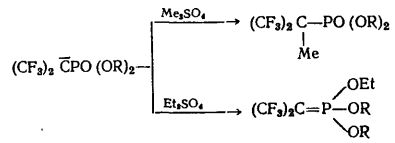
The highly electrophilic pentafluoroisopropenylphosphonates (XXI) add on an F^- anion to the C=C double bond under mild conditions. Treatment with CsF in polar aprotic solvents at low temperatures gives relatively stable solutions of salts (XLII), which contain an α-phosphonate-substituted carbanion:[80]



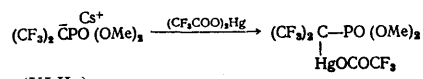
(XXIa, b) (XLIIa, b)

R = Me (a), Et (b)

This mesomeric carbanion can be alkylated on either the carbon atom or oxygen atom:[80]

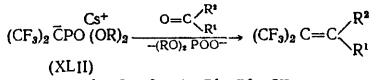


The mercuration of salt (XLIIa) has also been reported:[45]



(XLIIa)

There is considerable interest in the use of salts (XLII) in the Wittig–Horner reaction. On treatment with carbonyl compounds, fluorine-containing olefins are formed:[80]



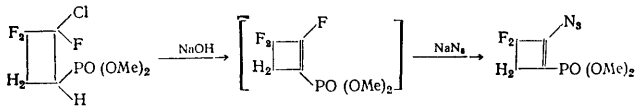
(XLII)

R^1=H, R^2=Ph; R^1=R^2=CF_3

In the Wittig–Horner reaction here a nonstandard method is used to obtain the initial α-phosphonate-substituted carbanion. Instead of the usual deprotonation of α-*H*-phosphonate,[94] use is made of the addition of a nucleophile (F^-) to an α,β-unsaturated phosphonate.†

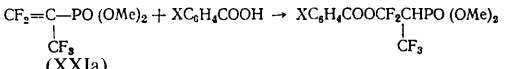
(e) Other Reactions

The action of sodium azide in the presence of alkali on cyclic phosphonate (XLIII) gives an unsaturated azidophosphonate, probably as a result of substitution of the vinyl fluorine atom in the cyclobutenylphosphonate (XLIV) formed as an intermediate:[96]



(XLIII) (XLIV)

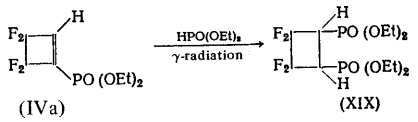
In a similar manner to perfluoromethacrylates,[21,89] pentafluoroisopropenylphosphonate (XXIa) readily adds on carboxylic acids:[80]



(XXIa)

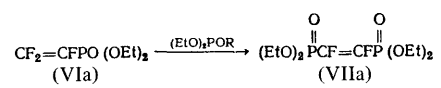
X=H, *m*-Cl

The reaction of 2-*H*-perfluorocyclobutenylphosphonate (IVa) with diethyl phosphite occurs under conditions for radical formation and gives addition product (XIX):[39]



(IVa) (XIX)

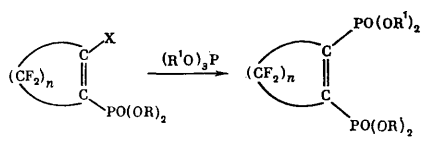
When trifluorovinylphosphonate (VIa) is reacted with neutral phosphites, a vinyl fluorine atom is replaced and *bis*-phosphonate (VIIa) is formed:[31]



(VIa) (VIIa)

R=Et, Me_3Si

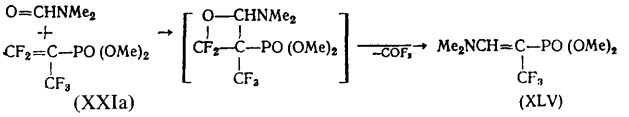
A similar substitution of the vinyl halogen atom also occurs for cyclic unsaturated phosphonates:[14,74]



n=2,3; X=Cl, Br, I

ω-Iodoperfluoroalkenylphosphonates (VIIIa–c) do not react with triethyl phosphite even on heating.[34]

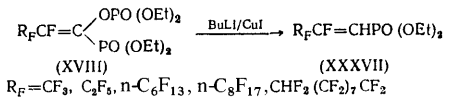
Pentafluoroisopropenylphosphonate (XXIa) reacts with dimethylformamide to give enaminophosphonate (XLV), probably through the intermediate formation of a cycloadduct:[80]



(XXIa) (XLV)

The analogous reactions of perfluoromethacrylic acid derivatives have been widely reported.[21]

α-Phosphoryloxy-substituted phosphonates (XVIII) when treated with butylcopper are converted to α-*H*-perfluoroalkenylphosphonates (XXXVII):[61]



(XVIII) (XXXVII)

R_F=CF_3, C_2F_5, n-C_6F_{13}, n-C_8F_{17}, $CHF_2(CF_2)_7CF_2$

* * *

In the summary presented above the variety of reactions of fluoroalkenylphosphonates, which combine the properties of fluorine-containing olefins and phosphonic acid derivatives, should be noted. There is definite interest in a systematic study of this class of compounds especially since some of them may have practical application.

REFERENCES

1. V.K.Promonenkov and S.Z.Ivin, Uspekhi Khim., 1968, **37**(9), 1577 [Russ.Chem.Rev., 1968(9)].
2. B.I.Ionin, G.M.Bogolyubov, and A.A.Petrov, Uspekhi Khim., 1967, **36**(4), 587 [Russs.Chem.Rev., 1967(4)].
3. D.Purdela and R.Vilceanu, "Chemistry of Organophosphorus Compounds" (Translated into Russian), Izd.Khimiya, Moscow, 1972.
4. B.E.Ivanov and Ya.A.Levin, in "Sintez i Modifikatsiya Polimerov" (The Synthesis and Modification of Polymers), Izd.Nauka, Moscow, 1976, p.72.
5. M.Kato, K.Akiyma, Y.Akasuka, and M.Yamabe, Reports Res.Lab.Asahi Glass Co., 1982, **32**, 117.
6. M.Kato, K.Akiyma, and M.Yamabe, Reports Res.Lab.Asahi Glass Co., 1983, **33**, 135.
7. M.Kato, S.Munekata, and M.Yamabe, 183 ACS Nat.Meeting. Div.Fluor.Chem.(USA), 1982(25).
8. P.Dietrich, G.Angler, U.Gross, K.Lumkwitz, D.Prescher and J.Schulze, BRD P. 2 808 754; Chem.Abs., 1979, **90**, 40551.
9. H.-D.Block, BRD P. 2 535 640; Chem.Abs., 1977, **87**, 23489.
10. A.W.Frank, J.Org.Chem., 1965, **30**, 3663.
11. W.W.Briner and J.S.Widder, US P.3 535 421; Chem. Abs., 1971, **74**, 15734.
12. US P. 4 565 808; [?AISS-Fluorine DWH] AIPS "Ftor", 1987, Set.3, No.501.

† Addition of mercaptides to α-alkoxycarbonylvinylphosphonates has been used in the same way.[95]

13. I.L.Knunyants, V.V.Tyuleneva, E.Ya.Pervova, R.N.Sterlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1964, 1797.
14. G.Bauer and G.Hägele, Z.Naturforsch., 1979, **34b**, 1252.
15. I.L.Knunyants, U.Utebaev, E.M.Rokhlin, et al., Izv.Akad. Nauk SSSR, Ser.Khim., 1976, 875.
16. U.Utebaev, E.M.Rokhlin, E.P.Lur'e, and I.L.Knunyants, Izv. Akad.Nauk SSSR, Ser.Khim., 1975, 1463.
17. U.Utebaev, Candidate's Thesis, Institute of Heteroorganic Compounds, USSR Academy of Sciences, Moscow, 1976.
18. I.L.Knunyants, U.Utebaev, E.M.Rokhlin, et al., Izv.Akad. Nauk SSSR, Ser.Khim., 1976, 895.
19. A.F.Gontar', N.A.Tul'kunova, E.G.Bykhovskaya, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2379.
20. V.V.Tyuleneva, Candidate's Thesis, Institute of Heteroorganic Compounds, USSR Academy of Sciences, Moscow, 1963.
21. E.M.Rokhlin, E.G.Abduganiev, and U.Utebaev, Uspekhi Khim., 1976, **45**(7), 1177 [Russ.Chem.Rev., 1976(7)].
22. E.P.Lur'e, E.G.Gal'pern, N.P.Gambaryan, et al., Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 619.
23. I.L.Knunyants, E.Ya.Pervova, and V.V.Tyuleneva, Dokl. Akad.Nauk SSSR, 1959, **129**, 576.
24. I.L.Knunyants, R.N.Sterlin, V.V.Tyuleneva, and L.N.Pinkina, Izv.Akad.Nauk SSSR, Otdel Khim.Nauk., 1963, 1123.
25. R.Dietrich and G.Hägele, Phosphorus and Sulfur, 1981, **10**, 127.
26. U.von Allwörden and G.-V.Röschenthaler, Chem.-Zeitung, 1985, **109**, 81.
27. I.L.Knunyants, E.Ya.Pervova, and V.V.Tyuleneva, Izv.Akad. Nauk SSSR, Ser.Khim., 1963, 1576.
28. N.P.Gambaryan, D.P.Del'tsova,V.A.Livshchits, and E.G.Ter-Gabrielyan, Izv.Akad.Nauk SSSR, Ser.Khim., 1986, 2344.
29. A.E.Feiring, M.C.Hovey, and S.D.Arthur, J.Fluor.Chem., 1984, **24**, 125.
30. J.C.Moilliet, IX Symp.Intern.Fluor Chim.(France), 1979; AIPC "Ftor" [?AISS-Fluorine DWH], 1980, Set.3, No.826–836.
31. A.A.Kadyrov, E.M.Rokhlin, and M.V.Galakhov, Izv.Akad. Nauk SSSR, Ser.Khim., 1988, 1885.
32. I.L.Knunyants, M.V.Urushadze, and E.M.Rokhlin, Izv. Akad.Nauk SSSR, Ser.Khim., 1971, 1365.
33. B.Boutevin, Y.Hervaud, and Y.Pietrasanta, Phosphorus and Sulfur, 1982, **11**, 373.
34. I.L.Knunyants and E.Ya.Pervova, Izv.Akad.Nauk SSSR, Ser.Khim., 1962, 1409.
35. H.R.Davis, US P.2 742 510.
36. A.W.Frank and C.F.Baranauckas, US P. 3 505 433; Chem. Abs., 1970, **72**, 121705.
37. J.D.Park and O.K.Furuta, Tetrahedron Lett., 1969, 393.
38. S.Z.Ivin, V.K.Promonenkov, and E.A.Fokin, Zhur.Obshch. Khim., 1969, **39**, 1058.
39. T.Ueda, K.Inukai, and H.Muramatsu, Bull.Chem.Soc.Japan, 1969, **42**, 1684.
40. Yu.A.Sizov, Vandidate's Thesis, VAKhZ, Moscow, 1974.
41. Yu.V.Zeifman, E.G.Ter-Gabrielyan, N.P.Gambaryan, and I.L.Knunyants, Uspekhi Khim., 1984, **53**(3), 431 [Russ.Chem. Rev., 1984(3)].
42. I.L.Knunyants, E.G.Bykhovskaya, V.N.Volkovitskii, et al., Zhur.Vses.Khim.Obshch. im Mendeleeva, 1972, **17**, 598.
43. K.Inukai, A.Ueda, and H.Muramatsu, Bull.Chem.Soc.Japan, 1967, **40**, 1288.
44. K.Inukai and A.Ueda, J.P. 15 402; Chem.Abs., 1969, **70**, 68507.
45. A.A.Kadyrov, Candidate's Thesis, Institute of Heteroorganic Compounds, USSR Academy of Sciences, Moscow, 1984.
46. Yu.M.Zinov'ev, T.G.Spiridonova, and L.Z.Soborovskii, Zhur.Obshch.Khim., 1959, **29**, 3594.
47. Yu.M.Zinov'ev and L.Z.Soborovskii, Zhur.Obshch.Khim., 1959, **29**, 3954.
48. C.B.C.Boyce, S.B.Webb, L.Phillips, and U.R.Ager, J.Chem. Soc.Perkin Trans.I, 1974, 1644.
49. T.Ishihara, T.Maekawa, Y.Yamasaki, and T.Ando, J.Fluor. Chem., 1987, **34**, 323.
50. I.L.Knunyants, E.M.Rokhlin, and A.A.Kadyrov, Izv.Akad. Nauk SSSR, Ser.Khim., 1981, 237.
51. A.A.Kadyrov and E.M.Rokhlin, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2583.
52. J.Heine and G.-V.Röschenthaler, Chem.-Zeitung., 1986, **110**, 91.
53. J.Heine and G.-V.Röschenthaler, Chem.Ber., 1987, **120**, 1445.
54. H.Goldwhite, D.G.Rowsell, and C.Valdez, J. Organometal. Chem., 1968, **12**, 133.
55. N.I.Gazieva, A.I.Shchekotikhin, and V.A.Ginsburg, USSR P.225 190; Byul.Izobret., 1968(27), 18.
56. G.M.Blackburn and M.J.Parratt, J.Chem.Soc.Perkin Trans.I, 1986, 1417.
57. G.M.Blackburn and M.J.Parratt, J.Chem.Soc.Perkin Trans.I, 1986, 1425.
58. M.S.Raasch, J.Org.Chem., 1978, **43**, 2500.
59. T.Ishihara, 3. Regular Meeting Sov.-Jap.Fluor.Chem.(Japan), 1983(7).
60. T.Ishihara, T.Maekawa, and T.Ando, Tetrahedron Lett., 1984, **25**, 1377.
61. T.Ishihara, T.Maekawa, Y.Yamasaki, and T.Ando, J.Fluor. Chem., 1986, **34**, 271.
62. T.Ishihara, J.Org.Chem., 1987, **52**, 300.
63. O.I.Kolodiaznyi, Tetrahedron Lett., 1985, **26**, 439.
64. O.I.Kolodyazhnyi D.B.Golokhov, and V.P.Kukhar', Zhur. Obshch.Khim., 1986, **56**, 1035.
65. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1984, **54**, 966.
66. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1986, **56**, 283.
67. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1982, **52**, 447.
68. H.Collet, P.Calas, and A.Commeyras, J.Chem.Soc.Chem. Comm., 1984, 1152.
69. T.V.Khim, E.I.Kiseleva, and A.D.Sinitsa, Zhur.Obshch.Khim., 1987, **57**, 807.
70. G.M.Blackburn and D.E.Kent, J.Chem.Soc.Chem.Comm., 1981, 511.
71. B.G.Christensen, T.R.Beattie, and D.W.Graham, US P.3 822 296; AOPS "Ftor" [?AISS-Fluorine DWM], 1975, Set 4, No.483–492.
72. K.G.Sharp and I.Schwager, Inorg.Chem., 1976, **15**, 1697.
73. M.I.Kabachnik, C.Y.Chang, and E.N.Tsvetkov, Zhur.Obshch. Khim., 1962, **32**, 3351.
74. A.W.Frank, J.Org.Chem., 1966, **31**, 1521.
75. A.W.Frank and C.F.Baranauckas, US P. 3 678 100; Chem.Abs., 1972, **77**, 140277.
76. A.W.Frank and C.F.Baranauckas, US P. 3 629 326; Chem.Abs., 1972, **77**, 5606.
77. A.W.Frank, J.Org.Chem., 1966, **31**, 1917.
78. A.N.Pudovik and R.G.Kuzovleva, Zhur.Obshch.Khim., 1965, **35**, 354.
79. A.N.Pudovik, G.E.Yastrebova, V.I.Nikitina, and Yu.Yu.Samitov, Zhur.Obshch.Khim., 1968, **38**, 292.

80. A.A.Kadyrov and E.M.Rokhlin, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 1353.
81. I.L.Knunyants and Yu.A.Cheburkov, Izv.Akad.Nauk SSSR, Otdel Khim.Nauk., 1961, 1057.
82. A.W.Frank, J.Org.Chem., 1966, **31**, 1920.
83. T.Ishihara, Y.Yamasaki, and T.Ando, Tetrahedron Lett., 1985, **26**, 79.
84. Y.Yamasaki, T.Maekawa, T.Ishihara, and T.Ando, Chem. Lett., 1985, 1387.
85. P.B.D.de la Mare and R.Bolton, in "Electrophilic Additions to Unsaturated Systems" (Translated into Russian), Izd.Mir, Moscow, 1968, p.140.
86. A.Roedig, Methoden der org.Chemie (Houben-Weyl). B. V/4. Stuttgart: G.Thieme Verlag, 1960, p.38.
87. Yu.V.Zeifman, L.T.Lantseva, A.A.Kadyrov, and E.M.Rokhlin, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 1116.
88. V.A.Garibina, A.V.Dogadina, V.I.Zakharov, et al., Zhur. Obshch.Khim., 1979, **49**.
89. A.A.Kadyrov, E.M.Rokhlin, and I.L.Knunyants, Izv.Akad. Nauk SSSR, Ser.Khim., 1982, 2344.
90. A.A.Kadyrov and E.M.Rokhlin, in "IV Vsesoyuznaya Konferentsiya po Khimii Ftororganicheskikh Soedinenii" (Proceedings of the IVth All-Union Conference on the Chemistry of Organofluorine Compounds), Tashkent, 1982, p.210.
91. D.Redmore, Chem.Revs., 1971, **71**, 315.
92. T.Ishihara, T.Maekawa, and T.Ando, Tetrahedron Lett., 1986, **27**, 357.
93. T.Ishihara, Y.Yamasaki, and T.Ando, Tetrahedron Lett., 1986, **27**, 2879.
94. W.S.Wadsworth, Org.React., 1977, **25**, 73.
95. M.F.Semmelhack, J.C.Tomesh, M.Czarny, and S.Boettger, J.Org.Chem., 1978, **43**.
96. G.Buhr, US P. 2 349 108; Chem.Abs., 1975, **83**, 113750.

Nesmeyanov Institute of
Heteroorganic Compounds,
USSR Academy of Sciences,
Moscow