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Chemistry of P–F Ylides

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Abstract — Results of the research into ylides containing fluorine atoms on the phosphorus atom of the P=C group are summarized. These compounds are convenient reagents for preparing various organic and organophosphorus compounds hardly available by other methods. Main synthetic routes to P-fluoroylides are considered. Chemical and physical properties of the ylides are reviewed. The peculiar chemistry of these compounds is shown, that significantly differs from the chemistry of triphenylphosphonium ylides. Prospective synthetic applications of P-fluoroylides are analyzed.

INTRODUCTION

Phosphorus ylides are important and versatile reagents of organic synthesis [1–3]. Among various types of these compounds obtained over the past years, much interest has been focused on P–Halogen-containing ylides [4]. P–halogen ylides exhibit specific properties which permit to prepare from them synthetically important compounds unavailable through the use of triphenylphosphonium ylides [8–18]. For example, phosphorus ylides containing fluorine atoms on the phosphorus atom, so-called P-fluorine ylides, have attracted chemist's attention by their availability, fair stability, and high reactivity, as well as by interesting chemical properties [4, 5, 19].

P-Fluoroylides can be prepared by means of simple chemical reactions [20–60]. The presence of the labile fluorine atoms on phosphorus predetermines unusual properties of these compounds, which is interesting not only in theoretical [60–64], but also in preparative aspects [1–3, 19, 65–90]. P-Fluoroylides can enter cycloaddition and heterocyclization reactions. They exhibit a high phosphorylating activity, what permits preparation of phosphorus-containing alkenes. Furthermore, P-fluoroylides are convenient objects for research into interesting theoretical problems concerning the structure and reactivity of organophosphorus compounds [7, 91–96]. These compounds hold undeniable promise for further investigations as reagents for preparing various hardly available types of organophosphorus compounds.

In view of the aforesaid, in the present article we have summarized the results of our investigations on the synthesis and properties of P-fluoroylides. In this review we relied on our published results and data unpublished, for various reasons, in available literature, and reported at conferences [97–105], mentioned in monographs [1, 2], and described in dissertations [22, 72].

1. SYNTHESIS OF P-FLUOROYLIDES

Detailed studies of P-fluoroylides allowed convenient synthetic approaches to these compounds to be developed. These methods were used to prepare a variety of P-fluoroylides bearing different substituents on the phosphorus and carbon atoms of the P=C group (Scheme 1). The most important methods of synthesis of P-Fluoroylides are the following [5–7]:

(a) dehydrofluorination of fluorophosphoranes;

(b) reaction of P-fluoroylides with chlorine-containing electrophiles, that involve substitution of hydrogen atoms on the carbon atom by various groups;

(c) reaction of P-fluoroylides with carbon tetrahalides, that involve substitution of hydrogen atoms on the α-carbon atom with halogen;

(d) substitution of the chlorine atom in P-chlorine ylides by fluorine by reaction with metal fluorides;

(e) reaction of fluorophosphines with carbenes (or carbenoids).

The above synthetic methods allow P-fluoroylides of practically any structure by to be prepared by means of simple chemical reactions, using cheap chemical reagents.

The best synthetic route to P-fluoroylides is the dehydrofluorination of fluorophosphoranes, resulting in formation of a P=C ylide bond (method A, Table 1). This method was used to prepare P-fluoroylides with one or two fluorine atoms on phosphorus.

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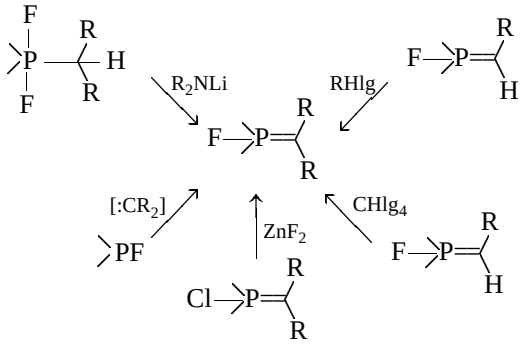
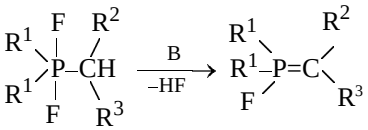
Scheme 1.

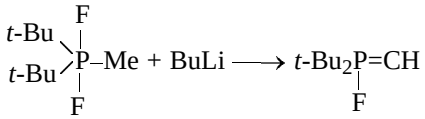


Dehydrofluorination of dialkyltrifluorophosphoranes or dialkylaminoalkylphosphoranes can be accomplished by means of butyllithium, lithium bis(trimethylsilyl)amide, lithium diisopropylamide, and, in some cases, triethylamine. Dehydrofluorination of fluorophosphoranes leads to formation of both P-fluoroylides and P,P-difluoroylides in high yields [15, 19, 20].



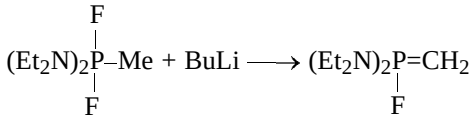
R^1 = Alk, Ph, Alk_2N, AlkO, F; R^2 = H, Alk, Cl; R^3 = H, Alk, Ar, Cl, CR^2R^3 = 9-fluorenyl, B = BuLi, *i*-Pr_2NLi, $(Me_3Si)_2NLi$, Et_3N.

Dehydrofluorination of fluorophosphoranes can be illustrated by experimental procedures for preparing P-fluoroylides. This method, for instance, gave ylides of simple structure, such as di-*tert*-butylfluorophosphonium methylide (Table 1) [21, 22].



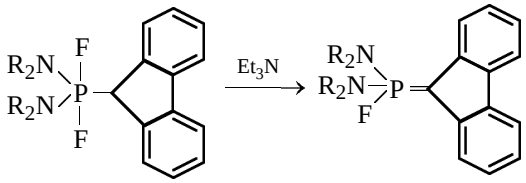
Di-*tert*-butylfluorophosphonium methylide [21, 22]. To a solution of di-*tert*-butyldifluoro(methyl)phosphorane (0.02 mol) in hexane (10 ml), a solution of butyllithium (0.024 mol) in hexane (10 ml) was added dropwise with stirring and cooling to –70°. The reaction mixture was heated to 20°C, the precipitate of lithium chloride was filtered off, the solvent was removed, and the residue was distilled in a vacuum. Yield 80%, bp 65°C (12 mm Hg). The ylide was obtained as a colorless liquid fuming in air. The product can be handled in a tightly closed vessel in a refrigerator (Table 1).

The yields of P-fluoroylides depend on the dehydrofluorination temperature. For example, the optimal temperature for dehydrofluorination of bis(diethylamino)difluoro(methyl)phosphorane is about 0°C, and decrease of the reaction temperature to –60 to –70°C much decreases the yield of P-fluoroylides.



Bis(diethylamino)fluorophosphonium methylide [21, 22]. To a solution of bis(diethylamino)difluoro(methyl)phosphorane (0.05 mol) in 20 ml of pentane, 27.5 ml of 2.0 M solution of butyllithium was added dropwise with stirring at 0–5°C under nitrogen. The reaction mixture was then heated to 20°C and left to stand for 1 h. Lithium chloride was filtered off, and the residue was distilled in a vacuum. Yield 70%, colorless oil, bp 35°C (0.08 mm Hg).

Diethylamine readily dehydrofluorinates difluoroalkylphosphoranes containing electron-acceptor groups on the α-carbon atom, such as bis(dialkylamino)difluoro(9-fluorenyl)phosphoranes (Table 1), [22, 23].



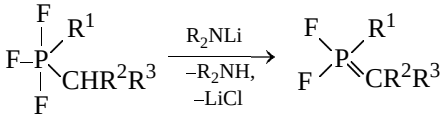
Bis(diethylamino)fluorophosphonium fluorenylide [22, 23]. Triethylamine, 0.1 mol, was added in one portion at 0°C to a solution of 0.05 mol of bis(diethylamino)difluoro(9-fluorenyl)phosphorane in 30 ml of diethyl ether, and the mixture was stirred for 30 min. The precipitate was was filtered off, the filtrate was evaporated, and the residue was crystallized from hexane–benzene (10 : 1). Yield 60%, yellowish orange crystals, mp 95°C.

Table 1. P-fluoroylides $R^1R^2P(F)=CR^3R^4$

R^1	R^2	R^3	R^4	Yield, %	Method[a]	bp, °C (*p*, mm Hg)	Reference
Me_2N	Me_2N	H	H	48.5	A	42 (10)	[7, 19]
Et_2N	Et_2N	H	H	70	A	35 (0.08)	[14, 37]
Et_2N	Et_2N	Ph	H	76.3	A	97–115 (0.008)	[7, 19]
Me_2N	Me_2N	$SiMe_3$	H	48.5	A, F	78 (10)	[19, 38]
Et_2N	Et_2N	$SiMe_3$	H	85	B	70 (0.06)	[14, 18]
i-Pr_2N	*i*-Pr_2N	$SiMe_3$	$SiMe_3$	85	H	–[b]	[60]
i-Pr_2N	*i*-Pr_2N	(*i*-$Pr_2N)_2P$	H	70	H		[61]
Me_2N	Me_2N	CO_2Me	H	58.2	E	47–50 (0.001)	[7]
t-Bu	*t*-Bu	H	H	80	A	65 (12)	[37]
t-Bu	*t*-Bu	Pr	H	65	A	65 (0.08)	[37]
t-Bu	*t*-Bu	Ph	H	70	A	100 (0.08)	[14]
t-Bu	*t*-Bu	Me	Et	65	A	45–48 (10)	[14, 37]
t-Bu	*t*-Bu	Cl	Cl	92	G	69–71[c]	[58]
t-Bu	*t*-Bu	Br	Br	55	G	120[c]	[58]
Et_2N	Et_2N	Me	H	60	A	35 (0.08)	[37]
Et_2N	Et_2N	Me	Me	80	A	70 (0.08)	[18]
Et_2N	Et_2N	*i*-Pr	H	60	A	60 (0.08)	[37]
Me_2N	Me_2N	Cl	Cl	65	G	17–19[c]	[58]
Et_2N	Et_2N	Cl	Cl	70	E	100 (0.05)	[57]
				80	G	87–88 (0.02)	[58]
Pr_2N	Pr_2N	Cl	Cl	66	G	120 (0.02)	[58]
$(CH_2)_5N$	$(CH_2)_5N$	Cl	Cl	90	E	–[b]	[57]
Et_2N	Et_2N	Br	Br	90	E	–[b]	[57]
Et_2N	Et_2N	Me	Cl	70	E	80 (0.06)	[57]
Et_2N	Et_2N	$CR^2R^3=CAr_2$[d]		45–60	A, B, F	95[c]	[23]
t-Bu	EtO	*i*-Pr	H	60	A	75 (10)	[31]
t-Bu	BuO	*i*-Pr	H	70	A	102 (15)	[31]
t-Bu	PhO	*i*-Pr	H	70	A	86 (0.06)	[31]
Ph	Ph	$SiMe_3$	H	50	C	–[b]	[21, 23]
Et_2N	F	H	H	95	A	32 (30)	[21, 23]
Et_2N	F	Pr	H	80	A	60 (12)	[21, 23]
Et_2N	F	Et	Me	80	A	78–80 (12)	[22, 28]
t-Bu	F	Pr	H	65	A	45–48 (12)	[22, 28]
t-Bu	F	*i*-Pr	H	60	A	45 (12)	[21, 23]
t-Bu	F	Me	Et	65	A	45–47 (150)	[28, 29]
s-Bu	F	Me	Et	80	A	50–52 (10)	[21, 24]
Et_2N	F	Cl	Cl	80	A, D	40–42 (0.05)	[22, 24, 59]
Me_2N	Me_2N	$(Me_2N)_2P(F)Cl$	Cl	90	G	99–101[c]	[58]
Me_2N	Me_2N	$(Me_2N)_2P(Bu)CH$	H	–	A	–	[49, 50]

[a] Methods A–H are mentioned in the text. [b] Oily liquid. [c] Melting point. [d] CR^3R^4 = CAr_2 = 9-fluorenyl.

Dehydrofluorination of trifluoroalkylphosphoranes with lithium or sodium amides leads to formation of ylides containing one or two fluorine atoms on phosphorus. For example, the reaction of butyl(diethylamino)trifluorophosphorane with lithium diisopropylamide in THF at –20 to 20°C leads to formation of P,P-difluoroylides in high yields (Table 1). The products were purified by vacuum distillation.



R^1 = *s*-Bu, *t*-Bu, Et_2N; CR^2R^3 = CH_2, CHMe, CHPr, CHPr-*i*, C(Me)Et; CHPh, $CHSiMe_3$; R_2NLi = (*i*-$Pr_2N)_2$·NLi, $(Me_3Si)_2NLi$.

n-Butyllithium, too, can be used for dehydrofluorination of phosphoranes. The highest yields of the products are achieved when the alkyl groups are branched and create steric hindrances for substitution of butyl for fluorine. Alkyltrifluorophosphoranes were prepared by the reaction of dialkylchlorophosphines with antimony trifluoride. P,P-difluoroylides are colorless liquids that can be distilled in a vacuum without decomposition. They are easily hydrolyzed with air moisture but can be handled at 0°C in a tightly closed flasks.

$$s\text{-Bu}_2\text{PCl} + \text{SbF}_3 \longrightarrow s\text{-Bu}_2\text{PF}_3,$$

$$s\text{-Bu}_2\text{PF}_3 + \text{BuLi} \longrightarrow s\text{-BuP(F}_2\text{)=C(Me)Et}.$$

***sec*-Butyldifluorophosphomium *sec*-butylide [22, 23].** *a*. Antimony trifluoride, 0.1 mol, was added in small portions to 0.1 mol of di-*sec*-butylchlorophosphine. The reaction mixture was stirred at 80°C for 4 h. The resulting dark reaction mixture was cooled to room temperature, and trifluorophosphorane was extracted with diehyl ether. The solvent was removed at reduced pressure, and the residue was distilled in a vacuum. Yield 70%, colorless mobile liquid with a sharp odor, bp 58–60°C (10 mm Hg).

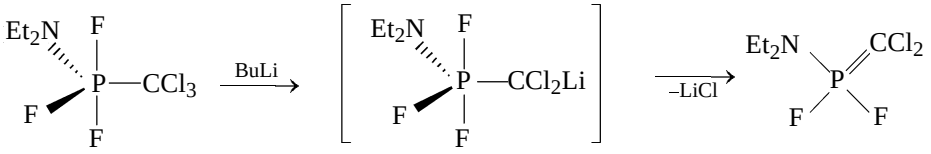
b. A solution of 0.023 mol of lithium diisopropylamide in 15 ml of an ether–hexane mixture, 1 : 1, was added dropwise to a solution of 0.02 mol of di-*sec*-butyltrifluophoshorane in 15 ml of diethyl ether at –60°C. The reaction mixture was heated to room temperature and stirred for about 10 min. After that the reaction mixture was heated to 35°C and filtered. The solvent was removed at reduced pressure, and the residue was distilled in a vacuum. Yield 80%, colorless mobile liquid fuming in air, bp 50–52°C (10 mm Hg). The product can be handled for several days in a refrigerator in a tightly closed vessel.

$$\text{Et}_2\text{N}(s\text{-Bu})\text{PCl} + \text{SbF}_3 \longrightarrow \text{Et}_2\text{NP(F}_3\text{)Bu-}s,$$

$$\text{E}_2\text{NP(F}_3\text{)Bu-}s + \text{BuLi} \longrightarrow s\text{-BuP(F}_2\text{)=C(Me)Et}.$$

(Diethylamino)difluorophosphonium *sec*-butylide [21, 22]. To a solution of 0.02 mol of butyl(diethylamino)trifluorophosphorane in 10 ml of THF, a solution of 0.022 mol of lithium diisopropylamide in 10 ml of THF was added with stirring at –20°C. After that the reaction mixture was heated to 20°C, and the precipitate of lithium chloride was filtered off. The solvent was removed, and the residue was distilled in a vacuum. Yield 80%, bp 60°C (12 mm Hg).

The reaction of (trichloromethyl)phosphoranes with butyllithium in ether gave P,P-difluoroylides in good yields [22, 24].

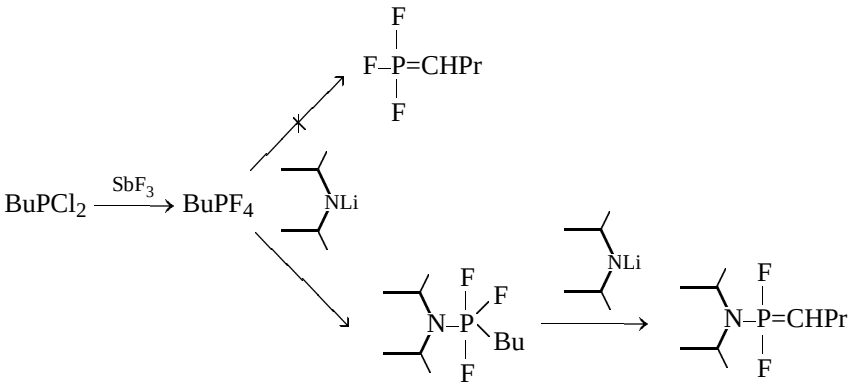


Dimethylamino(Difluoro)phosphonium dichloromethylide [22, 24]. To a solution of 0.007 mol of (diethylamino)(trichloromethyl)trifluorophophosphorane in 20 ml of diethyl ether, a solution of 0.02 mol of 2.3 N butyllithium in hexane was added dropwise with stirring at –100°C. The reaction mixture was stirred at –30°C for 30 min and then heated to 20°C, after which it was filtered, the solvent was removed in a vacuum, and the residue was distilled in a vacuum. Yield 70%, bp 40–42°C (0.05 mm Hg).

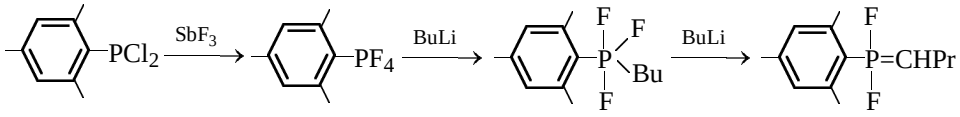
The reaction of alkyltetrafluorophosphoranes with sterically hindered lithium amides involves substitution of the fluorine atom on phosphorus by an amino group and provides trifluorophosphorane that then reacts with a further lithium amide molecule to give P,P-difluoroylide [19, 22]. No dehydrofluorination of alkyltetrafluorophosphoranes to form P-fluoroylides occurs in this case (Scheme 2).

Analogous reaction of tetrafluoro(mesityl)phos-

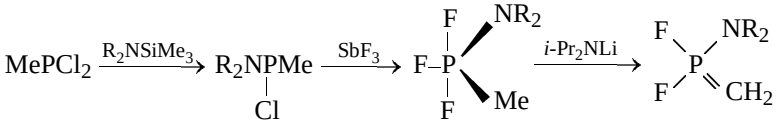
Scheme 2.



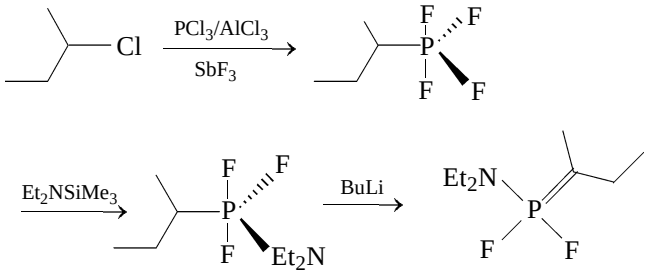
phorane with *n*-butyllithium leads to formation of fluorophosphorane which easily reacts with one more molecule of butyllithium to give P,P-difluoroylide [22].



The starting alkyltrifluorophosphoranes are available compounds that can be easily obtained from cheap starting compounds [22, 24–27]. For example, (dialkylamino)difluorophosphonium methylide was prepared in three stages from dichloro(methyl)phosphine [22].



A facile synthesis of (diethylamino)difluorophosphonium *sec*-butylide from *sec*-butyl chloride was also developed [21].

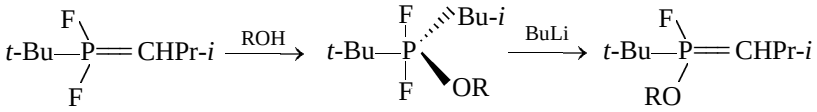


***sec*-Butyltetrafluorophosphorane**. *sec*-Butyldichlorophosphine, 0.15 mol, was cooled to 0°C by means of an ice bath, and then 0.2 mol of anhydrous antimony trifluoride was added with stirring in several poritons. The reaction mixture was heated to 20°C and stirred for 30 min, after which it was heated to 70°C, refluxed for about 2 h, and distilled in a vacuum. Yield 80%, mobile colorless liquid, bp 84–86°C.

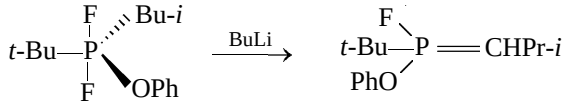
***sec*-Butyl(diethylamino)trifluorophosphorane [22, 28, 29]**. Diethyl(trimethylsilyl)amine, 0.2 mol, was added with stirring at 0°C to 0.15 mol of *sec*-butyltetrafluorophosphorane. The reaction mixture was heated to 20°C and stirred for about 30 min, after which it was refluxed for 2 h at 70°C. The target phosphorane was isolated by vacuum distillation as a colorless mobile liquid. Yield 75°C, bp 80–82°C (15 mm Hg).

(Diethylamino)difluorophosphonium *sec*-butylide [28, 29]. To a solition of *sec*-butyl(diethylamino)trifluorophosphorane, 0.02 mol, in 10 ml of THF, a solution of 0.022 mol of butyllithium in hexane was added dropwise with stirring at 0°C. The reaction mixture was heated to 20°C, and the precipitate of lithium chloride was filtered off. The solvent was evaporated, and the residue distilled in a vacuum to give the target product in 80% yield, bp 78–80°C (12 mm Hg).

Alkoxy- and aroxytrifluorophosphoranes are converted to P-fluoroylides under the action of butyllithium in an ether–hexane solution [24, 30, 31]. Unstabilized aroxy- and alkoxyfluorophosphonium ylides were purified by vacuum distillation. These compounds are thermally stable and, unlike other ylides containing alkoxy groups on phosphorus, do not enter the ylide–phosphonate rearrangement [1–3]. P-alkoxy-P-fluoroylides are easily dealkylated with benzoic acid to give fluorophosphinates. Hydrolysis of P-fluoroylides leads to formation of phosphinates.



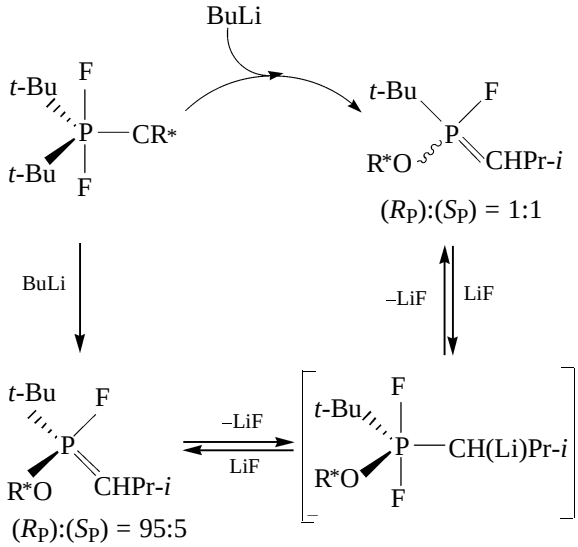
Butoxy-*tert*-butylfluorophosphonium butylylides [31]. To a solution of 0.012 mol of butoxy-*tert*-butyldifluoro(isobutyl)phosphorane in 5 ml of diethyl ether, 0.014 mol of a solution of butyllithium in hexane was added dropwise with stirring at 0°C. The reaction mixture was then heated to room temperature and left to stand for 30 min. Lithium fluoride was filtered off, the solvent was evaporated, and the residue was distilled in a vacuum to give the target product in 70% yield, bp 102°C (15 mm Hg).



***tert*-Butylfluoro(phenoxy)phosphonium isobutylide [31]**. To a solution of 0.01 mol of *tert*-butyldifluoro(isobutyl)phenoxyphosphorane in 5 ml of diethyl ether, a solution of 0.011 mol of butyllithium in hexane was added dropwise with stirring at 0°C. The reaction mixture was heated to room temperature and left to stand for 2 h. The precipitate of lithium fluoride was filtered off, the solvent was removed at reduced pressure, and the residue was distilled in a vacuum. Yield 70%, bp 86°C (0.06 mm Hg).

An interesting example of a thermodynamically controlled asymmetric synthesis is given by dehydrofluorination of alkoxydichlorophosphoranes containing chiral ligands. First difluorophosphorane is dehydrofluorinated to form a 1 : 1 mixture of P-fluoroylide diastereomers. Then in the presence of lithium salts this ratio slowly changes to 95 : 5, giving optically active P-fluoroylides. The first dehydrofluorination stage is sufficiently fast. Then the P-fluoroylide diastereomers reversibly take up lithium fluoride by the P=C bond to form a phospohorane intermediate product. Due to that an equilibrium between the P-ylide and this phosphorane is established, which causes slow transformation of the racemic P-fluoroylide to a more thermodynamically stable optically active P-fluoroylide diastereomer (Scheme 3) [32–36].

Scheme 3.

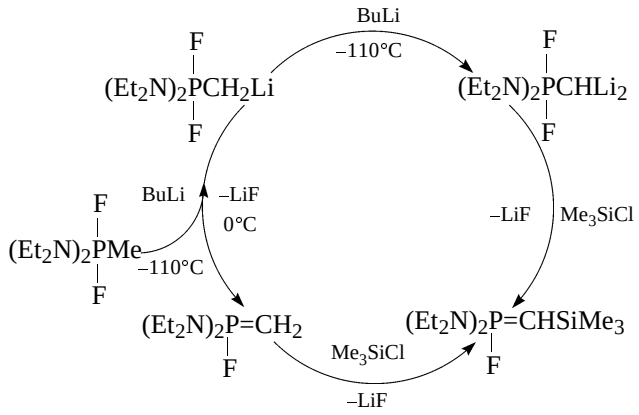


R*O = (–)(–)-1,2 : 5,6-Dicyclohexylideneglucofuranosyl, (–)-$Et_2NCH_2(Me)O$.

The transformation of fluorophosphoranes to ylides must proceed in ether at 0°C, since the reaction at –60°C to –80°C resulted in lower yields and purity of products, on account of the formation of dilithium

derivatives [18, 37]. At –60°C and below, alkyldifluorophosphoranes are easily metalated with the second molecule of butyllithium to give dilithium compounds that readily react with chlorotrimethylsilane to give C-silylated P-fluoroylides in high yields. The reaction of difluorophosphorane with butyllithium gives a C-lithiated difluorophosphorane that easily eliminates lithium fluoride at –20 to 0°C but is stable at lower temperatures. At –60°C and below, the lithium derivative is easily metalated with the second molecule of butyllithium to form a lithium-substituted difluorophosphorane (Scheme 4). Dilithium derivatives react with two mol of chlorotrimethylsilane, yielding C-silylated P-fluoroylides in high yields (method B) [18].

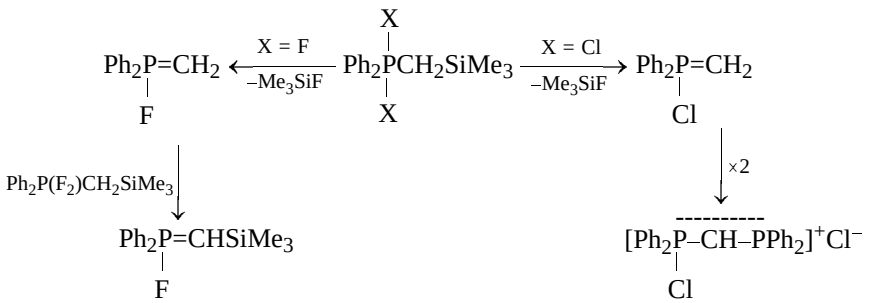
Scheme 4.



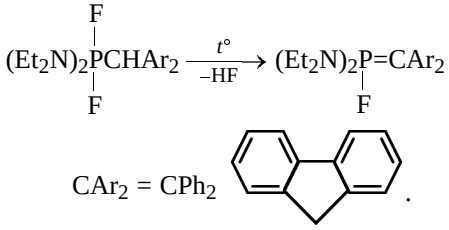
Bis(diethylamino)fluorophosphonium trimethylsilylmethylide (Scheme 4) [18]. To a solution of 0.05 mol of bis(diethylamino)difluoro(methyl)phosphorane in 50 ml of THF, 0.12 mol of a 0.2 N solution of butyllithium in hexane was added dropwise with stirring at –100°C. The reaction mixture was then left to stand for 2 h at –100°C to –80°C, after which 0.125 mol of chlorotrimethylsilane was added, and the resulting mixture was heated to 20°C. The precipitate of lithium fluoride was filtered off, the solvent was evaporated at reduced pressure, and the residue was distilled in a vacuum to give a colorless mobile liquid. Yield 85%, bp 70°C (0.06 mm Hg).

A comparatively facile synthesis of P-fluoroylides is based on elimination of X = Hal, H, or Me_3Si from fluorophosphoranes (method B) [12, 18, 22, 38]. Hence, difluorodiphenyl(trimethylsilylmethyl)phosphorane expels fluorotrimethylsilane at room temperature to give P-fluoroylide that enters ylide exchange with difluorophosphorane to give C-silyl-substituted P-fluoroylide (Scheme 4) [18]. At the same time, dichlorodiphenyl(trimethylsilylmethyl)phosphorane undergoes dimerization, yielding ylidophosphonium salt [14, 39]. The different behavior of P-chloro- and P-fluoroylides is evidently explained by the lability of chlorodiphenylphosphonium methylide (Scheme 5).

Scheme 5.

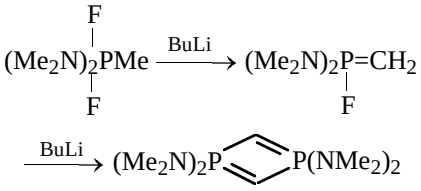


When heated in a vacuum, dufluorophosphoranes containing electron-acceptor substituents on the α-carbon atom are converted into P-fluoroylides, evolving hydrogen fluoride without base treatment [23].



Butyllithium reacts with bis(dimethylamino)difluoro(methyl)phosphorane in a 1 : 1 ratio in pentane at

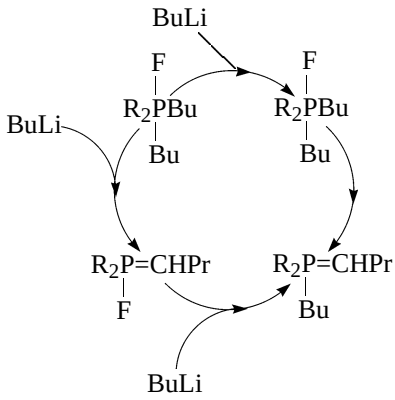
–80°C to form P-fluoroylide, while the reaction of difluorophosphorane with 2 mol of butyllithium in pentane at –95°C yields diphosphacyclobutadiene [40–47]. X-ray diffraction analysis showed that the four-membered ring in the molecule is planar and have completely equalized P–C bonds [20, 48, 49]. Fluck and co-workers [41–47] have thoroughly studied this diphosphacyclobutadiene to show that it enters cycloaddition reactions.



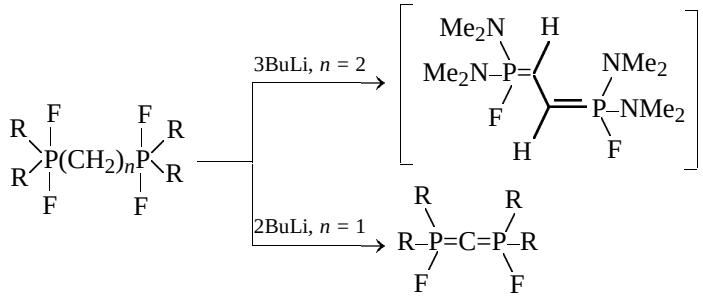
In some cases, treatment of difluorophosphoranes with alkyllithium compounds yielded, instead of dehydrofluorination, substitution of the halogen atom on phosphorus by the alkyl group. As a result, triorganylphosphonium ylides are formed rather than P-fluoroylides (Scheme 6).

Nevertheless, the dehydrofluorination of difluorophosphoranes with butyllithium or lithium hexamethyldisilazane most commonly proceeds smoothly to give P-fluoroylides containing different substituents R^1, R^2, R^3 on the phosphorus and carbon atoms of the P=C bond (Scheme 7) [2, 21, 24]. For example, the reaction of bis(difluorophosphoranyl)ethane with butyllithium leads to formation of bisylides in high yields [49], and the reaction of bis(difluorophosphoranyl)-methane with butyllithium gives carbodiphosphoranes. The structure of the latter was established by means of X-ray diffraction [1, 49, 50].

Scheme 6.



Scheme 7.



R = Ph (**a**), Me_2N (**b**).

A symmetrical P-fluoro-substituted carbodiphosphorane was obtained by dechlorination of a halogen-containing phosphonium salt of tris(dimethylamino)-phosphine (method D).

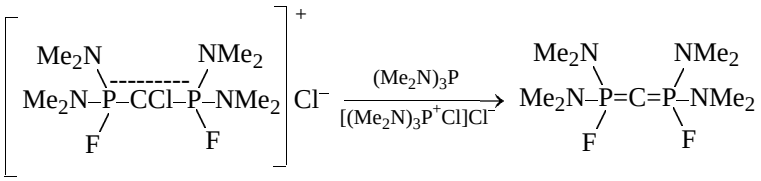
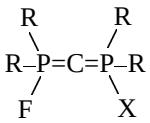


Table 2. Carbodiphosphoranes



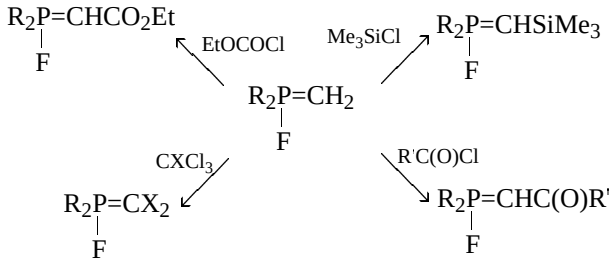
R	X	Method	Yield, %	bp, °C (*p*, mm Hg)	δ_P, ppm (*J*, Hz)	Reference
i-Pr_2N	H	**H**	70	116[a]	59.5 ($^1J_{PP}$ 32.9, $^1J_{PF}$ 951.8)	[61]
Me_2N	F	**A**	80	65–70 (0.004)	39.4 ($^1J_{PF}$ 958)	[50]
Me_2N	F	**B**	80	71–73 (0.03)	41.73 ($^1J_{PF}$ 966)	[51, 53]
Ph	F	**A**	80	90–93[a]	43.2 ($^1J_{PF}$ 1000)	[50]

[a] Melting point.

Difluorocarbodiphosphoranes are crystals or vacuum-distillable liquids (Table 2) [51–53].

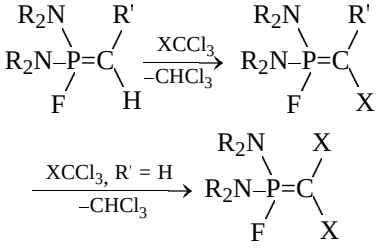
Hydrogen atoms and the trimethylsilyl group on the α-carbon atom of P-fluoroylides can be substituted via reactions with various electrophiles, which allows modification of P-fluoroylides to prepare their new representatives. Reactions of P-fluoroylides with chlorotrimethylsilane, alkyl chloroformates, and carboxylic acid chlorides proceed easily, providing new P-fluoroylides (method D, Scheme 8) [7, 14, 22, 51]. The reactions are carried out at 2 : 1 reagent ratios, because one mol of P-fluoroylide is consumed for deprotonation of the intermediate phosphonium salt (transylidation reaction). The yields of P-fluoroylides containing trimethylsilyl, acyl, alkoxycarbonyl, or phosphino groups on the α-carbon atom are about 50–85% [19, 22, 51, 57].

Scheme 8.



X = Cl, Br.

Substitution of hydrogen atoms at the ylide carbon atom with chlorine or bromine takes place in reactions of P-fluoroylides with carbon tetrachloride, carbon tetrabromide, or bromotrichloromethane in ether in the temperature range –10 to 20°C [51, 57].

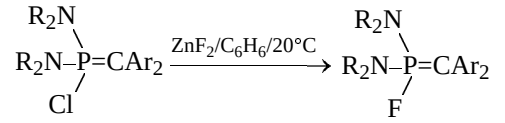


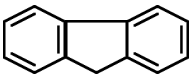
X = Cl, Br; R_2N = Et_2N, $(CH_2)_5NH$; R' = H, Alk.

Bis(diethylamino)fluorophosphonium dichloromethylide [23]. Carbon tetrachloride, 0.20 mol, was added dropwise with stirring under argon at 0 to –5°C to 0.05 mol of *bis*(diethylamino)fluorophosphonium methylide. The reaction mixture was let warm to 20°C and kept at this temperature for 10 min. The solvent was then removed at reduced pressure, and the residue was distilled in a vacuum to give a yellow liquid. Yield 70%, bp 100°C (0.05 mm Hg).

P-Fluoroylides were prepared by the reaction of P-chloroylides with zinc fluoride [23]. The exchange of the chlorine atom for fluorine proceeds in benzene at room temperature and is complete within 24 h. This method was used to prepare, in good yields, P-fluoro-

ylides stabilized by aryl groups on the α-carbon atom (method F).

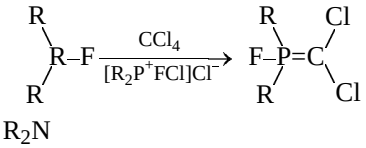


R = Et, *i*-Pr; CAr_2 = CPh_2,  .

Bis(diethylamino)fluorophosphonium fluorenylide [23]. To a solution of 0.005 mol of P-chloroylide in 15 ml of benzene, 0.0015 mol of zinc fluoride was added in one portion. The resulting mixture was stirred for 24 h at room temperature and then filtered and evaporated to dryness. The residue was crystallized from benzene–hexane, 1 : 10. Yield 45%, mp 95°C.

Fluorophosphines slowly react with carbon tetrachloride to give halophosphonium salts and P-fluoroylides in excellent yields (method J) [53, 58].

Di-*tert*-butylphosphonium dichloromethylide [58]. A solution of 0.1 mol of di-*tert*-butylfluorophosphine in 40 ml of carbon tetrachloride was kept at



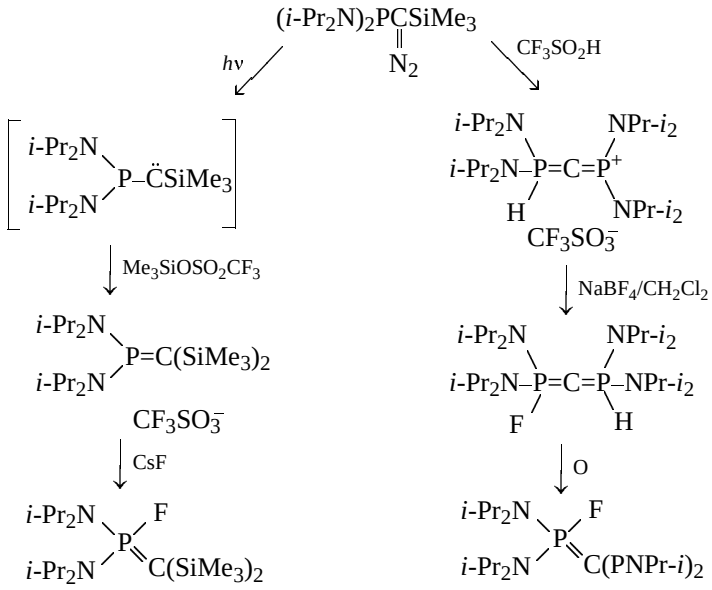
R = *t*-Bu, Me_2N, Et_2N, Pr_2N.

room temperature for 10 days and then heated for 3 days at 35°C. The crystalline precipitate was filtered off, the solvent was removed in a vacuum, and the residue was crystallized from pentane. Yield 92%, mp 69–71°C.

[Bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane was reported to generate phosphinocarbene under UV irradiation. The carbene reacted at room temperature in benzene with trimethylsilyl triflate and cesium fluoride to give P-fluoroylides in high yield (method H, Table 1).

Phosphinodiazomethane reacts also with sodium tetrafluoroborate to give PH-carbodiphosphorane (Table 2) that easily rearranges into P-fluoroylide (Scheme 9) [60, 61].

Scheme 9.



2. PHYSICOCHEMICAL PROPERTIES OF P-FLUOROYLIDES

P-Fluoroylides are crystalline substances or liquids. Most P-fluoroylides are colorless, and only some of them are colored. For example, fluorenylides are red and diphenylmethylides are orange [1, 2, 22].

P-Fluoroylides and P,P-difluoroylides are fairly stable compounds. They do not form dimers contrary to their closest analogs, P-fluoroiminophosphoranes that extremely easily dimerize to form cyclic diazaphosphetidines [1–]. Theoretical studies carried out before the first synthesis of P-fluoroylides predicted

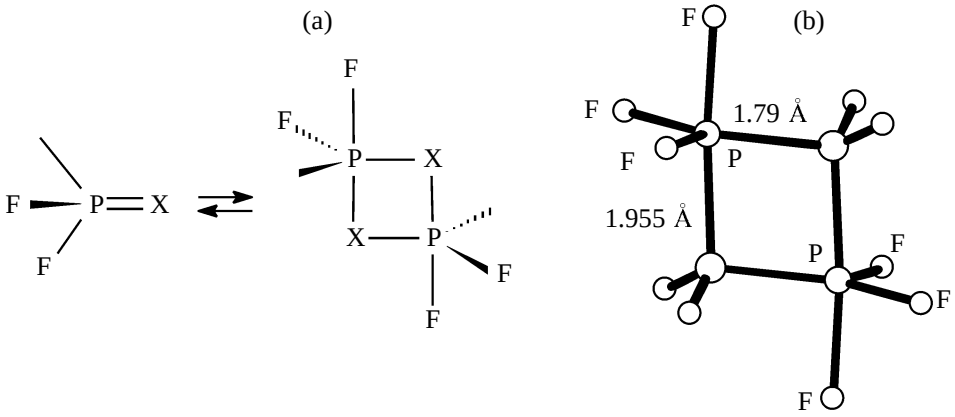


Fig. 1. (a) Dimerization of P-fluoroylides and P-fluoroiminophosphoranes and (b) PM_3-calculated structure of the $F_3P{=}CH_2$ dimer.

that these compounds should be still less stable than P-fluoroiminophosphoranes [62–64]. However, these predictions proved not to be the case. Evidently, the calculations neglected the low electronegativity and apicophilicity of carbon compared to nitrogen, which decreases stability of the axial–equatorial four-membered diphosphetidine ring and thus prevents dimerization of P-fluoroylides. Semiempirical PM_3 calculations (Fig. 1), as well as *ab initio* calculations at the SCF 6.31G* level showed that in this case the axial P–C bond must be very long (1.95 Å) and, therefore, too weak.

P-Fluoroylides can be kept in a refrigerator in tightly closed vessels filled with argon. They can be distilled in a vacuum without decomposition [1]. The stability of P-fluoroylides is increased by electron-acceptor substituents on the α-carbon atom, that decrease the negative charge on the latter, as well as by bulky substituents (*tert*-butyl, isopropyl, diisopropylamino, etc.) on the prosphorus and carbon atoms. Bulky substituents screen the P–C bond and complicate nucleophilic attack of the ylide carbon atom on the positively charged phosphorus atom.

The structure of P-fluoroylides was thoroughly studied by means of various physicochemical methods including IR and ^1H, ^{19}F, ^{13}C, and ^{31}P NMR spectroscopy and X-ray diffraction [1, 2, 20, 50].

The dependence between the environment of the ylide carbon atom and the $^2J_{CH}$ and $^1J_{CP}$ constants is shown in Table 1 [22, 13]. The P=C carbon signals appear in the range δ_C 20–80 ppm. These signals are doublets with the large $^1J_{PC}$ constants (150–200 Hz), which reflects the carbanionic character of the ylide carbon atom. The ^{13}C NMR spectra of P-fluoroylides have a doublet of triplets at 18–33 ppm ($^1J_{PC}$ 182–263 and $^2J_{CF}$ 21–25 Hz) from the F–P=C group [21, 22, 56]. In the case of unstabilized P-fluoroylides, the $^1J_{PC}$ constants are very large (250–300 Hz) [1, 2, 24]. Such coupling constants point to a distortion of the pyramidal configuration of the ylide carbon atom. Triphenylphosphonium methylide has a fairly small $^1J_{PC}$ coupling constant (52 Hz), and the $^1J_{CH}$ constant is 133 Hz, which corresponds to the *sp*-hybridized state of the ylide carbon atom (Table 3).

The chemical shifts in the ^{31}P NMR spectra of P-fluoroylides strongly depend on the nature of substi-

Table 3. ^{13}C NMR spectra of certain P-haloylides

Compound	δ_C, ppm	$^1J_{CP}$, Hz	$^1J_{CH}$, Hz	Reference
$Ph_3P{=}CH_2$	–5	52	133	[73]
$(Et_2N)_2P(F){=}CHSiMe_3$	8	176	133	[22]
$(Et_2N)_2P(Cl){=}CHPh$	39	220	156	[22]
$(Et_2N)_2P(F){=}CHPh$	46	217	158	[7, 22]
$(Et_2N)_2P(F){=}CH_2$	14	210	156	[19, 22]
$Et_2NP(F_2){=}CHPr$	17	252	160	[22]
$Et_2NP(F_2){=}CCl_2$	47	330	–	[22]

Table 4. ^{19}F and ^{31}P NMR spectra of P-fluoroylides $R^1R^2P(F)=CR^2R^3$

R^1	R^2	R^3	R^4	δ_P, ppm	δ_F, ppm	$^1J_{PF}$, Hz	Reference
F	Et_2N	H	H	66.13 t	–69.7 d	1025	[22, 28]
F	Et_2N	Pr	H	59.40 t	–72.5 d	1045	[22, 28]
F	Et_2N	Et	Me	53.13 t	–87.1 d	1054	[22, 28]
F	*t*-Bu	*i*-Pr	H	89.80 t	–83.0 d	1050	[22, 28]
F	*t*-Bu	Me	Et	89.6 t	–83.04 d	1050	[21]
F	*s*-Bu	Me	Et	9.5 t	–80.5 d	1040	[24, 51]
F	Et_2N	Cl	Cl	52.0 t	–	1070	[24]
Et_2N	Et_2N	Me	H	62.8 d	–65.0 d	984	[22]
Et_2N	Et_2N	Ph	H	46 d	–69.3 d	949.9	[22]
Et_2N	Et_2N	*i*-Pr	H	57.9 d	–64.43 d	1029	[19, 37]
t-Bu	*t*-Bu	H	H	105.1 d	–83.64 d	1125	[37]
t-Bu	EtO	*i*-Pr	H	91.4 d	–70.7 d	1090	[22, 24]
t-Bu	*t*-Bu	Pr	H	85.8 d	–74.03 d	1150	[37]

tuents on phosphorus. For example, the δ_P, ppm, is 50–70 at R = Alk_2N, 90–100 at R = *i*-Pr, 80-90 at R = Alk, and 55 at R = Ph (Table 4).

The phosphorus signals of P-fluoroylides are doublets with $^1J_{PF}$ 1000–1100 Hz. The ^{19}F NMR spectra of P-fluoroylides contain doublets in the range 70–87 ppm with very large $^1J_{PF}$ constants of 1000 Hz (Fig. 2). The ^{31}P NMR spectra of P,P-difluoroylides show triplets in the range 50–90 ppm with the same $^1J_{PF}$ values (Table 2). These δ_P and δ_C values correspond to the onium nature of the phosphorus and the carbanionic nature of the ylide carbon atom, as well as to the high polarity of the P=C bond.

The X-ray analysis of P-fluoroylides points to an effective delocalization of the negative charge of the ylide carbon atom over its attached substituents. The ylide part of the molecules studied is planar [1, 49, 50].

3. CHEMICAL PROPERTIES OF P-FLUOROYLIDES

The chemical properties of P-haloylides, first of all of P-chloroand P-fluoroylides, due to the presence of a highly polar P=C bond and a labile halogen atom on phosphorus, are very specific and differ from the properties of triphenylphosphonium ylides [1, 2, 65–78]. For example, reactions of P-haloylides with carbonyl compounds proceed with preservation of the P–C bond and are accompanied by transformations involving alteration of the coordination number of the phoshorus atom. P-Haloylides also exhibit some other properties uncharacteristic of triphenylphosphonium ylides [12].

P-Fluoroylides react with carbonyl compounds to give stable [2+2]-cycloaddition products of the C=O to P=C bond, which much distinguishes such adducts from unstable adducts of carbonyl compounds with

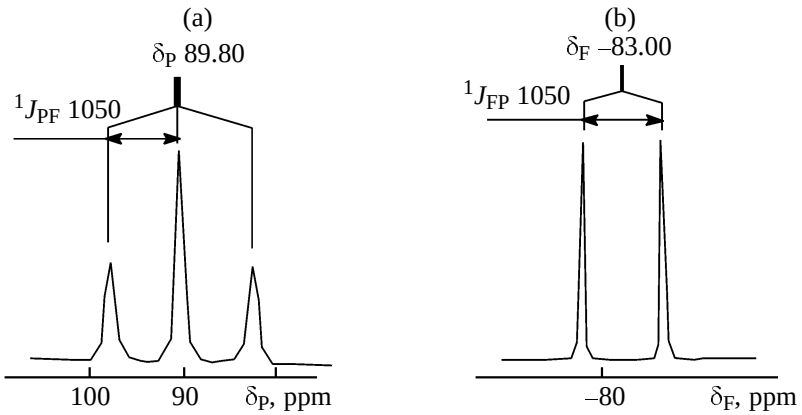
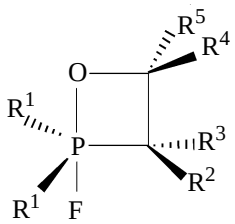


Fig. 2. (a) ^{31}P and (b) ^{19}F NMR spectra of *tert*-butyldifluorophosphonium butylide (δ, ppm; *J*, Hz).

Table 5. 2-Fluoro-1,2λ^5-oxaphosphetanes

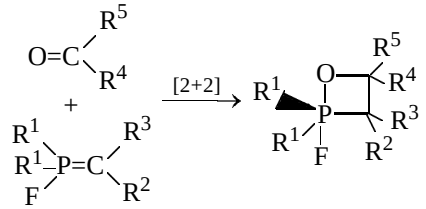


R^1	R^2	R^3	R^4	R^5	Yield, %	bp, °C (p, mm Hg)	δ_P, ppm	δ_F, ppm	$^1J_{PF}$, Hz	Reference
Et_2N	H	H	H	Bu	85	90 (0.06)	–42.15	31.30	767	[18]
Et_2N	H	H	H	C_6H_{13}	85	100 (0.06)	–42.25	31.12	766	[18]
Et_2N	H	H	Me	Me	70	75 (0.02)	–47.53	31.04	765	[18, 82]
Et_2N	H	H	Me	Et	85	85 (0.06)	–49.20	31.04	765	[18]
Et_2N	H	H	Me	Ph	99	[a]	–44.00	32.00	766	[18]
Et_2N	H	H	$(CH_2)_5$		90	110 (0.06)	–44.60	34.90	766	[18]
Et_2N	H	Me	$(CH_2)_5$		99	[a]	–44.00	21.00	853	[18]
Et_2N	H	H	Ph	Ph	99	[a]	–41.60	34.90	766	[18]
Et_2N	H	H	H	Ph	99	[a]	–42.13	31.18	768	[18, 82]
Et_2N	Cl	Cl	H	Pr	90	[a]	–47.00	5.40	853	[18]
Et_2N	Br	Br	H	Pr		[a]	–56.03	5.80	842	[18]
Et_2N	H	Me	CF_3	Ph	80	120 (0.06)	–36.39, –38.27 (7 : 1)[b]	–0.4	795, 795	[18]
Ph	Ph	H	CH_3	H	95	[a]	–43.50	47.8	670	[18]
Et_2N, F	H	Pr	CF_3	Ph	85	105 (0.06)	–26.7	–46.9, –65 (CF_3)	915, 1025	[18]
Et_2N	H	Ph	CF_3	Ph	85	<20[c]	–38.96	27	792.6	[18]
t-Bu	H	Pr	CF_3	Ph	70	125 (0.06)	–7.73, –8.79 (9 : 1)[b]	–1.03	768, 770	[18]
t-Bu	H	Pr	H	Ph	75	120 (0.08)	–10.1, –9.62 (15 : 1)[b]	9.9	762, 762	[18]
t-Bu	H	H	H	Ph	70	<20[c]	–5.9	13	750	[18]
Ph	Ph	$SiMe_3$	Ph	H		[a]	–43.5	28.76	670	[18]
Et_2N	H	$SiMe_3$	Ph	H	90	[a]	–39.27, –42.11 (4 : 1)[b]	40.19, 38.84	768, 768	[18]
Et_2N	H	*i*-Pr	H	Ph	70	110 (0.06)	–33.7, –33.54 (15 : 1)[b]	7.2	827, 827	[18, 37]
t-Bu	H	H	C=NPh		50	84–86[c]	–18.85	5.55	820	[18, 37]
t-Bu	H	H	C=O			[a]	2.0.01	–26.23	785	[18, 37]

[a] Oil. [b] Diastereomers. The diastereomeric composition of the products was evaluated by NMR spectroscopy. [c] Melting point.

triphenylphosphonium ylides [18, 37]. Cycloadducts of P-fluoroylides with carbonyl compounds, 2-fluoro-1,2λ^5-oxaphosphetanes, are much more stable than 2-chloro- or 2-bromo-1,2λ^5-oxaphosphetanes [18, 37, 73, 81].

2-Fluoro-1,2λ^5-oxaphosphetanes are usually isolated and purified by vacuum distillation. Their stability is explained by the high electronegativity of the fluorine atom as compared to chlorine and bromine. The P–F bond in 2-fluoro-1,2λ^5-oxaphosphetanes is very strong, and, therefore, these compounds do not



R^1 = Alk, Ph; CR^2R^3 = CH_2, CHAlk, $CAlk_2$, CHPh, $CHSiMe_3$, CCl2, CBr_2; CR^4R^5 = C=O, CNPh, CHAlk, $CAlk_2$, CHPh, CPh_2, CH_2CH=CH2.

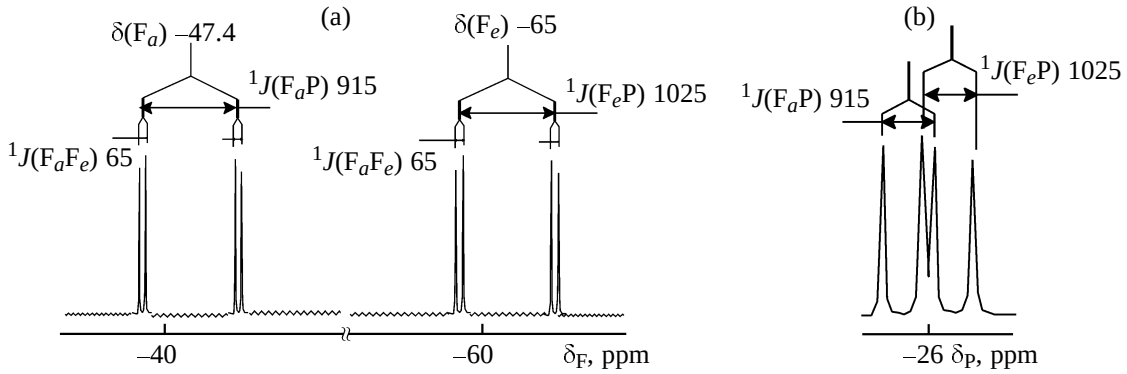
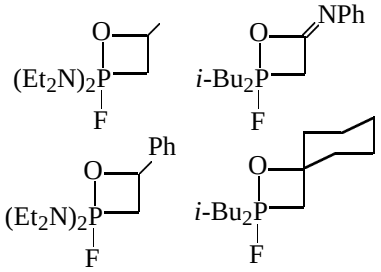


Fig. 3. (a) ^{19}F and (b) ^{31}P NMR spectra of 2-(diethylamino)-2,2-difluoro-4-phenyl-3-propyl-4-(trifluorophenyl)-1,2λ^5-oxaphosphetane.

dissociate with formation of cyclic phosphonium salts, what is observed, for example, with 2-chloro-1,2λ^5-oxaphosphetanes [15, 68–70, 72]. Various stable 2-fluoro-1,2λ^5-oxaphosphetanes were synthesized, isolated pure, and characterized (Table 5) [17, 28, 72]. Typical representatives of such compounds are shown in Scheme 10 [18, 21, 22, 37].

Scheme 10.



2,2-Di-*tert*-butyl-2-fluoro-2-phenyl-3-propyl-1,2λ^5-oxaphosphetane (Scheme 11, Table 5). A solution of 0.0011 mol of benzaldehyde in 3 ml of ether was added to a solution of 0.0011 mol of *tert*-butylphosphonium butylide in 6 ml of diethyl ether at –20°C. The reaction mixture was heated to 0°C and left to stand at this temperature for 15 min. After heating to 20°C, the solvent was removed at reduced pressure, and the residue was distilled in a vacuum. Yield 75%, bp 120°C (0.08 mm Hg). Colorless viscous liquid, diastereomeric ratio 15 : 1).

2-(Diethylamino)-2,2-difluoro-4-phenyl-3-propyl-4-(trifluoromethyl)-1,2λ^5-oxaphosphetane (Table 5) [21, 22]. A solution of 0.011 mol of trifluoroacetophenone in 1 ml of diethyl ether was added to a solution of 0.01 mol of (diethylamino)difluorophosphonium butylide in 1 ml of diethyl ether at –10°C. After that the reaction mixture was heated to room temperature and left to stand for 2 h. The solvent was then removed at reduced pressure, and the residue was distilled in a vacuum. Yield 85%, bp 105–107°C (0.08 mm Hg). Colorless viscous liquid. The NMR spectra revealed only one diastereomer of the adduct.

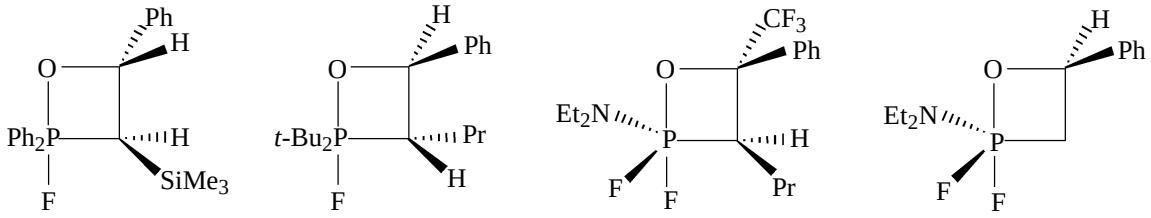
The ^{31}P NMR spectra of 2-fluoro-1,2λ^5-oxaphosphetanes display a doublet in the range –6 to –45 ppm, belonging to the five-coordinate phosphorus with corresponding coupling constants on axial fluorine atoms (760–850 Hz [47]). The ^{19}F NMR spectra of 2-fluoro-1,2λ^5-oxaphosphetanes contain a doublet in the range –27 to –35 ppm (J_{PF} 760 and 850 Hz). The presence in the ^{31}P NMR spectra of 2,2-difluoro-1,2λ^5-oxaphosphetane of a doublet of doublets at –27 ppm with J_{PF} 915 and 1025 Hz is consistent with the equatorial location of the fluorine atoms and the axial–equatorial position of the four-membered ring [80, 81]. The ^{19}F NMR spectra contain two doublets of doublets at –47 and –65 ppm with expected coupling constants for the axial and equatorial fluorine atoms: ^1J(PF$_a$) 915 Hz, ^1J(PF$_e$) 1025 Hz, and ^2J(F$_a$F$_e$) 62 Hz (Fig. 3).

Stereochemistry of the reaction of P-fluoroylides with carbonyl compounds was studied. By means of NMR spectroscopy it was established that 2-fluoroxaphosphetanes containing chiral phosphorus or endocyclic carbon atoms exist as mixtures of diastereomers whose ratio depends on the nature of the starting reagents.

The diastereomers of 2-fluoroxaphosphetanes having chiral endocyclic C^3 and C^4 atoms are formed with a high stereoselectivity, the diastereomer of *cis* configuration being preferred (Scheme 11). The diastereomeric purity of the compounds, assessed by NMR spectroscopy, was 80–96%. α,α,α-Trifluoro-

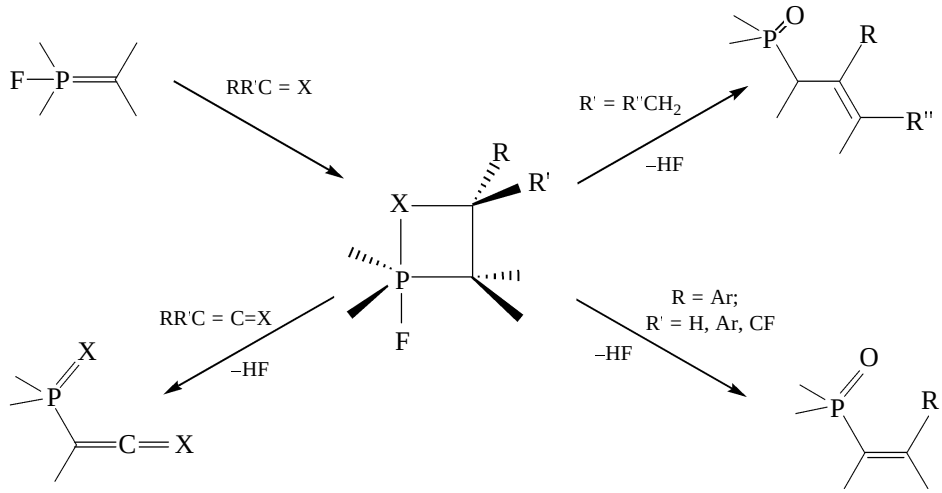
acetophenone highly selectively reacted with P,P-difluoroylides (*de* ~100%) to give a single diastereomer [32, 21]. At the same time, 2-fluoroxaphosphetanes containing a chiral phosphorus atom were formed with a low stereoselectivity (*dr* 3:1–4:1) (Scheme 11) [18, 37, 82].

Scheme 11.

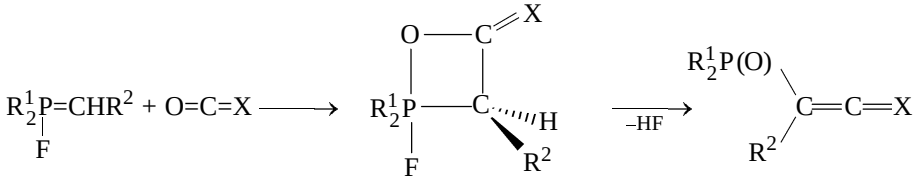


2-Fluoro-1,2λ^5-oxaphosphetanes depending on their structure at elevated temperatures are converted to various phosphorylated unsaturated alicylic compounds, such as allylphosphonates, vinylphosphonates, and phosphorylated heterocumulenes. The reaction involves preservation of the P–C bond (abnormal Wittig reaction), contrary to the classical Wittig reaction (Scheme 12) [14, 18].

Scheme 12.

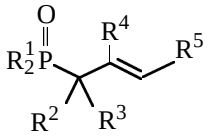


Adducts of P-fluoroylides with carbon dioxide were isolated as colorless liquids or crystalline compounds. Their structure was confirmed by the NMR spectra. When heated, the cycloadducts converted into phosphorylated ketenes. Stable [2+2]-cycloadducts of 2-fluoroylides with alkyl and aryl isothiocyanates were synthesized and then converted to phosphorylated ketenimines.



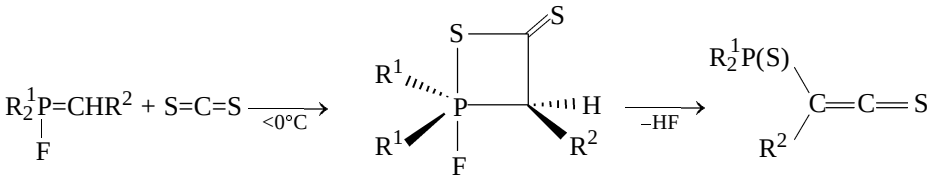
X = O, NPh.

Table 6. Allylphosphonates



R^1	R^2	R^3	R^4	R^5	Yield, %	bp, °C (*p*, mm Hg)	Reference
Et_2N	H	H	H	Pr	70	120 (0.06)	[18]
Et_2N	H	H	H	C_5H_{11}	70	140 (0.08)	[17, 18]
Et_2N	H	H	Me	H	55	105 (0.08)	[17, 18]
Et_2N	H	H	Me	Me	60	95 (0.06)	[14, 18]
Et_2N	H	H	Ph	H	65	145 (0.08)	[17, 18]
Et_2N	H	H	$(CH_2)_4$		85	145 (0.08)	[17, 18]
Et_2N	H	Me	$(CH_2)_4$		75	110 (0.06)	[18]
Et_2N	Me	Me	$(CH_2)_4$		70	110 (0.06)	[18]

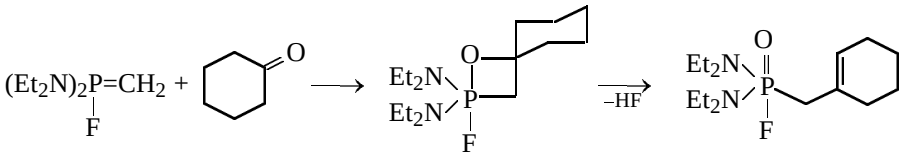
The reaction of P-fluoroylides with carbon disulfide gives unstable cycloadducts that at temperatures above 0°C convert to phosphorylated thioketenes in high yields. Phosphorylated thioketenes are red liquids distillable in a vacuum and susceptible to various transformations [13, 37].



R^1 = Alk, Ph; R^2 = Alk.

(Di-*tert*-butylphosphinothioyl)propylthioketene. A solution of 0.01 mol of carbon disulfide in 2 ml of pentane was added at –40°C to a solution of 0.02 mol of di-*tert*-butylphosphonium butylide in 10 ml of pentane. The reaction mixture was then heated to 0°C and left to stand for 10 min, after which it was heated to 20°C and stirred for 30 min. The solvent was removed at reduced pressure, and the residue was distilled in a vacuum. Yield 85%, bp 115–120°C (0.08 mm Hg), dark red liquid.

2-Fluoro-1,2λ^5-oxaphosphetanes containing an alkyl group at C^3 eliminate hydrogen fluoride to give allylphosphonates (Scheme 12, Table 6). The reaction occurs by the 1,4-elimination-like scheme [14, 18].



(1-Cyclohexylmethyl)phosphonic bis(diethylamide). *a*. A solution of 0.022 mol of cyclohexanone in 5 ml of diethyl ether was added to a solution of 0.02 mol of bis(diethylamino)fluorophosphonium methylide in 5 ml of ether at 0°C. The reaction mixture was heated to room temperature and left to stand for 3–4 h. The solvent was then removed at reduced pressure, and the residue was distilled in a vacuum.

Table 7. (*E*)-Vinylphosphonates

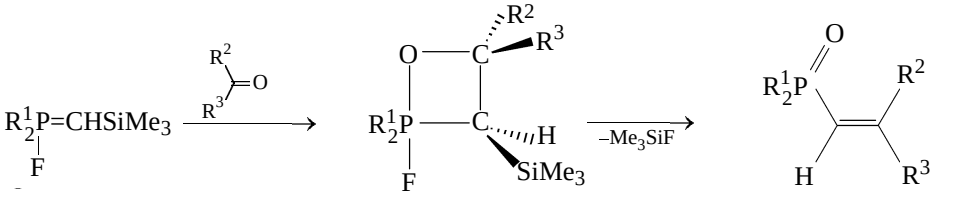
R^1	R^2	R^3	Yield, %	bp, °C (*p*, mm Hg)	Reference
Ph	H	Ph	40	165[a]	[18, 82]
Et_2N	H	Ph	85	103.5[a]	[18]
Et_2N	H	Pr	72	120 (0.05)	[18]
Et_2N	H	Bu	68	120 (0.04)	[18]
Et_2N	H	C_6H_{13}	80	135 (0.06)	[18]
Et_2N	H	C_8H_{17}	79	145 (0.05)	[18]
Et_2N	CF_3	Ph	74	140 (0.03)	[18]
t-Bu	H	Ph	80	138[a]	[37, 82]

[a] Melting point.

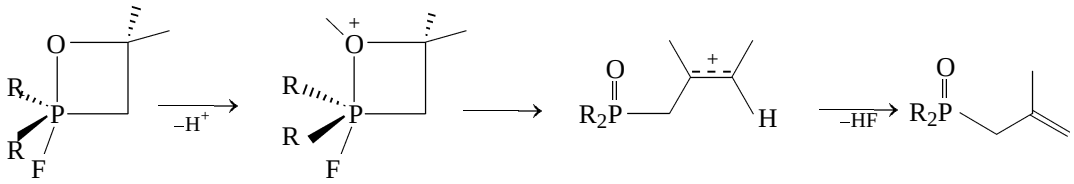
2-Fluoroxaphosphetane was obtained as a colorless liquid, yield 80%, bp 110°C (0.06 mm Hg).

a. 2-Fluorooxaphosphetane was heated under argon with stirring at 120°C. Evolution of hydrogen fluoride was observed over the course of several minutes. The reaction mixture was heated for an additional 15–20 min at 120–140°C and then distilled in a vacuum. Yield 75%, bp 145°C (0.08 mm Hg).

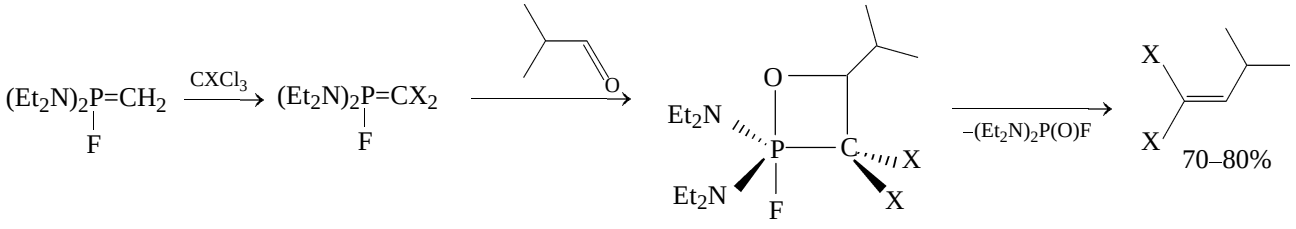
Silicon-containing 2-fluorooxaphosphetanes convert exclusively via 1,2 elimination of the trimethylsilyl group to give stereochemically pure (*E*)-vinylphosphonates in good yields (Table 7) [14, 18].



Lewis and Brønsted acids actively catalyze the transformation of 2-fluorooxaphosphetanes to allylphosphine oxides. Reaction is autocatalytic, because the evolving hydrogen fluoride catalyzes decomposition of 2-fluorooxaphosphetanes. The protonation of 2-fluorooxaphosphetanes provides oxonium salts that convert into carbenium intermediates that, in their turn, give allylphosphonates under the conditions of E$_N$1 elimination of hydrogen fluoride [13, 18].



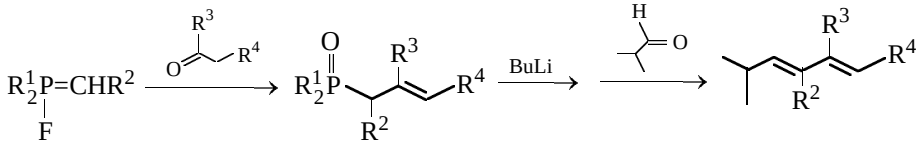
P-Fluoroylides react with carbonyl compounds to give fluorinecontaining alkenes [13, 17, 37, 82–85]. 2-Fluorooxaphosphetanes containing chlorine and bromine on C^3 decompose on heating, yielding 1,1-dihaloalkenes and phosphinoyl fluorides. It is proposed that the electronegative fluorine atoms favors transfer of the CX_2 group in the axial position, which results in cleavage of the carbon–phosphorus bond and formation of diazaalkene [18, 57].



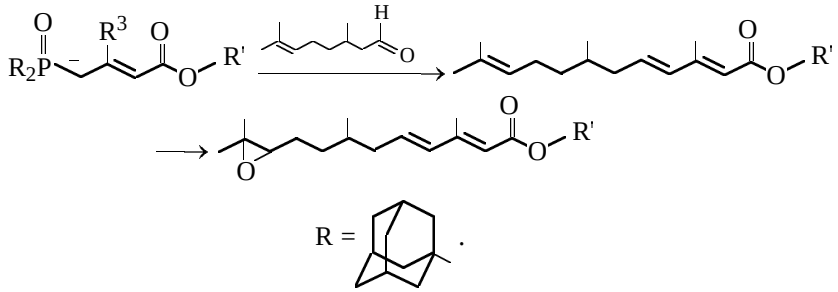
X = Cl, Br.

The reaction of P-fluoroylides with carbonyl compounds is a convenient synthetic approach to allylphosphonates. The latter are widely used for preparing natural compounds. In this case, the carbonyl compounds can be used twice for constructing the diene structure: first in reaction with P-fluoroylide and then in the Wittig reaction with allylphosphonate.

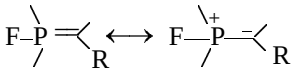
This reaction was used for preparing analogs of the juvenile hormone (Scheme 13) [22, 86].



Scheme 13.

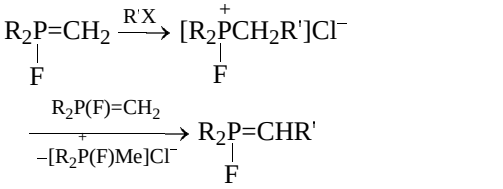


The P=C bond in P-fluoroylides is strongly polarized, as a result of which the negative charge is strongly localized on the carbon atom [1, 2, 6]. Therefore, P-fluoroylides easily take up variuos electrophiles to form phosphonium salts or betains.



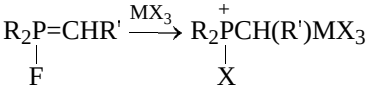
Phosphonium salts obtained by reactions of P-fluoroylides with such electrophiles as chlorotrimethylsilane, formyl chloride, carboxylic or phosphorous acid chlorides containing an electron-acceptor substituent R' on the α-carbon atom, are easily dehydrochlorinated with the initial P-fluoroylide to give C-substituted P-fluoroylides [19, 22, 38, 88].

Phosphonium salts obtained by reactions of P-fluoroylides with alkyl halides do not enter the transylidation reaction, since the alkyl group renders hydrogen atoms on the α-carbon atom less mobile [41].



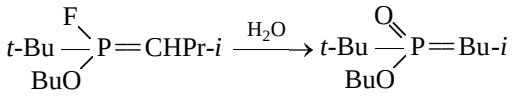
X = Cl, I; Y = F; R = Alk, Alk_2N; R' = Me, Me_3Si, R_2P, EtOCO, RC(O).

P-Fluoroylides take up Lewis acids (boron trifluoride, aluminum chloride) to give betains. However, nowadays this reaction presents the theoretical interest only [22, 41].

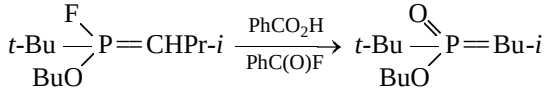


The mobile halogen atom of P-haloylides, attached to the electrophilic positively charged phosphorus atom can be easily substituted with various groups by means of reactions with nucleophiles [38, 52, 71, 89–92].

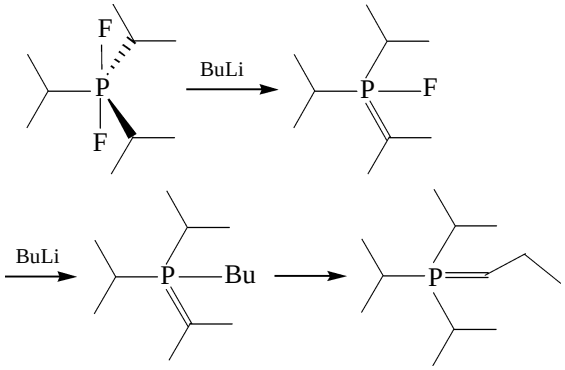
P-Fluoroylides are extremely easily hydrolyzed to form the corresponding phosphine oxides in quantitative yields.



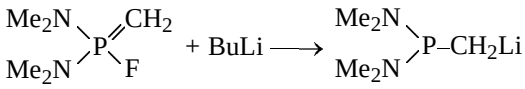
Alkoxyfluorophosphonium ylides are dealkylated with acids into phosphinic fluorides [31].



It was reported that difluorotriisopropylphosphorane reacts with butyllithium to give butylidenetriisopropylphosphorane [92].

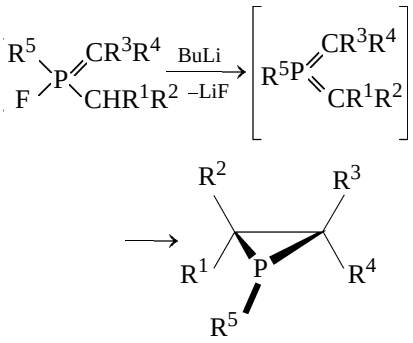


The reaction of bis(dimethylamino)phosphonium methylide with butyllithium results in exclusive formation of trivalent phosphorus derivatives [50].



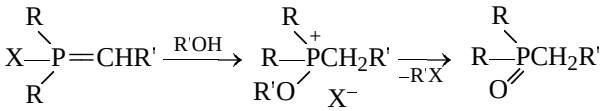
P-Fluoroylides containing secondary alkyl groups on phosphorus are easily dehydrofluorinated with organolithium compounds. Evidently, the latter agents effect metalation of the carbon atom to form a bisalkylidenephosphorane. In the absence of sterically congested substituents that stabilize the multiple P=C bond, the bisalkylidenephosphorane undergoes cyclization leading to phosphiranes. Dehydrofluorination of P,P-difluoroylides proceeds smoothly under the action of lithium diisopropylamide to form fluorophosphiranes. These compounds are liquids that can be distilled in a vacuum [94]. The ^{31}P NMR spectra of the fluorophosphiranes contain upfield signals (doublets, $^{1}J_{FF}$ ca. 1100 Hz), supportive of their structure. Fluorophosphiranes with different substituents R and R' are formed as mixtures of *syn* and *anti* isomers.

Cyclic P-fluorophosphiranes are stable compounds which can be distilled in a vacuum. The signals of phosphiranes in the ^{31}P and ^{19}F NMR spectra locate extremely downfield. They have large J_{PF} coupling constants reaching 1000 Hz. The NMR spectra of fluorophosphiranes containing different substituents on the α-carbon atom reveal *syn* and *anti* isomers. The fluorine atoms in these compounds are easily substituted with dialkylamino groups in reactions with lithium amides to give P-diethylaminophosphiranes in high yields [24, 94].



2,3-Diethyl-2,3-dimethyl-1-fluorophosphirane [94]. A solution of 0.072 mol of butyllithium in hexane was added dropwise to a solution of 0.03 mol of di-*sec*-butyltrifluorophosphorane in 10 ml of diethyl ether at –60°C. The reaction mixture was stirred for 15 min at this temperature and then heated to 20°C. After that it was left for 1 h at room temperature and then filtered. The solvent was removed from the filtrate at reduced pressure, and the residue was distilled in a vacuum. Yield 80%, bp 35–40°C (15 mm Hg).

Reactions of P-fluoroylides with nucleophiles containing a mobile hydrogen atom lead to formation of adducts by the P=C bond [87, 89, 92]. The reactions of P-fluoroylides with HX strongly differ from analogous reactions of other P-halo(chloro, bromo, or iodo)ylides. For example, P-chloroylides take up alcohols to give alkoxyphosphonium salts in quantitative yields. Reactions of P-fluorolides with alcoh ols, too, provide phosphonium salts [89].



At the same time, P,P-difluoroylides which have a highly polar P=C bond take up nucleo-

Table 8. Phosphiranes

R^1	R^2	R^3	R^4	R^5	bp, °C (*p*, mm Hg)	δ_P, mmp (*J*, Hz)	Reference
Me	Et	Me	Et	F	35–40 (150)	31.45 ($^1J_{PF}$ 964), 32.7 ($^1J_{PF}$ 964)	[24, 94]
Ph	H	Ph	H	$PhCH_2$	77–79[a]	–181.7	[93]
Ph	H	Ph	H	Et_2N	[b]	–89.3	[93]
Me	Me	Me	Me	*i*-Pr	44–46 (10)	–139.6	[93]

[a] Melting point. [b] Oily substance.

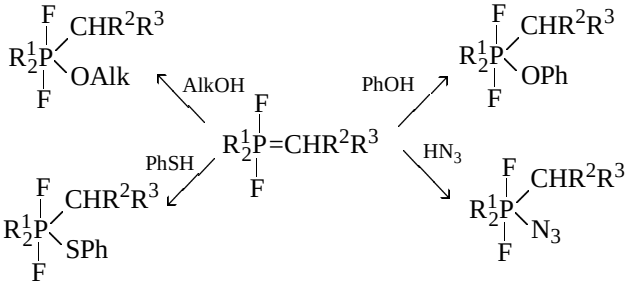
Table 9. P-Difluorophosphoranes $R^1P(F_2)(X)CHR^2R^3$

R^1	R^2	R^3	X	Yield, %	bp, °C (*p*, mm Hg)	δ_P, ppm (*J*, Hz)	Reference
t-Bu	Me	Et	MeO	95	65 (12)	–14.27 (780)	[21]
t-Bu	*i*-Pr	H	EtO	95	68 (12)	–13.07 (780)	[21]
Et_2N	Pr	H	MeO	95	26–30 (0.1)	–41.6 (780)	[21]
Et_2N	Me	Et	EtO	95	35 (0.1)	–44.1 (767)	[21]
t-Bu	Me	Et	*i*-BuO	98	50–60 (0.1)	–14.74 (807)	[21, 32]
t-Bu	*i*-Pr	H	$Et_2NCH_2CH(Me)O$	95	75 (0.08)	–14.7 (807)	[21, 32]
Et_2N	H	H	PhO	95	70 (0.07)	–46.7 (769)	[21]
Et_2N	Pr	H	PhO	90	80 (0.01)	–47.3 (790)	[21]
Et_2N	Pr	H	PhS	90	[a]	–28.9 (816)	[21]
Et_2N	Pr	H	N_3	90	[a]	–42.7 (775)	[21]

[a] Oil.

philes with a mobile hydrogen atom to give difluorophosphoranes in quantitative yields. The reactions of P,P-difluoroylides with alcohols, phenols, and thiophenols easily proceed in ether or benzene below 0°C to form difluorophosphoranes in almost quantitative yields [21, 22]. Contrary to the above-described alkoxyfluorophosphoranes which are extremely unstable, adducts of alcohols with P-fluoroylides are stable at room temperature. The stability of these alkoxyfluorophosphoranes is evidently explained by their high purity. Addition of nucleophiles containing a mobile hydrogen atom to P,P-difluoroylides is a convenient route to hardly available alkoxyfluorophosphoranes and azidofluorophosphoranes (Scheme 14, Table 9) [21, 95].

Scheme 14.



***tert*-Butylisobutyldifluoro(ethoxy)phosphorane**. Ethanol, 0.02 mol, was added to a solution of 0.02 mol of *tert*-butyldifluorophosphonium isobutylide in 10 ml of ether at –60°C. After that the reaction mixture was heated to 20°C, the solvent was removed at reduced pressure, and the residue was distilled in a vacuum. Yield 80%, bp 67°C (12 mm Hg).

SUMMARY

P-Fluoroylides are available compounds which can be prepared by simple methods from cheap starting materials. P-Fluoroylides exhibit diverse reactivity and can be used as starting materials in organic synthesis. The fluorine atoms on phosphorus affect the chemical properties and reactivity of P-fluoroylides, which imparts to the latter new chemical properties and synthetic potential. Research into P–F ylides will undoubtedly be continued, and, probably, these reagents will find practical application. Further studies, for example, may dwell on synthesis of ylides containing three fluorine atoms on phosphorus. Furthermore, P-fluoroylides can be used as starting materials for preparing inorganic polymers and biologically active compounds.

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