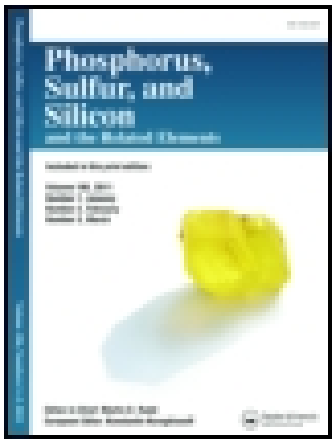


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Synthesis and Properties of Four-Membered Phosphorus Heterocycles - 2-Fluoro-1,2Λ^5-Oxaphosphetanes

Anastasia O. Kolodiazhna[a] & Oleg I. Kolodiazhnyi[a]

[a] Institute of Bioorganic Chemistry and Petrochemistry of National Academy of Sciences of Ukraine, Ukraine, Kiev, 02094, Murmanska Street, 1

Accepted author version posted online: 08 Jun 2015.

SYNTHESIS AND PROPERTIES OF FOUR-MEMBERED PHOSPHORUS HETEROCYCLES - 2-FLUORO-1,2λ^5-OXAPHOSPHETANES

Anastasia O. Kolodiazhna, Oleg I. Kolodiazhnyi*

Institute of Bioorganic Chemistry and Petrochemistry of National Academy of Sciences of Ukraine, Ukraine, 02094, Kiev, Murmanska Street, 1

*Address correspondence to Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Murmanskaia 1, Kyiv 02094, Ukraine. e-mail: olegkol321@rambler.ru

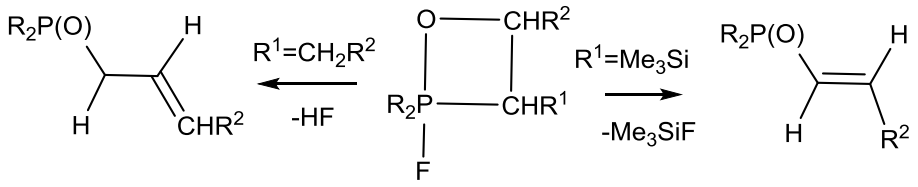
Received x xxx 2015; accepted xx xxx 2015.

Dedicated to Editor-in-Chief Emeritus of this Journal Professor Robert R. Holmes.

Abstract

The preparation of four-membered phosphorus(V)-heterocycles, ***2****-fluoro-1,2λ^5-oxaphosphetanes, by reaction of P-fluoroylides with carbonyl compounds is described. The reaction is stereoselective and leads preferentially to the formation of threo-1,2λ^5-oxaphosphetanes. Oxaphosphetanes were isolated as individual compounds and their structures were confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectra. The fluoro-1,2λ^5-oxaphosphetanes may be*

easily converted to various alkenylphosphonates: allyl- or vinylphosphonates. This reaction represents a good method for the preparation of phosphorylated alkenes



Keywords

1,2λ^5-Oxaphosphetanes, phosphoranes, allylphosphonates, vinylphosphonates, P-fluoroylides

INTRODUCTION

One of the most interesting and intriguing classes of organophosphorus compounds is 1,2-oxaphosphetanes – four-membered heterocycles containing pentacoordinated phosphorus.[1-3]

The reaction of phosphorus ylides with carbonyl compounds, leading to the formation of olefins, is one of the major reaction in synthetic organic chemistry.[4] Extensive experimental[5,6] and theoretical work[7,8] has been devoted to clarify the reaction mechanism. A variety of different species, betaines,[8] diradicals, and 1,2-oxaphosphetanes,[1-3] were proposed as possible reactive intermediates. However, only 1,2-oxaphosphetanes were fully identified and some of them (A-C) were isolated (Scheme 1).[9-11] Among the stable oxaphosphetanes the biggest interest is in the 2-halogen-1,2-oxaphosphetanes D, which possess relatively high stability and various reactivity.[12-15]

DISCUSSION

The available methods for the synthesis of 2-fluoro-1,2λ^5-oxaphosphetanes can be used for investigation of the reaction mechanism of phosphorus ylides with carbonyl compounds as well as for preparing stable oxaphosphetanes thats can be used as initial reactants for organic synthesis. The 2-fluoro-1,2λ^5-oxaphosphetanes are the most stable representatives of this type of compounds. They can be purified by distillation under vacuum and stored in a refrigerator. At the same time they possess interesting chemical properties and enter to various chemical transformations.

The 2-fluoro-1,2λ^5-oxaphosphetanes were prepared by reaction of P-fluoroylides with carbonyl compounds. Earlier we developed convenient methods for the synthesis of P-fluoroylides. For example, they can be obtained in high yields by dehydrofluorination of alkyltrifluorophosphoranes.[13-15]

In the present article we have studied 2-fluoro-1,2λ^5-oxaphosphetanes **2a-h** which were prepared by reaction of P-fluoroylides **1a-d** with aldehydes and ketones leading to the formation of [2+2]-cycloaddition products **2a-h** in very high yields (Scheme 2). The 2-fluorooxaphosphetanes **2** are stable compounds at room temperature, which were isolated and studied by means of NMR spectroscopy. The 2-fluoro-3-silyl-1,2λ^5-oxaphosphetanes **2a-j**, containing C-3 and C-4-asymmetric atoms, exist as mixture of *erythro*- and *threo*-diastereomers. The ^{19}F and ^{31}P NMR spectra for compounds **2a-j** showed two sets of signals in the ratio ~4: 1 for the diastereomers.

The ^{31}P NMR chemical shifts of 2-fluorooxaphosphetanes were found at -37 to -43 ppm as doublets with a large constant $^1J_{PF}$ ~750-780 Hz and the values δ_F were found out at -45 ppm, doublets with the constant $^1J_{PF}$ 750-780 Hz. In ^{1}H NMR spectra were found signals of Me_3Si group, C(3)H proton at 4.80-5.0 ppm, double doublet with $^2J_{PH}$ ~14 and $^3J_{HF}$ ~7.5 Hz; OC(4)H at 5.2 – 5.4 ppm. In the ^{13}C NMR spectra, the signal δ_C of C-4 was found at +80 ppm and the signal of C-2 at +30 ppm as double doublets, $^1J_{PC}$ ~130 Hz, and $^2J_{FC}$ ~50 Hz, correspondingly. The spectroscopic data of 2-fluorooxaphosphetanes **2a-h** are typical for pentacoordinated phosphorus compounds.[16]

The transformations of 2-fluoro-1,2λ^5-oxaphosphetanes proceeded without P—C bond cleavage leading to a number of interesting organophosphorus compounds. Thus, 2-fluorooxaphosphetanes **2a-h** hydrolyze with formation of 2-hydroxyphosphonates **3**, which were isolated as crystalline compounds. The treatment of 2-fluorooxaphosphetanes **2a-h** with an ether solution of HCl led to the formation of 2-chlorooxaphosphetanes **4**. In contrast to 2,2,2-triphenyloxaphosphetanes, upon heating, the decyclization of 2-fluorooxaphosphetanes 2 occurred, leading to the formation of phosphorylated alkenes – allyl- or vinylphosphonates. The direction of reaction depends on substituents R^2 and R^3 at C–3 and C–4 of oxaphosphetane cycle. The 2-fluorooxaphosphetanes bearing R^2=H, Alk, Ar, at C-3 and R^3=Alkyl at C-4 proceeded with HF elimination to give allylphosphonates **5a,b**.[16c] The reaction was catalyzed by boron trifluoride etherate. The 2-fluorooxaphosphetanes bearing R=Me_3Si substituent at C-3 eliminated Me_3SiF to afford vinylphosphonates **6a-l** (Table 1). This reaction is a convenient method for the preparation of phosphorylated alkenes that are versatile building blocks for organic synthesis.[17]

Upon heating to 60 to 80 °C, the 2-fluoro-3-silyloxaphosphetanes **2a-h** converted into vinylphosphonates **6** in high yields. The reaction is regioselective and afforded pure *trans*-vinylphosphonates **6a-m**, without inclusion of allylphosphonates **5**. The *trans*-geometric configuration of vinylphosphonates **6a-m** was proven by NMR spectra which have disclosed signals, of two double doublets of olefin protons at 6-8 ppm with $^3J_{HH}$ =~16-18 Hz and $^2J_{PH}$ =~17-20 Hz. It is known that $^3J_{HH}$ of *cis*-vinylphosphonates are 11 – 14 Hz, and $^3J_{PH}$ are

approximately 40-57 Hz.[15-18] The *trans*-vinylphosphonates **6a-c** were synthesized earlier, their spectroscopic data were identical with those previously reported.[13,18]

The most stable were 2-fluoro-3-silyloxaphosphetanes **2g**, bearing CF_3 group at C-4. Upon heating to +100 °C the oxaphosphetanes **2g** eliminated Me_3SiF affording a mixture of *E*- and *Z*-vinylphosphonates **6k** in the ratio 2:1. However the slow conversion of **2g** at +20 °C over several days provided almost pure *E*-vinylphosphonates ***E*-6k**, containing only 2-3% of *Z*-isomer.

Probably, this effect can be explained by formation of carbocation intermediate **G** and rotation of substituents around the C-C bond (Scheme 5). In addition, the initial 2-fluorooxaphosphetanes **2a-h** exist as mixture of *threo*- and *erythro*-diastereomers, but they converted into pure *E*-vinylphosphonates. We suppose that the 2-fluorooxaphosphetanes under condition of acid catalysis (with HF or BF_3) *via* the formation of an oxonium intermediate **F**, convert to carbocation intermediate **G** which has a planar configuration. The removal of a proton from the carbocation intermediate **G** depends on electronic effects of the substituents. Alkyl groups possessing the +*I*-effect and the effect of hyperconjugation stabilize the positive charge and reduce the energy of activated state. Therefore, the activated state **G'** is energetically more favorable than the activated state, leading to the formation of vinylphosphonate. However, the presence of Me_3Si at C-3 in **G'** leads to the elimination of Me_3SiF, which has a high energy of formation, that creates a preference for the formation of vinylphosphonates (Scheme 5).[3]

The formation of carbocation intermediate **G** was experimentally confirmed (Scheme 6). The treatment of 2-hydroxyphosphonate with trifluoracetic acid and refluxing for several hours, generated the carbocation intermediate **G**, as a result of acid-catalyzed dehydration of alcohol **3**.[9]

Then the intermediate **G** converted into allylphosphonate **5a**, which is identical to the one obtained from 2-fluorooxaphosphetane **2i**.

The reaction of ylides **1** with carbonyl compounds proceeded with an equimolecular ratio of reagents upon cooling in diethyl ether. The reaction can be carried out in *one-pot* without isolation of oxaphosphetanes. In the reaction flask at low temperature, was placed the ether solution of P-fluoroylide and carbonyl compound. Next solvent was evaporated and the residue was heated to 60 to 100 ^{o}C. The course of reaction was monitored by TLC and by emission of gaseous Me_3SiF. The vinylphosphonates **6** were purified by distillation under vacuum or by column chromatography and obtained in good yields. The reaction of ylides **1a-c** with unsaturated aldehydes led to the formation of dienophosphonates **6i,j.** The IR spectra of these dienes contained intensive absorption bands of 1560 and 1620 cm^{-1} corresponding to unsymmetrical and symmetrical valence vibrations of *trans*-C=C—C=C bonds, and also bands 3010, 3030, 3090 – 3100 for valence vibration-frequencies and 930 – 940 cm^{-1} for the deformation frequencies of vinyl groups. In the ^{1}H NMR spectrum the signal assigned to four diene protons was observed in the field of 6-8 ppm.[19-21]

The reaction of ylides with aldehydes is regioselective. For example, the reaction of ylide **1c** with terephthalic aldehyde in the 2:1 ratio of initial reagents led to formation of a 1,4-bis-vinylphosphonobenzene **6m** and in the 1:1 ratio afforded phosphonovinylbenzaldehyde **6l,** which are interesting as starting reagents for organic synthesis. The reaction was performed at +20 °C in THF. Elemental analysis and spectroscopic data of phosphonovinylbenzaldehyde **6l** responded to the structure. IR spectra contained absorbtions at 2700 (CH) and 1690 cm^{-1} (C=O),

showing the presence of an aldehyde group, and also bands at 1550 (C=C), 1205, 1215 cm^{-1} (P=O). The ^{1}H NMR spectra of compound revealed the singlet of an aldehyde proton at 11.5 ppm, double doublets of vinyl protons at 6.5 ppm (PCH=C) and 7.7 ppm (PC=CH) with coupling constants $^{3}J_{HH}$ 17 Hz, $^{3}J_{PH}$ 19 Hz and $^{2}J_{PH}$ 17.5 Hz. There was also a double doublet of ortho-protons for the 1,4-disubstituted benzene ring.

CONCLUSION

In conclusion, we have studied the reaction of P-fluoroylides with aldehydes and ketones leading to the formation of 2-fluoro-1,2λ^{5}-oxaphosphetanes, that could be converted into phosphorylated alkenes by heating. The structure of the alkenes depended upon the nature of substituents at C-3 and C-4 atoms in a four-membered cycle. The 2-fluorooxaphosphetanes, bearing alkyl groups at the C-4 atom, as a result of 1,4-elimination of hydrogen fluoride, afforded allylphosphonates. The 2-fluorooxaphosphetanes bearing the trimethylsilyl group at the C-3-atom, through 1,2-elimination of trimethylsilylfluoride afforded *E*-vinylphosphonates. The conversion of 2-fluorooxaphosphetanes into alkenphosphonates proceeded *via* the formation of a carbenium ion intermediate.

EXPERIMENTAL

IR spectra were obtained in KBr pellets and recorded with a Vertex 70 IR Fourier spectrophotometer. The mass spectra were recorded on an AEIMS-902 model. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured in C_6D_6 and $CDCl_3$ solution with TMS as internal or 85% H_3PO_4 as an external standard with Varian VXR-300 and Gemini 2000 (400 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million. Coupling constants (J) are

reported in Hz. Solvents were preliminarily distilled in an inert atmosphere: diethyl ether, hexane, benzene, and carbon tetrachloride over phosphorus pentoxide, methanol and triethylamine over sodium, and ethyl acetate over calcium chloride. All commercially available reagents were used without further purification. Melting points are uncorrected. The P-fluoroylides **1a-d** were prepared by reaction of trifluroalkylphosphonates with butyllithium using methods earlier reported by us.[12,15] Other reagents were purchased from Merck (Germany), Fluka (Buchs, Switzerland), and Acros and were used without further purification. TLC was performed on plates coated with silica gel 60 with an F_{254} indicator; column chromatography was carried out on silica gel 60 (230–240 mesh).

2,2-Bis(diethylamino)-2-fluoro-3-(trimethylsilyl)-4-phenyl-1,2-λ^5-oxaphosphetane (2a)

(*Typical experiment*)

To a solution of ylide **1c** (0.02 moles) in 5 mL of diethyl ether at 0 °C was added 0.022 moles of benzaldehyde. The reaction mixture was left for 3 – 4 h at +20 °C. Then the solvent was evaporated under reduced pressure. The product is unstable, therefore was used without purification. Colorless liquid. Yield 95 %.

^{1}H NMR ($CDCl_3$): δ 0.18 d ($^3J_{PH}$ 1.0 Hz, 9H, Me_3Si); 1.21, t ($^3J_{PH}$ 7 Hz, 6H, CH_3); 1.33 t ($^3J_{PH}$ 7 Hz, 6H, CH_3); 3.21 m (8H, CH_2N); 4.80, d.d ($^2J_{PH}$ 14 Hz, $^3J_{FH}$ 7.5 Hz, 1H, PCH); 5.23 d.d ($^3J_{PH}$ 5 Hz, $^3J_{HH}$ 7.5 Hz, 1H, OCH); 7.5 m; 7.73 m; 8.07 m (5H, C_6H_5) (major diastereomer). ^{13}C NMR (C_6H_6): δ_C 1.81, dd ($^3J_{CP}$ 8 Hz, $^4J_{CF}$ 2 Hz, Me_3Si); 15.73, dd ($^2J_{CP}$ 8 Hz, $^3J_{CF}$ 3 Hz, CH_3);

29.1, d.d ($^1J_{CP}$ 130 Hz, $^2J_{CF}$ 28 Hz, PCH); 37.9 dd ($^2J_{CP}$ 7 Hz, $^3J_{CF}$ 6 Hz, NCH_2); 82; 124.29; 125.93; 127.08; 148.2 (major diastereomer).

^{31}P NMR ($CDCl_3$): δ_P = –39.18, d, $^1J_{PF}$ 780 Hz; –38.53, d, $^1J_{PF}$ 762 Hz. ^{19}F NMR ($CDCl_3$): δ_F = –41.0, d, $^1J_{PF}$ 780 Hz, δ_F = –39.6, d, $^1J_{PF}$ 760 Hz (4:1). Anal. Calcd. for $C_{19}H_{36}FN_2OPSi$: P, 8.01%. Found: P, 8.00%.

Other 2-fluoro-oxaphosphetanes **2b-h** were prepared analogously to compound **2a**. These compounds were used for further synthesis without purification. Parameters of ^{19}F and ^{31}P spectra are presented below in the Table 2.

2,2-Bis(diethylamino)-2-fluoro-4-spiro-cyclohexane-1,2λ^5-oxaphosphetane (2i)

To a solution of ylide **1d** (0.02 moles) in 5 mL of diethyl ether at 0 °C was added 0.022 moles of cyclohexanone. The reaction mixture was left for 3 – 4 h at +20 °C. Then the solvent was evaporated and the residue was distilled under vacuum. Colorless liquid. Yield 90 %. Bp 110 ^{oC} (0.02 mmHg).

^{1}H NMR ($CDCl_3$): δ 1.1 t ($^3J_{HH}$ 7 Hz, 12H, CH_3CH_2); 1.48 m (10H, C_5H_{10}); 2.90 m (8H, CH_2N); 5.5 d ($^2J_{HP}$ 25 Hz, 2H, PCH_2). ^{13}C NMR (C_6H_6): δ_C 13.78; 22.27; 23.84; 37.15 d ($^3J_{CP}$ 8.5 Hz, C_5H_{10}); 40.43 dd ($^2J_{CP}$ 7.5 Hz, $^3J_{CF}$ 7 Hz, CN); 51.16 d.d ($^1J_{CP}$ 139 Hz, $^2J_{CF}$ 51, PC); 66.0 d.d (^2Jcp 20 Hz, $^3J_{CF}$ 9 (OC). ^{31}P NMR (C_6D_6): δ_P = -44.0, d ($^1J_{PF}$ 756 Hz)**;** δ_F -42.2, d ($^1J_{PF}$ 756). MS (m/e): 306 (M^+) M 306.40. Anal. Calcd. for $C_{15}H_{32}FN_2OP$: N 9.14; P 10.11. Found: N 9.02; P 10.02.

2,2-Bis(diethylamino)-2-fluoro-4,4-dimethyl-1,2λ^5-oxaphosphetane (2j)

Preparation was analogous to **2a**. Yield 70%. Bp 70-75 ^{oC} (0.02 mmHg).

^{1}H NMR ($CDCl_3$): δ 1.08 t ($^3J_{HH}$ 7 Hz, 12H, CH_3); 1.31 s; 1.34 s [$(CH_3)_2C$]; 2.78 t ($^2J_{HP}$ 15.5 Hz,1H, PCH^a); 3.08 t ($^2J_{PH}$ 15.5 Hz, 1H, PCH^b); 3.19 m; 3.25 m (8H, CH_2N).

^{13}C NMR (C_6H_6): δ_C 13.6 (CH_3); 27.5 d ($^3J_{CP}$ 9 Hz); 30.6 d [$^3J_{CP}$ 9 Hz, $(CH_3)_2C$]; 36.6 m (CH_2N); 42.05 dd ($^1J_{PC}$ 130 Hz, $^3J_{FC}$50 Hz, CH_2); 66.5 (CMe_2).

^{31}P NMR (C_6D_6): δ_P = -47.5, d ($^1J_{PH}$ 765 Hz). ^{19}F NMR (C_6D_6): δ_F = -45.95 Hz, d ($^1J_{PH}$ 765 Hz).

MS (m/e) 266 (M+), M=266.34.

Anal. Calcd. for $C_{12}H_{28}FN_2OP$: C 54.12; H 10.60. Found: C 54.02; H 10.42%.

[(1-Hydroxycyclohexyl)methyl]-phosphonic bis(diethylamide) (3)

^{1}H NMR ($CDCl_3$): δ 1.07 t ($^4J_{HH}$ 7 Hz, 12H, CH_3) 1.3-1.6 m (10H, CH_2); 2.1 d (2H, $^2J_{PH}$ 19 Hz, PCH_2); 2.9 m (8H, CH_2N). ^{31}P NMR (C_6D_6): δ_P = 29.28. MS (*m/e*): 304 (M^+) (M 304.23).

Anal. Calcd. for $C_{15}H_{33}N_2O_2P$: C, 59.18; H, 10. Found: C, 59.61; H, 11.15%.

2-Chloro-2-phenylethylphosphonic bis(diethylamide) (4)

To a solution of 2-fluoroxaphosphetane (0.01 mol) in 5 mL of ether at -70 °C was added ether solution of hydrogen chloride (0.01 mol). The temperature was raised to room temperature. The precipitate of the hydrochloride of phosphonate **4** was filtered off and treated with triethylamine

in ether. A product dissolved on ether, was combined with a mother solution. The solvent was evaporated; the residue was recrystallized in pentane (-70 °C). Yield 70%, mp 42-43 °C.

^{1}H NMR ($CDCl_3$): δ 0.8 t ($^3J_{HH}$ 7 Hz, 6H, CH_3CH_2); 1.08, t ($^3J_{HH}$ 7 Hz, 6H, CH_3CH_2); 2.56 d.d ($^3J_{HH}$ 7 Hz, $^2J_{HP}$ 13.0 Hz, 1H, PCH); 2.59 dd ($^3J_{HH}$ 6.5 Hz, $^2J_{HP}$ 13 Hz, 1H, PCH'); 2.63 m; 2.97 m (8H, NCH_2); 5.31 dt ($^3J_{HH}$ 7 Hz, $^3J_{HP}$ 8.5 Hz, 1H, CHC1); 7.27 m (5H, C_6H_5). ^{31}P NMR (C_6D_6): δ_P = 29.28 ppm.

Anal. Calcd. for $C_{16}H_{28}ClN_2OP$; Cl 10.72; N 8.47; P 9.36. Found: Cl 11.07; N 8.46; P 8.98%.

1-Cyclohexen-1-yl-methylphosphonic bis(diethylamide) (5a)

a) The 2-fluoro-1,2λ^5-oxaphosphetanes (0.015 moles) was heated carefully to 120 – 140 °C and gaseous hydrogen fluoride emission was observed .Then the reaction mixture was distilled under vacuum.

Bp 145 ^{o}C (0.08 mmHg). Yield 85 %.

b) To 2-fluorooxaphosphetane **2** (0.015 mol.) was added several drops of boron trifluoride etherate. The reaction mixture was left for several hours at ambient temperature or at weak heating. Gaseous hydrogen fluoride emission was observed. Then the reaction mixture was distilled under vacuum. Bp 145 ^{o}C (0.08 mmHg). Yield 80 %.

c) A solution of bis(diethylamide) - [(1-hydroxycyclohexyl)methyl]-phosphonate 3 (0.015 mol) in trifluoroacetic acid (10 mL) was heated for 2 h. Then the solution was evaporated under pressure reduced (10 mmHg) and residue was distilled under vacuum (0.06 mmHg). Yield 50%.

Bp 140 ^{o}C (0.06 mmHg). The product was additionally purified by column chromatography with silica gel (eluent ethyl acetate/hexane).

^{1}H NMR ($CDCl_3$): δ 1.02 t ($^{3}J_{HH}$ 7 Hz, 12H, CH_3CH_2); 1.53, m; 1.94 m; 2.11 m [$(CH_2)_4$]; 2.35 d ($^{2}J_{HP}$ 16.6 Hz, 2H, PCH_2); 2.93 dq ($^{3}J_{HP}$ 10 Hz, 8H, NCH_2); 5.39 m (CH=C).

^{13}C NMR (C_6H_6), δ_C 12.73; 20.5; 21.34; 23.89; 28.01; 34.08 d ($^{1}J_{CP}$ 109, PC); 37.35; 123.34 d ($^{2}J_{CP}$ 12 Hz, PCC=C); 129.28.

^{31}P NMR (C_6D_6): δ_P = 32.6 ppm. *m/z* 286 (M+) (M 286.39).

Anal. Calcd. for $C_{15}H_{31}N_2OP$: C 62.91, H 10.91, P 10.82%. Found: C 62.60, H 10.72, P 10.99%.

(2-Methyl-2-propenyl)-phosphonic bis(diethylamide) (5b)

Was prepared analogously to **5a**. Yield 50%, bp 100 ^{o}C (0.08 mmHg).

^{1}H NMR ($CDCl_3$): δ 1.01 t ($^{3}J_{HH}$ 7 Hz, 12H, CH_3CH_2); 1.81 s (3H, CH_3C=C); 2.42 d ($^{2}J_{HP}$ 16.6 Hz, 2H, PCH_2); 2.93 dq ($^{3}J_{HP}$ 10 Hz, 8H, NCH_2); 4.7 d ($^{4}J_{HP}$ 2 Hz, 1H, CH^{a}=C); 4.9 d ($^{4}J_{HP}$ 2 Hz, 1H, CH^{b}=C); ^{31}P NMR (C_6D_6): δ_P = 31.74. MS (*m/e*) 246 (M+) (M 246.33).

Anal. Calcd. for $C_{12}H_{27}N_2OP$. C 58.51; H 11.05; P 12.57%. Found: C 59.21; H 11.55; P 12.26%.

Vinylphosphonates 6a-m (*general method*).

2-Fluorooxaphosphetanes **2a-h** were heated to 80 – 100 °C. The evolution of gaseous Me_3SiF was observed. The reaction mixture was then crystallized in hexane or heptane, and distilled under vacuum or chromatographed on column with silica gel

Di-tert–butyl(2-phenylethenyl)phosphine oxide (6a)

The ylide **1b** (0.01 mol) was mixed with benzaldehyde (0.01 mol) and the mixture was heated at 150 °C for 30 – 40 min to the end of Me_3SiF emission. The residue was cooled and recrystallized from heptane. Yield 80 %, mp 138 °C.[13]

^{1}H NMR ($CDCl_3$): δ 1.53 d ($^3J_{HH}$ 13.7 Hz, 9H,CH_3C); 7.08 d.d ($^3J_{HH}$ 18 Hz, $^2J_{PH}$ 22.5 Hz, 1H, PCH=C); 7.95 dd ($^3J_{HH}$ 18 Hz, 1H, C=CH); 7.8 m (5H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 50 ppm.

Diphenyl(2-phenylethenyl)phosphine oxide (6b).

To a stirring solution of ylide **1a** (0.01 mole) in ether (10 mL) at -70 ^{o}C was added benzaldehyde (0.011 mol). Then the temperature of reaction mixture was raised to +20 ^{o}C and the mixture was left for 12 hr. The course of reaction was monitored by ^{31}P NMR. The ^{31}P NMR spectrum showed the full conversion of ylide **1a** into 2-fluoroxaphosphetane **2c** in several hours: δ_P -43.5 ppm, doublet, $^1J_{PF}$ 620 Hz. The solvent was evaporated under vacuum and the residue was heated up to 80 – 100 °C, then the reaction mixture was treated with water and separated by column chromatography on silica gel with ethyl acetate as an eluent. Yield 40%, m.p. 165 °C that corresponds to the published data.[18]

^{1}H NMR ($CDCl_3$): δ 6.35, d.d ($^{3}J_{HH}$ 17.0 Hz, $^{2}J_{HP}$ 24.0 Hz, 1H, PCH=C); 7.3 m; 7.75 m (16H, PC=CH+ C_6H_5). ^{31}P NMR (C_6D_6): δ_P = 22.0 ppm.

_E_-(2-Phenylethenyl)phosphonic bis(diethylamide) (6c)

To a solution of ylide **1c** (0.01 mol) at -70 ^{o}C was added benzaldehyde (0.015 mol), the temperature was raised to room and the mixture was stirred for 14 h. The reaction mixture was evaporated under pressure reduced (10 mmHg) at +20 ^{o}C, then the residue was heated at 100 °C for 15 min. under vacuum (0.05 mm Hg) and the residue was recrystallized in hexane. Yield 80%, mp 103.5 °C.

^{1}H NMR ($CDCl_3$): δ 1.38 t (^{3}Jнн 7 Hz, 12H, CH_3CH_2); 3.38 dq (^{3}Jнн 7 Hz, ^{3}Jрн 11 Hz, 8H, CH_2N); 6.60 d.d ($^{3}J_{HH}$ 17.2 Hz, J_{PH} 18 Hz, 1H, PCH=C); 7.75 d.d ($^{3}J_{HH}$ 17.5, $^{3}J_{PH}$ 19, 1H, C=CH); 7.65 m (5H, C_6H_5). ^{13}C NMR (C_6D_6): δ 13.70; 41.85; 114.50, d ($^{1}J_{PC}$ 152.0 Hz, PCH=C); 128.70; 131.66 d ($^{2}J_{PC}$ 24.0 Hz, PC=C), 144.17, 161.90 d ($^{3}J_{PC}$ 30 Hz). ^{31}P NMR ($CDCl_3$): δ_P 24.50 ppm.

1_E_-1-propenyl]-phosphonic bis (diethylamide) (6d)

Preparation was analogous to **6c**.Yield 72%. Bp 80^{o}C (0.05 mmHg).

^{1}H NMR ($CDCl_3$): δ 0.92 t ($^{3}J_{HH}$ 7.7 Hz, 12H, CH_3); 1.85 d ($^{4}J_{PH}$ 8 Hz, 3H, CH_3); 2.98 dq ($^{3}J_{HH}$ 7 Hz, $^{3}J_{PH}$ 10 Hz, 8H, CH_2N); 5.66 d.d ($^{2}J_{PH}$ 20 Hz, $^{3}J_{HH}$16 Hz, 1H, PCH=C); 6.61 ddq (^{3}Jнр 18 Hz, ^{3}Jнн 16 Hz, ^{3}Jнн 6 Hz, 1H, PC=CH). ^{31}P NMR (C_6D_6): δ_P 24.7 ppm.

Anal. Calcd. for $C_{11}H_{25}N_2OP$. P, 13.33%. Found: P, 13.43%

1*E*-1-Pentenylphosphonic bis(diethylamide) (6e)

was prepared analogously to **6c**. Yield 70%, bp 110^{o}C (0.05 mmHg).

^{1}H NMR ($CDCl_3$): δ_H 0.86 t ($^{3}J_{HH}$ 7.7 Hz, 3H, CH_3); 1.03 t (^{3}Jнн 7 Hz, 12H, C$\underline{H}_3CH_2N$); 1.42m (2H, CH_2); 2.13 d.t (^{3}Jнн 7 Hz, $^{3}J_{PH}$ 7 Hz, 2H, CH_2); 3.08 dq ($^{3}J_{HH}$ 7 Hz, $^{3}J_{PH}$ 10 Hz, 8H, CH_2N); 5.65 d.d.t ($^{2}J_{PH}$ 20 Hz, $^{3}J_{HH}$16 Hz, $^{4}J_{HH}$, 1.4 Hz, 1H, PCH=C); 6.65 d.d.t ($^{3}J_{HP}$ 18 Hz, ^{3}Jнн 16 Hz, ^{3}Jнн 6 Hz, 1H, PC=CH). ^{31}P NMR (C_6D_6): δ_P 24.2 ppm.

1*E*-1-Hhexenylphosphonic bis(diethylamide) (6f)

was prepared analogously to **6c**. Yield 68%, bp 120-123 ^{oC} (0.04 mmHg).

^{1}H NMR ($CDCl_3$): δ 0.83 t (^{3}Jнн 7 Hz, 3H, CH_3); 1.01 t (^{3}Jнн 6.8 Hz, 12H, C$\underline{H}_3CH_2N$); 1.20-1.40 m (4H, CH_2); 2.16 d.t ($^{3}J_{HH}$ 6.8 Hz, 2H, CH_2); 2.98 dq ($^{3}J_{HH}$ 7 Hz, $^{3}J_{HP}$ 12 Hz, 8H, NCH_2); 5.63, d.d.t ($^{3}J_{HH}$ 16.8 Hz, $^{2}J_{HP}$ 21 Hz, $^{4}J_{HH}$ 1.5 Hz, 1H, PCH=C); 6.61 d.d.t ($^{3}J_{HP}$ 19 Hz, $^{3}J_{HH}$ 16.8 Hz, $^{3}J_{HH}$ 6.7 Hz, 1H, PC=CH). ^{31}P NMR (C_6D_6): δ_P 23.95 ppm.

1*E*-1-octenylphosphonic bis(diethylamide) (6g)

Was prepared analogously to **6c**.Yield 80%, bp 135 (0.06 mmHg).

^{1}H NMR ($CDCl_3$): δ 0.83 t ($^{3}J_{HH}$ 7 Hz, 3H, CH_3), 1.02 t ($^{3}J_{HH}$ 6.9 Hz, 12H, CH_3CH_2N); 1.22 m (8H, CH_2); 2.15 d.t ($^{3}J_{HH}$ 6 Hz, $^{3}J_{HH}$ 6.8 Hz, 2H, CH_2C=); 2.97 ddq ($^{3}J_{HH}$ 7.8 Hz, $^{3}J_{HP}$ 11.7 Hz, 8H, NCH_2); 5.61 d.d.t ($^{2}J_{HP}$ 21.3 Hz, $^{3}J_{HH}$ 16.8 Hz, $^{4}J_{HP}$ 1.5 Hz, 1H, PCH=C); 6.61 d.d.t ($^{3}J_{HP}$ 19.3 Hz, $^{3}J_{HH}$ 16.8 Hz, $^{4}J_{HH}$ 6.7 Hz, 1H, PC=CH). ^{13}C NMR ($CDCl_3$): δ 12.17; 12.15; 20.68; 26.17; 26.85; 28.70; 32.22 d ($^{3}J_{CP}$ 18.9 Hz, PC=CC); 119.1 d ($^{1}J_{CP}$ 153.14 Hz, PC=); 148.36.

^{31}P NMR (C_6D_6): δ_P = 24.1 ppm. *m/z* 302 (M+) M= 302.436.

Anal. Calcd. for $C_{16}H_{35}N_2OP$: C, 63.54; H, 11.66; P, 10.24%. Found: C, 63.66; H, 11.72; P, 10.04%.

(1*E*)-1-Decenylphosphonic bis(diethylamide) (6h)

Preparation was analogous to **6c**. Yield 79%, bp 145-150 °C (0.05 mmHg).

^{1}H NMR ($CDCl_3$): δ 0.81, t ($^{3}J_{HH}$ 7 Hz, 3H, CH_3), 1.01 t ($^{3}J_{HH}$ 7 Hz, 12H, $C\underline{H_3}CH_2N$)*;* 1.20 м 10H, CH_2); 2.13 d.t ($^{3}J_{HH}$ 7 Hz, $^{3}J_{HH}$ 7 Hz, 2H, CH_2C=); 2.98 dq ($^{3}J_{HP}$ 10.5 Hz, 8H, NCH_2); 5.64 d.d.t ($^{2}J_{HP}$ 20.5 Hz, $^{3}J_{HP}$ 16.8 Hz, $^{4}J_{HH}$ 1.5 Hz, 1H, PCH=C); 6.61 d.d.t ($^{3}J_{HP}$ 19 Hz, $^{3}J_{HH}$ 16.8 Hz, $^{3}J_{HH}$ 6.5 Hz, 1H, PC=CH). ^{31}P NMR (C_6D_6): δ_P = 24.1 ppm.

Anal. Calcd. for $C_{18}H_{39}N_2OP$: C, 65.42; H 11.89; P, 9.37%. Found: C, 66.12; H 12.09; P, 9.01%

4-Phenyl-(1*E*,3*E*)-butadienylphosphonic bis(diethylamide) (**6i)**

To a solution of **1a** (0.02 mol) in diethyl ether (10 mL) was added cinnamic aldehyde (0.02 mol) at 0 – +5°C. The mixture was left for 18 h at room temperature and then was evaporated under pressure reduced. The residue was distilled under vacuum

Yield 70 %, b. p.170-175 °C (0.06 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.4 t ($^{3}J_{HH}$ 7 Hz, 12H, CH_3); 3.30 dq ($^{3}J_{PH}$ 10 Hz, 8H, CH_2N); 6.30 m (1H, CH=C); 7.30 m (3H, C=CH+CH=CH); 7.80 m (5H, C_6H_5).

^{31}P NMR ($CDCl_3$): δ_P 23.30 ppm.

Anal. Calcd. for $C_{18}H_{29}N_2OP$: C, 67.47; H, 9.12; P, 9.67%. Found: C, 67.77; H, 9.20; P, 9.66%.

1*E*,3*E*-4,8-Dimethyl-1,3,7-nonatrienylphosphonic bis(diethylamide) (6j)

Yield 40%, bp 160 °C (0.08 mmHg). δ_H 1.04 t ($^{3}J_{HH}$ 7 Hz, $\underline{CH_3}CH_2N$); 1.60 m (3H, CH_3); 1.70 m (3H, CH_3); 1.81 m (3H, CH_3); 2.1 m (4H, CH_2); 3.0 m (8H, CH_2N); 5.11 t ($^{3}J_{PH}$ 8 Hz, 1H, $CH=CMe_2$); 5.49 t ($^{3}J_{HP}$ 17 Hz, 1H, C=CHP); 5.9 d ($^{3}J_{HP}$ 12Hz, 1H, C=CH); 6.6 m (1H, C=CH)

MS (*m/e*)= 340 (M+) M 340.48

Anal. Calcd. for $C_{19}H_{37}N_2OP$. C, 67.02; H, 10.95; P, 9.10%. Found: C, 67.57; H, 10.20; P, 9.46%.

3,3,3-Trifluoro-2-phenylpropenephosphonic bis(diethylamide) (6k)

a) The 2-fluorooxaphosphetanes **2g (0.02 mol)** was heated to 80 – 100 °C. The evolution of gaseous Me_3SiF was observed. The reaction mixture was then distilled under vacuum or

chromatographed on column with silica gel. Yield 70 %, bp 150 ^{o}C (0.07 mmHg). The mixture of *E*- and *Z*-isomers in ratio 2:1 was obtained. We assume that the major isomer is *E*-alkene **6k**, because δ_H of vinyl proton and δ_P of this compound are shifted to down field relative to those of minor *Z*-isomer. In earlier reported ^{31}P NMR spectra of vinylphosphonates, the signals of Z-isomers appeared at higher field than the ones of *E*-isomers.[20, 22,23a-c]

b) The 2-fluorooxaphosphetanes 2g (0.02 mol) was left at 20 °C for a week. The reaction mixture was then distilled under vacuum. Yield 75 %, b. p.150 ^{o}C (0.07 mmHg). The almost pure *E*-isomer was obtained.

(*E*-isomer): ^{1}H NMR ($CDCl_3$): δ 1.38 t ($^{3}J_{HH}$ 7 Hz, 12H, CH_3); 3.27 dq ($^{3}J_{PH}$ 10 Hz, 8H, CH_2N); 6.80 dq ($^{2}J_{PH}$ 12 Hz, $^{4}J_{HF}$ 1.5 Hz, 1H, C=CH); 7.60 m (5H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 23.50 ppm ^{19}F NMR ($CDCl_3$), δ_F –68.11

(*Z*-isomer): ^{1}H NMR ($CDCl_3$): δ 1.28 t ($^{3}J_{HH}$ 7 Hz, CH_3CH_2); 3.27 m (CH_2N); 6.4 d ($^{2}J_{HP}$ 9 Hz, C=CH); 7.6 m (C_6H_5). ^{31}P NMR ($CDCl_3$): δ 18.20 ppm

Anal. Calcd. for $C_{17}H_{26}F_3N_2OP$. C, 56.35; H, 7.23; P, 8.55%. Found: C, 56.15; H, 7.03; P, 8.10%.

1*E*-4-Formylphenylethenylphosphonic bis(diethylamide) (6l)

A solution of ylide **1c** (0.02 mol) in 10 mL of diethyl ether was added to 0.025 mol of terephthalic aldehyde in THF (3 mL) at 0 °C. The reaction mixture was left for a night. Then the solvent was evaporated under reduced pressure (10 mmHg). The residue was recrystallized in a

mixture of ether/pentane at 0 °C. Yield 50 %, mp 92.5 – 94 °C. After second recrystallization in hexane, mp 98 °C. ^{1}H NMR ($CDCl_3$): δ 1.40 t ($^{3}J_{HH}$ 7 Hz, 12H, CH_3CH_2); 3.41 d.d ($^{3}J_{HH}$ 7 Hz, $^{3}J_{PH}$ 10.5 Hz, 8H, CH_2N); 8.10 d.d (4H, C_6H_4); 6.80 d.d ($^{3}J_{HH}$ 17.5 Hz, $^{2}J_{PH}$ 17.5 Hz, 1H, PCH=C); 7.85, d.d ($^{3}J_{HH}$ 17.5 Hz, $^{3}J_{PH}$ 19 Hz, 1H, C=CH); 8.00 d; 8.10 d ($^{4}J_{HH}$ 9 Hz, 4H, C_6H_4); 10.30 s (1H, C(O)H). ^{13}C NMR ($CDCl_3$): δ 14.01; 41.7 d, *J* 6; 105.2 d ($^{1}J_{PC}$ 160 Hz); 130.1; 131.5; 136.0; 142.5; 154.2 d ($^{2}J_{PC}$ 32); 191.5. ^{31}P NMR ($CDCl_3$), δ_P: 23.7 ppm.

Anal. Calcd. for $C_{17}H_{27}N_2O_2P$: C 63.34; H 8.44; P 9.61%. Found: C 63.13; H 8.41; P 9.52 %:

Bis(1*E*, 1'*E*)-(2-tetraethyldiamidophosphonoethenyl)benzene (6m)

To a solution of ylide **1c** (0.025 mol) in diethyl ether (10 mL) was added dropwise a solution of terephthalic aldehyde (0.01 mol) in THF at -70 ^{o}C. The temperature was raised to a room and the reaction mixture was left for a night. The solvent was evaporated, the residue was recrystallized in heptane to give a yellow crystalline product, yield 50%. After second recrystallization in heptane m.p. 188.5-190 °C. ^{1}H NMR ($CDCl_3$): δ 1.05 t ($^{3}J_{HH}$ 7 Hz, 24H, CH_3CH_2); 3.03 dq ($^{3}J_{HH}$ 7 Hz, $^{3}J_{PH}$ 11 Hz, 16H, NCH_2); 6.33 d.d ($^{3}J_{HH}$ 17 Hz, $^{2}J_{PH}$ 17 Hz, 2H, PCH=C); 7.30 d.d ($^{3}J_{HH}$ 17 Hz, $^{3}J_{PH}$ 19 Hz, 2H, C=CH); 7.44 m (4H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 14.00 d ($^{3}J_{PC}$ 8 Hz); 41.80; 105.70 ($^{1}J_{PC}$ 180 Hz, PCH=); 129.80; 137.70; 154.20 ($^{2}J_{PC}$ 32 Hz). ^{31}P NMR ($CDCl_3$): δ_P 24.80 ppm.

Anal. Calcd. for $C_{20}H_{48}H_2O_2P_2$: C 61.16; H 9.47; N 10.97%. Found C 61.31; H 9.66; N10.85%.

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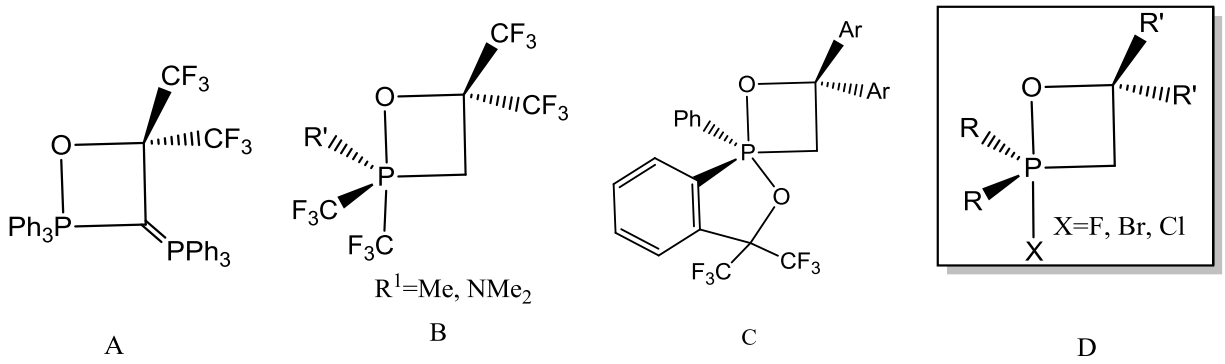
Table 1 Vinylphosphonates **6a-m**

Comp-d	R^1	R^3	R^4	Yield,%[a)]	bp ^oC (p mmHg)/ mp ^oC (solvent)	δ_P, ppm
6a	t-Bu	H	Ph	50	138 (heptane)	35.0
6b	Ph	H	Ph	40	165 (heptane)	22.0
6c	Et_2N	H	Ph	85	103.5 (hexane)	24.7
6d	Et_2N	H	Me	80	120 (0.05)	24.7
6e	Et_2N	H	Pr	72	120 (0.05)	24.3
6f	Et_2N	H	Bu	68	120-123 (0.04)	23.95
6g	Et_2N	H	C_6H_{13}	80	135 (0.06)	24.1
6h	Et_2N	H	C_8H_{17}	79	145-150 (0.05)	24.1
6i	Et_2N	H	PhCH=CH-	60	170 (0.06)	23.30
6j	Et_2N	H	Me_2C=CHCH_2CH_2C(Me)CH=C-	35	160 (0.08)	25.0
6k	Et_2N	CF_3	Ph	74	140 (0.03)	17.0; 18.7[b)]
6l	Et_2N	H	-C_6H_4CHO-4	50	98 (hexane)	23.7
6m	Et_2N	H	-C_6H_4CH=CHP(O)$(NEt_2)_2$	50	190 (heptane)	24.8

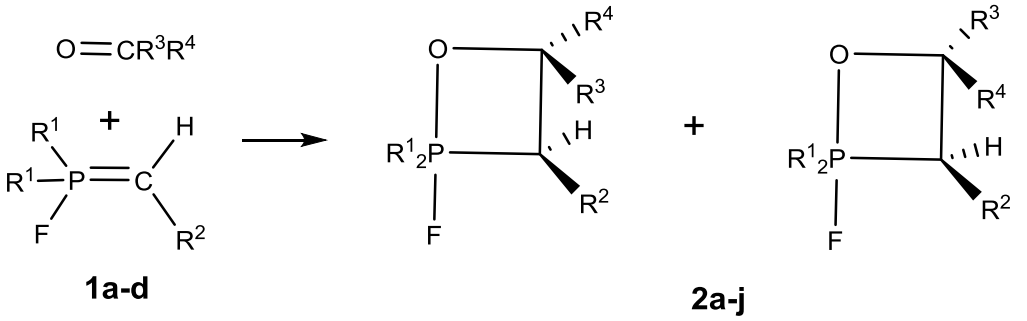
[a)] yield of the isolated product; [b)] mixture of *E/Z*-diastereomers in 97:3 ratio

.**Table 2**. 2-Fluoro-3-Silyl-1,2λ^5-oxaphosphetanes **2a-h**

№ comp-d	R^1	R^2	R^3	δ_P, ppm	δ_F, ppm	J_{PF}, Hz	*Threo/Erythro*
2a	Et_2N	H	Ph	—39.18	—40.89	670	3 : 2
				—38.83	—39.54		
2b	t-Bu	H	Ph	–11.0	-	768	4 : 1
2c	Ph	H	Ph	—43.50	—29.5	670	-
2d	Et_2N	H	Pr	—39.27 —42.11	—43.71 —42.61	768 768	4 : 1
2e	Et_2N	H	Bu	—39.22 —42.32	—43.71 —42.61	763 763	4 : 1
2f	Et_2N	H	C_6H_{13}	—39 .20 —42.10	—43.71 —42.61	763 763	3 : 1
2g	Et_2N	H	C_8H_{17}	—39 .88 —42.20	—42.85 —42.07	763 763	4 : 1
2h	Et_2N	CF_3	Ph	—38.60 —37 .45	—41.11 —49.01	777 774	3 : 1



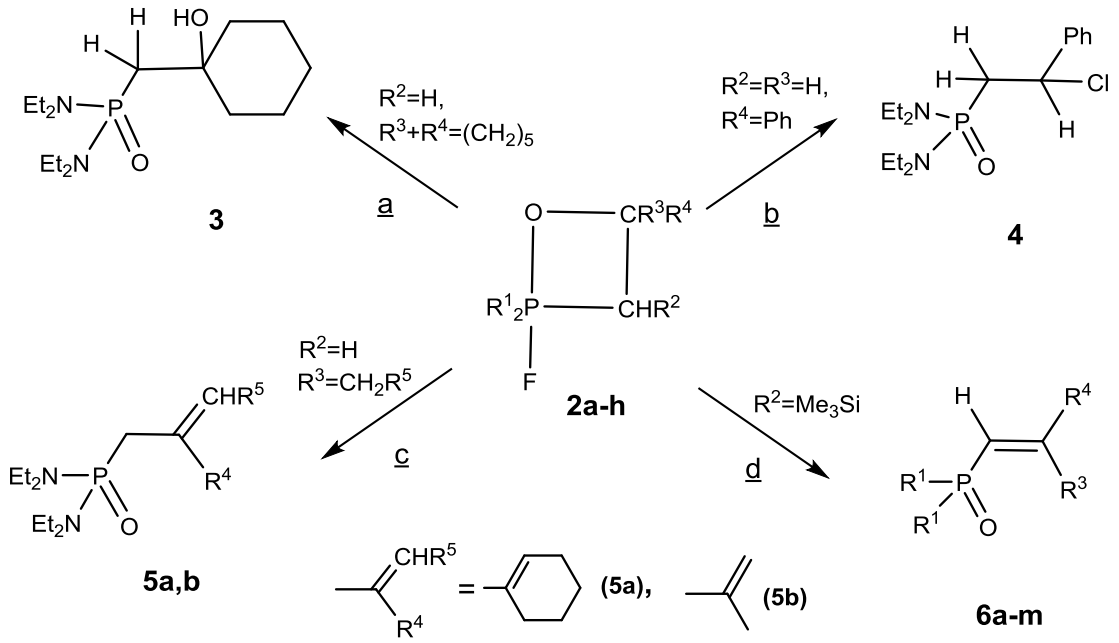
Scheme 1. Examples of stable oxaphosphetanes



R^1=Ph, R^2=Me_3Si (**1a**); R^1=t-Bu, R^2=Me_3Si (**1b**); R^1=Et_2N, R^2=Me_3Si (**1c**); R^1=Et_2N, R^2=H (**1d**);

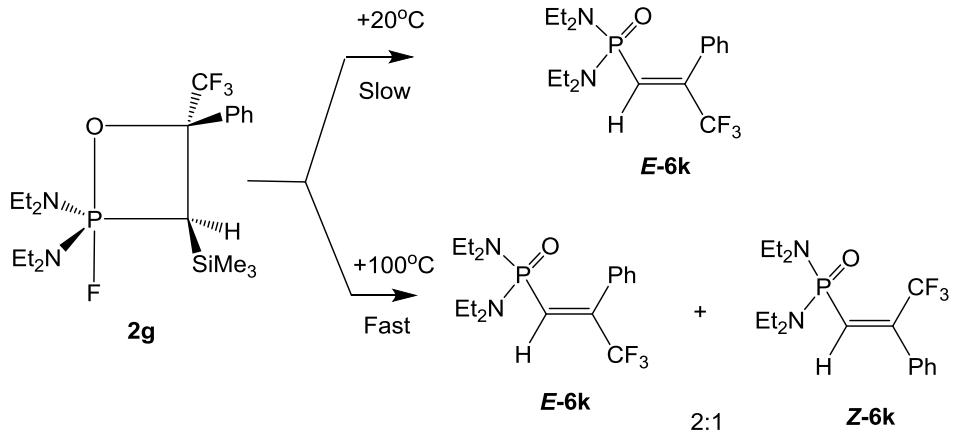
R^1=Et_2N, R^2=Me_3Si, R^3=Ph, R^4=H (**2a**); R^1=t-Bu, R^2=Me_3Si, R^3=Ph, R^4=H (**2b**); R^1=Ph, R^2=Me_3Si, R^3=Ph, R^4=H, (**2c**); R^1=Et_2N, R^2=Me_3Si, R^3=Pr, R^4=H (**2d**); R^1= Et_2N, R^2=Me_3Si, R^3=Bu, R^4=H (**2e**); R^1= Et_2N, R^2=Me_3Si, R^3=C_6H_{13}, R^4=H (**2f**); R^1= Et_2N, R^2=Me_3Si, R^3=C_8H_{17}, R^4=H (**2g**), R^1=Ph, R^2=Me_3Si, R^3=Ph, R^4=CF_3 (**2h**); R^1=Et_2N, R^2=H, R^3+R^4=$(CH_2)_5$ (**2i**); R^1=Et_2N, R^2=H, R^3=R^4=Me, (**2j**);

Scheme 2. Synthesis of 2-fluoro-1,2λ^5-oxaphosphetanes **2a-j**

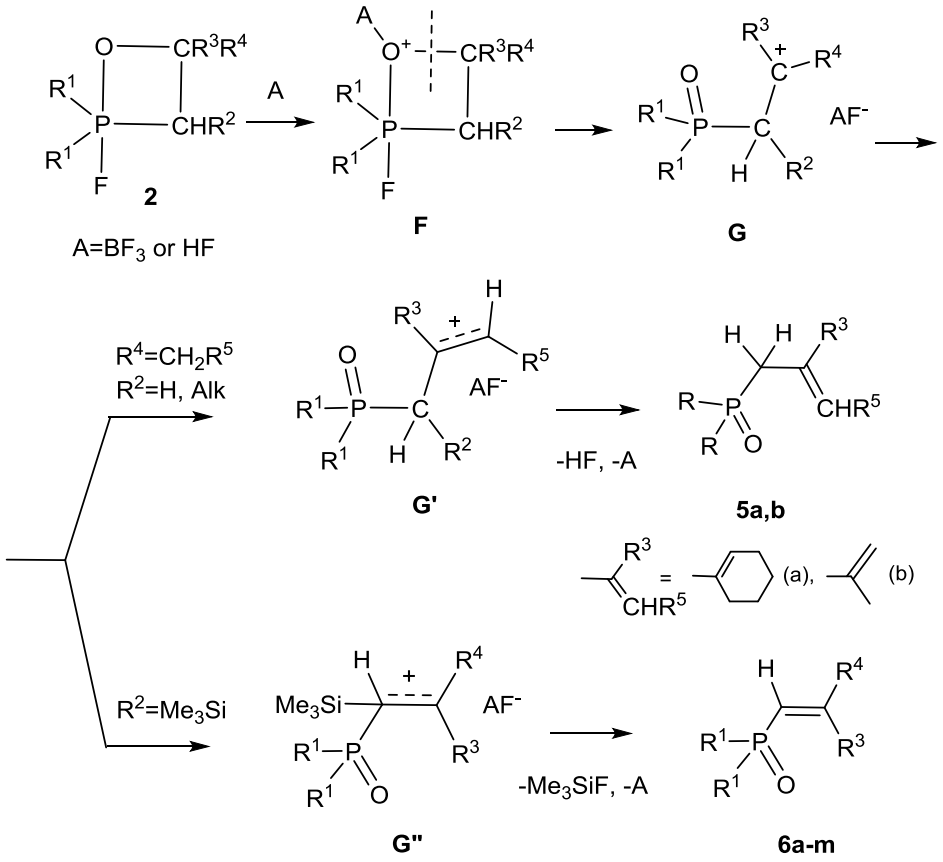


a=H_2O (-HF); b=HCl, ether (-HF); c=100-120^oC, ~0.5 hr (-HF) or $BF_3{\cdot}Et_2O$,+20^oC, 168 hr; d=60-80^oC (-Me_3SiF)

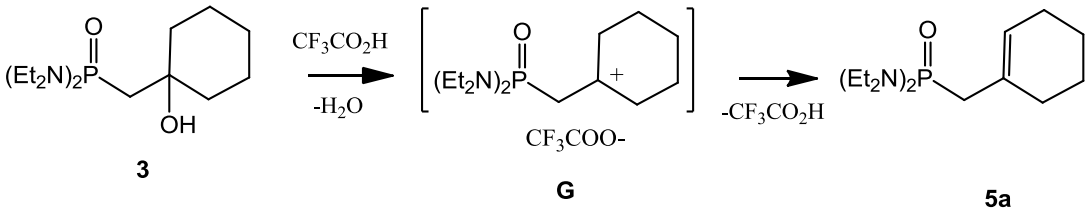
Scheme 3. Chemical properties of 2-fluoro-1,2λ^5-oxaphosphetanes **2a-i**



Scheme 4 Effect of temperature on the stereoselectivity of 2-fluoro-1,2λ^5-oxaphosphetane 2g conversion into vinylphosphonates 6k



Scheme 5. The mechanism for the 2-fluoro1,2λ^5-oxaphosphetane conversion into allyl- or vinylphosphonates



Scheme 6. The conversion of hydroxyphosphonate **3** into the allylphosphonate **5a**