

New P-Fluorinated Ylides and Phosphoranes

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ABSTRACT: *Methods for the preparation of P-fluorinated phosphorus ylides as well as new P-fluoro, P,P-difluoro- and P-fluoro, P-alkoxyylides, and the corresponding fluorophosphoranes are described.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 659–664, 1998

INTRODUCTION

Phosphorus ylides, containing halogen atoms at the phosphorus atom (P-halogenoylides), have attracted considerable interest in the last few years [1,2]. To continue systematic studies of the P-halogenoylides, we have synthesized new P-fluorinated ylides and P-fluorinated phosphoranes that have shown interesting chemical and stereochemical properties [3,4].

Phosphorus ylides bearing fluorine atoms at the phosphorus atom attracted the rapt attention of researchers in the last few years owing to their accessibility, high reactivity, and interesting chemical properties. The presence of the mobile fluorine atom at the phosphorus atom in the molecule of these compounds defines interesting properties of P-fluoroylides.

RESULTS AND DISCUSSION

P-Fluoroylides can easily be prepared from P-chloroylides **1** by the action of zinc fluoride. Reaction in benzene at room temperature is completed within 24 hours. The crude zinc fluoride containing traces of

moisture is more active than the carefully dried and purified reactant. By this method, fluorenylides **2** were obtained in high yields. Alternatively, arsenic trifluoride could be used in the exchange. P-Fluoroylides **2** were isolated in the form of deeply colored orange crystalline substances that were subsequently purified by crystallization from hexane. They readily add hydrogen chloride to give fluorophosphonium chlorides **4**, which were isolated as solids insoluble in ether. Reactions of the chlorophosphonium chlorides **3** with arsenic trifluoride in chloroform solution lead to the exchange of only one chlorine atom to furnish the fluorophosphonium chlorides **4**. Their ^{31}P NMR spectra unambiguously reveal their phosphonium character with tetracoordinate phosphorus. Heating of chlorides **3** with an excess of arsenic trifluoride in the absence of solvent affords the difluorophosphoranes **5**, which are very soluble in diethyl ether. Their ^{31}P NMR spectra confirm the presence of the pentacoordinate phosphorus atom. Under heating in vacuo, the compounds **5** lose hydrogen fluoride to revert into P-fluoroylides **2**. The dehydrohalogenation with triethylamine also give compounds **2** in good yields (Scheme 1).

Polyfluorophosphoranes can be transformed into P-fluoroylides by the action of various bases: tertiary amines, lithium amides, butyllithium [5–7]. These bases smoothly dehydrofluorinate the trifluorophosphorane **6** to afford the P-difluoroylide **7** in high yield. The use of a sterically hindered lithium amide avoids the replacement of the fluorine by an aminogroup (Scheme 2) that was reported earlier by us [3,4].

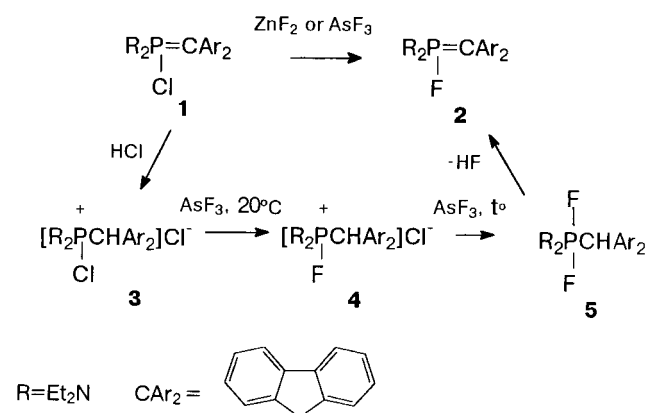
The alkyltetrafluorophosphorane **8** enters into a substitution reaction with lithium diethylamide to give the fluorophosphorane **9**, which then reacts with a second molecule of the lithium amide to give

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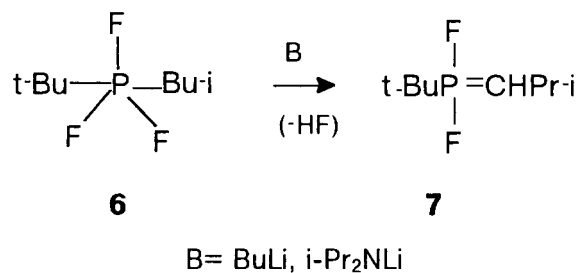
the P,P-difluoroyle 10. The highest yield of 10 was obtained when the trifluorophosphorane was prepared with $\text{Et}_2\text{NSiMe}_3$ and its dehydrofluorination was performed with $i\text{-Pr}_2\text{NLi}$ (Scheme 3).

The P,P-difluoroyle 13 was synthesized by reaction of trifluorophosphorane 11 with butyllithium. Likely, the reaction proceeds via the exchange of a chlorine atom on the trichloromethyl group with lithium, following which, the lithium fluoride is eliminated with the formation of P,P-difluoroyle 13 (Scheme 4).

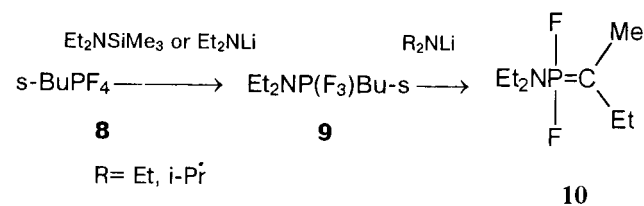
P,P-Difluoroyle 7,13 are stable colorless liquids that are easily hydrolyzed by moisture of the air. These compounds can be purified by distillation in a vacuum without decomposition and can be stored



SCHEME 1



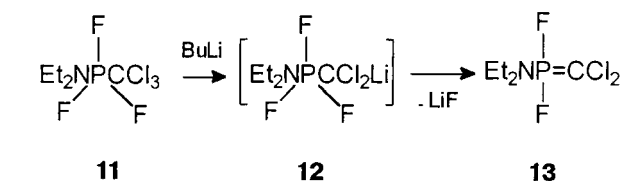
SCHEME 2



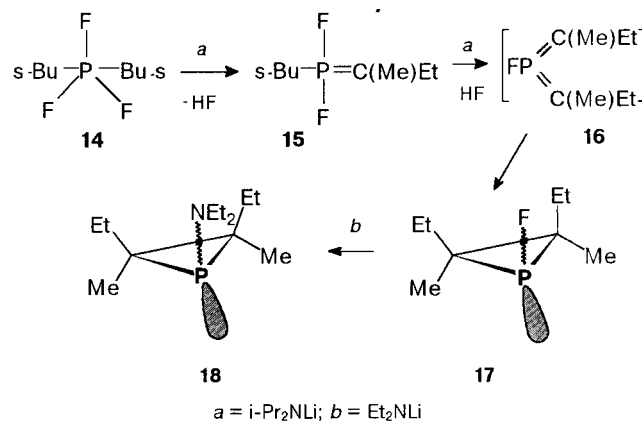
SCHEME 3

for a long time at a temperature below 0°C , if they are carefully protected from moisture. The structures of P-fluoroyle 7,13 were confirmed by spectroscopic data. The ^{19}F NMR signal is a doublet at $\delta = 70\text{--}87$, and the ^{31}P NMR signal is a triplet at $\delta = 50\text{--}90$ with $^1J_{\text{PF}}$ ca. 1000 Hz. The ^{13}C NMR signal of the P = C group is a double triplet at $\delta = 18\text{--}33$, with $^1J_{\text{CP}}$ 182–263 Hz and $^2J_{\text{CF}}$ 21–25 Hz. These values correspond to the phosphonium character of the phosphorus and to the carbanion character of the α -carbon atom, which corresponds to a high polarity of the P = C bond. In the case of nonstabilized P-fluoroyle, $^1J_{\text{P=C}}$ values are approximately 250–300 Hz [1–3].

P,P-Difluoroyle bearing *sec*-butyl groups at the phosphorus atom can easily be dehydrofluorinated by bases. Thus, dehydrofluorination of the dialkyltrifluorophosphorane 14 with lithium diisopropylamide affords in very good yield the P,P-difluoroyle 15. It can be dehydrofluorinated by a second molecule of lithium diisopropylamide with the formation of the P-fluoro-bis(alkylidene)phosphorane 16, which is unstable [8,9] and converts to the P-fluorophosphirane 17 (Scheme 5). Phosphorus chemical shifts of the fluorophosphiranes are found in a weak field and are doublets with $^1J_{\text{PF}}$ ca. 1000 Hz. The fluorine atom of 17 is easily substituted by a diethylamino group by reaction with lithium die-



SCHEME 4

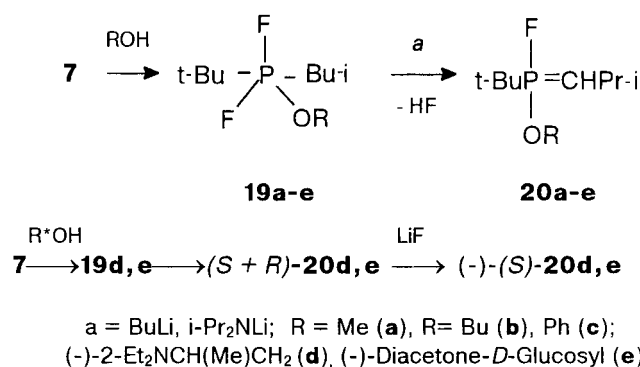


SCHEME 5

thylamide to result in P-diethylaminophosphirane **18** in good yield [10]. Similar results are obtained by use of lithium diisopropylamide. The chemical shift of **18**, δ_P -70 and -80 (*cis*- and *trans*-isomers), is in accord with the structure of the compound.

P,P-Fluoroylides readily add nucleophiles bearing a mobile hydrogen to form various difluorophosphoranes [3]. P,P-Fluoroylides such as **7** smoothly react with alcohols or phenols in ether below 0°C to afford difluorophosphoranes such as **19** in very good yields. In contrast to previously reported alkoxyfluorophosphoranes, the compounds prepared by addition of alcohols to P,P-difluoroylides are stable at room temperature, which is likely explained by their high purity. Dehydrofluorination of alkoxy and aroxydifluorophosphoranes **19** can be performed easily by action of butyllithium in ether-hexane solution. The resulting aroxyfluorophosphonium and alkoxyfluorophosphonium ylides such as **20** were purified by distillation in a vacuum. Ylides with alkoxy groups at the phosphorus are thermally stable compounds.

The additions of optically active alcohols to P,P-difluoroylides **7** afford difluorophosphoranes **19d,e** bearing a chiral alkoxy group [11]. The treatment of difluorophosphoranes **19** with butyllithium in hexane or in ether-hexane solution below 0°C gives P-fluoroylides containing alkoxy groups at the phosphorus atom in very good yields. The careful study of reaction mixtures by means of ^{31}P - ^1H and ^{19}F NMR spectra showed the presence of the diastereomers of the ylides that are initially formed in the ratio 1:1. However, in the presence of lithium salts found in the solution, the diastereomer proportion changes gradually to 4:1 (**20d**) and 95:5 (**20e**) in 12–16 hours at 20°C . The isolation of ylides from the reaction mixture and their purification preempts the epimerization. In this case, the proportion of diastereoisomers does not change. The epimerization of



SCHEME 6

the ylides can be explained; the dehydrofluorination of difluorophosphoranes proceeds very fast, evidently under conditions of kinetic control. After that, the ylides add reversibly lithium halogenides to the multiple P=C bond to form intermediates containing an achiral pentacoordinated phosphorus atom that are then converted slowly and predominantly into the thermodynamically more stable diastereomer.

The structures of the P-fluoroalkoxyylids were confirmed by ^1H , ^{19}F , and ^{31}P NMR spectroscopy. The ^{19}F and ^{31}P NMR spectra of the ylides show a doublet at $\delta = -7$ and at $\delta = 87\text{--}90$, respectively, with $^1J_{\text{PF}} = 1100$ Hz [12,13]. The P-alkoxyphosphonium ylides **20** are stable and can be purified by distillation in vacuum.

EXPERIMENTAL

Melting points are uncorrected. The NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 (^1H) and 121.8 MHz (^{31}P). Reaction rate measurements were performed in NMR tubes at constant temperatures ($-20 \pm 0.5^\circ\text{C}$) – ($+60 \pm 0.5^\circ\text{C}$). All chemical shifts are expressed in δ ($^\circ$). Chemical shifts of ^1H and ^{13}C are referenced to Me_4Si as an internal standard, those of ^{31}P to external 85% H_3PO_4 . All manipulations were carried out under argon. Organic solvents were dried using standard procedures.

Bis(diethylamino)fluorophosphonium fluorenylide (2)

Method a. To a solution of 0.05 mol of difluorophosphorane **5** in 15 mL of diethyl ether, 0.1 mol of triethylamine was added at 0°C . The mixture was stirred for 30 minutes, then the precipitate was filtered off, the filtrate was evaporated, and the residue was recrystallized from a hexane–benzene mixture (10:1). Yield 60%, mp 95°C .

Method b. To a solution of P-chloroylide **1** (0.005 mol) in 5 mL of benzene, zinc fluoride (0.15 mol) was added, and the mixture was stirred for 24 hours at room temperature. Then the reaction mixture was filtered, the filtrate evaporated, and the residue crystallized from a benzene–hexane mixture (1:10). Yield 45%, mp 95°C .

Method c. To 0.005 mol of P-chloroylide **1** in 5 mL of diethyl ether, 0.02 mol of arsenic trichloride was added. Then volatile products were evaporated, and the desired product was extracted from the res-

idue by ether. After evaporation of solvent, the residue was crystallized from a hexane–benzene mixture. Yield 30%, mp 95°C.

^1H NMR (CDCl_3): $\delta = 1.13$ (t, $J = 7$ Hz, CH_3); 3.18 (m, CH); 7–7.5 (m, C_6H_4)

^{31}P NMR $\delta_{\text{P}} = 60.42$ (d, $J = 975$ Hz)

^{19}F NMR: $\delta_{\text{F}} = 69.5$ (d, $J = 975$ Hz)

Calcd for $\text{C}_{21}\text{H}_{28}\text{FN}_2\text{P}$: F, 5.30; P, 8.64. Found: F, 5.05; P, 8.56.

Bis(diethylamino)fluorenylfluorophosphonium chloride (4)

Method a. To a solution of 0.01 mol of bis(diethylamino)fluorenylchlororophosphonium chloride (**3a**) in 10 mL of chloroform, 0.01 mol of arsenic trifluoride was added. After 30 minutes, the solvent was evaporated under reduced pressure. The residue was washed with ether and then dried in a vacuum of 0.01 mmHg.

Method b. To a solution of 0.01 mol of P-fluoroylide (**2**) in 15 mL of ether at -50°C , the solution of 0.01 mol of hydrogen chloride in ether was added dropwise. Then the colorless precipitate was filtered off, washed with ether, and dried in a vacuum of 0.01 mmHg.

^{31}P NMR, $\delta_{\text{P}} = 63.5$ (d, $^1J_{\text{PF}} = 1079$ Hz)

^{19}F NMR, $\delta_{\text{F}} = -78.9$ (d, $^1J_{\text{PF}} = 1079$ Hz)

Calcd for $\text{C}_{21}\text{H}_{29}\text{F}_2\text{N}_2\text{P}$: Cl, 8.98; F, 4.81; P, 7.84. Found: Cl, 8.87; F, 4.76; P, 7.85.

Bis(diethylamino)fluorenyldifluorophosphorane (5)

A mixture of 0.01 mol of phosphonium salt **4** with 0.03 mol of arsenic trifluoride was heated to $50\text{--}60^\circ\text{C}$ for 30 minutes. Then the excess of arsenic trifluoride was removed in a vacuum. The residue was extracted with ether. The solvent was evaporated in vacuum to furnish the spectroscopically pure difluorophosphorane, sublimed in a vacuum of 0.01 mmHg.

^{31}P NMR spectrum, $\delta = -51.5$ (t, $^1J_{\text{PF}} = 1079$ Hz)

Calcd for $\text{C}_{21}\text{H}_{29}\text{F}_2\text{N}_2\text{P}$: F, 10.04; P, 8.18. Found: F, 9.99; P, 8.21.

Diethylamino-sec-butyl-trifluorophosphorane (9)

Into a one-necked, round-bottomed flask, the *sec*-butyltetrafluorophosphorane **8** (0.04 mol) was placed, cooled to 0°C , and mixed with diethylaminotrimethylsilane (0.042 mol). Then, the temperature was raised to 60°C and the mixture refluxed for 2 hours.

The reaction mixture was distilled under reduced pressure to give the desired product in a yield of 75%, bp $80\text{--}82^\circ\text{C}$ (15 mmHg).

^{31}P NMR spectra (CDCl_3): $\delta = -34.05$ dt, $J_{\text{PF}} = 855$ Hz.

Diethylamino-difluorophosphonium-2-butylide (10)

A solution of lithium diisopropylamide (0.02 mol) in THF was added dropwise at -60°C with stirring to a solution of diethylamino-*(s)*-butyltrifluorophosphorane **9** (0.007 mol) in 10 mL of THF. The temperature of the mixture was raised slowly to $+20^\circ\text{C}$. Then the precipitate of LiF was filtered off, the solvent was evaporated under reduced pressure, and the residue was distilled in a vacuum. Yield 80%, bp $78\text{--}80^\circ\text{C}$ (12 mmHg).

^{31}P NMR, $\delta_{\text{P}} = 53,13$ (t, $J_{\text{PF}} = 1054$ Hz)

^{19}F NMR, $\delta_{\text{F}} = -87,08$ (d, $J_{\text{PF}} = 1054$ Hz)

^{13}C NMR (C_6D_6), δ 12.65 (dt, J 18.48, 4 Hz $\overline{\text{CC}}$); 14.65 dt, J 1, 1 Hz ($\overline{\text{CH}_3\text{CN}}$); 15.97 (dt, J 9.2, 5.7 Hz, $\overline{\text{CH}_3\text{C}}$); 23.61 (dt, J 16.1, 4.1 Hz, $\overline{\text{CH}_2\text{C}=\text{}}$); 25.6 (dt, J 268.3, 25.2, $\text{P}=\overline{\text{C}}$); 43.24 (J 3, 2.7 Hz, CH_2N)

Diethylamino-difluorophosphonium-dichloromethylide (13)

A solution of butyllithium (0.02 mol, 2.3 N) in hexane was added dropwise at -100°C with stirring to a solution of diethylaminotrifluorotrichloromethylphosphorane **11** (0.007 mol) in 20 mL of diethyl ether. The mixture was stirred at -30°C for 30 minutes, and then the temperature was raised to $+20^\circ\text{C}$. The mixture was filtered, the solvent was evaporated from the filtrate in a vacuum, and the residue was distilled. Yield 70%, bp $40\text{--}42^\circ\text{C}$ (0.05 mmHg).

^{31}P NMR (C_6D_6), $\delta = 52$ (t, $J_{\text{PF}} = 1070$ Hz)

^{13}C NMR (C_6D_6), $\delta = 47$ (d, $^1J_{\text{C}=\text{P}} = 330$ Hz)

Calcd for $\text{C}_5\text{H}_{10}\text{Cl}_2\text{F}_2\text{NP}$: P, 13.83. Found: P, 13.99.

Bis(sec-butyl)trifluorophosphorane (14)

Bis(*sec*-butyl)phosphine (0.1 mol) was placed into a one-necked round-bottomed Pyrex flask (100 mL). Then antimony trifluoride was added in small portions into the flask. The reaction mixture was stirred at 80°C for a 4 hours. Then the deep dark reaction mixture was cooled to room temperature, and the trifluorophosphorane was extracted with the diethyl ether. The solvent was removed under reduced pressure, and the residue was distilled in a vacuum. Yield 70%, bp $58\text{--}60^\circ\text{C}$ (10 mmHg).

^{31}P NMR (CDCl_3): $\delta = 6.17$, dt, $^1J_{\text{PF}} = 989$ and 854 Hz

^{19}F NMR: $\delta = -41.98$ (dt $J_{\text{PF}} = 854, 44.25$ Hz, axial F); -95.15 (d, $J_{\text{PF}} = 977$ Hz, equatorial F) [13]
Calcd for $\text{C}_8\text{H}_{18}\text{F}_3\text{P}$: F, 28.16; P, 15.25. Found: P, 28.19; F, 15.32.

Sec-Butyl-difluorophosphonium-2-butylyde (15)

A solution of lithium bis(diisopropyl)amide (0.023 mol) in ether-hexane (ca. 1:1) solution was added dropwise to a solution of bis(*sec*-butyl)trifluorophosphorane **14** (0.02 mol) in 15 mL of diethyl ether at -60°C . Then the reaction mixture was warmed to room temperature and stirred for 10 minutes at this temperature and then at $+35^\circ\text{C}$. The reaction mixture was filtered, the solvent was evaporated from the filtrate under reduced pressure, and the residue was distilled in a vacuum. Yield 80%, bp $50\text{--}52^\circ\text{C}$ (10 mmHg).

^{31}P NMR (CDCl_3): $\delta = 83.9$ (t, $J_{\text{PF}} = 1040$ Hz)

^{19}F NMR (CDCl_3): $\delta = -79.5$ (d, $J_{\text{PF}} = 1040$), -81.55 (d, $J_{\text{PF}} = 1040$ Hz) (magnetically not equivalent signals because of the *s*-Bu group presence)
Calcd for $\text{C}_8\text{H}_{17}\text{F}_2\text{P}$: F, 20.85; P, 17.0. Found: F, 20.56; P, 17.21.

2,3-Dimethyl-2,3-diethyl-1-fluorophosphirane (17)

A solution of butyllithium (0.072 mol, 2.1 N) in hexane was added dropwise to a solution of bis(*sec*-butyl)trifluorophosphorane (0.03 mol) in 10 mL of diethyl ether at -60°C . The reaction mixture was stirred for 15 minutes at this temperature. Then the reaction mixture was warmed to $+20^\circ\text{C}$, left for 1 hour, and filtered. The solvent was removed from the filtrate under reduced pressure, and the residue was distilled in a vacuum. Yield 88%, bp $35\text{--}40^\circ\text{C}$ (15 mmHg).

^{31}P NMR (CDCl_3): $\delta = 29.23$ (d, $J_{\text{PF}} = 950$ Hz); 32.62 (d, $J_{\text{PF}} = 955$ Hz); 35.03 (d, $J_{\text{PF}} = 964$ Hz) (1:6:9 ratio, geometrical isomers)

^{19}F NMR: $\delta = -249.4$, d ($J_{\text{PF}} = 963.4$ Hz), -249.57 (d, $J_{\text{PF}} = 955$ Hz); -250.8 (d, $J_{\text{PF}} = 940$ Hz), (ratio 6:9:1)

^{13}C NMR: $\delta = 40.45$ dd, $J_{\text{CP}} = 46.5$, $J_{\text{CF}} = 6$ Hz; 39.88 (dd, $J_{\text{CP}} = 46.5$, $J_{\text{CF}} = 6$ Hz); 40.2 (dd, $J_{\text{CP}} = 46.5$, $J_{\text{CF}} = 6$ Hz) (three carbon atoms of phosphirane ring); 10.44 s; 10.56 s, 10.74 s (CH_3); $11.4\text{--}12.3$ m (CH_3CH_2); $24.5\text{--}26.0$ (CH_2)

Calcd for $\text{C}_8\text{H}_{16}\text{FP}$: F, 11.71; P, 19.10. Found: F, 11.86; P, 19.12.

Ethoxy-tert-butyl-isobutyldifluorophosphorane (19a)

To a solution of 0.02 mol of *tert*-butyl-isobutyldifluorophosphoniumisobutylyde (**7**) [7] in 10 mL of ether

was added 0.02 mol of ethanol at -60°C . Then the temperature was raised to $+20^\circ\text{C}$, the solvent was removed under reduced pressure, and the residue was distilled in a vacuum. Yield 80%, bp 67°C (12 mmHg).

^{19}F NMR spectrum (CDCl_3), $\delta = -40.3$ (dd $J = 789$ Hz, -41.4 Hz); 40.6 (dd $J = 787, 40.6$ Hz)

^{31}P NMR: (CDCl_3), $\delta = -14.07$ (t, $J = 788$ Hz)
Calcd for $\text{C}_{15}\text{H}_{34}\text{F}_2\text{NOP}$: F, 12.12. Found: F, 11.95.

Ethoxy-tert-butyl-fluorophosphoniumisobutylyde (20a)

A solution of butyllithium (0.035 mol, 2.1 N) in hexane was added dropwise to a solution of ethoxy-*tert*-butyl-isobutyldifluorophosphorane (0.03 mol) in 10 mL of diethyl ether at -60°C and stirred for 15 minutes. Then the reaction mixture was warmed to $+20^\circ\text{C}$, left for 1 hour at this temperature, and filtered. The solvent was removed from the filtrate under reduced pressure, and the residue was distilled in vacuum. Yield 60%, bp 75°C (10 mmHg).

^1H NMR (CDCl_3): $\delta = 1.037$ (d, $J = 10.4$ Hz, CH_3C), 1.03 (t, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$); 1.29 (d, $J = 4.4$ Hz, CH_3CH), 2.5 m (CH), 4.0 m, OCH_2)

^{19}F NMR (CDCl_3): $\delta_{\text{F}} = -70.07$, d $J = 1090$ Hz
 ^{31}P NMR (CDCl_3)

^{31}P NMR (CDCl_3): $\delta 91.4$ (d, $J = 1080$ Hz)
Calcd for $\text{C}_{10}\text{H}_{22}\text{FOP}$: F, 9.59; P, 9.59. Found: F, 9.72; P, 10.00.

Butoxy-tert-butylfluorophosphoniumisobutylyde (20b)

Butoxy-*tert*-butylfluorophosphonium isobutylyde (**20b**) was prepared analogously to **20a**. Yield 70%, bp 102°C (15 mmHg)

^1H NMR (CDCl_3): $\delta = 1.13$ (d, $J = 10.6$ Hz, CH_3C); 0.89 (t, $J = 4.8$ Hz, CH_3), 1.38 (d, $J = 4.6$ Hz, CH_3CH), 1.31 (dd, $J = 4.6, 1.26$ Hz P=CH), $1.4\text{--}1.6$ m (CH_3CH_2), 2.62 m (CH), $3.8\text{--}4.0$ (OCH_2)

^{19}F NMR (CDCl_3), $\delta = -64.8$ (d $J = 1086$ Hz)

^{31}P NMR (CDCl_3), $\delta = 87.5$ (d, $J = 1078$ Hz)
Calcd for $\text{C}_{12}\text{H}_{26}\text{FOP}$: F, 8.04; P, 13.11. Found: F, 8.17; P, 13.41.

Phenoxy-tert-butylfluorophosphoniumisobutylyde (20c)

Phenoxy-*tert*-butylfluorophosphonium isobutylyde (**20c**) was prepared analogously to (**20a**). Yield 70%, bp 86°C (0.06 mmHg).

^{19}F NMR spectrum (CDCl_3), δ_{p} , -88.1 (d, $J = 1075$ Hz)

^{31}P NMR spectrum (CDCl_3), $\delta_{\text{p}} = 83.2$ (d, $J = 1075$ Hz)

Calcd for $C_{14}H_{22}FOP$: F, 7.41; P, 12.08. Found: F, 7.49; P, 12.17.

Dicyclohexylidene-glucofuranosyl-tert-butyl-isobutyldifluorophosphorane (19d)

Yield 95%.

^{19}F NMR ($CDCl_3$), $\delta_P = 40.3$ (dd $J = 789, 41.4$ Hz); 0.6 (dd $J = 787, J = 40.6$ Hz)

^{31}P NMR ($CDCl_3$), $\delta_P = -11.48$ (d, $J_{PF} = 788$ Hz) · $[\alpha]_D - 6.75$

Calcd for $C_{20}H_{44}F_2O_6P$: F, 7.28; P, 5.94 Found: F, 7.10; P, 5.65.

Dicyclohexylidene-glucofuranosyl-tert-butylfluorophosphoniumisobutylide (20d)

Yield 60%.

^{19}F NMR spectrum ($CDCl_3$), $\delta = 70.1$ (d $J = 1100$ Hz)

^{31}P NMR spectrum ($CDCl_3$), $\delta = 86.4$ (d, $J = 1089$ Hz) and 87.7 (d, $J = 1089$ Hz). Mixture of diastereomere 95:5.

(1-Diethylamino-2-propoxy-tert-butylfluorophosphoniumisobutylide (20e)

Yield 60%, bp $75^\circ C$ (0.08 mmHg).

^{19}F NMR ($CDCl_3$), $\delta = -70.8$ (d, $J = 1075$ Hz) and -71.9 (d, $J = 1075$ Hz)

^{31}P NMR ($CDCl_3$), $\delta = 87.5$ (d, $J = 1078$ Hz) and 88.8 (d, $J = 1078$ Hz). Mixture of diastereomere 4:1.

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