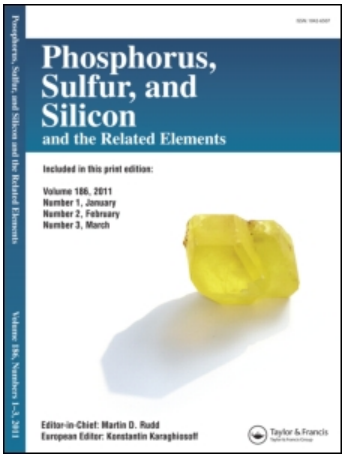


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# SYNTHESIS AND PROPERTIES OF P,P-DIFLUOROYLIDS

O. I. Kolodiazhnyi[a]; S. N. Ustenko[a]
[a] Institute of Bioorganic Chemistry of the Ukrainian Academy of Sciences, Kiev, USSR

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# SYNTHESIS AND PROPERTIES OF P,P-DIFLUOROYLIDS

O. I. KOLODIAZHNYI* and S. N. USTENKO

*Institute of Bioorganic Chemistry of the Ukrainian Academy of Sciences, Kharkovskoie shosse, 50, Kiev-160, 253160, USSR*

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Ylids containing two fluorine atoms at the phosphorus atom of the P=C group were prepared by reaction of trifluorophosphoranes with sterically hindered amides of lithium. The ylid structure was studied by means of NMR spectra and chemical reactions. The ylids add to the multiple P=C bond alcohols, phenol, thiophenol, $HN_3$ to form difluorophosphoranes, react with carbonyl compounds by a [2 + 2]-cycloaddition to give four membered phosphorus heterocycles, 2,2-difluoro-1,2$\lambda^5$-oxaphosphetanes.

*Key words:* P,P-difluoroylids; alkoxyfluorophosphoranes; phenoxyfluorophosphoranes; azidodifluorophosphorane; 2,2-difluoro-1,2$\lambda^5$-oxaphosphetanes; [2 + 2]-cycloaddition.



## INTRODUCTION

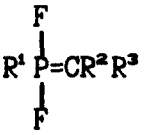
Phosphorus ylids, containing halogen atom at the phosphorus atom (P-halogenoylids) have attracted considerable interest in the last few years.[1–7] These easily accessible compounds possess high reactivity and interesting chemical properties.[8–13] By means of P-halogenoylids (**1**) one can prepare various phosphorus compounds, inaccessible or not easily accessible by another synthetic ways: phosphorus ketenes,[8] thioketenes,[9] iminoketenes,[8] vinylphosphonates,[10] allylphosphonates,[11–13] etc.

However, in contrast to the ylids (**1**), containing one halogen atom (X=Cl, Br, F), the ylids having two or three halogen atoms at the phosphorus atom were almost unknown. A single ylid (**2**) of this type was synthesized and described previously by us.[14]

(1)



(2)



(3)

Presently, the ylids having several halogen atoms at the phosphorus atom are interesting from the theoretical and synthetic view. Electronegative halogen atoms must increase a positive charge on the phosphorus atom and raise the efficiency of the [3d–2p] $\pi$-connection.

In this case the "ylene" character of ylids increases. It is well-known that the "ylen" structure has minimum contribution in the ground state of the ylids containing an alkyl or aryl group at the phosphorus atom.[15,16]

The influence of the halogen atoms on the reactivity of phosphorus ylids is also of interest.

In this paper we wish to report the synthesis of the first ylids containing two fluorine atoms at the phosphorus atom (**3**) (P,P-difluoroylids).

## RESULTS AND DISCUSSION

The P,P-difluoroylids (**3**) has been prepared by dehydrofluorination of corresponding alkyltrifluorophosphoranes. As dehydrofluorinating reagents has been used the sterically hindered lithium amides. This avoids the replacement of the fluorine atom at the phosphorus atom on the amino-group and realizes the elimination of the HF from the corresponding alkyltrifluorophosphoranes (**4**). The reaction of compounds (**4**) with $R_2NLi$, where R = i-Pr, $SiMe_3$, proceeds in tetrahydrofurane (THF) below 0°C and leads to the formation of P,P-difluoroylids (**3**) in very good yields (Table I).

$$R^1P(F_3)CHR^2R^3 \xrightarrow[-R_2NH]{R_2NLi} R^1P(F_2)=CR^2R^3$$

(4 a-e) (3 a-e)

| (3),(4) | a | b | c | d | e |
|---|---|---|---|---|---|
| $R^1$ | $Et_2N$ | $Et_2N$ | $Et_2N$ | t-Bu | t-Bu |
| $R^2$ | H | H | Me | Me | H |
| $R^3$ | Pr | Et | Et | Et | i-Pr |

TABLE I

Characterization data of P,P-difluoroylids (**3a-e**)

| Compound | Yield (%) | b.p. °C (mmHg) | $\delta_P$ (ppm) | $\delta_F$ (ppm) | $J_{PF}$ (Hz) |
|---|---|---|---|---|---|
| 3a | 95 | 30 (30) | 66.13 t | -69.66 d | 1025 |
| 3b | 80 | 60 (12) | 59.4 t | -72.5 d | 1045 |
| 3c | 80 | 78-80 (12) | 53.13 t | -87.08 d | 1054 |
| 3d | 70 | 45 (14) | 97.22 t | -83.04 d | 1058 |
| 3e | 65 | 45-48 (10) | 89.8 t | -87.0 d | 1050 |

TABLE II
Carbon-13 data for P,P-difluoroylids (3)

| Compound | $^{13}$C-NMR ($\delta$, ppm, J, Hz, $C_6D_6$) |
|---|---|
| 3b | 13.17 s $CH_2CH_2CH_3$); 14.32 s ($CH_3CH_2$); 17.7 dt, $J_{CP}$ 252.7, $J_{CF}$ 23.61 (P=C); 25.15 dt, $J_{CP}$ 8.4, $J_{CF}$ 3.5 ($CH_2CH_2CH_3$); 28.15 dt, $J_{CP}$ 11, $J_{CF}$ 6 ($CH_2CH_2CH_3$); 43.05 dt, $J_{CP}$ 3.5, $J_{CF}$ 1.6 ($CH_2N$). |
| 3c | 12.65 dt, $J_{CP}$ 19.48, $J_{CF}$ 4 ($CCH_2CH_3$); 14.65 dt, $J_{CP}$ 1, $J_{CF}$ 1 ($CH_3CH_2N$); 15.97 dt, $J_{CP}$ 9.2, $J_{CF}$ 6.7 ($CCH_3$); 23.61 dt, $J_{CP}$ 16.1, $J_{CF}$ 4.1 ($CH_2C$=); 25.6 dt, $J_{CP}$ 268.3, $J_{CF}$ 25.2 (P=C); 43.24 dt, $J_{CP}$ 3, $J_{CF}$ 2.7 ($CH_2N$). |
| 3d | 24.26 d (P=CCH); 26.05 s [ $(CH_3)_3C$ ]; 27.24 dt, $J_{CP}$ 11.5, $J_{CF}$ 5.2 ( $(CH_3)_2C$); 31 dt, $J_{CP}$ 54. $J_{CF}$ 11.9 (PC); 33.4 dt, $J_{CP}$ 182; $J_{CF}$ 21 (P=C). |
| 3e | 12.7 dt, $J_{CP}$ 17, $J_{CF}$ 4.5 ($CCH_3$); 15.71 dt, $J_{CP}$ 8.4, $J_{CF}$ 8.4 ($CH_3CH_2$); 23.66 dt, $J_{CP}$ 15, $J_{CF}$ 4.5 ($CH_3CH_2$); 25.8 dt, $J_{CP}$ 1.5, $J_{CF}$ 1 [ $(CH_3)_3C$]; 31 dt, $J_{CP}$ 195 (P=C); 31.87 dt, $J_{CP}$ 102, $J_{CF}$ 13 (P=C). |



The P,P-difluoroylids (**3**) are stable, colorless, and highly reactive to moisture. These compounds are distilled without decomposition under reduced pressure and can be preserved for a long time below 0°C, when they are carefully protected from air. The structure of the ylids (**3**) is confirmed by spectroscopic data. The $F^{19}$ NMR spectra of the ylids show a doublet of signals centered at −70–87 ppm with a very large constant, $^1J_{PF}$ 1050 Hz. The $^{31}$P NMR spectra disclose the presence of a triplet of signals centered at +53 − +97 ppm with the same coupling constant $^1J_{PF}$. In $^{13}$C NMR spectra the ylids (**3**) exhibit double triplets of signals at 18–33 ppm with coupling constant $^1J_{CP}$ 182–263 Hz and $^2J_{CF}$ 21–25 Hz related to the carbon atom of the C=P group (Table II).

These values of $\delta_P$ and $\delta_C$ correspond to the phosphonium character of the phosphorus atom and carboanion character of the $\alpha$-carbon atom that indicate on the high polarity of the P=C bond.[17] In accordance with the high polarity of the P=C bond, the ylids (**3**) readily add nucleophiles containing mobile hydrogen atoms to form various difluorophosphoranes (**5–8**).

The reactions of the ylids (**3**) with alcohols, phenols, thiophenol, $HN_3$ proceed smoothly in ether or benzene below 0°C to afford difluorophosphoranes (**5–8**) in very high yields (Tables III and IV). In contrast to the previously described alk-

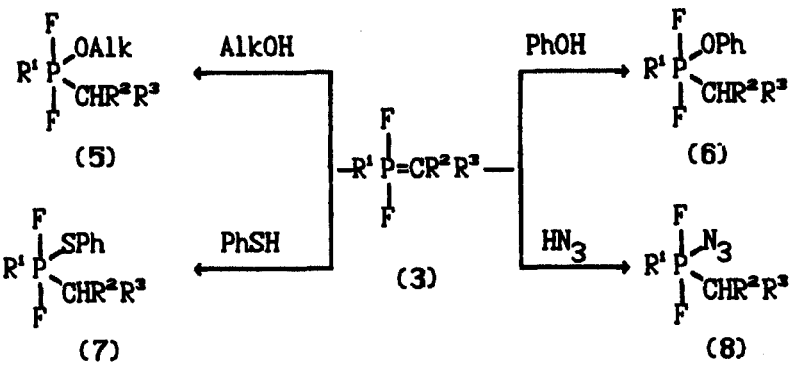
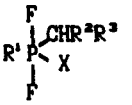



TABLE III

Characterization data of difluorophosphoranes (5–8)



| Compound | $R^1$ | $CHR^2R^3$ | X | Yield (%) | b.p. °C (mm Hg) | $\delta_P$ (ppm) | $\delta_F$ (ppm) | $^1J_{PF}$ (Hz) | Mol. Formula[a] |
|---|---|---|---|---|---|---|---|---|---|
| 5a | $Et_2N$ | Bu | MeO | 95 | 25–30 (0.1) | -41.6 t | -44.5 d | 780 | $C_9H_{22}F_2NOP$ |
| 5b | $Et_2N$ | s-Bu | EtO | 95 | 35(0.1) | -44.1t | -44.03 d | 167 | $C_{10}H_{24}F_2NO$ |
| 5c | t-Bu | s-Bu | MeO | 95 | 65 (12) | -14.27t | -52.91dd<br>-50.13dd | 780[b]<br>780 | $C_9H_{21}F_2OP$ |
| 5d | t-Bu | s-Bu | i-BuO | 98 | 50–60 (0.1) | -14.74t | -51.23dd<br>-48.58dd | 807[c]<br>807 | $C_{12}H_{27}F_2OP$ |
| 5e | t-Bu | i-Bu | EtO | 95 | 66–68 (12) | -13.07t | -40.0 d | 780 | $C_{10}H_{23}F_2OP$ |
| 6a | $Et_2N$ | Me | PhO | 95 | 70 (0.07) | -46.7 t | - | 769 | $C_{11}H_{18}F_2NO$ |
| 6b | $Et_2N$ | Bu | PhO | 90 | 80 (0.01) | -47.3 t | -37.0 d | 790 | $C_{14}H_{24}F_2NO$ |
| 7 | $Et_2N$ | Bu | PhS | 90 | - | -28.9 t | -20.81 d | 816 | $C_{14}H_{24}F_2NP$ |
| 8[d] | $Et_2N$ | Bu | $N_3$ | 90 | - | -42.7 t | - | 775 | $C_7H_{19}F_2N_4P$ |

a. Satisfactory results of the elemental analysis are obtained: C 0.15, H 0.1, P 0.15, F 0.1

b. $^2J_{FF}$ 42.5 Hz;

c. $^2J_{FF}$ 42.5 Hz;

d. IR spectrum, $\nu_{N_3}$ 2128 $cm^{-1}$.

TABLE IV
$^1$H-NMR spectra of the prepared compounds (3–8)

| Compound | Solvent | $^1$H-NMR ($\delta$, ppm, J, Hz) |
|---|---|---|
| 3b | $C_6D_6$ | 0.861 t, $J_{HH}$ 7.2 ($CH_3$); 1.06 t, $J_{HH}$ 7.2($CH_3$);1.31 m; 1.538 m ($CH_2CH_2CH_3$); 2.11 dtt, $J_{HH}$ 7, $J_{HP}$ 24.2, $J_{HF}$1.4 (P=CH); 2.86 dtq, $J_{HH}$7, $J_{HP}$12.6, $J_{HF}$14 ($CH_2N$) |
| 3d | $C_6D_6$ | 0.935 d, $J_{HP}$16.8 [$(CH_3)_3C$]; 1.2 d, $J_{HP}$6.6 [$(CH_3)_2$)C]; 1.63 ddt, $J_{HP}$50, $J_{HF}$10, $J_{HH}$7.5 (P=CH); 2.6 m [$CH(CH_3)_2$] |
| 3e | $C_6D_6$ | 1.06 d, $J_{HP}$17 [ $(CH_3)_3C$]; 1.08 t, $J_{HP}$8 ($CH_3CH_2$);1.7 dt, $J_{HP}$9.7, $J_{HF}$9.7 ($CCH_3$); 2.1 dq, $J_{HH}$7.5, $J_{HP}$19.5 ($CCH_3$). |
| 5b | $CDCl_3$ | 0.863 t, $J_{HH}$7.4 ($CH_3CH_2C$); 0.99-1.1 m ($CH_3C$); 1.002 m, $J_{HH}$7 ($CH_3CH_2N$); 1.162 t, $J_{HH}$7 ($CH_3CH_2O$);1.8 m ($CHCH_2$), 2.92 m ($CCH_2N$); 3.85 dq, $J_{HH}$7, $J_{HP}$94 ($CH_2O$). |
| 5e | $CDCl_3$ | 1.07 dd, $J_{HH}$6.6, $J_{HP}$1.5 [$(CH_3)_2C$]; 1.29 dt, $J_{HP}$18.9, $J_{HF}$2.7 [$(CH_3)_3C$];1.87 dtt, $J_{HH}$6.6, $J_{HP}$13.2. $J_{HF}$12.6 ($PCH_2$ 2.285 m [$CH(CH_3)_2$]; 3.96 dq, $J_{HH}$7.2, $J_{HP}$7.5 ($OCH_2$). |
| 5c | $CDCl_3$ | 0.925 d, $J_{HH}$6.6 [$(CH_3)_2CH$]; 0.96 t, $J_{HH}$7.2 ($CH_3CH_2$), 1.18 dd, $J_{HH}$7.2. $J_{HP}$21.6 ($CHCH_3$); 1.22 d, $J_{HP}$18.6 [$(CH_3)_3C$]; 1.9 m (PCH); 3.64 dd, $J_{HH}$6.6, $J_{HP}$4.8 ($OCH_2$). |
| 6a | $CDCl_3$ | 1.095 t, $J_{HH}$7 ($CH_3CH_2$); 1.69 dt, $J_{HP}$19.6, $J_{HF}$12.6 ($PCH_3$) 3.037 m ($CH_2N$); 6.99-7.26 m ($C_6H_5$). |
| 8 | $CDCl_3$ | 0.909 t, $J_{HH}$7 ($CH_3$); 1.099 t, $J_{HH}$7 ($CH_3$); 1.343 m; 1.6 m ($CH_2$); 1.9 m ($PCH_2$); 3.1 m ($CH_2N$). |

oxyfluorophosphoranes,[18] the compounds (3) prepared by addition of alcohols to ylids are stable at room temperature.

The stability of the alkoxyfluorophosphoranes (5) can be explained probably by the purity of obtained compounds and in the case of compounds (5) (R = *t*-Bu) also by the sterical influence of the bulky *tert*-butyl group.

The compounds (5) are stable at brief heating to +80–100°C and can be preserved for a long time at room temperature.

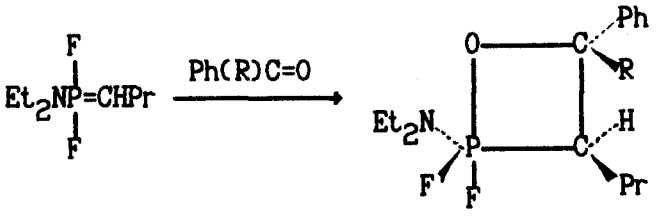
The phosphoranes (**6, 7**) containing phenoxy- and thiophenoxy groups are also stable. Azidodifluorophosphorane (**8**) is stable in solution and can be characterized by IR and NMR spectra. The IR spectrum of this compound reveals the presence of strong $N_3$ absorption band at 2128 $cm^{-1}$. The chemical shifts $\delta_P$ of the compounds (**5–8**) are in up field of $^{31}P$ NMR spectra, triplets with coupling constant $^1J_{PF}$ 770–800 Hz, in accordance with pentacoordinate state of the phosphorus atom (Table III).

The spectra $^{19}F$ NMR of compounds (**5–8**) disclose the presence of doublets of signals with constant $^1J_{PF}$ 770–800 Hz.

The signals $^{19}F$ of the compounds (**5**) having an asymmetric center on the $\alpha$-carbon atom of s-Bu group are doubled and represent two double doublets. In this case the coupling constant of the two chemically nonequivalent fluorine atoms appears, $^1J_{FF}$, 42.5 Hz.

The nucleophilicity of the P,P-difluoroylids (**3**) toward C=O group is weaker than in case of ylids (**1**) having one fluorine atom at the phosphorus atom (X=F).

Nevertheless, the ylids (**3**) react with the benzaldehyde and trifluoroacetophenone to afford the stable [2 + 2]-cycloadducts (**9**). The compounds (**9b**) (R=$CF_3$) is distilled under reduced pressure without decomposition, the compound (**9a**) (R=H) is not distilled but it is stable at room temperature and can be characterized by means of spectroscopy.




(3b) (9a,b)

R=H (9a), $CF_3$ (9b)

The $^{31}P$ NMR spectrum of the oxaphosphetane (**9b**) shows the presence of a double doublet at −26.7 ppm with constants $^1J_{PFa}$ 915 Hz, $^1J_{PFe}$ 1025 Hz in accordance with axial and equatorial position of the fluorine atoms and axial-equatorial position of the four-membered cycle. The $^{19}F$ NMR spectrum of the compound (**9b**) contains two double doublet with constants $^1J_{PFa}$ and 915 Hz, $^1J_{PFe}$ 1025 Hz and $^2J_{FaFe}$ 62 Hz. Apparently [2 + 2]-cycloaddition of the C=O group to the ylid (**9**) proceeds with high stereo selectivity, because the $^{19}F$ and $^{31}P$ NMR spectra show the signals belonging to the single diastereomer of the compound (**9b**). The signals of the second diastereomer, the existence of which one can suppose as a consequence of the presence of two asymmetric endocyclic C-3 and C-4 carbon atoms are absent.

The $^{13}C$ NMR spectrum reveals the presence of the signals at 62.5 ppm ($J_{CP}$ 150 Hz, $J_{CF}$ 53 Hz) and 75.6 ppm due to the C-3 and C-4 carbon atoms in complete accordance with the assigned structure of oxaphosphetane cycle.[19,20] The far downfield shift and the large $J_{CP}$ value indicate equatorial placement of the C-3 carbon atom.[21,22]

## EXPERIMENTAL

$^1H$, $^{13}C$, $^{19}F$ and $^{31}P$ NMR spectra were recorded on a "Varian VXR-300" spectrometer at 300, 75.35, 281.7, 126.16 MHz. All chemical shifts are expressed in $\delta$ (ppm). $^1H$ and $^{13}C$ chemical shifts are expressed relative to $Me_4Si$ as internal standard. $^{19}F$ NMR and $^{31}P$ NMR spectra are referenced to internal $CFCl_3$ and external 85% $H_3PO_4$ respectively. IR spectra were run on a "Specord IR 85" spectrometer.

All manipulations were carried out under inert atmosphere ($N_2$ or Ar), solvents were distilled under inert atmosphere from the following drying agents: diethyl ether, hexane ($P_2O_5$); THF (sodium/benzophenone).

*Butylidene-diethylamino-difluorophosphorane* (**3b**). To a solution of 0.02 mol of diethylaminobutyltrifluorophosphorane (**4b**) in 10 ml of THF is added 0.022 mol of i-$Pr_2NLi$ in 10 ml THF at $-20°C$. After heating of the reaction mixture up to room temperature the precipitate of LiCl was filtered under reduced pressure. Yield 80%.
Calcd for $C_8H_{17}F_2N_2P$: F 19.36, P 17.19. Found: F 19.01, P 17.52.
Ylid (**3c**) was obtained from (**4c**) in a similar manner.

*Methylene-diethylamino-difluorophosphorane* (**3a**). To a solution of 0.02 mol of diethylaminomethyltrifluorophosphorane (**4a**) in 10 ml of ether is added with stirring 0.02 mol of $(Me_3Si)_2NLi$ in THF at 0°C. After stirring for a further 0.5 hour the solid (LiCl) was filtered off and the filtrate was evaporated and distilled under reduced pressure. Yield 60%.

*Isobutylidene-tert-butyl-difluorophosphorane* (**3d**). To a solution of 0.02 mol of *tert*-butyl-isobutyltrifluorophosphorane (**4d**) in 10 ml ether was added with stirring 0.022 mol of butyl lithium in hexane at $-10°C$. After stirring for a 0.5 hour the precipitate of LiCl was filtered off and the filtrate was evaporated. The residue was distilled under reduced pressure. Yield 70%.
The product was obtained as clear and colorless liquid.
Calcd for $C_8H_{18}F_3P$: F 28.19, P 15.32. Found: F 28.05, P 15.16.
Similarly, ylid (**3e**) was obtained from (**4e**).
The physical and spectral data of the ylids (**3a–e**) are listed in Tables I, II and IV.

*Reactions of ylids* (**3**) *with alcohols, phenol, thiophenol and* $HN_3$. *General procedure*: To a solution of 0.015 mol of an ylid (**3**) in 5 ml of ether was added with stirring 0.015 mol of alcohol at $-10°C$. The solution was allowed to stand for 15 min at room temperature. After the evaporation of solvent the residue was distilled under reduced pressure.
The reactions of ylids (**3**) with phenol, thiophenol, $HN_3$ were performed in the same manner. Yields and physical data are given in Tables III and IV.

*2,2,-Difluoro-2-diethylamino-3-propyl-4-trifluoromethyl-4-phenyl-1,2*$\lambda^5$*-oxaphosphetane* (**9b**). To a solution of 0.01 mol of the ylid (**3b**) in 1 ml of ether was added of 0.011 mol of $\alpha,\alpha,\alpha$-trifluoroacetophenone at $-10°C$. After standing of the mixture at room temperature for 2 hours it was distilled in vacuum.
The product was obtained as clear and colorless liquid.
Yield 85%, b.p. 105–107°C (0.06 mm Hg).
NMR spectra ($\delta$, ppm; $J$, Hz; $CDCl_3$):
$\delta_H$: 0.712 $t$ ($J_{HH}$ 7.4, $CH_3$); 1.096 $t$ ($J_{HH}$ 7, $\underline{CH_3}CH_2N$); 1.3 m; 1.5 m ($\underline{CH_2}\underline{CH_2}$); 3.0–3.3 m ($CH_2N$); 4.0–4.1 m (PCH); 7.30–7.60 m ($C_6H_5$). $\delta_C$: 14.29 s ($\underline{CH_3}CH_2CH_2$); 16.13 s ($\underline{CH_3}CH_2$); 21.22 *dd* ($J_{CP}$ 14, $J_{CF}$ 2.8, $CH_3CH_2\underline{CH_2}$); 28.7 *d* ($J_{CP}$ 11, $CH_3\underline{CH_2}CH_2$); 45.0 m (NC); 62.5 *ddd* ($J_{CP}$ 150, $J_{CF}$ 53 P$\underline{C}$); 75.0 m ($\underline{C}$–O); 128.17 s; 120.9 s; 129.54 s; 134.8 *d*; $J_{CP}$ 3.5 ($C_6H_5$). $\delta_F$: −46.9 *dd* ($J_{PF^a}$ 915, $J_{F^aF^e}$ 61, P$\underline{F}^a$); −65 *dd* ($J_{PF^e}$ 1025, $J_{F^aF^e}$ 61, P$\underline{F}^e$); −77.74 s ($CF_3$). $\delta_P$: −26.7 *dd* ($J_{PF^a}$ 915, $J_{PF^e}$ 1025). Calcd for the $C_{16}H_{23}F_5ONP$: F 26.11, P 8.57, N 5.37. Found F 26.20, P 8.75, N 5.41.

*2,2-Difluoro-2-diethylamino-3-propyl-4-phenyl-1.2*$\lambda^5$*-oxaphosphetane* (**9a**). To a solution of 0.01 mol of the ylid (**3b**) was added of 0.01 mol of benzaldehyde at 0°C. After standing of the reaction mixture at room temperature for a 0.5 hour the oxaphosphetane (**9a**) was obtained as a colorless liquid. The product was only characterized $^{19}F$ and $^{31}P$ NMR spectra because of its instability.
NMR spectra ($\delta$, ppm; $CDCl_3$): $\delta_F$: −48.7 *dd* ($J_{PF^a}$ 873 Hz, $J_{F^aF^e}$ 66 Hz, P$F^a$); −52.6 *dd* ($J_{PF^e}$ 909, $J_{F^aF^e}$ 66, P$\underline{F}^e$). $\delta_P$: −27.1 *dd* ($J_{PF^a}$ 876 Hz, $J_{PF^e}$ 908 Hz).

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