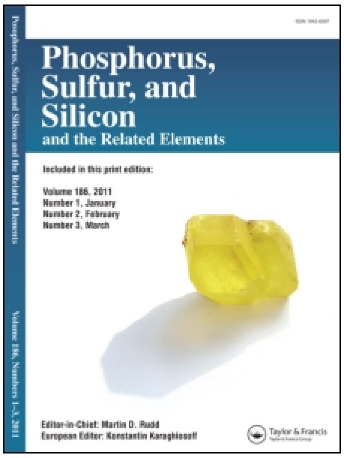

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EXAMPLES OF 1,3,2-DIOXABENZO-PHOSPHOR(III)INANES

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EXAMPLES OF 1,3,2-DIOXABENZO-PHOSPHOR(III)INANES

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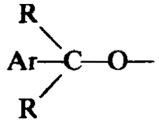
The concept allowing to synthesize hitherto unknown 1,3,2-dioxabenzo-phosphor(III)inanes is introduced. On the basis of ^1H, ^{19}F, and ^{31}P NMR evidence it was shown that the nature of the exocyclic substituent at the phosphorus atom can have a significant influence on the conformational features of the bicyclic phosphorinane ring system as well as on the chemical properties of this system. The study of the reactions between 2-dialkylaminobenzo-1,3,2-dioxaphosphor(III)inanes and proton containing nucleophiles confirmed the structures of the obtained compounds and exhibited their synthetic value.

Key words: Benzo-1,3,2-dioxaphosphor(III)inanes, phosphorylation, NMR spectroscopy, trifluoromethyl, saligenines, structure.

INTRODUCTION

Much attention is being paid to 1,3,2-dioxaphosphor(III)inanes because of their expectancy both for studying of fundamental stereochemical problems[1] and for solution of modern synthetic ones, e.g. for the creation of cell growth regulators which are analogues of adenosinemonocyclophosphate.[2] However some principal classes of such heterocycles were not known so far. One can note unsuccessful attempts to synthesize benzo-1,3,2-dioxaphosphorinanes by phosphorylation of saligenines with trialkylphosphites or other trivalent phosphorus agents.[3–5] Alkylation of the trivalent phosphorus with the readily formed benzyl cation at one of synthetic stages seems to be one of the reasons of these failures. Such an alkylation leads to phospholanes instead of the expected phosphorinanes. This assumption was confirmed by the experiments on phosphorylation of saligenine nitrous analogues with trivalent phosphorus reagents which resulted in benzo-1,3,2-diazaphosphorinanes.[6]

In connection with the above mentioned we assumed that a promising synthetic route to 1,3,2-dioxabenzophosphor(III)inanes would be the application of saligenines with groups hindering the heterolysis of the

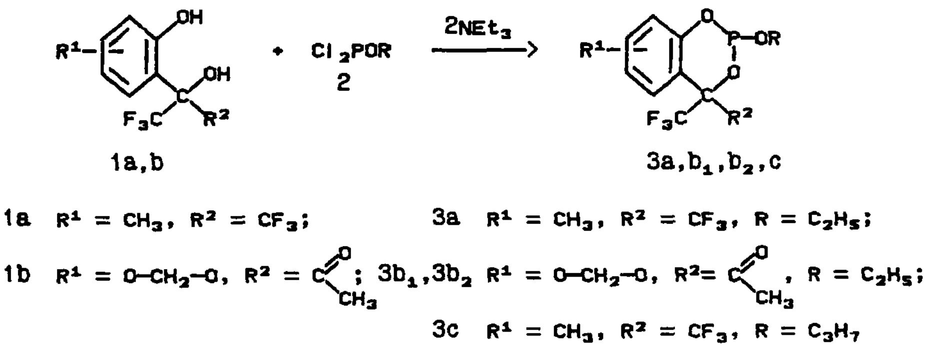


$Ar{-}CR_2{-}O{-}$

bond (R-groups). Trifluoromethyl groups may be regarded as such substituents. In accordance with these considerations we began the investigation on cyclophosphorylation of 0-1,1,1,3,3,3-hexafluorohydroxyisopropylphenols **1**.

RESULTS AND DISCUSSION

In the present work two methods of phosphorylation were used. The first one is based on the phosphorylation of dissolved phenols **1** with alkyldichlorophosphites **2** in the presence of triethylamine. Substituted 0-1,1,1,3,3,3-hexafluorohydroxyisopropylphenols **1a, b** were shown to give the expected phosphorinanes **3a, b** in 81–87% yield:

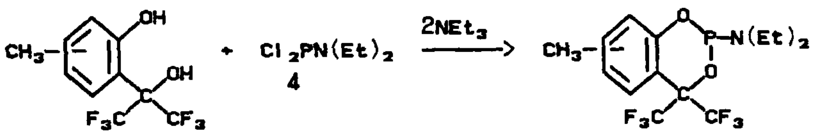


1a,b

3a,b$_1$,b$_2$,c

The products were identified by means of ^{31}P, ^{19}F, and ^{1}H NMR spectroscopy. The compound **3b** was proved to be formed in two geometric isomers (see Experimental).

The phosphorylation with diethylamidodichlorophosphophosphites proceeds analogously, the amide **5a** being formed in 81% yield:

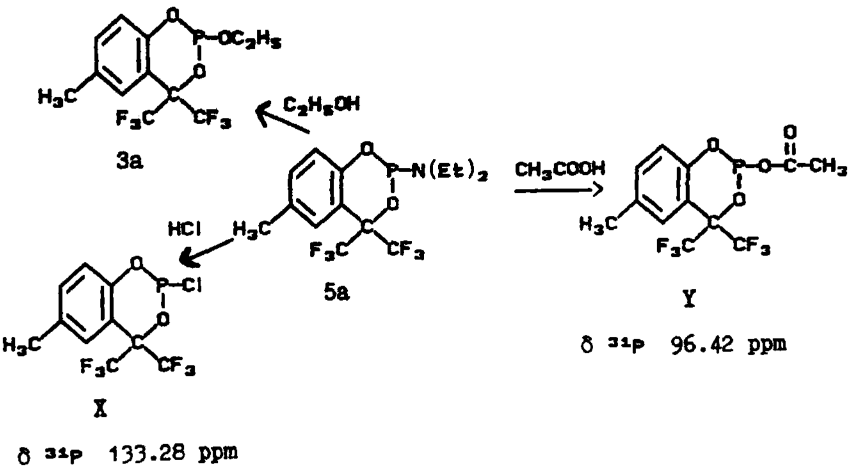


1a

5a

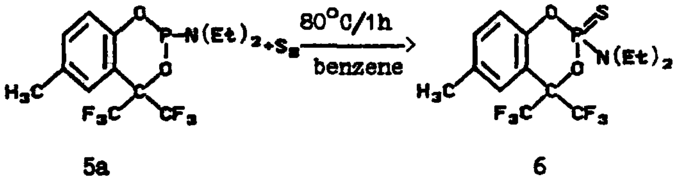
The same compound (**5a**) as well as its N,N′-dimethyl analogue **5b** were efficaciously obtained by the phosphorylation of the saligenine **1a** with phosphorous hexaalkyltriamides.

The amide **5a** was introduced into reactions with proton-donor nucleophiles, for example:



The obtained derivatives X and Y were not isolated because of their thermal lability. They were defined by means of ^{31}P NMR spectroscopy.

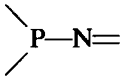
The amide **5a** was oxidized with sulfur:



The reaction is found to occur very easily and to be of preparative value. It is important to point out that the phosphite **3a** adds sulfur under much more severe conditions, which seems to be due to the difference in steric organization of the benzophosphorinanes in question. The NMR data confirm this supposition. In the ^{31}P NMR spectrum the phosphite **3a** shows a singlet, proving the absence of considerable P—F coupling. The ^{19}F NMR spectrum does not show P—F coupling either. At the same time, the spectrum of phosphamide **5a** differs from that of phosphite **3a** very much. Its ^{31}P NMR spectrum shows an expected quadruplet with coupling constant J (PF) of 23 Hz. The very same constant is found in the ^{19}F NMR spectrum but only for one of the CF_3 groups. So, in the phosphite **3a** the two trifluoromethyl groups are situated symmetrically relative to the phosphorus surroundings but in the phosphamide **5a** these groups are sharply different to each other.

The structural analysis using Dreiding models shows that one of the CF_3 groups is located over the phosphorus atom. Such a steric approach of fluorine and phosphorus atoms results in transannular coupling and has been reported earlier for some four- and five-membered phosphorus cycles containing CF_3-substituents at the carbon atoms.[6,7]

The distinction between two similar benzophosphorinanes (**3a** and **5a**) is most probably due to different conjugation in P—O and P—N fragments. In the last case the mesomeric donation is well known to be maximal towards phosphorus.[8] Such an effect results both in shortening of the



bond and in flattening of the phosphorus bonds which causes the two CF_3-groups to be different. The other consequence of the mesomeric effect is the increase of the electron density on the phosphorus atom which is manifested in the high feasibility of oxidating reactions.

While completing the synthetic line related to sulfurization of the phosphamide **5a**, we proved rigorously the structure of the obtained thionophosphamide **6** by means of X-ray structural analysis.

STRUCTURE DESCRIPTION

Figure 1 presents a general view of the molecule 6, bond length and valence angle values (with an accuracy of 0.002–0.010 Å and 0.2–0.6 deg. respectively). Non-H atom coordinates are given in Table I.† In the molecule **6** the average values of endocyclic angles and those of interatomic C—C distances in the phenol ring lie within the limits of tabulated ones. The fragment formed by the atoms bound to the aromatic cycle is planar within the limits ±0.002 Å and the deviations of other atoms O1 (0.001 Å), C7 (0.084 Å), and C10 (−0.062 Å) are negligible. The atoms O1 and C7 are included in the conjugation system, but the C7 atom is sp^3-hybridized, deviating from the plane defined by the atoms O1, C2, and C9 by 0.469 Å. It is obvious that some difference in the bond lengths of the C—O heterocycle is due to the contribution of the C7 atom sp^3-hybridization. Interatomic C···O distances are shortened as compared with those of bicyclic C-substituted 1,3,2-dioxaphosphorinanes (1.44 − 1.16 Å).[9,10]

The heterocycle has a tangled twist configuration (torsion angles are listed in Table II). For 1,3,2-phosphorinanes a chair conformation is usual wherein O—P—O and C—C—C planes make with the central tetra-atomic one the angles of 46 and 52° respectively.[9] In the molecule **6** the most planar ones are the fragments of atoms O1, C1, C2, C7 (±0.002 Å) and O1, O2, C2, C7 (±0.035 Å). Planarity of the central tetra-atomic fragment (O1, C1, O2, C7) is of ±0.087 Å and their dihedral angles with O—P—O and C—C—C planes are 40.1° and 8.4°, respectively.

The bond angles O1—C1—C2 (121.2°) and C1—C2—C7 (120.3°) as well as C1—C2 bond length are close to those in conjugated aromatic systems.

The complex configuration of the heterocycle resulting from asymmetric C-substitution appears to cause the difference in endocyclic angles on the oxygen atoms (116.0 and 124.3°) and the decrease of the O—P—O bond angle to 98.9° compared with unsubstituted, 4- and 6-, and 5-substituted derivatives of 1,3,2-dioxaphos-

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†For H atoms coordinates address to the authors.

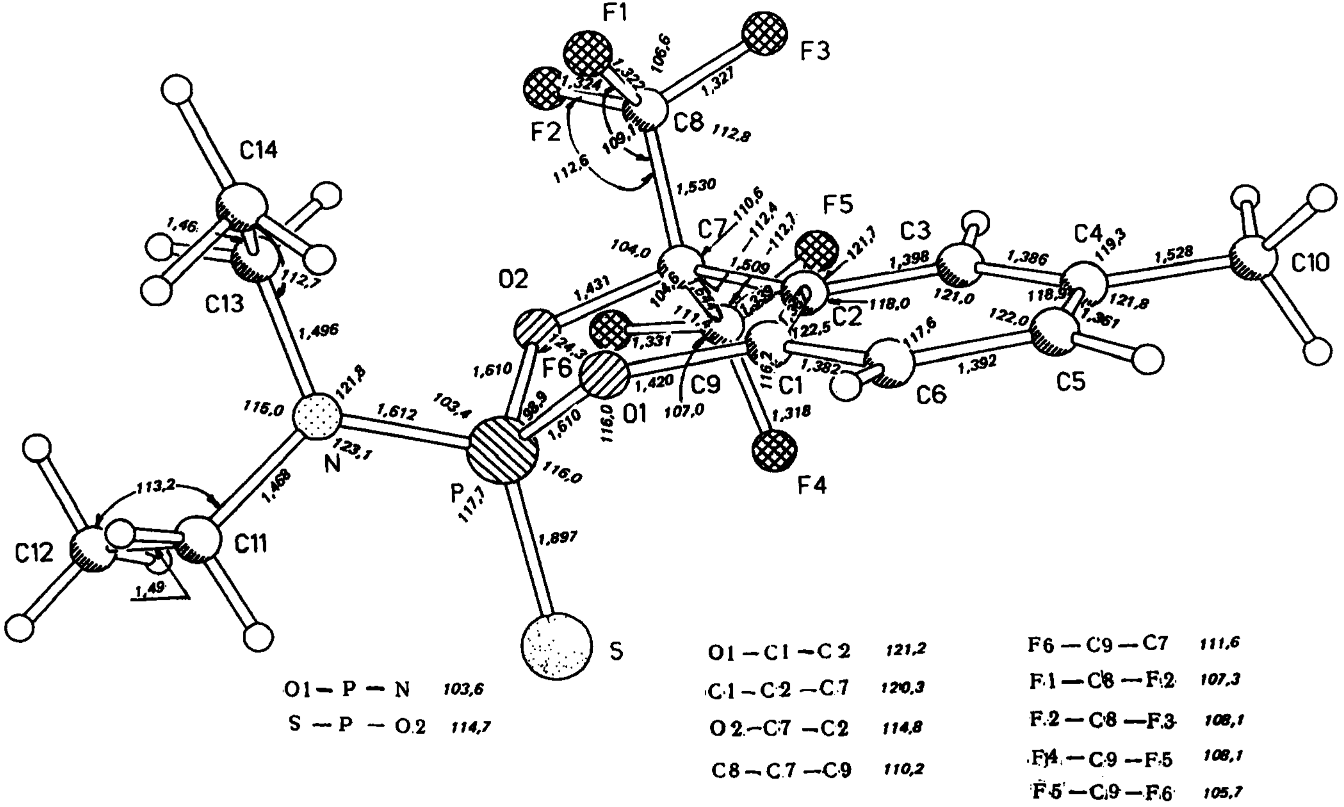


FIGURE 1 General view of molecule 6 with bond lengths and valence angle values included.

TABLE I

Atom coordinates ($\times 10^4$) and temperature factors ($A^2 \times 10^3$) of compound **6**

Atom	X	Y	Z	U_{eq}
S	6193(1)	2797(1)	3619(2)	93(1)*
P	5364(1)	3328(1)	5084(2)	61(1)*
F(1)	3763(3)	5192(3)	6230(5)	98(2)*
F(2)	2662(2)	4927(3)	4538(5)	104(2)*
F(3)	3573(3)	6097(2)	4518(5)	106(2)*
F(4)	5085(3)	4479(2)	1637(4)	94(2)*
F(5)	3973(3)	5525(2)	1847(4)	102(2)*
F(6)	3463(3)	4221(2)	2087(4)	92(1)*
O(1)	5954(3)	4049(2)	6051(4)	66(1)*
O(2)	4397(2)	3907(2)	4492(4)	57(1)*
N	4812(4)	2709(3)	6269(5)	71(2)*
C(1)	6224(4)	4829(3)	5329(6)	58(2)*
C(2)	5552(4)	5199(3)	4348(5)	49(2)*
C(3)	5868(4)	5971(3)	3688(7)	61(2)*
C(4)	6821(5)	6361(4)	4046(7)	65(2)*
C(5)	7448(4)	5982(4)	5062(7)	73(2)*
C(6)	7164(4)	5213(4)	5743(7)	73(2)*
C(7)	4497(4)	4786(3)	4020(6)	54(2)*
C(8)	3606(5)	5258(4)	4818(8)	74(3)*
C(9)	4261(5)	4754(4)	2380(7)	69(2)*
C(10)	7151(5)	7190(4)	3267(8)	93(3)*
C(11)	5068(6)	1787(4)	6421(8)	98(3)*
C(12)	4214(8)	1207(5)	5887(10)	132(4)*
C(13)	4048(6)	3054(4)	7364(7)	90(3)*
C(14)	4549(7)	3244(7)	8751(10)	145(4)*

---

* Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalised U(i,J) tensor.

TABLE II

Bond lengths (Å) of compound **6**

S-P	1.897(2)	P-O	1.610(4)
P-O(2)	1.610(3)	P-N	1.612(5)
F(1)-C(8)	1.322(9)	F(2)-C(8)	1.324(7)
F(3)-C(8)	1.327(7)	F(4)-C(9)	1.318(7)
F(5)-C9(0	1.339(7)	F(6)-C(9)	1.331(7)
O(1)-C(1)	1.420(6)	O(2)-C(7)	1.431(6)
N-C(11)	1.468(8)	N-C(13)	1.496(8)
C(1)-C(2)	1.367(7)	C(1)-C(6)	1.382(7)
C(2)-C(3)	1.398(7)	C(2)-C(7)	1.509(7)
C(3)-C(4)	1.386(8)	C(4)-C(5)	1.361(9)
C(4)-C(10)	1.528(8)	C(5)-C(6)	1.392(8)
C(7)-C(8)	1.530(8)	C(7)-C(9)	1.544(9)
C(11)-C(12)	1.49(1)	C(13)-C(14)	1.46(1)

TABLE III

Bond angles (degrees) of compound **6**

S-P-O(1)	116.0(2)	S-P-O(2)	114.7(2)
O(1)-P-O(2)	98.9(2)	S-P-N	117.7(2)
O(1)-P-N	103.6(2)	O(2)-P-N	103.4(2)
P-O(1)-C(1)	116.0(3)	P-O(2)-C(7)	124.3(3)
P-N-C(11)	123.1(4)	P-N-C(13)	121.8(4)
C(11)-N-C(13)	115.0(5)	O(1)-C(1)-C(2)	121.2(4)
C(1)-C(1)-C(6)	116.2(5)	C(2)-C(1)-C(6)	122.5(5)
C(1)-C(2)-C(3)	118.0(4)	C(1)-C(2)-C(7)	120.3(4)
C(3)-C(2)-C(7)	121.7(4)	C(2)-C(3)-C(4)	121.0(5)
C(3)-C(4)-C(5)	118.9(5)	C(3)-C(4)-C(10)	119.3(5)
C(5)-C(4)-C(10)	121.8(5)	C(4)-C(5)-C(6)	122.0(5)
C(1)-C(6)-C(5)	117.6(5)	O(2)-C(7)-C(2)	114.8(4)
O(2)-C(7)-C(8)	104.0(4)	C(2)-C(7)-C(8)	110.6(4)
O(2)-C(7)-C(9)	104.6(4)	C(2)-C(7)-C(9)	112.4(4)
C(8)-C(7)-C(9)	110.2(5)	F(1)-C(8)-F(2)	107.3(5)
F(1)-C(8)-F(3)	106.6(5)	F(2)-C(8)-F(3)	108.1(5)
F(1)-C(8)-C(7)	109.1(5)	F(2)-C(8)-C(7)	112.6(5)
F(3)-C(8)-C(7)	112.8(5)	F(4)-C(9)-F(5)	108.1(5)
F(4)-C(9)-F(6)	107.0(5)	F(5)-C(9)-F(6)	105.7(5)
F(4)-C(9)-C(7)	111.6(5)	F(5)-C(9)-C(7)	112.7(5)
F(6)-C(9)-C(7)	111.4(5)	N-C(11)-C(12)	113.2(6)
N-C(13)-C(14)	11		

Tortion angles

S	P	O1	c1	68.8
O2	P	O1	C1	-54.4
N	P	O1	C1	-160.6
S	P	O2	C7	-83.1
O1	P	O2	C7	41.0
N	P	O2	C7	147.4
S	P	N	C11	11.1
S	P	N	C13	-173.1
O1	P	N	C11	-118.5
O1	P	N	C13	57.4
O2	P	N	C11	138.7
O2	P	N	C13	-45.4
P	O1	C1	C2	39.7
P	O1	C1	C6	-144.4
O1	C1	C2	C3	179.5
O1	C1	C2	C7	0.5
C6	C1	C2	C3	3.7
C6	C1	C2	C7	-175.2
C1	C2	C3	C4	-1.6
C7	C2	C3	C4	177.3
C2	C3	C4	C5	-0.4
C2	C3	C4	C10	178.2
C3	C4	C5	C6	0.5
C10	C4	C5	C6	-178.1

TABLE III (*Continued*)

O1	C1	C6	C5	-179.6
O2	C1	C6	C5	-3.7
C4	C5	C6	C1	1.5
P	O1	C7	C2	-9.9
P	O2	C7	C8	-130.8
P	O2	C7	C9	113.6
C1	C2	C7	O2	-15.7
C1	C2	C7	C8	101.5
C1	C2	C7	C9	-135.0
C3	C2	C7	O2	165.4
C3	C2	C7	C8	-77.4
C3	C2	C7	C9	46.1
O2	C7	C8	F1	61.4
O2	C7	C8	F2	-57.6
O2	C7	C8	F3	179.7
C2	C7	C8	F1	-62.3
C2	C7	C8	F2	178.8
C2	C7	C8	F3	56.0
C9	C7	C8	F1	173.0
C9	C7	C8	F2	54.0
C9	C7	C8	F3	-68.7
O2	C7	C9	F4	-79.0
O2	C7	C9	F5	159.1
O2	C7	C9	F6	40.5
C2	C7	C9	F4	46.1
C2	C7	C9	F5	-75.8
C2	C7	C9	F6	165.6
C8	C7	C9	F4	169.8
C8	C7	C9	F5	47.9
C8	C7	C9	F6	-70.7
P	N	C11	C12	-107.5
C13	N	C11	C12	76.3
P	N	C13	C14	-96.2
C11	N	C13	C14	79.9

phorinanes, wherein the respective values are 114.3–119.2 and 101.5–105.6°, respectively.[11]

An analogous difference in the P—O—C bond angles is to be observed in cyclic nucleoside 3,5-monophosphate of twisted configuration (115.3 and 129.8°), wherein the O—P—O bond angle is 107.6°.[10] The nitrogen atom is planar, deviating from the plane passed through the atoms bound to it by 0.030 Å (the sum of its valent angles is 359.9°), and it is equatorial to the plane passed through the atoms O1, O2, C1, C2 (N = −0.014 Å). The sulfur atom deviates from this plane by 2.604 Å, i.e. it is axial.

The lengths of the bonds P—N and P═S are 1.612 Å and 1.897 Å respectively,[4] while the P—O bonds are equal to each other and longer than 1.58 Å,[2] typical for 1,3,2-dioxaphosphorinanes (Table III).

In the diethylamino group the C—C bonds are rather shortened and the C—N ones are near to tabulated values (C—C 1.513, C—N 1.467 Å).[12]

The structures of the trifluoromethyl groups is standard (C—C 1.530, C—F 1.322 Å)[12]; deviations of the atoms C8 and C9 from the planes defined by the fluor atoms bound to them, are 0.468 and 0.496 Å, respectively.

It should be mentioned that when the phosphorus changes from the trivalent to pentavalent state, the two CF_3-groups are situated almost symmetrically relative to the ring. In correspondence with this fact, the ^{31}P and ^{19}F NMR spectra take a more simple form compared with those of the trivalent amide **5a**. The P—F through space coupling disappears (see Experimental).

EXPERIMENTAL

^{31}P NMR spectra were recorded with a Bruker WP-80 spectrometer at 32.2 MHz. Chemical shifts were referenced relative to 85% H_3PO_4 at 30°C. ^1H NMR spectra were recorded with a Bruker H-360 at 360 MHz. Chemical shifts were referenced relative to TMS. ^{19}F NMR spectra were recorded with a Bruker AC-200 at 188.3 MHz. Chemical shifts were referenced to CF_3COOH.

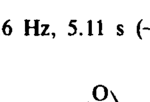
An X-ray diffraction study was carried out with an automatical Syntex PI diffractometer without monocromator (αMoKα-radiation, θ/2θ scanning, sin $\theta/\alpha_{max} = 0.539$).

Crystals of 1 ($C_{14}H_{16}NO_2F_6PS$) are ortho-rhombic: a = 12.634(2), b = 15.458(3), c = 9.231(1)Å, v = 1802(8)Å^3, Z = 4, space group $P2_12_12_1$, $d_{calc.} = 1.501$ g/cm^3. Unit cell parameters and intensities of 1072 independent reflections with $I \geqslant 3\sigma(I)$ were measured on the automatic Syntex PI diffractometer, Nb-filtered MoKα-radiation, θ/2θ scan technique, $\sin\theta/\alpha_{max} = 0.539$ Å^{-1}. The structure was solved using the direct method by SHELXTL program followed by least-squares refinements with anisotropic (for C, N, O, F, P, S) and isotropic (for H) thermal parameters. Refinement of the positional and thermal parameters of the H atoms resulted in final values of R = 0.032 and wR = 0.034.

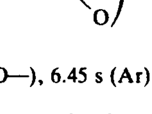
All the syntheses were performed using dry solvents under inert gas atmosphere.

2-Ethoxy-4,4-bis-trifluoromethyl(2'-methylbenzo)-1,3,2-dioxaphosphorinane (**3a**). Triethylamine (2 mL, 0.014 mol) was added to a solution of **1a** (2 g, 0.007 mol) in benzene. To the cooled and stirred mixture was added dropwise a solution of ethyldichlorophospite (1 g, 0.007 mol) in benzene. Then the reaction mixture was stirred for 1.5 hrs. The precipitate was filtered off, the solvent was evaporated under vacuum and cooling and the residue was distilled. Yield is 2 g (81%), b.p. 110°/10^{-4} mm Hg. Found, %: C 32.7, H 3.3, P 9.0. $C_{12}H_{11}F_6O_3P$. Calc., %: C 32.8, H 3.1, P 8.9. ^{31}P NMR (δ, ppm): 110.5 s, ^1H NMR (δ, ppm): 0.65 t ($\underline{CH_3}$—CH_2—), 1.81 s ($\underline{CH_3}$—Ar), 3.58 q (—CH_2—O), (P—O—CH_2—) 8.8 Hz, 6.72 s (Ar), 7.36 s (Ar), ^{19}F NMR (δ, ppm): 0.9 q, J_{F-F} 10 Hz, 5.3 q, J_{F-F} 10 Hz.

2-Ethoxy-4 trifluoromethyl-4-acetyl (2',3'-oxydimethylene)-1,3,2-dioxaphosphorinanes (**3b$_1$**, **3b$_2$**). The reaction was performed as above described. Yield is 76%, b.p. (°C): 110/10^{-4} mm Hg. Found, %: C 36.3, H 2.3, P 8.2. $C_{11}H_9F_6O_5P$. Calc., %: C 36.0, H 2.4, P 8.4. ^{31}P NMR (δ, ppm): δ_1 112.2 s, δ_2 109.6 s. ^1H NMR (δ, ppm): δ_1 0.88 t ($\underline{CH_3}$—CH_2—), 2.85 s



3.65 q (—$\underline{CH_2}$—CH_3), (—CH_2—O—P), 8.6 Hz, 5.11 s (—O—$\underline{CH_2}$—O—) 6.42 s (Ar), δ_2 1.1 t ($\underline{CH_3}$—CH_2—) 3.25 s



3.85 q (—$\underline{CH_2}$—CH_3), 5.22 s (—O—$\underline{CH_2}$—O—), 6.45 s (Ar).

2-Propoxy-4,4-bis-trifluoromethyl(2'methylbenzo)-1,3,2-dioxaphosphorinane (**3c**). The reaction was performed as above described. Yield is 87%, b.p. (°C): 85–86/10^{-4} mm Hg. Found, %: C 40.8, H 4.3, P 8.6. $C_{16}H_{15}F_6O_3P$. Calc., %: C 40.9, H 4.2, P 8.8. ^{31}P NMR (δ, ppm): 110.8; ^1H NMR (δ, ppm): 0.67 t ($\underline{CH_3}$—CH_2—CH_2—), 1.33 q (—$\underline{CH_2}$—CH_3), 1.83 s (CH_3—Ar), 3.61 q ($\underline{CH_2}$—O—), $J_{(CH2OP)}$ 8.8 Hz, 7.36 s (Ar).

2-Diethylamino-4,4-bis-trifluoromethyl(2'-methylbenzo)-1,3,2-dioxaphosphorinane (**5a**)

A. Triethylamine (0.6 mL, 0.004 mol) was added to a solution of **1a** (0.6 g, 0.002 mol) in benzene, then diethylamidodichlorophosphite **4** (0.4 g, 0.002 mol) in benzene was added dropwise under cooling and stirring. The reaction mixture was stirred for 1 h. The precipitate was filtered, the solvent evaporated under vacuum and cooling. The residue was distilled under vacuum. Colourless crystals were isolated in 0.63 g, 85% yield, b.p. 76–77°/1 mm Hg. Found, %: C 54.0, H 4.4, P 8.1. $C_{14}H_{16}F_6NO_2P$. Calc., %: C 44.8, H 4.2, P 8.2. ^{31}P NMR (δ, ppm): 131 q, $J_{(P-F)}$ 20.1 Hz. ^1H NMR (δ, ppm): 1.16 t ($\underline{CH_3}$—CH_2—), 2.18 s ($\underline{CH_3}$—Ar), 3.25 m (CH_3—$\underline{CH_2}$—), $J_{(PNCH2)}$ 10.25 Hz, 7.06 s (Ar), 7.68 s. (Ar). ^{19}F NMR (δ, ppm): 1.7 q J_{F-F} 10 Hz, 4.5 m, J_{F-P} 20.14 Hz.

B. **1** (1.2 g, 0.004 mol) and hexaethyltriamide phosphite (0.6 g, 0.004 mol) were mixed and the reaction mixture was heated up to 130°C and kept for 2 hrs until the diethylamine was completely distilled off. The residue was sublimated under vacuum. Yield is 0.8 g (56%).

2-Dimethylamino-4,4-bis-trifluoromethyl-(2-methylbenzo)-1,3,2-dioxaphosphorinane (**5b**). The reaction was performed as above described. Yield is 88%, b.p. (°C): 80–81/1 mm Hg. Found, %: C 41.8, H 3.3, P 9.0. $C_{12}H_{12}F_6NO_2P$. Calc., %: C 41.5, H 3.4, P 8.9. ^{31}P NMR (δ, ppm): 129.2 q, J_{P-F} 20 Hz.

2-Diethylamino-2-thio-4,4-bis-trifluoromethyl-(2-methylbenzo)-1,3,2-dioxaphosphorinane (**6**). Finepowdered sulfur (0.12 g) was added to a solution of amide **5a** (1 g) in benzene. The mixture was kept at 80°C for 1 h until total sulfur dissolution. The solution was cooled and the solvent evaporated. The residue was dissolved in hexane. The crystals of **6** were precipitated on cooling the solution to °C; they were filtered off. Yield is 1.1 g (95%), m.p. 82–84°C. Found, %: C 41.2, H 3.9, P 7.6. $C_{14}H_{16}F_6NO_2PS$. Calc., %: C 41.2, H 3.9, P 7.6. ^{31}P NMR (δ, ppm): 61.5 s.

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