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DIALKYL-N-ALKOXY-N-(4-TOLUENESULFONYL)PHOSPHORAMIDATES: SYNTHESIS AND STRUCTURE

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This study investigates the reaction between N-alkoxy-N-chloro-4-toluenesulfonamides and N-chloro-N-(methoxy)methanesulfonamide with trialkyl phosphites, resulting in the formation of dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoroamidates and dialkyl N-methoxy-N-methanesulfonylphosphoroamidates, respectively. The resulting dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoramidates and N-alkoxy-N-methanesulfonylphosphoramidates are identified as products of nucleophilic substitution at the amide nitrogen atom. The structures of these compounds have been confirmed by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy, mass spectrometry, and an XRD study. The XRD study of dimethyl N-methoxy-N-(4-toluenesulfonyl)phosphoroamidate and dimethyl N-ethoxy-N-(4-toluenesulfonyl)-phosphoroamidate reveals a pyramidal configuration at the amide nitrogen atom, along with the shortening of the N−O(Alk) bond and the elongation of the N−P and N−S bonds. In the asymmetric part of the unit cell, dimethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate exists in the form of two independent molecules that differ in the degree of pyramidality of the nitrogen atom and the lengths of its bonds.

Keywords: N-alkoxy-N-(chloro)sulfonamides, trialkyl phosphites, dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoramidates, dialkyl N-methoxy-N-methanesulfonylphosphoroamidates, structure, single crystal X-ray diffraction study.

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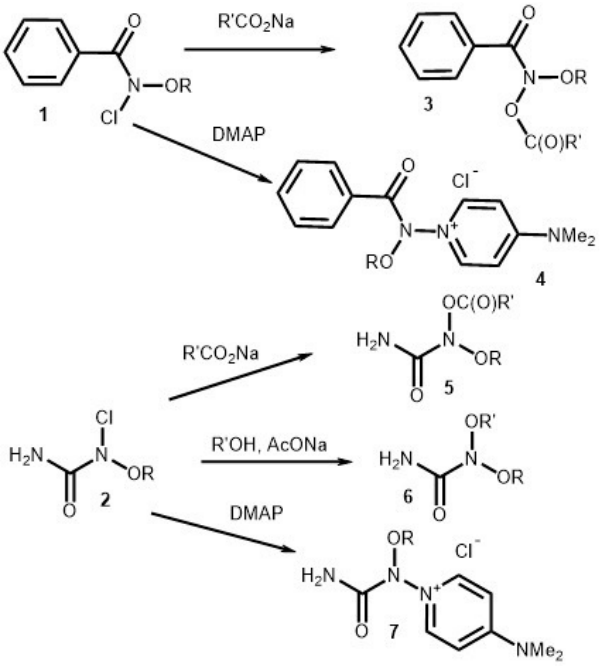
Introduction

The study of organophosphorus compounds remains a critical area of research due to their wide-ranging applications in fields such as medicinal chemistry and materials science. Among these, the derivatives of phosphoroamidates have gained particular interest for their unique reactivity and potential for functionalization. In the context of anomeric amides, such as N-alkoxy-N-chlorobenzamides **1** [1−6] and N-alkoxy-N-chloroureas **2** [7−10], the amide nitrogen atom is notably connected to two heteroatoms, adopting a pyramidal configuration. This structural feature is favorable for the $n_{O(Alk)} \rightarrow \sigma^*_{N-Cl}$ anomeric effect [1−10], which results in the shortening of the N−O(Alk) bond and the elongation of the N−Cl bond. This bond weakening facilitates the formation of nucleophilic substitution products when these anomeric amides interact with O- and N-nucleophiles [1−10] (Scheme 1).



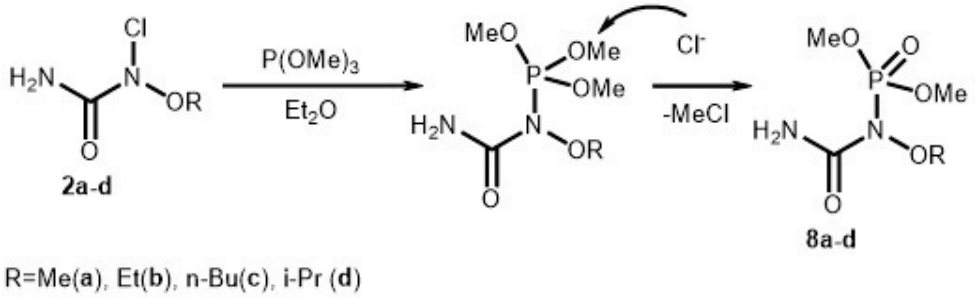
Scheme 1. Interaction of N-alkoxy-N-chlorobenzamides 1 and N-alkoxy-N-chloroureas 2 with the O- and N-nucleophiles [1–10]

Despite extensive research on these interactions, there has been a surprising lack of studies on the reaction of N-alkoxy-N-chlorobenzamides and N-alkoxy-N-chloroureas with phosphorus nucleophiles. In our earlier work, we addressed this gap by demonstrating the selective reaction of N-alkoxy-N-chloroureas **2a–d** with trimethyl phosphite, which led to the formation of N-alkoxy-N-phosphorylureas **8a–d** via an unusual Michaelis-Arbuzov reaction [11]. This finding opened new avenues for exploring the reactivity of anomeric amides with phosphorus nucleophiles, offering insights into their structural and chemical activity characteristics (Scheme 2).

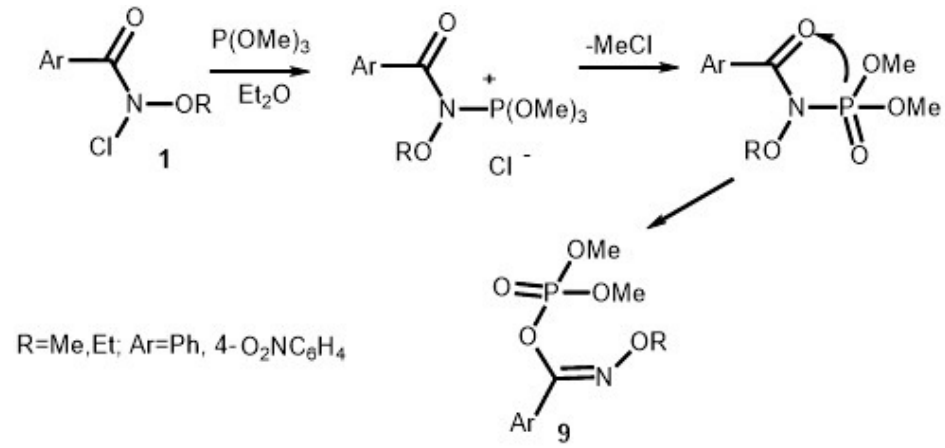
It was found that in N-alkoxy-N-phosphorylureas **8a–d**, the N-alkoxy nitrogen atom has an almost planar configuration unlike N-alkoxy-N-chloroureas **2a–d** [8,9], N-acyloxy-N-alkoxyureas 2 [9], and N,N-dialkoxyureas **4** [10].

N-Alkoxy-N-chlorobenzamides **1a–c** react with trimethyl phosphite, leading to the selective formation of N-alkoxy-1-(dimethoxyphosphoryloxy)benzimidates **9** [12] (Scheme 3).

However, the potential interaction of N-alkoxy-N-(chloro)sulfonamides and trialkyl phosphites had not been investigated.



Scheme 2. Interaction of N-alkoxy-N-chloroureas 2a–d with trimethyl phosphite [11]



Scheme 3. Interaction of N-alkoxy-N-chlorobenzamides**1a–c** with trimethyl phosphite [12]

Therefore, the objective of our current study was to explore this interaction and analyzethe structure of the resulting products.

Experimental

Materials and equipment

^{1}H NMR spectra were recorded on a VARIAN VNMRS 400 spectrometer (400 MHz). ^{13}C NMR spectra were recorded on a VARIAN VNMRS 400 spectrometer (100 MHz). $CDCl_3$ was used as the solvent. ^{1}H NMR chemical shifts relative to the residual solvent protons as an internal standard [$(CD_3)_2SO$: 2.500 ppm, $CDCl_3$: 7.260 ppm, CD_3CN: 1.940 ppm] were reported. The solvent carbon atoms served as an internal standard for ^{13}C NMR spectra [$CDCl_3$: 77.16 ppm]. ^{31}P NMR spectra were recorded on a VARIAN VNMRS 400 spectrometer (161.95 MHz), the solvent $CDCl_3$ was used; 98% H_3PO_4 was used as external standard. Mass spectra were recorded in fast atom bombardment mode (FAB) on a VG 70-70EQ mass spectrometer. The solvents were purified and dried according to standard procedures.

Synthesis

*N-Methoxy-4-tolyenesulfonamide (**10a**)*

The solution of N-methoxyamine (0.571 g, 12.134 mmol) in MeCN (5 mL) was added to the solution of TsCl (1.157 g, 6.069 mmol) in MeCN (5 mL), and then the solution of trietylamine (0.676 g, 6.675 mmol) in MeCN (5 mL) was added. The reaction mixture was maintained at 19^{0}C during 68 h, followed by boiling for 1 h. After that, MeCN was evaporated under vacuum, and the residue was extracted by benzene (30 mL). The PhH-extract was evaporated under vacuum, the residue was maintained at 60єC under vacuum (2 mmHg); then obtained residue was washed with water (15 mL), and dried under vacuum (2 mm Hg), giving 1.004 g (82%) of *N*-methoxy-4-tolyenesulfonamide **10a** as a colorless crystals, mp 109–110^{0}C (benzene–hexane).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=2.448 (3H, s, Me); 3.789 (3H, s, NOMe); 7.035 (1H, br.s, NHO); 7.350 (2H, d, ^3J=8.4 Hz, C(3)H,C(5)H $C_6H_4SO_2$); 7.814 (2H, d, ^3J=8.4 Hz, C(3)H,C(5)H $C_6H_4SO_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=21.78 Me; 65.14 NOMe; 128.65 C(2)H, C(6)H $C_6H_4SO_2$; 129.85 C(3)H, C(5)H $C_6H_4SO_2$; 133.72 C(4)–Me, $C_6H_4SO_2$; 145.03 C(1)–SO_2. Mass spectrum (FAB), m/z (I_{rel}, %): 202 $[M+H]^+$ (34); 201 M^+ (54); 155 Ts^+ (100); 91 (54). Found, %: C 47.69; H 5.66; N 6.92. $C_8H_{11}NO_3S$. Calculated, %: C 47.75; H 5.51; N 6.96.

*N-Ethoxy-4-tolyenesulfonamide (**10b**)*

N-Ethoxy-4-tolyenesulfonamide (**10b**) was synthesized according ref. [7], colorless crystals, mp. 86–88^{0}C (benzene–hexane).^{1}HNMR(400 MHz, $CDCl_3$, ppm): δ=1.194 (3H, t, ^{3}J=7.0 Hz, $NOCH_2Me$); 2.449 (3H, s, Me); 4.037 (2H, q, ^{3}J=7.0 Hz, $NOCH_2Me$); 6.865 (1H, s, NH); 7.352 (2H, d, ^{3}J=8.0 Hz, C(3)H,C(5)H$C_6H_4SO_2$); 7.813 (2H, d, ^{3}J=8.0 Hz, C(2)H,C(6)H$C_6H_4SO_2$).

*N-(Methoxy)methanesulfonamide (**11**)*

The solution of MsCl (1.230 g, 10.74 mmol) in MeCN (6 mL) was added to the solution of N-methoxyamine (1.036 g, 22.018 mmol) (6 mL) at –25^{0}C. The reaction mixture was maintained at 7^{0}C for 2 h, and then at 18^{0}C for 137 h; then the obtained solid was filtered off, and washed with MeCN (4 mL). The MeCN-filtrate was evaporated under vacuum, the residue was dried under vacuum (2 mmHg), and benzene (14 mL) was added. The obtained solid was filtered off and dried under vacuum (2 mm Hg), yielding 0.756 g (56%) of N-(methoxy)methanesulfonamide **11** as a colorless crystals, mp 94–95^{0}C (benzene). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=3.059 (3H, s, $MeSO_2$); 3.817 (3H, s, NOMe); 7.158 (1H, br. s, NHO). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=36.81 $MeSO_2$, 65.33 NOMe. Mass spectrum (FAB), m/z (I_{rel}, %):251 $[2M+H]^+$(100); 125 M^+ (100).

The PhH-filtrate was maintained at 7^{0}C for 10 h, the obtained precipitate was filtered off, and dried under vacuum (2 mm Hg), yielding an additional 0.362 g (27%) of N-(methoxy)methanesulfonamide **11**.

*N-Chloro-N-methoxy-4-tolyenesulfonamide (**12a**)*

The solution of *tert*-butyl hypochlorite (165 mg, 1.520 mmol) in CH_2Cl_2 (3 mL) was added to the solution of *N*-methoxy-4-tolyenesulfonamide **10a** (102 mg, 0.507 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was maintained at 5^{0}C for 2 h; then it was evaporated under vacuum, the residue was kept at 2 mm Hg for 20 min, washed with cold hexane, and dried under vacuum, yielding 112 mg (94%) of unstable N-chloro-N-methoxy-4-tolyenesulfonamide **12a** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=2.494 (3H, s, Me); 3.797 (3H, s, NOMe); 7.418 (2H, d, ^{3}J=8.4 Hz, C(3)H,C(5)H $C_6H_4SO_2$); 7.920 (2H, d, ^{3}J=8.4 Hz, C(2)H,C(6)H $C_6H_4SO_2$).

*N-Chloro-N-ethoxy-4-tolyenesulfonamide (**12b**)*

Unstable N-chloro-*N*-ethoxy-4-tolyenesulfonamide **12b** has been synthesized by chlorination of N-ethoxy-4-tolyenesulfonamide **10b** by tert-butyl hypochlorite according ref. [7], colorless oil, n_D^{30} 1.5332. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=1.236 (3H, t, ^{3}J=7.0 Hz, $NOCH_2Me$); 2.492 (3H, s, Me); 4.060 (3H, q, ^{3}J=7.0 Hz, $NOCH_2Me$); 7.414 (2H, d, ^{3}J=8.4 Hz, C(3)H,C(5)H$C_6H_4SO_2$); 7.914 (2H, d, ^{3}J=8.4 Hz, C(2)H,C(6)H$C_6H_4SO_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=13.25

$NOCH_2Me$; 21.99 Me; 72.39 $NOCH_2$; 127.75 C(4)−$MeC_6H_4SO_2$; 129.74 C(3)H, C(5)$HC_6H_4SO_2$; 131.42 C(2)H, C(6)$HC_6H_4SO_2$; 146.80 C(1)−SO_2.

*N-Chloro-N-(methoxy)methanesulfonamide (**13**)*

The solution of *tert*-butyl hypochlorite (205 mg, 1.893 mmol) in CH_2Cl_2 (2 mL) was added to the solution of N-(methoxy)methanesulfonamide **11** (79 mg, 0.631 mmol) in CH_2Cl_2 (3 mL) at 8^0C. The reaction solution was maintained at 8^0C for 2 h, then it was evaporated under vacuum; the residue was dried at 15^0C under vacuum (4 mm Hg) for 30 min, yielding 100 mg (99 %) of N-chloro-N-(methoxy)methanesulfonamide **13** as a colorless oil, n^{20}_D 1.4681. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=3.227 (3H, s, $MeSO_2$); 3.913 (3H, s, NOMe). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=31.86 $MeSO_2$, 63.68 NOMe. Mass spectrum (FAB, KCl), m/z (I_{rel}, %): 200 $[M+K]^+$ (32); 198 $[M+K]^+$ (100), 79 Ms^+ (13).

*Dimethyl N-methoxy-N-(4-toluenesulfonyl)phosphoramidate (**14**)*

A. The solution of trimethyl phosphite (126 mg, 1.013 mmol) in diethyl ether (6 mL) was added to the solution of N-chloro-N-methoxy-4-tolylsulfonamide **12a** (112 mg, 0.475 mmol) in diethyl ether (2 mL). The reaction mixture was maintained at 5^0C for 20 min, and then at 18^0C for 161 h in a sealed ampoule. The obtained solution was evaporated under vacuum; then the residue was heated at 65^0C during 20 min under vacuum (2 mm Hg). The obtained residue was treated with hexane (9 mL) at 10^0C during 20 h; then the precipitated solid was filtered off and dried under vacuum (2 mm Hg), giving 101 mg (69%) of dimethyl N-methoxy-N-(4-toluenesulfonyl)phosphoramidate **14** as a colorless crystals, mp 45−46^0C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=2.441 (3H, s, Me); 3.756 (6H, d, ^{HP}J=11.2 Hz, P(O)$(OMe)_2$); 3.959 (3H, s, NOMe); 7.334 (2H, d, ^{3}J=8.4 Hz, C(3)H, C(5)H $C_6H_4SO_2$); 7.883 (2H, d, ^{3}J=8.4 Hz, C(2)H, C(65)H $C_6H_4SO_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=21.80, s, Me; 55.36 d, ^{CP}J=6.03 Hz, P(O)$(OMe)_2$; 66.44 d, ^{CP}J=1.01 Hz NOMe; 129.11, s, C(2)H, C(6)H $C_6H_4SO_2$; 129.50 s C(3)H, C(5)H $C_6H_4SO_2$; 133.86, s, C(4)−Me, $C_6H_4SO_2$; 145.27, s, C(1)−SO_2. ^{31}P NMR (161.95 MHz, $CDCl_3$, ppm): −4.07. Mass spectrum (FAB), m/z (I_{rel}, %): 310 $[M+H]^+$ (100); 155 Ts^+ (28). Found, %: C 38.71; H 5.34; N 4.37. $C_{10}H_{16}NO_6PS$. Calculated, %: C 38.84; H 5.21; N 4.53.

The obtained filtrate was kept at -30^0C for 5 days; the obtained precipitate was filtered off, and dried under vacuum, yielding an additional 7 mg (5%) of compound **14**.

B. The solution of trimethyl phosphite (155 mg, 1.249 mmol) in diethyl ether (5 mL) was added to the solution of *N*-chloro-*N*-methoxy-4-tolylsulfonamide **12a** (139 mg, 0.590 mmol) in diethyl ether (2 mL) at 12^0C. The reaction mixture was maintained at 12^0C for 2 h, and then at 19^0C for 169 h in the sealed ampoule. The solvent was evaporated under vacuum; and the residue was heated at 65^0C for 40 min under vacuum (2 mm Hg). Hexane (10 mL) was added to the residue. The mixture was maintained at 18^0C for 169 h; the obtained precipitate was filtered off, and dried under vacuum (2 mm Hg), yielding 130 mg (71.2%) of dimethyl N-methoxy-N-(4-toluenesulfonyl)phosphoramidate **14**.

The hexane filtrate was maintained at -26^0C for 73 h, the obtained precipitate was quickly filtered off, and dried und vacuum (2 mm Hg), yielding an additional 29 mg (15.9%) of compound **14**.

*Dimethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate (**15**)*

A. The solution of trimethyl phosphite (96 mg, 0.773 mmol) in diethyl ether (2 mL) was added to the solution of *N*-chloro-*N*-ethoxy-4-tolyenesulfonamide **12b** (102 mg, 0.408 mmol) in diethyl ether (4 mL). The reaction mixture was maintained at 19^0C for 137 h in the sealed ampoule. The solvent was evaporated under vacuum, and the residue was heated at 75^0C for 1 h under vacuum (2 mm Hg), giving 129 mg (97%) of dimethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate **15** as a colorless crystals, mp 47−48^0C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.246 (3H, t, ^{3}J=7.0 Hz, $NOCH_2Me$); 2.446 (3H, s, Me); 3.761 (6H, d, ^{HP}J=11.6 Hz, P(O)$(OMe)_2$); 4.257 (2H, q, ^{3}J=7.0 Hz, $NOCH_2Me$); 7.338 (2H, d, ^{3}J=8.4 Hz, C(3)H, C(5)H $C_6H_4SO_2$); 7.884 (2H, d, ^{3}J=8.4 Hz, C(2)H, C(6)H $C_6H_4SO_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=13.72 $NOCH_2Me$; 21.86, Me; 55.39 d, ^{CP}J=6.04 Hz, P(O)$(OMe)_2$; 75.02 d, ^{CP}J=0.50 Hz, $NOCH_2$; 129.21, C(2)H, C(6)H $C_6H_4SO_2$; 129.50 C(3)H, C(5)H $C_6H_4SO_2$; 133.99, C(4)−Me, $C_6H_4SO_2$; 145.18, C(1)−SO_2. ^{31}P NMR (161.95 MHz, $CDCl_3$, ppm): −3.95. Mass spectrum (FAB), m/z (I_{rel}, %): 324 $[M+H]^+$ (100); 169 (17). Found, %: C 40.72; H 5.78; N 4.20. $C_{11}H_{18}NO_6PS$. Calculated, %: C 40.87; H 5.61; N 4.33.

B. The solution of trimethyl phosphite (143 mg, 1.153 mmol) in diethyl ether (5 mL) was added to the solution of *N*-chloro-*N*-ethoxy-4-tolyenesulfonamide **12b** (131 mg, 0.525 mmol) in diethyl ether (5 mL). The reaction mixture was maintained at 8^0C for 3 h, and then at 18^0C for 163 h in the sealed ampoule. The solvent was evaporated under vacuum, the residue was heated at

76°C for 1 h under vacuum (2 mm Hg); the residue was washed with hexane (8 mL) at 18°C for 25 h, and the obtained solid was filtered off, and dried under vacuum (5 mm Hg), giving 124 mg (73%) of dimethyl *N*-ethoxy-*N*-(4-toluenesulfonyl)phosphoramidate **15**.

The obtained filtrate was evaporated under vacuum, the residue was heated at 60°C for 1 h under vacuum (2 mm Hg), the residue was crystallized from hexane (5 mL), yielding an additional 35 mg (20%) of compound **15**.

Dimethyl N-methanesulfonyl-N-methoxyphosphoramidate (16)

A. The solution of trimethyl phosphite (248 mg, 1.998 mmol) in diethyl ether (6 mL) was added to the solution of N-chloro-N-(methoxy)methanesulfonamide **13** (159 mg, 0.999 mmol) in ether (2 mL) at −30°C. The reaction mixture was maintained at 20°C for 138 h in a sealed ampoule. The solvent was evaporated under vacuum, and the residue was heated at 60°C for 1 h under vacuum (2 mm Hg), giving 193 mg (83%) of dimethyl N-methanesulfonyl-N-methoxyphosphoramidate **16**, colorless oil, n_D^{26} 1.4450. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=3.151 (3H, s, $MeSO_2$); 3.935 (6H, d, ^{HP}J=11.6 Hz, P(O)$(OMe)_2$); 3.951 (3H, s, NOMe). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=37.49 s $MeSO_2$, 55.93 d, ^{CP}J=6.04 Hz, P(O)$(OMe)_2$; 66.45 d, ^{CP}J=2.01 Hz, NOMe. ^{31}P NMR (161.95 MHz, $CDCl_3$, ppm): −3.28. Mass spectrum (FAB), *m/z* (I_{rel}, %): 234 $[M+H]^+$ (100); 155 $[M+H-Ms]^+$ (44). Found, %: C 20.32; H 5.25; N 5.89. $C_4H_{12}NO_6PS$. Calculated, %: C 20.60; H 5.19; N 6.01.

B. The solution of trimethyl phosphite (210 mg, 1.694 mmol) in diethyl ether (7 mL) was added to the solution of N-chloro-N-(methoxy)methanesulfonamide **13** (135 mg, 0.846 mmol) in ether (4 mL) at 20°C. The reaction mixture was maintained at 20°C for 167 h in a sealed ampoule. The solvent was evaporated under vacuum, the residue was heated at 80°C for 20 min under vacuum (2 mm Hg), giving 176 mg (89%) of dimethyl N-methanesulfonyl-N-methoxyphosphoramidate **16**.

Diethyl N-methoxy-N-(4-toluenesulfonyl)phosphoramidate (17)

A. The solution of triethyl phosphite (173 mg, 1.044 mmol) in diethyl ether (5 mL) was added to the solution of *N*-chloro-*N*-methoxy-4-toluenesulfonamide **12a** (123 mg, 0.522 mmol) in diethyl ether (2 mL). The reaction mixture was maintained at 20°C for 192 h in a sealed ampoule. Then the solvent was evaporated under vacuum, and the residue was heated at 85°C during 40 min under vacuum (2 mm Hg). Then, the obtained residue was extracted by hexane (10 mL) at 20°C for 24 h; the extract was separated from the second liquid phase and evaporated under vacuum; the residue was heated at 85°C for 20 min, yielding 115 mg (65.3%) of diethyl *N*-methoxy-*N*-(4-toluenesulfonyl)phosphoramidate **17**, colorless oil, n_D^{25} 1.4500. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=1.252 (6H, td, ^{3}J=7.2 Hz, ^{HP}J=0.8 Hz, P(O)$(OCH_2Me)_2$); 2.435 (3H, s, Me); 3.960 (3H, s, NOMe); 4.014−4.122 (2H, m, P(O)(OCH_2Me); 4.143−4.241 (2H, m, P(O)(OCH_2Me); 7.320 (2H, d, ^{3}J=8.4 Hz, C(3)H, C(5)H $C_6H_4SO_2$); 7.879 (2H, d, ^{3}J=8.4 Hz, C(2)H, C(6)H $C_6H_4SO_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=16.04 d, ^{CP}J=7.04 Hz, P(O)(OCH_2Me); 21.81 s Me; 65.53 d, ^{CP}J=6.04 Hz, P(O)(OCH_2Me); 66.47 d, ^{CP}J=1.01 NOMe; 129.22 s, C(3)H, C(5)H $C_6H_4SO_2$; 129.40 s, C(2)H, C(6)H $C_6H_4SO_2$; 134.05, s C(4)−Me, $C_6H_4SO_2$; 145.10 C(1)−SO_2). ^{31}P NMR (161.95 MHz, $CDCl_3$, ppm): −6.740. Mass spectrum (FAB), m/z (I_{rel}, %): 338 $[M+H]^+$ (100). Found, %: C 42.85; H 5.91; N 4.03. $C_{12}H_{20}NO_6PS$. Calculated, %: C 42.73; H 5.98; N 4.15.

The second liquid phase was extracted by boiling hexane (10 mL), the extract was maintained at 10°C for 24 h, and the obtained precipitate was filtered off, yielding 5 mg (4.7%) of N-methoxy-4-tolyenesulfonamide **10a**, identified by ^{1}H NMR. The filtrate was evaporated under vacuum, the residue was heated at 70°C during 15 min under vacuum (2 mm Hg), yielding an additional 29 mg (16.5%) of compound **17**, identified by ^{1}H NMR.

Diethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate (18)

The solution of triethyl phosphite (116 mg, 0.695 mmol) in diethyl ether (4 mL) was added to the solution of N-chloro-N-ethoxy-4-toluenesulfonamide **12b** (124 mg, 0.497 mmol) in diethyl ether (2 mL) at 20°C. The reaction mixture was maintained at 19°C for 116 h, then the solvent was evaporated under vacuum, the residue was heated at 80°C for 30 min under vacuum (2 mm Hg). Then the obtained residue was treated by hexane (8 mL) at 20°C for 24 h; the extract was separated from the second phase, and evaporated under vacuum, the residue was heated at 85°C for 10 min, yielding 150 mg (86%) of diethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate **18** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ=1.236 (3H, t, ^{3}J=7.2 Hz, NOCH_2Me); 1.254 (6H, t, ^{3}J=7.2 Hz,P(O)$(OCH_2Me)_2$); 2.437 (3H, s, Me); 4.003−4.080 (2H, m, P(O)(OCH_2Me); 4.129−4.221 (2H, m, P(O)(OCH_2Me); 4.255 (2H, q ^{3}J=7.2 Hz,

$NOCH_2Me$); 7.320 (2H, d ^3J=8.4 Hz, C(3)H, C(5)H $C_6H_4SO_2$); 7.876 (2H, d ^3J=8.4 Hz, C(2)H, C(6)H $C_6H_4SO_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=13.69, s, $NOCH_2Me$; 16.045 d, ^{CP}J=7.04 Hz, P(O)(OCH_2Me); 21.80 s Me; 65.37 d ^{CP}J=6.04 Hz, P(O)(OCH_2Me); 74.90 s, $NOCH_2Me$; 129.26 s, C(3)H, C(5)H $C_6H_4SO_2$; 129.35 s, C(2)H, C(6)H $C_6H_4SO_2$; 134.14, s C(4)−Me, $C_6H_4SO_2$; 144.98 C(1)−SO_2. ^{31}P NMR (161.95 MHz, $CDCl_3$, ppm): −3.63. Mass spectrum (FAB), m/z (I_{rel}, %): 352 $[M+H]^+$ (100); 197 (9). Found, %: C 44.32; H 6.57; N 3.87. $C_{13}H_{22}NO_6PS$. Calculated, %: C 44.44; H 6.31; N 3.99.

*Diethyl N-methanesulfonyl-N-methoxyphosphoramidate (**19**)*

The solution of triethyl phosphite (245 mg, 1.477 mmol) in diethyl ether (2 mL) was added to the solution of N-chloro-N-(methoxy)methanesulfonamide 13 (168.3 mg, 1.055 mmol) in diethyl ether (4 mL) at −20°C. The reaction mixture was maintained at 18°C for 145 h; then the solvent was evaporated under vacuum, and the residue was heated at 85°C for 30 min under vacuum (2 mm Hg), yielding 230 mg (83%) of diethyl N-methanesulfonyl-N-methoxyphosphoramidate 19 as a colorless oil, n_D^{26} 1.4432. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ=1.389 (6H, td, ^3J=7.1 Hz, ^{HP}J=1.2 Hz, P(O)($OCH_2Me)_2$); 3.133 (3H, s, $MeSO_2$); 3.940 (3H, s, NOMe); 4.223−4.370 (4H, m, P(O)($OCH_2Me)_2$)). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=16.19, d, ^{CP}J=7.04 Hz, P(O)($OCH_2Me)_2$; 37.40, s, $MeSO_2$; 65.95, d, ^{CP}J=6.04Hz, P(O)($OCH_2Me)_2$; 66.44, d, ^{CP}J=2.01 Hz, NOMe. ^{31}P NMR (161.95 MHz, $CDCl_3$, ppm): −5.883. Mass spectrum (FAB), m/z (I_{rel}, %): 262 $[M+H]^+$ (100). Found, %: C 27.38; H 6.26; N 5.17. $C_6H_{16}NO_6PS$. Calculated, %: C 27.59; H 6.17; N 5.36.

X-ray diffraction study

*Dimethyl N-methoxy-N-(4-toluenesulfonyl)phosphoramidate (**14**)*

The colorless crystals of compound **14** ($C_{10}H_{16}NO_6PS$) are monoclinic, from hexane, at −100.5°C, **a**=14.9246(6) Å, **b**=11.3134(5) Å, **c**=8.2825(4) Å, β=95.113(3)°, V=1392.92(11) Å^3, M_r=309.27, Z=4, space group $P2_1/c$, d_{calc}=1.475 g/cm^3, μ(MoK_α)=0.368 mm^{-1}, F(000)=648.

Intensities of 16788 reflections (2445 independent, R_{int}=0.0425) were measured on the «Bruker APEX-II CCD» diffractometer (graphite monochromated MoK_α radiation, CCD detector, φ and ω-scanning, $2\Theta_{max}$=50°). The structure was solved by direct method using SHELXTL package [13]. Positions of the hydrogen atoms were located from electron density difference maps and refined by «riding» model with U_{iso}=nU_{eq} (n=1.5 for methyl groups and n=1.2 for other hydrogen atoms) of the carrier atom. The MeON group hydrogens are refined in an isotropic approximation. Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms using 2445 reflections was converged to wR_2=0.0906 (R_1=0.0341 for 2111 reflections with F>4σ(F), S=1.059).

The atomic coordinates, molecular geometry parameters, and crystallographic data of compound **14** are preserved at the Cambridge Crystallographic Data Center, 12 Union Road, CB2, 1EZ UK [fax:+44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk and are available on request quoting the deposit number CCDC 2379521 (**14**).

*Dimethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate (**15**)*

The colorless crystals of compound **15** ($C_{11}H_{18}NO_6PS$) are monoclinic, from hexane, at −100.5°C, **a**=12.7349(5) Å, **b**=8.0280(4) Å, **c**=29.5093(12) Å, β=91.202(3)°, V=3016.2(2) Å^3, M_r=323.29, Z=8, space group $P2_1/n$, d_{calc}=1.424 g/cm^3, μ(MoK_α)=0.343 mm^{-1}, F(000)=1360.

Intensities of 38270 reflections (5307 independent, R_{int}=0.1058) were measured on the «Bruker APEX-II CCD» diffractometer (graphite monochromated MoK_a radiation, CCD detector, φ and ω-scanning, $2\Theta_{max}$=50°). The structure was solved by direct method using SHELXTL package [13]. Positions of the hydrogen atoms were located from electron density difference maps and refined by «riding» model with U_{iso}=nU_{eq} (n=1.5 for methyl groups and n=1.2 for other hydrogen atoms) of the carrier atom. Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms using 5307 reflections was converged to wR_2=0.1584 (R_1=0.0747 for 3759 reflections with F>4σ(F), S=1.083).

The atomic coordinates, molecular geometry parameters, and crystallographic data of compound **15** are preserved at the Cambridge Crystallographic Data Center, 12 Union Road, CB2, 1EZ UK [fax:+44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk and are available on request quoting the deposit number CCDC 2379522 (**15**).

Results and discussion

Synthesis and identification

Chlorination of *N*-alkoxysulfonamides **10a,b** and **11** by tert-butyl hypochlorite afforded N-alkoxy-N-chloro-4-toluenesulfonamides12a,b and N-chloro-N-methoxy-methanesulfonamide **13** (Scheme 4).

The interaction of N-alkoxy-N-

(chloro)sulfonylamides12a,b and 13 with trialkyl phosphites selectively yields dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoramidates and dialkyl N-methoxy-N-methanesulfonylphosphoramidates **14–19**, respectively (Scheme 5).

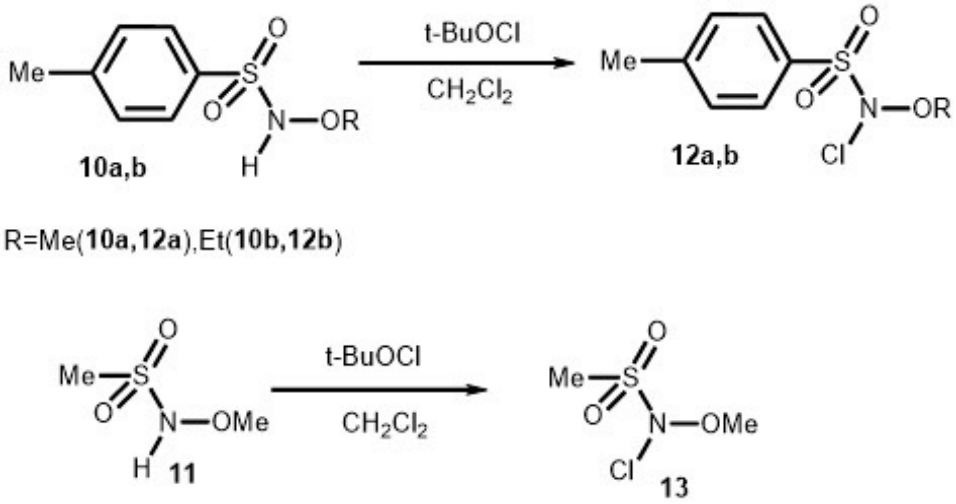
This reaction is a new convenient method of the N–P bond formation. A potential novel strategy for the synthesis of N-phosphoryl sulfonamides is proposed.

Compounds **14–19** may be regarded as products of the nucleophilic substitution at nitrogen. It is surprising because earlier we had found that N-chloro-N-ethoxy-4-tolyenesulfonamide **12b** did not react with AcONa in MeCN [7].

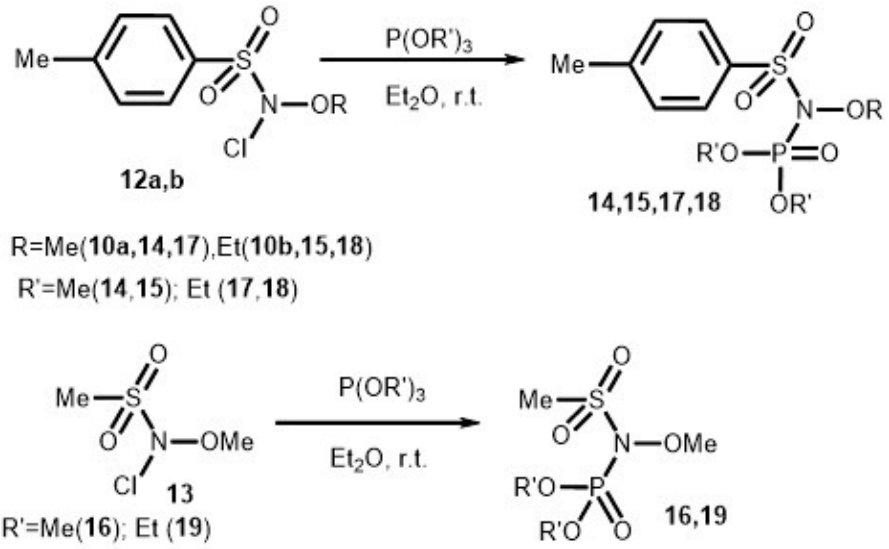
A proposed alternative pathway for the synthesis of compounds **14–19** is shown below. It involves two steps. First, nucleophilic substitution at the nitrogen of N-alkoxy-N-(chloro)sulfonamides 12a,b and 13 by trialkyl phosphites leads to the formation of labile N-alkoxy-N-(trialkoxyphosphonium)sulfonamide chlorides **A** (Scheme 6).

At the second stage the *O*-dealkylation of the phosphonium salts **A** by the chloride anion occurs (this is the unusual kind of Michaelis–Arbuzov rearrangement). It yields the waiting dialkyl N-alkoxy-N-R-sulfonylphosphoramimates **16–19**.

The structure of N-alkoxy-N-phosphorylureas **16–19** has been proved by the ^{1}H, ^{13}C, ^{13}P NMR



Scheme 4. Synthesis of N-alkoxy-N-(chloro)sulfonamides **12a,b** and **13**



Scheme 5. Synthesis dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoramidates and dialkyl N-methoxy-N-methanesulfonylphosphoramidates **14–19**

spectra and mass spectra. In addition, the structure of compound **14** has been confirmed by the single crystal X-ray diffraction (XRD) study (Fig. 1).

The ^{1}H NMR spectra of compounds **16–19** show such a common characteristic as doublet of dimethoxyphosphoryl moiety and singlet of MeON-group (Table 1).

In the ^{31}P NMR spectra of compounds **16–19**, the chemical shifts of the phosphorus atom lie in the range of −3.28 to −6.74 ppm.

The ^{13}C NMR spectra of compounds **16–18** demonstrate numerous shared features and common characteristics. They include the chemical shifts of the NOMe carbon atoms ($NOCH_2$ for compound **18**), the carbon atoms of dimethoxyphosphoryl group and the carbon atom of C=N bond (Table 2).

The mass spectra of compounds **14–19** display protonated molecular ion $[M+H]^+$ peaks at the appropriate *m/z* values with 100% intensity.

Structural features

The structure of the compounds **14** and **15** has many interesting peculiarities that merit to be additionally reviewed in this article. The structure of dimethyl N-methoxy-N-(4-toluenesulfonyl)phosphoramidate **14** is represented in Fig. 1.

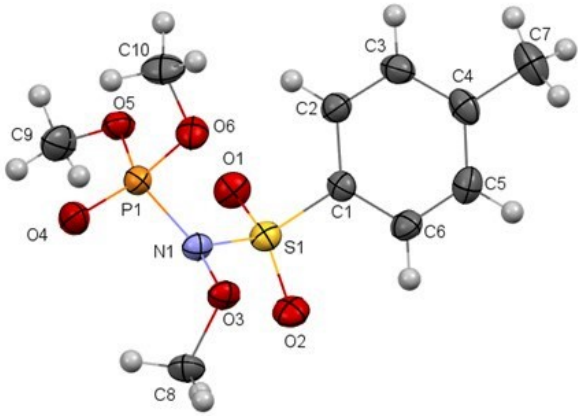
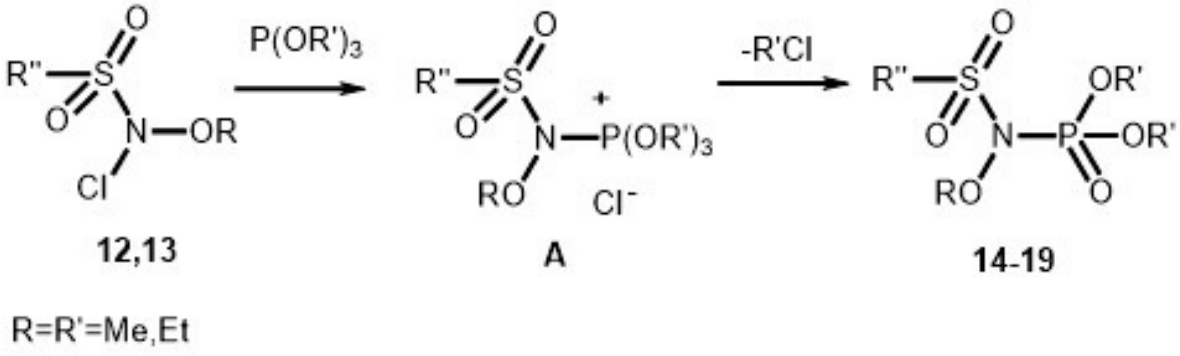


Fig. 1. Molecular structure of dimethyl N-methoxy-N-(4-toluenesulfonyl)phosphoramidate 14 according to X-ray diffraction data. Thermal ellipsoids are shown at 50% probability level



Scheme 6. A probable scheme of the formation of compounds **14–19**

Table 1

Typical ^{1}H NMR and ^{31}P chemical shifts of dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoramidates and dialkyl N-methoxy-N-methanesulfonylphosphoramidates 14–19 (ppm, in $CDCl_3$)

Compound	^{1}H NMR, σ			^{31}P NMR, σ
	NOMes	$NOCH_2Me$	$P(O)(OR)_2$	
14	3.959	–	3.756	–4.07
15	–	1.246 t, 4.257 q	3.761	–3.95
16	3.948	–	3.934	–3.28
17	3.960	–	1.252 td, 4.014–4.122 m 4.143–4.241 m	–6.74
18	–	1.236t, 4.255 q	1.236 t, 4.003–4.080 m 4.129–4.221 m	–3.63
19	3.940	–	1.389 td 4.223–4.370 m	–5.88

Surprisingly, in compound **14**, the N(1) atom has pyramidal configuration, and the sum of bond angles (Σβ) is 347.6⁰. In N-alkoxy-N-(dimethoxyphosphoryl)ureas **8a**,**c**, the same nitrogen atom has the planar configuration; Σβ is 357.94(16)⁰ and 359.3(6)⁰ in urea **8a** and **8c**, respectively [11].

The N(1)−O(3)Me bond is shortened (1.439(2) Å) relative to the average N_{sp3}−O bond (1.463 Å) [14] and relative to the N−O bond of N-alkoxy-N-(dimethoxyphosphoryl)ureas 8a,c. In N-methoxy-N-(dimethoxyphosphoryl)ureas **8a**, the length of the N−O(Me) bond is 1.412(2) Å;in N-n-butyloxy-N-(dimethoxyphosphoryl)ureas **8c**, the length of the N−O(Bu^n) bond is 1.401(7) Å [11].

The N(1)−S(1) bond (1.6744(16) Å) and N(1)−P(1) bond (1.699(16) Å) are elongated relative to the average N−S bond (1.642 Å, [14]) and N−P bond (1.683 Å, [14]). In N-methoxy-N-(dimethoxyphosphoryl)ureas **8a**, the length of the N−P bond is shorter (1.6861(12) Å) [11]. In N-n-butyloxy-N-(dimethoxyphosphoryl)ureas **8c**, the length of the N−P bond is shorter too (1.653(7) Å) [11].

It may be supposed that the observed pyramidality of N(1) nitrogen atom in N-methoxy-N-(4-toluenesulfonyl)phosphoramidate **14**, the shortening of the N(1)−O(3)Me bond, elongations of the N(1)−P(1) bond and N(1)−S(1) bonds are all caused by the weakening of the conjugation of the lone electron pair (LP) of N(1) nitrogen atom with the phosphoryl and sulfonyl groups. We also assume that it is the possible action of the $n_{O(Me))}\rightarrow\sigma^*_{N-P}$ and the $n_{O(Me)}\rightarrow\sigma^*_{N-S}$ anomeric effects that have caused these structural features.

It is plausible that the observed conformation O=P−N−S=O fragment is unfavorable for conjugation of the LP of N(1) atom with the phosphoryl and sulfonyl groups.

In the molecule **14**, the P(1)=O(4) group is anti-periplanar oriented toward the N(1)−S(1) bond (the S(1)−N(1)−P(1)−O(4) torsion angle is 163.08(12)⁰).

In the dimethoxyphosphoryl moiety, the C(9)H_3-methyl group and C(10)H_3-methyl group are orthogonal and anti-periplanar oriented toward the N(1)−P(1). The N(1)−P(1)−O(5)−C(9) torsion angle is 83.2(2)⁰, and the N(1)−P(1)−O(6)−C(10) torsion angle is −179.2(2)⁰.

The C(8)H_3 group is in +*ac*-conformation toward the N(1)−P(1) bond. The torsion angle P(1)−N(1)−O(3)−C(8) is 106.1(1)⁰.

The 4-tolyl substituent is in +sc-conformation relative to the N(1)−P(1) bond and it is deployed relative to the N(1)−S(1) bond. The C(1)−S(1)−N(1)−P(1) torsion angle is 71.2(1)⁰, and the C(2)−C(1)−S(1)−N(1) torsion angle is −78.1(2)⁰.

The structure of dimethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate **15** is represented in Fig. 2.

There are two independent molecules of the compound **15** (**15A** and **15B**) in the asymmetric part of the unit cell. These molecules differ in the degree of pyramidality of the nitrogen atom and the lengths of its bonds.

This existence of urea derivatives as a mixture of the two forms which differ by the pyramidality degree of the nitrogen atom and the lengths of the nitrogen atom bonds is known for N-chloro-N-ethoxyurea [9], N-chloro-N-methoxy-N'-4-nitrophenylurea [10], and 1-alkoxy-3-aryl-3a,8a-dihydroxy-1,3,3a,8a-tetrahydroindeno[1,2-d]imidazole-2,8-diones [15].

Table 2

Typical ^{13}C NMR chemical shifts of carbon atoms dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoramidates and dialkyl N-methoxy-N-methanesulfonylphosphoramidates 14−19 (in $CDCl_3$)

Compound	Shifts, ppm			
	NOMe	NOEt	$P(O)(OMe)_2$	$P(O)(OEt)_2$
14	66.44 d	–	55.36 d	–
15	–	13.72 s 75.02 d	55.39 d	–
16	66.45 d	–	55.93 d	–
17	66.47 d	–	–	16.04 d 65.53 d
18	–	13.69 s 74.90 s	–	16.045 d 65.37 d
19	66.44 d	–	–	16.19 d 65.95 d

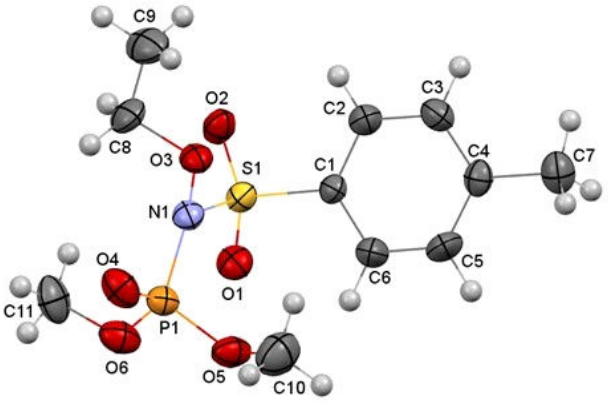


Fig. 2. Molecular structure of dimethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate **15** according to X-ray diffraction data. Thermal ellipsoids are shown at 50% probability level

The molecules **15A** and **15B** differ by the pyramidality degree of the nitrogen atom and the lengths of some bonds. In the molecule **15A**, the N(1) nitrogen atom has almost planar configuration (Σβ is 353.4^0). In the molecule **15B**, the N(1) nitrogen atom has pyramidal configuration (Σβ is 340.3^0). The same phenomenon has been established for N-chloro-N-ethoxyurea earlier [9].

In the molecule **15A**, the N(1)−P(1) bond (1.702(4) Å) and the N(1)−S(1) bond (1.668(4) Å) are shorter than the N(1)−P(1) bond (1.722(4) Å) and the N(1)−S(1) bond (1.685(4) Å) in the molecule **15B**, respectively. However, in both molecules **15A** and **15B**, the N(1)−P(1) bond is longer than the N−P bond in N-alkoxy-N-(dimethoxyphosphoryl)ureas **8a,8c** [11].

It may be supposed that the observed structural difference between molecule **15A** and molecule **15B** is caused by some following factors:

(a) by the mutual orientation of SO_2-group and P=O-group (the O(4)−P(1)−N(1)−S(1) torsion angle is 176.2(3)^0 and 54.3(3)^0 in the molecules **15A** and **15B**, respectively);

(b) by the degree of rotation of SO_2-group around the N(1)−S(1) single bond (the P(1)−N(1)−S(1)−O(1) torsion angle is 23.1(3)^0 and 47.2(3)^0 in the molecule **15A** and **15B**, respectively).

Thus, the observed conformation O=P−N−S=O fragment in the molecule **15A** promotes conjugation of the LP of N(1) atom with the phosphoryl and sulfonyl groups. This conjugation caused the almost planar configuration of N(1) nitrogen atom and shortening of the N(1)−P(1) and N(1)−S(1) bonds in the molecule **15A**.

In the molecule **15A**, the N-ethoxy group is slightly rotated relative to the P(1)−O(4) bond (the O(4)−P(1)−N(1)−O(3) torsion angle is 27.5(3)^0). Its ethyl substituent is located almost orthogonally to the P(1)−N(1) bond and it is antiperiplanar to the N(1)−O(3) bond (the P(1)−N(1)−O(3)−C(8) torsion angle is −94.5(4)^0, and the N(1)−O(3)−C(8)−C(9) torsion angle is −164.2(4)^0).

In the molecule **15B**, the N-ethoxy group is in −*sc*-position of application to the P(1)−O(4) bond (the O(4)−P(1)−N(1)−O(3) torsion angle is −74.1(3)^0). Its ethyl substituent is in −*ac*-conformation relative to the N(1)−P(1) bond and it is antiperiplanar to the N(1)−O(3) bond (the P(1)−N(1)−O(3)−C(8) torsion angle is −116.5(3)^0, and the N(1)−O(3)−C(8)−C(9) torsion angle is −173.2(4)^0).

In both molecules **15A** and **15B**, the N(1)−O(3)Et bond is shortened (1.424(2) Å and 1.434(5) Å in **15A** and **15B**, respectively) relatively to the average N_{sp3}−O bond (1.463 Å) [14].

In the molecule **15A**, the tolyl substituent is located practically orthogonally to the N(1)−P(1) bond (the P(1)−N(1)−S(1)−C(1) torsion angle is −92.8(3)^0). In the molecule **15A**, the tolyl substituent is significantly rotated relatively to the N(1)−P(1) bond (the P(1)−N(1)−S(1)−C(1) torsion angle is −68.6(3)^0).

In both molecules **15A** and **15B**, the tolyl substituent is deployed orthogonally to the N(1)−S(1) bond (the N(1)−S(1)−C(1)−C(2) torsion angle is −104.0(4)^0 and −84.4(4)^0 in the molecule **15A** and **15B**, respectively).

Conclusions

This study presents a novel and efficient synthetic approach to dialkyl N-alkoxy-N-R-sulfonylphosphoramidates. We have found that the reaction of N-alkoxy-N-(chloro)-R-sulfonamides **12**, **13** with trialkylphosphites is a novel synthetic pathway to dialkyl N-alkoxy-N-R-sulfonylphosphoramidates **14−19** by means of the nucleophilic substitution at the nitrogen atom accompanied by Michaelis-Arbuzov rearrangement.

The structural elucidation of dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoramidates and dialkyl N-methoxy-N-methanesulfonylphosphoramidates **14−19** was confirmed by ^{1}H, ^{13}C, ^{31}P NMR spectra, mass spectra, and by the single crystal X-ray diffraction study of dimethyl N-methoxy-N-(4-toluenesulfonyl)phosphoramidate **14** and dimethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate **15**. This study has demonstrated that the amide nitrogen atom has pyramidal configuration, the N−P and N−S bonds elongation and the N−O(Alk) bond shortening take place. It is supposed that these phenomena are caused by the weakening of the conjugation of the lone pair of N(1) nitrogen atom

with the phosphoryl and sulfonyl groups as well as by the possible actions of the $n_{O(Me)}\rightarrow\sigma^*_{N-P}$ and the $n_{O(Me)}\rightarrow\sigma^*_{N-S}$ anomeric effects. It was found that in the asymmetric part of the unit cell dimethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate **15** exists in the form of two independent molecules that differ in the degree of pyramidality of the nitrogen atom and the lengths of its bonds.

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ДІАЛКІЛ-*N*-АЛКОКСИ-*N*-(4-ТОЛУОЛСУЛЬФОНІЛ)ФОСФОРОАМІДАТИ: СИНТЕЗ І БУДОВА

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Досліджено взаємодію N-алкокси-N-хлоро-4-толуолсульфонамідів та N-метокси-N-(хлоро)метансульфонаміду з триалкілфосфітами, яка призводить до утворення діалкіл-N-алкокси-N-(4-толуолсульфоніл)фосфороамідатів та діалкіл-N-метокси-N-метансульфоніл-фосфороамідатів, відповідно. Синтезовані діалкіл-N-алкокси-N-(4-толуолсульфоніл-)фосфороамідати та діалкіл-N-алкокси-N-метансульфонілфосфороамідати ідентифіковані як продукти нуклеофільного заміщення при амідному атомі азоту. Структури цих сполук були підтверджені ^{1}H, ^{31}P, та ^{13}C ЯМР спектроскопією, мас-спектрометрією, та рентгеноструктурним дослідженням. Рентгеноструктурне дослідження диметил-*N*-метокси-*N*-(4-толуолсульфоніл)фосфороамідату та диметил-*N*-етокси-*N*-(4-толуол-сульфоніл)-фосфороамідату виявило пірамідальну конфігурацію в амідному атомі азоту разом із укороченням зв'язку N–O(Alk) та подовженням зв'язків N–P та N–S. В асиметричній частині елементарної комірки диметил-*N*-етокси-*N*-(4-толуолсульфоніл)фосфороамідат існує у вигляді двох незалежних молекул, які відрізняються ступенем пірамідальності атома азоту і довжиною його зв'язків.

Ключові слова: *N*-алкокси-*N*-(хлоро)сульфонаміди, триалкілфосфіти, діалкіл-*N*-алкокси-*N*-(4-толуолсульфоніл)фосфороамідати, діалкіл-*N*-метокси-*N*-метансульфонілфосфоро-амідати, будова, рентгенівське дифракційне дослідження монокристалів.

DIALKYL-*N*-ALKOXY-*N*-(4-TOLUENESULFONYL)PHOSPHORAMIDATES: SYNTHESIS AND STRUCTURE

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This study investigates the reaction between N-alkoxy-*N*-chloro-4-toluenesulfonamides and N-chloro-*N*-(methoxy)methanesulfonamide with trialkyl phosphites, resulting in the formation of dialkyl N-alkoxy-*N*-(4-toluenesulfonyl)phosphoroamidates and dialkyl N-methoxy-N-methanesulfonylphosphoroamidates, respectively. The resulting dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoramidates and N-alkoxy-N-methanesulfonylphosphoramidates are identified as products of nucleophilic substitution at the amide nitrogen atom. The structures of these compounds have been confirmed by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy, mass spectrometry, and an XRD study. The XRD study of dimethyl N-methoxy-N-(4-toluenesulfonyl)phosphoroamidate and dimethyl N-ethoxy-N-(4-toluenesulfonyl)-phosphoroamidate reveals a pyramidal configuration at the amide nitrogen atom, along with the shortening of the N−O(Alk) bond and the elongation of the N−P and N−S bonds. In the asymmetric part of the unit cell, dimethyl N-ethoxy-N-(4-toluenesulfonyl)phosphoramidate exists in the form of two independent molecules that differ in the degree of pyramidality of the nitrogen atom and the lengths of its bonds.

Keywords: N-alkoxy-N-(chloro)sulfonamides; trialkyl phosphites; dialkyl N-alkoxy-N-(4-toluenesulfonyl)phosphoramidates; dialkyl N-methoxy-N-methanesulfonylphosphoroamidates; structure; single crystal X-ray diffraction study.

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