ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 7, pp. 1258–1262. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © L.L. Tolstikova, A.V. Bel'skikh, B.A. Shainyan, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 7, pp. 1092–1096.

The Reaction of *N*-Sulfinyltrifluoromethanesulfonamide with Triethylphosphate and Triethylphosphite

L. L. Tolstikova, A. V. Bel'skikh, and B. A. Shainyan

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: bagrat@irioch.irk.ru

Received March 1, 2010

Abstract—The reaction of *N*-sulfinyltrifluoromethanesulfonamide CF_3SO_2NSO with triethylphosphate and triethylphosphite results in *N*-(trifluoromethanesulfonyl)triethoxyphosphazene $CF_3SO_2N{=}P(OEt)_3$, which upon heating is converted into the diethyl ester of *N*-trifluoromethylsulfonylamidophosphoric acid $CF_3SO_2NHP(O)\cdot(OEt)_2$. The latter was also prepared by alcoholysis of *N*-(trifluoromethanesulfonyl)trichlorophosphazene or of potassium salt of dichloroanhydride of *N*-trifluoromethylsulfonylamidophosphoric acid, or by the reaction of the salt CF_3SO_2NHNa with diethylchlorophosphate. Compound $CF_3SO_2N{=}P(OEt)_3$ does not rearrange into the isomeric diethyl ester of *N*-ethyl-*N*-(trifluoromethylsulfonyl)amidophosphoric acid $CF_3SO_2N(Et)P(O)(OEt)_2$, contrary to the statement in the literature on the easy rearrangement of phosphazenes $R_FSO_2N{=}P(OEt)_3$ into amidates $R_FSO_2N(Et)P(O)(OEt)_2$.

DOI: 10.1134/S1070363210070066

The reaction of *N*-sulfinylsulfonamides RSO_2NSO (R = Me, p-Tol) with triphenylphosphine, triphenylphosphine oxide, triphenylphosphine sulfide and triethylphosphite affords phosphazenes $RSO_2N{=}PR'_3$ (R' = Ph, EtO) in moderate to good yields [1]. The reaction of polyfluoroalkane-sulfonylazides $R_FSO_2N_3$ and *N,N*-dichloropolyfluoroalkanesulfonamides $R_FSO_2NCl_2$ with trialkyl-(aryl)phosphines and triethylphosphite proceeds with the formation of similar polyfluorinated products $R_FSO_2N{=}PR'_3$ [2–5]. The difference is that in the reaction of $R_FSO_2N_3$ with triethylphosphite the isolated product was $R_FSO_2N(Et)\cdot P(O)(OEt)_2$, which, as the authors believe [3], is the product of rearrangement of the initially formed phosphazene $R_FSO_2N{=}P(OEt)_3$. The reaction of *N*-sulfinylsulfonamides RSO_2NSO with trialkylphosphates is not described in the literature, except for the reaction of *p*-$TolSO_2NSO$ with *O,O,O*-triethylphosphothioate $(EtO)_3P{=}S$ leading to the target product in a very low yield [1].

The analysis of the literature has shown that trialkoxyphosphazenes are prepared either by the exhaustive alcoholysis of trichlorophosphazenes $RSO_2N{=}PCl_3$ [6, 7] or by the reaction of azides of sulfonic acids with triethylphosphite [3]. There are only two examples of the synthesis of trialkoxyphosphazenes from *N*-sulfinylsulfonamides: *p*-$TolSO_2N{=}P(OEt)_3$ by the reaction with $(EtO)_3P{=}S$ in 10% yield, and $MeSO_2N{=}P(OEt)_3$ by the reaction with $(EtO)_3P$ in 51% yield accompanied by the substantial oxidation of the starting phosphite [1]. Reactions of *N*-sulfinylsulfonamides with trialkylphosphates have not been studied. The literature data on the fluorinated phosphazenes $R_FSO_2N{=}P(OR)_3$ are confined to the single early work of Yagupolskii et al. on the formation of $CF_3SO_2N{=}P(OC_6H_{13})_3$ by the reaction of alcoholysis of $CF_3SO_2N{=}PCl_3$ with sodium hexanolate in benzene [8]. The formation of one more similar structure, $H(CF_2)_2SO_2N{=}P(OEt)_3$, was only assumed by Zhu [3]. In connection with this and in continuation of our studies in the field [9], in the present paper we have investigated the reaction of *N*-sulfinyltrifluoromethanesulfonamide with triethylphosphate and triethylphosphite with the formation of *N*-(trifluoromethanesulfonyl)triethoxyphosphazene as well as some other approaches to this product and its further transformations.

The reaction of *N*-sulfinyltrifluoromethanesulfonamide CF_3SO_2NSO (**I**) with triethylphosphate in benzene results in the formation of *N*-(trifluoro-

methanesulfonyl)triethoxyphosphazene $CF_3SO_2N{=}P(OEt)_3$ (**II**) in 96% yield.

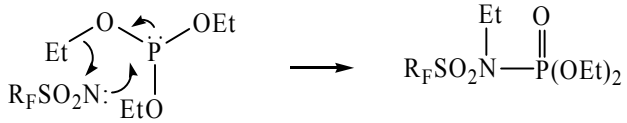
$$\underset{\textbf{I}}{CF_3SO_2N{=}S{=}O} + O{=}P(OEt)_3 \xrightarrow[-SO_2]{} \underset{\textbf{II}}{CF_3SO_2N{=}P(OEt)_3}$$

$$\not\rightarrow \quad \underset{\textbf{III}}{CF_3SO_2N(Et)P(O)(OEt)_2} \qquad (1)$$

The structure of product **II** is proved by the presence in the ^1H and ^{13}C NMR spectra of the signals of the ethyl group split on phosphorus atom and shifted downfield relative to the signals of triethylphosphate, as well as a quartet of the CF_3 group in the ^{13}C NMR spectrum. The signal in the ^{31}P NMR spectrum is also slightly shifted downfield with respect to triethylphosphate.

The peak of molecular ion in the mass spectrum of compound **II** is absent. The electrospray ionization mass spectrum taken in solution shows a hydrolytic cleavage to triethylphosphate and triflamide with the proton transfer from $CF_3SO_2NH_2$ to $(EtO)_3P{=}O$ and fragmentation of the formed ion *m/z* 183 $[(EtO)_3POH]^+$ by successive expulsion of three molecules of ethylene. The absence of the peaks of ions *m/z* 69 $[CF_3]^+$ and 133 $[CF_3SO_2]^+$ typical for triflate derivatives proves the suggested scheme of fragmentation.

Contrary to the statement on the easy rearrangement of compound $H(CF_2)_2SO_2N{=}P(OEt)_3$, a close analog of **II**, into the isomeric product $H(CF_2)_2SO_2N(Et)P(O)(OEt)_2$ [3], we did not observe such a rearrangement **II** → **III** under the conditions of reaction (1) (6 h, 80°C) in the ^1H NMR spectra. Note that [3] does not contain any indications on the initial formation of phosphazene $H(CF_2)_2SO_2N{=}P(OEt)_3$, which further, as the author believes, suffers rearrangement into $H(CF_2)_2SO_2N(Et)P(O)(OEt)_2$. The final product was isolated in 40% yield by vacuum distillation at high temperature {its boiling point is not given in [3], but for the structurally close analogs it is about ~200°C (1 mm Hg) [10]}. Taking into account our data, as well as the fact that no rearrangements of the products of the reaction of azides of sulfonic acids with trialkylphosphites $ArSO_2N{=}P(OR)_3$ were reported in the literature [6, 7], the formation of diethyl ester of *N*-ethyl-*N*-(fluoroalkyl)amidophosphoric acid in [3], presumably, is the result of the attack of sulfonylnitrene RSO_2N: on the O–Et bond with its rupture and formation of the N–P bond:

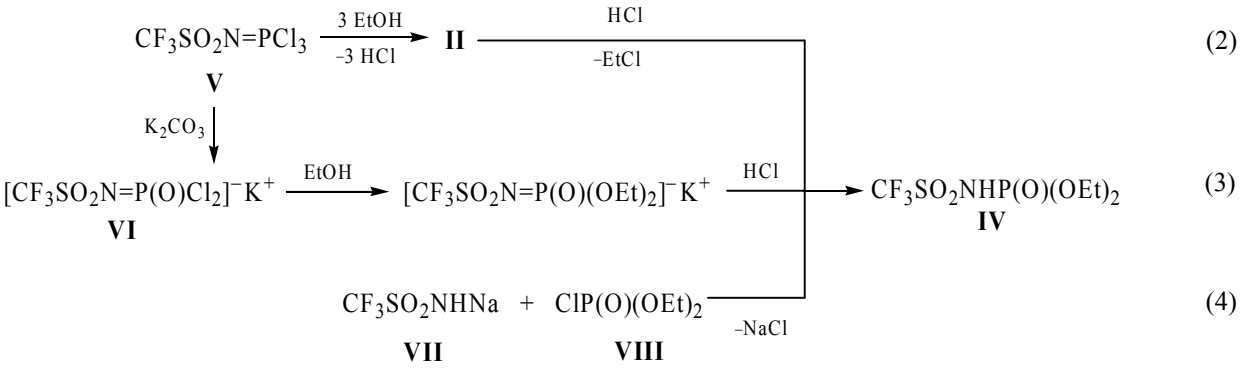


In the literature the rearrangement of the *N*-phenyl analog of compound **II**, *N*-phenylphosphorimidate $PhN{=}P(OEt)_3$ into *N*-ethyl-*N*-phenylphosphoramidate $PhN(Et)P(O)(OEt)_2$ is described, occurring in parallel with the minor side process of elimination of ethylene leading to *N*-phenylphosphoramidate $PhNHP(O)(OEt)_2$ [11]. Both processes are slow but are sharply accelerated in the presence of electrophiles in the reaction mixture. Since the mechanism of the rearrangement [11] includes the initial nucleophilic attack of the imine nitrogen atom on the electrophilic center (α-carbon atom) of the second molecule of phosphorimidate, the absence of such rearrangement in our case is in agreement with extremely low nucleophilicity of the nitrogen atom connected in molecule **II** with trifluoromethanesulfonyl group.

The fractional vacuum distillation of phosphazene **II** at ~100°C (1 mm Hg) leads to the formation of its mixture with a new product, the ^1H NMR spectrum of which contains the signals of the methylene and methyl groups with splitting similar to that in product **II**, but shifted by 0.2 and 0.07 ppm downfield, and the signal of NH protons; the IR spectrum also contains the band of stretching vibrations ν_{NH} at 3200–3300 cm^{-1}. These characteristics correspond to those of the diethyl ester of *N*-trifluoromethylsulfonylamidophosphoric acid $CF_3SO_2NHP(O)(OEt)_2$ (**IV**) prepared in [10] by the reaction of triflamide with diethylphosphite $(EtO)_2P(O)H$ in the presence of KOH and the phase transfer catalyst. We also synthesized compound (**IV**) independently by different methods: by the reaction of *N*-(trifluoromethanesulfonyl)trichlorophosphazene (**V**) [12] with excess ethanol [Eq. (2)], by alcoholysis of potassium salt of dichloroanhydride of trifluoromethanesulfonamidophosphoric acid (**VI**) [Eq. (3)], and by the reaction of sodium salt of triflamide **VII** with diethylchlorophosphate **VIII** [Eq. (4)].

The NMR spectra of the samples of compound **IV** obtained by reactions (2)–(4) coincide with each other and with the literature data [10].

The formation of *N*-(arylsulfonyl)trialkoxyphosphazenes by the action of excess alcohol on *N*-(arylsulfonyl)trichlorophosphazenes and their thermally or acid-catalyzed rearrangement into dialkyl esters of arylsulfonamidophosphoric acids are well known



(2)

(3)

(4)

[6, 12], as well as the formation and alcoholysis of the salts of dichloroanhydrides of arensulfonamidophosphoric acids [13].

It should be noted that compound **IV** is readily hydrolized, so, triflamide and derivatives of phosphoric acid are formed as side products in reactions (2)–(4), as follows from the presence of two signals in the ^{19}F NMR spectrum and several signals in the ^{31}P NMR spectrum.

N-Sulfinylytrifluoromethanesulfonamide **I** also actively reacts with triethylphosphite $P(OEt)_3$. The data of the NMR spectroscopy of the reaction mixture after removal of the solvent show that it contains products **II** and **IV**, the latter being predominant. Taking into account that the reaction proceeds exothermally with vigorous evolution of gaseous products, the following scheme of formation of **IV** can be assumed.

$$\mathbf{I} + P(OEt)_3 \xrightarrow[-[SO]]{} \mathbf{II}$$

$$\xrightarrow[-C_2H_4]{} \underset{\mathbf{IV}}{CF_3SO_2NHP(O)(OEt)_2} \quad (5)$$

Product **II** is also formed by the reaction of triflamide $CF_3SO_2NH_2$ (**IX**) with dichloro(triethoxy)-phosphorane $Cl_2P(OEt)_3$ (**X**) prepared in situ from triethylphosphite and PCl_5, although the reaction is followed by the formation of substantial amount of unidentified product, characterized by a complex multiplet of a CH_2 group at 4.1 ppm, which does not coincide with the signal of the CH_2 group in **IV**. We failed to separate the products of the reaction.

$$\underset{\mathbf{IX}}{CF_3SO_2NH_2} + \underset{\mathbf{X}}{Cl_2P(OEt)_3} \xrightarrow[-2HCl]{} \mathbf{II} \quad (6)$$

Therefore, the reaction of *N*-sulfinyltrifluoromethanesulfonamide with triethylphosphate and triethylphosphite proceeds with the formation of *N*-(trifluoromethanesulfonyl)triethoxyphosphazene. Upon heating, the latter eliminates ethylene to give diethyl ester of *N*-trifluoromethylsulfonylamido-phosphoric acid $CF_3SO_2NHP(O)(OEt)_2$, which is readily hydrolyzed to triflamide and diethylphosphate; no formation of diethyl ester of *N*-ethyl-*N*-(trifluoromethanesulfonyl)amidophosphoric acid, $CF_3SO_2N(Et)\cdot P(O)(OEt)_2$, the product of rearrangement earlier suggested in the literature is observed.

EXPERIMENTAL

IR spectra were recorded on a Bruker Vertex 70 instrument in thin film or in KBr pellets. NMR spectra were taken on a Bruker DPX-400 spectrometer at working frequencies 400 (^1H), 100 (^{13}C), 376 (^{19}F), 162 (^{31}P) MHz in $CDCl_3$, using the signals of the residual protons of the solvent (for ^1H), or carbon atoms (for ^{13}C) as an internal standard, chemical shifts are given relative to TMS (^1H, ^{13}C), CCl_3F (^{19}F), H_3PO_4 (^{31}P). Electron impact mass spectra (70 eV) were obtained in the direct injection regime on a GCMS-QP5050A Shimadzu instrument with quadruple mass analyzer. High resolution spectrum of compound **II** was obtained on a Micromass Q-TOF_{micro} mass spectrometer in the ESI MS regime.

N-(Trifluoromethanesulfonyl)trichlorophosphazene (**V**) was prepared as described in [14], its spectral characteristics were described by us earlier [9]. Diethylchlorophosphate **X** was obtained according to [15]. ^1H NMR spectrum, δ, ppm: 4.24 m (4H, CH_2), 1.38 m (6H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 65.73 d (CH_2, J_{CP} 6.6 Hz), 15.59 d (CH_3, J_{CP} 8.1 Hz). ^{31}P NMR, δ_P, ppm: 4.4.

Trifluoro-*N*-(triethoxy-λ^5-phosphoranylidene)-methanesulfonamide (II). *a*. To the solution of 1.25 g (6.4 mmol) of compound **I** in 16 ml of benzene the solution of 1.17 g (6.4 mmol) of triethylphosphate in

2 ml of benzene was added in an argon atmosphere at room temperature while vigorous stirring. The mixture was stirred for 2 h at room temperature and 8 h at 80°C, cooled, evaporated to give 1.92 g (96%) of crude **II** as a brown liquid with bp 72–80°C (1 mm Hg). The ^{31}P NMR spectrum of the product distilled after one month storage at room temperature showed the presence of ~2% of compound **IV**. IR spectrum, ν, cm^{-1}: 2990, 1394, 1386, 1231, 1192, 1157, 1032, 983, 825, 804, 612, 497. ^{1}H NMR spectrum, δ, ppm: 4.05 d.q (2H, CH_2, J_{PH} 7.6, J_{HH} 7.1 Hz), 1.28 d.t (3H, CH_3, J_{PH} 0.9, J_{HH} 7.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 119.64 q (CF_3, J_{CF} 319.3 Hz), 64.04 d (CH_2, J_{CP} 5.6 Hz), 15.88 d (CH_3, J_{CP} 6.4 Hz). ^{19}F NMR spectrum, δ_F, ppm: –79.61. ^{31}P NMR spectrum, δ_P, ppm: –1.17. HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_7H_{16}F_3NO_5PS$: 314.0439; found 314.0428. Found, %: C 27.55; H 5.31; N 3.73; P 8.92; S 9.36. $C_7H_{15}F_3NO_5PS$. Calculated, %: C 26.84; H 4.83; N 4.47; P 9.89; S 10.24.

b. To the solution of 0.62 g (3.2 mmol) of compound **I** in 4 ml of benzene the solution of 0.53 g (3.2 mmol) of triethylphosphite in 1 ml of benzene was added at vigorous stirring; the reaction mixture slightly self-heated. The mixture was stirred 4 h at room temperature and evaporated to obtain 1.00 g (100%) of light-yellow liquid containing, according to ^{1}H NMR spectrum, the mixture of products **II** and **IV** in the 1:3 ratio.

c. To the solution of 0.42 g (2 mmol) PCl_5 in 3 ml of CCl_4 0.33 g (2 mmol) of triethylphosphite was added at stirring. The reaction mixture was stirred for 10 min at room temperature, 0.30 g (2 mmol) of triflamide was added, the mixture was stirred for 2 h at room temperature and 8 h at reflux. The solvent was removed in a vacuum to obtain 0.5 g (79%) of the mixture of product **II** and an unidentified product in the ratio of 1:2 as a mixture of crystals and liquid.

Diethyl ester of *N*-trifluoromethylsulfonylamidophosphoric acid (IV). *a*. To 0.57 g (2 mmol) of *N*-(trifluoromethanesulfonyl)trichlorophosphazene (**V**) 2 ml of ethanol was added at vigorous stirring at room temperature; the reaction mixture self-heated to boiling. The mixture was blown with argon, stirred at room temperature for a week. After removal of solvent and vacuum distillation 0.25 g (40%) of product **IV** with bp 126°C (1 mm Hg) was obtained. IR spectrum, ν, cm^{-1}: 3363, 2992, 2945, 1399, 1201, 1144, 1037, 939, 613, 497. ^{1}H NMR spectrum, δ, ppm: 6.62 s (NH), 4.26 d.q (2H, CH_2, J_{PH} 15.3, J_{HH} 7.2 Hz), 1.35 d.t (3H, CH_3, J_{PH} 0.9, J_{HH} 7.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 119.54 q (CF_3, J_{CF} 317.2 Hz), 67.04 d (OCH_2, J_{CP} 7.2 Hz), 15.60 d (CH_3, J_{CP} 6.0 Hz). ^{19}F NMR spectrum, δ_F, ppm: –79.23. ^{31}P NMR spectrum, δ_P, ppm: –2.23. ESI MS, *m/z* (I_{rel}, %) ion: 286 $[M + H]^+$ (2), 183 (100) $[(EtO)_3POH]^+$, 155 (76) $[(EtO)_2P(OH)_2]^+$, 127 (30) $[EtOP(OH)_3]^+$, 99 (40) $[P(OH)_4]^+$, 81 (10) $[H_2PO_3]^+$, 45 (6) $[EtO]^+$. The presence of $[M + H]^+$ ion in the mass spectrum of compound **IV**, formed presumably as a result of internal ionization was also mentioned in [10].

b. To the solution of 1.08 g (3.79 mmol) of compound **V** in 7 ml of hexane the excess of potassium carbonate (1.00 g, 6.4 mmol) was added at room temperature at vigorous stirring; the mixture slightly self-heated with evolution of CO_2. The mixture was stirred for 4 h at room temperature, 2 ml of ethanol was added; substantial self-heating and evolution of HCl was observed. The mixture was stirred for 20 min at room temperature, treated with 10% aqueous HCl, the hexane layer was separated, the water layer was extracted with chloroform (3×2 ml); the combined organic solutions were dried over $CaCl_2$ and the solvent was removed in a vacuum to obtain 0.94 g of the mixture of product **IV** and the products of its hydrolysis.

c. To the solution of 0.29 g (1.7 mmol) of diethylchlorophosphate **X** in 5 ml of THF 0.29 g (1.7 mmol) of sodium salt of triflamide **VII** was added at 2°C in the argon atmosphere at vigorous stirring. The mixture was heated to room temperature, the precipitate was filtered off, washed with THF, the filtrate was evaporated to obtain 0.23 g of the mixture of **IV** and the products of its hydrolysis.

ACKNOWLEDGMENTS

This work was performed with the financial support from the Russian Foundation for Basic Research (grant no. 10-03-00110). The authors are grateful to Ines Starke (Potsdam University) for taking high resolution and ESI MS of compound **II**.

REFERENCES

1. Senning, A., *Acta Chem. Scand*., 1965, vol., 19, no. 7, p. 1755.
2. Zhu, S.-Z., *Tetrahedron Letters*, 1992, vol. 33, no. 43, p. 6503.
3. Zhu, S.-Z., *J. Chem. Soc. Perkin Trans 1*, 1994, p. 2077.

4. Zhu, S.-Z., Xu, B., Qin, C., and Xu, G., *Inorg. Chem*., 1997, vol. 36, no. 21, p. 4909.
5. Zhu, S.-Z. and He, P., *Curr. Org. Chem*., 2004, vol. 8, no. 2, p. 97.
6. Derkach, G.I., Zhmurova, I.N., Kirsanov, A.V., Shevchenko, V.I., and Shtepanek, A.S., *Fosfazo-soedineniya* (Phospfaza Compounds), Kiev: Naukova Dumka, 1965.
7. Kirsanov, A.V. and Shevchenko, V.I., *Zh. Obshch. Khim*., 1954, vol. 24, no. 3, p. 474.
8. Radchenko, O.A., Nazaretyan, V.P., and Yagupol'-ski, L.M., *Zh. Obshch. Khim*., 1976, vol. 46, no. 3, p. 565.
9. Tolstikova, L.L., Bel'skikh, A.V., and Shainyan, B.A., *Zh. Obshch. Khim.,* 2009, vol. 79, no. 8, p. 1394.
10. Zhu, S., Zhang, J., and Xu, B., *J. Fluor. Chem*., 1996, vol. 78, p. 183.
11. Challis, B.C., Challis, J.A., and Iley, J.N., *J. Chem. Soc., Perkin Trans 2*, 1978, no. 8, p. 813.
12. Kirsanov, A.V. and Shevchenko, V.I., *Zh. Obshch. Khim*., 1956, vol. 26, no. 2, p. 504.
13. Levchenko, E.S. and Kirsanov, A.V., *Zh. Obshch. Khim*., 1957, vol. 27, no. 11, p. 3078.
14. Roesky, H.W., Holtschneider, G., and Giere, H.H., *Z. Naturforsch. B*, 1970, vol. 25, no. 3, p. 252.
15. Kormachev, V.V. and Fedoseev, M.S., *Preparativnaya khimiya fosfora* (Preparative Chemistry of Phosphorus), Perm': Ural. Otd. Ross. Akad. Nauk, 1992.