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Reaction of *N*-Sulfinyltrifluoromethanesulfonamide with Triphenylphosphine and Triphenylphosphine Oxide

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Abstract—The reaction of *N*-sulfinyltrifluoromethanesulfonamide with triphenylphosphine and triphenylphosphine oxide or of trifluoromethanesulfonamide with dichloro(triphenyl)phosphorane leads to trifluoro-*N*-(triphenyl-λ^5-phosphanylidene)methanesulfonamide, which is hydrolyzed to trifluoromethanesulfonamide and triphenylphosphine oxide via the intermediate trifluoro-*N*-[hydroxy(triphenyl)phosphoranyl]methanesulfonamide.

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Reactions of *N*-sulfinylsulfonamides RSO_2NSO (R = Me, *p*-Tol) with triphenylphosphine, -oxide, -sulfide, -phenylimine afford phosphazenes $RSO_2N{=}PPh_3$ in moderate to good yields [1, 2].

$$RSO_2N{=}S{=}O + Ph_3P{=}X \rightarrow RSO_2N{=}PPh_3 + XSO, \quad (1)$$
$$X = LP, O, S, NPh.$$

Mixed triarylphosphazosulfonylaryls $ArSO_2N{=}PAr'_2Ar''$, $ArSO_2N{=}PAr'Ar''Ar'''$ are prepared by the reaction of dichloro(triarylphosphoranes with arenesulfonamides or *N,N*-dichlorosulfonamides [Eqs. (1), (2)] and by oxidative imination of triarylphosphines with *N,N*-dichlorosulfonamides [Eq. (4)], sodium salts of *N*-chlorosulfonamides [Eq. (5)] or arenesulfonylazides [Eq. (6)] [3].

$$ArSO_2NH_2 + Cl_2PR_3 \xrightarrow{-HCl} ArSO_2N{=}PR_3 \quad (2)$$

$$ArSO_2NCl_2 + Cl_2PR_3 \xrightarrow{-Cl_2} ArSO_2N{=}PR_3 \quad (3)$$

$$ArSO_2NCl_2 + PR_3 \xrightarrow{-Cl_2} ArSO_2N{=}PR_3 \quad (4)$$

$$ArSO_2NNaCl + PR_3 \xrightarrow{-NaCl} ArSO_2N{=}PR_3 \quad (5)$$

$$ArSO_2N_3 + PR_3 \xrightarrow{-N_2} ArSO_2N{=}PR_3 \quad (6)$$

As noted in [3], reaction (6) is the least practical since it is followed by the formation of difficultly separable side products, although the triphenylphosphine reacts smoothly with polyfluorinated sulfonylazide under mild conditions to form the corresponding phosphazene in 66% yield, which is readily hydrolyzed in air [4].

$$R_FSO_2N_3 + Ph_3P \xrightarrow[-N_2]{} R_FSO_2N{=}PPh_3$$
$$\xrightarrow{H_2O} R_FSO_2NH_2 + Ph_3PO, \quad (7)$$
$$R_F = H(CF_2)O(CF_2)_2.$$

The oxidative imination of triphenylphosphine with *N,N*-dichloro(polyfluoroalkane)sulfonamides also proceeds in high yields (>70%) [5].

$$PPh_3 + R_FSO_2NCl_2 \xrightarrow[C_6H_6\ (Et_2O)]{Zn} R_FSO_2N{=}PPh_3, \quad (8)$$
$$R_F = I(CF_2)_2O(CF_2)_2;\ H(CF_2)_2O(CF_2)_2.$$

The known methods of synthesis of fluorinated phosphazenes $R_FSO_2N{=}PPh_3$ are limited to the aforementioned reactions (7), (8) [4, 5]. In connection with this and in continuation of our studies of the phosphorus-containing derivatives of triflamide [6] we have studied the reaction of *N*-sulfinyltrifluoromethanesulfonamide CF_3SO_2NSO (**I**) with triphenylphosphine and triphenylphosphine oxide.

The reaction of compound **I** with triphenylphosphine in benzene at room temperature results in the formation of trifluoro-*N*-(triphenyl-λ^5-phosphanylidene)methanesulfonamide $CF_3SO_2N{=}PPh_3$ (**II**) in nearly quantitative yield.

$$CF_3SO_2N{=}S{=}O + PPh_3 \rightarrow CF_3SO_2N{=}PPh_3 + SO. \quad (9)$$
I **II**

The reaction of compound **I** with triphenylphosphine oxide in benzene also results in product **II**, although the reaction proceeds much more slowly. According to the ^{31}P NMR spectroscopy data, the conversion of triphenylphosphine oxide after 2 h at 80°C was as low as 7%.

$$CF_3SO_2N{=}S{=}O + O{=}PPh_3 \xrightarrow{-SO_2} CF_3SO_2N{=}PPh_3. \quad (10)$$
I **II**

We believe that the reasons for a substantially lower activity of triphenylphosphine oxide as compared to triphenylphosphine in the reaction with compound **I** are similar to those in the reaction of oxidation of sulfides into sulfoxides and of sulfoxides into sulfones as we have considered earlier [7]. Reaction (9) consists in a nucleophilic attack of the lone pair of the phosphorus atom in Ph_3P on the electron-deficient nitrogen atom in $TfN^+–S^-{=}O$; similar to that the oxidation of sulfides is a nucleophilic attack of the lone pair (LP) of the sulfur atom on the oxygen atom of the oxidant. On the contrary, reaction (10) is a nucleophilic attack of the nitrogen LP in compound **I** on the electrophilic phosphorus atom of $Ph_3P{=}O$, like the oxidation of sulfoxides consists in a nucleophilic attack of the oxidant on the sulfur atom in R_2SO. Extremely low basicity of nitrogen atom in compound **I** results in the low reactivity of triphenylphosphine oxide.

Product **II** was independently synthesized by the reaction of *N*-trifluoromethanesulfonamide $CF_3SO_2{\cdot}NH_2$ **III** with dichloro(triphenyl)phosphorane prepared *in situ* by the chlorination of triphenylphosphine with phosphorus pentachloride.

$$CF_3SO_2NH_2 + PPh_3Cl_2 \xrightarrow{-HCl} CF_3SO_2N{=}PPh_3. \quad (11)$$
III **II**

The structure of product **II** was proved by the presence of doublet signals of the C_o, C_m, C_p carbon atoms split by coupling with the phosphorus atom in the ^{13}C NMR spectrum and a quartet of doublets of the CF_3 group. A specific difference of the ^{13}C NMR spectra of compound **II** and triphenylphosphine oxide is that in Ph_3PO the C_i atom gives the most downfield signal (133 ppm), while in product **II** it is the most upfield signal of the phenyl group (126 ppm). In the ^1H NMR spectrum of product **II** the signals of the H_o, H_m, H_p protons are separated, in contrast to the PPh_3 spectrum where they all resonate as a singlet at 7.36 ppm. The ^1H NMR spectrum of product **II** is qualitatively similar to that of triphenylphosphine oxide but the signals are shifted downfield by 0.10 (H_o, H_m) and 0.14 ppm (H_p) relative to the corresponding signals of $Ph_3P{=}O$. The signal in the ^{31}P NMR spectrum is also shifted downfield relative to triphenylphosphine by 26 ppm.

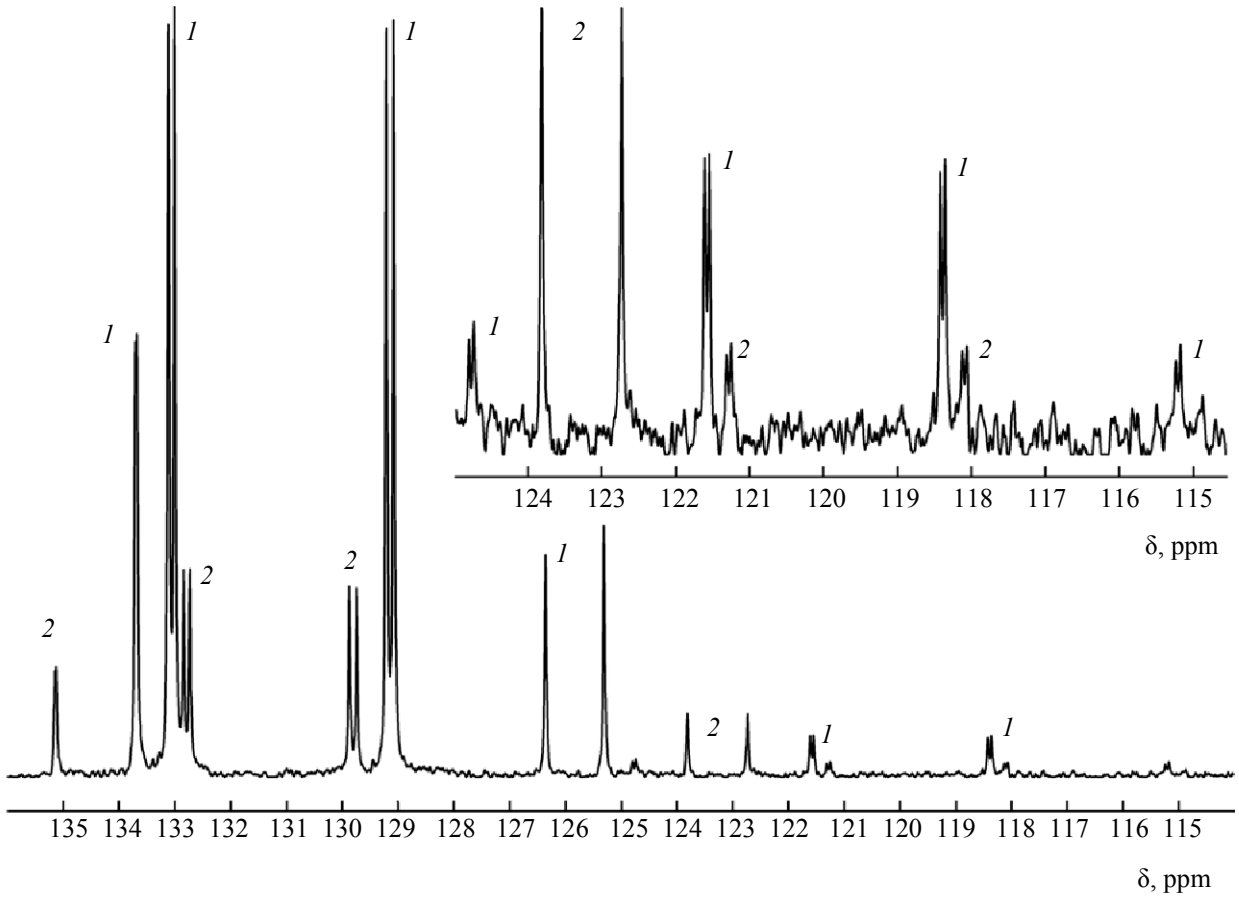
The molecular ion peak is lacking in the mass spectrum of compound **II**. The main fragment ion $[Ph_3PNSO_2]^+$ with *m*/*z* 340 corresponds to elimination of CF_3 from the molecular ion. Similar fragmentation is characteristic of trifluoro-*N*-(trichloro-λ^5-phosphanylidene)methanesulfonamide $CF_3SO_2N{=}PCl_3$ [8].

After staying in the solution, new signals of a minor product appear in the NMR spectra of product **II**, as shown in the figure by the example of the ^{13}C NMR spectrum.

Complete resemblance of the ^{13}C NMR spectra is indicative of the presence of the same groups in the formed product as in compound **II**, that is, Ph_3P and NSO_2CF_3. In the ^{31}P NMR spectrum, two signals at 52 (minor) and 21 ppm are observed, and the J_{CP} constants in the ^{31}P NMR spectrum measured for these signals from ^{13}C satellites coincide with the J_{CP} constants in the ^{13}C NMR spectrum for the C_i carbon signals in the minor product and in compound **II**, respectively. In the ^{19}F NMR spectrum two signals are present at –78.45 ppm (minor) and –79.34 ppm (major). In the ^1H NMR spectrum, apart from the signals of aromatic protons, a downfield signal appears at 11.5 ppm. The similarity of the ^{13}C NMR spectra and substantial difference of the ^{31}P chemical shifts, as well as almost complete coincidence of the minor ^{19}F signal with that of triflamide (–78.52 ppm) allow to conclude that the minor product is the product of hydration of trifluoro-*N*-(triphenyl-λ^5-phosphanylidene)methanesulfonamide (**II**), trifluoro-*N*-[hydroxy(triphenyl)phosphoranyl]-methanesulfonamide (**IV**), which is the intermediate product of hydrolysis before the formation of triflamide and triphenylphosphine oxide.

$$CF_3SO_2N{=}PPh_3 \xrightarrow{H_2O} CF_3SO_2NH{-}PPh_3(OH) \rightarrow CF_3SO_2NH_2 + O{=}PPh_3. \quad (12)$$
II **IV** **III**

Therefore, the reaction of *N*-sulfinyltrifluoromethanesulfonamide with triphenylphosphine and triphenylphosphine oxide, as well as the reaction of trifluoromethanesulfonamide with dichloro(triphenyl)-



^{13}C NMR spectrum of the partly hydrolyzed compound **II**. (*1*) signals of trifluoro-*N*-(triphenyl-λ^5-phosphanylidene)-methanesulfonamide (**II**) and (*2*) signals of trifluoro-*N*-[hydroxy(triphenyl)phosphoranyl]methanesulfonamide (**IV**).

phosphorane leads to trifluoro-*N*-(triphenyl-λ^5-phosphoranylidene)methanesulfonamide. The latter is easily hydrolyzed in the air or upon staying in the solution to trifluoromethanesulfonamide and triphenylphosphine oxide via the intermediate formation of the product of hydration, trifluoro-*N*-[hydroxy(triphenyl)phosphoranyl]methanesulfonamide.

EXPERIMENTAL

IR spectra were registered on a Bruker Vertex 70 spectrophotometer in KBr pellets. ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR spectra were recorded on a Bruker DPX 400 spectrometer at working frequencies of 400 (^{1}H), 100 (^{13}C), 162 (^{31}P), 376 MHz (^{19}F) in $CDCl_3$, chemical shifts are given relative to TMS (^{1}H, ^{13}C), H_3PO_4 (^{31}P) and CCl_3F (^{19}F). Electron impact mass spectrum (70 eV) was obtained on a GCMS-QP5050A Shimadzu chromatomass spectrometer (quadruple mass analyzer), capillary column SPB-5mS (60 m, 0.25 mm) in the temperature programming mode from 70 to 250°C with the rate of 10°/min, gas-carrier helium. The temperature of injector and ionic source 250°C.

Reaction of *N*-trifluoromethanesulfonamide with dichlorotriphenylphosphorane. To a solution of 0.42 g of phosphorus pentachloride in 4 ml of CCl_4 0.40 g of triphenylphosphine was added at stirring. The reaction mixture was refluxed with stirring for 20 min, then 0.30 g of trifluoromethanesulfonamide was added and stirred for 2 h at room temperature. The solvent was removed in a vacuum. The yield of trifluoro-*N*-(triphenyl-λ^5-phosphanylidene)methane-sulfonamide (**II**) 0.82 g (100%), mp 124–126°C. IR spectrum, ν, cm^{-1}: 3059, 1589, 1485, 1439, 1318, 1251, 1210, 1111, 1096, 997, 794, 729, 691, 612, 534, 501. ^{1}H NMR, δ, ppm: 7.56 m (6H, H_o), 7.67 m (3H, H_p), 7.77 m (6H, H_m). ^{13}C NMR, δ_C, ppm: 120.07 q. d (CF_3SO_2, J_{CF} 320.7, 6.2 Hz), 125.92 d (C_i, J 105.7 Hz), 129.23 d (C_m, J 13.4 Hz), 133.15 d (C_o, J 11.2 Hz), 133.78 d (C_p, J 2.5 Hz). ^{31}P NMR, δ_P, ppm: 21.40. ^{19}F NMR, δ_F, ppm: –79.34. Mass spectrum, *m*/*z* (ion, I_{rel}, %): 340

($Ph_3PNSO_2^+$, 100), 201 (Ph_2PO^+, 38), 122 ($PhPN^+$, 38), 77 (Ph^+, 53), 69 (CF_3^+, 11), 51 (CHF_2^+, 38), 46 (SN^+, 12). Found, %: C 55.44; H 3.68; F 13.57; N 3.42; P 7.56; S 8.06. $C_{19}H_{15}F_3NO_2PS$. Calculated, %: C 55.75; H 3.69; F 13.92; N 3.42; P 7.57; S 7.83.

Trifluoro-*N*-[hydroxy(triphenyl)phosphoranyl]-methanesulfonamide (IV). ^{13}C NMR, δ_C, ppm: 119.77 q. d (CF_3SO_2, J_{CF} 320.8, 6.3 Hz), 123.36 d (C_i, J 108.8 Hz), 129.89 d (C_m, J 13.4 Hz), 132.88 d (C_o, J 11.6 Hz), 135.23 d (C_p, J 2.3 Hz). ^{31}P NMR, δ_P, ppm: 52.42. ^{19}F NMR, δ_F, ppm: –78.45.

Reaction of *N*-sulfinyltrifluoromethanesulfonamide with triphenylphosphine. To a solution of 0.39 g of *N*-sulfinyltrifluoromethanesulfonamide in 5 ml of benzene in argon atmosphere at room temperature 0.52 g of triphenylphosphine in 5 ml of benzene was added with vigorous stirring; the mixture slightly self-heated and turned yellow. The reaction mixture was stirred for 16 h at room temperature, the solvent was removed in a vacuum to obtain 0.82 g (100%) of product **II** as cream color crystals.

Reaction of *N*-sulfinyltrifluoromethanesulfonamide with triphenylphosphine oxide. To the solution of 0.24 g of *N*-sulfinyltrifluoromethanesulfonamide in 5 ml of benzene in argon atmosphere at room temperature 0.33 g of triphenylphosphine oxide was added with vigorous stirring. The mixture was stirred at 80°C for 2 h and evaporated. The residue (0.50 g), from the data of ^1H, ^{13}C, ^{31}P NMR spectra, was the mixture of triphenylphosphine oxide and product **II** in the ratio of 13:1.

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