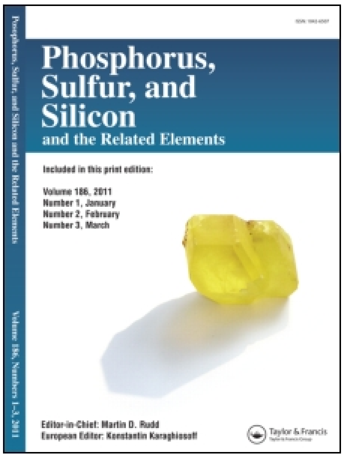

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SYNTHESIS OF SULFAMOYL AZIDE AND REACTION WITH TRISUBSTITUTED PHOSPHINES

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A new synthetic route to (trisubstitutedphosphoranylidene)sulfamides via the reaction of sulfamoyl azide with trisubstituted phosphines is described.

Key words: Sulfamoyl azide, trisubstituted phosphine, (trisubstitutedphosphoranylidene)sulfamides.

We reported earlier the first synthesis of organophosphorus ester chlorides of the type $(RO)_3P{=}NSO_2Cl$, the chlorosulfonylimino(trialkoxy or triphenoxy)phosphoranes,[1] ((trialkoxy or triphenoxyphosphoranylidene)sulfamoyl chlorides) from the reaction of chlorosulfonyl azide and suitably substituted phosphines.

Other (trisubstitutedphosphoranylidene)sulfamoyl chlorides have been prepared by the reaction of sulfuryl chloride with triphenylphosphine imine[2] and the Kirsanov reaction,[3,4] involving the reaction of sulfamic acid with suitably halogenated phosphorane. In the work of Kirsanov and co-workers,[2] (trisubstitutedphosphoranylidene)sulfamides **2** were prepared by the reaction of (trisubstitutedphosphoranylidene)sulfamoyl chlorides **1** with ammonia and amines (see Equation 1).

$$\underset{\mathbf{1}}{(C_6H_5)_3P{=}NSO_2Cl} + \underset{R\,=\,H,\ \text{alkyl, aryl}}{RNH_2} \rightarrow \underset{\mathbf{2}}{(C_6H_5)_3P{=}NSO_2NHR} \qquad (1)$$

In our continued work on the synthesis of (trisubstitutedphosphoranylidene)-sulfamoyl derivatives for chemical and biological studies, we report here the use of sulfamoyl azide for the synthesis of (trisubstitutedphosphoranylidene)sulfamides.

Treatment of sulfuryl chloride with excess sodium azide in acetonitrile gave sulfuryl azide as reported earlier.[5] Direct reduction of this acetonitrile solution of sulfuryl azide with sodium borohydride (1/2 mole equivalent) afforded an oil and a mixture of sulfamic acid and sulfur. The infrared spectrum of the oil suggested the formation of sulfamoyl azide **3** with N_3, SO_2 and NH_2 functional groups showing their characteristic stretching frequencies in the expected regions (Table I). Its formation is further confirmed by mass spectrum. Its mass spectrum exhibits the molecular ion at m/e 122 and this fragments further in a manner similar to organosulfonyl azides[6] by first losing N_3 radical to give the parent peak at m/e 80:

$$\underset{(12.0\%)^7}{\underset{m/e\ 122;\ 9.6\%}{N_3SO_2NH_2^+}} \xrightarrow{-N_3\cdot} \underset{(100\%)^7}{\underset{m/e\ 80;\ 100\%}{SO_2NH_2^+}}$$

Sulfamoyl azide had earlier been prepared by Shozda and Vernon,[7] from the reaction of sodium azide with sulfamoyl chloride:

$$H_2NSO_2Cl + NaN_3 \rightarrow H_2NSO_2N_3 \qquad (2)$$

It was obtained as a low melting explosive solid. The fragmentation pattern of the compound, obtained in this work, is identical to the reported mass spectrum.[7]

Sulfamic acid was confirmed by its melting point, infrared and mass spectrum. The mass spectrum exhibits the (M-1) ion at m/e 96 (63.6% relative intensity) and base peak at m/e 80 (attributable to either $H_2NSO_2^+$ or SO_3^+).

The formation of sulfur was confirmed by its melting point (118°C) and mass spectrum. The fragmentation pattern is identical to the published mass spectrum of S_8^+, with molecular ion at m/e 256 (relative intensity 57.1%).

The by-products, sulfur and sulfamic acid, were not formed when the acetonitrile solution containing the sulfuryl azide was diluted with toluene. This was then washed with dilute alkali, followed by dilute HCl and then water. The organic portion was separated, dried over anhydrous Na_2SO_4 and then reduced with $NaBH_4$.

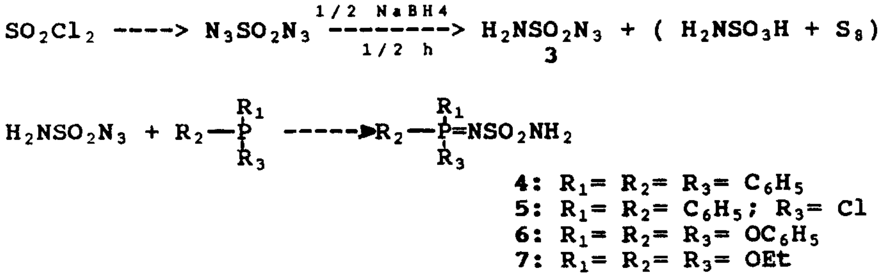
Equimolar amounts of sulfamoyl azide **3** and the appropriate trisubstituted phosphine were reacted in a suitable solvent under gentle reflux to give the corresponding (trisubstitutedphosphoranylidene)sulfamide **4–7** (Scheme I).

TABLE I

Infrared data of the sulfonyl azides and the (phosphoranylidene)sulfamides

Compd.	IR Absorption ν (cm^{-1})	M^+ (rel. int.)
$N_3SO_2N_3$	2145(N_3); 1378, 1177(SO_2); (other 1636w)	-
3	3395,3303(NH_2); 2149(N_3); 1381, 1181 (SO_2); (other, 1551m)	122(9.6)
4	3372, 3287 (NH_2); 1254, 1173, 1134 (SO_2,P=NSO_2)[1];(other,1586, 1563,1439)	356(23.3)
*5(oil)	3338, 3268,3122(NH_2); 1261, 1176,1130 (SO_2,P=NSO_2)[1];(other,1590, 1439,1400)	-
6	3350, 3280(NH_2); 1345, 1293, 1242, 1204,1185,1161(SO_2,P=NSO_2)[1]; (other, 3030, 1590, 1485)	$(M-NH_2)^+$ at m/e 388(5.2)
7	3371, 3232(NH_2); 1285, 1250, 1180 1158 (SO_2, P=NSO_2)[1]	$(M-15)^+$ at m/e 245 (20.0)

*Note: Compound 5 could not be obtained in analytically pure form.



$$SO_2Cl_2 \longrightarrow N_3SO_2N_3 \xrightarrow[1/2\ h]{1/2\ NaBH_4} \underset{\mathbf{3}}{H_2NSO_2N_3} + (H_2NSO_3H + S_8)$$

$$H_2NSO_2N_3 + R_2\!-\!\overset{R_1}{\underset{R_3}{P}} \longrightarrow R_2\!-\!\overset{R_1}{\underset{R_3}{P}}\!=\!NSO_2NH_2$$

4: $R_1 = R_2 = R_3 = C_6H_5$
5: $R_1 = R_2 = C_6H_5$; $R_3 = Cl$
6: $R_1 = R_2 = R_3 = OC_6H_5$
7: $R_1 = R_2 = R_3 = OEt$

SCHEME I

EXPERIMENTAL

1. *Preparation of Sulfamoyl Azide*

To sulfuryl azide (prepared from freshly distilled sulfuryl chloride (25 ml, 308 mmol) and sodium azide (70.0 g, 1075 mmol))[5] in dry acetonitrile (1000 ml) was added sodium borohydride (5.8 g, 154 mmol) in small portions with stirring, after which the mixture was refluxed for 1 h. The reaction mixture was cooled in ice and then treated with dilute H_2SO_4 (0.05 M), followed by extraction with ether. The ether extract was washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent at room temperature gave a mixture of sulfamoyl azide as an oil[9] and solid (sulfamic acid and sulfur). Addition of toluene or benzene separated the oil from the solid. Weight of oil = 18.4 g (49% yield based on the starting sulfuryl chloride), sulfamic acid (10.5 g, 35%) and sulfur (0.9 g). The oil was used directly for the synthesis of **4–7**.

2. *Reaction of Sulfamoyl Azide with Trisubstituted Phosphines*

General procedure. The reaction of triphenylphosphine with sulfamoyl azide is representative of the procedure employed.

To 1.0 g (8.2 mmol) of sulfamoyl azide in toluene was added triphenylphosphine (2.2 g, 8.4 mmol), stirred to dissolution and then heated gradually to reflux. Refluxing was continued for 6 h. The solvent was evaporated and the residue recrystallised from ethanol to give white crystals (2.5 g, 85% yield). M.P. = 196–198°C (lit.[2], 197–198°C). ^1H NMR (DMSO-d_6): 7.75–7.48 (m, Ar); 5.97 (s, NH_2, D_2O exchangeable).

(Triphenoxyphosphoranylidene)sulfamide **6**, was obtained as a soft white solid melting at 72–75°C. Recrystallization from toluene gave white crystals (78% yield). M.P. = 149–151°C. ^1H NMR (DMSO-d_6): 7.43–7.37 (m, 6H, Ar), 7.28–7.19 (m, 9H, Ar), 6.95 (br, s, NH_2, D_2O exchangeable). $C_{18}H_{17}N_2O_5PS$ required: C = 53.46; H = 4.24; N = 6.93. Found: C = 53.49; H = 4.10; N = 6.71. (Triethoxyphosphoranylidene)sulfamide **7**, was obtained as an oil. ^1H NMR ($CDCl_3$): 4.15 (q, 6H); 1.38 (t, 9H). $C_6H_{17}N_2O_5PS$ required: C = 27.69; H = 6.58; N = 10.76. Found: C = 27.50; H = 6.59; N = 10.64.

3. *Spectroscopy*

The IR spectra were recorded on a PERKIN ELMER IR spectrometer, type 299. A BRUCKER WM-250 NMR spectrophotometer was used to record the NMR spectra in $CDCl_3$ or DMSO-d_6 (TMS as internal standard). A VARIAN MAT 312 mass spectrometer was used to record the mass spectra at 70 ev.

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9. Care must be taken in handling sulfamoyl azide as it is an explosive material (see Reference 7).