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Chemistry of (Triphenylphosphoranylidene)sulfamoyl Chloride. I. Reaction with Amines and Alcohols

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Received October 9, 1974 AIC40700R

Compounds of the type Ph_3PNSO_2OR and Ph_3PNSO_2NHR (R = Me, Et, *n*-Pr, *n*-Bu, and *o*-, *m*-, *p*-BrC_6H_4) have been prepared in good yield by the reaction of (triphenylphosphoranylidene)sulfamoyl chloride, Ph_3PNSO_2Cl, with alcohols in pyridine or with amines in chloroform; derivatives of secondary amines may also be prepared by the latter method. Heating the methyl ester in pyridine to moderately high temperatures produces a compound containing the $Ph_3PNSO_2O^-$ ion which yields the free acid upon acidification. The infrared spectra of the title compound and the alkyl esters in the 1100–1300-cm^{-1} region are presented and discussed.

Introduction

The reaction of dry sulfamic acid with dichlorotriphenylphosphorane in refluxing acetonitrile[1] or benzene yields the novel compound (triphenylphosphoranylidene)sulfamoyl chloride, Ph_3PNSO_2Cl (**1**), the first known representative of a series of compounds of general formula Ar_3PNSO_2Cl. As part of a general investigation of the chemistry of these compounds, the reaction of the sulfamoyl chloride **1** with selected alcohols and primary and secondary amines has been studied.

Experimental Section

Reagents. Gaseous dimethylamine (Matheson) was used as received; methylamine was used as a 40% aqueous solution while all other amines and the three isomeric bromophenols were reagent grade materials (Eastman) and used without further purification. Aliphatic alcohols (reagent grade) were dried over Drierite for several days, filtered from the desiccant, and distilled from the corresponding magnesium alkoxide. Pyridine was dried by distillation from KOH pellets; chloroform was the commercially available "anhydrous" reagent and was used without further treatment.

The synthesis of **1** has been described previously;[1] however, a significant improvement results if benzene is substituted for acetonitrile as solvent. In a number of runs using 1.00 mol of sulfamic acid, 2.05 mol of dichlorotriphenylphosphorane, and 1.5–2.0 l. of dry benzene, yields of 91–94% were consistently obtained. The product precipitates as small, white crystals during the course of the reaction which is essentially complete after 24 hr at reflux (a small amount of HCl can still be detected after this time, but it probably results from traces remaining dissolved in the solvent). The analytically pure product is obtained directly from the reaction mixture by filtering the golden brown solution, washing the product several times with dry benzene, and drying in vacuo; mp 213.0–216.0°. *Anal.* Calcd for $C_{18}H_{15}ClNO_2PS$: C, 57.54; H, 4.08; N, 3.86. Found: C, 57.54; H, 3.99; N, 3.73.

Procedure. One of two general procedures was followed depending upon whether chloroform or pyridine was used as solvent. Examples of each of these procedures are given along with additional comments concerning other compounds whose syntheses are not described in detail. It should be noted that for the reactions run in chloroform, no special effort was made to exclude atmospheric moisture; on humid days, the transfer of pyridine to the reaction flask was done in a nitrogen-filled glove bag.

***N*-Methyl-*N'*-(triphenylphosphoranylidene)sulfamide.** A 7.52-g (20.0-mmol) amount of **1** was added in small portions to a mechanically stirred mixture of 100 ml of chloroform and 10.00 ml of a 40% aqueous solution of methylamine contained in a 300-ml, two-necked flask (the flask was kept stoppered between additions). The chloride reacted immediately as evidenced by its dissolution in the reaction mixture; external cooling was not necessary. After all of the sulfamoyl chloride had been added, the clear solution was stirred for 1 additional hr, transferred to a separatory funnel, and washed with water until the water extract was just faintly basic to litmus. After drying of the solution overnight with anhydrous sodium sulfate, the solvent was removed in vacuo using a rotary evaporator to yield a white solid which was finally dried in vacuo at 40°.

Table I. (Triphenylphosphoranylidene)sulfamides

No.	Compd	Yield,[a] %	Mp,[b] °C	Recrystallizn solvent
2	Ph_3PNSO_2NHMe	71	158.2–159.2	EtOH–cyclohexane
3	Ph_3PNSO_2NHEt	81	130.0–132.1	PhH–cyclohexane
4	Ph_3PNSO_2NH-*n*-Pr	82	151.5–152.4	EtOH
5	Ph_3PNSO_2NH-*n*-Bu	82	140.2–141.2	EtOH
6	$Ph_3PNSO_2NHC_6H_4Br$-*o*	73	178.0–179.0	EtOH
7	$Ph_3PNSO_2NHC_6H_4Br$-*m*	80	193.1–194.8	EtOH
8	$Ph_3PNSO_2NHC_6H_4Br$-*p*	73	194.5–195.5	EtOH
9	$Ph_3PNSO_2NMe_2$	87	156.2–157.2[c]	PhH–cyclohexane
10	$Ph_3PNSO_2N(n\text{-}Bu)_2$	88	147.0–148.0[d]	PhH–cyclohexane

[a] After purification; crude yields were >90%. [b] All melting points are uncorrected. [c] Reference 2: 156–158°. [d] Reference 2: 149°.

Reactions involving all other aliphatic amines, except dimethylamine (vide infra), were performed similarly except that a single-necked, 200-ml flask was used and stirring was accomplished magnetically; some degree of external cooling was also usually necessary. The quantity of amine taken was some 10–15% in excess of that required for the reaction and to act as hydrogen chloride acceptor; it was measured out volumetrically and added to the flask using a volumetric pipet. Work-up was as above or was done by evaporating the solvent and washing the resulting solid with water until it was free of amine hydrochloride. If an oil resulted (the case with ethylamine), trituration with ether rendered it crystalline.

***N,N*-Dimethyl-*N'*-(triphenylphosphoranylidene)sulfamide.** Gaseous dimethylamine was passed into a magnetically stirred suspension of 7.52 g of **1** in 100 ml of chloroform contained in a 300-ml, two-necked flask equipped with a gas inlet tube and reflux condenser fitted with a drying tube ($CaSO_4$); the very exothermic reaction was moderated by cooling with ice water. Amine was passed into the solution for about 15 min after the last of the sulfamoyl chloride had disappeared. Dry nitrogen was then passed through the solution to remove some of the excess amine and work-up was as described for the *N*-methyl derivative.

Methyl (Triphenylphosphoranylidene)sulfamate. (a) A 7.52-g sample of **1** was added in small portions and against a countercurrent of dry nitrogen to a magnetically stirred solution of 1.00 ml of dry MeOH in 30 ml of dry pyridine contained in a 100-ml, three-necked, standard taper (19/22) flask equipped with a thermometer–gas inlet adapter, stopper, and reflux condenser with drying tube; the reaction was only slightly exothermic and external cooling was unnecessary.

After all the chloride had been added (a small amount of solid remained undissolved in the flask), the flask was heated in an oil bath at 100° for about 30 min; crystals of a white solid formed upon cooling the contents to room temperature. The contents of the flask were then poured, with stirring, into a beaker containing concentrated HCl (1.80 mol/mol of pyridine used) and ca. 100 g of crushed ice. The crystals which formed were suction filtered on a sintered-glass filter funnel, washed twice with distilled water, and dried in vacuo at 40°; yield 6.07 g.

A portion of this solid produced a vigorous effervescence when treated with 5% sodium bicarbonate; hence, another portion of the solid was added to 5% sodium bicarbonate and filtered from the insoluble residue (identified as Ph_3PO), and the filtrate was acidified with cold, dilute sulfuric acid. The white solid which precipitated was filtered, washed with cold water, dried in vacuo, and finally recrystallized from acetonitrile. The infrared spectrum and analytical data suggest that this compound should be formulated as (triphenylphosphoranylidene)sulfamic acid, Ph_3PNSO_2OH; mp 225–226° dec. *Anal.* Calcd for $C_{18}H_{15}NO_3PS$: C, 60.50; H, 4.51; N, 3.92. Found: C, 60.34; H, 4.61; N, 4.05.

(b) The procedure was as described above, except that the flask was heated with a heating mantle until the solution *just* cleared (internal temperature 47°), after which the heat source was removed and stirring was continued for several hours. Following the treatment with cold HCl, the product was filtered, washed successively with water, 5% $NaHCO_3$ (no effervescence), and water, and then sucked as dry as possible on the frit. Final drying was done in vacuo at 40°. The compound was identified as the methyl ester.

The reactions with the other aliphatic alcohols and the isomeric bromophenols and bromoanilines were similar except that 50 ml of pyridine was used and the internal temperature was kept at 70° for ca. 15 min in the case of the aliphatic alcohols while reflux temperatures (1–2 hr) were used for the aromatic derivatives; the wash with $NaHCO_3$ was used only with the alkyl sulfamates and produced very little, or no, gas evolution. Reactions with the aromatic amines were accompanied by color changes: light green, as the chloride was added, to red-orange, as the solution was heated, to light green, at the completion of the reaction, for *p*-bromoaniline; yellow to orange-red to yellow-green for *m*-bromoaniline; light green throughout for the ortho amine; the crude products were light green and were decolorized with Norit A to give the pure, white products.

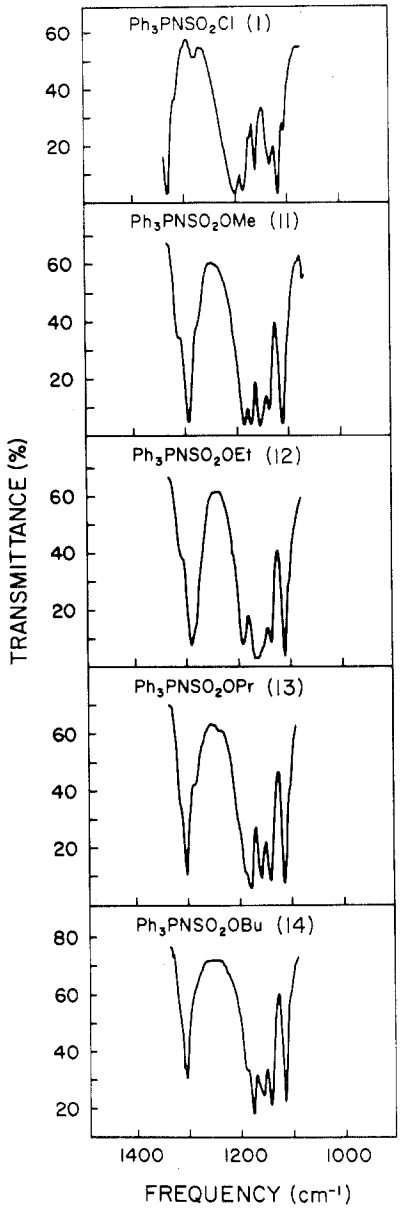

Figure 1. Infrared spectra of compounds **1** and **11–14** in the 1100–1300-cm^{-1} region.

Results and Discussion

Data regarding yields, melting points, and solvents used for recrystallization of the *N*-alkyl(aryl)-*N'*-(triphenylphospho-

Table II. (Triphenylphosphoranylidene)sulfamates

No.	Compd	Yield,[a] %	Mp,[b] °C	Recrystallizn solvent
11	Ph_3PNSO_2OMe	83	185.2–186.5	PhH
12	Ph_3PNSO_2OEt	80	170.1–171.4	PhH–cyclohexane
13	Ph_3PNSO_2O-*n*-Pr	82	109.7–110.5	PhH–cyclohexane
14	Ph_3PNSO_2O-*n*-Bu	79	113.1–114.5	PhH–cyclohexane
15	$Ph_3PNSO_2OC_6H_4Br$-*o*	78	202.5–204.0	Methyl ethyl ketone
16	$Ph_3PNSO_2OC_6H_4Br$-*m*	68	140.8–141.8	EtOH
17	$Ph_3PNSO_2OC_6H_4Br$-*p*	79	214.8–217.5	$CHCl_3$–EtOH

[a] After recrystallization; crude yields were >88%. [b] All melting points are uncorrected.

ranylidene)sulfamides and the two *N,N*-dialkyl derivatives are presented in Table I; Table II gives the corresponding data for the alkyl(aryl) (triphenylphosphoranylidene)sulfamates. All of the compounds prepared are white, nonhygroscopic, crystalline solids, and all gave satisfactory elemental analyses.

None of the compounds listed have been previously reported in the literature except the sulfamides **9** and **10**.[9] Moeller and Vandi have prepared compounds of this type by treating *N,N*-dialkyl-*N*-(trichlorophosphoranylidene)sulfamides with phenylmagnesium bromide in benzene or ether.[2] The yields using this procedure are lower than those from the method reported here and their method is not applicable for the preparation of *N*-alkyl derivatives. Since the dialkylsulfamides from dimethyl to dibutyl had been previously prepared, only two secondary amines were chosen to illustrate the present method.

The reaction between **1** and primary and secondary aliphatic amines proceeds readily in chloroform solution with essentially no side reactions taking place; the same is true for the reactions in pyridine solution of the three isomeric bromoanilines; the method appears to be general. In the preparation of esters of (triphenylphosphoranylidene)sulfamic acid, however, some evidence for side reactions similar to those encountered in the preparation of esters of arylsulfonic acids was obtained.

When sulfonyl chlorides are treated with alcohols in pyridine solution, several side reactions are possible which lead to sulfonic acids after treatment with acid in the work-up:[3-5] (1) formation of alkylpyridinium salts and (2) formation of alkyl chlorides. Both side reactions become serious at temperatures above 0° and depend upon the sulfonyl chloride used and the type of alcohol. In the attempted preparation of the sulfamate **11** at high temperatures, the free acid would be generated when the reaction mixture is treated with hydrochloric acid regardless of which side reaction, if not both, had taken place. At present, the data do not enable any conclusions to be made concerning the nature of any side reactions involved. The formation of triphenylphosphine oxide is most likely due to hydrolysis of the P=N bond during the treatments with hydrochloric and sulfuric acids rather than during the reaction in pyridine; hydrolysis and precipitation of the oxide also occur when a solution of the sulfamic acid in sodium bicarbonate is allowed to stand at room temperature.

Infrared Spectra. The 1100–1300-cm^{-1} region of the infrared spectra of compounds **1** and **11–14** is reproduced in Figure 1 (as KBr pellets). The strong band near 1300 cm^{-1} is assigned to the SO_2 asymmetric stretching vibration; this band has been shown by isotopic studies[7] to be a pure SO_2 frequency and not a combination band as suggested by Moeller and Vandi.[2] The strong band near 1100 cm^{-1} is present in the spectra of all of the compounds listed in the tables and is essentially invariant in both position and intensity; it is associated with a "*P*-phenyl" vibration.

The positions of the P=N stretching and SO_2 symmetric stretching frequencies are less certain. The work of Wiegrabe, Bock, and Lüttke[7,8] has indicated that, for compounds containing the $P{=}NSO_2{-}$ group, both vibrations may lie in the 1100–1200-cm^{-1} region. This range is probably correct for the compounds shown in Figure 1, but the complexity of this spectral region is such as to make a definite assignment untenable. It is hoped that infrared measurements on ^{15}N-labeled compounds will be made to clarify the location of these bands.

Acknowledgment. The author wishes to thank Mr. Malcolm Stone for the C, H, and N analyses.

Registry No. **1**, 41309-06-2; **2**, 54484-05-8; **3**, 54484-06-9; **4**, 54484-07-0; **5**, 54484-08-1; **6**, 54484-09-2; **7**, 54484-10-5; **8**, 54484-11-6; **9**, 33610-48-9; **10**, 54484-12-7; **11**, 41309-07-3; **12**, 41309-08-4; **13**, 54484-13-8; **14**, 54484-14-9; **15**, 54484-15-0; **16**, 54484-16-1; **17**, 54484-17-2; (triphenylphosphoranylidene)sulfamic acid, 41309-05-1; methylamine, 74-89-5; dimethylamine, 124-40-3; MeOH, 67-56-1.

Supplementary Material Available. Analytical data for compounds **2–17** will appear as Table III following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC40700R.

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(9) **Note Added in Proof.** The preparation of the title compound and the esters **11** and **12** by alternative methods has also been described in the Russian literature: A. S. Shtepanek, V. A. Zasorina, and A. V. Kirsanov, *J. Gen. Chem. USSR* (*Engl. Transl.*), **43**, 21 (1973). Melting points are comparable except for that of the sulfamoyl chloride (209.5–211°).