N-(Triphenylphosphoranylidene)sulphamoyl Pseudohalides. Part I. Preparation of the Azide and its Reaction with Phosphites and Thiophosphites

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The preparation of *N*-(triphenylphosphoranylidene)sulphamoyl azide, $Ph_3P{:}N{\cdot}SO_2N_3$, by reduction of the hydrazide with nitrous acid or by reaction of sodium azide with the chloride in methyl ethyl ketone, is described. The azide reacts with phosphites and thiophosphites to produce compounds of the type $Ph_3P{:}N{\cdot}SO_2{\cdot}N{:}P(OR)_3$ (R = Me, Et, Pr^n, Bu^n, or Ph), and $Ph_3P{:}N{\cdot}SO_2{\cdot}N{:}P(SR)_3$ (R = Et or Pr^n), respectively.

As part of a continuing investigation of the chemistry of *N*-(triphenylphosphoranylidene)sulphamoyl chloride,[1] $Ph_3P{:}N{\cdot}SO_2Cl$ (I), the conversion of (I) to the azide has been studied and the latter characterized by reaction with trialkyl phosphites and trialkyl trithiophosphites.

RESULTS AND DISCUSSION

The azide, $Ph_3P{:}N{\cdot}SO_2N_3$ (II), was prepared either by the reduction of the hydrazide with sodium nitrite in acid solution,[2] or by reaction of the chloride (I) with sodium azide in solvents such as acetone, acetonitrile, or methyl ethyl ketone (mek) at reflux temperatures.

$$Ph_3P{:}N{\cdot}SO_2{\cdot}NH{\cdot}NH_2 + NaNO_2 + HCl \longrightarrow Ph_3P{:}N{\cdot}SO_2N_3 + NaCl + 2H_2O \quad (1)$$

$$Ph_3P{:}N{\cdot}SO_2Cl + NaN_3 \longrightarrow Ph_3P{:}N{\cdot}SO_2N_3 + NaCl \quad (2)$$

Exchange was slower in acetone (b.p. 56 °C) than in acetonitrile (b.p. 80 °C) or mek (b.p. 79 °C) and extended reaction times, of the order of several days, were required to effect high conversion to the azide. All three solvents suffer from the disadvantage that some decomposition takes place during the reaction, as evidenced by a discolouration of the solution, but it is not clear whether such discolouration is the result of thermal decomposition of the azide or attack of the azide on the carbonyl or cyano-group of the solvent. Acetonitrile gave the most intense discolouration (reddish brown) for the same reaction time and some attack on the solvent therefore seems likely. The extent of decomposition in acetonitrile is such that a number of recrystallizations were necessary to obtain a pure product (treatment with decolourizing carbon was ineffective); since the time for complete exchange in mek and acetonitrile is similar and decomposition is less extensive in mek, this solvent was used for subsequent preparations of the azide.

Anhydrous methanol was also examined as a solvent for the exchange reaction, since it is known that aliphatic sulphonyl chlorides undergo exchange with NaN_3 in this solvent.[3] Although azide was detected in the solid obtained after work-up of the reaction mixture, the bulk material was identified as methyl *N*-(triphenylphosphoranylidene)sulphamate[1] in 84% yield. It is reasonable to expect that alcoholysis will compete with the exchange reaction and, in the present case, is the favoured reaction with the azide apparently serving as an acid acceptor. Although no experiments were made to detect hydrogen azide in the reaction mixture, this hypothesis is supported by the observation that the yield of the methyl ester from the reaction of (I) with methanol in the absence of the azide is substantially lower.

Synthesis of the azide by reduction of the hydrazide [equation (1)] has the advantage that it occurs at low temperatures (0—5 °C) and no decomposition was noted; however, the hydrazide and its hydrochloride are not very soluble in water and the azide, which is also water insoluble, often contains both substances as impurities. Although the azide can be readily separated from the impurities, the conversion *via* equation (2) is preferred since it gives high yields and does not involve formation of the hydrazide as an additional step in the conversion of (I) to the azide. For this reason, no attempt was made to optimize the yield in equation (1).

One of the reactions which azides are known to undergo is that with trivalent phosphorus compounds to produce imines.[4,5] The reaction of the azide (II) with phosphites and thiophosphites proceeds according to

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[1] An earlier paper reported the reaction of the chloride with alcohols and amines (*Inorg. Chem.*, 1975, in the press).

[2] N. A. Goldberg and G. P. Balabanov, *J. Org. Chem.* (*U.S.S.R.*), 1965, **1**, 1625.

[3] J. Goerdeler and H. Ullmann, *Chem. Ber.*, 1961, **94**, 1067.

[4] G. Singh and H. Zimmer, *Organometallic Chem. Rev.*, 1967, **2**, 279.

[5] G. M. Kosolapoff and L. Maier, 'Organic Phosphorus Compounds,' Wiley–Interscience, New York, 1972, vol. 3, ch. 5A.

equation (3), where X = O or S and R = Me, Et, Pr^n,

$$\mathrm{Ph_3P{:}N{\cdot}SO_2N_3 + (RX)_3P \longrightarrow Ph_3P{:}N{\cdot}SO_2{\cdot}N{:}P(XR)_3 + N_2} \quad (3)$$

Bu^n, or Ph. Details concerning reaction conditions, yields, analytical data, *etc.*, are presented in the Table. In general, azide (II) reacts much more readily with phosphites than thiophosphites, in agreement with the findings of Goerdeler and Ullmann.[3]

The solvents used to prepare derivatives of phosphites were usually unsuitable for the thiophosphites. In a run using excess of $(EtS)_3P$ in methylene chloride, no nitrogen evolution was detected and an i.r. examination of the reaction mixture after 20 h at reflux indicated that azide was still present. Formation of imines by reaction of azides and phosphines is known to proceed *via* decomposition of an intermediate complex of azide and phosphine (' Staudinger intermediates,' several of which have been isolated [6]) and it is possible that, in methylene chloride, either the complex is not sufficiently stable for its formation to occur or that its rate of dissociation is greater than its rate of decomposition to nitrogen and imine.[6] It is also possible that the decomposition temperature of the adduct between $(EtS)_3P$ and the azide is greater than the temperature of refluxing methylene chloride, for the expected product was obtained when *p*-xylene was substituted for methylene chloride, but only after extended refluxing.

Data for the new compounds $\mathrm{Ph_3P{:}N{\cdot}SO_2{\cdot}N{:}P(XR)_3}$, (III)

Compound	Reaction medium	Yield (%)	M.p. (θ_c/°C) [a]	Recrystallizing solvent	Found (%) C	Found (%) H	Found (%) N	Calc. (%) C	Calc. (%) H	Calc. (%) N
(III; X = O, R = Me)	C_6H_6	79	137·0—138·1	C_6H_{12}–C_6H_6	53·15	5·15	5·85	52·7	5·05	5·85
(III; X = O, R = Et)	CH_2Cl_2	90	91·2—92·0	C_6H_{12}–C_6H_6	55·65	5·85	5·30	55·4	5·80	5·40
(III; X = O, R = Pr^n)	Pr^{n}OH	91	77·5—78·5	Et_2O	57·7	6·35	4·95	57·65	6·45	5·00
(III; X = O, R = Bu^n)	CH_2Cl_2 [b]	78	43·5—44·5		59·6	6·70	4·30	59·6	7·00	4·65
(III; X = O, R = Ph)	Pr^{n}OH	83	169·5—172·5	EtOH	64·6	4·65	4·20	65·05	4·55	4·20
(III; X = S, R = Et)	p-Xylene	55	93·8—94·4	Et_2O	50·75	5·30	4·90	50·7	5·30	4·90
(III; X = S, R = Pr^n)	n-Pentyl alcohol	77	89·0—90·0	Et_2O	53·3	6·05	4·50	53·1	5·95	4·60
$\mathrm{Ph_3P{:}N{\cdot}SO_2{\cdot}NH{\cdot}NH_2}$	*c*	95	161 [d]	EtOH	58·05	4·90	11·2	58·2	4·90	11·3
$\mathrm{Ph_3P{:}N{\cdot}SO_2N_3}$, (II)	*c*	95	145 [d]	Pr^{n}OH	56·5	4·05	14·65	56·55	3·95	14·65

[a] Uncorrected. [b] Removal of solvent left a sweet-smelling syrup which solidified slowly only after being chromatographed on neutral alumina with diethyl ether as eluant, followed by removal of the ether *in vacuo*. [c] See text. [d] Decomposes with gas evolution.

Alcohols were also examined as reaction media, but a reasonable yield of imine was obtained only with tri-n-propyl trithiophosphite in n-pentyl alcohol; the use of alcohols is limited for thiophosphites since exchange reactions producing phosphites and thiols are possible.[7] Moreover, redox reactions may also accompany reactions with thiophosphites as evidenced by the isolation of *N*-(triphenylphosphoranylidene)sulphamide, $\mathrm{Ph_3P{:}N{\cdot}SO_2{\cdot}NH_2}$, from the reaction of triethyl trithiophosphite with the azide in n-pentyl alcohol. Similar behaviour has been observed for the reaction of benzenesulphonyl azide with triphenylphosphine in chloroform [6] and acetonitrile.[8]

Unfortunately, no pattern emerges from these observations since the amide was not detected in the reaction of $(PrS)_3P$ with the azide (II) in alcohol. It is clear, however, that reactions of azides with thiophosphites are more likely to result in reactions leading to products other than imines and this may be related to the lower stability of the intermediate adducts compared to those from phosphites, and to the greater tendency of thiophosphites to engage in reactions leading to cleavage of the phosphorus–sulphur bond.

EXPERIMENTAL

Reagents.— *N*-(Triphenylphosphoranylidene)sulphamoyl chloride, (I), was synthesized as previously described;[1,9] triethyl, tri-n-propyl, and tri-n-butyl trithiophosphites were synthesized according to literature methods.[10] Tri-n-propyl phosphite was synthesised by a procedure similar to that used for the synthesis of the thiophosphites, while the remaining phosphites and all other reagents were available commercially and used as received. All solvents were dried by standard techniques. *N*-(Triphenylphosphoranylidene)-sulphamoyl hydrazide was prepared by reaction of (I) with excess of an 85% aqueous solution of hydrazine hydrate in chloroform; the yield was quantitative.

N-(*Triphenylphosphoranylidene*)*sulphamoyl Azide*, (II).—(a) The hydrazide (9·28 g, 25 mmol) was added to a solution of concentrated HCl (4·5 cm^3) in water (100 cm^3) contained in a three-necked flask (500 cm^3) equipped with a mechanical stirrer, thermometer, and dropping funnel containing a solution of $NaNO_2$ (200 g, 29 mmol) in water (50 cm^3). The flask contents were cooled to 5 °C and the $NaNO_2$ slowly added to the stirred suspension of hydrazide. After all the nitrite had been added, the mixture was allowed to warm to room temperature and stirring was continued for 1 h. The solid was filtered off, washed with water, and dried *in vacuo* at room temperature. Finally it was slurried well with warm benzene, filtered from insoluble matter, and the benzene removed on a rotary evaporator to give 4·97 g (52%) of a pale brown *solid* which was recrystallized from absolute ethanol. The i.r. spectrum (KBr pellet) contained a strong band at 2 100 cm^{-1} which is attributed to the azide asymmetric-stretching frequency.[11] The azide is not shock sensitive and does not decompose explosively when heated.

(b) Compound (I) (75·1 g, 0·200 mol) and sodium azide (19·5 g, 0·300 mol) were added to a dry two-necked flask

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[6] J. E. Leffler and Y. Tsuno, *J. Org. Chem.*, 1963, **28**, 902.

[7] C. Wu and F. Welch, U.S.P. 3,351,683.

[8] J. E. Franz and C. Osuch, *Tetrahedron Letters*, 1963, **13**, 841.

[9] D. Arrington, *Synthesis React. Inorg. Metal-org. Chem.*, 1974, **4**, 107.

[10] A. Lippert and E. Reid, *J. Amer. Chem. Soc.*, 1938, **60**, 2370.

[11] L. Bellamy, ' The Infra-red Spectra of Complex Molecules,' John Wiley, New York, 1958, p. 273.

(1 l) equipped with a mechanical stirrer and reflux condenser with drying tube. After adding dry methyl ethyl ketone (500 cm^3), the mixture was stirred and heated under reflux in an oil-bath for *ca.* 30 h. The heat source was then removed and the mixture allowed to cool spontaneously, with stirring, to room temperature. The flask contents were then poured, with vigorous stirring, into water (1 200 cm^3) contained in a flask (2 l) and the resulting yellow curdy precipitate was filtered off, washed well with water, partially dried on the frit, and finally dried *in vacuo* at 50 °C. The pure azide was obtained by recrystallization from ethanol, n-propanol, or dichloromethane–n-propanol. (The pure solid azide should not be heated at 60 °C or higher for partial decomposition occurs which discolours the solid.)

(Triethoxophosphoranylidene)(triphenylphosphoranylidenesulphamoyl)amine, (III; X = O, R = Et).—Compound (II) (3·82 g, 10·0 mmol) was dissolved in CH_2Cl_2 (25 cm^3) contained in a three-necked flask (100 cm^3) equipped with a thermometer, dropping funnel, and condenser with drying tube; stirring was accomplished magnetically. A solution of the phosphite (2·10 cm^3, *ca.* 12·1 mmol) in methylene chloride (10 cm^3) was slowly added from the dropping funnel; the reaction was only mildly exothermic and cooling was unnecessary. After all the phosphite had been added, the clear solution was heated under reflux for 2—3 h. The solution was then cooled, filtered, and the solvent stripped off on a rotary evaporator. The resulting oily residue solidified on trituration with diethyl ether and the *solid* purified by recrystallization from hexane–benzene.

The reactions with other phosphites were similar; specific details are presented in the Table.

(Triethylthiophosphoranylidene)(triphenylphosphoranylidenesulphamoyl)amine, (III; X = S, R = Et).—The azide (II) (7·13 g, 20·0 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and the thiophosphite (4·50 g, 21·0 mmol) added as a solution in CH_2Cl_2 as above. After 20 h at reflux, an i.r. examination of the solution indicated the presence of free azide; hence the CH_2Cl_2 was distilled off and replaced by dry *p*-xylene (30 cm^3). Heating under reflux was maintained until no azide could be detected in the solution (*ca.* 8 h); the solution was yellow-brown at this point. Solvent was removed by distillation *in vacuo* to leave a viscous brown residue which solidified on cooling. This residue was taken up in CH_2Cl_2 and chromatographed on neutral alumina with CH_2Cl_2 as eluant, followed by chloroform. The first fraction gave, after removal of solvent, a pale brown *product*; subsequent fractions were white. An analytical sample was obtained by extraction of the purer fractions with diethyl ether for several days in a Soxhlet apparatus.

(Tri-n-propylthiophosphoranylidene)(triphenylphosphoranylidenesulphamoyl)amine, (III; X = S, R = Pr^n).—The scale and general procedure was the same as for the reaction with $(EtO)_3P$, except that n-pentyl alcohol (10 cm^3) was used as the reaction medium. Refluxing was continued for 1·5 h, after which time the cooled solution was poured into diethyl ether (60 cm^3) and placed in the freezing compartment of a refrigerator overnight. The *crystals* which deposited were filtered off, washed with diethyl ether, and dried. An analytical sample was obtained by extraction with diethyl ether.

In spite of a number of experiments using tri-n-butyl trithiophosphite in a variety of solvents, no imine could be isolated from the reaction mixture and most of the azide was either recovered unchanged or had decomposed during the reaction to give intractable evil-smelling oils or gummy solids. Work with this thiophosphite was therefore discontinued.

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