

CHEMISTRY OF AZIDES. II. REACTION WITH TRIPHENYLPHOSPHINE

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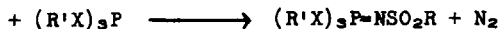
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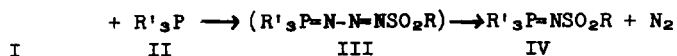
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Sulfonyl azides have been reported to react with phosphites<sup>1</sup>,  
thiophosphites<sup>1</sup> and phosphines<sup>2</sup> to give phosphinimines.



RSO<sub>2</sub>N<sub>3</sub>



X = O or S, I, II, III, and IV R=R'=Ph

Isolation of intermediates of type III were not reported.

Horner and Gross<sup>2</sup> and Leffler and co-workers<sup>3</sup> have reported  
stable adducts from reaction of II with o-azidobenzoic acid  
and triphenylmethyl azide, respectively.

While reaction of azide, I, with phosphine, II, is reported<sup>2</sup>  
to give imine, IV, we have found that in benzene or ether at  
room temperature an excellent yield of adduct, III, was ob-  
tained. Para-toluenesulfonyl azide and diethylsulfamyl

<sup>1</sup> J. Goerdeler and H. Ullman, Chem. Ber. 94, 1067 (1961).

<sup>2</sup> L. Horner and A. Gross, Ann 591, 117 (1955).

<sup>3</sup> J. E. Leffler, H. Honsberg, Y. Tsuno and I. Forsblad,  
J. Org. Chem. 26 4810 (1961).

azide reacted in similar fashion. Phosphites were found to react as reported<sup>1</sup>.

In refluxing benzene triphenylphosphine and benzenesulfonyl azide gave the expected imine, IV, in 85% yield. However, we have also discovered that in refluxing acetonitrile or chloroform, still another reaction occurred and triphenylphosphine oxide, phenyl sulfide and phenyl disulfide were identified.

The following examples are typical of the methods employed. An equimolar amount of benzenesulfonyl azide (I), dissolved in ether (or benzene), was added dropwise to a solution of triphenylphosphine in the same solvent at about 25° with agitation. No gas evolved and the oil, which formed initially, solidified rapidly. After standing fifteen minutes, the solids were filtered, washed with fresh solvent, and recrystallized (from CHCl<sub>3</sub> by addition of ether, no heating) to give beautiful, yellow crystals (III), m.p. 87.5°(d). Found: C, 64.9; H, 4.70; N, 9.30. Calc. for C<sub>24</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub>PS: C, 64.7; H, 4.53; N, 9.43. The infrared spectrum of the solid (mineral oil) showed no azide absorption at 4.7 μ. In solution (CHCl<sub>3</sub>) the azide band was present<sup>4</sup>. The P<sup>31</sup> NMR spectrum (oscilloscope scan) of the adduct in CHCl<sub>3</sub> showed a weak, temporary band at -25 ppm (H<sub>3</sub>PO<sub>4</sub> reference). No bands could be observed from +10 to

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<sup>4</sup> This behavior was also reported by Leffler, et al for their trityl azide-phosphine adduct.

+50 ppm<sup>5</sup>. The solution evolved nitrogen rapidly thus precluding a more intensive investigation.

Dropwise addition of a benzene solution of azide, I, to a molar equivalent of phosphine, II, in hot benzene caused vigorous gas evolution. The solution was then heated (steam bath) thirty minutes and cooled. The white solid which formed was collected, washed with fresh benzene and dried under vacuum to give an 85% yield of imine, IV, m.P. 157.8-158.8° (lit.<sup>2</sup> 154°). Found: P, 7.1; S, 7.4. Calc. for C<sub>24</sub>H<sub>20</sub>NO<sub>2</sub>PS: P, 7.4; S, 7.7.

Preliminary results on the reaction of molar equivalents of triphenylphosphine with benzene sulfonyl azide in hot chloroform or acetonitrile gave poor yields of the expected imine, IV. Instead, triphenylphosphine oxide was isolated (Runs 1 and 2). The presence of a nitrogen atmosphere (Run 3) did not materially alter the results. Phenyl disulfide was isolated from the reaction mixture in 65% yield when two moles of phosphine, II, were mixed with one of azide, I, in acetonitrile (Run 4). In Runs 5-8 the total reaction mass was sampled and analyzed by programmed temperature GLC using triphenylmethane as an internal standard. The percent of each product found is shown in bracketed figures in the Table. The phosphine imine, IV, did not elute from the column.

<sup>5</sup> The absence of a strong positive shift argues against a cyclic structure



-SO<sub>2</sub>R, since the pentasubstituted phosphorous would be expected to show such a shift<sup>6</sup>.

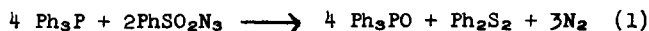
<sup>6</sup> R.A.Y. Jones & A.R. Katritzky, Angew. Chem. Inter. Ed. 1, 32 (1962).

REACTIONS OF BENZENESULFONYL AZIDE (I) WITH TRIPHENYLPHOSPHINE (II)<sup>a</sup>

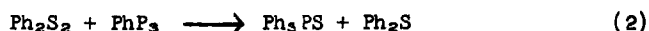
Run No.	Millimoles of Reactant		Millimoles of Products			Ph <sub>3</sub> PO 4.68 <sup>c,d</sup>
	I	II	N <sub>2</sub>	Ph <sub>2</sub> S	Ph <sub>3</sub> S <sub>2</sub>	
1 <sup>b</sup>	10	10	--	--	--	4.68 <sup>c,d</sup>
2 <sup>e</sup>	10	10	--	--	--	9.11
3 <sup>e,f</sup>	10	10	--	g	g	8.26
4 <sup>e</sup>	5.0	10	--	--	1.62 <sup>h</sup>	8.99
5 <sup>e</sup>	100 <sup>j</sup>	1.00	0.651(0.75) <sup>k</sup>	(6.8) <sup>l</sup> 0.157	(2.7) <sup>l</sup> 0.053	(51.0) <sup>l</sup> 0.788
6 <sup>b</sup>	0.889	0.889	0.754(0.67) <sup>k</sup>	(1.4)-----	(2.7)-----	(35.4)-----
7 <sup>e</sup>	1.00	2.00	--	(4.3) 0.161	(8.2) 0.262	(79.0) 1.98
8 <sup>b</sup>	2.00	4.00	--	(1.2) 0.095	(4.1) 0.280	(51.4) 2.73

- a. All reactions were carried out at the boiling point of the solvent for thirty minutes.
- b. Chloroform solvent.
- c. Imine, IV, 0.161 millimoles, was also isolated. None was isolated in Runs 2-8 but infrared bands at 7.9  $\mu$  and 12.4  $\mu$  showed this compound to be present to some degree.
- d. The presence of sulfonyl azide was detected in the infrared spectrum (strong 4.7  $\mu$  band) in all runs using 1:1 mole ratio. The azide was identified, in this run, by addition of I in ether to form adduct III.
- e. Acetonitrile solvent.
- f. Nitrogen atmosphere present.
- g. Presence indicated by GLC.
- h. M.p. 54-57° alone, 58-59° when mixed with an authentic sample (m.p. 60.0-60.5°).
- i. Figures in ( ) represent % present from GLC analysis, probably accurate to  $\pm 10\%$  of the amount reported.
- j. Unreacted I present, 0.457 millimoles by infrared.
- k. Theoretical yield based on equation (1).

The results obtained suggest that three separate (and possibly simultaneous) reactions can occur when triphenylphosphine is mixed with benzenesulfonyl azide: formation of adduct, III, formation of imine, IV (possibly via III) and oxygen transfer according to equation (1).



Phenyl sulfide could be accounted for by a sulfur transfer side reaction.<sup>7</sup>



According to equation (1), the reaction of equivalent amounts of reagents should leave one-half of the sulfonyl azide (I) unreacted, three-fourths of the molar amount of azide used will appear as nitrogen, all of the triphenylphosphine (II) should appear as triphenylphosphine oxide and one-half of the azide will be converted to reduced forms of sulfur compounds. In acetonitrile, we obtained (Run 5) 45.7% of the azide unreacted, 87.7% of the calculated amount of nitrogen, 78.8% of II as phosphine oxide and 52.6% of the expected amount of sulfur as  $\text{Ph}_2\text{S}$  and  $\text{Ph}_2\text{S}_2$ . When the stoichiometric ratio of reactants was used (Run 7) virtually all (99%) of II was recovered as the oxide (this is probably fortuitous) and 68.5% of the azide was accounted for as phenyl-sulfide or disulfide. Sulfur not accounted for<sup>10</sup> may be due to the

<sup>7</sup> Although disulfides are reported to react with trivalent phosphorus compounds to give phosphine sulfides and sulfides, the reaction of  $\text{Ph}_2\text{S}_2$  with  $\text{Ph}_3\text{P}$  appears to be more complex<sup>8</sup>.

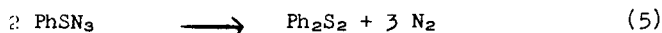
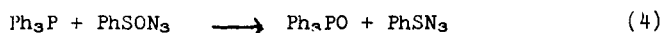
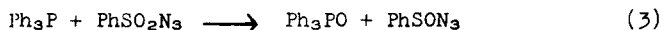
<sup>8</sup> J. I. G. Cadogan, Quart. Rev. 1962, 227.

<sup>9</sup> A. Schonberg, Chem. Ber. 68, 163 (1935).

<sup>10</sup> Elemental analysis of a total crude batch (similar to Run 8) showed no loss of sulfur. However, the GLC column employed did not separate  $\text{Ph}_3\text{PS}$  from  $\text{Ph}_3\text{PO}$ .

presence of  $\text{Ph}_3\text{PS}$  in the  $\text{Ph}_3\text{PO}$  fraction, intermediates that do not elute or that decompose on the GLC column or to the imine, IV, formed simultaneously.

A feasible mechanistic scheme can be written on the basis of a similar reaction between phosphites and sulfonyl chlorides<sup>11</sup>.



Equations (3) and (4) parallel those of Poshkus and Herweh except for the use of a phosphine instead of a phosphite and the substitution of an azide group in place of a chloride atom. The formation of phenyl disulfide from a sulfonyl azide, equation (5), has been reported in attempts to prepare these azides from sulfonyl chlorides<sup>12</sup>.

In chloroform solution (Runs 6 and 8), the results showed that generally less phosphine oxide was formed than in a comparable run in acetonitrile. Infrared evidence suggested that more imine, IV, was formed when chloroform was used as solvent. However, until good analytical methods for all the components of this complex reaction mixture are worked out, details of the proposed scheme cannot be verified. Further work along these lines is in progress.

11 A. C. Poshkus and J. E. Herweh, J. Am. Chem. Soc. 79, 4245 (1957).

12 N. Kharasch in Organic Sulfur Compounds Vol. I, p.337 Edited by N. Kharasch. Pergamon Press, 1961.