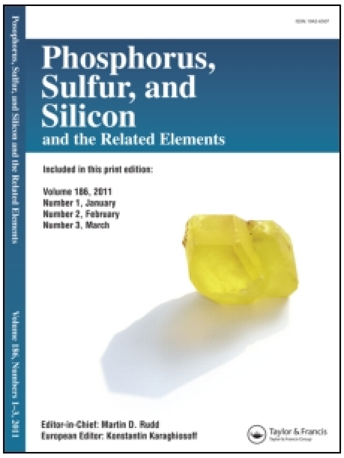

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Desulfurization of Diphenyl Disulfide with Triphenylphosphine

D. L. Middleton[a]; E. G. Samsel[a]; G. H. Wiegand[a]
[a] Department of Chemistry, Idaho State University, pocalo, Idaho, U.S.A.

To cite this Article Middleton, D. L. , Samsel, E. G. and Wiegand, G. H.(1979) 'The Desulfurization of Diphenyl Disulfide with Triphenylphosphine', Phosphorus, Sulfur, and Silicon and the Related Elements, 7: 3, 339 — 340

To link to this Article: DOI: 10.1080/03086647908077491

URL: http://dx.doi.org/10.1080/03086647908077491

Phosphorus and Sulfur, 1979, Vol. 7, pp. 339–340
0308-664X/79/0703-0339$04.50/0

SHORT COMMUNICATION

The Desulfurization of Diphenyl Disulfide with Triphenylphosphine

D. L. MIDDLETON, E. G. SAMSEL, and G. H. WIEGAND

Department of Chemistry, Idaho State University, Pocatello, Idaho 83209, U.S.A.

(*Received March 15, 1979*)

When diphenyl disulfide and triphenylphosphine are fused (neat) at 250–300°C in an inert atmosphere, diphenyl sulfide and triphenylphosphine sulfide are produced. This reaction has also been carried out under reflux in tetralin, M-Pyrol, tetradecane, and hexadecane. Probable mechanisms for the desulfurization involve nucleophilic attack of triphenylphosphine at sulfur to form a phosphonium mercaptide, followed by either nucleophilic attack of the mercaptide ion at the aromatic carbon atom bearing sulfur or formation of a phosphorane with subsequent intramolecular collapse to form products.

Although tertiary phosphines are known to readily desulfurize a host of dialkyl, arylalkyl, alkenylalkyl, and dialkenyl disulfides (Eq. 1),

$$RSSR' + R''_3P \longrightarrow RSR' + R''_3PS \qquad (1)$$

desulfurization of diaryldisulfides has not been accomplished to any appreciable extent.[1] We wish to report that when an intimate mixture of carefully dried triphenylphosphine and diphenyl disulfide are fused (neat) under dry nitrogen at 250–300°C, the disulfide is cleanly desulfurized to give diphenyl sulfide and triphenylphosphine sulfide (Eq. 2).

$$PhSSPh + Ph_3P \xrightarrow{250\text{–}300°C} PhSPh + Ph_3PS \qquad (2)$$

Distillation of the reaction mixture, after heating, at 4.0–4.5 torr and about 650 torr has afforded yields of diphenyl sulfide as high as 55 % and 79 %, respectively. It also has been possible to carry out this reaction in tetralin, M-Pyrol (N-methyl-2-pyrrolidone), tetradecane, and hexadecane under reflux.

That this reaction yields only diphenyl sulfide and triphenylphosphine sulfide was shown by TLC and GC analysis[2] of the reaction mixture resulting from the fusion of the two reactants (neat). Small amounts of triphenylphosphine oxide were formed, however, if oxygen was not rigorously excluded during the fusion, and benzenethiol and triphenylphosphine oxide were formed if moisture was present, as has been reported previously.[3] The stoichiometry of Eq. 2 was shown to be correct by GC analyses of reaction mixtures obtained at various time increments up to 2 hours at 250°C. When equimolar amounts of triphenylphosphine and diphenyl disulfide were heated together, these reactants disappeared at the same rate, while the products, diphenyl sulfide and triphenylphosphine sulfide, appeared at a rate equal to that of disappearance of the reactants. For example, after 34 minutes at 250°C diphenyl sulfide and triphenylphosphine sulfide were each formed in 17 % yields, while the reactants decreased by the same amount. After 120 minutes, the amounts of diphenyl disulfide, triphenylphosphine, diphenyl sulfide, and triphenylphosphine sulfide were, respectively, 37 %, 33 %, 63 %, and 67 %.

Although diphenyl disulfide can undergo dissociation to sulfenyl radicals under the reaction conditions, it is questionable whether the desulfurization proceeds via a radical mechanism, since products which would arise from such a process[4] were found to be absent. More likely, a nucleophilic attack of triphenylphosphine upon diphenyl disulfide to form a phosphonium mercaptide (Eq. 3)

$$Ph_3P + PhSSPh \longrightarrow Ph_3\overset{+}{P}SPh,\ PhS^- \qquad (3)$$

occurs. This process has been reported earlier,[3] and our evidence supports those conclusions. For example, a mixture of triphenylphosphine and diphenyl disulfide gave a positive onium salt test,[5] and a spot which gave a positive test was observed in the TLC analysis of the mixture after partial reaction. Also, a mixture of the two reagents in acetonitrile after standing for four days at room temperature gave an immediate intense onium salt test.

Formation of triphenylphosphine sulfide and diphenyl sulfide could then occur by subsequent nucleophilic attack of mercaptide ion at the aromatic carbon atom bearing the sulfur atom in the phosphonium cation (Eq. 4).

$$Ph_3\overset{+}{P}SPh + PhS^- \longrightarrow Ph_3PS + PhSPh \qquad (4)$$

Another pathway would be the formation of the phosphorane **I**,[3a] followed by intramolecular collapse to yield products. Phosphoranes having two sulfur atoms bound to phosphorus recently have been prepared and characterized, and in one instance a phosphorane similar to **I** was shown to be

$Ph_3P(SPh)_2$

I

in equilibrium with its corresponding phosphonium salt.[6] Although a free radical process for this latter step cannot be precluded, radicals formed would have to react faster with each other than they could dissociate.

ACKNOWLEDGEMENTS

Support of this work by grants from Research Corporation and the Idaho State University Faculty Research Committee is gratefully acknowledged.

REFERENCES AND NOTES

1. D. N. Harpp and J. G. Gleason, *J. Am. Chem. Soc.*, **93**, 2437 (1971), and references contained therein.
2. Gas chromatographic analyses were carried out using a 6 foot × $\frac{1}{8}''$ stainless steel column packed with 10% W-98 silicone rubber on Chromsorb W.
3. See, for example; a) L. E. Overman, D. Matzinger, E. M. O'Connor, and J. D. Overman, *J. Am. Chem. Soc.*, **96**, 6081 (1974);
   b) L. E. Overman and E. M. O'Connor, *J. Am. Chem. Soc.*, **98**, 771 (1976).
4. E. E. Reid, *The Organic Chemistry of Bivalent Sulfur*, Vol. III (Chemical Publishing Co., Inc., New York, N.Y., 1960), p. 370.
5. a) H. A. Potratz and J. M. Rosen, *Anal. Chem.*, **21**, 1276 (1949);
   b) for use of this method as an onium salt test see G. H. Wiegand and W. E. McEwen, *J. Org. Chem.*, **33**, 2671 (1968); W. E. McEwen, G. H. Briles, and B. E. Giddings, *J. Am. Chem. Soc.*, **91**, 7079 (1969); W. E. McEwen, W. I. Shiau, Y. I. Yeh, D. N. Schulz, R. U. Pagilagan, J. R. Levy, C. S. Symmes, Jr., G. D. Nelson, and I. Granoth, *J. Am. Chem. Soc.*, **97**, 1787 (1975).
6. B. C. Burros, N. J. De'Ath, D. B. Denney, D. Z. Denney, and I. J. Kipnis, *J. Am. Chem. Soc.*, **100**, 7300 (1978).