

also contain *p,p'*-DDT. However, these levels are too low to account for the disproportionate ratios.

In Table II are presented the results of an experiment where the exposure to *o,p*-DDT was repeated at a lower level and for a shorter time. While the excess *p,p'*- over the *o,p*-DDT is smaller under these conditions (approximately 2:1), the possible contribution from diet residuals has been reduced about tenfold. Here it is even more apparent that the explanation for the findings in both experiments cannot be attributed to the presence of contaminating sources of *p,p'*-DDT in the control diets.

In order to confirm that the *p,p'*-DDT found in fat by gas chromatography and presumed to originate from *o,p*-DDT is, in fact, *p,p'*-DDT, independent identification was made by micro infrared spectroscopy. The infrared spectrum of *p,p'*-DDT derived from fat was compared with a standard crystalline preparation of *p,p'*-DDT. Precise correspondence of the strong bands at 9.15, 9.85, 12.80, and 13.05 μ and the medium strength bands at 11.80 and 11.95 μ was observed. These bands are characteristic of the *para,para'* isomer of DDT. Comparison with a standard crystalline preparation of *o,p*-DDT showed that the bands at 9.51 and 9.62 μ characteristic for this isomer were absent.

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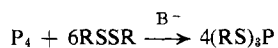
Organic Phosphorus-Sulfur Chemistry.

I. A Novel Synthesis of Tertiary Trithiophosphites

Sir:

Trialkyl trithiophosphites have been prepared by the interaction of yellow phosphorus and dialkyl disulfides at 170–210°. Since homolysis of disulfides occurs at these temperatures,² the reaction presumably involves free radicals.

We wish to report an ionic reaction of yellow phosphorus with organic disulfides in a dipolar aprotic



solvent. Unlike the thermal process,¹ which requires extended reaction time and often superatmospheric pressures, the new reaction proceeds exceptionally smoothly under very mild conditions. A general procedure is as follows. About 1 ml. of 15 *N* potassium hydroxide is added to a stirred mixture of 1 g.-atom of finely divided phosphorus and 1.5 moles of disulfide in 500 ml. of acetone at room temperature under nitrogen. The reaction is slightly exothermic and is usually complete within 30 min. The product is isolated by vacuum distillation in greater than 90% yield. If yellow phosphorus is present in excess, dark solids having high phosphorus content are formed at the end of the reac-

(1) D. R. Stevens and R. S. Spindt, U. S. Patent 2,542,370 (1951); G. D. McLeod, U. S. Patent 2,768,194 (1956); G. D. McLeod and E. L. d'Ouville, U. S. Patent 2,819,290 (1958).

(2) For a summary of the evidence, see W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y. 1962, pp. 42–45.

tion in addition to the trithiophosphite. The reaction may be carried out more conveniently by using molten phosphorus (m.p. 44°). The reaction is generally applicable to simple aliphatic and aromatic disulfides.

Group I-A bases such as hydroxides, alkoxides, mercaptides, alkyls, amides, hydrides, and phosphides are effective catalysts. Grignard reagents and calcium amide may also be used as catalysts. The reaction is rapid in dipolar aprotic solvents such as acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide; but it proceeds extremely slowly in protic solvents such as methanol or in ethereal solvents such as tetrahydrofuran.

Data indicate that the reaction most probably involves bimolecular nucleophilic substitutions at phosphorus and at sulfur. The detailed mechanism is necessarily complex, since all of the six P–P bonds in the P₄ tetrahedron must be progressively cleaved, with each cleavage producing at least one new organophosphorus intermediate.

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About the Ahrland–Chatt–Davies Classification of Rhodium and Iridium into Type (a) or (b) Central Atoms

Sir:

The Ahrland–Chatt–Davies¹ classification of the elements and ions according to their relative affinities for ligands, together with Pearson's² generalization that hard (type (a)) acids prefer to associate with hard bases, and soft (type (b)) acids prefer soft bases, has proved to be a useful tool for explaining or predicting the stability of compounds. For elements on the border line where it is not possible to assign hardness or softness unambiguously, several explanations can be found as to why an atom or ion sometimes exhibits hard and sometimes soft character. These include the ionization state,³ the steric factor,⁴ and the nature of other ligands in the complex.^{3,5}

Ahrland, Chatt, and Davies¹ classify rhodium as a type (b) element, but close to the border line of type (a), and iridium as class (b). Pearson² does not classify rhodium, and derives for iridium(III) class (a) behavior on the basis of equilibrium data⁶ for the hydrolysis of [Ir(NH₃)₅X]²⁺, where X refers to a halide ion.

Thiocyanate when coordinated to these metals may serve as a test case for this classification since this anion is known to be a difunctional ligand which can be attached to the metal cation either through the soft sulfur or the hard nitrogen atom. This property together with Pearson's rule that hard acids prefer hard bases and soft acids prefer soft bases facilitates the description of these central atoms as relatively more hard or

(1) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

(2) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(3) C. K. Jørgensen, *Inorg. Chem.*, **3**, 1201 (1964).

(4) F. Basolo, W. H. Baddley, and J. L. Burmeister, *ibid.*, **3**, 1202 (1964).

(5) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

(6) A. B. Lamb and L. T. Fairhall, *J. Am. Chem. Soc.*, **45**, 378 (1923).