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Reversible Reaction between Cyclic Phosphonite and Aromatic Cyclic Disulfide To Form a Spiro Dithiophosphorane. Observation of Reductive Elimination of a Phosphorus(V) Compound

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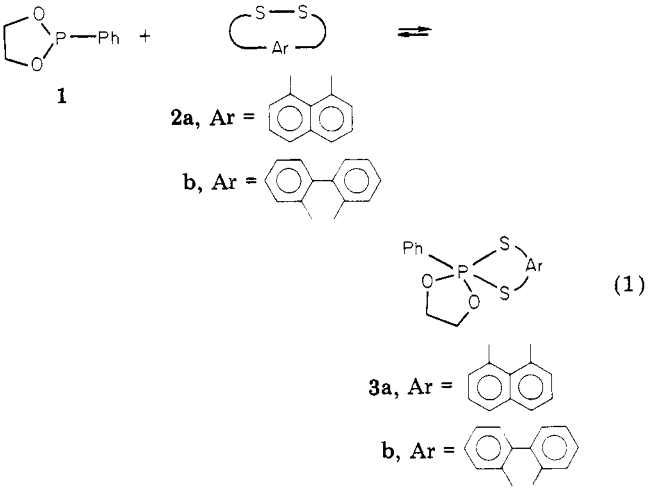
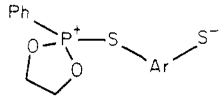
A binary system of a trivalent phosphorus compound and a disulfide has been utilized in organic syntheses.[1-3] Recently,[4] we have reported a phosphorane synthesis using diphenyl disulfide as a coupling agent. In this paper is described a novel reaction system consisting of a cyclic phosphonite, **1**, and aromatic cyclic disulfides **2** which produces a sulfur-containing phosphorane, **3**[5,6] (eq 1). This system is reversible, the direction of reaction depending on the solvent. In the reverse reaction, the spiro P(V) phosphorane[6] is reduced to phospholane **1** with elimination of disulfide **2**. Thus, it may be called a "reductive elimination" by analogy with reactions of transition-metal complexes.



The phosphoranes **3a** and **3b** were successfully isolated in crystalline form by reaction of **1** with **2a** or **2b** in acetonitrile. Both compounds were characterized as described in the Experimental Section. The chemical shifts[7] in their ^{31}P NMR spectroscopies (**3a**, −17.6 ppm; **3b**, 17.0 ppm) are strongly indicative of the dioxydithiophosphorane structure. The relatively low-field shift for **3b**, which has previously been observed for dithiooxyphosphoranes,[7] may be brought about by the strained seven-membered ring. The possibility of zwitterionic structure **4** is excluded by the ^1H NMR spectrum as well as by the solubility properties[8] for both **3a** and **3b**.



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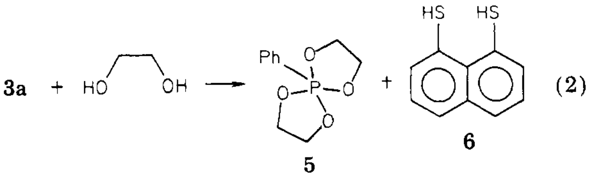
On lowering the temperature of a $CDCl_3$ solution of **3a**, the doublet signal of ^1H NMR due to OCH_2CH_2O (δ 3.95, J_{P-H} = 15 Hz) collapsed into a broad complicated multiplet (δ 3.5–4.7) below −30 °C (coalescence temperature ~0 °C). This observation suggests that **3a**, having a six-membered ring, enters into permutational isomerization[9] at room temperature. However, its structure,[10] which may be either trigonal bipyramidal (TP) or square pyramidal (SP), is not yet known. In the case of **3b** in C_6D_6, the coalescence temperature was observed around at 10–20 °C.

Additional evidence supporting structure **3a** was its conversion with an equimolar amount of ethylene glycol at room temperature to **5** and **6** (eq 2). Both products were isolated in high yields. Among the very large number of phosphoranes,[6] **3a** is the first example involving a sulfur-containing six-membered ring, and **3b** is the second example[11] containing a seven-membered ring.



In solvents other than acetonitrile, the reverse reaction was predominant, the starting materials **1** and **2** being formed at room temperature on solution of **3** in solvents.[12] The rate of the reverse reaction was increased with increasing of solvent polarity in the order of PhCN > CH_2Cl_2 > $CHCl_3$ > benzene. The rate of decomposition of **3a** was

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(4) Kimura, Y.; Miyamato, M.; Saegusa, T. *J. Org. Chem.* **1982**, *47*, 916.

(5) Recently, several phosphoranes in which one or two sulfur atoms are bonded to phosphorus have been prepared: (a) Peake, S. C.; Schmutzler, R. *J. Chem. Soc. A* **1970**, 1049. (b) Bone, S. A.; Trippett, S.; Whittle, P. *J. Chem. Soc., Perkin Trans. 1* **1977**, 80. (c) Brierley, J.; Trippett, S.; White, M. W. *Ibid.* **1977**, 273. (d) Antczak, S.; Bone, S. A.; Brierley, J.; Trippett, S. *Ibid.* **1977**, 278. (e) Eisenhut, M.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Chem. Commun.* **1973**, 144. (f) Day, R. O.; Sau, A. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3790.

(6) Review on phosphorane: (a) Ramirez, F. *Acc. Chem. Res.* **1968**, *1*, 168. (b) Ramirez, F. *Synthesis* **1974**, 90. (c) Hellwinkel, D. "Organo Phosphorus Compounds", Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 3, pp 185–339. (d) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Wiley: New York, 1976; pp 253.

(7) Oxyphosphoranes in which two sulfur atoms are bonded to phosphorus are reported to have chemical shifts ranging from δ −20 to +20. See ref 14 for an example.

(8) Both **3a** and **3b** were soluble in chloroform, dichloromethane, benzonitrile, benzene, tetrahydrofuran, pyridine, and toluene but insoluble in diethyl ether, acetone, and water. They decomposed to unknown products in dimethylformamide and dimethylacetamide.

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(12) Examined in all of the good solvents described in ref 8.

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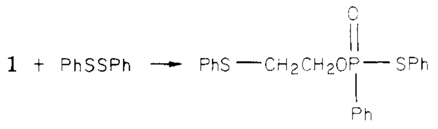
generally faster than that of **3b**. For example, in chloroform at room temperature, the change of **3a** was complete overnight, while **3b** scarcely decomposed at room temperature in 3 days. At 50 °C the half-life time of **3b** became 3 h.

Since both forward and reverse reactions were almost quantitative without any side reaction, several cycles of these two reactions could be carried out by changing solvents. The forward reaction was completed in acetonitrile, and then acetonitrile was distilled off under reduced pressure. When dichloromethane or chloroform was added to the product, the reverse reaction occurred and was soon completed. The extent of the reactions in both directions exceeded 95% (by ^1H NMR spectroscopy).

Of interest also is the effect of temperature. In acetonitrile, at temperatures above 60 °C, the equilibrium was entirely on the side of **1** and **2a**, but when the acetonitrile solution was cooled to room temperature, the equilibrium was shifted to the side of **3a** which precipitated because its solubility in acetonitrile is very low at room temperature. In comparison with **3a**, **3b** was more thermodynamically stable; **3b** remained unchanged and undesolved in acetonitrile up to 120 °C. The shift of the equilibrium to the side of **3** is due at least partly to the low solubility of **3** in the solvent. In fact, even in a polar solvent such as PhCN, **3** went to the left side because the solubility of **3** in PhCN is much higher than that in CH_3CN.

The following facts are noteworthy. (1) The reaction is quite specific for **1**. We have not observed any reaction with six other trivalent phosphorus compounds.[13] (2) When **1** was exposed to diphenyl disulfide as an acyclic analogue of **2** in acetonitrile, the regular Arbusov-type reaction took place within a few minutes at room temperature to produce **7** almost quantitatively (eq 3).[4] (3)



$$1 + PhSSPh \longrightarrow PhS{-}CH_2CH_2O\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}{-}SPh \qquad (3)$$

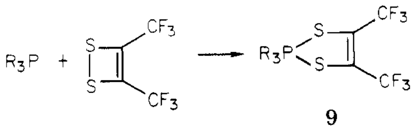
7

The backward reaction was promoted enormously by a small amount of pyridine. On the basis of these observations, a scheme of reversible reactions involving a zwitterion intermediate **4** is presented (eq 4). However,

$$\mathbf{1} + \mathbf{2} \rightleftharpoons \mathbf{4} \rightleftharpoons \mathbf{3} \qquad (4)$$

full elucidation of this interesting phenomenon, especially the thermodynamics of the system, requires further study.

In relation to the present finding, Denney et al.[14] prepared an analogous phosphorane, **9**, by the use of dithiete **8** (eq 5) but found no reverse reaction. In addition, a



8 **9**

different mode of decomposition of phosphorane has been reported by the same group.[15]

Experimental Section

Both ^1H and ^{31}P NMR spectra were measured with a Hitachi A60 spectrometer at 60 and 24 MHz, respectively. Infrared spectra were measured with a Hitachi Model 215 grating spectrometer. Melting points were determined on a Kofler apparatus which were uncorrected.

Materials. 2-Phenyl-1,3,2-dioxaphospholane (**1**),[16] 1,2-dithiaacenaphthene (**2a**),[17] and dibenzo[*c,e*]-1,2-dithiin (**2b**)[18] were prepared according to literature procedures. All solvents were purified by the distillation under nitrogen.

2-Phenylspiro[1,3,2-dioxaphospholane-2,2′-naphtho[1,8-*d,e*][1,3,2]dithiaphosphorin] (3a). An equimolar mixture of **1** (504 mg, 3 mmol) and **2a** (571 mg, 3 mmol) in acetonitrile (2 mL) was kept at room temperature with stirring for 1 h under a nitrogen atmosphere. The characteristic red color due to **2a** disappeared gradually, and pale yellow crystalline solids deposited from the solution. After 3 h the solids were isolated by filtration, washed twice with diethyl ether, and dried in vacuo. **3a**: 1.05 g (98%); mp 80–81 °C dec (to **1** and **2**); ^1H NMR (C_6D_6) δ 3.18 (d, $^3J_{P-H}$ = 15 Hz, OCH_2CH_2O, 4 H), 6.7–8.1 (m, aromatic H, 11 H); ^{31}P NMR (C_6H_6, 85% H_3PO_4 external standard) δ −17.6; IR (KBr) 3050 (ν_{ArH}), 1050 (ν_{P-O-C}) cm^{-1}. Anal. Calcd for $C_{18}H_{15}O_2PS_2$: C, 60.32; H, 4.22; P, 8.64. Found: C, 60.01; H, 4.13; P, 8.41.

2-Phenylspiro[dibenzo[*d,f*]-1,3,2-dithiaphosphepin-2,2′-[1,3,2]dioxaphospholane] (3b). A mixture of 504 mg of **1** and 649 mg of **2b** in 5 mL of acetonitrile was kept at 50 °C as above, producing a white crystalline solid, **3b**: 969 mg (84%); mp 140–143 °C dec (to an unknown polymer); ^1H NMR (C_6D_6) δ 3.32 (d, $^3J_{P-H}$ = 18 Hz, OCH_2CH_2O, 4 H), 6.8–8.1 (m, aromatic H, 13 H); ^{31}P NMR (C_6H_6, 85% H_3PO_4 external standard) δ 17.0; IR (KBr) 1060 (ν_{P-O-C}) cm^{-1}. Anal. Calcd for $C_{20}H_{17}O_2PS_2$: C, 62.48; H, 4.46; P, 8.06. Found (very hygroscopic): C, 62.08; H, 4.64; P, 7.91.

Reaction of 3a with 1,2-Ethanediol. Under a nitrogen atmosphere 358 mg (1.0 mmol) of **3a** was added portionwise into a solution of 62 mg (1.0 mmol) of 1,2-ethanediol in 2 mL of benzonitrile with stirring during 15 min at room temperature. Diethyl ether (15 mL) was then added to the mixture, and the system was maintained at −30 °C, precipitating out white crystalline solids which were filtered and dried to give **4**: 210 mg (92%); mp 121 °C (lit.[6] mp 123 °C). Then, the filtrate was evaporated to dryness at reduced pressure, and the residue was washed twice with ethanol to give yellow crystals, 177 mg (92%). They were essentially pure 1,8-dimercaptonaphthalene [mp 115 °C (lit.[17] mp 113–114 °C)], its IR spectrum being identical with the one of the authentic dithiol.

Reverse Reaction of 3. A typical example is as follows. Under a nitrogen atmosphere 0.2 g of **3a** was placed in an NMR sample tube (10ϕ in diameter) and dissolved in 2 mL of $CDCl_3$ at room temperature. During the dissolution, the characteristic red color due to **2a** began to appear. The ^{31}P NMR spectrum taken immediately after the complete dissolution of **3** showed two signals at δ −17.7 (due to **3a**) and 162 (due to **1**), both signals being of the similar intensity. After 30 min, the former disappeared, and the latter became strong in the dark red system. The reverse reaction was also observed by ^1H NMR at a lower concentration. In an NMR tube (5ϕ) 10 mg of **3a** was allowed to dissolve in 0.3 mL of $CDCl_3$ as above and was submitted to ^1H NMR measurement. The doublet signal due to $O{-}CH_2CH_2{-}O$ of **3a** turned into the sharp multiplet of **1** at a much slower rate. When the sample was allowed to stand overnight at room temperature, the spectrum [δ 3.9–4.1 (several sharp signals), 7.0–8.2 (m)] was about the same as that of the mixture of **1** and **2a**. In a similar manner, the reverse reaction of **3b** was carried out at 50 °C.

Registry No. **1**, 1006-83-3; **2a**, 209-22-3; **2b**, 230-26-2; **3a**, 86853-79-4; **3b**, 86853-80-7; **5**, 34736-73-7; **6**, 25079-77-0.

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[13] Those examined were triethyl phosphite, tri-*n*-butylphosphine, triphenylphosphine, 2-methoxy-1,3,2-dioxaphospholane, and 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaphospholane, etc.

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