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REDUCTION WITH TRICHLOROSILANE. VI. DESULFURATION OF PHOSPHINE SULFIDES AND PHOSPHOROTHIONATE WITH TRICHLOROSILANE

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It was found that trisubstituted phosphine sulfides and triphenyl phosphorothionate were reduced to the phosphines and triphenyl phosphite with trichlorosilane under γ irradiation.

Trichlorosilane (TCS) has been known to reduce aliphatic esters,[1,2] lactones,[3] and acetals[4] to aliphatic ethers, cyclic ethers, and ethers, respectively, under free radical conditions, and to reduce N,N-disubstituted amides[5] to tert-amines under refluxing. TCS also has been known to reduce phosphine oxides[6,7] to phosphines by refluxing. In the present communication the novel desulfuration of trisubstituted phosphine sulfides and phosphorothionate with TCS under γ irradiation is described.

Degassed TCS (1 mmol) was added via a vacuum line to a degassed solution of phosphine sulfide or phosphorothionate (0.1 mmol) in benzene (0.5 ml) in a glass tube, the open end of which was then sealed. The tube was irradiated with a ^{60}Co source. The results of the products by the glpc (FID) analysis are shown in Table 1. Effects of the

Table 1. Reduction of Phosphine Sulfides and Phosphorothionate with Trichlorosilane

Reactant	Dose (rad)	Yield (%) of desulfuration product	Recovery (%)
$Ph_3P=S$	5.6×10^7	34	59
$n\text{-}Bu_3P=S$	5.0×10^7	21	79
$(PhO)_3P=S$	5.6×10^7	10	75

dose and molar ratio of TCS/sulfide on the desulfuration reaction of triphenyl phosphine sulfide are shown in Figs. 1 and 2, respectively. The results indicate the greater molar ratio of TCS/sulfide and more dose seem to favor desulfuration. The G value (number of molecules formed per 100 eV of energy absorbed) calculated from Fig. 1 (a) is 1.7. This result suggests that no chain reaction occurs in this reaction. The same mixture (1 mmol of TCS, 0.1 mmol of the phosphine sulfide, and 0.5 ml of benzene), under the irradiation of 4.8×10^7 r, gave 0.8 mmol of recovered TCS, 0.024 mmol of the phosphine, 0.01 mmol of tetrachlorosilane, and 0.02 mmol of hydrogen. Stoichiometric relation between TCS and the phosphine sulfide cannot be observed, although in the reductions of esters,[1,2] lactones,[3] acetals,[4] and phosphine oxides[6] with TCS such relation were observed.

Mislow et al.[8] proposed eq. 1 for the stereospecific desulfuration of optically

$$abcP{=}S + Cl_3SiSiCl_3 \longrightarrow abc\overset{+}{P}{-}\underset{\underset{^{-}SiCl_3}{\uparrow}}{S}{-}SiCl_3 \longrightarrow abcP + Cl_3SiSSiCl_3 \qquad (1)$$

active phosphine sulfides with hexachlorodisilane.

In the present communication the interaction of phosphine sulfides and phosphorothionate with hexachlorodisilane which is produced in the reaction mixture by γ irradiation of TCS as shown in eq. 2 is more understandable than the direct interaction with

$$2HSiCl_3 \xrightarrow{\sim\!\!\sim} Cl_3SiSiCl_3 + H_2 \qquad (2)$$

TCS. All the results mentioned above, namely, approximately equimolar relation between phosphine and hydrogen, no chain reaction, and no stoichiometric relation between phosphine production and TCS consumption observed in the present communication support this assumption.

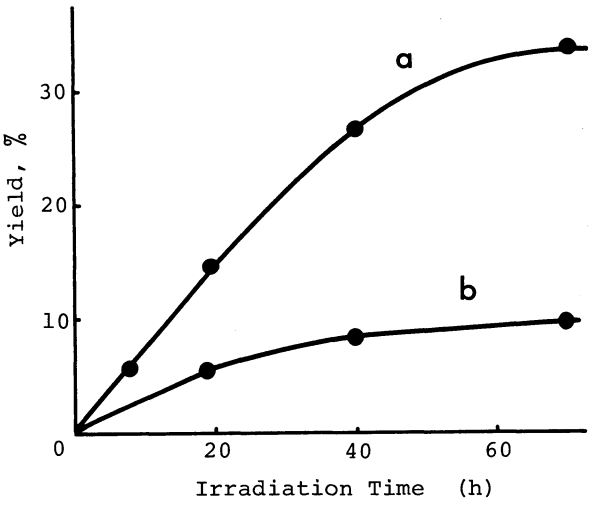

Fig. 1 Effect of the dose on the desulfuration reaction of triphenyl phosphine sulfide (a) and triphenyl phosphorothionate (b). TCS/sulfide = 10, dose rate = 8.0×10^5 r/h.

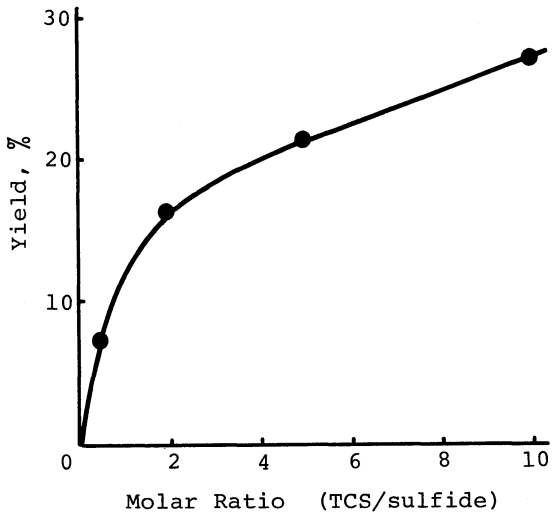

Fig. 2 Effect of the molar ratio of TCS/sulfide on the desulfuration reaction of triphenyl phosphine sulfide. Total dose = 5.3×10^7 r.

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