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Reaction of Thiocarbonyl Compounds with Tributylphosphine[1]

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Synopsis. The reaction of thiobenzophenone (**1**) with tributylphosphine (**3**) gives an oligomer at room temperature, but it gives tributylphosphine sulfide (**4**), 1,1,2,2-tetraphenylethane, and tetraphenylethylene (**6**) at 100 °C. The reaction of thiofluorenone with **3** gives **4**, bifluorenylidine (**8**), and bifluorenyl (**9**) at room temperature. These possible mechanisms are discussed by carbene intermediates.

The deoxygenation and desulfurization of organic compounds by trivalent phosphorus compounds is well known.[2] Some of these reactions may proceed *via* carbene intermediates, but there have been only a few attempts to identify carbenes in the reaction with trivalent phosphorus compounds.[3] The reaction of benzophenone with triisopropyl phosphite to give a mixture of diisopropyl benzhydrylphosphonate, triisopropyl phosphate, tetraphenyl–ethylene, and propylene, probably proceeds *via* an ionic path.[4]

On the other hand, it was postulated[5] that hexafluoroacetone reacts with phosphite *via* a carbene intermediate to give trialkoxybis(trifluoromethyl)methylene phosphorane. The reaction of cyclic 1,2-thiocarbonates with trimethyl phosphite gives olefinic product, together with a small amount of orthoformate derivative formed by carbene reaction.[6] Also the formation of fluorene, bifluorenyl, and tribiphenylenepropane by the reaction of fluorene with tributylphosphine in hydrogen donating solvents[7] suggests the intermediacy of carbene.

The thiophilicity of trivalent phosphorus compounds should be higher than the oxophilicity in the reaction of ketonic compounds, and we reported previously the facile reaction of thiobenzophenone with phosphite.[8] This paper deals with evidence for carbene formation during the desulfurization of some thioketones by phosphine, and their higher reactivities.

Results and Discussion

No reaction of thiobenzophenone (**1**) with triphenylphosphine (**2**) occurred even at 160 °C for 24 h. An apparent reaction of **1** on addition of tributylphosphine (**3**) proceeds at room temperature, but the reaction gave only an oligomer of **1** in good yield without desulfurization. When the oligomer was dissolved in inert solvents, the dark blue color of the monomer was reappeared, and it strongly suggests that the formation of the oligomer is reversible.

The acid-catalyzed dimerization and trimerization of thioaldehydes, dialkyl thioketones, and alkyl aryl thioketones are well known.[9,10] On the other hand, cyclization of monothiobenzil and dithiobenzil derivatives to four-membered ring including one or two sulfur atoms was recently reported.[11,12]

But only a few report was known concerning the formation of polymeric thiobenzophenone.[13] This is the first report on the reversible formation of oligomer.

$$n\text{-Ph}_2\text{CS}(\mathbf{1}) \xrightarrow{n\text{-Bu}_3\text{P}} (\text{Ph}_2\text{CS})_n \qquad (n=2 \text{ or } 3)$$

However, the reaction of **1** with **3** under N_2 at 100 °C for 10 h gives mainly tributylphosphine sulfide (**4**, 89%), 1,1,2,2-tetraphenylethane (**5**, 65%), and tetraphenylethylene (**6**, 28%). The formation of **5** and **6** suggests the intermediacy of carbene in the reaction, i.e., these products may be produced by the coupling of diphenyl carbene or diphenylmethyl radical arising from abstraction of sulfur from **1** by phosphine, followed by hydrogen atom abstraction.

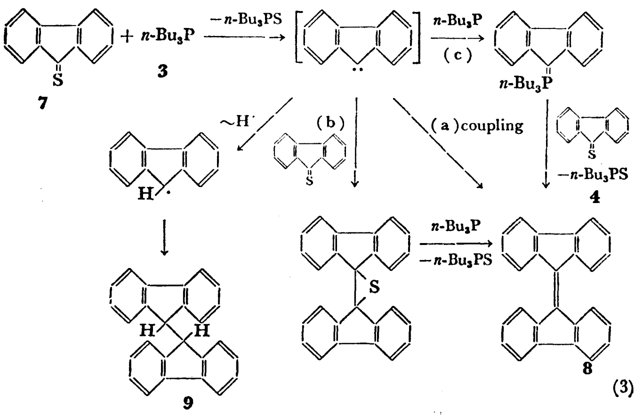
$$\underset{\mathbf{1}}{\text{Ph}_2\text{CS}} + \underset{\mathbf{3}}{n\text{-Bu}_3\text{P}} \rightarrow \underset{\mathbf{4}}{n\text{-Bu}_3\text{PS}} + \underset{\mathbf{5}}{(\text{Ph}_2\text{CH-})_2} + \underset{\mathbf{6}}{\text{Ph}_2\text{C=CPh}_2} \tag{2}$$

The photochemical reaction of diphenyldiazomethane in some solvents gives benzophenonazine and tetraphenylethane, those yields depending upon solvents used[14] where the formed diphenylcarbene couples with starting material to give benzophenonazine, and/or abstracts hydrogen atom from the solvent followed by coupling to give tetraphenylethane. In our present reaction, the formed carbene may react with thiobenzophenone to give tetraphenylethylene, and/or may abstract a hydrogen atom from phosphine followed by coupling to give tetraphenylethane. (See Scheme 1).

The reaction of thiofluorenone (**7**) with tributylphosphine (**3**) proceeds at room temperature. The products are mainly **4** (95%), bifluorenylidine (**8**, 63%), and bifluorenyl (**9**, 23%). It is known that the reaction of fluorenone with tributylphosphine at 155—165 °C for 76 h affords bifluorenylidene (40%),[7] and that the photochemical reaction of diazofluorene in cyclohexane affords bifluorenyl (24%).[14] Hence following reaction pathways are conceivable for our reaction of thiofluorenone to form **4**, **8** and **9**.

Fluorenyl carbene abstracts a hydrogen atom from tributylphosphine (**3**), then couples each other to form bifluorenyl (**9**), because **9** was obtained even in the reaction in neat. Three pathways are concievable for the formation of **8**, i.e., (i) coupling of two molecules of fluorenyl carbene (path a), (ii) formation of episulfide followed by desulfurization (path b), and (iii) formation of phosphorane followed by Wittig reaction with thiobenzophenone (path c).[3b,15] Phosphines have been utilized as carbene acceptors,[16] but path c is less probable in this reaction because of the little effect on the product distribution by adding benzaldehyde to the reaction mixture.[17] The desulfurization from episulfide by phosphine and coupling of carbene is very fast, so that both paths a and b cannot be ruled out. The analogous reaction mechanism may be applicable for the reaction of **1** with **3**.

The facile reaction of thiofluorenone with tributylphosphine at room temperature for 3 h in comparison



Scheme 1.

with the reaction of thiobenzophenone, which required 10 h reaction at 100 °C, is attributable to the driving force due to the stability of the formed carbene; *i.e.* fluorenyl carbene may be more stable than diphenyl carbene in view of its resonance forms. Gas phase reaction of diphenyl carbene gives about 30% yield of fluorene.[18)]

The thiophilicity of trivalent phosphorus compounds towards thiocarbonyl compounds surpasses the oxophilicity towards the corresponding carbonyl compounds.[8,19)] The reaction of **7** with **3** proceeds at room temperature, while the reaction of fluorenone with **3** necessitates the higher temperature of 155—165 °C,[7)] and the reaction of benzophenone with triisopropyl phosphite needs more drastic conditions, *i.e.*, 72 h reaction at 170 °C, while those of thiobenzophenone with trialkyl phosphites can proceed at 100 °C for 10 h.[4,8)]

Experimental

All melting points and boiling points were uncorrected. A Yanagimoto GCG 550F and Hitachi K53 gas chromatographs were used with a 1 m×3 mm column packed with Silicone GE SE 30 (8%) coated on Chromosorb W. IR spectra were measured by a Perkin-Elmer Model 337 spectrophotometer. NMR spectra were measured by a JNM-C60-HL NMR instrument of Japan Optics Laboratory. Mass spectra were measured by a Hitachi RMS-4 mass spectrometer.

Reaction of Thiobenzophenone with Tributylphosphine. The reaction of thiobenzophenone (**1**) with excess tributylphosphine (**3**) (*ca.* 3 equivalents) at room temperature for 10 min gave oligomer of **1** (quantitative), which was dissociated to its monomer on dissolving in benzene and chloroform, mp 130 °C.

The NMR spectra show only aromatic protons (δ=7.18—7.72), and IR spectra show C-S absorption (651 cm^{-1}), but no C=S absorption. The reported mp of polymeric thiobenzophenone is 146.5 °C[13)]

The mixture of **1** (0.67 g) and **3** (1.7 g) was heated under N_2 for 10 h at 100 °C. The products were tetraphenylethylene (28%), tetraphenylethane (65%), and tributylphosphine sulfide (89%), which were identified by NMR, IR, VPC. and mp by comparison with the authentic samples. In addition to these compounds, other two minor unidentified products were obtained.

*Reaction of Thiofluorenone (**7**) with Tributylphosphine(**3**).* The reaction of thiofluorenone (**7**) with **3** was carried out for 3 h at room temperature. Bifluorenylidine (63%), bifluorenyl (23%), and tri-*n*-butylphosphine sulfide (95%) were separated from the reaction mixture by TLC (Kiesel gel G/benzene) and identified by VPC analysis by comparison with the authentic samples. The formation of 9-diphenylenephenanthrone was also observed, and was identified by IR (KBr, C=O, 1700 cm^{-1}), NMR ($CDCl_3$, δ=6.2—7.9, aromatic protones), mp 201.5—203 °C (recrystallized from petroleum ether–benzene), and elemental analysis. Found: C, 90.90; H, 5.06%. Calcd for $C_{26}H_{16}O$: 90.70; H, 5.13%.

Reaction of **1** *with* **2**. A mixture of **1** (0.71 g) with **2** (3.71 g) was heated in a sealed tube under N_2 for 24 h at 160 °C, but no reaction product was observed by VPC analysis.

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