Tetrahedron. Vol. 30, pp. 3709 to 3712. Pergamon Press 1974. Printed in Great Britain

REACTION OF THIOBENZOPHENONE WITH TRIALKYL AND TRIARYL PHOSPHITES[1]

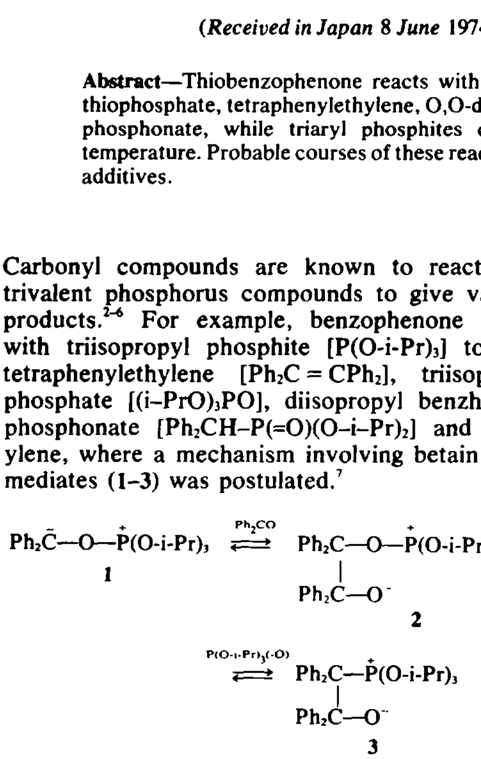
Y. OGATA,* M. YAMASHITA and M. MIZUTANI

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

(*Received in Japan* 8 *June* 1974; *Received in UK for publication* 19 *June* 1974)

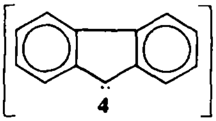
Abstract—Thiobenzophenone reacts with trimethyl and triethyl phosphites at 100° to give trialkyl thiophosphate, tetraphenylethylene, O,O-dialkyl S-benzhydryl thiophosphate, and dialkyl benzhydrylphosphonate, while triaryl phosphites do not react with thiobenzophenone even at elevated temperature. Probable courses of these reactions are discussed on the basis of the products and effect of additives.

Carbonyl compounds are known to react with trivalent phosphorus compounds to give various products.[2-6] For example, benzophenone reacts with triisopropyl phosphite [$P(O\text{-}i\text{-}Pr)_3$] to give tetraphenylethylene [$Ph_2C=CPh_2$], triisopropyl phosphate [$(i\text{-}PrO)_3PO$], diisopropyl benzhydrylphosphonate [$Ph_2CH\text{-}P(=O)(O\text{-}i\text{-}Pr)_2$] and propylene, where a mechanism involving betain intermediates (1–3) was postulated.[7]



$$\underset{\mathbf{1}}{Ph_2\overset{-}{C}\text{—}O\text{—}\overset{+}{P}(O\text{-}i\text{-}Pr)_3} \overset{Ph_2CO}{\rightleftharpoons} \underset{\mathbf{2}}{\begin{array}{l}Ph_2C\text{—}O\text{—}\overset{+}{P}(O\text{-}i\text{-}Pr)_3\\ \;|\\ Ph_2C\text{—}O^-\end{array}} \overset{P(O\text{-}i\text{-}Pr)_3(\text{-}O)}{\rightleftharpoons} \underset{\mathbf{3}}{\begin{array}{l}Ph_2C\text{—}\overset{+}{P}(O\text{-}i\text{-}Pr)_3\\ \;|\\ Ph_2C\text{—}O^-\end{array}}$$

In contrast, fluorenone reacts with tributylphosphine to give bifluorenylidene, while it gives fluorene, bifluorenyl and tribiphenylpropane in a solvent acting as a hydrogen source. The intervention of carbenoid species 4 has been suggested.[8]



4

Although the reactions of trivalent phosphorus compounds with carbonyl compounds have been often reported, there are only a few reports on the reaction of trivalent phosphorus compounds with thiocarbonyl compounds which should be more reactive.[9,10] The present paper is a summary of data on the reaction of thiobenzophenone with some phosphites.

RESULTS

A mixture of thiobenzophenone (**5**) and triethyl phosphite (**6**) on heating (Experimental) at 100° yielded triethyl thiophosphate (**7**), tetraphenylethylene (**8**), O,O-diethyl S-benzhydryl thiophosphate (**9**), and diethyl benzhydrylphosphonate (**10**).

$$\underset{\mathbf{5}}{Ph_2CS} + \underset{\mathbf{6}}{P(OEt)_3} \longrightarrow$$

$$\underset{\mathbf{7}\,(64\%)}{(EtO)_3PS} + \underset{\mathbf{8}\,(5\%)}{Ph_2C{=}CPh_2} + \underset{\mathbf{9}\,(15\%)}{Ph_2CHS\text{—}P({=}O)(OEt)_2}$$

$$+\underset{\mathbf{10}\,(66\%)}{Ph_2CH\text{—}P({=}O)(OEt)_2} \qquad (1)$$

The yields of **9** and **10** varied with runs, but that of **7** and **8** were nearly constant. Our attempted trapping experiments of diphenylcarbene with cyclohexene, dimethyl maleate, ethyl alcohol and cumene all failed. To test the intermediary formation of ylide, the reaction was carried out in the presence of benzaldehyde or acetophenone, but the olefins expected from the Wittig reaction of ylide $Ph_2C=P(OEt)_3$, e.g., 1,1,2-triphenylethylene, could not be detected. Hence, the ylide is not an intermediate in this reaction.

The gaseous product evolved in this reaction was analyzed by GLC, but ethylene, ethane, butane, methyl alcohol, and ethyl alcohol were not detected. Further, the gas was passed through a CCl_4 solution of bromine, but no ethylene bromide was formed, so that ethylene, if formed, would soon be polymerized.

When a mixture of **9** and **6** was heated in a sealed tube at 100° no **10** was produced, hence **10** is not a secondary product from **9**.

$$\underset{\textbf{9}}{Ph_2CHS{-}P({=}O)(OEt)_2} + \underset{\textbf{6}}{P(OEt)_3}$$
$$\underset{\textbf{10}}{Ph_2CH{-}P({=}O)(OEt)_2} + \underset{\textbf{7}}{SP(OEt)_3} \qquad (2)$$

The reaction of diethyl phosphite with thiobenzophenone in a sealed tube at 100° affords no **9**, and the reactants were recovered; hence **9** is not produced by this reaction.

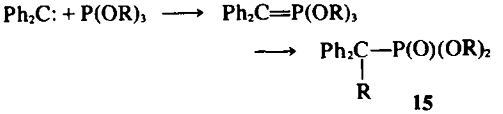
If α-hydrogen atom of **9** and **10** would come from alkyl group of the phosphite (Eq 1), the hydrogen transfer from alkyl group might be retarded in trimethyl phosphite, because the ease of α-hydrogen abstraction should be $\mathrm{Me} \ll \mathrm{Et}$. To test this possibility, trimethyl phosphite (**11**) and **5** were heated in a sealed tube at 100°. The products were trimethyl thiophosphate (**12**, 31%), **8** (5%), O,O-dimethyl S-benzhydryl thiophosphate (**13**, 16%), and dimethyl benzhydrylphosphonate (**14**, 51%), which were the products quite similar to those from triethyl phosphite (**6**).

The reaction of thiobenzophenone with triphenyl phosphite was attempted at 120° but the reactants were recovered, probably because triphenyl phosphite bears a P atom of weaker nucleophilicity and no H atom to be abstracted. Also no reaction occurred even at 165° with a mixture of **5** and tri(p-methoxyphenyl) phosphite, in which the nucleophilicity of the P atom would be higher than that of triphenyl phosphite.

DISCUSSION

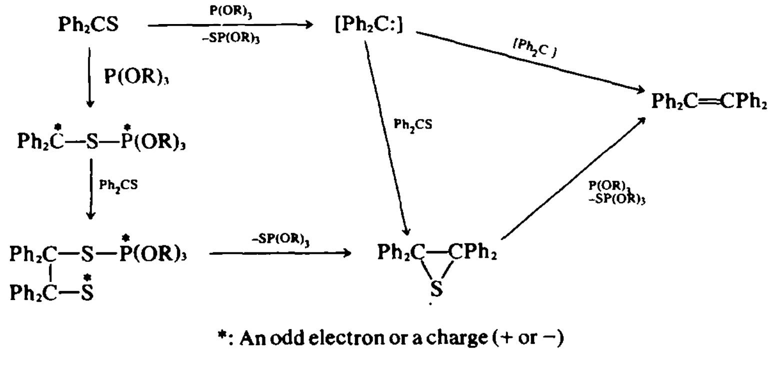
It is not clear whether phosphite attacks the thiocarbonyl carbon or the S atom. Trivalent phosphorus compounds may be a thiophilic reagent in view of the following facts, and hence the reaction of trialkyl phosphite with thiobenzophenone may proceed more readily than that with benzophenone. (i) Triphenyl and tributyl phosphines do not react with molecular oxygen in the absence of initiators, while they react exothermally with elemental sulfur at room temperature. (ii) Deoxygenation of *cis*-epoxides with trivalent phosphorus compounds gives *trans*-olefins, so that the P atom must attack on a C atom of epoxide to induce the inversion of configuration. In contrast, the desulfurization of *cis*-episulfides with trivalent phosphorus compounds gives *cis*-olefins, hence a direct attack on the S atom is probable in the latter case.[11,12] (iii) The energy level difference between the ground state and the excited state of benzophenone is 74 kcal/mol for the first singlet level (S_1) and 69 kcal/mol for the first triplet level (T_1). Whereas, thiobenzophenone has values of 40-42 kcal/mol for S_1 and T_1, so that a lone pair electron of phosphorus is more easily transferred to the thiocarbonyl carbon of thiobenzophenone because of its low LVMO energy level.

If the P atom of phosphite attacks directly on the S atom of thiobenzophenone to abstract it, diphenyl carbene would be produced. But no diphenylcarbene was trapped by olefins (e.g., cyclohexene) and no diphenylmethane was formed on addition of hydrogen sources such as cyclohexene or ethyl alcohol. This is probably due to the higher reactivity of thiobenzophenone and trialkyl phosphite with diphenylcarbene than that of trapping reagents. In fact, it was reported[13] and it was confirmed in our hands that diphenylcarbene prepared from diphenyldiazomethane can easily add to thiobenzophenone, where the product was tetraphenylethylene sulfide, which was desulfurized easily by trialkyl phosphite to give tetraphenylethylene (Experimental). If diphenylcarbene would add to trialkyl phosphite, it should give trialkoxyphosphorane, which should rearrange to give phosphonate.[14,15] In our experiments, the rearranged product **15** was not formed by the reaction of phosphites with thiobenzophenone; therefore, possibility of Eq 3 can be ruled out.



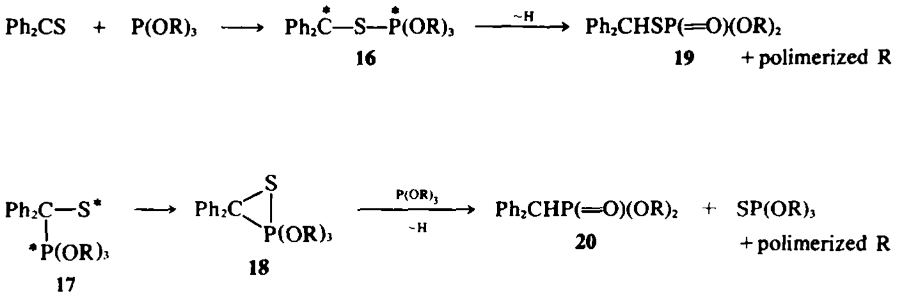
$$Ph_2C{:} + P(OR)_3 \longrightarrow Ph_2C{=}P(OR)_3 \longrightarrow \underset{\textbf{15}}{Ph_2\underset{\displaystyle R}{\underset{|}{C}}{-}P(O)(OR)_2} \qquad (3)$$

These observations suggest that a mechanism involving betain and/or carbene intermediates followed by the formation of tetraphenylethylene sulfide which is easily desulfurized by trialkyl phosphite is reasonable for the formation of tetraphenylethylene.



*: An odd electron or a charge (+ or −)

The mechanism of formation of **9** and **10** is still obscure, but a tentative mechanism is conceivable as follows.



R: Me, Et
*: An odd electron or a charge (+ or −)

It is still unknown whether the primary intermediates **16** and **17** are radical or zwitterion and how the alkyl group of the phosphite is eliminated to give **19** and **20**. We observed that the hydrogen transfer from alkyl group of phosphite to the benzhydryl carbon did occur, but that the shift of alkyl group such as the rearrangement observed in Arbuzov reaction did not occur. This supports a scheme involving a radical intermediate, since the migration of alkyl carbonium ion would occur in an ionic intermediate such as that of Arbuzov reaction. The hydrogen transfer and then alkyl group elimination should give olefins, but the expected ethylene was not detected in the case of triethyl phosphite. Nascent ethylene from triethyl posphite and methylene from trimethyl phosphite may be polimerized to tarry materials.

No reaction of triphenyl and tri(*p*-methoxyphenyl) phosphites with thiobenzophenone is presumably ascribed to the absence of an H atom to be abstracted and the lower nucleophilicities of aryl groups [σ_I is +0·25 for OMe, +0·27 for OEt, and +0·39 for OPh, and the inductive effect is triplicated in $(RO)_3P$].[16]

EXPERIMENTAL

IR and NMR spectra were recorded by a Perkin-Elmer Model 337 infrared spectrophotometer and a JNM-C60-HL spectrometer, respectively. The products were analyzed by a Yanagimoto gas chromatograph with flame ionization dector, Model GCG 550F using stainless steel column of 1·5 m packed with 8% Silicone GE SE-30 on 80–100 mesh silanized Chromosorb W at a flow rate 25 ml/min of N_2. The temperature were: column, 80–290°; injection, 220°; detector, 250°. For TLC separation, Kieselgel G nach Stahl (type 60) of Merck was used.

Materials. Thiobenzophenone was prepared by the reaction of benzophenone with hydrogen sulfide in EtOH,[17] and purified before use by distillation, column chromatography (silica gel-benzene), and then recrystallization from light petroleum under CO_2 (m.p. 49–50°). Phosphites were prepared by the reaction of PCl_3 with the corresponding alcohols or phenols; b.p: $P(OMe)_3$, 56° (101 mm); $P(OEt)_3$, 61–63° (25 mm);[18] $P(OPh)_3$, 210–220° (5 mm); and $(p\text{-}MeOC_6H_4O)_3P$, 250–260° (4 mm).[19]

The reaction of thiobenzophenone (**5**) *with triethyl phosphite* (**6**). Thiobenzophenone (0·119 g) and triethyl phosphite (0·400 g, 4 equivalents) were placed in a thick glass tube, and after the air was replaced by N_2 gas, the tube was sealed. The mixture was heated at 100° for 10 h, producing yellow liquid. The products were separated by TLC (silica gel-benzene). Products **7** and **8** were identified by the comparison of their IR and GLC peaks with the authentic specimen. Products **9** and **10** were identified by means of NMR and IR spectra. **9**: NMR (CCl_4), δ (ppm) = 7–7·5 (multiplet, 10 H), 5·57 (doublet, 1 H, J_{PH} = 11·3 Hz), 3·83 (multiplet, 4 H), 1·12 (triplet, 6 H, J = 7 Hz). IR, 1250 cm^{-1} (ν_{P-O}); **10**:NMR ($CDCl_3$), δ (ppm) = 7·1–7·6 (multiplet, 10 H), 4·40 (doublet, 1 H, J_{PH} = 24·6 Hz), 3·90 (multiplet, 4 H), 1·10 (triplet, 6 H, J = 7 Hz), IR, 1245 cm^{-1} (ν_{P-O}).

The gas in the tube was analyzed by GLC using a 1·5 m column of 30% (95% Di-n-butyl maleate-5% β,β'-oxydipropionitrile) on 40–60 mesh silanized C-22 and a 2 m column of Silica gel 60–80 mesh. Ethane, ethylene, butane, methyl alcohol, and ethyl alcohol were not detected.

The reaction of thiobenzophenone (**5**) *with trimethyl phosphite* (**11**). A mixture of **5** (0·193 g) and **11** (0·486 g, 4 equivalents) was heated at 100° for 10 hr in a sealed tube. The mixture was separated by TLC. Products **8** and **12** were identified by means of IR and GLC by comparison with authentic samples. Products **13** and **14** were identified by NMR and IR spectra. **13**: NMR ($CDCl_3$), δ (ppm) = 7·2–7·6 (multiplet, 10 H), 5·61 (doublet, 1 H, J_{PH} = 12 Hz), 3·54 (doublet, 6 H, J_{PH} = 12 Hz), IR, 1255 cm^{-1} (ν_{P-O}); **14**: NMR ($CDCl_3$), δ (ppm) = 7·2–7·6 (multiplet, 10 H), 4·43 (doublet, 1 H, J_{PH} = 26 Hz), 3·53 (doublet, 6 H, J_{PH} = 11 Hz), IR, 1240 cm^{-1} (ν_{P-O}).

Reaction of thiobenzophenone (**5**) *with triphenyl or tri*(p-*methoxyphenyl*) *phosphite.* A mixture of **5** (0·508 g) and triphenyl phosphite (3·26 g, 4 equiv) was heated at 120° for 10 h, but the reaction did not proceed. The similar reaction of **5** with tri(*p*-methoxyphenyl) phosphite at 165° for 30 h gave also the recovered reactants.

The reaction of diphenyldiazomethane with thiobenzophenone.[13] A petroleum ether soln of diphenyldiazomethane[20] was added to thiobenzophenone (1·53 g) in petroleum ether at room temp until the color of thiobenzophenone disappeared. Colorless crystals were precipitated immediately. Recrystallization from petroleum ether-chloroform afforded tetraphenylethylene sulfide, m.p. 185° (lit.[13] 175° and 178°). The product was confirmed by IR, NMR, and UV spectra, and detection of S by the sodium melting technique.

The reaction of tetraphenylethylene sulfide with triethyl phosphite. Tetraphenylethylene sulfide (0·067 g) was heated with triethyl phosphite (0·073 g) at 80° for 5 hr. The products were identified as tetraphenylethylene (m.p. and m.m.p. 228–230°) and triethyl thiophosphite by means of their GLC peaks in comparison with the authentic specimen.

REFERENCES

[1] Contribution No. 201

[2] V. A. Kukhtin and K. M. Kirillova, *Zh. Obshch. Khim.* **31**, 2226 (1961); *Chem. Abstr.* **56**, 3507 (1962)

[3] B. A. Arbuzov and V. M. Zoroastrova, *Izvest. Akad. Nauk.* 1030 (1960); *Chem. Abstr.* **54**, 24627 (1960)

[4] V. A. Ginsburg and A. Y. Yakubovich, *Zh. Obshch. Khim.* **30**, 3979 (1960); *Chem. Abstr.* **55**. 22099 (1961)

[5] F. Ramirez, H. Yamanaka and O. H. Basedow, *J. Am. Chem. Soc.* **83**, 173 (1961)

[6] I. A. Degen, D. G. Saunders and B. P. Woodford, *Chem. & Ind.* **19**, 267 (1969)

[7] A. C. Poshkus and J. E. Herweh, *J. Org. Chem.* **29**, 2567 (1964)

[8] I. J. Borowitz, M. Anschel and P. D. Readio, *Ibid.* **36**, 553 (1971)

[9] D. Horton and C. G. Tindall Jr., *Ibid.* **35**, 3558 (1970)

[10] T. Mukaiyama, H. Nambu and M. Okamoto, *Ibid.* **27**, 3651 (1962)

[11] N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.* **81**, 578 (1959)

[12] D. B. Denny and M. J. Boskin, *Ibid.* **82**, 4736 (1960)

[13] H. Staudinger and J. Siegwart, *Helv. Chim. Acta* **3**, 833 (1920)

[14] W. J. Middleton and W. H. Sharkey, *J. Org. Chem.* **30**, 1384 (1965)

[15] E. J. Corey and G. Märkl, *Tetrahedron Letters* 3201 (1967)

[16] M. Charton, *J. Org. Chem.* **29**, 1222 (1964)

[17] B. F. Gofton and E. A. Braude, *Org. Syn.* Coll. Vol. IV, 927 (1963)

[18] A. H. Ford-Moore and B. J. Perry, *Ibid.* Coll. Vol. IV, 955 (1963)

[19] H. B. Gottlieb, *J. Am. Chem. Soc.* **54**, 748 (1932)

[20] L. I. Smith and K. L. Howard, *Org. Syn.* Coll. Vol. III, 351 (1955)