Metal Phosphinylides and Phosphinothioylides. IV.[1] Reactions with Tetrahydrofuran

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Diphenylphosphinic (**1**) and diphenylphosphinothioic chlorides (**2**) were allowed to react in tetrahydrofuran (THF) in the presence of metal or metal salts at 120—150 °C. In the cases of lithium and magnesium, $[Ph_2PX]^-$ (X=O, S) thus formed attacked the α-carbon of THF to give ring-opening products, which were produced by deoxygenation, sulfurization, and reaction with **1** and **2**. In the cases of iron, copper, and their salts, *O*-4-chlorobutyl diphenylphosphinate (**12**) and diphenylphosphinothioate (**13**) were obtained in a homolytic fashion. The formation mechanisms have been discussed.

In a previous paper,[2] it was reported that reactions of $[Ph_2PX]\,M$ (X=O, S; M=Li, FeCl) with *p*-benzoquinone gave different type compounds, depending on the metals employed. The reactions show anionic and homolytic characters in the cases of M=Li and FeCl, respectively.

It is known that lithium dimethylphosphide (Me_2PLi) reacts rapidly with tetrahydrofuran (THF) to give 4-hydroxybutyldimethylphosphine by a nucleophilic attack on the α-carbon atom of THF.[3]

In order to clarify this difference still more, reactions of diphenylphosphinic (**1**) and diphenylphosphinothioic chlorides (**2**) with THF were carried out in the presence of several metals or metal salts.

The reaction of diphenylphosphinic chloride (**1**) with lithium in THF at 150 °C gave 29% of diphenylphosphine oxide (**3**), 3% of tetraphenyldiphosphine dioxide (**4**), and a trace amount of 4-substituted butyldiphenylphosphine oxide (**5**). The structure of **5** is unknown because of difficulties of purification but it is considered to be **8** (see below) mainly from the spectral data. A similar reaction of diphenylphosphinothioic chloride (**2**) gave 13% of **3**, 46% of tetramethylene bis(diphenylphosphinodithioate) (**6**), and 16% of *S,S*-tetramethylene diphenylphosphinothioate diphenylphosphinodithioate (**7**). The formation of **3** indicates the occurrence of desulfurization during the reaction.[4]

$$\underset{\mathbf{1}}{Ph_2P(O)Cl} + Li + THF \longrightarrow \underset{\mathbf{3}}{Ph_2P(O)H} + \underset{\mathbf{4}}{Ph_2P(O){-}P(O)Ph_2} + \underset{\mathbf{5}}{Ph_2P(O)(CH_2)_4Y}$$

$$\underset{\mathbf{2}}{Ph_2P(S)Cl} + Li + THF \longrightarrow \underset{\mathbf{3}}{Ph_2P(O)H} + \underset{\mathbf{6}}{Ph_2P(S)S(CH_2)_4SP(S)Ph_2} + \underset{\mathbf{7}}{Ph_2P(S)S(CH_2)_4SP(O)Ph_2}$$

Reaction of **1** with magnesium in THF at 150 °C gave 21% of 1,4-bis(diphenylphosphino)butane 1,4-dioxide (**8**) and a trace amount of **5**. A similar reaction of **2** gave 6% of diphenylphosphinic acid, 21% of diphenylphosphinodithioic acid (**9**), a trace of tetraphenyldiphosphine disulfide (**10**), and 18% of *O,S*-tetramethylene diphenylphosphinothioate diphenylphosphinodithioate (**11**). The formation of diphenylphosphinic acid and **9** also indicates the occurrence of desulfurization during the reaction.

$$\mathbf{1} + Mg + THF \longrightarrow \underset{\mathbf{8}}{Ph_2P(O)(CH_2)_4P(O)Ph_2} + \mathbf{5}$$

$$\mathbf{2} + Mg + THF \longrightarrow Ph_2P(O)OH + \underset{\mathbf{9}}{Ph_2P(S)SH} + \underset{\mathbf{10}}{Ph_2P(S)P(S)Ph_2} + \underset{\mathbf{11}}{Ph_2P(S)S(CH_2)_4OP(S)Ph_2}$$

Reactions of **1** and **2** in the presence of a catalytic amount of iron, copper, cuprous chloride, and oxide in THF at 150 °C gave *O*-4-chlorobutyl diphenylphosphinate (**12**) and diphenylphosphinothioate (**13**). In some cases, 1:2 product (**14**) was also obtained. These products are quite different from those in the cases with lithium and magnesium. The results are summarized in Table 1.

$$\mathbf{1}\text{ or }\mathbf{2} + M\text{ or }MA + THF \longrightarrow Ph_2P(X)O(CH_2)_4Cl + Ph_2P(X)[O(CH_2)_4]_2Cl$$

M=Fe, Cu
MA=Cu_2Cl_2, Cu_2O
12 X=O
13 X=S
14 a, X=O; b, X=S

TABLE 1. YIELDS OF **12**, **13**, AND **14** (AT 150 °C)

1 or **2**	M or MA	**12** (%)	**13** (%)	**14** (%)
1	Fe	22	—	—
	Cu	36	—	—
	Cu_2Cl_2	23	—	4
	Cu_2O	18	—	—
2	Fe	—	27	10
	Cu	—	28	5
	Cu_2Cl_2	—	46	—
	Cu_2O	—	59	—

In order to obtain some information on the formation mechanism of **12** and **13**, **1** and **2** were allowed to react in THF in the presence of a catalytic amount of various metals and metal salts at 120 °C for 6 hr; the yields of **12** and **13** were determined by gas chromatography (glc). The results are shown in Table 2.

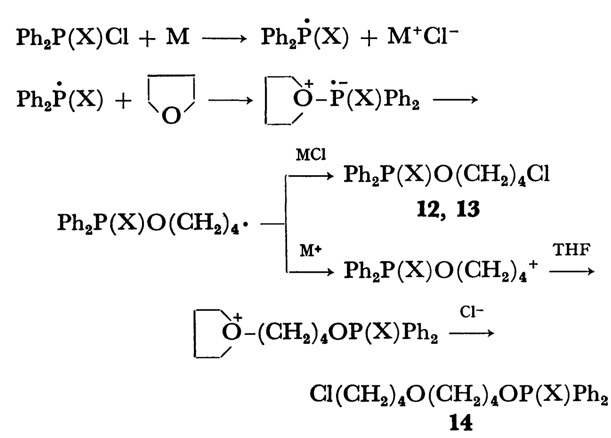
As seen in Table 2, copper and the salts are favorable over iron and the salts as catalyst. Moreover, Friedel-Crafts catalysts such as ferric and aluminum chlorides are not so good, except for zinc chloride.

TABLE 2. YIELDS OF **12** AND **13** (AT 120 °C FOR 6 hr)

Cat.	**12** (%)	**13** (%)
none	—	—
Cu	37	8
Cu_2Cl_2	34	25
$(i\text{-PrO})_3P \cdot CuCl$	39	16
$CuCl_2$	57	28
Fe	15	4
$FeSO_4$	7	<1
$FeCl_3$	5	<1
$ZnCl_2$	36	9
$AlCl_3$	2	<1

These facts suggest that the reactions in the presence of copper, copper salts, iron, and ferrous salts proceed in a homolytic fashion, because it has been known that the reactions of cuprous and ferrous salts with carbon tetrachloride,[5] sulfonyl chlorides,[6] and *N*-chloroamines[7] generate trichloromethyl, sulfonyl, and amino radicals, respectively.

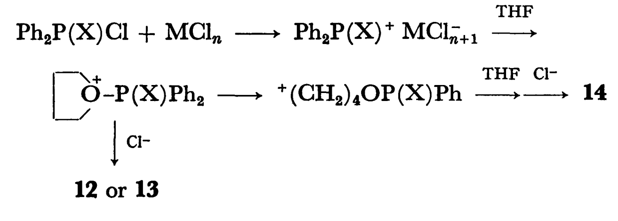
Thus, the formations of **12**, **13**, and **14** are reasonably explained as follows:



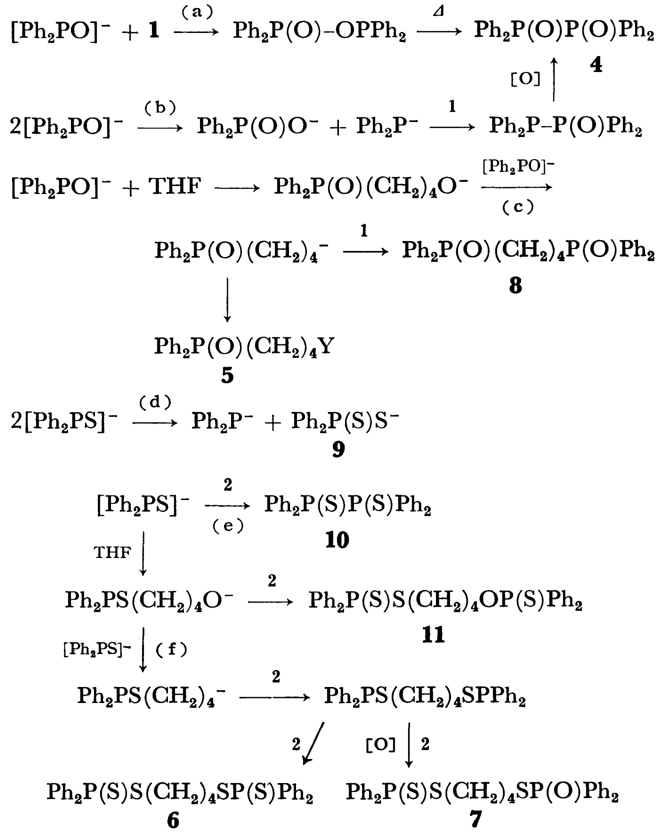
Since neither addition nor polymerization occurred in the presence of acrylonitrile, styrene, vinyl acetate, and dienes under the same conditions, it is considered that the reactions are homolytic but that free radicals are not produced in these reactions.

In the above mechanisms, the second step is analogous to the reactions of alcohols with $Ph_2P\cdot$[8] and $Ph_2P(S)\cdot$ radicals.[9]

In the presence of Friedel-Crafts catalysts, the formation of **12**, **13**, and **14** is explained as follows:



In the cases with lithium and magnesium, the formation of products is explicable by anionic mechanisms as follows:



The steps (a) and (e) have been discussed in a previous paper.[9] The steps (c) and (f) are deoxygenation by trivalent phosphorus.[2] The steps (b) and (d) are disproportionation involving oxygen and sulfur atoms.

Experimental

All melting and boiling points are uncorrected. The IR spectra were recorded on a Hitachi EPI-G2 spectrophotometer. NMR spectra were measured with Hitachi R-24 and R-20B spectrometers using TMS as an internal standard, and MS spectra were determined with a Hitachi RMU-6L mass spectrometer. All reactions were carried out under nitrogen in a sealed tube.

Materials. Diphenylphosphinic[10] (**1**) and diphenylphosphinothioic chlorides[11] (**2**) were prepared by the reported methods.

Reaction with 1 and Lithium. A mixture of 1.83 g (7.7 mmol) of **1** and 70 mg (10 mg-atom) of lithium metal in 5 ml of THF was heated for 24 hr at 150 °C. The reaction mixture was poured into water and extracted with chloroform. After removal of the solvent from the dried extracts, ether was added to the residue. From the solution, **3** (0.457 g, 29%) was obtained (identified by IR and NMR). The insoluble part was purified by dry column chromatography (DCC) on an alumina column with acetone to give 49 mg (3%) of **4**, which was identified by IR,[9] and a small amount of **5**, which was difficult to purify. IR (neat): 3300 (br), 1185, and 1120 cm^{-1}; NMR ($CDCl_3$): δ 1.3—1.8(m), 1.8—2.7(m), 3.2—3.8(m), and 7.2—8.0(m).

Reaction with 2 and Lithium. A mixture of 1.52 g (6 mmol) of **2** and 55 mg (7.9 mg-atom) of lithium metal in 5 ml of THF was allowed to react and treated similarly. Ether was added to the residue to crystallize 0.354 g (26%) of diphenylphosphinothioic anhydride[9] (by IR). The ether solution was treated by DCC on silica gel with ethyl acetate to separate oily fractions. One of the fractions was identified with **3** (0.152 g, 13%) by IR but was difficult to purify. The other fractions were treated again by DCC with ether to give crystalline and oily materials. The crystals (**6**) were recrystallized from *n*-hexane–dichloromethane, yield 0.304 g (46%), mp 91—92 °C. NMR ($CDCl_3$): δ 1.60 (m, 4H, $2CH_2$), 2.85 (dd, J_{PSCH} 13.2, J_{HCCH} 6.6 Hz, 4H, 2-SCH_2), and 7.30—8.15 (m, 20H, 4Ph); Mass: *m/e* 554 (M^+) and 217 (Ph_2PS^+, 100%).

Found: C, 61.33; H, 5.19%. Calcd for $C_{28}H_{28}P_2S_4$: C, 60.63; H, 5.09%.

The oily product (**7**) was 0.128 g (16%) and also difficult to purify. IR (neat): 1197 (P=O), 1100 (P-Ph), 655, and 530 cm^{-1} (P=S); NMR ($CDCl_3$): δ 1.6 (m, 4H, $2CH_2$), 2.6—2.9 (m, 4H, 2-SCH_2), and 6.3—7.1 (m, 20H, 4Ph); Mass: *m/e* 538 (M^+).

Reaction with 1 and Magnesium. A mixture of 1.45 g (6.1 mmol) of **1** and 0.134 g (5.5 mg-atom) of magnesium in 5 ml of THF was heated under the same conditions. The reaction mixture was poured into water and neutralized with 2 M hydrochloric acid to give precipitates. The aqueous solution was extracted with chloroform. Evaporation of the dried extracts gave a considerable amount (0.70 g, 53%) of diphenylphosphinic acid, which was removed by filtration of the alcoholic solution through an alumina column. The eluate was purified by DCC on a silica gel column with ether to give crystalline material (**8**), which was recrystallized from 95% ethanol, mp 264—266 °C, yield 0.198 g (21%); IR (KBr): 1185 (P=O) and 1120 cm^{-1} (P-Ph); NMR ($CDCl_3$): δ 1.5—2.0 (m, 4H, $2CH_2$), 2.0—2.5 (m, 4H, $2CH_2$), and 7.3—8.0 (m, 20H, 4Ph); Mass: *m/e* 458 (M^+).

Found: C, 73.61; H, 5.90%. Calcd for $C_{28}H_{28}O_2P_2$: C, 73.35; H, 6.16%.

Reaction with 2 and Magnesium. A mixture of 1.70 g (6.7 mmol) of **2** and 0.162 g (6.7 mg-atom) of magnesium in 5 ml of THF was heated similarly. After removal of unchanged magnesium (91 mg), the reaction mixture was decomposed with 30% aqueous ammonium chloride, extracted with chloroform, and the extracts were dried with anhydrous magnesium sulfate. The concentration gave crystals. The crystalline part was subjected to DCC on silica gel with chloroform to give 0.180 g (21%) of **9** and 10 mg of **10**, which were identified by IR. A similar treatment of the filtrate gave 83 mg (6%) of diphenylphosphinic acid and 0.209 g (18%) of **11**, mp 72—73 °C (from ether); IR (KBr): 1100 (P-Ph), 1020 (C-O), 945 (P-O), 660, and 545 cm^{-1} (P=S); NMR ($CDCl_3$): δ 1.75 (m, 4H, $2CH_2$), 2.95 (m, J_{PSCH} 13.8 Hz, 2H, SCH_2), 3.95 (m, J_{POCH} 7.8 Hz, 2H, OCH_2), and 7.20—8.15 (m, 20H, 4Ph); Mass: *m/e* 538 (M^+). However, the analytically pure sample could not be obtained because it was difficult to make the separation of a trace of impurity.

Reaction with 1 and Iron. A mixture of 1.43 g (6.0 mmol) of **1** and 31 mg (0.56 mg-atom) of reduced iron powder in 5 ml of THF was heated similarly. The resulting precipitates (iron diphenylphosphinate) was filtered off, and the filtrate was treated by DCC with ether to give 0.414 g (22%) of **12** as oil; IR (neat): 1220 (P=O), 1135 (P-C), 1030 (C-O), and 970 cm^{-1} (P-O); NMR ($CDCl_3$): δ 1.9 (m, 4H, $2CH_2$), 3.53 (m, 2H, CH_2Cl), 4.05 (m, J_{POCH} 15.6 Hz, 2H, OCH_2), and 7.35—8.0 (m, 10H, 2Ph).

Found: C, 62.14; H, 5.80; Cl, 11.23%. Calcd for $C_{16}H_{18}O_2ClP$: C, 62.24; H, 5.83; Cl, 11.51%.

Reaction with 2 and Iron. A mixture of 1.67 g (6.6 mmol) of **2** and 53 mg (0.96 mg-atom) of reduced iron powder in 5 ml of THF was heated similarly. A similar treatment gave 0.575 g (27%) of **13**, bp 117 °C/0.05 mmHg, and 0.268 g (10%) of **14b**, which was difficult to purify.

13: IR (neat): 1120 (P-C), 1030 (C-O), 960 (P-O), 640, and 520 cm^{-1} (P=S); NMR ($CDCl_3$): δ 1.83 (m, 4H, $2CH_2$), 3.43 (m, 2H, CH_2Cl), 3.98 (m, J_{POCH} 8.4 Hz, 2H, OCH_2), and 7.25—8.05 (m, 10H, 2Ph).

Found: C, 59.29; H, 5.30; Cl, 11.48; S, 10.14%. Calcd for $C_{16}H_{18}ClOPS$: C, 59.17; H, 5.59; Cl, 10.91; S, 9.87%.

14b: IR (neat): 1435 (P-C), 640, and 520 cm^{-1} (P=S); NMR ($CDCl_3$): δ 1.73 (m, 8H, $4CH_2$), 3.40 (m, 6H, $3CH_2$), 4.03 (m, J_{POCH} 7.8 Hz, 2H, OCH_2), and 7.3—8.1 (m, 10H, 2Ph).

Found: C, 61.33; H, 6.51%. Calcd for $C_{20}H_{26}ClO_2PS$: C, 60.52; H, 6.56%.

Copper and Cuprous Salts-catalyzed Reactions with 1 and 2. A mixture of **1** or **2** (about 6 mmol) and catalyst (about 0.5 mmol/mmol of one Cu atom) in 5 ml of THF was heated for 24 hr at 150 °C. The reaction mixture was filtered and the filtrate was treated by DCC to separate the reaction products (**12**, **13**, and **14**). The results are summarized in Table 1.

14a: oil: IR (neat); 1435 (C-P), 1215 (P=O), 1135 (P-Ph), and 995 cm^{-1} (P-O).

Found: C, 63.01; H, 7.13; Cl, 9.30%. Calcd for $C_{20}H_{26}ClO_3P$: C. 63.07; H, 6.83; Cl, 9.36%.

Reactions with 1 and 2 in the Presence of Various Catalysts. A mixture of **1** or **2** (about 6 mmol) and catalyst (about 0.1 mmol) in about 6.3 g of THF was heated at 120 °C for 6 hr. The reaction mixture was treated with methanol, concentrated, and determined by gas chromatography (column: H 523 on Diasolid at 210 °C). The results are summarized in Table 2.

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References

1) For Part III see: M. Yoshifuji, H. Gomi, and N. Inamoto, This Bulletin, **47**, 2905 (1974).

2) K. Goda, H. Gomi, M. Yoshifuji, and N. Inamoto, *ibid.*, **47**, 2453 (1974).

3) R. E. Goldsberry, D. E. Lewis, and K. Cohn, *J. Organometal. Chem.*, **15**, 491 (1968).

4) T. Emoto, H. Gomi, M. Yoshifuji, R. Okazaki, and N. Inamoto, This Bulletin, **47**, 2449 (1974).

5) M. Asscher and D. Vofsi, *J. Chem. Soc.*, **1963**, 1887, 3921.

6) M. Asscher and D. Vofsi, *ibid.*, **1964**, 4962.

7) F. Minisci and R. Galli, *Tetrahedron Lett.*, **1964**, 167, 3197.

8) R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc. C*, **1966**, 722.

9) T. Emoto, R. Okazaki, and N. Inamoto, This Bulletin, **46**, 898 (1973).

10) W. A. Higgins, P. W. Vogel, and W. G. Craig, *J. Amer. Chem. Soc.*, **77**, 1864 (1955).

11) L. Maier, *Helv. Chim. Acta*, **47**, 120 (1964).