

Metal Phosphinylides and Phosphinothioylides. II.¹⁾ Effects of Metals on the Reactions of $[\text{Ph}_2\text{PX}]\text{M}$ with Benzaldehyde and *p*-Benzoquinone

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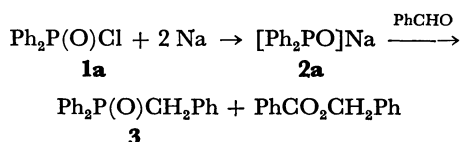
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Reactions of $[\text{Ph}_2\text{PO}]\text{M}$ with benzaldehyde gave benzyl benzoate and benzyldiphenylphosphine oxide (**3**) in the case of $\text{M}=\text{Na}$, **3**, α -hydroxybenzyldiphenylphosphine oxide, benzyl alcohol, benzoin and benzil in the case of $\text{M}=\text{MgCl}$, and **3** in the case of $\text{M}=\text{ZnCl}$. Reactions of $[\text{Ph}_2\text{PX}]\text{M}$ with *p*-benzoquinone gave 2,5-dihydroxyphenyldiphenylphosphine oxide or sulfide and *p*-hydroxyphenyl diphenylphosphinate in the cases $\text{X}=\text{O}$, S and $\text{M}=\text{Li}$, MgCl , Al, and 1,4-phenylene bis(diphenylphosphinate) or bis(diphenylphosphinothioate) in the cases $\text{X}=\text{O}$, S and $\text{M}=\text{FeCl}$. The reaction mechanisms have been discussed.

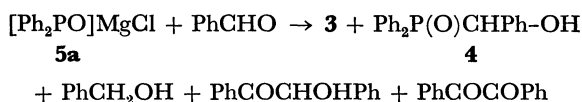
The formation of $[\text{Ph}_2\text{PX}]\text{M}$ ($\text{X}=\text{O}$, S; $\text{M}=\text{Li}$, Na, MgCl) was reported in the preceding paper,¹⁾ reactions of $[\text{Ph}_2\text{PO}]\text{Li}$ or $[\text{Ph}_2\text{PS}]\text{M}$ ($\text{M}=\text{Li}$, MgCl) with benzaldehyde giving α -hydroxybenzyldiphenylphosphine oxide or sulfide in good yields.

This paper describes the effects of metals on reactions of $[\text{Ph}_2\text{PO}]\text{M}$ with benzaldehyde, and those on the reactions of $[\text{Ph}_2\text{PX}]\text{M}$ ($\text{X}=\text{O}$, S) with *p*-benzoquinone.

Reactions with Benzaldehyde. When sodium diphenylphosphinylide (**2a**) prepared from diphenylphosphinyl chloride (**1a**) and two equivalents of sodium in tetrahydrofuran (THF) was allowed to react with benzaldehyde for 24 hr at room temperature and then for 2 hr at the refluxing temperature, benzyl benzoate (65%) and benzyldiphenylphosphine oxide (**3**) (7%) were obtained, instead of α -hydroxybenzyldiphenylphosphine oxide (**4**).

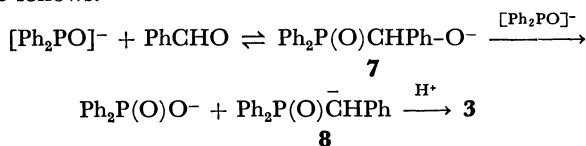


A similar reaction of diphenylphosphinylmagnesium chloride (**5a**) with benzaldehyde gave **4** in only 6% yield, together with **3** (1%), benzyl alcohol (30%), benzoin (5%) and benzil (9%).



The reaction of diphenylphosphinylzinc chloride (**6a**) with benzaldehyde gave only 8% of **3** as an isolated product.

Formation of **3** is explicable by the deoxygenation of intermediate anion (**7**) by diphenylphosphinylide anion as follows.

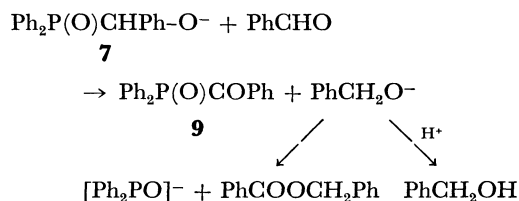


The driving force may be due to the formation of stabilized anion (**8**).

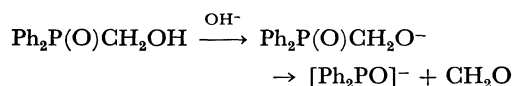
In the case of **5a**, **3** was formed in a trace amount, the normal product (**4**) being also obtained. The result is attributable to the fact that the concentration of free anion (**7**) in this case was lower than that in the case of **2a**, due to the formation of the covalent mag-

nesium derivative of **7**.

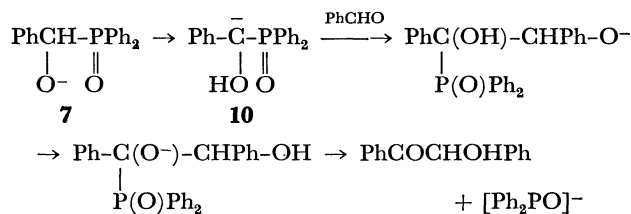
The formation of benzyl alcohol and benzoate is explained by an intermolecular hydride shift from **7** to benzaldehyde to give benzyloxide anion and benzyldiphenylphosphine oxide (**9**). The mechanism is analogous to that in the Cannizzaro reaction.



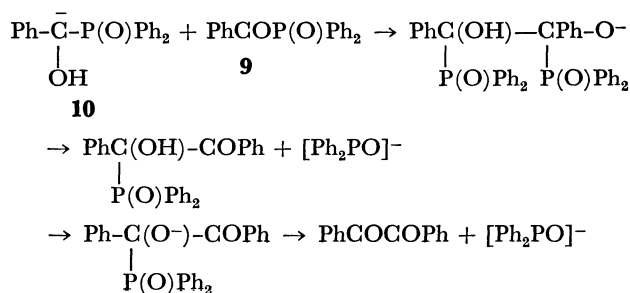
In the case of **5a** benzyl alcohol is produced due to a low concentration of free benzyloxide anion. However, in the case of **2a**, benzyl benzoate is formed through attack of free benzyloxide anion on the carbon atom of the carbonyl group in **9**, since diphenylphosphinylide anion is considered to be a good leaving group on the basis of the following decomposition.²⁾



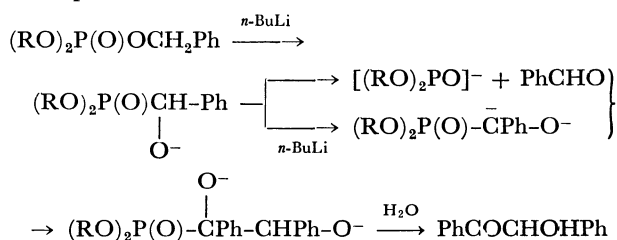
The formation of benzoin is considered to be analogous to benzoin condensation, indicating that diphenylphosphinylide anion behaves in a similar way to that of cyanide anion.



Benzil is formed through an attack of the anion (**10**) on the carbonyl carbon atom of **9**.

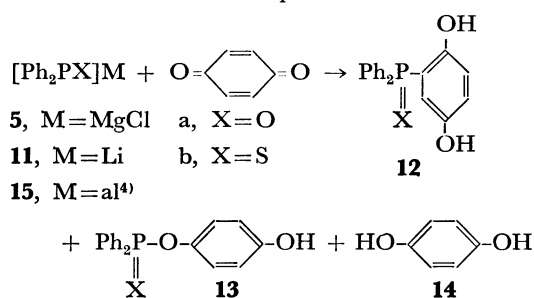


An analogous formation of benzoin has recently been reported.³⁾



In conclusion, since the formation of **7** is reversible, long reaction time results in the formation of several abnormal products. The products depend on the extent of ionic character of the initial addition product (**7**), which depends on metal in $[\text{Ph}_2\text{PO}]\text{M}$.

*Reactions with *p*-Benzoquinone.* Reactions of $[\text{Ph}_2\text{PX}]\text{M}$ ($\text{X}=\text{O}, \text{S}$) with *p*-benzoquinone were carried out at room temperature in THF.



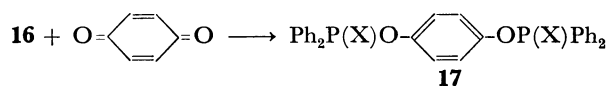
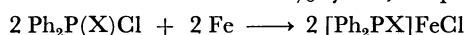
The reaction of lithium diphenylphosphinylide (**11a**) gave 2,5-dihydroxyphenyldiphenylphosphine oxide (**12a**) (20%), *p*-hydroxyphenyl diphenylphosphinate (**13a**) (18%) and hydroquinone (**14**) (33%).

The reaction of **5a** gave 17% of **12a**, 17% of **14**, and 8% of magnesium diphenylphosphinate.

The reaction of **15a** gave 8% of **13a**, 20% of **14** and compounds containing aluminum as the main product. A similar reaction of **15b** gave 9% of **13a** and similar aluminum-containing products as main products. The formation of **13a** indicates desulfurization during the course of the preparation of **15b**.¹⁾ The above aluminum-containing compounds are considered to be a mixture of aluminum chelate of **12** and aluminum diphenylphosphinate, but attempts to isolate **12** were unsuccessful.

Reaction of **11b** gave also 30% of **12b**.

A reaction mixture of diphenylphosphinyl (**1a**) or diphenylphosphinothiyl chloride (**1b**) with reduced iron powder in THF reacted with *p*-benzoquinone to give 1,4-phenylene bis(diphenylphosphinate) (**17a**) or bis(diphenylphosphinothioate) (**17b**) by considerably fast reaction in 78 or 79% yield, respectively.

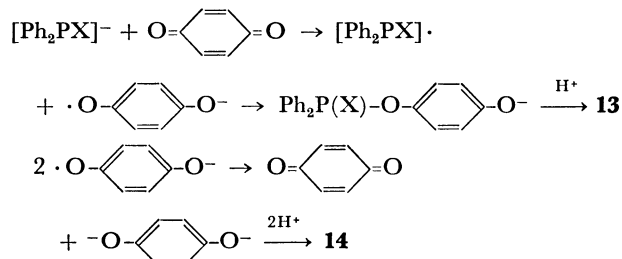


Solutions of **16** were pale green and the ¹H-NMR spectra could be measured without difficulty. Thus, the iron atom in **16** is considered to be bivalent.

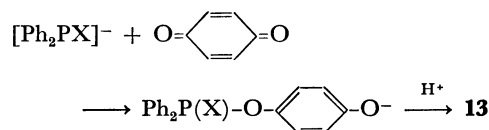
Compounds **12** are considered to be formed through

a nucleophilic addition to quinone nucleus, since diphenylphosphine oxide and sulfide give **12a**⁵⁾ and **12b** with *p*-benzoquinone, respectively. It is noteworthy that **12b** is formed in a better yield in the absence of any base than in the presence of base, isolation being very easy.

The formation of **13** and **14** is considered to be due to electron transfer mechanism.



However, the following direct addition to the oxygen atom of quinone cannot be ruled out for the formation of **13**.



Since **16** did not react with benzyl chloride, acetaldehyde, diethyl disulfide, olefins, dienes, and naphthalene, it does not have an anionic character and does not generate free radicals under similar conditions.

Moreover, **16a** reacted with air to give iron diphenylphosphinate, which gave diphenylphosphinic acid after alkaline hydrolysis. It is suggested that the reactions proceed through an coordinate complex between **16** and quinone in a homolytic fashion without formation of free radicals.

Experimental

All melting and boiling points are uncorrected. IR and mass spectra were measured with a Hitachi EPI-G2 spectrophotometer and a Hitachi RMU-6L mass spectrometer, respectively. ¹H-NMR spectra were measured with Hitachi R-20B and R-24 spectrometers, using TMS as an internal standard. ³¹P-NMR spectra were measured with Hitachi R-20-R-204-P and R-20B-R-204-PB spectrometers, using 85% phosphoric acid as an external standard.

Starting materials were prepared as described previously.¹⁾ All the reactions were carried out under nitrogen.

Reactions of Benzaldehyde. a) *With $[\text{Ph}_2\text{PO}]\text{Na}$ (**2a**):* A solution of **2a** was prepared from 2.27 g (9.6 mmol) of diphenylphosphinyl chloride (**1a**) and 0.47 g (20 mg atom) of sodium metal in 14 ml of THF at room temperature for 24 hr. To the filtrate was added 2.39 g (23 mmol) of benzaldehyde. The mixture was stirred for 24 hr at room temperature and then refluxed for 2 hr. The reaction mixture was poured into water and extracted with ether. The dried extract was evaporated and the residue was separated by dry column chromatography (DCC) on silica gel with ether to give 0.187 g (7%) of benzyl diphenylphosphine oxide (**3**) and 1.55 g (65%) of benzyl benzoate which was identified by the IR spectrum.

3: mp 190–192 °C (from ethanol) (lit.⁶⁾ 192–193 °C); NMR (CDCl_3): δ 3.6 (d, J_{PCH} 13.8 Hz, 2H, PCH_2), 7.15 (s, 5H, Ph), and 7.35–7.9 (m, 10H, 2Ph).

b) With $[Ph_2PO]MgCl$ (**5a**): A mixture of 2.97 g (12.6 mmol) of **1a** and 0.568 mg (23.7 mg atom) of magnesium in THF (32 ml) was stirred at room temperature for 1 hr and then refluxed for 1 hr. To the filtrate was added 2.13 g (20 mmol) of benzaldehyde and the mixture was treated similarly. Separation by DCC gave 0.64 g (30%) of benzyl alcohol, 0.112 g (5%) of benzoin, 0.197 g (9%) of benzil, which were identified by the IR spectra, 0.227 g (6%) of α -hydroxybenzylidenediphenylphosphine oxide, mp 172–174 °C (lit.^{2b} 176 °C), and 34 mg (1%) of **3**, mp 190–192 °C, which were identified by the IR and NMR spectra.

c) With $[Ph_2PO]ZnCl$ (**6a**): A mixture of 1.47 g (6.2 mmol) of **1a** and 0.954 g (15 mg atom) of zinc dust in 15 ml of THF was stirred at room temperature for 24 hr. To the solution was added 2.32 g (22 mmol) of benzaldehyde. The mixture was stirred for 24 hr at room temperature and then refluxed for 2 hr. After removal of unchanged zinc dust and THF, the residue was crystallized to give 0.813 g (60%) of diphenylphosphinic acid and 0.149 g (8%) of **3**, successively.

Reactions of *p*-Benzoquinone. a) With $[Ph_2PO]Li$ (**11a**): A solution of **11a** was prepared from 1.53 g (6.5 mmol) of **1a** and 0.19 g (27 mg atom) of lithium metal in 15 ml of THF by stirring for 3 hr at room temperature and then heating for 1 hr, and decanted under nitrogen. To the solution was added 0.562 g (5.2 mmol) of *p*-benzoquinone in 15 ml of THF and the mixture was allowed to stand overnight. The resulting blue solution was poured into water, acidified with 2M hydrochloric acid, and extracted with chloroform and ethyl acetate, successively. The ethyl acetate extracts gave 0.19 g (33%) of hydroquinone (**14**) after evaporation, which was identified by comparison of IR and tlc with those of an authentic sample. The chloroform extracts were chromatographed on silica gel with chloroform to give two crystalline compounds. One was recrystallized twice from 95% ethanol to give **12a**, mp 218–220 °C, yield 0.341 g (20%). IR (KBr): 3150 (OH) and 1140 cm^{-1} (P=O); Mass: m/e 310 (M^+).

Found: C, 69.93; H, 5.06%. Calcd for $C_{18}H_{15}O_3P$: C, 69.67; H, 4.87%.

The other was recrystallized from benzene-methanol to give **13a**, mp 190–192 °C, yield 0.267 g (18%); IR (KBr): 3200 (OH) and 1218 cm^{-1} (P=O); NMR ($CDCl_3$): δ 6.75 (q, J 9 Hz, 4H) and 7.4–8.2 (m, 10H).

Found: C, 69.92; H, 4.85%. Calcd for $C_{18}H_{15}O_3P$: C, 69.67; H, 4.87%.

b) With $[Ph_2PO]MgCl$ (**5a**): A solution of **5a**, prepared from 1.50 g (6.3 mmol) of **1a** and 0.257 g (11 mg atom) of magnesium in 15 ml of THF, was added to 0.545 g (5 mmol) of *p*-benzoquinone in THF (15 ml) and stirred for 14 hr at room temperature. The resulting greenish precipitates turned brown in the air. The precipitates were added to 2M hydrochloric acid, but were not completely soluble. A small amount of methanol was then added for complete dissolution and the reaction mixture was treated with DCC on silica gel with ether. Each fraction was extracted with methanol to give 0.342 g (17%) of **12a**, 94 mg (17%) of **14**, mp 172–173 °C (identified by tlc and IR), and 0.124 g (8%) of magnesium salt, mp > 300 °C, which was dissolved in 10% NaOH solution and neutralized with hydrochloric acid to give diphenylphosphinic acid after extraction with chloroform.

c) With $[Ph_2PO]Al$ (**15a**): A solution of **15a**, prepared from 1.65 g (7.0 mmol) of **1a**, 0.263 g (9.7 mg atom) of aluminum foil and 54 mg (0.2 mmol) of mercuric chloride in 15 ml of THF by heating for 6 hr, was added to 0.932 g (8.6 mmol) of *p*-benzoquinone in 15 ml of THF. The reaction mixture was chromatographed on silica gel after filtration to give 0.134 g (8%) of **13a** and 0.183 g (20%) of **14**. The

precipitates (1.33 g) contained aluminum which was difficult to remove.

d) With $[Ph_2PS]Al$ (**15b**): A solution of **15b**, prepared from 1.89 g (7.5 mmol) of **1b**, 0.435 g (16 mg atom) of aluminum foil and 54 mg (0.2 mmol) of mercuric chloride in 15 ml of THF by heating for 3 hr, was added to 0.693 g (6.4 mmol) of *p*-benzoquinone in 15 ml of THF, and stirred for 15 hr at room temperature. After filtration of precipitates, the filtrate was chromatographed to give 47 mg (0.4 mmol) of recovered quinone and 0.221 g (9%) of **13a**. The precipitates (1.26 g) contained aluminum.

e) With Diphenylphosphine Sulfide: A mixture of 1.64 g (7.5 mmol) of the sulfide and 0.97 g (9.0 mmol) of *p*-benzoquinone in 50 ml of THF was stirred for one day at room temperature. After evaporation, a dark brown tarry substance was subjected to DCC on silica gel with chloroform to afford 1.71 g (70%) of **12b**, which was further purified by column chromatography on alumina with ethanol and recrystallized from ethanol-*n*-hexane, mp 148–149 °C. IR (KBr): 3320, 3275 (OH), and 640 cm^{-1} (P=S); NMR ($CDCl_3$): δ 6.12 (s, 1H, OH), 6.22 (d, J_{PCH} 14.4 Hz, 1H), 6.8–6.9 (m, 2H), 7.2–7.85 (m, 10H, 2Ph), and 9.07 (s, 1H, OH); δ_p ($CHCl_3$): –37.2 ppm; Mass: m/e 326 (M^+).

Found: C, 66.30; H, 4.59%. Calcd for $C_{18}H_{15}O_2PS$: C, 66.25; H, 4.63%.

f) With $[Ph_2PS]Li$ (**11b**): To a solution of **11b** prepared from diphenylphosphine sulfide (1.44 g, 6.6 mmol) in THF (50 ml) and *n*-butyllithium (7.7 mmol) was added dropwise 0.81 g (7.5 mmol) of *p*-benzoquinone in 20 ml of THF with stirring, and the mixture was stirred for one day at room temperature. After removal of THF, the residue was treated with 2M hydrochloric acid, and extracted with chloroform. Removal of the chloroform from the dried extract gave a tarry product, which was subjected to column chromatography with ethyl acetate to give 0.646 g (30%) of **12b**. Crude **12b** was purified by DCC on silica gel with ether and recrystallized from chloroform-*n*-hexane, mp 155–157 °C. The NMR, IR, and mass spectral data were identical with those of a sample obtained in e).

g) With $[Ph_2PO]FeCl$ (**16a**): A mixture of 1.48 g (6.3 mmol) of **1a** and 0.30 g (5.4 mg atom) of reduced iron powder in 15 ml of THF was stirred overnight. To the solution was added 0.338 g (3.1 mmol) of *p*-benzoquinone in 15 ml of THF and stirred for 30 min at room temperature. The resulting precipitates were filtered off. The filtrate was again filtered through alumina to remove diphenylphosphinic acid and the filtrate was evaporated. The residue was treated with ether. Insoluble part (**17a**) was recrystallized from 2-propanol, mp 210–212 °C, yield 1.24 g (78%). IR (KBr): 1235 (P=O), 1180 (Ph–O), and 920 cm^{-1} (P–O); NMR ($CDCl_3$): δ 7.25 (s, 4H) and 7.5–8.2 (m, 20H); δ_p ($CHCl_3$): –30.5 ppm.

Found: C, 70.38; H, 4.58%. Calcd for $C_{30}H_{24}O_4P_2$: C, 70.56; H, 4.74%.

The precipitates (0.287 g) were insoluble in organic solvents. When the precipitates were dissolved in 10% NaOH solution and neutralized with hydrochloric acid, diphenylphosphinic acid was obtained.

h) With $[Ph_2PS]FeCl$ (**16b**): A reaction mixture of 1.55 g (6.1 mmol) of **1b** and 0.270 g (4.7 mg atom) of reduced iron powder in 15 ml of THF was added to 0.254 g (2.3 mmol) of quinone in 15 ml of THF and 1.00 g (79%) of **17b** was obtained, mp 220–221 °C (from 2-propanol). IR (KBr): 1170 (C–O), 1120 (P–Ph), 900 (P–O), and 550 cm^{-1} (P=S); NMR ($CDCl_3$): δ 6.9 (s, 4H) and 7.35–8.2 (m, 20H).

Found: C, 66.20; H, 4.22%. Calcd for $C_{30}H_{24}O_2P_2S_2$: C, 66.41; H, 4.46%.

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References and Notes

- 1) For Part I see: T. Emoto, H. Gomi, M. Yoshifuji, R. Okazaki, and N. Inamoto, *This Bulletin*, **47**, 2449 (1974).
 - 2) a) R. C. Miller, C. D. Miller, W. Rogers, Jr., and L. A. Hamilton, *J. Amer. Chem. Soc.*, **79**, 424 (1957); b) L. Horner, P. Beck, and V. G. Toscano, *Chem. Ber.*, **94**, 1317 (1961).
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 - 4) The structure of **15** is obscure in the case of aluminum. M is therefore represented as "al".
 - 5) I. G. M. Campbell and I. D. R. Stevens, *Chem. Commun.*, **1966**, 505.
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