BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (11), 2905—2906 (1974)

Metal Phosphinylides and Phosphinothioylides. III.[1] Reactions of Lithium Diphenylphosphinylide and Diphenylphosphinothioylide with Acetone and Bromoacetone

Masaaki Yoshifuji, Hideyuki Gomi, and Naoki Inamoto
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received May 14, 1974)

Synopsis. Reaction of acetone with $[Ph_2PO]Li$ gave 1-hydroxy-1-methylethyl- (**2a**), 1,1-dimethyl-3-oxobutyldiphenylphosphine oxides (**3a**) and 2,6-bis(diphenylphosphinyl)-2,6-dimethylheptan-4-one (**4a**). The corresponding sulfide **2b** was obtained in the case of $Ph_2P(S)H$, and **3b** and **4b** in the case of $[Ph_2PS]Li$ (**5b**). Bromoacetone reacted with **5b** through substitution reaction.

It has been reported that the reaction of acetone with diphenylphosphinylmagnesium bromide (**1a**), prepared from three molar amounts of phenylmagnesium bromide and diethyl phosphite, gave phosphine oxides **2a** and **4a**, the latter being considered to be formed by addition of **1a** to phorone formed from acetone and ethoxide ion.[2]

$$[Ph_2PX]M + Me_2CO \longrightarrow \underset{\mathbf{2}}{Ph_2P(X)CMe_2OH}$$

1, M=MgBr; a, X=O
5, M=Li; b, X=S

$$+ \underset{\mathbf{3}}{Ph_2P(X)CMe_2CH_2COMe}$$

$$+ \underset{\mathbf{4}}{(Ph_2P(X)CMe_2CH_2)_2CO}$$

If **4a** is formed by the suggested mechanism, **3a** should be formed by addition of **1a** to mesityl oxide produced during the course of reaction.

This paper describes reactions of acetone and some ketones with lithium diphenylphosphinylide (**5a**) or diphenylphosphinothioylide (**5b**).

Reaction of **5a** with acetone afforded three phosphine oxides **2a**, expected **3a** and **4a**. The separation of these compounds was difficult, and **2a** and **3a** were isolated only in 7.4 and 20% yields, respectively. **4a** was identified by NMR, which exhibited signals at δ 1.37 (d, J_{PCCH} 16.8 Hz, Me), 2.67 (d, J_{PCCH} 7.8 Hz, CH_2), and 7.3—8.2 (m, Ph), from the crude mixture. The data were in agreement with the reported one.[2]

Reaction of **5b** with acetone did not give **2b**, but gave **3b** (43%), **4b** (23%) and 2-diphenylphosphinothioyl-6-diphenylphosphinyl-2,6-dimethylheptan-4-one (**6**) (4%).

$$Ph_2P(S)CMe_2CH_2COCH_2CMe_2P(O)Ph_2 \quad \mathbf{6}$$

By the reaction of **5b** with mesityl oxide, **3b** was also obtained in 40% yield. No **4b** could be isolated from **5b** and phorone. The following stepwise mechanism would be more reasonable. Slightly excess amount of *n*-butyllithium acts as a base for the condensation of acetone.

$$2Me_2CO \xrightarrow{n\text{-BuLi}} Me_2C{=}CHCOMe \xrightarrow{\mathbf{5}} \mathbf{3} \xrightarrow[Me_2CO]{n\text{-BuLi}}$$

$$Ph_2P(X)CMe_2CH_2COCH{=}CMe_2 \xrightarrow{\mathbf{5}} \mathbf{4}$$

Formation of **6** indicates desulfurization of **5b** during the course of preparation or reaction,[3] and then oxidation of the phosphorus atom in the intermediate product during the treatment.

Reaction of diphenylphosphine sulfide (**7**) with acetone gave **2b** in 23 and 86% yields in tetrahydrofuran (THF) and in acetone, respectively. The yields were determined by means of NMR, since **2b** decomposed with recrystallization from benzene–ethanol and on silica gel column.

Acetophenone and benzophenone did not react with **5b**.

Reaction of **5b** with bromoacetone gave 2-oxopropyldiphenylphosphine sulfide (**8**) in 65% yield. The result is in contrast to the reaction with chloroacetone,[4] which gives phosphinyl-substituted epoxide.

$$Ph_2P(S)CH_2COMe \quad \mathbf{8}$$

Experimental

All boiling and melting points are uncorrected. ^{1}H-NMR spectra were measured with a Hitachi R-24 spectrometer using TMS as an internal standard. ^{31}P-NMR spectra were measured with a Hitachi R-20B-R-204-PB spectrometer using 85% H_3PO_4 as an external standard. All the reactions were carried out under nitrogen atmosphere.

Reaction of Acetone with 5a. Acetone (5.15 g, 89 mmol) was added to a solution of **5a** prepared from diphenylphosphine oxide[5] (4.07 g, 20 mmol) and *n*-BuLi (21 mmol) in THF (80 ml), and the mixture was stirred for 19 hr at 30 °C and refluxed for 18 hr. After evaporation, the residue was treated with water and extracted with chloroform. Removal of the solvent from the dried extract gave a tarry mixture of **2a**, **3a**, and **4a** (by NMR), which was chromatographed on silica gel with ethyl acetate and methanol to afford **3a** (1.23 g, 20%), mp *ca.* 75 °C (lit,[6] 76.5—77.5 °C), and **2a** (0.39 g, 7.4%), mp 140—142 °C (from acetone) (lit,[2] 144—145 °C), δ_P ($CHCl_3$): −34.2 ppm. Acidification of the aqueous layer gave diphenylphosphinic acid (1.88 g, 43%).

Reaction of Acetone with 5b. A mixture of **5b**, prepared from **7**[7] (4.54 g, 21 mmol) and *n*-BuLi (23 mmol) in THF (60 ml), and acetone (4.57 g, 79 mmol) was stirred for 5 hr and refluxed for 15 hr. After a similar work-up to that with **5a**, ether was added to the residue to precipitate **4b**. The filtrate was chromatographed on silica gel with benzene and chloroform to afford **6**, oily **3b** and tarry products. On adding ether to the tarry products, **4b** precipitated, and **3b** was obtained from the filtrate.

3b: yield 2.82 g (43%). The IR and NMR spectra were in agreement with those of a sample obtained from **5b** and mesityl oxide.

4b: mp 178—179 °C (from EtOH), yield 1.36 g (23%). IR (KBr): 1705 cm^{-1} (C=O); NMR ($CDCl_3$): δ 1.45 (d, J_{PCCH} 18 Hz, 12H, 4Me), 2.81 (d, J_{PCCH} 9.2 Hz, 4H, $2CH_2$), and 7.4—8.2 (m, 20H, 4Ph); δ_P (CHCl$_3$): −60.3 ppm.

Found: C, 68.96; H, 6.01; S, 11.43%. Calcd for $C_{33}H_{36}OP_2S_2$: C, 68.97; H, 6.31; S, 11.43%.

6: mp 151—152 °C (from EtOH), yield 0.24 g (4%). IR (KBr): 1710 (C=O), 1180 (P=O), and 540 cm^{-1} (P=S); NMR (CDCl$_3$): δ 1.35 (d, J_{PCCH} 16.2 Hz, 6H, P(O)CMe$_2$), 1.55 (d, J_{PCCH} 17.6 Hz, 6H, P(S)CMe$_2$), 2.64 (d, J_{PCCH} 8.4 Hz, 2H, CH$_2$ (P(O) side)), 2.83 (d, J_{PCCH} 9 Hz, 2H, CH$_2$ (P(S) side)), and 7.3—8.2 (m, 20H, 4Ph); δ_P (CHCl$_3$): −37.0 (P=O) and −62.0 ppm (P=S).

Found: C, 70.75; H, 6.43; S, 5.58%. Calcd for $C_{33}H_{36}O_2P_2S$: C, 70.95; H, 6.50; S, 5.74%.

*Reaction of Acetone with **7**.* 1) A mixture of **7** (1.49 g, 6.8 mmol) and acetone (12.76 g, 220 mmol) in THF (45 ml) was stirred for 17 hr at room temperature and then refluxed for 16 hr. Removal of THF gave white crystals (1.60 g). The NMR spectrum showed them to be a mixture of **7** and **2b**. The yield of **2b** was estimated to be 23% by means of NMR.

2) A solution of **7** (1.27 g, 5.8 mmol) in acetone (100 ml) was stirred for 19 hr at room temperature and then refluxed for 22 hr. The yield of **2b** was estimated to be 86%; δ_P (CHCl$_3$): −55.6 ppm. The melting point of the mixture was 110—117 °C (lit,[8] **2b**: 118—120 °C).

*Reaction of **5b** with Mesityl Oxide.* To a solution of **5b** prepared from **7** (4.00 g, 18 mmol) and *n*-BuLi (20 mmol) in THF (40 ml) was added mesityl oxide (2.54 g, 26 mmol) in THF (10 ml). The mixture was stirred for 35 hr at room temperature and then for 4 hr at 40 °C. Similar treatment gave a tarry product, which was chromatographed on silica gel with benzene and distilled under reduced pressure to give oily **3b** (2.30 g, 40%), bp 222 °C/1.5 mmHg. IR (neat): 1720 (C=O) and 645 cm^{-1} (P=S); NMR (CDCl$_3$): δ 1.51 (d, J_{PCCH} 18 Hz, 6H, CMe$_2$), 2.07 (s, 3H, COMe), 2.93 (d, J_{PCCH} 9 Hz, 2H, CH$_2$), and 7.3—8.3 (m, 10H, 2Ph); δ_P (CHCl$_3$): −60.7 ppm.

Found: C, 68.53; H, 6.41; S, 10.27%. Calcd for $C_{18}H_{21}OPS$: C, 68.33; H, 6.69; S, 10.13%.

*Reaction of **5b** with Bromoacetone.* To a solution of **5b** prepared from **7** (2.22 g, 10 mmol) and *n*-BuLi (13 mmol) in THF (30 ml) was added dropwise bromoacetone[9] (2.19 g, 16 mmol) in THF (20 ml) under ice-cooling, and the mixture was stirred for 16 hr at room temperature. After a similar work-up, the tarry residue was subjected to alumina dry column chromatography with chloroform. No crystals were obtained, but the following NMR spectrum showed that the main product was **8**, 1.82 g (65%). IR (neat): 1720 (C=O) and 620 cm^{-1} (P=S); NMR (CDCl$_3$): δ 2.31 (s, 3H, Me), 3.75 (d, J_{PCH} 15 Hz, 2H, CH$_2$), and 7.4—8.2 (m, 10H, 2Ph).

One of the authors (N. I.) thanks the Ministry of Education for financial support.

References

1) For Part II see K. Goda, H. Gomi, M. Yoshifuji, and N. Inamoto, This Bulletin, **47**, 2453 (1974).

2) P. F. Cann, S. Warren, and M. R. Williams, *J. Chem. Soc., Perkin I*, **1972**, 2377.

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

4) G. Sturtz, *Bull. Soc. Chim. France*, **1964**, 2333.

5) G. I. Derkach and A. V. Kirsanov, *Zh. Obshch. Khim.*, **29**, 1815 (1959); *Chem. Abstr.*, **54**, 8682a (1960).

6) P. F. Cann, D. Howells, and S. Warren, *J. Chem. Soc., Perkin II*, **1972**, 304.

7) G. Peters, *J. Amer. Chem. Soc.*, **82**, 4751 (1960).

8) G. Peters, *J. Org. Chem.*, **27**, 2198 (1961).

9) P. A. Levene, "Organic Syntheses," Coll. Vol. II, p. 88 (1943).