Facile Synthesis of 2-Phenyl-1,2-oxaphospholane and Its Related New Compounds. The Family of Deoxophostones and Deoxothiolphostones

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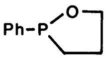
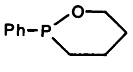
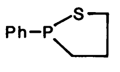
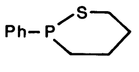
Synopsis. 2-Phenyl-1,2-oxaphospholane (**1a**), 2-phenyl-1,2-oxaphosphorinane (**1b**), 2-phenyl-1,2-thiaphospholane (**1c**), and 2-phenyl-1,2-thiaphosphorinane (**1d**) were prepared readily by the reaction of dichlorophenylphosphine with an ω-chloroalkanol or an ω-chloroalkanethiol followed by cyclization with the aid of lithium metal. Compounds **1b**—**d** have been obtained for the first time.

Recently, we have reported the cationic ring-opening polymerization of a five-membered deoxophostone (2-phenyl-1,2-oxaphospholane, (**1a**)) to give poly (phosphine oxide).[1] During the course of these studies we have found a new facile method to prepare **1a** and its family compounds. The present paper deals with the synthesis of five- and six-membered deoxophostones and their sulfur analogues of deoxothiolphostones,[2] *i.e.*, **1a**, 2-phenyl-1,2-oxaphosphorinane (**1b**), 2-phenyl-1,2,-thiaphospholane (**1c**), and 2-phenyl-1,2-thiaphosphorinane (**1d**).

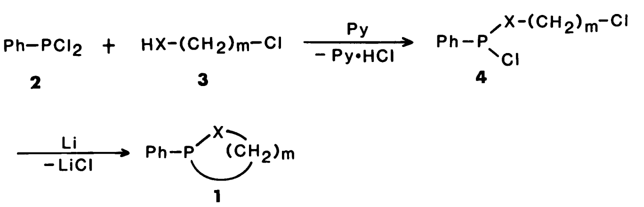

1a


1b


1c


1d

The synthetic route is given in Scheme 1.



a, X=O; *m*=3 **c**, X=S; *m*=3
b, X=O; *m*=4 **d**, X=S; *m*=4

Scheme 1.

To dichlorophenylphosphine (**2**) with pyridine in tetrahydrofuran (THF) was added an ω-chloroalkanol or ω-chloroalkanethiol **3** and refluxed for 1 h. At this time, The ^{31}P NMR spectrum of the reaction mixture showed a single peak assignable to phosphonochloridite (**4**): **4a**, 175.0 ppm; **4b**, 175.3 ppm; **4c**, 141.7 ppm; **4d**, 141.6 ppm. Without isolation, **4** in THF was reacted with lithium metal. The ^{31}P NMR spectrum of the respective reaction mixture showed many peaks. With adding diethyl ether to the mixture, precipitated insoluble parts which probably consisted of LiCl and polymeric by-products. In the ^{31}P NMR spectrum of the soluble part the peak due to **1** was main. The distillation *in vacuo* gave **1** in a moderate or low yield. ^{31}P, ^{1}H, ^{13}C NMR data as well as MS data supporting the structures of **1a**—**d** are given in the experimental section.

Few routes to prepare **1a** have previously been reported, which required several steps and the overall yield was lower than that of the present method.[3,5] These methods involve phosphines having a P–H bond which are very stinking and poisonous. On the other hand, the present method is more facile, not necessary to handle stinking phosphines, and more generally applicable to prepare not only **1a** but also **1b**—**d**. Five-membered deoxothiolphostone **1c** had been known only as a ligand of an Fe-complex.[6] Six-membered deoxophostone **1b** and deoxothiolphostone **1d** have not been known so far. Although the isolated yields are not high, the present study provides the first instance of the isolation of **1b**, **1c**, and **1d**. These new compounds are very attractive reagents which allow investigation of reactivities and stereochemical problems in phosphorus chemistry. The ring-opening polymerization of **1c** and **1d** will be reported soon.[7]

Experimental

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Hitachi R-20B (^{1}H NMR) or a Hitachi R-900 (^{13}C and ^{31}P NMR) spectrometer. Mass spectra were obtained with JEOL JMS-DX300. THF, diethyl ether, and pyridine were dried respectively over $LiAlH_4$, CaH_2, or KOH, and distilled. Commercially available dichlorophenylphosphine, 3-chloro-1-propanol, and 4-chloro-1-butanol were purified by distillation. 3-Chloro-1-propanethiol was prepared according to the reported procedures.[8] 4-Chloro-1-butanethiol was prepared by the HCl-catalyzed methanolysis[8] of S-(4-chlorobutyl) thioacetate, which was obtained from the substitution reaction[9] of 4-chlorobutyl tosylate with potassium thioacetate; overall yield 38%, bp 89—95 °C (57—65 Torr, 1 Torr=133.322 Pa).

The following all operations were carried out under nitrogen atmosphere.

2-Phenyl-1,2-oxaphospholane 1a: To a mixture of dichlorophenylphosphine (2.01 g, 11.2 mmol), pyridine (0.95 ml, 11.8 mmol), and 10 ml of THF was added 3-chloro-1-propanol (1.06 g, 11.2 mmol) in 4 ml of THF at 0 °C. After refluxing for 1 h, the precipitate of pyridinium hydrochloride was removed by filtration. The filtrate was added to 8 ml of THF containing small pieces of lithium metal (0.172 g 24.8 mg-atom) at −78 °C and stirred overnight gradually up to room temperature. THF was evaporated *in vacuo,* and 30 ml of diethyl ether was added to the residue to extract the product. The mixture was well stirred and filtered. After concentration of the filtrate, the residue was subjected to distillation *in vacuo* to give 0.69 g of **1a** (37% yield), bp 62—65 °C (0.13 Torr)[3]. $^{31}P\{^1H\}$NMR($CDCl_3$) +110.2 ppm (relative to 85% H_3PO_4 external standard); ^1H NMR δ($CDCl_3$) 1.4—2.5 (m, 4H, $PC\underline{H}_2C\underline{H}_2$), 3.6—4.3 (m, 2H, $OC\underline{H}_2$), and 7.1—7.4 ppm (m, 5H, $C_6\underline{H}_5$); $^{13}C\{^1H\}$NMR($CDCl_3$) 23.3 (s, $P\underline{C}H_2$), 32.2 (d, J_{CCP}=20.9 Hz, $PCH_2\underline{C}H_2$) 72.4 (d, J_{COP}=14.0 Hz, $O\underline{C}H_2$), 126.9 (s, P-Ph; δ-C) 128.0 (d, J_{CCP}=14.8 Hz, P-Ph; β-C), 128.1 (s, P-Ph; γ-C), and 144.8 ppm (d, J_{CP}=36.7 Hz, P-Ph; α-C).

These procedures for the preparation of **1a** were similarly applied to those of **1b—d**.

*2-Phenyl-1,2-oxaphosphorinane **1b***: From dichlorophenylphosphine (2.19 g, 12.2 mmol), 4-chloro-1-butanol (1.33 g, 12.2 mmol), pyridine (1.04 ml, 12.8 mmol), and lithium metal (0.186 g 26.8 mg-atom), 0.39 g of **1b** was obtained; 18% yield, bp 76—79 °C (0.55 Torr). $^{31}P\{^1H\}$NMR($CDCl_3$) +111.1 ppm; ^1H NMR δ($CDCl_3$) 1.2—2.4 (m, 6H, $PC\underline{H}_2C\underline{H}_2C\underline{H}_2$), 3.4—3.9 (m, 2H, $OC\underline{H}_2$), and 7.1—7.5 (m, 5H, $C_6\underline{H}_5$); $^{13}C\{^1H\}$NMR($CDCl_3$) 19.3 (d, J_{CP}=3.5 Hz, $P\underline{C}H_2$), 25.5 (d, J_{CCP}=22.6 HZ, $PCH_2\underline{C}H_2$), 27.6 (d, J_{CCOP}=3.5 Hz, $OCH_2\underline{C}H_2$), 63.4 (d, J_{COP}=7.8 Hz, $O\underline{C}H_2$), 127.8 (s, P-Ph; δ-C), 128.6 (d, J_{CCCP}=2.6 Hz P-Ph; γ-C), 129.0 (d, J_{CCP}=14.1 Hz, P-Ph; β-C), and 140.7 (d, J_{CP}=31.4 Hz, P-Ph; α-C); *m/z* 180 (M^+, 69%).

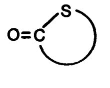
*2-Phenyl-1,2-thiaphospholane **1c***: From dichlophenylphosphine (48 ml, 0.355 mol), 3-chloro-1-propanethiol (39.2 g, 0.355 mol), pyridine (30 ml, 0.371 mol), and lithium metal (4.93 g, 0.710 g-atom), 6.59 g of **1c** was obtained; 10% yield, bp 102—104 °C (0.50 Torr). $^{31}P\{^1H\}$NMR($CDCl_3$) + 22.3 ppm; ^1H NMR δ($CDCl_3$) 1.1—3.1 (m, 6H, $SC\underline{H}_2C\underline{H}_2C\underline{H}_2P$) and 6.8—7.6 (m, 5H, $C_6\underline{H}_5$); $^{13}C\{^1H\}$NMR($CDCl_3$) 28.9 (d, J_{CSP}=7.3 Hz, $S\underline{C}H_2$), 35.2 (s, $P\underline{C}H_2$), 36.0 (d, J_{CCP}=23.2 Hz, $PCH_2\underline{C}H_2$), 128.1 (s, P-Ph; δ-C) 128.1 (d, J_{CCCP}=3.7 Hz, P-Ph; γ-C), 130.0 (d, J_{CCP}=17.1 Hz, P-Ph; β-C), and 140.4 (d, J_{CP}=40.3, P-Ph, α-C); *m/z* 182 (M^+, 100%).

*2-Phenyl-1,2-thiaphosphorinane **1d***: From dichlorophenylphosphine (12.65 g, 0.071 mol), 4-chloro-1-butanethiol (9.52 g, 0.071 mol), pyridine (6.0 ml, 0.074 mol), and lithium metal (0.985 g, 0.142 g-atom), 0.659 g of **1d** was obtained; 5% yield, bp 99—103 °C (0.32 Torr). $^{31}P\{^1H\}$NMR($CDCl_3$) +4.8 ppm; ^1H NMR δ($CDCl_3$) 1.0—3.0 (m, 8H, $S\underline{C}H_2C\underline{H}_2C\underline{H}_2C\underline{H}_2P$) and 6.9—7.8 (m, 5H, $C_6\underline{H}_5$); $^{13}C\{^1H\}$NMR-($CDCl_3$) 20.1 (s, $P\underline{C}H_2$ or $PCH_2CH_2\underline{C}H_2$), 23.5 (d, J_{CCP}=22.6 Hz, $PCH_2\underline{C}H_2$), 24.5 (d, J_{CSP}=10.5 Hz, $S\underline{C}H_2$), 27.8 (s, $P\underline{C}H_2$ or $PCH_2CH_2\underline{C}H_2$), 127.2 (s, P-Ph; δ-C), 128.6 (d, J_{CCCP}=3.5 Hz, P-Ph; γ-C), 130.5 (d, J_{CCP}=14.8, P-Ph; β-C), and 137.1 ppm (d, J_{CP}=32.2 Hz, P-Ph; α-C); *m/z* 196 (M^+, 100%).

References

1) S. Kobayashi, M. Suzuki, and T. Saegusa, *Polymer Bull.*, **4**, 315 (1981); *ibid.*, **8**, 417 (1982); *Macromolecules*, **17**, 107 (1984).

2) A trivial name of "deoxophostone" for **1a** was used by Grayson and Farley.[3] A "phostone" is recognized as a derivative of lactone.[4] We followed logically these naming for new phosphorus heterocycles **1c** and **1d** as "deoxothiolphostones". Then, the inter-relationships are schematically shown as follows: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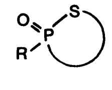
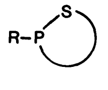

thiolphostone


deoxothiolphostone

3) M. Grayson and C. E. Farley, *J. Chem. Soc., Chem. Commun.*, **1967**, 830. This literature reported bp of **1a** as 112 °C (0.5 Torr). However, we prepared **1a** according to the present method as well as to this literature's method, distilled it several times, and confirmed that the present bp value is correct.

4) J.-N. Collard and C. Benezra, *Tetrahedron Lett.*, **23**, 3725 (1982).

5) K. Issleib and H.-R. Roloff, *Chem. Ber.*, **98**, 2091 (1965); S. Antczak and S. Trippett, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 1326; F. Mathey and F. Mercier, *J. Chem. Soc., Chem. Commun.*, **1980**, 191.

6) F. Mathey, M.-B. Comarmond, and D. Moras, *J. Chem. Soc., Chem. Commun.*, **1979**, 417.

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8) B. Sjöberg, *Chem. Ber.*, **74**, 64 (1941).

9) J. H. Chapman and L. N. Owen, *J. Chem. Soc.*, **1950**, 579.