Direct Deoxygenation of the Hydroxy Group of Methyl 1-Hydroxyalkyl-(phenyl)-phosphinates using Diphosphorus Tetraiodide

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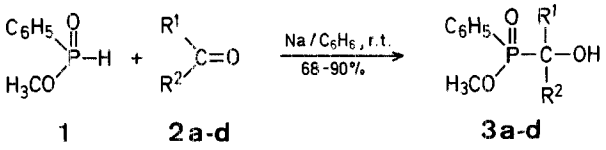
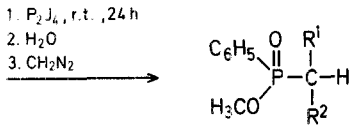
The hydroxy group of methyl 1-hydroxyalkyl-(phenyl)-phosphinates **3**, prepared from methyl phenylphosphinate **1** and aldehydes or ketones **2**, is directly deoxygenated on treatment with diphosphorus tetraiodide to give the methyl alkyl-(phenyl)-phosphinates **4**.

Additions of phosphorus compounds having a P-H bond to carbonyl compounds are known to give phosphorus compounds possessing a hydroxy group on the α-carbon atom[1-5]. The conversion of the hydroxy group directly into hydrogen was unsuccessful until our preceding work on α-hydroxyalkylphosphine oxide derivatives using diphosphorus tetraiodide was published[6]. In this communication we describe the synthesis of methyl 1-hydroxyalkyl-(phenyl)-phosphinate derivatives **3a–d** and their direct deoxygenation, promoted by the methoxy-phenylphosphinyl group, with diphosphorus tetraiodide[7].



1 2a-d 3a-d



4a-d

2,3,4	R^1	R^2
a	CH_3	CH_3
b	CH_3	H
c	C_2H_5	CH_3
d	C_2H_5	H

Methyl 1-hydroxyalkyl-(phenyl)-phosphinates **3a–d** were prepared by the reaction of aldehydes or ketones **2a–d** with methyl phenylphosphinate **(1)** in the presence of base[8]. Direct deoxygenation of **3a–d** to give methyl alkyl-(phenyl)-phosphinates **4a–d** with diphosphorus tetraiodide was successful after work-up with diazomethane (Table).

Only a few reports concerning the deoxygenation of alcohols with diphosphorus tetraiodide to give the parent hydrocarbons are known[9,10]. In the case of phosphonates also, no direct deoxygenation of an α-hydroxy group of (1-hydroxyethyl)-phosphonate derivatives has been reported. However, it has been reported that the functional group interconversion of the α-hydroxy group into hydrogen can be carried out to prepare the parent ethanephosphonate derivatives, in yields of 48–77%, by hydrogenation or hydrogenolysis of the corresponding vinyl- or chloro-derivatives[11].

In summary, the present method should provide a facile preparative method for phosphinates from carbonyl compounds and phosphorus compounds having a P-H bond.

Table. Compounds **3** and **4** prepared

Product	Yield [%]	m.p. [°C] or b.p. [°C]/torr	Molecular Formula[a]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]	I.R. (KBr) ν [cm^{-1}]	M.S. m/e (M^+)
3a	68	110–111°	$C_{10}H_{15}O_3P$ (214.2)	1.42, 1.47 (2d, 3H each, J = 15.0 Hz, $2CH_3$); 3.94 (d, 3H, J = 10.0 Hz, OCH_3); 5.11 (s, 1H, OH); 7.5–8.4 (m, $5H_{arom}$)	3300 (OH)	214
3b	90	232–237°/0.1	$C_9H_{13}O_3P$ (200.2)	1.37 (dd, 3H, J_{HH} = 7.0 Hz, J_{HP} = 15.0 Hz, CH_3); 3.71 (d, 3H, J = 10.0 Hz, OCH_3); 3.7–4.2 (m, 1H, CH); 5.39 (s, 1H, OH); 7.0–8.0 (m, $5H_{arom}$)	3350 (OH)	200
3c	76	200–202°	$C_{11}H_{17}O_3P$ (228.2)	0.92 (t, 3H, J = 7.0 Hz, CH_2CH_3); 1.28, 1.30 (2d, 3H, J = 15.5 Hz, $C—CH_3$); 1.63 (dq, 2H, J_{HP} = 15.5 Hz, J_{HH} = 7.0 Hz, CH_2CH_3); 3.66 (d, 3H, J = 10.5 Hz, OCH_3); 4.26 (s, 1H, OH), 7.1–7.8 (m, $5H_{arom}$)	3300 (OH)	228
3d	74	47–49°	$C_{10}H_{15}O_3P$ (214.2)	0.80 (t, 3H, J = 7.0 Hz, CH_2CH_3); 1.0–2.0 (m, 2H, CH_2CH_3); 3.5–4.0 (m, 1H, CH); 3.45 (d, 3H, J = 10.0 Hz, OCH_3); 4.05 (s, 1H, OH); 7.0–7.7 (m, $5H_{arom}$)	3300 (OH)	214
4a[12]	74	95–100°/1.5	$C_{10}H_{15}O_2P$ (198.2)	0.95, 1.20 (2dd, 3H each, J_{HP} = 15.0 Hz, J_{HH} = 7.0 Hz, $2CH_3$); 1.5–2.5 (m, 1H, CH); 3.50 (d, 3H, J = 10.0 Hz, OCH_3); 7.2–7.7 (m, $5H_{arom}$)	1240 (P=O)	198
4b[13]	80	106–107°/0.8	$C_9H_{13}O_2P$ (184.2)	1.00 (dt, 3H, J_{HP} = 15.0 Hz, J_{HH} = 7.0 Hz, CH_3); 1.5–2.0 (m, 2H, CH_2); 3.62 (d, 3H, J = 10.8 Hz, OCH_3); 7.0–7.5 (m, $5H_{arom}$)	1250 (P=O)	184
4c	75	104–106°/0.7	$C_{11}H_{17}O_2P$ (212.2)	0.81–1.3 (m, 8H, CH_3, C_2H_5); 1.5–2.0 (m, 1H, CH); 3.55 (d, 3H, J = 10.0 Hz, OCH_3); 7.0–7.7 (m, $5H_{arom}$)	1240 (P=O)	212
4d	77	117–119°/2	$C_{10}H_{15}O_2P$ (198.2)	0.95, 1.00 (2t, 3H, J = 7.0 Hz, CH_2CH_3); 1.2–2.2 (m, 4H, $—CH_2CH_2—$); 3.60 (d, 3H, J = 10.8 Hz, OCH_3); 7.0–7.8 (m, $5H_{arom}$)	1250 (P=O)	198

[a] Satisfactory microanalyses obtained: C ±0.41, H ±0.29.

Methyl 2-Hydroxy-2-propyl-(phenyl)-phosphinate (3a); Typical Procedure:

To a mixture of methyl phenylphosphinate (**1**; 2.0 g, 13 mmol) and sodium metal (0.20 g, 8.7 mmol) in benzene (10 ml) is added acetone (**2a**; 4.0 g, 6.9 mmol). After 12 h at room temperature the solvent is removed, and the residue is taken up in chloroform (3 × 30 ml). The chloroform solution is washed with water (2 × 10 ml) and dried with anhydrous sodium sulfate. Evaporation of the solvent in vacuo gives the product **3a**; yield: 1.9 g (69%); m.p. 110–111 °C.

$C_{10}H_{15}O_3P$ (214.2) calc. C 56.07 H 7.06 found 56.01 6.92

M.S.: m/e = 214 (M^+); I.R. (KBr): ν = 3300 cm^{-1} (OH).

Methyl Phenyl-(2-propyl)-phosphinate (4a); Typical Procedure:

A mixture of diphosphorus tetraiodide (2.7 g, 4.8 mmol) and **3a** (0.52 g, 2.4 mmol) in chloroform (5 ml) is stirred at room temperature for 24 h. The mixture is then extracted with chloroform (3 × 30 ml), the extract is washed with water (2 ml), and treated with an ether solution of diazomethane [generated from *p*-toluenesulfonylmethylnitrosamide (0.89 g, 4.2 mmol) in ether (8 ml) according to Ref.[14] at 20 °C for 0.5 h. The product is separated by preparative thin layer chromatography on silica gel with ethyl acetate/petroleum ether (2/1, v/v) as eluent to give **4a**; yield: 0.35 g (74%); b.p. 95–100 °C/1.5 torr.

$C_{10}H_{15}O_2P$ (198.2) calc. C 60.60 H 7.63 found 60.19 7.34

M.S.: m/e = 198 (M^+); I.R. (film): ν = 1240 cm^{-1} (P=O).

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