Synthesis of Diphenyl-(1-nitromethyl-1-alkyl)-phosphine Oxides and their Conversion to Diphenyl-(1-formyl-1-alkyl)-phosphine Oxides

Manabu YAMADA, Mitsuji YAMASHITA*

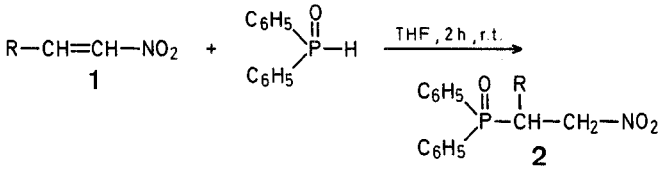
Department of Synthetic Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432, Japan

Saburo INOKAWA

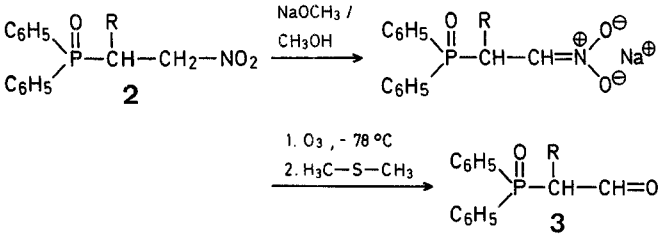
Department of Chemistry, Faculty of Science, Okayama University, Okayama 700, Japan

The conversion of nitro compounds into carbonyl compounds is a useful synthetic transformation. This reaction is generally carried out under one of a variety of conditions: strongly acidic (Nef reaction[1]), basic oxidative[2-8], neutral oxidative[9], and neutral reductive[7,10,11,12]. However, the conversion of organophosphorus compounds with a nitro group at the β-carbon atom (β-nitrophosphines) into compounds with an aldehyde group on the α-carbon atom has not been reported. Numerous attempts by us to affect this conversion under various conditions[5,7,8,10,12] were unsuccessful.

This report describes the synthesis of diphenyl-(1-nitromethyl-1-alkyl)-phosphine oxides **2** and their conversion to the diphenyl-(1-formyl-1-alkyl)-phosphine oxides **3**. Compounds **2** are prepared by the addition of diphenylphosphine oxide to a nitroalkene **1** in tetrahydrofuran at room temperature (Table).



Conversion of compounds **2** to **3** was achieved by treating **2** with ozone[4] in the presence of sodium methoxide at −78 °C (Table).



Sodium borohydride reduction of compounds **3** should provide a useful method for the preparation of diphenyl-(1-alkyl-2-hydroxyethyl)-phosphine oxides. Compounds **3** were char-

Table. Compounds **2** and **3** prepared

Product No.	R	Yield [%]	m.p. [°C]	Molecular formula[a]	M.S. *m/e* (M^+)	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]	m.p. [°C] of 2,4-DNP
2a	CH_3	93	120–123°	$C_{15}H_{16}NO_3P$ (289.3)	289	1550, 1370; 1180; 710	1.24 (dd, 3 H, J_{HH} = 7 Hz, J_{HP} = 16 Hz); 3.1–3.7 (m, 1 H); 4.52 (dd, 2 H, J_{HH} = 5 Hz, J_{HP} = 7 Hz); 7.0–8.1 (m, 10 H_{arom})	—
2b	C_2H_5	95	115–117°	$C_{16}H_{18}NO_3P$ (303.3)	303	1545, 1375; 1185; 710	0.95 (t, 3 H, J = 7 Hz); 1.4–1.9 (m, 2 H); 3.1–3.6 (m, 1 H); 4.58 (dd, J_{HH} = 5 Hz, J_{HP} = 7 Hz); 7.3–8.2 (m, 10 H_{arom})	—
2c	*i*-C_3H_7	95	160°	$C_{17}H_{20}NO_3P$ (317.3)	317	1545, 1375; 1180; 710	1.02 (d, 6 H, J = 7 Hz); 2.0–2.5 (m, 1 H); 3.2–3.6 (m, 2 H); 7.0–8.2 (m, 10 H_{arom})	—
2d	C_6H_5	86	208–209°	$C_{20}H_{18}NO_3P$ (351.3)	351	1545, 1375; 1185, 710	4.3–4.7 (m, 2 H); 4.8–5.3 (m, 1 H); 7.1–8.2 (m, 15 H_{arom})	—
3a	CH_3	90	130–131°	$C_{15}H_{15}O_2P$ (258.3)	258	1650	1.34 (dd, 3 H, J_{HH} = 7 Hz, J_{HP} = 16 Hz); 3.3–3.8 (m, 1 H); 7.2–8.0 (m, 10 H_{arom}); 9.60 (d, 1 H, J = 3 Hz)	—[c]
3b	C_2H_5	99	147–148°	$C_{16}H_{17}O_2P$ (272.3)	272	1650	0.94 (t, 3 H, J = 7 Hz); 1.6–2.4 (m, 2 H); 3.4–3.8 (m, 1 H); 7.2–8.0 (m, 10 H_{arom}); 9.84 (d, 1 H, J = 3 Hz)	190–192°
3c	*i*-C_3H_7	90	168–169°	$C_{17}H_{19}O_2P$ (286.3)	286	1640	1.10 (d, 6 H, J = 7 Hz); 1.9–2.5 (m, 1 H); 3.1–3.5 (m, 1 H); 7.2–8.0 (m, 10 H_{arom}); 9.26 (d, 1 H, J = 5 Hz)	201–203°
3d[b]	C_6H_5	67	189–190°	$C_{20}H_{17}O_2P$ (320.3)	320	1705	4.5–5.1 (m, 1 H); 6.9–8.2 (m, 15 H_{arom}); 9.95 (br. s, 1 H)	154–160° (dec)

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.18, N ±0.32.
[b] Aldehyde **3d** is oxidized to the corresponding acid during work-up.
[c] Not crystallized.

0039-7881/82/1232-1026 $ 03.00

acterized by microanalysis, I.R., ^{1}H-N.M.R., and mass spectrometry, and by conversion to 2,4-dinitrophenylhydrazones.

Diphenyl-3-nitro-2-propylphosphine Oxide (2a; R = CH_3); Typical Procedure:

To a solution of 1-nitro-1-propene (**1a**; 1.04 g, 12 mmol) in anhydrous tetrahydrofuran (15 ml) is added a solution of diphenylphosphine oxide (2.42 g, 12 mmol) in anhydrous tetrahydrofuran (5 ml) at 0 °C. The solution is stirred for 2 h at room temperature, the solvent is evaporated under reduced pressure, and the residue is recrystallized from carbon tetrachloride to give pure **2a**; yield: 3.21 g (93%); m.p. 120–123 °C.

$C_{15}H_{16}NO_3P$	calc.	C 62.28	H 5.58	N 4.84
(289.3)	found	62.38	5.76	4.89

Diphenyl-1-oxo-2-propylphosphine Oxide (3a; R = CH_3); Typical Procedure:

Compound **2a** (1.00 g, 3.5 mmol) in anhydrous methanol (30 ml) is treated with sodium methoxide (0.19 g, 3.5 mmol) and the mixture is stirred at room temperature for 10 min. The solution is then cooled to −78 °C and a stream of ozone is bubbled until the solution acquires a light blue color. After 30 min, the mixture is purged with nitrogen, treated with dimethyl sulfide (5 ml) at −78 °C, and slowly allowed to warm to room temperature. The mixture is allowed to stand for 16 h, volatile material is removed using a rotary evaporator, the residue is taken up in chloroform (40 ml), and washed with water (20 ml) and brine (20 ml). The chloroform extract is dried with sodium sulfate and evaporated under reduced pressure. The residue is recrystallized from carbon tetrachloride to give pure **3a**; yield: 0.8 g (90%); m.p. 130–131 °C.

$C_{15}H_{15}O_2P$	calc.	C 69.97	H 5.86
(258.2)	found	69.79	5.85

Received: June 9, 1982

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0039-7881/82/1232-1027 $ 03.00