Novel Preparation of Diphenylvinylphosphine Oxides via Direct Deoxygenation of 1,2-Epoxyethyldiphenylphosphine Oxides with Diphosphorus Tetraiodide

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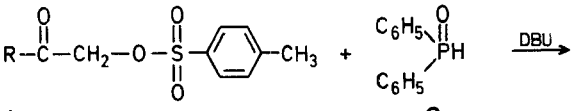
(1-Hydroxyethyl)-diphenylphosphine oxides were easily prepared by addition of diphenylphosphine oxide to ketones or aldehydes in good yields[1]. The reaction of 2-oxopropyl *p*-toluenesulfonate with dimethyl phosphonate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature was reported to give dimethyl 1,2-epoxy-1-methylethanephosphonate[2], addition of dimethyl phosphonate to the carbonyl group followed by replacement of the *p*-toluenesulfoxyl group having taken place.

Deoxygenation with diphosphorus tetraiodide has been reported to give sulfide, nitrile, and olefin from sulfoxide, oxime, and epoxide, respectively[3,4]. Previous work on the preparation of vinyl derivatives of phosphorus compounds was concerned mainly with Grignard[5], elimination[6], and substitution reactions[7], which were not applicable to carbohydrates. The present communication deals with a novel synthesis of epoxyphosphine oxides from α-keto tosylates and their conversion into vinylphosphine oxides by action of diphosphorus tetraiodide.

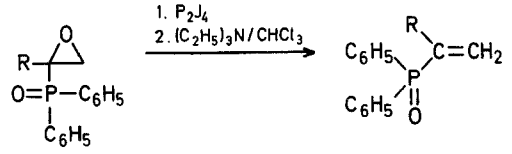
Reaction of 2-alkyl-2-oxoethyl *p*-toluenesulfonates (**1**) with diphenylphosphine oxide (**2**) in the presence of DBU at 5 °C gave (1-alkyl-1,2-epoxyethyl)-diphenylphosphine oxides (**3**) in good yield (Table 1).

Reaction of epoxide **3** with diphosphorus tetraiodide in the presence of triethylamine at room temperature gave the corresponding vinylphosphine oxide **4** in good yield (Table 2). In an earlier paper[8], the authors reported the synthesis of vinylphosphonate from acylphosphonate via Wittig reaction. On the other hand, vinylphosphonates were obtained from 1-alkyl-1-hydroxyethylphosphonates by reaction with thionyl chloride[9], where an isomeric product other than the vinyl one was formed. Therefore the present method is a mild, convenient, and regioselective reaction to prepare vinyl derivatives of phosphorus compounds.



1a R = CH_3
b R = C_2H_5
c R = *c*-C_6H_{11}
d R = C_6H_5

2



3 **4**

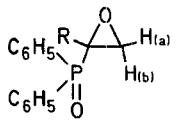
(1-Methyl-1,2-epoxyethyl)-diphenylphosphine Oxide (3a; R = CH_3); Typical Procedure:

A mixture of diphenylphosphine oxide (**2**; 7.0 g, 35 mmol) and 2-oxopropyl *p*-toluenesulfonate (8.0 g, 35 mmol) in dry benzene (20 ml) in the presence of DBU (5.6 g, 37 mmol) is allowed to stand for 48 h in refrigerator. Evaporation of the solvent in vacuo gives a crude product. Purification by extraction of DBU with dilute hydrochloric acid from the chloroform solution and recrystallization from benzene gives pure **3a**; yield: 7.6 g (84%) m.p. 113–115 °C.

For the Preparation of Diphenyl(1-methylvinyl)-phosphine Oxide (4a; R = CH_3) from 3a with Diphosphorus Tetraiodide; Typical Procedure:

A chloroform (5 ml) solution of **3a** (0.50 g, 1.9 mmol) and diphosphorus tetraiodide[11] (1.2 g, 2.1 mmol) is allowed to stir for 24 h at room temperature, then triethylamine (10 ml) is added to the solution. The mixture is further allowed to stir for an additional 6 h at room temperature. The mixture is decanted several times with chloroform (5 × 20 ml), then the solution is washed with water (3 × 10 ml), and dried with anhydrous sodium sulfate. Evaporation of the solvent followed by separation by thin layer chromatography on silica gel affords pure **3a**; yield: 0.43 g (79%); m.p. 126–128 °C.

Table 1. Compounds **3** prepared

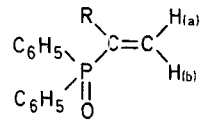


3a-d

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. ($CDCl_3$/TMS) δ [ppm]
3a	CH_3	84	113–115°	$C_{15}H_{15}O_2P$ (258.3)	258	1210 (P=O); 1030 (C—O—C); 720 (C—P)	1.45 (d, J = 10 Hz, CH_3); 2.42 [dd, J = 5 Hz, 9 Hz, H(a)]; 2.57 [dd, J = 5 Hz, 8 Hz, H(b)]; 7.1–8.0 (m, $2C_6H_5$)
3b	C_2H_5	90	87–89°	$C_{16}H_{17}O_2P$ (272.3)	272	1210 (P=O); 1030 (C—O—C); 720 (C—P)	0.85 (t, J = 8 Hz, CH_3); 1.95 (dq, J = 8 Hz, 8 Hz, CH_2); 2.42 [dd, J = 5 Hz, 5 Hz, H(a)]; 2.75 [dd, J = 5 Hz, 5 Hz, H(b)]; 7.2–8.2 (m, $2C_6H_5$)
3c	*c*-C_6H_{11}	80	96–98°	$C_{20}H_{23}O_2P$ (326.4)	326	1210 (P=O); 1050 (C—O—C); 720 (C—P)	0.7–2.1 (m, C_6H_{11}); 2.30 [dd, J = 5 Hz, 6 Hz, H(a)]; 2.71 [dd, H(b)]; 7.2–8.3 (m, $2C_6H_5$)
3d	C_6H_5	83	168–170°	$C_{20}H_{17}O_2P$ (320.3)	320	1180 (P=O); 1030 (C—O—C); 720 (C—P)	2.72 [dd, J = 3 Hz, 6 Hz, H(b)]; 2.87 [dd, J = 5 Hz, 6 Hz, H(a)]; 7.1–8.1 (m, $3C_6H_5$)

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.18.

Table 2. Compounds **4** prepared



4 a-d

Product No.	R	Yield [%]	m.p. [°C]	Molecular Formula[a] or Lit. m.p. [°C]	M.S. *m/e* (M^+)	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
4a	CH_3	79	126–128°	126–128°	242	1180 (P=O); 880 (C=CH_2); 720 (C—P)	1.99 (d, J = 12 Hz, CH_3); 5.61 [d, J = 19 Hz, H(b)]; 5.90 [d, J = 41 Hz, H(a)]; 7.3–7.9 (m, $2C_6H_5$)
4b	C_2H_5	76	43–45°	$C_{16}H_{17}OP$ (256.3)	256	1190 (P=O); 880 (C=CH_2); 720 (C—P)	1.10 (t, J = 7 Hz, CH_3); 2.35 (dq, J = 2 Hz, 7 Hz, CH_2); 5.63 [d, J = 21 Hz, H(b)]; 5.93 [d, J = 43 Hz, H(a)]; 7.3–7.9 (m, $2C_6H_5$)
4c	*c*-C_6H_{11}	70	29–31°	$C_{20}H_{23}OP$ (310.4)	310	1180 (P=O); 890 (C=CH_2); 730 (C—P)	0.6–2.5 (m, C_6H_{11}); 5.43 [d, J = 22 Hz, H(b)]; 5.87 [d, J = 44 Hz, H(a)]; 7.0–7.9 (m, $2C_6H_5$)
4d	C_6H_5	80	114–115°	114–115°[7]	304	1190 (P=O); 930 (C=CH_2); 720 (C—P)	5.55 [d, J = 19 Hz, H(b)]; 6.13 [d, J = 40 Hz, H(a)]; 7.0–7.9 (m, $3C_6H_5$)

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.18.

Received: June 12, 1984

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