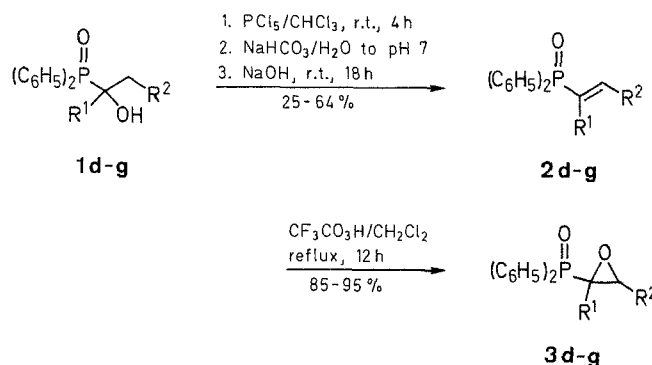


Epoxides are known to be cleaved by attack of nucleophiles at the less hindered site to give open-chain hydroxy compounds. Ring opening generally occurs at the less substituted site or at the site having no electron-withdrawing groups.¹ In the case of 1,2-epoxyalkylphosphonates, orientation of the ring opening by a nucleophile is similar: cleavage occurs at C-2 of the oxirane ring.^{2,3} Using alkyllithium as a nucleophile, 1,2-epoxyalkylphosphonates decompose to allylic alcohols.⁴ In this communication, we describe the reaction of 1,2-epoxyalkyldiphenylphosphine oxides with lithium aluminum hydride to give 2-hydroxyalkyldiphenylphosphine oxides.

1,2-Epoxyalkyldiphenylphosphine oxides **3a-c** are prepared by the reaction of 2-oxoalkyl *p*-toluenesulfonates with diphenylphosphine oxide in good yield,⁵ and compounds **3d-g** are prepared by the following method: 1-Hydroxyalkyldiphenylphosphine oxides **1d-g**⁶ are converted to 1-alkenyldiphenylphosphine oxides **2d-g** by successive treatment with phosphorus(V) chloride and aqueous potassium hydroxide.



Abnormal Ring Opening of 1,2-Epoxyalkyldiphenylphosphine Oxides with Lithium Aluminum Hydride to Form 2-Hydroxyalkyldiphenylphosphine Oxides

Hiroyuki Imoto, Mitsuji Yamashita*

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

Ring opening of 1,2-epoxyalkyldiphenylphosphine oxides with LiAlH_4 gives 2-hydroxyalkyldiphenylphosphine oxides in good yield. This is the first example of ring opening of 1,2-epoxyalkyldiphenylphosphine oxides to give the corresponding 2-hydroxy derivatives.

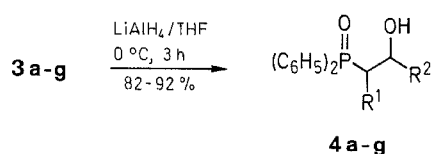
Epoxidation of **2d-g** with trifluoroperacetic acid gives phosphine oxides **3d-g** with retention of configuration.⁷

The ring cleavage of **3a-g** with lithium aluminum hydride gives compounds **4a-g** in good yield.

Table 1. Compounds **2d-g** Prepared

Product	Yield (%)	mp (°C)	Molecular Formula ^a or Lit. mp (°C)	MS (M^+) m/z	IR (KBr) ν (cm^{-1})	$^1\text{H-NMR}$ (CDCl_3/TMS) δ , J (Hz)
2d	28	103-105	$\text{C}_{17}\text{H}_{19}\text{OP}$ (270.3)	270	1630 (C=C); 1200 (P=O)	0.89 (t, 3H, $J_{\text{HH}} = 8$, CH_2CH_3); 1.84 (dd, 3H, $J_{\text{HH}} = 7$, $J_{\text{HP}} = 3$, CHCH_3); 2.36 (dq, 2H, $J_{\text{HH}} = 8$, $J_{\text{HP}} = 15$, CH_2); 6.18 (dq, 1H, $J_{\text{HH}} = 7$, $J_{\text{HP}} = 22$, CH); 7.2-7.9 (m, 10H _{arom})
2e	25	86-88	87-89 ⁸	298	1630 (C=C); 1200 (P=O)	0.77 (t, 3H, $J_{\text{HH}} = 7$, $\text{CH}_2\text{CH}_2\text{CH}_3$); 0.89 (t, 3H, $J_{\text{HH}} = 7$, CH_2CH_3); 1.9-2.4 (m, 6H, 3CH ₂); 6.05 (dt, 1H, $J_{\text{HH}} = 7$, $J_{\text{HP}} = 21$, CH); 7.2-7.8 (m, 10H _{arom})
2f	64	113-115	118-120 ⁹	282	1630 (C=C); 1190 (P=O)	1.5-2.4 (m, 8H, C_6H_8); 6.37 (d, 1H, $J_{\text{HP}} = 20$, CH); 7.2-7.9 (m, 10H _{arom})
2g	28	74-76	oil ⁹	296	1630 (C=C); 1190 (P=O)	1.3-2.1 (m, 10H, C_7H_{10}); 6.55 (dt, 1H, $J_{\text{HH}} = 6$, $J_{\text{HP}} = 17$, CH); 7.3-7.8 (m, 10H _{arom})

^a Satisfactory microanalyses obtained: C ± 0.30 , H ± 0.18 , P ± 0.15 .



Orientation of this cleavage is abnormal: i.e., attack of hydride ion occurs at C-1, but not at C-2 of the epoxide to afford 2-hydroxyalkylphosphine oxides. This is the first example where 1,2-epoxyalkylphosphorus compounds are cleaved at the (C-1)-O bond to give 2-hydroxyalkyl compounds.

(1-Ethyl-1-propenyl)diphenylphosphine Oxide (2d; R¹ = C₂H₅, R² = CH₃); Typical Procedure:

To a stirred solution of (1-ethyl-1-hydroxypropyl)diphenylphosphine oxide (1d; 2.12 g, 7.4 mmol) in CHCl₃ (15 mL) is added phosphorus(V) chloride (3.7 g, 18 mmol) at 0°C. Stirring is continued for 4 h at room

temperature and the solution then neutralized with saturated aqueous NaHCO₃. To the solution is added KOH (1.0 g), the mixture is stirred for 18 h at room temperature, and extracted with CHCl₃ (4 × 25 mL). The extract is washed with 2 N HCl (10 mL) and with H₂O (3 × 15 mL), and dried (Na₂SO₄). Removal of the solvent under reduced pressure gives 2d; yield: 0.60 g (28 %); mp 103–105°C.

C₁₇H₁₉OP calc. C 75.54 H 7.09 P 11.46
(270.3) found 75.76 7.24 11.52

For spectral data, see Table 1.

(1,2-Epoxy-1-ethylpropyl)diphenylphosphine Oxide (3d; R¹ = C₂H₅, R² = CH₃); Typical Procedure:

To a stirred suspension of 30% aqueous H₂O₂ (1.2 mL) in CH₂Cl₂ (10 mL) is added trifluoroacetic anhydride (2.0 mL), dropwise, over 5 min at 0°C. Then the solution is allowed to warm to room temperature, and stirred for 30 min. A solution of phosphine oxide 2d (1.23 g, 4.6 mmol) in CH₂Cl₂ (10 mL) is then added over 12 h under reflux. The mixture is extracted with CH₂Cl₂ (30 mL) and the extract is washed with 10% aqueous KHSO₃ (10 mL), saturated aqueous KHCO₃

Table 2. Compounds 3d–g Prepared

Product	Yield (%)	mp (°C)	Molecular Formula ^a	MS (M ⁺) m/z	IR (KBr) ν (cm ⁻¹)	¹ H-NMR (CDCl ₃ /TMS) δ, J (Hz)
3d	95	154–156	C ₁₇ H ₁₉ O ₂ P (286.3)	286	1205 (P=O); 870 (oxirane)	1.04 (t, 3H, J _{HH} = 8, CH ₂ CH ₃); 1.32 (d, 3H, J _{HH} = 5, CHCH ₃); 1.6–2.4 (m, 2H, CH ₂); 2.6–2.9 (m, 1H, CH); 7.3–8.2 (m, 10H _{arom})
3e	94	75–77	C ₁₉ H ₂₃ O ₂ P (314.4)	314	1200 (P=O); 860 (oxirane)	0.88 (t, 3H, J _{HH} = 6, CH ₂ CH ₂ CH ₃); 0.98 (t, 3H, J _{HH} = 7, CH ₂ CH ₃); 1.3–2.2 (m, 6H, 3CH ₂); 2.61 (dt, 1H, J _{HH} = 7, J _{HP} = 6, CH); 7.2–8.1 (m, 10H _{arom})
3f	90	148–149	C ₁₈ H ₁₉ O ₂ P (298.3)	298	1200 (P=O); 870 (oxirane)	1.1–2.4 (8H, C ₆ H ₈); 2.7–3.0 (m, 1H, CH); 7.2–8.1 (m, 10H _{arom})
3g	85	110–112	C ₁₉ H ₂₁ O ₂ P (312.4)	312	1200 (P=O); 850 (oxirane)	1.0–2.3 (m, 10H, C ₇ H ₁₀); 2.6–2.9 (m, 1H, CH); 7.2–8.1 (m, 10H _{arom})

^a Satisfactory microanalyses obtained: C ± 0.24, H ± 0.16, P ± 0.13.

Table 3. Compounds 4 Prepared

Product	Yield (%)	mp (°C)	Molecular Formula ^a or Lit. mp (°C)	MS (M ⁺) m/z	IR (KBr) ν (cm ⁻¹)	¹ H-NMR (CDCl ₃ /TMS) δ, J (Hz)
4a	83	141–142	141–142 ¹⁰	260	3300 (OH); 1180 (P=O)	1.09 (dd, 3H, J _{HH} = 7, J _{HP} = 16, CH ₃); 2.3–2.9 (m, 1H, CH); 3.5–3.9 (m, 2H, CH ₂ OH); 4.02 (s, 1H, OH); 7.2–7.9 (m, 10H _{arom})
4b	84	105–106	105–106 ¹⁰	274	3300 (OH); 1180 (P=O)	0.83 (t, 3H, J _{HH} = 7, CH ₂ CH ₃); 1.3–1.9 (m, 2H, CH ₂ CH ₃); 2.1–2.6 (m, 1H, CH); 3.74 (dd, 2H, J _{HH} = 5, J _{HP} = 16, CH ₂ OH); 4.08 (s, 1H, OH); 7.1–7.9 (m, 10H _{arom})
4c	85	185–187	168–170 ¹⁰	322	3400 (OH); 1180 (P=O)	2.77 (t, 1H, J _{HH} = 6, CH); 3.7–4.4 (m, 2H, CH ₂ OH); 4.47 (s, 1H, OH); 7.0–8.0 (m, 3 × C ₆ H ₅ , 15H _{arom})
4d	89	83–86	C ₁₇ H ₂₁ O ₂ P (288.3)	288	3380 (OH); 1180 (P=O)	0.79 (t, 3H, J _{HH} = 7, CH ₂ CH ₃); 1.18 (d, 3H, J _{HH} = 7, CHCH ₃); 1.3–2.3 (m, 3H, CHCH ₂); 3.64 (s, 1H, OH); 3.9–4.6 (m, 1H, CHOH); 7.2–8.0 (m, 10H _{arom})
4e	91	157–159	C ₁₉ H ₂₅ O ₂ P (316.4)	316	3400 (OH); 1180 (P=O)	0.5–1.0 (m, 6H, 2CH ₃); 1.0–2.0 (m, 6H, 3CH ₂); 2.0–2.4 (m, 1H, PCH); 3.7–4.2 (m, 1H, CHOH); 4.26 (s, 1H, OH); 7.2–8.0 (m, 10H _{arom})
4f	92	122–125	C ₁₈ H ₂₁ O ₂ P (300.3)	300	3400 (OH); 1190 (P=O)	0.9–2.0 (m, 8H, C ₆ H ₈); 2.0–2.3 (m, 1H, PCH); 3.9–4.3 (m, 1H, CHOH); 4.06 (s, 1H, OH); 7.2–8.0 (m, 10H _{arom})
4g	82	132–134	C ₁₉ H ₂₃ O ₂ P (314.4)	314	3370 (OH); 1170 (P=O)	1.1–2.0 (m, 10H, C ₇ H ₁₀); 2.0–2.4 (m, 1H, PCH); 4.09 (s, 1H, OH); 4.0–4.4 (m, 1H, CHOH); 7.2–8.0 (m, 10H _{arom})

^a Satisfactory microanalyses obtained: C ± 0.28, H ± 0.20, P ± 0.13.

(2 × 20 mL), and H₂O (10 mL). The organic layer is dried (Na₂SO₄) and the solvent removed under reduced pressure to give **3d**; yield: 1.24 g (95%); mp 154–156°C.

C ₁₇ H ₁₉ O ₂ P	calc.	C 71.32	H 6.69	P 10.82
(286.3)	found	71.53	6.82	10.93

For spectral data, see Table 2.

(2-Hydroxy-1-methylethyl)diphenylphosphine Oxide (4a; R¹ = CH₃, R² = H); Typical Procedure:

To a stirred solution of epoxide **3a** (0.262 g, 1.0 mmol) in THF (10 mL) is added LiAlH₄ (0.050 g, 1.3 mmol) at 0°C and stirring is continued for 3 h at 0°C. Then, H₂O (1 mL) is added and the solution is neutralized with 2 N HCl. The solvent is removed under reduced pressure, the product is taken up in CHCl₃ (3 × 15 mL), and the extract is washed with H₂O (2 × 10 mL) and dried (Na₂SO₄). Removal of the solvent under reduced pressure gives **4a**; yield: 0.219 g (83%); mp 141–142°C (Lit.¹⁰ mp 141–142°C).

For spectral data, see Table 3.

Received: 3 April 1987; revised: 2 November 1987

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