

The product of a Pummerer reaction⁸⁾ of the phosphirane oxide **4** (i.e., compound **6**) gave additional strong information regarding the structure of compound **4**. If the Pummerer reaction product **6** has a trans configuration for two acetoxyl groups or for two phenylthio groups, the two methyl protons of the acetoxyl groups should be observed separately from the two singlet signals in the ¹H NMR spectrum. On the other hand, if the configuration of **6** is cis for these two groups, the two methyl protons should be observed as one singlet, owing to the symmetry. The treatment of compound **4** with acetic anhydride afforded a crystalline phosphirane oxide derivative **6** which had two acetoxyl groups on the α and α' positions of the phosphorus atom. The ¹H NMR spectrum of compound **6** clearly showed two kinds of acetoxyl signals at δ 3.00 and 3.32 (three protons each). These observations clearly established the structure of phosphirane oxide **4** to be either (2*S*, 3*S*) or (2*R*, 3*R*) as shown in the scheme. The sp³ α and α' carbon signals of the phosphorus atom were observed downfield (69.5 and 73.6 ppm) compared with various publish-

ed reports^{2,5)} regarding ¹³C NMR spectrum, since the carbon atoms are connected to oxygen and sulfur atoms.

Experimental

Apparatus. The IR spectra were measured on a Japan Spectroscopic Co., Ltd. JASCO A-3 spectrophotometer; the ¹H NMR spectra were run on a Hitachi R-24B (60 MHz) spectrometer; the mass spectra were measured by a Hitachi RMU, DMG, GC-MS spectrometer; the high-performance liquid chromatography was carried out using a Japan Spectroscopic Co., Ltd. UNIFLOW-211 and melting points were measured on a Yanagimoto Seisakusho micro melting-point apparatus.

Synthesis of Bis(phenylthiomethyl)phenylphosphine (1). A Grignard reagent was prepared from chloromethyl phenyl sulfide (3.7 g, 23.4 mmol) and magnesium metal (0.57 g, 23.4 mg atom) in freshly distilled tetrahydrofuran or ether (30 ml) under a dry nitrogen atmosphere. Phenylphosphonous dichloride (2.0 g, 11.2 mmol) in tetrahydrofuran (20 ml) was added to a solution of the Grignard reagent and the resulting solution was stirred for 5 h at room temperature. An aqueous solution of ammonium chloride (20 ml) was added to the reaction mixture; then, the solution was extracted with ether (3×30 ml). The organic layer was washed with water (3×10 ml) and dried over anhydrous sodium sulfate; the solvent was then evaporated. The residue was separated by column chromatography on silica gel (eluent: hexane) to afford compound **1** as colorless crystals in 45% yield, mp 71–72°C (from ethanol). ¹H NMR (CDCl₃) δ=2.92 (s, 4H, 2CH₂) and 6.98 (br s, 15H, 3Ph). Found: C, 74.54; H, 5.96%. Calcd for C₂₀H₁₉PS: C, 74.51; H, 5.94%.

Synthesis of Bis(phenylsulfinylmethyl)phenylphosphine Oxide (2). A 30% aqueous solution of hydrogen peroxide (0.37 g) was added to a solution of compound **1** (0.5 g, 1.55 mmol) in acetic acid (10 ml) and was stirred for 1 h at 0°C. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 0.5 h, followed by the usual work-up. Isolation of the product by column chromatography on silica gel (eluent: benzene/ethyl acetate=1/1 in v/v) afforded compound **2** as a white crystalline material in 80% yield, mp 125–127°C. ¹H NMR (CDCl₃) δ=2.92 and 3.20 (s×2, 4H, 2CH₂), and 7.36–7.43 (m, 15H, 3Ph). IR (ν_{max}^{KBr}) cm⁻¹, 1100 (P=O) and 1150 (S=O). Found: C, 64.82; H, 5.15%. Calcd for C₂₀H₁₉PSO₃: C, 64.85; H, 5.17%.

Synthesis of 3. After the addition of a dichloromethane (20 ml) solution of bromine (0.25 g, 1.59 mmol), *N*-bromosuccinimide (0.14 g, 0.76 mmol), and pyridine (1 ml) to a solution of compound **2** (0.28 g, 0.76 mmol) in dichloromethane (10 ml), the mixture was stirred for 3 h at room temperature. The reaction mixture was poured into water (30 ml) and the organic layer was separated, washed with water, dried over anhydrous sodium sulfate, and then the solvent was evaporated. The separation of the product by thin-layer chromatography on silica gel afforded a crystalline compound **3** in 60% yield, mp 119–124°C. Compound **3** was a mixture of diastereoisomers which were detected by an HPLC retention time of 4.2 and 4.4 min (eluent: chloroform/methanol=20/1 in v/v) at the ratio of 1.5 to 1.0, respectively. ¹H NMR (CDCl₃) δ=3.09–3.81 (m, 2H, CH₂), 4.81–5.30 (m, 1H, CH–Br), and 7.43–7.85 (m, 15H, 3Ph); IR (ν_{max}^{KBr}) cm⁻¹, 1100 (P=O), 1160 (S=O), and 690 (C–Br); MS, *m/z*, 480 (M⁺) and 482 (M⁺⁺). Found: C, 49.57; H, 3.69%. Calcd for C₂₀H₁₈PS₂BrO₃: C,

49.90; H, 3.77%.

Synthesis of 1-Phenyl-2,3-bis(phenylsulfinyl)phosphirane 1-Oxide (4). A solution of compound **3** (0.1 g, 0.21 mmol) and an excess amount of triethylamine (3 ml) in tetrahydrofuran (5 ml) was stirred for 12 h at room temperature. The solvent was evaporated and the residue was separated by thin-layer chromatography on silica gel (eluent: benzene/ethyl acetate=1/1 in v/v) to afford the phosphirane oxide, **4**, and the olefinic product, **5**, in 75 and 3% yields, respectively. The phosphirane oxide, **4**, (syrup): ¹H NMR (CDCl₃) δ=4.34 (dd, *J*_{PCH}=7.5 Hz, 2H, 2CH) and 7.55–7.93 (m, 15H, 3Ph); IR (ν_{max}^{KBr}) cm⁻¹, 1450 (P–C_{arom}), 1130 (P=O), 1050 (S=O), and 700 (P–C); MS *m/z*, 400 (M⁺). Found: C, 60.11; H, 4.31%. Calcd for C₂₀H₁₇O₃PS₂: C, 59.99; H, 4.28%.

The olefinic product, **5**, (syrup): ¹H NMR (CDCl₃) δ=6.10 (d, *J*_{HCCP}=15.0 Hz, 1H, P=C–CH), 7.00 (d, *J*_{HP}=444.0 Hz, 1H, PH), and 7.2–7.6 (m, 15H, 3Ph); IR (ν_{max}^{neat}) cm⁻¹, 2350 (P–H), 1580 and 840 (C=C); MS *m/z*, 400 (M⁺).

Pummerer Reaction of Phosphirane Oxide Derivative 4 with Acetic Anhydride. A solution of phosphirane oxide **4** (0.1 g, 0.25 mmol), acetic anhydride (0.06 g, 0.55 mmol), and a trace of *p*-toluenesulfonic acid in dichloromethane (5 ml) was stirred for 12 h at room temperature; then, the solvent was evaporated. The isolation of the crude product by thin-layer chromatography on silica gel afforded (2*S*, 3*S* or 2*R*, 3*R*)-1-phenyl-2,3-diacetoxy-2,3-bis(phenylthio)phosphirane 1-oxide (**6**) in 85% yield, mp 135–136°C. ¹H NMR (CDCl₃) δ=3.00, 3.32 (s, 6H, 2OAc), and 7.52 (m, 15H, 3Ph); ³¹P NMR (CDCl₃) δ_P=–62.7 ppm (from 85% H₃PO₄); ¹³C NMR (CDCl₃) δ=34.2 (s, CH₃), 34.5 (s, CH₃), 69.5 (d, *J*_{CP}=37.8 Hz, C^α), 73.6 (d, *J*_{CP}=35.2 Hz, C^α), 127.4 (P–arom), 128.1 (P–arom), 129.3 (P and S arom), 129.5 (S–arom), 130.4 (S–arom), 140.9 (S–arom), 143.3 (P–arom), 226.3 (s, C=O), 230.3 (s, C=O); IR (ν_{max}^{KBr}) cm⁻¹, 1590 (C=O), 1450 (P–Ph), 1150 (P=O), 750 (C–S–C), and 690 (C–P); MS *m/z*, 484 (M⁺). Found: C, 59.52; H, 4.34%. Calcd for C₂₄H₂₁O₅PS₂: C, 59.50; H, 4.37%.

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