

PREPARATION AND CHARACTERIZATION OF STERICALLY PROTECTED
 PRIMARY PHOSPHINE SULFIDE AND OXIDE

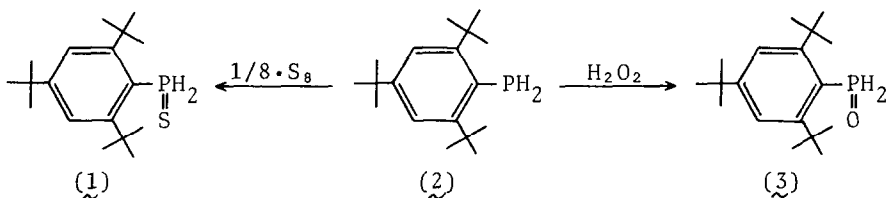
Masaaki Yoshifuji*, Katsuhiko Shibayama, Kozo Toyota, and Naoki Inamoto
 Department of Chemistry, Faculty of Science, The University of
 Tokyo, Hongo, Tokyo 113, Japan

Sterically protected primary phosphine sulfide (1) and oxide (3), were prepared from 2,4,6-tri-tert-butylphenylphosphine (2) and were characterized as stable compounds.

By introducing an extremely bulky group into a molecule, we have been successful in preparing some unusual but isolable phosphorus containing compounds of interest.^{1,2}

We now report our preliminary results on the preparation and characterization of sterically protected primary phosphine sulfide and phosphine oxide.³

Apparent formation of a primary phosphine sulfide, C₆H₅P(S)H₂, has been reported by Köhler and Michaelis⁴ and later by Maier⁵, however, it has neither been isolated as a stable compound nor well characterized since it readily decomposes to evolve hydrogen sulfide.



2,4,6-Tri-tert-butylphenylphosphine (2)² was allowed to react with one equivalent of elemental sulfur at 40°C in benzene for 3 days in the presence of one equivalent of pyridine or 2,6-lutidine to give 2,4,6-tri-tert-butylphenylphosphine sulfide (1), which was purified through silica-gel column chromatography and recrystallization from pentane (45% yield based on 2 consumed). Mp 114 - 117°C; ³¹P NMR (CDCl₃; ext. 85% H₃PO₄) δ_P -24.7 ppm (t, ¹J_{PH} = 466.3 Hz), ³¹P{¹H} NMR spectrum appeared as a quintet on adding D₂O (ArylP(S)D₂, ¹J_{PD} = 72.0 Hz); ¹H NMR(CDCl₃) 7.86 (2H, d, ¹J_{PH} = 466.2 Hz, PH₂), 7.50 (2H, d, ⁴J_{PH} = 4.8 Hz, arom.), 1.67 (18H, d, ⁵J_{PH} = 1.1 Hz, o-Bu^t), 1.31 (9H, s, p-Bu^t); ¹³C{¹H} NMR (CDCl₃) δ 155.3 (d, o-arom., ²J_{CP} = 7.3 Hz), 153.8 (d, p-arom., ⁴J_{CP} = 3.1 Hz), 123.9 (d, m-arom., ³J_{CP} = 12.2 Hz), 122.7 (d, ipso-arom., ¹J_{CP} = 71.4 Hz), 39.0 (d, o-C(CH₃)₃, ³J_{CP} = 3.1 Hz), 35.2 (p-C(CH₃)₃), 34.2 (d, o-C(CH₃)₃, ⁴J_{CP} = 1.8 Hz), 31.0 (p-C(CH₃)₃); IR (KBr) ν_{PH} 2480, 2430, 2330, 2270 cm⁻¹ and ν_{PS} 660 cm⁻¹; mass spectrum m/e 310 (M⁺, 75%),

309 ($M^+ - H$, 75%), 277 ($ArylPH^+$, 100%); high resolution MS m/e 310.1908, calcd for $C_{18}H_{31}PS$ 310.1883.

The oxidation of primary phosphines is quite difficult to control and such compounds at the first oxidation stage even if generated have poor thermal stability.^{6,7} Since the steric protection by the 2,4,6-tri-*tert*-butylphenyl group in the sulfide (1) proved effective, an attempt to isolate the corresponding phosphine oxide was made as follows. The phosphine (2) was allowed to react with equimolar amount of aqueous ethanolic hydrogen peroxide at room temperature to give the primary phosphine oxide (3) almost quantitatively. Mp 172 - 172.5°C (from EtOH - Et₂O); ³¹P NMR (CDCl₃) -10.0 ppm (t, ¹J_{PH} = 490.7 Hz); ³¹P{¹H} NMR appeared as a quintet on adding D₂O (ArylP(O)D₂, ¹J_{PD} = 73.9 Hz); ¹H NMR (CDCl₃) 7.85 (2H, d, ¹J_{PH} = 481.6 Hz, PH₂), 7.49 (2H, d, ⁴J_{PH} = 4.2 Hz, arom.), 1.62 (18H, s, o-Bu^t), 1.32 (9H, s, p-Bu^t); ¹³C{¹H} NMR (CDCl₃) 156.8 (d, o-arom., ²J_{CP} = 8.3 Hz), 154.3 (d, p-arom., ⁴J_{CP} = 2.9 Hz), 124.9 (d, ipso-arom., ¹J_{CP} = 95.2 Hz), 38.6 (d, o-C(CH₃)₃, ³J_{CP} = 3.9 Hz), 35.2 (p-C(CH₃)₃), 33.9 (o-C(CH₃)₃), 31.0 (p-C(CH₃)₃); IR (KBr) ν_{PH} 2440 cm⁻¹ and ν_{PO} 1172 cm⁻¹; MS m/e 294 (M^+ , 14%), 57 (Bu⁺, 100%). The oxide (3) was very stable for a long period of time at room temperature even in the solid state probably due to the steric protection from the intermolecular oxidation-reduction and from aerial oxidation, in contrast to octylphosphine oxide, which liquified within 1 h at room temperature in the solid state,⁶ reported by Buckler and Epstein.

The very stable primary phosphine sulfide (1) and oxide (3) thus obtained⁸ might serve as good model compounds for the study of the P=S and P=O species. Further studies on the reaction of such compounds are in progress.

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- 8 The sulfide (1) and oxide (3) in solution on long standing in air gave the corresponding thiophosphinic acid, ArylP(S)(H)(OH) (mp 139 - 141°C, δ_p (CDCl₃) 50.7 ppm, d, J = 556.5 Hz) and phosphinic acid, ArylP(O)(H)(OH) (mp 161 - 162°C, δ_p (CDCl₃) 25.7 ppm, d, J = 575.7 Hz), respectively.

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