Oxidation of a Diphosphene and Dechlorination of an Arylphosphonic Dichloride: Isolation of the Diphosphene Oxide Masaaki Yoshifuji,* Kaori Ando, Kozo Toyota, Ichiro Shima, and Naoki Inamoto Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

The dechlorination reaction of the phosphonic dichloride $ArP(O)CI_2$ ($Ar = 2,4,6-But_3C_6H_2$) with magnesium gave the sterically protected diphosphene oxide ArP(O)=PAr as a stable compound.

We are interested in the isolation of reactive phosphoruscontaining species by steric protection. Among them, diphosphene is of current interest because of its unusual phosphorusphosphorus double bond.^{1,2} We now report the oxidation of *E*-bis-(2,4,6-tri-t-butylphenyl)diphosphene (1) with *m*-chloroperbenzoic acid via a new reactive intermediate, 1,2-bis-(2,4,6-tri-t-butylphenyl)diphosphene 1-oxide (2), and the isolation of (2) by the dechlorination of 2,4,6-tri-t-butylphenylphosphonic dichloride (3) with magnesium.

To a solution of (1) (0.086 mmol) in dichloromethane (4 ml) m-chloroperbenzoic acid (80%) (0.085 mmol) in dichloromethane (6 ml) was added dropwise at 0 °C under argon. The orange solution of (1) immediately became colourless. Removal of the solvent and chromatography on silica gel (CCl₄) gave 2,4,6-tri-t-butylphenylphosphine (4) in 56% yield and addition of ethereal diazomethane to this product mixture gave the phosphonate(5) in 58 % yield [${}^{1}H$ n.m.r. δ (CCl₄) 7.88— 6.96 (m, 6H, arom.), 3.85 (d, 3H, ³J_{PH} 12 Hz, OMe), 1.48 (s, 18H, o-Bu^t), and 1.32 (s, 9H, p-Bu^t); mass spectrum, m/z 478 $(M^+, 36\%), 463 (M^+ - Me, 42\%), 443 (M^+ - Cl, 14\%), and$ 421 $(M^+ - Bu^t, 100\%)$]. The phosphine (4)² [³¹P n.m.r. δ (CDCl₃; external 85% H₃PO₄) -129.9 p.p.m. (t, ¹J_{PH} 210.6 Hz)] was identical to that obtained from the reaction between 2,4,6-tri-t-butylphenylphosphonous dichloride and lithium aluminium hydride. The formation of (5) indicates the intermediacy of the diphosphene monoxide (2).



In an attempt to isolate the phosphinoylidene intermediate,³ the phosphonic dichloride (3) (0.301 mmol) in tetrahydrofuran (3 ml) was allowed to react with magnesium turnings (0.35 mgatom)† at 0 °C with ultrasonic irradiation (1.5 h). The colour of the reaction mixture immediately turned to green then gradually to yellow. The solvent was removed by rotary evaporation, pentane-insoluble inorganic salts were filtered off, and the filtrate was concentrated to give yellow crystals of (2) in 71% yield, an unexpected phosphorus analogue of the

$$ArP(O)Cl_2 + Mg \longrightarrow (2)$$
(3)

azoxy-compounds {m.p. 174—176 °C; i.r. (KBr) v(P=O) 1205 cm⁻¹; ¹H n.m.r. δ (CDCl₃) 7.40—7.37 (m, 4H, arom.), 1.64 (s, 18H, *o*-Bu^t), 1.58 (s, 18H, *o'*-Bu^t), and 1.30 (s, 18H, *p*- and *p'*-Bu^t). The ³¹P n.m.r. spectrum of (2) in CDCl₃ contained an AB pattern centred at 206.5 (Ar*P*=) and 69.8 p.p.m. [Ar*P*(O)=] with a large coupling constant ¹*J*_{PP} 683.6 Hz. The ¹*J*_{PP} in (2) is one of the largest values ever observed for a directly bonded P–P linkage,⁴ which indicates an unusual electron correlation in (2). High resolution mass spectrum, m/z 568.3955, C₃₆H₅₈OP₂ requires 568.3961; u.v. (CH₂Cl₂) λ_{max} (ϵ) 245 (14 300), 292 (4300), and 342 nm (1500); m_{T} (in C₆H₆) 589}.

$$(2) + H_2O \longrightarrow (4) + ArP(O)(OH)_2$$

$$(6)$$

† A large excess of magnesium leads to intractable materials.

The hydrolysis of (2) was very fast to give the phosphine (4) and 2,4,6-tri-t-butylphenylphosphonic acid (6). The acid (6) was identical with that formed by reaction of the corresponding phosphonic dichloride (3) and sodium hydroxide in aqueous acetone (77% yield), (6); m.p. 105–106.5 °C, ³¹P n.m.r. δ (CDCl₃) 26.9 p.p.m., ¹H n.m.r. δ (CDCl₃) 8.77–8.40 (br. s, 2H, OH), 7.29 (d, 2H, ⁴J_{PH} 5.4 Hz, arom.), 1.38 (s, 18H, *o*-Bu^t), and 1.27 (s, 9H, *p*-Bu^t), field desorption mass spectrum *m*/*z* 326 (*M*⁺).

The dechlorination with magnesium is in contrast to that of the corresponding phosphonothioic dichloride which gives E-2,3-bis(2,4,6-tri-t-butylphenyl)-1,2,3-thiadiphosphiran.⁵

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