Oxidation of a Diphosphene and Dechlorination of an Arylphosphonic Dichloride: Isolation of the Diphosphene Oxide

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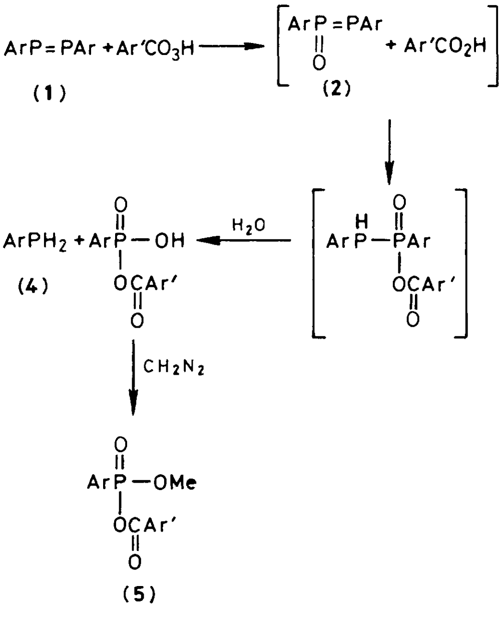
The dechlorination reaction of the phosphonic dichloride $ArP(O)Cl_2$ ($Ar = 2,4,6\text{-}Bu^t{}_3C_6H_2$) with magnesium gave the sterically protected diphosphene oxide $ArP(O){=}PAr$ as a stable compound.

We are interested in the isolation of reactive phosphorus-containing species by steric protection. Among them, diphosphene is of current interest because of its unusual phosphorus–phosphorus 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 (CCl_4) 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 [^1H n.m.r. δ (CCl_4) 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] [^{31}P n.m.r. δ($CDCl_3$; external 85% H_3PO_4) −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**).



$Ar = 2,4,6\text{-}Bu^t{}_3C_6H_2$
$Ar' = m\text{-}ClC_6H_4$

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 mg-atom)† 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

$$\underset{(\mathbf{3})}{\mathrm{ArP(O)Cl_2}} + \mathrm{Mg} \longrightarrow (\mathbf{2})$$

azoxy-compounds {m.p. 174—176 °C; i.r. (KBr) ν(P=O) 1205 cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$) 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 ^{31}P n.m.r. spectrum of (**2**) in CDCl$_3$ contained an AB pattern centred at 206.5 (Ar*P*=) and 69.8 p.p.m. [Ar*P*(O)=] with a large coupling constant $^1J_{PP}$ 683.6 Hz. The $^1J_{PP}$ 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, $C_{36}H_{58}OP_2$ requires 568.3961; u.v. (CH$_2$Cl$_2$) λ_{max} (ϵ) 245 (14 300), 292 (4300), and 342 nm (1500); m_r (in C$_6$H$_6$) 589}.

$$(\mathbf{2}) + \mathrm{H_2O} \longrightarrow (\mathbf{4}) + \underset{(\mathbf{6})}{\mathrm{ArP(O)(OH)_2}}$$

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, ^{31}P n.m.r. δ(CDCl$_3$) 26.9 p.p.m., ^{1}H n.m.r. δ (CDCl$_3$) 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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† A large excess of magnesium leads to intractable materials.