Journal of Organometallic Chemistry, 310 (1986) 21–25
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOSPHORUS–PHOSPHORUS SINGLE OR DOUBLE BOND FORMATION FROM $PCl_{3-n}R_n$ ($n = 1$ or 2) AND A BIS-IMIDAZOLIDINE REDUCING AGENT

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(Received February 21st, 1986)

Summary

1,3,1′,3′-Tetraethyl-bis(2,2′-imidazolidene), L_2^{Et} (I), is a mild homogeneous reducing agent which reduces P–Cl bonds in phosphonous or phosphinous chlorides to give compounds with phosphorus–phosphorus bonds. High yields of diphosphines P_2R_4 are produced from the corresponding phosphinous chlorides ($PClR_2$). Phenyl- and t-butyl-phosphonous dichlorides are reduced to cyclopolyphosphines $(PR)_n$, which appear to be the kinetically controlled products. 2,4,6-Tri(t-butyl)phenylphosphonous dichloride ($PArCl_2$) is reduced to either 1,2-dichloro-1,2-bis(2,4,6-tri-t-butylphenyl)diphosphine $(PArCl)_2$ or *trans*-bis[(2,4,6-tri-t-butyl)phenyl]diphosphene (P_2Ar_2) depending on the initial stoichiometry.

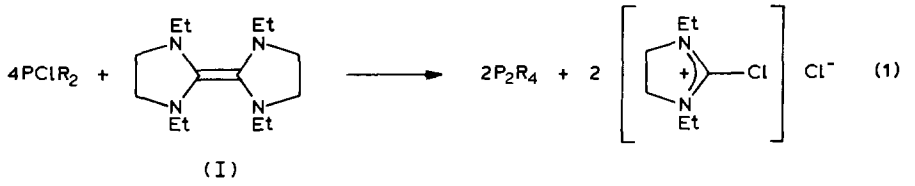
Introduction

Heterogeneous reduction of phosphinous halides (PR_2X) to diphosphines (P_2R_4) or of phosphonous dihalides (PRX_2) to cyclopolyphosphines $(PR)_n$ by metals is a sluggish reaction which needs high temperatures and long reaction times [1]. In contrast, the homogeneous reduction of a hindered phosphinous halide by a bis-imidazolidine [$=\overline{CN(R)CH_2CH_2NR}$] ($\equiv L_2^R$) to the persistent phosphinyl radical ($\dot{P}R_2$), which is generally in equilibrium with its dimer, the diphosphine (P_2R_4), is rapid at room temperature when initiated photolytically [2,3]. Consequently, we decided to explore the synthetic utility of a bis-imidazolidine, such as I, as a reducing agent for phosphonous dihalides as well as less hindered phosphinous halides.

0022-328X/86/$03.50

Results and discussion

Reductions of diarylphosphinous chlorides to the tetra-aryldiphosphines proceeded much more rapidly and under much milder conditions with the bis-imidazolidene (I) than with the metal reducing agents used previously [1]. The stoichiometry of the reaction was that shown in eq. 1 (R = aryl).



(I)

Photo-initiation was not required for the reactions reported here. The carbonium salt by-product precipitated out from the toluene solution during the reaction; hence, the mixture was easy to work up, and P_2R_4 was obtained in good yield (see Table 1). Since the reduction of hindered phosphinous chlorides by bis-imidazolidenes leads to phosphinyl radicals [2,3], it seems likely that the present reactions also proceed via phosphinyl radicals ($\dot{P}R_2$), which dimerise to yield the diphosphines.

Reduction of t-butylphosphonous dichloride by the bis-imidazolidene (I) led cleanly to the cyclotetraphosphine $(PBu^t)_4$ as the sole product; this was also obtained by reduction of the dichloride by a metal [4].

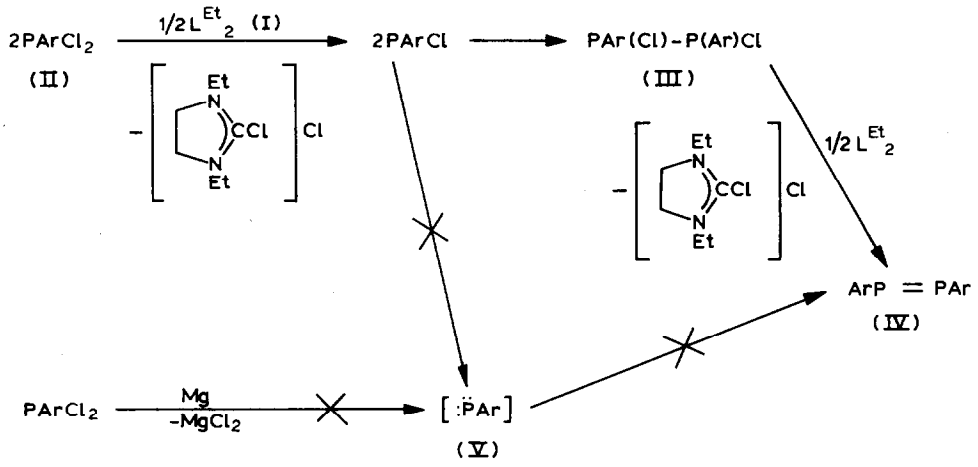
Reduction of phenylphosphonous dichloride by zinc, in a slow thermal reaction, yielded the cyclopentaphosphine $(PPh)_5$ as the major product, together with smaller amounts of cyclotetraphosphine and cyclohexaphosphine [5]. It seems probable that this was the thermodynamic product mixture under these conditions. In contrast, we now report that bis-imidazolidene reduction of PCl_2Ph gives a mixture of 55% of cyclotetraphosphine and 45% of cyclopentaphosphine, with no detectable cyclohexaphosphine. This mixture, obtained at ambient temperature under mild conditions, may be kinetically determined. It is possible that bis-imidazolidene reduction will prove to favour the formation of cyclopolyphosphines which are not as readily accessible by other reduction methods.

The preparation of phosphorus–phosphorus double-bonded compounds, diphosphenes, from P^{III} precursors is a topic of current interest [9–15]. The work described below on the bis-imidazolidene reduction of $PArCl_2$ helps to elucidate the mechanism of the reactions whereby a symmetrical diphosphene is prepared from a

TABLE 1

PREPARATION OF DIPHOSPHINES P_2R_4 BY REACTION 1

R in P_2R_4	Yield (%)	M.p. (lit.) (°C)
C_6H_5	88	120 (121–122 [6])
2,4,6-$(CH_3)_3C_6H_2$	73	210–215 (dec.) (200–215 [7])
$(CH_3)_3C$	57	47 (48 [4])
c-C_6H_{11}	50	171 (173 [8])



SCHEME 1. Reaction sequence in the reduction 2,4,6-tri(t-butyl)phenylphonous dichloride $PArCl_2$ (II) and the bis-imidazolidene L_2^{Et} (I), and inoperative alternatives (via V).

phosphonous dichloride. 2,4,6-Tri-(t-butyl)phenylphosphonous dichloride, $PArCl_2$ (II), was treated with L_2^{Et} (I). The initial product was the 1,2-dichlorodiphosphine (III) together with a small amount of the diphosphene (IV). Use of a slight excess of I under more vigorous conditions gave only IV.

Thus, in the preparation of diphosphenes by reduction from phosphonous dichlorides there is unlikely to be a phosphinidene intermediate (V), as has been proposed [9]. Formation of the dichlorodiphosphine (III) is now demonstrated to occur along the pathway from II to IV. Compound III has not previously been observed because an excess of a dechlorinating/reducing agent has always been employed.

These data are summarised in Scheme 1. From earlier ESR experiments [11], it was demonstrated that the initial transient product of reduction of PCl_2Ar by L_2^{Et} is the radical ṖArCl. It is now evident that ṖArCl dimerises to the diphosphine III; this radical, as well the analogous ṖArX (X = OBu^t, SPr, SBu^t, Cl, $N(SiMe_3)_2$, $CH(SiMe_3)_2$, Ph, $C_6H_2Me_3$-2,4,6, Ar, or OAr], have previously been identified as products from L_2^{Et} (I) and PAr(Cl)X [11].

Experimental

General procedures

Except where otherwise noted starting materials were commercial products (Aldrich, Strem, or Alfa), and were distilled or crystallised before use; their purities were checked by NMR spectroscopy. Proton NMR spectra were recorded with a Varian EM-60 or an EM-90 spectrometer; ^{31}P NMR spectra were recorded at 36.4 MHz with a Bruker HFX-10 spectrometer; positive values of δ correspond to resonances at low field relative to external 85% H_3PO_4 at $\delta = 0$. Reactions were run under argon in a Schlenk line. Solvents were dried over sodium and distilled under nitrogen.

Starting materials

A mixture of *N,N*-dimethylformamide dimethylacetal (17.9 g, 20.0 cm^3, 151 mmol) and *N,N'*-diethylethylenediamine (15.1 g, 18.3 cm^3, 130 mmol) in dry benzene was heated in a distillation vessel during 3 h to 110°C and the methanol/benzene azeotrope that was produced was collected. The vessel was cooled and the remaining benzene was removed in vacuo. The residue was distilled under vacuum to yield 1,3,1',3'-tetraethyl-2,2'-bis(imidazolidene) (I) (11.5 g, 70%, b.p. 86–88°C at 3 Torr), which is sensitive to air and moisture; I is a low melting solid (m.p. 48°C) [16], and is conveniently used in toluene solution.

Bromomesitylene (19.9 g, 15.1 cm^3, 100 mmol) in diethyl ether (30 cm^3) was added slowly to n-butyllithium in hexane (52 cm^3 of a 2.53 mol dm^{-3} solution; 130 mmol of $LiBu^n$) and the mixture was heated at reflux for 3 h. A copious deposit of crystalline mesityllithium was produced. The mixture was cooled to 0°C and phosphorus trichloride (6.8 g, 4.36 cm^3, 50 mmol) in diethyl ether (20 cm^3) was slowly added. The mixture was stirred at 25°C for 15 h and then filtered. Vacuum distillation gave mesitylphosphonous dichloride (1.5 g, b.p. 145–150°C at 2 Torr; ^{31}P NMR: δ 161 ppm) and dimesitylphosphinous chloride (4.8 g, 31%, b.p. 180–185°C at 2 Torr; ^1H NMR (δ in ppm, CD_2Cl_2): 2.20 (s), 6-CH_3; 2.30 [d, J(PH) 2.4 Hz], 2,4-CH_3; 6.8 (d), 3,5-H, J(PH) 3.2 Hz; ^{31}P NMR, δ 76 ppm.

Diphosphines: general procedure

A solution of the bis-imidazolidene (I) (0.60 mmol, 20% excess) in toluene (1 cm^3) was added slowly at 0°C to a stirred solution of the phosphinous chloride (2.0 mmol) in toluene (5 cm^3). The mixture was stirred at 0°C for 2 h, and then filtered. Toluene was evaporated from the filtrate in vacuo at room temperature to yield the diphosphine.

Tetra-t-butylcyclotetraphosphine

This was prepared by the above general procedure, starting from t-butylphosphonous dichloride (2.0 mmol) and the bis-imidazolidene (I) (1.0 mmol) in toluene (8 cm^3). Examination of the product solution after filtration by ^{31}P NMR spectroscopy showed only one peak, at 62.9 ppm, characteristic of the cyclotetraphosphine (cf. [4]: δ 58 ppm); this compound was isolated in 57% yield.

Phenylcyclopolyphosphines

Reaction between phenylphosphonous dichloride (2.0 mmol) and the bis-imidazolidene (I) (1.0 mmol) in toluene (8 cm^3) was carried out by the above general procedure. Examination of the product solution after filtration by ^{31}P NMR spectroscopy showed peaks only at 9.9 ppm (singlet; integrated area, 55% of total signal) attributed to the cyclotetraphosphine (cf. [5] δ 9.0 ppm), and at 5.1 ppm (complex multiplet, 45% of signal) attributed to the cyclopentaphosphine (cf. [17] δ 4.7 ppm) [7]. The isolated yield of the combined cyclopolyphosphines was 72%.

1,2-Dichloro-1,2-bis(2,4,6-tri-t-butylphenyl)diphosphine and trans-bis(2,4,6-tri-t-butylphenyl)diphosphene

A solution of the bis-imidazolidene (I) (0.23 g, 0.90 mmol) in toluene (10 cm^3) was added dropwise to 2,4,6-tri-t-butylphenylphosphonous dichloride [9] (1.17 g, 3.37 mmol) in toluene (20 cm^3). A white flocculent precipitate was immediately

formed and the solution became yellow. After 2 h stirring the precipitate was filtered off and the solvent removed from the filtrate in vacuo at room temperature. Examination of the residue by ^{31}P NMR spectroscopy showed it to be the almost pure diphosphine (δ 75.7 ppm) containing a little diphosphene (δ 494 ppm).

The diphosphene was formed quantitatively (^{31}P NMR) when an excess of the bis-imidazolidene (I) (ca. 10%) was used, and the mixture refluxed for 1 h.

Acknowledgement

We thank the National Institutes of Health for grants under the Minorities Biomedical Research Support Program and the Minorities Access to Research Careers Program; NATO for a grant under its Scientific Research Program, and S.E.R.C. for a studentship (to S.J.S.).

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