Synthesis of the first *p*-diphosphaquinone and its bis(pentacarbonylchromium) complex

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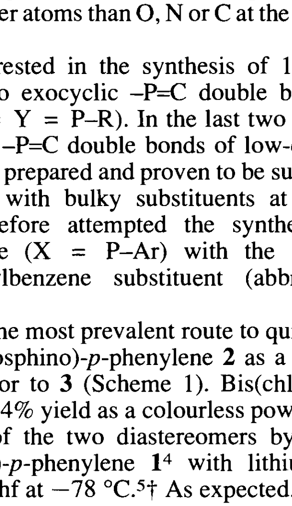
The first synthesis of a *p*-diphosphaquinone and the isolation of its bis(pentacarbonylchromium) complex is reported.

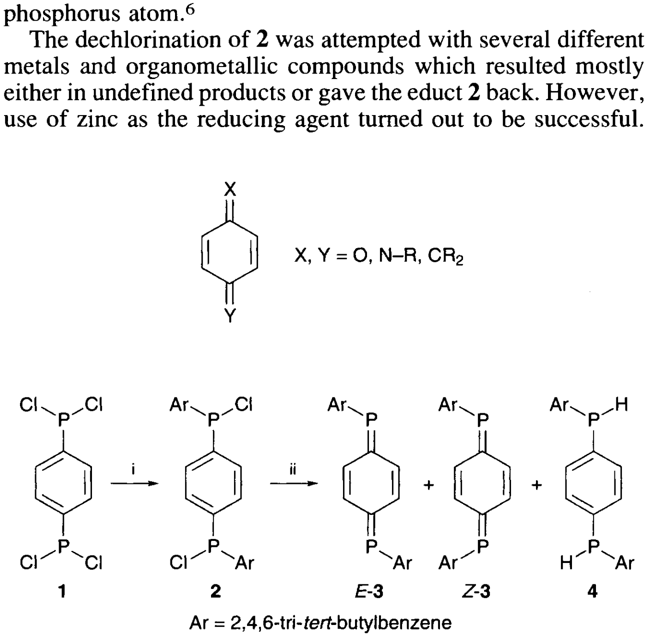
Apart from the classical 1,4-quinones (X, Y = O) stable 1,4-quinonoid systems are the quinone imines (X = O, Y = N–R), the quinodimines (X, Y = N–R), the quinomethanes (X = O, Y = CR_2) and the quinodimethanes (X, Y = CR_2).[1] Mono- and di-thioquinones have been observed as short-lived species in the gas phase and in an argon matrix.[2] To our knowledge, however, no 1,4-quinones have been prepared with other atoms than O, N or C at the *exo* double-bond positions.

We were interested in the synthesis of 1,4-benzoquinone systems with two exocyclic –P=C double bonds with $\lambda^3\sigma^2$-phosphorus (X = Y = P–R). In the last two decades, various compounds with –P=C double bonds of low-coordinate phosphorus have been prepared and proven to be surprisingly stable, especially those with bulky substituents at the phosphorus atom.[3] We therefore attempted the synthesis of a $\lambda^3\sigma^2$-diphosphaquinone (X = P–Ar) with the well established 2,4,6-tri-*tert*-butylbenzene substituent (abbreviated as Ar throughout).

In analogy to the most prevalent route to quinones, we chose the bis(chlorophosphino)-*p*-phenylene **2** as a possible 'hydroquinone' precursor to **3** (Scheme 1). Bis(chlorophosphine) **2** was obtained in 84% yield as a colourless powder consisting of a 1 : 4 mixture of the two diastereomers by treating bis(dichlorophosphino)-*p*-phenylene **1**[4] with lithium-2,4,6-tri-*tert*-butylbenzene in thf at −78 °C.[5]† As expected, the bulkiness of the protecting group leads to selective monosubstitution at the phosphorus atom.[6]

The dechlorination of **2** was attempted with several different metals and organometallic compounds which resulted mostly either in undefined products or gave the educt **2** back. However, use of zinc as the reducing agent turned out to be successful. When a solution of **2** in thf was heated at reflux in the presence of a large excess of zinc powder the solution turned orange within a short time. After refluxing for 3 h all starting material was consumed. The ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of the reaction mixture proved the apparent formation of the 1,4-diphosphaquinone with signals in the typical range for phosphaalkenes[7] at δ_P 260.1 for the *E* isomer and at δ_P 261.8 for the *Z* isomer. The structural assignment of the two diastereomers could be made on the basis of the coupling constants for the phenylene protons in the proton spectrum and showed the *E* isomer to be the major product (ratio *E*:*Z* = 5 : 1).‡



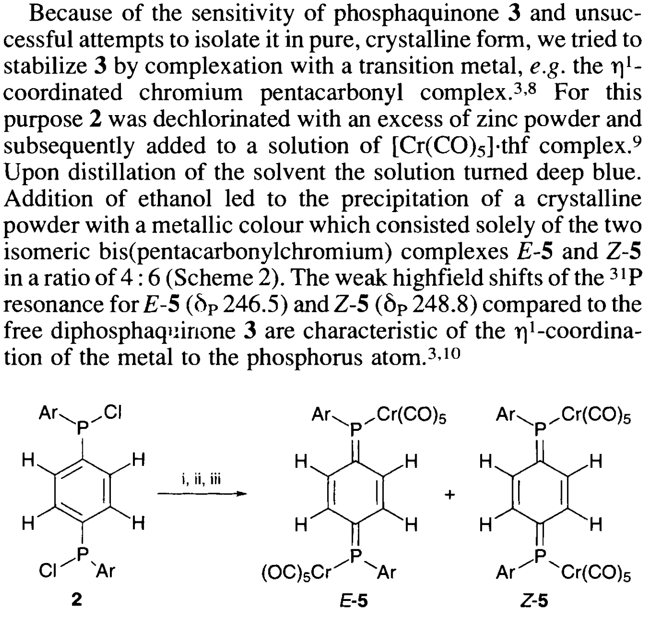


Scheme 1 *Reagents and conditions*: i, N_2, 2 ArLi, thf, −78 °C to room temp., 84% yield; ii, N_2, Zn, thf, 3 h reflux, 100% conversion

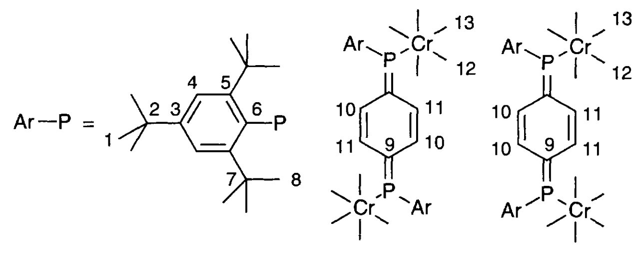
The dechlorination of **2**, however, did not give **3** as the only product, but gave also the bisphosphine **4** (ratio obtained for **3**:**4** = 3 : 2).§ Even if less zinc was used and the reaction was interrupted before all **2** had reacted, the **3**:**4** ratio was about the same. This could indicate an intermediate competing reaction to give either **4** or **3** rather than a subsequent reduction of **3** to **4**.

Further verification for the formation of **3** was obtained with a field desorption mass spectrum of the yellow crystalline mixture of **3** and **4** with the only molecular peaks detectable at 628 and 630. Diphosphaquinone **3** is stable in solution or as a solid in the absence of oxygen but isomerizes (*E*-**3** ⟶ *Z*-**3** and *vice versa*) when irradiated with light. When a solution of **3** and **4** was kept for 2 days in open daylight under a nitrogen atmosphere the ^{31}P NMR spectrum demonstrated the isomerization of **3** with the *E*-**3**:*Z*-**3** ratio being changed to about 1 : 1, whereas no change in the **3**:**4** ratio was observed. In the presence of oxygen rapid decomposition of **3** takes place as seen by the disappearance of the yellow colour of the solid or the solution and confirmed by the ^{31}P NMR spectrum of the decomposed mixture.

Because of the sensitivity of phosphaquinone **3** and unsuccessful attempts to isolate it in pure, crystalline form, we tried to stabilize **3** by complexation with a transition metal, *e.g.* the η^1-coordinated chromium pentacarbonyl complex.[3,8] For this purpose **2** was dechlorinated with an excess of zinc powder and subsequently added to a solution of $[Cr(CO)_5]\cdot$thf complex.[9] Upon distillation of the solvent the solution turned deep blue. Addition of ethanol led to the precipitation of a crystalline powder with a metallic colour which consisted solely of the two isomeric bis(pentacarbonylchromium) complexes *E*-**5** and *Z*-**5** in a ratio of 4 : 6 (Scheme 2). The weak highfield shifts of the ^{31}P resonance for *E*-**5** (δ_P 246.5) and *Z*-**5** (δ_P 248.8) compared to the free diphosphaquinone **3** are characteristic of the η^1-coordination of the metal to the phosphorus atom.[3,10]



Scheme 2 *Reagents and conditions*: i, N_2, Zn, thf, 3 h reflux; ii, $[Cr(CO)_5]\cdot$thf, 5 min reflux; iii, evaporation of solvent, precipitation with ethanol



Scheme 3

The structure of **5** was further supported by field desorption mass spectrometry (M^+, 1012) and ^{1}H and ^{13}C NMR spectroscopy.¶ The quinonoid structure of *E*-**5** and *Z*-**5** is notably supported by the chemical shifts of the P=C double-bond carbons [*E*-**5** : $\delta_{C(10)}$ 166.70; *Z*-**5** : $\delta_{C(10)}$ 166.41].

Footnotes

† Compound **2**, colourless powder, mp 209–213 °C; ^{31}P NMR (162 MHz, $CDCl_3$): δ_P 75.2 (major isomer), 76.6 (minor isomer). Both isomers show two peaks in the ^{31}P NMR spectrum due to the isotopic shift (2 Hz) of the chlorine atoms.[5] ^{1}H NMR (400 MHz, $CDCl_3$): major/minor isomer 1.33/1.35 (s, 18 H, *p*-Bu^t), 1.39/1.40 (br s, 36 H, *o*-Bu^t), 6.50/6.54 (br s, 4 H, C_6H_4), 7.42/7.46 [pt, ^4J(P–H) 2.4 Hz, 4 H, C_6H_2]. **2** is resistant to hydrolysis to give the bisphosphine oxide but readily cleaves off the 2,4,6-tri-*tert*-butylbenzene substituent in the presence of an acid.

‡ Mixture of **3** and **4**, yellow powder; ^{1}H NMR (400 MHz, $CDCl_3$): *E*-**3**/*Z*-**3** isomer 1.38/n.k. (s, 18 H, *p*-Bu^t), 1.41/n.k. (br s, 36 H, *o*-Bu^t), 5.44/5.24 [m, ^3J(H–H) 9.4 Hz for *E*-**3**, m for *Z*-**3**, 2 H, C_6H_4], 6.87/7.20 (m, 2 H, C_6H_4), 7.46/n.k. (s, 4 H, C_6H_2) (n.k. = not known).

§ Compound **4**, colourless crystalline powder, mp 192–196 °C, was obtained as a racemate by reduction of **2** with $LiAlH_4$; the X-ray structure of **4** after crystallization from CH_2Cl_2–ethanol confirms surprisingly the existence of the *R*,*R*-enantiomer; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.33 (s, 18 H, *p*-Bu^t), 1.40 (br s, 36 H, *o*-Bu^t) 5.95 [d, ^1J(P–H) 229.4 Hz, P-H], 5.96 [d, ^1J(P–H) 229.8 Hz], 6.430 (m), 6.434 (m, C_6H_4), 7.45 [d, ^4J(P–H) 2.1 Hz, C_6H_2]; ^{13}C NMR (100 MHz, $CDCl_3$) : δ 31.28 (s, C-1), 35.08 (s, C-2), 150.25 (s, C-3), 122.26 [d, ^3J(P–C) 4.1 Hz, C-4], 155.89 (br s, C-5), 127.93 [d, ^1J(P–C) 25.9 Hz, C-6], 38.30 (s, C-7), 33.36 [pt, *N*(P–C) 7.1 Hz, C-8], 138.73 [d, ^1J(P–C) 14.5 Hz, C-9], 130.47/130.64 [2 pt, *N*(P–C) 9.6/9.9 Hz]; ^{31}P NMR (162 MHz, $CDCl_3$) : δ −64.53, −64.57 (the 2 signals are probably a result of the formation of a 1 : 1 diastereomeric mixture of *rac*- and *meso*-**4** in solution).

¶ Compound **5**, bronze crystalline powder (Scheme 3): mp > 320 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *E*-**5**/*Z*-**5** 1.37/1.31 (s, 18 H, *p*-Bu^t), 1.51/1.47 (br s, 36 H, *o*-Bu^t), 6.46/6.38 [m, ^3J(H–H) 9.6 Hz for *E*-**5**, 2 H, C_6H_4], 7.11/7.48 [m, ^3J(H–H) 9.6 Hz for *E*-**5**, 2 H, C_6H_4], 7.59/7.52 (br s, 4 H, C_6H_2); ^{13}C NMR (100 MHz, $CDCl_3$): *E*-**5**/*Z*-**5** 31.06/30.99 (s, C-1), 35.00/34.89 (s, C-2), 152.12/151.86 (s, C-3), 125.67/125.93 (pt, C-4), 153.93/153.30 (pt, C-5), 128.91/128.91 [d, ^1J(P–C) 22.4 Hz, C-6], 40.23/40.39 (s, C-7), 34.96/35.04 (s, C-8), 166.70/166.41 (pt, C-9), 127.75/125.93 (pt, C-10), 125.20/127.13 (pt, C-11), 215.16/215.09 (pt, C-12), 221.93/221.93 [d, ^2J(P–C) 3 Hz, C-13].

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