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A new type of water-soluble phosphine for biphasic catalysis *

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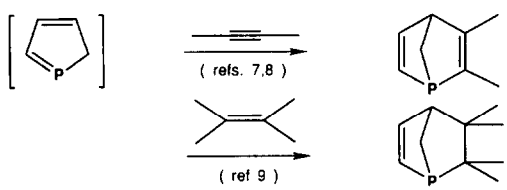
Abstract

The reaction of the [4 + 2] dimer of 3,4-dimethyl-2*H*-phosphole with maleic anhydride in boiling THF gives the 2*H*-phosphole-maleic anhydride [4 + 2] endocyclo-adduct in 60% yield. Upon treatment with sodium hydroxide, this cyclo-adduct is transformed into the sodium salt of 3,4-dimethyl-1-phospha-2-norbornene-5,6-dicarboxylic acid which is very soluble in water (≥ 300 g/l) and is not extracted from water by organic solvents such as toluene and dichloromethane.

1. Introduction

Since the successful development of the Veba-Rhône Poulenc process for the hydroformylation of olefins in a two-phase system [1], a number of new water-soluble phosphines have been described for use in biphasic catalysis [2]. Some of the latest include phosphines containing sugar substructures [3], phosphonate chains [4], sulfonated diphosphines derived from a biphenyl backbone [5], and chiral sulfonated phosphines for the asymmetric hydrogenation of dehydropeptides [6].

During recent years, we have described a simple route for the synthesis of bicyclic phosphines with phosphorus atoms at the bridgehead from transient 2*H*-phospholes (eqns. (1), (2)).



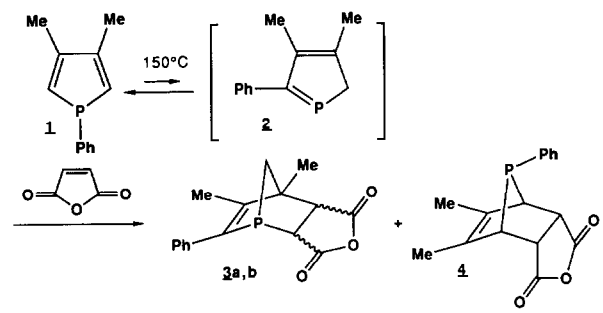
(1)

(2)

These phosphines have significant activity in the rhodium-catalyzed hydrogenation [10] and hydroformylation of olefins [11]. They can also be prepared in optically pure form [12] and they display an interesting specificity since the asymmetric phosphorus centre cannot racemise. Thus, we felt that the synthesis of water-soluble bicyclic phosphines of this type would be worthwhile.

2. Results and discussion

In a preliminary attempt, we decided to take advantage of the equilibrium which appears upon heating between 1-phenyl-1*H*-phospholes and 2-phenyl-5*H*-phospholes [7,8]. We planned to trap selectively the 5*H*-phosphole with maleic anhydride in order to introduce two hydrophilic carboxylate groups into the resulting phosphine. In fact, maleic anhydride is reactive enough to also add to the 1*H*-phosphole to give a 7-phosphanorbornene side-product, as does *N*-phenylmaleimide [13] (eqn. (3)).



(3)

The desired 1-phosphanorbornene (**3**) is obtained as a mixture of two isomers with an endo or exo junction. The 7-phosphanorbornene (**4**) has an anti geometry at

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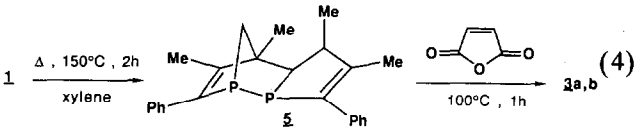
* Dedicated to Professor Lappert for his 65th birthday as a tribute to an outstanding Main-Group and Transition-Metal chemist.

P as shown by its ^{31}P resonance at relatively high field ($\delta(^{31}P)$ **4** + 49 ppm; see [13,14]) and the high ^{2}J(C–P) coupling of the Me-*C* sp^2 carbon atoms, 18.3 Hz (see [15]). The endo junction in **4** is not definitively proven but it seems logical for steric reasons and is suggested by the magnitude of the ^{3}J(H–P) coupling of the hydrogen atoms at the junction. The value of 13.3 Hz is similar to those recorded by Quin [16] for anti endo-fused 7-phosphanorbornenes of proven structure.

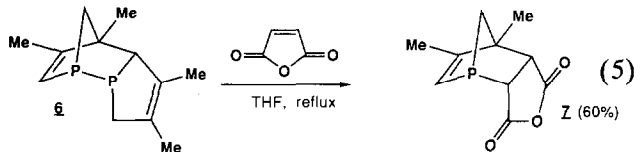
In order to avoid the formation of **4**, we then investigated the reaction of the preformed [4 + 2] dimer of 5*H*-phosphole (**2**) [17] with maleic anhydride. Since the dimer–monomer equilibrium comes into effect already at around 100°C, the reaction with maleic anhydride is cleaner and produces only **3** (eqn. (4)).



(4)

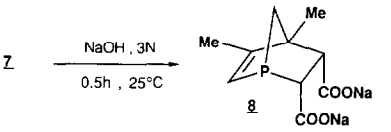
The product obtained after chromatography on silica gel is a mixture of the two endo and exo isomers, easily distinguished by ^{31}P NMR spectroscopy: $\delta(^{31}P)$ **3a** + 1.4 ppm; $\delta(^{31}P)$ **3b** + 5.4 ppm (in $CDCl_3$). Upon standing in solution, **3b** tends to form **3a** slowly during several days. The key feature allowing us to establish the stereochemistry of **3a** and **3b** is the ^{2}J(H–P) coupling within the P–CH–COO unit. This coupling is weak (2.9 Hz) in **3b** and strong (10.6 Hz) in **3a**. According to our previous work [9], these data mean that **3b** has an exo and **3a** an endo junction.

The endo anhydride readily dissolves in aqueous base. However, since both the yield of **3a** and the hydrophilicity of the corresponding carboxylate were not satisfactory, we chose to prepare a similar structure without the phenyl substituent. We started from the [4 + 2] dimer of 3,4-dimethyl-2*H*-phosphole (**6**) obtained by protonation of the 3,4-dimethylphospholide anion [18]. The reaction with maleic anhydride yields **7** as pure isomer in satisfactory yield (eqn. (5)).



(5)

The ^{2}J(H–P) coupling within the P–CH–COO unit is high (10.6 Hz), thus establishing the endo stereochemistry at the junction. The anhydride **7** readily reacts with aqueous base to give the dicarboxylate **8** (eqn. (6)).



(6)

Both the ^{2}J(H–P) coupling within the P–CH–COO unit (8.1 Hz) and the ^{3}J(H–H) coupling between the protons at the endo junction (10.8 Hz) in **8** are similar to those in **7**, thus showing that the two carboxylate groups are on the endo side. The dicarboxylate **8** is highly soluble in water (≥ 300 g/l) and is not extracted from water either by toluene or by dichloromethane. Upon treatment with 3 N hydrochloric acid, it gives the corresponding diacid **9** which precipitates and can be solubilized by dichloromethane. The diacid [$\delta(^{31}P)$ **9** −17.0 ppm in $CDCl_3$] slowly loses water to regenerate the anhydride [$\delta(^{31}P)$ (**7**) −14.8 ppm]. We are currently investigating the coordination chemistry of **8**.

3. Experimental section

All reactions were carried out under argon and silica gel (70–230 mesh) was used for chromatographic separations. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P). Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 spectrometer by the direct inlet method. Elemental analyses were performed by the 'Service d'analyse du CNRS' at Gif-sur-Yvette, France.

3.1. Synthesis of 1-phosphanorbornene (3)

A solution of 1.9 g of phosphole **1** [19] (10 mmol) in 10 ml of dry xylene was heated under reflux for 2 h. The solution was kept at 100°C, and 1.0 g of maleic anhydride (10 mmol) in 10 ml of toluene was added in 1 h. After cooling, 3 ml of hexane were added and the crude solution was chromatographed. Elution with hexane toluene (30:70) gave 500 mg of a mixture of two isomers **3a**/**3b** (70:30), yield 18%.

3a (endo): ^{1}H NMR ($CDCl_3$): δ 1.60–1.80 (m, 2H, CH_2); 1.73 (s, 3H, CH_3); 1.93 (s, 3H, CH_3); 3.30 (d, 1H, $^{3}J(H_\alpha–H_\beta) = 8.4$ Hz, H_β); 3.89 (dd, 1H, $^{3}J(H_\alpha–H_\beta) = 8.4$ Hz; ^{2}J(H–P) = 10.6 Hz, H_α). ^{13}C NMR ($CDCl_3$): δ 14.7 (CH_3); 20.1 (CH_3); 46.0 (d, ^{1}J(C–P) = 27.8 Hz, CH_2); 51.4 (s, $C_\beta H$); 52.7 (d, ^{1}J(C–P) = 8.3 Hz, $C_\alpha H$); 65.1 (d, ^{2}J(C–P) = 6.1 Hz, *C*–Me); 136.4 (d, ^{2}J(C–P) = 20.3 Hz, =*C*–Me); 139.7 (d, ^{1}J(C–P) = 23.0 Hz, =*C*–Ph); 170.3 and 170.4 (CO). ^{31}P NMR ($CDCl_3$):

δ 1.4 ppm. MS: *m/z* (relative intensity) 286 (M^+, 8), 188 ($M^+ - C_4H_2O_3$, 100). IR (CH_2Cl_2): γ (C=O) 1780 cm^{-1}.

3b (exo): ^1H NMR ($CDCl_3$): δ 1.30–1.80 (m, 2H, CH_2); 1.67 (s, CH_3); 1.91 (s, CH_3); 2.85 (d, $^3J(H_\alpha-H_\beta)$ = 7.6 Hz, H_β); 3.38 (dd, 1H, $^2J(H-P)$ = 2.95 Hz, $^3J(H_\alpha-H_\beta)$ = 7.6 Hz, H_α). ^{13}C NMR ($CDCl_3$): δ 12.9 (CH_3); 17.9 (CH_3); 49.5 (d, $^1J(C-P)$) = 40.0 Hz, CH_2); 49.7–53.5 (2CH). ^{31}P NMR ($CDCl_3$): δ 5.4 ppm.

3.2. Synthesis of 7-phosphanorbornene (4)

A mixture of 1.9 g of phosphole **1** (10 mmol) and 1.0 g of maleic anhydride (10 mmol) was heated under reflux in xylene (15 ml) for 1 h. The brown solution was extracted at room temperature with dichloromethane. After concentration, 7-phosphanorbornene (**4**) crystallized, m.p. 188°C, yield 600 mg (20%). ^1H NMR ($CDCl_3$): δ 1.80 (s, 6H, CH_3); 3.38 (m, 2H, $^3J(H-H)$ = 1.8 Hz, $^2J(H-P)$ = 13.4 Hz, CH–P); 3.59 (pseudo t, 2H, $^3J(H-H)$ = 1.8 Hz, CH–CO). ^{13}C NMR ($CDCl_3$): δ 13.4 (s, CH_3); 49.9 (s, CH); 50.2 (s, CH); 135.0 (d, $^2J(C-P)$ = 18.3 Hz, =*C*–Me); 172.0 (s, CO). ^{31}P NMR ($CDCl_3$): δ 49.9 ppm. MS: *m/z* (relative intensity) 286 (M^+, 45), 108 ($P-Ph^+$, 100).

3.3. Synthesis of 1-phosphanorbornene (7) (endo)

The dimer **6** [18], prepared from 7.6 g of phosphole **1** (40 mmol), was heated under reflux in THF (50 ml) and a solution of 4.0 g of maleic anhydride in THF (20 ml) was added in 0.5 h. The solution was concentrated and chromatographed on a short column of silica gel. Elution with dichloromethane yielded 4.8 g of 1-phosphanorbornene (**7**) (60%), m.p. (toluene) 92°C. ^1H NMR ($CDCl_3$): δ 1.60 (2H, CH_2); 1.66 (s, CH_3); 1.89 (s, CH_3); 3.29 (d, 1H, $^3J(H-H)$ = 8.54 Hz, CH_β); 3.85 (dd, 1H, $^2J(H-P)$ = 10.6 Hz, $^3J(H_\alpha-H_\beta)$ = 8.54 Hz, CH_α); 5.98 (d, 1H, $^2J(H-P)$ = 46.1 Hz, =CH). ^{13}C NMR ($CDCl_3$): δ 18.2 (s, CH_3); 19.4 (s, CH_3); 45.9 (d, $^1J(C-P)$ = 27.0 Hz, CH_2); 51.2 (s, CH); 54.4 (d, $J(C-P)$ = 7.9 Hz, CH); 63.6 (d, $^2J(C-P)$ = 6.0 Hz, *C*Me); 125.3 (d, $^1J(C-P)$ = 26.9 Hz, =CH); 163.7 (s, =*C*Me); 170.6 (s, CO). ^{31}P NMR ($CDCl_3$): δ −14.9 ppm. MS: *m/z* (relative intensity) 210 (M^+, 11), 112 ($M^+ - C_4H_2O_3$, 100). IR (CH_2Cl_3): γ (CO) 1780 cm^{-1}.

3.4. Synthesis of the dicarboxylate (8)

The anhydride **7** (945 mg, 4.5×10^{-3} mol) was dissolved in 3 ml of a deoxygenated 3 N solution of NaOH at room temperature. This took 0.5 h. After the solution had become homogeneous, it was extracted with dichloromethane or toluene. No ^{31}P NMR signal was detected in the organic phase. Evaporation of the water phase yielded pure **8**.

8: ^1H NMR (D_2O): δ 1.30 (d, 2H, $^2J(H-P)$ = 8.6 Hz, CH_2); 1.46 (s, 3H, CH_3); 1.94 (s, 3H, CH_3); 2.91 (d, $^3J(H_\alpha-H_\beta)$ = 10.8 Hz, CH_β); 3.51 (dd, $^2J(H-P)$ = 8.10 Hz, $^3J(H_\alpha-H_\beta)$ = 10.8 Hz, CH_α); 5.97 (d, 1H, $^2J(H-P)$ = 44.0 Hz, =CH). ^{13}C NMR (D_2O): δ 19.0 (s, CH_3); 20.0 (s, CH_3); 50.7 (s, CH_β); 52.5 (d, $^1J(C-P)$ = 13.7 Hz, CH_2); 56.3 (s, CH_α); 61.6 (d, $^2J(C-P)$ = 4.2 Hz, *C*Me); 124.7 (d, $^1J(C-P)$ = 18.4 Hz, =CH), 163.2 (d, $^2J(C-P)$ = 3.8 Hz, =*C*–Me); 180.6 and 180.9 (2s, CO). ^{31}P NMR (D_2O): δ −29.47 ppm.

3.5 Synthesis of diacid (9)

An excess of 3 N hydrochloric acid (4 ml) was added to the aqueous solution of dicarboxylate, **8**, prepared as described above. The white precipitate was extracted twice with dichloromethane (2 × 5 ml), yielding quantitatively the diacid **9**. ^1H NMR ($CDCl_3$): δ 1.35 (2H, CH_2); 1.49 (s, 3H, CH_3); 2.04 (s, 3H, CH_3); 2.86 (d, 1H, $^3J(H_\alpha-H_\beta)$ = 10.32 Hz, CH_β); 3.68 (dd, $^3J(H_\alpha-H_\beta)$ = 10.32 Hz, $^2J(H-P)$ = 8.44 Hz, CH_α); 5.84 (d, 1H, $^2J(H-P)$ = 46.5 Hz = CH). ^{13}C NMR ($CDCl_3$): δ 19.3 and 19.8 (2s, CH_3); 47.8 (d, $^1J(C-P)$ = 25.3 Hz, CH_2); 52.3 (s, CH); 52.7 (s, CH); 61.0 (d, $^2J(C-P)$ = 4.9 Hz, *C*–Me); 125.4 (d, $^1J(C-P)$ = 25.6 Hz, =CH); 163.6 (s, =*C*Me); 177.7 (s, CO). ^{31}P NMR ($CDCl_3$): δ −17.0 ppm. MS: *m/z* (relative intensity) 228 (M^+, 6), 112 ($M^+ - C_4H_4O_4$, 100).

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