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Monodechlorination of 6,6-Dichloro-3-phosphabicyclo[3.1.0]hexane 3-Oxides by Catalytic Hydrogenation†

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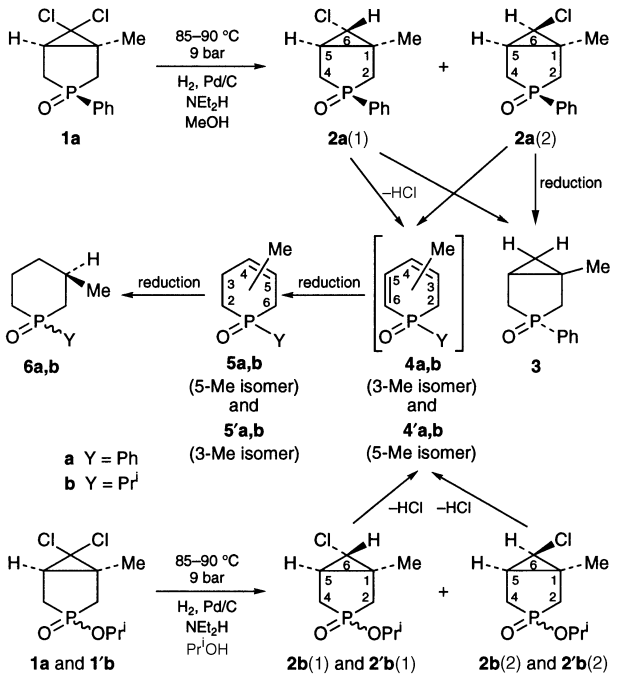
Catalytic hydrogenation of the title compounds at *ca.* 88 °C and 9 bar in the presence of diethylamine led to a reasonable portion of monochlorocyclopropanes together with *ca.* 38% of hexahydrophosphinine oxides.

There are only a few reports on the reductive monodechlorination of geminal dichlorocyclopropanes in the literature.[1–4] We have recently found that the hydrogenation of dichlorophosphabicyclohexanes at *ca.* 88 °C and 9 bar in the presence of triethylamine afforded hexahydrophosphinines by reductive cyclopropane ring opening.[5] Under the conditions applied, it was not possible to stop at the intermediate stages. Therefore we could not isolate and characterise the intermediates. Here we show how to perform the hydrogenations to yield a reasonable quantity of the monochloro species.



Scheme 1

It was not possible to achieve monodechlorination by carrying out the hydrogenations of the title compounds (*e.g.* **1a**) at lower temperatures than 85–90 °C,[5] as no reaction occurred below 85 °C. Hydrogenation of **1a** at *ca.* 88 °C in the presence of diethylamine instead of triethylamine afforded, however, the monochloro species **2a**(1) and **2a**(2) in reasonable quantities. According to ^{31}P NMR, the proportion of **2a**(1) and **2a**(2) was 40%, with the remainder being the fully dehalogenated cyclopropane **3** (20%) and the hexahydrophosphinine oxide **6a** (40%) (Scheme 1, Table 1). A similar hydrogenation of the isopropoxy starting material consisting of 36% of **1b** and 64% of **1′b** gave the monochloro products as a mixture of four isomers [**2b**(1), **2b**(2), **2′b**(1) and **2′b**(2)] in 64% yield, together with 36% of **6b** (Scheme 1, Table 1). Our results are in accord with literature data showing that the outcome of the dehydrohalogenation may depend on the nature of the base employed.[1] Partial or complete separation of the isomers **2a** and **2′b** was achieved by repeated column chromatography: isomer **2a**(1) was isolated in a pure form, **2′b** as a 61–39% mixture of isomers **2′b**(1) and **2′b**(2).

The stereostructure of the starting material **1a** is known from an earlier X-ray study[6] and the structures of the isomers of the isopropoxy compound (**1b** and **1′b**) were assigned on the basis of an analogy.[7] As only the C-6 centre of the starting materials (**1** and **1′**) is involved in the hydrogenolysis, the relative configurations of the other asymmetric centres should remain unchanged. The distinction between isomer (1) and isomer (2) of **2** (and **2′**) is possible on the basis of the stereospecific $^3J_{HH}$ couplings at C(6)—H. The X-ray structure[6] of the starting material **1a** served as a good basis for the estimation of the torsion angles in the two isomers. Hence, the H—C(5)—C(6)—H dihedral angle is *ca.* 147° for isomer (1) of **2** and **2′**, and *ca.* 0° for isomer (2) of the same products, suggesting $^3J_{HH}$ couplings of 4.8 and 8.0 Hz, respectively.[8] Isomer (1) and isomer (2) of the products (**2** and **2′**) were assigned on the basis of the measured couplings of *ca.* 3 and

Table 1 Products from the hydrogenation of the phosphabicyclohexanes

	δ_P[a] (product composition in %)[b]							
Starting compound	**2**(1)	**2**(2)	**2′**(1)	**2′**(2)	**3**	Major	**6**	Minor
1a	71.8 (26)	80.0 (14)			73.2 (20)	37.0 (35.1)[5] (29)		34.6 (33.0)[5] (11)
1b+**1′b**	79.1[c] (15)	82.8[c] (9)	80.6 (15)	88.2 (25)		51.0 (50.5)[5] (28)		49.9 (49.1)[5] (8)

[a]In $CDCl_3$. [b]On the basis of the ^{31}P NMR intensities. [c]Tentative assignments.

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Table 2 Partial ^{1}H NMR data for the monochloro products

	δ_H[a] (multiplicity, J in Hz)		
	2a(1)	**2′b**(1)	**2′b**(2)
C(6)—H	2.68 (d, $^3J_{HH}$ = 2.9)	2.95 (d, $^3J_{HH}$ = 3.0)	3.25 (dd, $^3J_{HH}$ = 7.3, $^4J_{PH}$ = 3.5[b])

[a]In $CDCl_3$. [b]Confirmed by ^{31}P decoupled spectra.

Table 3 ^{13}C NMR data for the monochlorophosphabicyclohexanes

	δ_C[a] (J_{PC} in Hz)									
Compound	C-1	C-2	C-4	C-5	C-6	C(1)—Me	C-1′	C-2′	C-3′	C-4′
2a(1)	28.4	38.1	32.2	30.8	45.1	19.2	132.5	130.2[b]	129.0[b]	132.2
	(7.3)	(66.8)	(66.7)	(5.6)	(3.8)	(7.4)	(88.3)	(9.2)	(11.1)	(2.1)
2′b(1)	24.9	34.2	28.8	27.8	44.3	19.2		70.1	24.1	
	(11.4)	(89.2)	(88.7)	(8.7)	(4.0)	(9.7)		(6.5)	(3.7)	
2′b(2)	22.5	28.8	23.6	23.7	45.8	21.5		69.3	24.4	
	(12.1)	(88.7)	(89.0)	(8.6)	(6.3)	(10.6)		(6.5)	(3.6)	

[a]In $CDCl_3$. [b]May be reversed.

7.3 Hz, respectively (Table 2). Isomers **2a**(1), **2′b**(1) and **2′b**(2) were also characterised by ^{13}C NMR (Table 3) and MS data.

Interruption of the hydrogenation of **1a** at an earlier stage resulted in a mixture containing 11% of **2a**(1), 7% of **2a**(2), 7% of **3**, 23% of **6a** and 6% of **1a** according to ^{31}P NMR. The remaining part at δ_P 30.7 (37%) and at δ_P 28.5 (9%) consisted of intermediate isomers. The major component was separated by column chromatography and assigned structure **5a** by ^{13}C NMR and MS. Thus, it was confirmed that the hydrogenation of **1** takes place through the tetrahydrophosphinine oxide **5**, formed from the dihydrophosphine oxide **4**.

Experimental

The same instruments were used as previously reported.[5] The NMR spectra were recorded in $CDCl_3$ solution. Coupling constants (J) are given in Hz. The starting materials **1a** and **1b** were prepared as described earlier.[9,10]

Hydrogenation of **1a**. 6-*Chloro*-1-*methyl*-3-*phenyl*-3-*phosphabicyclo*[3.1.0]*hexane* 3-*Oxide* **2a**(1) *and* 1-*Methyl*-3-*phenyl*-3-*phosphabicyclo*[3.1.0]*hexane* 3-*Oxide* **3**.—A mixture of **1a** (1.5 g, 5.46 mmol), Pd–C (0.9 g, 10%) and diethylamine (1.4 ml, 13.7 mmol) in methanol (50 ml) was hydrogenated at 85–90 °C and 9 bar until 1.8 equiv. of hydrogen was absorbed. Filtration and evaporation left an oil that was analysed by ^{31}P NMR and GCMS (Table 1). Column chromatography (silica gel, 3% methanol in chloroform) afforded 0.21 g (16%) of **2a**(1), 0.31 g (27%) of **6a** and a fraction of 0.2 g consisting of *ca.* 50% of **3**.

2a(1). δ_P 70.9; δ_H see Table 2 and 1.56 (s, 3 H, 1-Me), 1.65 (dd, $^3J_{PH}$ = 21.9, $^3J_{H(4)H}$ = 7.8, 1 H, 5-H), 2.29–2.44 [m, 3 H, C(2)—H_2, C(4)—Hα], 2.63 [ddd, $^3J_{HH}$ = 7.7, $^2J_{PH}$ = $^2J_{HH}$ = 18.3, 1 H, C(4)—Hβ], 7.49–7.69 (m, 5 H, Ar); δ_C see Table 3; m/z (rel. int.) 240 (M^+, 5), 225 (2), 205 (100), 125 (15), 77 (12), 91 (9); HRMS, M^+ (Found: 240.0499. $C_{12}H_{14}OPCl$ requires 240.0471 for the ^{35}Cl isotope).

3. δ_P 72.3; m/z 206 (M^+) (Found: M^+ 206.0899. $C_{12}H_{15}OP$ requires M_r 206.0861).

5-*Methyl*-1-*phenyl*-1,2,3,6-*tetrahydrophosphinine* 1-*Oxide* **5a**.—Compound **5a** was obtained by column chromatography (silica gel, 3% MeOH in $CHCl_3$) after interrupting the above hydrogenation. Yield: 21%. δ_P 30.5; δ_C 22.1 (J = 4.9, C-3), 23.8 (J = 67.4, C-6), 25.7 (J = 11.1, Me), 31.4 (J = 66.2, C-2), 122.5 (J = 12.6, C-4), 128.3 (J = 11.5, C-2′),* 129.5 (J = 9.3, C-3′),* 131.5 (C-4′), 132.5 (J = 96.6, C-1′) (assignments marked * may be reversed); m/z (rel. int.) 206 (M^+, 100), 191 (28), 125 (68), 91 (29), 77 (26). (Found: M^+ 206.0895. $C_{12}H_{15}OP$ requires M_r 206.0861).

Hydrogenation of **1b** *and* **1′b**. 6-*Chloro*-1-*methyl*-3-*isopropoxy*-3-*phosphabicyclo*[3.1.0]*hexane* 3-*Oxides* **2b′**(1) *and* **2′b**(2).—The mixture of isomers (**1b** and **1′b**) was hydrogenated in isopropyl alcohol as described above for **1a**. Column chromatography of the mixture (Table 1) led to 0.25 g (21%) of **2′b** consisting of 61% or **2′b**(1) and 39% of **2′b**(2) and 0.30 g (30%) of **6b**. For **2′b**(1): δ_P 80.9. For **2′b**(2): δ_P 88.4. For the mixture: δ_H, Table 2; δ_C, Table 3; CI–MS, m/z 223 (M + H); m/z (rel. int.) 222 (M^+, 1), 207 (5), 187 (25), 180 (18), 145 (100).

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