A New Approach to Phosphinines by Three-Step Aromatization of 1-Ethoxy-1,2-dihydrophosphinine 1-Oxides

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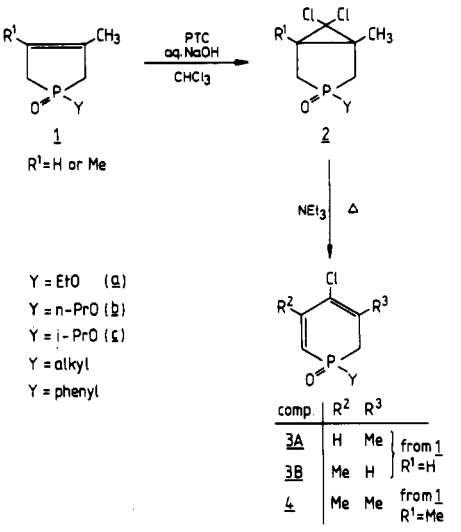
We have recently developed a simple method for the ring enlargement of P-substituted 3-methyl- and 3,4-dimethyl-2,5-dihydro-1*H*-phosphole 1-oxides to 1,2-dihydrophosphinine oxides.[1-4] Dichlorocarbene is added to the dihydro-1*H*-phosphole oxide (1) in the first step.[1,3,4] The dichlorocyclopropane ring is then opened[2-4] to give the ring-expanded products **3** and **4** in good yields (Scheme I). This method offers easier access to valuable dihydrophosphinine oxides (**3** and **4**) than the earlier procedures.[5] 1,2-Dihydrophosphinine oxides are excellent starting materials for other P-heterocycles.[6] The present paper describes their use in the synthesis of phosphinines.

Phosphinine derivatives, such as substituted and fused phosphinines, can be prepared in different ways.[7,8] One approach involves the aromatization of P-substituted dihydrophosphinines.[8-11] Starting with *P*-chlorodihydrophosphinines, the yields were poor,[10] special techniques were necessary,[11] and in some cases the product was not isolated in a pure form.[11]

We hoped that *P*-alkoxy-1,2-dihydrophosphinine oxides might also be converted to phosphinines by reducing the phosphorus to the tervalent state and increasing the unsaturation of the ring. To realize this new approach, the mixture of the double-bond isomers (**A** and **B**) of the ethoxy-substituted dihydrophosphinine oxide (**3a**) chosen as starting material was transformed to the phosphinic acid chlorides (**5A** and **5B**) by reaction with phosphorus pentachloride. The mixture of intermediates **5A** and **5B** so obtained was used without purification in the next step, which consisted of deoxygenation by phenylsilane. The phosphinous chlorides (**6A** and **6B**) formed were too unstable to be detected by spectroscopic methods as they lose hydrogen chloride spontaneously, under the conditions of the reduction. Scheme II shows that the same product

Scheme I[1-4]



Scheme II

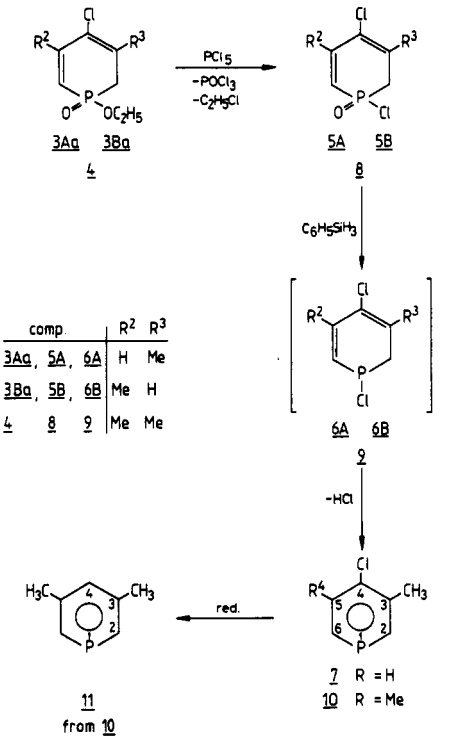


Table I. ^{13}C NMR Spectral Data for Phosphinines 7, 10, and 11

compd	^{13}C δ (J_{PC})[a]					
	C_2	C_6	C_3	C_5	C_4	CH_3
7	156.1 (53.5)	152.6 (52.0)	142.6 (16.2)	135.9 (14.7)	137.5 (23.4)	23.6 (2.2)
10	153.1 (49.8)		143.2 (16.2)		*b*	24.8 (2.2)
11	150.1 (49.8)		144.0 (14.6)		132.3 (18.3)	24.7 (2.2)

[a] $CDCl_3$ solutions; J_{PH} given in Hz. [b] Not resolved.

(**7**) is formed from both double-bond isomers (**A** and **B**) of the starting material (**3a**). The three-step procedure gives the 4-chloro-3-methylphosphinine (**7**) in a gross yield of ~35% after fractional distillation. It is not necessary to remove the hydrogen chloride side product by 1 equiv of a tertiary amine, as this does not increase the yield,

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Table II. ^1H NMR Spectral Data for Phosphinines 7, 10, and 11

compd	^1H δ (mult, integral, J_{PH})[a]			
	H_2	H_6	H_4 or H_5	CH_3
7	8.32 (ddd, 1 H, ^2J = 36)	8.46 (dm, 1 H, ^2J = 36)	7.81 (dm, 1 H, ^3J = 10)	2.52 (d, 3 H, ^4J = 2)
10	7.84 (d, 2 H, ^2J = 38)			2.02 (d, 6 H, ^4J = 2)
11	7.73 (d, 2 H, ^2J = 38)		6.59 (s, 1 H)	1.91 (d, 6 H, ^4J = 0.7)

[a] $CDCl_3$ solutions; J_{PH} given in Hz.

but causes workup difficulties, and contaminates the phosphinine 7. Other P-alkoxy dihydrophosphinine oxides, such as the *n*-propoxy- or isopropoxy derivatives (**3b** and **3c**, respectively), can also be used instead of the ethoxy compound **3a** in the preparation of phosphinine 7. In these cases, the phosphinine 7 could be obtained in a ~20% yield.

An attempt was also made to convert the dimethyldihydrophosphinine oxide 4 to the corresponding phosphinine 10. The formation of product 10 was, however, accompanied by side reactions, such as decomposition and further reduction to phosphinine 11 (Scheme II). As we could not avoid the undesired reduction by the use of less phenylsilane and also because the two phosphinines (10 and 11) have close boiling points, it was not possible to obtain product 10 in a pure form. The structure of 10 could, however, be reassuringly confirmed by GC–MS and by NMR (see below). The use of more reducing agent led to phosphinine 11 as a single product, which could be isolated in pure form and in reasonable yield. Other dimethylphosphinines, such as the 2,6-dimethyl-[12] and the 3,4-dimethyl derivatives,[13] have also been described but were synthesized by other approaches.

Structures of the phosphinines prepared (7, 10, and 11) are supported by ^{13}C and ^1H NMR and by mass spectrometry. NMR spectra of the products (Tables I and II) display the expected features, such as strong downfield shifts for the α-carbon atoms and α-protons ($\delta_{C(2)}$ and $\delta_{C(6)}$ ~153 ppm and $\delta_{H(2)}$ and $\delta_{H(6)}$ ~8.1 ppm, respectively) and the unusually large J_{PC} and J_{PH} couplings, especially for the α-carbon atoms and α-protons ($^1J_{PC}$ ~52 Hz and $^2J_{PH}$ ~37 Hz, respectively). These parameters together with the ^{31}P NMR chemical shifts of +197 ppm for 7 and +204.3 ppm for 11 are consistent with the aromatic structure and similar to those described for other phosphinines.[7,9,11] In accordance with expectations,[7,9] the mass spectra of the products (7, 10 and 11) show intense molecular ions (with the expected isotopic distribution for the 4-chloro derivatives). Compounds 7 and 10 may lose a chlorine atom or hydrogen chloride in the ion source of the mass spectrometer. Regarding phosphinine 10, the $M - HCl^{+}$ species can be further stabilized by extrusion of the P-atom and by elemental steps to give a tropylium cation (m/e = 91).

Products 7 and 10 are the first examples of 4-chlorophosphinines. Preparation of 2-halogenophosphinines by cycloaddition followed by aromatization has recently been reported by Mathey[14] and by Bickelhaupt.[15] While the 2-iodo- and 2-bromophosphinines are useful starting materials in the synthesis of functionalized derivatives,[15,16] the 2-chlorophosphinines were inert to substitution.[14] The simplicity of our method for the synthesis of 4-chlorophosphinines will allow us to explore their chemistry.

Experimental Section

^{31}P, ^1H, and ^{13}C NMR spectra were recorded on a JEOL FX 100 instrument operating at 40.26, 100.0, and 25.0 MHz, respectively. Chemical shifts are downfield relative to 85% phosphoric acid (^{31}P NMR) and to tetramethylsilane (^1H and ^{13}C NMR) and have a positive sign. Coupling constants are given in Hz. Mass spectra were obtained on a MS 25-RFA instrument at 70 eV.

4-Chloro-3-methylphosphinine (7). Phosphorus pentachloride (3.2 g, 15.4 mmol) was added to the mixture of **3Aa** (26%) and **3Ba** (24%)[3] (3.0 g, 14.5 mmol) in dichloromethane (30 mL). The contents of the flask were stirred for 15 min at room temperature and for 3.5 h at reflux. Evaporation of the volatile components in vacuo provided the double-bond isomers **A** and **B** of phosphinic chloride **5** (2.9 g) in a form suitable for further transformation. **5A** (75%): ^{31}P NMR (C_6D_6) δ +37.6; ^{13}C NMR ($CDCl_3$) δ 22.6 ($^3J_{PC}$ = 10.9, CH_3), 39.2 ($^1J_{PC}$ = 82.8, C_2), 120.5 ($^1J_{PC}$ = 107, C_6), 122.8 ($^3J_{PC}$ = 24.2, C_4), 133.1 ($^2J_{PC}$ = 10.3, C_3), 144.3 (C_5); ^1H NMR ($CDCl_3$) δ 1.82 (s, 2.25 H, CH_3). **5B** (25%): ^{31}P NMR (C_6D_6) δ +37.6; ^{13}C NMR ($CDCl_3$) δ 23.8 ($^3J_{PC}$ = 15.4, CH_3) 33.9 ($^1J_{PC}$ = 83.5, C_2), 119.7 ($^1J_{PC}$ = 112.1, C_6), 123.7 ($^2J_{PC}$ = 11.7, C_3), 130.7 ($^3J_{PC}$ = 25.6, C_4), 151.2 (C_5); ^1H NMR ($CDCl_3$) δ 1.91 (s, 1.75 H, CH_3). For the mixture of **5A** and **5B**: MS m/e (rel intensity) 196 (M^+, 23), 160 (80), 77 (100).

Dichloromethane (30 mL) was added to **5** (2.9 g, ~14.5 mmol) from the previous reaction, and the solution was degassed by nitrogen. Phenylsilane (0.72 mL, 5.80 mmol) was then added, and the mixture was stirred at the boiling point under nitrogen for 4 h. The solution was concentrated in vacuo, and volatile components of the residue were distilled at 0.3 Torr into a flask cooled by a dry ice–acetone mixture. The contents of the flask were then fractionated in vacuo to give 7 (0.73 g, 35%): bp 82–84 °C (20 Torr); ^{31}P NMR ($CDCl_3$) δ +197.0; ^{13}C NMR, Table I; ^1H NMR, Table II; MS m/e (rel intensity) 144 (M^+, 100), 143 (24), 109 (42), 108 (45), 107 (70), 78 (52). Anal. Calcd for C_6H_6ClP: C, 49.86, H, 4.18. Found: C, 50.20; H, 3.99.

3,5-Dimethylphosphinine (11). Phosphinic chloride **8** was prepared from **4**[4] by the procedure used for **5**: ^{13}C NMR ($CDCl_3$) δ 23.8 ($^3J_{PC}$ = 11.7, C_3-CH_3), 25.0 ($^3J_{PC}$ = 17.6, C_5-CH_3), 40.1 ($^1J_{PC}$ = 82.8, C_2), 118.0 ($^1J_{PC}$ = 113.6, C_6), 126.9 ($^3J_{PC}$ = 21.3, C_4), 133.1 ($^2J_{PC}$ = 10.3, C_3), 153.3 ($^2J_{PC}$ = 2.9, C_5); ^1H NMR ($CDCl_3$) δ 2.0 (s, 3 H, CH_3), 2.05 (s, 3 H, CH_3), 6.0 (d, 1 H, CH=, $^2J_{PH}$ = 8); MS m/e (rel intensity) 210 (M^+, 34), 174 (60), 91 (100). **8** was treated with 0.7 equiv of phenylsilane as described for **5**. Yield of 11: 28%; bp 76–78 °C (20 Torr); ^{31}P NMR ($CDCl_3$) δ +204.3; ^{13}C NMR, Table I; ^1H NMR, Table II; MS m/e (rel intensity) 124 (M^+, 100), 109 (48), 91 (29); M^+_{found} = 124.0420, C_7H_9P requires 124.0442.

Using 0.4 equiv of phenylsilane, a mixture containing ~70% of **10** and ~30% of 11 was formed: bp 76–80 °C (20 Torr). For **10**: ^{13}C NMR, Table I; ^1H NMR, Table II; GC–MS m/e (rel intensity) 158 (M^+, 100), 143 (11), 123 (22), 122 (8), 121 (20), 91 (77); M^+_{found} = 158.0034, C_7H_8ClP requires 158.0052 for the ^{35}Cl isotope.

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