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1-CHLORO-1H-PHOSPHIRENES - A NEW SYNTHESIS FROM PHOSPHAALKENES AND CARBENES [1]

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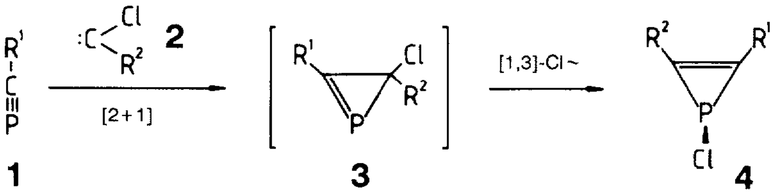
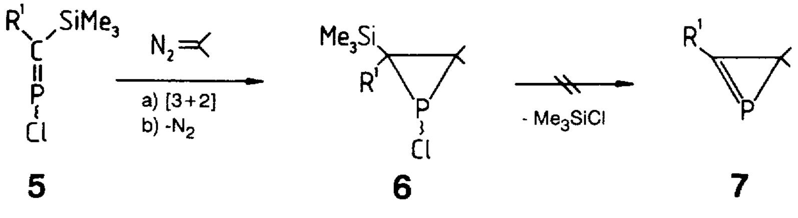
Abstract: The chlorocarbenes **2**, generated thermally from the diazirines **8**, take part in [2 + 1]-cycloaddition reactions with the phosphaalkenes **5** to furnish the dichlorophosphiranes **9**. At 130 °C, the latter products **9** undergo elimination of chlorotrimethylsilane to form the 1-chloro-1H-phosphirenes **4**.

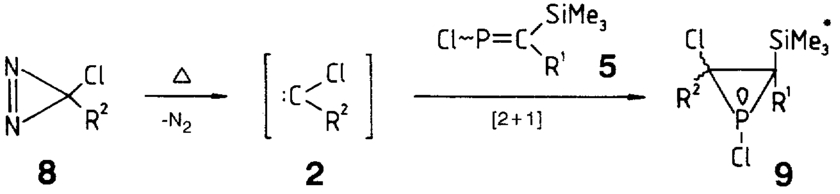
While 1-alkyl- or 1-aryl-1H-phosphirenes have been known for some years [2], free 1-chloro-1H-phosphirenes **4** without stabilization by complex formation have just recently been prepared for the first time [3]. They were obtained from the reactions of the phosphaalkynes **1** with the chlorocarbenes **2** whereby the primarily formed 2H-phosphirenes **3** could not be isolated since they underwent isomerization to **4** by rapid [1,3]-chlorine shifts. Since chlorine substituents can readily take part in nucleophilic substitution reactions, the 1-chloro-1H-phosphirenes represent interesting building blocks for organophosphorus chemistry. In this communication, we report on a new, high-yielding synthesis of **4** which is independent of the kinetically stabilized phosphaalkynes **1** and which starts rather from the P-chloro-substituted phosphaalkenes **5** and chlorocarbenes. The formation of the endocyclic C/C double bond is achieved by elimination on the phosphirane ring.





It is of interest to note that the thermal cleavage of chlorotrimethylsilane from the chlorophosphirane ring for introduction of a P/C double bond (6 $\not\longrightarrow$ 7) has not yet been successful [4]. The starting materials for the elimination are accessible from **5** by cycloaddition of secondary diazo compounds with subsequent cleavage of nitrogen [4]. Also, base-catalyzed HCl eliminations from comparable systems have been unsuccessful to date [5], although 2*H*-phosphirenes **7** have been prepared by other routes [6].

When the phosphaalkenes **5a** [7] and **b** [8] are heated in benzene with the diazirine **8a** [9] (glass pressure vessel, see Table 1) or when the thermally less stable **8b** [10] is allowed to react with the same reaction partners at room temperature (see Table 1), the dichlorophosphiranes **9a-d**, which are all sensitive towards hydrolysis, are obtained in 47 - 89% yield as either colourless crystals (**9a**: m.p. 77 °C; **9c**: m.p. 97 °C) or non-crystallizable oils (**9b, d**).



8a: R^2 = Ph ; 8b: R^2 = OPh	5a: R^1 = Ph; 5b: R^1 = $SiMe_3$	9: R^1,R^2 see Table 1

Table 1. Reaction conditions, yields, and NMR spectroscopic data of the 1,2-dichlorophosphiranes **9a-d**.

Phosphirane	R^1	R^2	Reaction Conditions	Yield [%]	^{31}P-NMR[a] [ppm]	^{13}C-NMR [ppm][b,c] R^1-$\underline{C}$	R^2-$\underline{C}$
9a	Ph	Ph	C_6H_6/5 min/125 °C	57	-52.8	46.4 (61.1)	63.8 (51.5)
9b	$SiMe_3$	Ph	C_6H_6/5 min/125 °C	89	-36.6	32.8 (68.1)	66.2 (57.2)
9c	Ph	OPh	C_6H_6/48 h/25 °C	47	-49.7	45.9 (58.8)	92.3 (54.4)
9d	$SiMe_3$	OPh	C_6H_6/48 h/25 °C	59	-35.3	32.1 (62.3)	93.5 (61.0)

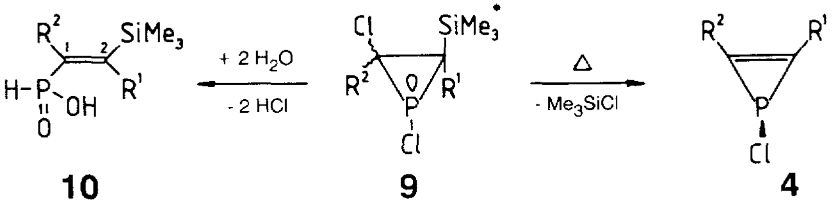
[a] **9a,b**: $CDCl_3$; **9c,d**: C_6D_6; 85% phosphoric acid as external standard.
[b] **9a,b**: $CDCl_3$; **9c,d**: C_6D_6; tetramethylsilane as internal standard.
[c] $^1\underline{J}_{C,P}$ coupling constants [Hz] in parenthesis.

The constitutions of the 1,2-dichlorophosphiranes **9a-d** were confirmed by the characteristic ^{31}P-NMR resonances for $\lambda^3\sigma^3$-phosphorus atoms with a chlorine substituent (δ = -35.3 to -52.8) as well as the ^{13}C-NMR resonances which are split by $^1\underline{J}_{C,P}$ coupling constants of 51.5 to 68.1 Hz (see Table 1) [11].

Molecules of the type **9** possess two (for R^1 = $SiMe_3$) or three (for R^1 = Ph) centres of chirality so that the occurrence of diastereomers is to be expected. However, the NMR data of both the crude and the pure products show that only one diastereomer has been formed in each case.

NMR spectroscopic studies of other phosphiranes [4,11] have shown that substituents in a <u>trans</u>-position to the free electron pair of the phosphorus atom exhibit smaller coupling constants than substituents in a <u>cis</u>-position. On the basis of these results, the observation that only the SiMe$_3^*$ groups exhibit a coupling in the ^{1}H-NMR [δ = -0.29 to 0.15 (each d, $^4J_{H,P}$ = 1.5 to 2.4 Hz)] and ^{13}C-NMR [δ = -1.7 to 1.6 (each d, $^3J_{C,P}$ = 6.2 to 12.0 Hz)] indicates that these groups are each in a <u>cis</u>-relationship to the free electron pairs of the phosphorus atoms. The configuration at the carbon atom of the three-membered ring bearing the R^2 substituent is, in contrast, still unclarified.

On attempts to purify the dichlorophosphirane **9b** by flash chromatography [12] (silica gel/diethyl ether), it undergoes hydrolysis to the vinylphosphonous acid **10b** [colourless crystals; m.p. 135 °C; ^{1}H-NMR (CDCl$_3$): δ = -0.20, 0.34 (each s, 9H, SiMe$_3$), 7.00 (d, $^1J_{H,P}$ = 561 Hz, 1H, PH), 7.28 (m, 5H, aromatic), 12.56 (br. s, 1H, POH); ^{13}C-NMR (CDCl$_3$): δ = 2.0, 3.6 (each s, Si($\underline{C}$H$_3$)$_3$), 127.9, 128.3, 130.6 (each s, aromatic C), 139.4 (d, $^2J_{C,P}$ = 14.5 Hz, <u>ipso</u>-aromatic C), 159.1 (d, $^1J_{C,P}$ = 114.9 Hz, C-1), 164.9 (d, $^2J_{C,P}$ = 13.5 Hz, C-2); ^{31}P-NMR (CDCl$_3$): δ = 23.4]. Under the above-mentioned conditions the phosphirane **9d** undergoes unspecific decomposition whereas products **9a** [13] and **c** can be purified in this manner.



10a: R^1 = R^2 = Ph	**10b**: R^1 = SiMe$_3$, R^2 = Ph	**9**: R^1,R^2 see Table 1	**4**: R^1,R^2 see Table 2

Table 2. Boiling point, yield, and NMR spectroscopic data for the 1-chloro-1<u>H</u>-phosphirenes **4a–d**.

Phosphirene	R^1	R^2	B.p.[a] [°C/mbar]	Yield [%]	^{31}P-NMR[b] [ppm]	^{13}C-NMR [ppm][c,d] R^1-$\underline{C}$	R^2-$\underline{C}$
4a	Ph	Ph	200/2·10^{-3}	78	-81.5	135.7 (66.0)	
4b	SiMe$_3$	Ph	150/2·10^{-3}	52	-83.4	153.2 (76.7)	139.1 (72.2)
4c	Ph	OPh	150/2·10^{-3}	46	-43.0	108.4 (49.8)	150.2 (80.0)
4d	SiMe$_3$	OPh	100/5·10^{-3}	51	-39.8	109.4 (54.2)	167.5 (83.6)

[a] Oven temperature of the bulb-to-bulb distillation.

[b] **4a–c**: CDCl$_3$; **4d**: CD$_2$Cl$_2$; 85% phosphoric acid as external standard.

[c] **4a–c**: CDCl$_3$; **4d**: CD$_2$Cl$_2$; tetramethylsilane as internal standard.

[d] $^1J_{C,P}$ coupling constants [Hz] in parenthesis.

When the 1,2-dichlorophosphiranes **9a–d** are heated at 130°C in the absence of a solvent and then worked-up by bulb-to-bulb distillation, the title substances **4a–d** can be isolated in 46–78% yield in the form of oxidation- and hydrolysis-sensitive crystals (**4a**: m.p. 91 °C) or oils (**4b–d**).

The appearance of resonances for two olefinic carbon atoms with $^1\underline{J}_{C,P}$ coupling constants as well as the expected high field absorptions for the $\lambda^3\sigma^3$-phosphorus atoms in the respective NMR spectra (see Table 2) unequivocally confirm the structures of the 1H-phosphirenes **4a–d**. The mass spectra exemplarily recorded for compounds **4b** and **c** exhibit, among others, peaks for the molecular ions (13 and 6% relative intensities) as well as fragments at m/z = 174 and 194 (28 and 100% relative intensities, respectively) which demonstrate the cleavage of the P-Cl moiety.

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13. In addition, 15% of **10a** can be obtained from the eluate as colourless crystals with m.p. 141 °C. Selected NMR data: ^{1}H-NMR ($CDCl_3$): δ = 7.38 (d, $^1\underline{J}_{H,P}$ = 561 Hz, 1H, PH), 12.82 (br. s, 1H, POH); ^{13}C-NMR ($CDCl_3$): δ = 146.0 (d, $^1\underline{J}_{C,P}$ = 129.8 Hz, C-1), 162.7 (d, $^2\underline{J}_{C,P}$ = 26.3 Hz, C-2); ^{31}P-NMR ($CDCl_3$): δ = 24.5.

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