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A VERY SIMPLE ONE-POT SYNTHESIS OF 2-CHLOROPHOSPHININES

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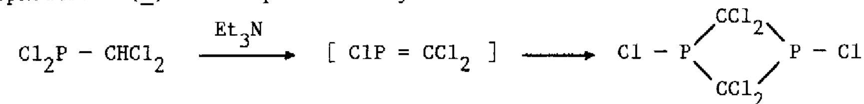
Summary : 2-Chlorophosphinines are obtained by reaction of dichloromethyldichlorophosphine with conjugated dienes and triethylamine at *ca* 80°C.

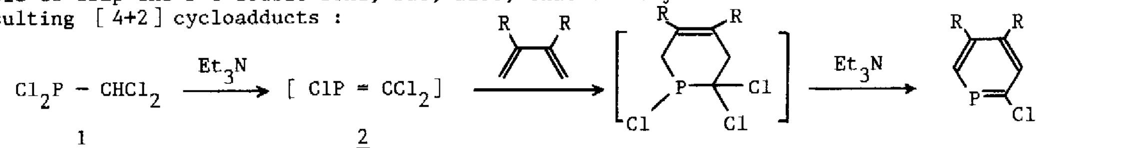
Although they are now known since a long time, the study of phosphinines is still hampered by two synthetic problems . Indeed, on one side, the access to weakly substituted phosphinines remains difficult. For example, the only route to parent phosphinine is the original multistep method of Ashe [1] with its low overall yield. On the other hand, only a limited number of functional phosphinines has been reported in the literature until now [2-8] and no easy and general access to these species is known. We wish to describe hereafter a new and very simple one-pot synthesis of the still unknown 2-chlorophosphinines which may partly solve these two synthetic problems.

Our starting point was an observation made by russian chemists [9] who stated that triethylamine was able to dehydrochlorinate dichloromethyldichlorophosphine (1) to give a transient trichlorophosphaalkene (2) which spontaneously dimerizes :



1 2

Since it is well known that chlorine substitution stabilizes phosphaalkenes [10], we suspected that the half-life of 2 would be long enough so that reactive conjugated dienes could trap it via a [4+2] cycloaddition. Hence, we decided to perform this dehydrochlorination in the presence of a series of 1,3-dienes. In so doing, we discovered not only that it was indeed possible to trap the P=C double bond, but, also, that triethylamine was able to aromatize the resulting [4+2] cycloadducts :



1 2 3 R=Me 4 R=H 5 R=Me

The synthesis of 2-chlorophosphinine is described hereafter as an example :
Dichlorophosphine 1 (10g, 5.38×10^{-2} mol), Et_3N (32.5g, 3.22×10^{-1} mol), butadiene (14.5g, 2.69×10^{-1} mol) and 50 mL of dry benzene were heated 5h at 80°C in a pressure vessel. After cooling, 200 mL of pentane were added; after filtration and evaporation of the solvent, the organic residue was distilled (60°C, 10^{-1} mm Hg). Yield 2.31g (33%) of 2-chlorophosphinine (4)[11]. A similar experiment with 2,3-dimethylbutadiene gave 35% of 4,5-dimethyl-2-chlorophosphinine (5)[12]. With a smaller excess of Et_3N at 70°C, a peak at +70.8 ppm was observed in the ^{31}P NMR spectrum of the crude reaction mixture, probably corresponding to the initial [4+2] cycloadduct 3. Both phosphinines were fully analyzed as their P-$W(CO)_5$ complexes 6 from 4, and 7 from 5, obtained by reaction with $W(CO)_5(MeCN)$ in THF at 60°C for 1h in respectively 75 and 88% yields. The extreme simplicity of this synthesis of 2-chlorophosphinines will allow us to investigate in some depth their chemistry.

References and Notes

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11. 4 : ^{31}P NMR ($CDCl_3$) : δ 200.7 ppm ; ^{1}H NMR ($CDCl_3$) : δ 7.5 (m, $^3J(H_4-H_3)={}^3J(H_4-H_5)$=7.8 Hz, $^4J(H_4-P)$=3.9 Hz, $^4J(H_4-H_6)$= 1.7 Hz, 1H, H_4), 7.75 (q, $^3J(H_5-H_6)$=8 Hz, $^3J(H_5-H_4)$=7.8 Hz, $^3J(H_5-P)$ not measured , $^4J(H_5-H_3)$=1.4 Hz, 1H, H_5), 7.9 (dd, $^3J(H_3-H_4)$=7.8 Hz, $^3J(H_3-P)$= 3.3 Hz, $^4J(H_3-H_5)$=1.4 Hz, 1H, H_3), 8.7 (dd, $^2J(H_6-P)$=40.3 Hz, $^3J(H_6-H_5)$=8 Hz, $^4J(H_6-H_4)$ =1.7 Hz, 1H, H_6) ; ^{13}C NMR ($CDCl_3$) : δ 131.3 (d, ^2J(C-P)=26.7 Hz, C_3 or C_5), 131.6 (d, ^2J(C-P)=25.3 Hz, C_5 or C_3), 135.6 (d, ^3J(C-P)=12.2 Hz, C_4), 156.3 (d, ^1J(C-P)=54.5 Hz, C_6), 164.9 (d, ^1J(C-P)=59.7 Hz, C_2) ppm.
6 : ^{31}P NMR ($CDCl_3$) : δ 178.8 ppm, $^1J(^{31}P-^{183}W)$=280.8 Hz ; ^{1}H NMR ($CDCl_3$) : δ 7.4 (m, $^4J(H_4-P)$ ∿ $^3J(H_4-H_5)$ ∿ $^3J(H_4-H_3)$ ∿ 8.5 Hz, $^4J(H_4-H_6)$=1.5 Hz, 1H, H_4), 7.7 (m, $^3J(H_5-P)$=23.5 Hz, ^3J $H_5-H_6)$=9.7 Hz, $^3J(H_5-H_4)$=8.5 Hz, $^4J(H_5-H_3)$=1.2 Hz, 1H, H_5), 8.0 (dd, $^3J(H_3-P)$=12.2 Hz, $^3J(H_3-H_4)$=8.5 Hz, $^4J(H_3-H_5)$=1.2 Hz, 1H, H_3), 8.4 (ddd, $^2J(H_6-P)$=26.7 Hz, $^3J(H_6-H_5)$=9.7 Hz, $^4J(H_6-H_4)$=1.5 Hz, 1H, H_6) ; ^{13}C NMR ($CDCl_3$) : δ 128.0 (d, ^1J(C-P)=25.4 Hz, C_6), 135.4 (d, ^2J(C-P)=17.5 Hz, C_5), 137.0 (d, ^3J(C-P)=8.9 Hz, C_4), 151.4 (d, ^2J(C-P)=18.1 Hz, C_3), 158.4 (d, ^1J(C-P)=21.6 Hz, C_2-Cl), 193.7 (d, ^2J(C-P)=9.2 Hz, CO cis), 198 (d, ^2J(C-P)=33.4 Hz, CO trans) ppm ; I.R. (pentane) : γ (CO) 2080, 1980, 1960 cm^{-1}.
12. 5 : ^{31}P NMR ($CDCl_3$) : δ 179.8 ppm ; ^{1}H NMR ($CDCl_3$) : δ 2.35 (d, ^4J(H-P)=3.8 Hz, 3H, CH_3), 2.39 (s, 3H, CH_3), 7.71 (d, ^3J(H-P)=3.5 Hz, 1H, H_3), 8.31 (d, ^2J(H-P)=39.7 Hz, 1H, H_6) ; ^{13}C NMR ($CDCl_3$) : δ 22 (s, CH_3), 22.5 (d, ^3J(C-P)=3 Hz, CH_3), 137.4 (d, ^2J(C-P)=12.6 Hz, C_3), 141.1 (d, ^3J(C-P)=15.1 Hz, C_4), 141.1 (d, ^2J(C-P)=15.6 Hz, C_5), 155.7 (d, ^1J(C-P)=50.8 Hz, C_6), 161.2 (d, ^1J(C-P)=54.3 Hz, C_2-Cl) ppm.
7 : ^{31}P NMR ($CDCl_3$) : δ 159.3 ppm, $^1J(^{31}P-^{183}W)$=278.3 Hz ; ^{1}H NMR ($CDCl_3$) : δ 2.36 (d, ^4J(H-P)= 6.4 Hz, 3H, CH_3), 2.4 (d, ^5J(H-P)=1.4 Hz, 3H, CH_3), 7.86 (d, ^3J(H-P)=13.2 Hz, 1H, H_3), 8.1 (d, ^2J(H-P)=25.9 Hz, 1H, H_6) ; ^{13}C NMR ($CDCl_3$) : δ 22.1 (d, ^4J(C-P)=3 Hz, CH_3), 22.9 (d, ^3J(C-P)=10.3 Hz, CH_3), 138.9 (d, ^2J(C-P)=23 Hz, C_5), 140 (d, ^2J(C-P)=8.7 Hz, C_3), 146.0 (d, ^3J(C-P)=17.9 Hz, C_4), 150.8 (d, ^1J(C-P)=19.7 Hz, C_6), 155.9 (d, ^1J(C-P)=25.2 Hz, C_2-Cl), 194.0 (d, ^2J (C-P)=9.3 Hz, CO cis), 198.5 (d, ^2J(C-P)=32.2 Hz, CO trans) ppm ; I.R. (pentane) : γ (CO) 2080, 1980, 1960 cm^{-1} ; mass spectrum (E.I., 70 eV, ^{184}W) : m/z 482 (M, 19%), 426 (M-2CO, 27%), 398 (M-3CO, 4%), 370 (M-4CO, 13%), 342 (M-5CO, 83%).

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