

METHYLIDENEPHOSPHINE¹.

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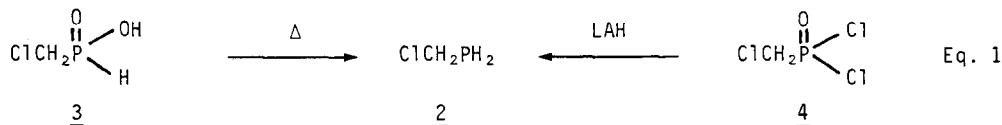
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Abstract : Methylidenephosphine 1 was formed by gas-phase or liquid-phase HCl-elimination from chloromethylphosphine 2 and unambiguously characterized by chemical trapping and spectroscopic analysis (MS, IR, ³¹P NMR).

Methylidenephosphine 1, a fundamental phosphalkene of considerable theoretical² and synthetic interest, has been identified in the gas phase by microwave spectroscopy from the pyrolysis of (CH₃)₂PH or TMSCH₂PH₂, but these approaches have only analytical significance³. In 1966, Goldwhite and coworkers postulated that the reaction between chloromethylphosphine 2 and aqueous sodium hydroxide involved unsaturated phosphine 1 as an intermediate⁴. We now report that 1 is effectively formed from 2 by HCl-elimination, either in solution at low temperature with a Lewis base or in gas-phase reactions (by Flash Vacuum Thermolysis (FVT) or Vacuum Gas Solid Reaction (VGSR)⁵), and can be unambiguously characterized by chemical trapping and spectroscopic analysis (MS, IR, ³¹P NMR).

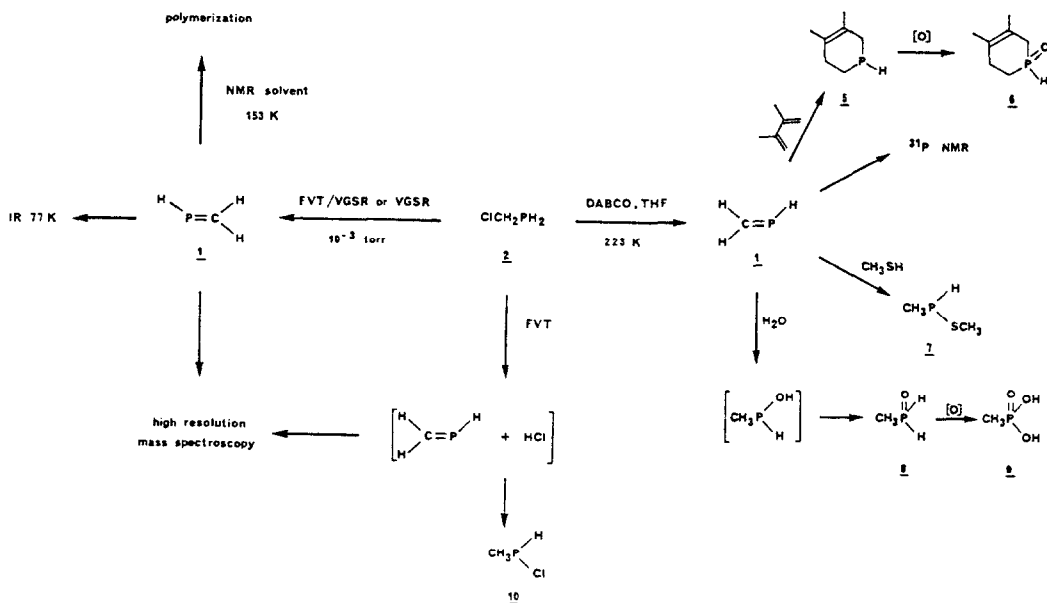
The chloromethylphosphine precursor 2 can be prepared according to the literature⁴ by thermal decomposition of the chloromethylphosphinic acid 3. Since this reaction is not easy or safe, the reduction of the chloromethylphosphonic dichloride⁶ 4 was preferred (eq. 1).



Recent knowledge of the high reactivity of unsaturated phosphalkenes, especially nucleophilic additions⁷ and cycloadditions⁸, makes possible the chemical trapping of the parent compound 1. All the following reactions were performed at 223 K in THF with DABCO as Lewis base. Thus, the reaction with 2,3-dimethyl-1,3-butadiene leads to the tetrahydrophosphinine 5 (³¹P -86,7 ppm, ¹J_{PH} 190 Hz) which was further oxidized⁹ to the corresponding cyclic phosphine oxide 6¹⁰. The NMR spectra of methanethiol adduct 7 can be recorded at room temperature (³¹P, ¹³C, ¹H)¹¹. All these reactions have to be carried out with a dry and freshly distilled solvent : in the presence of a trace of water, phos-

phine oxide 8 was observed¹² and further oxidation leads to the already known methylphosphonic acid 9¹³. FVT of 2 leads to the unstable P-chloromethylphosphine 10 ($\delta^{31\text{P}}$ -124.5, $^1\text{J}_{\text{PH}}$ 190 Hz)¹⁴. Due to a rapid polymerization of 10 (T 203 K) and lack of reproducibility, this reaction represents only analytical significance.

Methylidene phosphine 1 has also been characterized in the gas phase by coupling reactors with a mass spectrometer¹⁵. After verification that the pyrolytic process did not occur in the ion source, conditions of the following experiments were optimized by real time gas analysis¹⁶. The three sequences, FVT/MS (oven 1123 K), FVT/VGSR/MS (oven 1123 K, solid K_2CO_3 323 K) or VGSR/MS (solid K_2CO_3 373 K) gave reproducible results with the loss of HCl as the sole process. High resolution measurement was performed for the characterization of the molecular ion¹⁸. The low temperature IR spectrum of 1 (KBr, 77 K) gives a strong band ν_{PH} at 2260 cm^{-1} ¹⁹; the large band at 850 cm^{-1} was tentatively assigned to the $\nu_{\text{C}=\text{P}}$ stretching²⁰. Compound 1 is not stable in solid state at 77 K: polymerization is observed by a rapid decrease of the two main bands (total disappearance occurs after 30 min) with formation of a polymer of low solubility.



Another experiment shows the high reactivity of 1 : all attempts to transfer 1 under neutral gas from the cold trap to the NMR tube were unsuccessful due to instantaneous polymerization of the solution at approximately 153 K even with a solvent of very low melting point (CFCl_3 , $(\text{CH}_3)_2\text{O}$). Other evidence for the formation of 1 was given by a direct ^{31}P high field NMR analysis during its formation in solution (^{31}P 121.5 MHz, δ_{P} 231, $^1\text{J}_{\text{PH}}$ 130 Hz, $^1\text{J}_{\text{PH}}$ 29 Hz)²¹. In spite of numerous efforts, we could never obtain the corresponding ^1H or ^{13}C NMR spectra.

Methylenephosphine 1 has been characterized unambiguously by spectroscopic analysis. Use in synthesis seems to be possible since this species can be formed in mild conditions, at controlled temperature and in very high dilution.

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10. ^{31}P NMR of 10 : δ 2.2 (dm, $\text{J}_{\text{PH}} = 460$ Hz). Mass spectrum : M^+ m/z 144(15), 84(100), 56(68), 54(29), 52(23). High Resolution measurement : calcd. for $\text{C}_7\text{H}_{13}\text{OP}$ 144.0704, found 144.0702.
11. ^1H NMR : δ 1.25 (dd, 3H, $\text{J}_{\text{PH}} = 7.3$ Hz, $\text{J}_{\text{HH}} = 7.5$ Hz, $\text{CH}_3\text{-P}$), δ 2.1 (d, 3H, $\text{J}_{\text{PH}} = 8$ Hz, S-CH_3), δ 4.6 (dq, 1H, $\text{J}_{\text{PH}} = 200$ Hz, P-H). ^{31}P NMR : δ -37 (dm, $\text{J}_{\text{PH}} = 200$ Hz). ^{13}C NMR : δ 17.2 ($\text{J}_{\text{PC}} = 18.6$ Hz, $\text{CH}_3\text{-P}$) δ 7.7 ($\text{J}_{\text{PC}} = 20.6$ Hz), S-CH_3).
12. ^1H NMR : δ 1.63 (dt, 3H, $\text{J}_{\text{PH}} = 14$ Hz, $\text{J}_{\text{HH}} = 4.5$ Hz, $\text{CH}_3\text{-P}$), δ 7.05 (dq, 2H, $\text{J}_{\text{PH}} = 470$ Hz, P(O)H_2). ^{31}P NMR : δ 1.6 (dq, $\text{J}_{\text{PH}} = 470$ Hz). ^{13}C NMR : δ 13.6 ($\text{J}_{\text{PC}} = 66$ Hz).
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18. High Resolution measurement of molecular ion $\text{CH}_2=\text{P}-\text{H}^+$: calcd. for CH_3-P : 45.9972, found 45.9975. mass spectrum : m/z (rel. int.) M^+ 46(100), 45(56), 44(47), 32(5).
19. IR spectrum of 2 (NaCl film, 77 K) : 730 vs, 840 s, 930 s, 1070 s, 1215 m, 1390 m, 2310 s, 3000 vw.
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21. This result seems to imply an equivalence of the two methylene protons since a large difference between cis and trans $^2J_{\text{PH}}$ coupling constants values has been lastly mentioned²². The presence of an ammonium salt can induce exchange of the proton bonded at phosphorus. However, we cannot exclude a deceptively simple spectrum.
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