

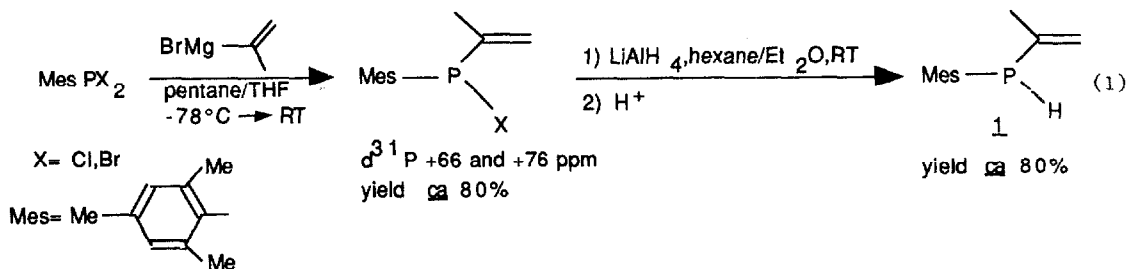
THERMAL ISOMERIZATION OF A SECONDARY
 VINYLPHOSPHINE INTO A PHOSPHAALKENE

François MERCIER, Catherine HUGEL-LE GOFF, François MATHEY

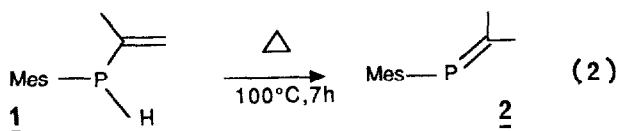
Laboratoire de Chimie du Phosphore et des Métaux de Transition - DCPH -
 Ecole Polytechnique, 91128 PALAISEAU Cédex (France)

Summary : When heated at 100°C, (mesityl)(propen-2-yl)phosphine rearranges via a radical mechanism to give (mesityl)(isopropylidene)phosphine.

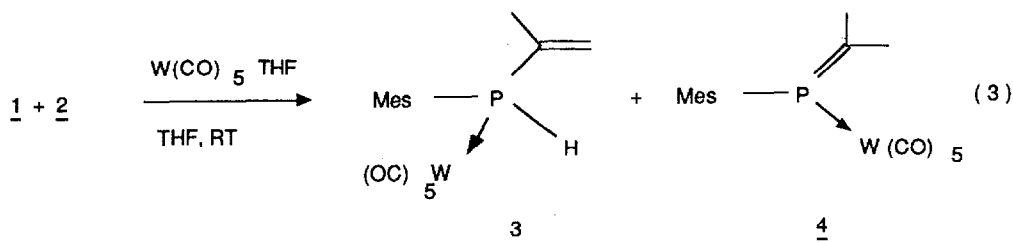
Primary and secondary vinylphosphines were long thought to be intrinsically unstable until the recent work of Ripoll [1] who described the synthesis and the characterization of the parent molecule CH₂=CH-PH₂. Since that time, several stable secondary vinylphosphines >C=C-P(H)R have been described in the literature. In most cases, it appears that stability is provided via the use of reasonably bulky R groups (e.g. R=*t*-Bu [2]). In the course of the study of one such phosphine, we have discovered an unprecedented secondary vinylphosphine → phosphalkene rearrangement. The starting phosphine 1 [3] was prepared according to eq 1 :



Upon heating at 100°C for 7h, 1 undergoes a rearrangement into (mesityl)(isopropylidene) phosphine 2 (eq 2). The conversion ratio lies ca 80-90%. The phosphalkene 2 cannot be separated from its PH isomer but its formation was easily deduced from the inspection of the ¹H, ¹³C, and ³¹P NMR spectra of the crude reaction mixture [4].



Above 130°C, 2 gives a new product in which the double bond has been hydrogenated ($\delta^{31}\text{P}$ -64 ppm). Treatment of the 1 + 2 mixture by $\text{W}(\text{CO})_5$ THF affords the corresponding complexes 3 and 4 (eq 3) :



The two complexes were separated by chromatography on silica gel with hexane as eluent and fully characterized [5]. Concerning the mechanism of this isomerization, we cannot discriminate at the moment between a photochemical (Solar light) supra [1,3] sigmatropic shift, a thermal antarafacial shift or a radical pathway involving the initial homolytic cleavage of the relatively weak P-H bond. As far as we know, the only more or less related finding which has been described in the literature concerns the rearrangement of secondary alkynylphosphines into phosphallenes under basic conditions [6].

References and Notes

1. M.-C. Lasne, J.-L. Ripoll¹, A. Thuillier, J. Chem. Soc., Chem. Commun., 1428 (1986)
2. F. Mercier, C. Hugel-Le Goff, F. Mathey, Organometallics, 7, 955 (1988)
3. 1 : ^{31}P NMR (C_6D_6) : δ -74 ppm, $^1\text{J}(\text{P-H})$ 222 Hz ; ^1H NMR (C_6D_6) : δ 1.76 (d, $^3\text{J}(\text{H-P})$ 8 Hz, 3H, propenyl Me), 2.10 (s, 3H, Me para), 2.40 (s, 6H, Me ortho), 4.75 (d, $^1\text{J}(\text{H-P})$ 219 Hz, 1H, PH), 5.01 (d, $^3\text{J}(\text{H-P})$ 9.8 Hz, 1H, =CH₂), 5.20 (d, $^3\text{J}(\text{H-P})$ 23 Hz, 1H, =CH₂), 6.76 (s, 2H, Mes, H meta) ppm ; ^{13}C NMR (C_6D_6) : δ 21.11 (s, Me para), 22.98 (d, $^3\text{J}(\text{C-P})$ 11.7 Hz, Me ortho), 23.54 (d, $^2\text{J}(\text{C-P})$ 15.8 Hz, propenyl Me), 120.49 (d, $^2\text{J}(\text{C-P})$ 17.6 Hz, =CH₂), 141.62 (d, $^1\text{J}(\text{C-P})$ 18.4 Hz), 143.13 (d, $^1\text{J}(\text{C-P})$ 12.8 Hz) ppm ; mass spectrum (70eV) : m/z 193 (M+H, 100%), 192 (M⁺, 32%).
4. 2 : ^{31}P NMR (C_6D_6) : δ + 210.6 ppm ; ^1H NMR (C_6D_6) : δ 1.73 (dd, $^3\text{J}(\text{H-P})$ 13 Hz, $^4\text{J}(\text{H-H})$ 1 Hz, Me-C=), 2.14 (dd, $^3\text{J}(\text{H-P})$ 22.6 Hz, $^4\text{J}(\text{H-H})$ 1 Hz, Me-C=) ppm ; ^{13}C NMR (C_6D_6) : δ 190.55 (d, $^1\text{J}(\text{C-P})$ 41 Hz, C=P) ppm.
5. 3 : ^{31}P NMR (C_6D_6) : δ -46.6 ppm, $^1\text{J}(\text{P-}^{183}\text{W})$ 224.6 Hz, $^1\text{J}(\text{P-H})$ 341.8 Hz ; ^1H NMR (C_6D_6) : δ 1.42 (d, $^3\text{J}(\text{H-P})$ 9.7 Hz, 3H, propenyl Me), 1.97 (s, 3H, Me para), 2.17 (s, 6H, Me), 5.44 (d, $^3\text{J}(\text{H-P})$ 47.3 Hz, 1H, =CH₂), 5.86 (d, $^3\text{J}(\text{H-P})$ 22.3 Hz, 1H, =CH₂), 6.23 (d, $^1\text{J}(\text{H-P})$ 342 Hz, 1H, PH), 6.58 (d, $^4\text{J}(\text{H-P})$ 2.6 Hz, 2H, Mes, H meta) ppm ; mass spectrum (70 eV, ^{184}W) : m/z 516 (M⁺, 38%), 376 (M-5CO, 68%), 373 (100%).
6. 4 : Orange crystals, mp 80°C (pentane) ; ^{31}P NMR (C_6D_6) : δ + 162.7 ppm, $^1\text{J}(\text{P-}^{183}\text{W})$ 254 Hz ; ^1H NMR (C_6D_6) : δ 1.51 (dd, $^3\text{J}(\text{H-P})$ 25.4 Hz, $^4\text{J}(\text{H-H})$ 1 Hz, 3H, Me-C=), 1.97 (dd, $^3\text{J}(\text{H-P})$ 31 Hz, $^4\text{J}(\text{H-H})$ 1 Hz, 3H, Me-C=), 2.00 (s, 3H, Me para), 2.26 (s, 6H, Me ortho), 6.65 (d, $^4\text{J}(\text{H-P})$ 2.2 Hz, 2H, Mes, H meta) ppm ; ^{13}C NMR (C_6D_6) : δ 183.57 (d, $^1\text{J}(\text{C-P})$ 44 Hz, C=P), 195.75 (d, $^2\text{J}(\text{C-P})$ 10 Hz, CO cis), 199.34 (d, $^2\text{J}(\text{C-P})$ 27.6 Hz, CO trans) ppm ; IR (decalin) : ν (CO) 2070, 1945 cm^{-1} ; mass spectrum (70 eV, ^{184}W) : m/z 516 (M⁺, 35%), 376 (M-5CO, 77%), 374 (100%).
6. See for example : G. Märkl, H. Herold, Tetrahedron Lett., 29, 2935 (1988).