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THE NUCLEOPHILIC ATTACK OF A VINYL-HALO-PHOSPHINE BY A TERTIARY AMINE : A NEW ACCESS TO PHOSPHAALKENES

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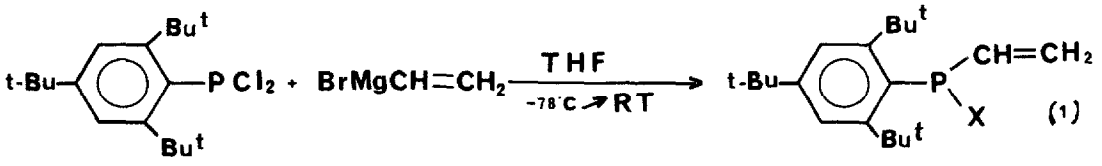
Summary: The reaction of DABCO with (2,4,6-tris-tertiobutylphenyl)(vinyl) halo phosphine (X= Cl, Br) yields the corresponding 1-(2,4,6-tris-tertiobutylphenyl)-2-ammoniomethyl phosphaethene via a SN2'-like attack at the vinylic CH_2.

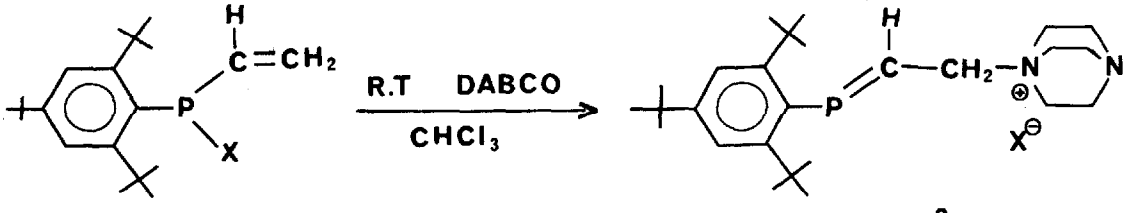
Our recent work on the chemistry of η^3-1-phosphaallyl complexes[1] and on the thermal isomerisation of secondary vinylphosphines into the corresponding phosphaalkenes [2] has suggested some parallelism between the chemical behaviours of the allyl and 1-phosphaallyl groups. We wish to report hereafter on a new experiment which further strengthens this parallelism.

The starting vinyl-halophosphine 1 [3] was obtained as a ca 50/50 mixture of chloro- and bromo-derivatives according to eq 1 :



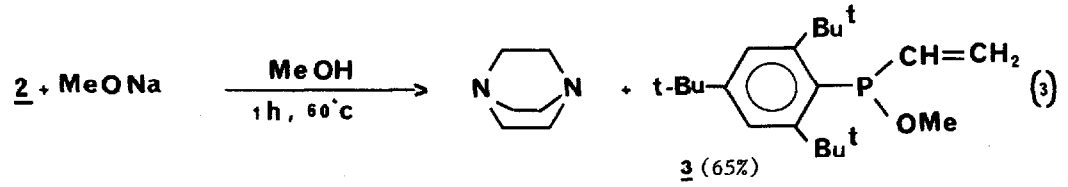
1 : X = Cl, Br ; yield ca 65%

When allowed to react with a stoichiometric amount of a nucleophilic amine such as DABCO, 1 is converted into an ammonium substituted phosphaalkene such as 2 (eq 2) :



1 2

The ammonium salt 2 [4] was precipitated and washed twice with diethylether. Then, it was recrystallized in a 1/1 mixture of $CHCl_3$ and Et_2O (45% yield of pure product). According to the elemental analysis, the counterion in 2 is almost exclusively $Br^\ominus$. This observation suggests that the reaction preferentially takes place with the bromo-vinylphosphine. A classical SN2' mechanism could explain this selectivity. Anyhow, both the higher strength of the C-N bond by comparison with the P-N bond and the steric bulk of the supermesityl substituent at phosphorus favour the attack of the tertiary amine at the β-vinylic carbon. As expected, 2 reacts with sodium methylate at 60°C in methanol solution (eq 3). The vinylphosphinite 3 [5] was purified by chromatography on silica gel with hexane/CH_2Cl_2 50/50 as eluent. A SN2' mechanism is very likely once again involved. The initial attack of $MeO^\ominus$ at phosphorus is probably driven by the high oxophilicity of phosphorus.



3 (65%)

References and Notes

1. F. Mercier, J. Fischer, F. Mathey, Angew. Chem., Int. Ed. Engl., 25, 357 (1986) ; F. Mercier, C. Hugel-Le Goff, F. Mathey, Organometallics, 7, 955 (1988) ; C. Hugel-Le Goff, F. Mercier, L. Ricard, F. Mathey, J. Organometal. Chem., 363, 325 (1989).
2. F. Mercier, C. Hugel-Le Goff, F. Mathey, Tetrahedron Lett., 30, 2397 (1989).
3. 1: ^{31}P NMR ($CDCl_3$): δ + 67.9 (Cl), + 64.3 (Br) ; ^{1}H NMR ($CDCl_3$): δ1.31 (s, 9H, Bu^t para),1.55 and 1.61 (2s, 18H, Bu^t ortho) ; mass spectrum (70eV) : m/z (relative intensity) 384 [M^+ + 1 (Br), 3%], 339 [M^+ (Cl), 6%] , 303 (M^+-X, 100%).
4. 2: ^{31}P NMR ($CDCl_3$): δ + 313.6 (vs H_3PO_4) ; ^{1}H NMR ($CDCl_3$) : δ 1.34 (s, 9H, Bu^t para), 1.47 (s, 18H, Bu^t ortho), 3.26 (broad t, ^{3}J(H-H) 6.4 Hz, 6H, CH_2N), 3.71 (broad t., 6H, CH_2N^+), 4.60 (dd, ^{3}J(H-P) 17.7 Hz, ^{3}J(H-H) 9.3 Hz, 2H, CH_2C=), 7.06 (dt, ^{2}J(H-P) 23.7 Hz, 1H, HC=P), 7.41 (s, 2H, H meta) ; ^{13}C NMR ($CDCl_3$): δ31.06 (s, Me para), 33.82 and 33.92 (2s, Me ortho), 34.67 (s, Bu^t C para), 37.74 (s, Bu^t C ortho), 45.27 (s, CH_2N), 51.83 (s, CH_2N^+), 65.71 (d, ^{2}J(C-P) 40.6 Hz, $\underline{CH_2}$-C=), 121.8 (s, CH meta), 135.95 (d, ^{1}J(C-P) 55.4 Hz,C ipso), 150.39 (s, C para), 153.29 (s, C ortho), 156.48 (d, ^{1}J(C-P) 40.0 Hz, $\underline{C}$=P). The compound crystallizes with one molecule of chloroform. Anal. Calcd for $C_{27}H_{45}BrCl_3N_2P$: C, 52.74 ; H, 7.37 ; N, 4.55 ; Br, 12.99 ; Cl, 17.29. Found: C, 52.77 ; H, 7.47 ; N, 4.80 ; Br, 10.51 ; Cl, 16.99.
5. 3: ^{31}P NMR ($CDCl_3$) : δ+ 109.8 ; ^{1}H NMR ($CDCl_3$):δ 1.31 (s, 9H, Bu^t para), 1.50 (s, 18H, Bu^t ortho), 3.65 (d, ^{3}J(H-P) 14.9 Hz, 3H, MeO), 4.80 (m, 1H, CH_2), 5.40 (m, 1H, CH_2), 6.50 (m, 1H, CHP) 7.41 and 7.42 (2s, 2H, CH ar.) ; ^{13}C NMR ($CDCl_3$): δ 31.30 (s, Me para), 34.00 and 34.18 (2s, Me ortho), 35.00 (s, Bu^t C para), 39.02 (s, Bu^t C ortho), 57.71 (d, ^{2}J(C-P) 31.2 Hz, MeO), 121.27 (d, ^{2}J(C-P) 18.4 Hz, CH_2=), 122.59 and 122.71 (2s, C meta), 135.60 (d, ^{1}J(C-P) 53.9 Hz, C ipso), 144.84 (d, ^{1}J(C-P) 26.5 Hz, =CH-P), 150.50 (s, C para), 156.12 and 156.40 (C ortho) ; mass spectrum (EI, 70eV) : m/z 334 (M^+, 19%), 319 (M^+-CH_3, 62%), 278 (100%).

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