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ON THE REACTION OF N-VINYLIMINOPHOSPHORANES. SYNTHESIS AND REACTION OF 1,2-λ^5-AZAPHOSPHORINE RING SYSTEM

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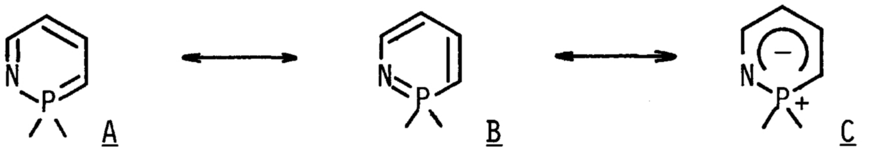
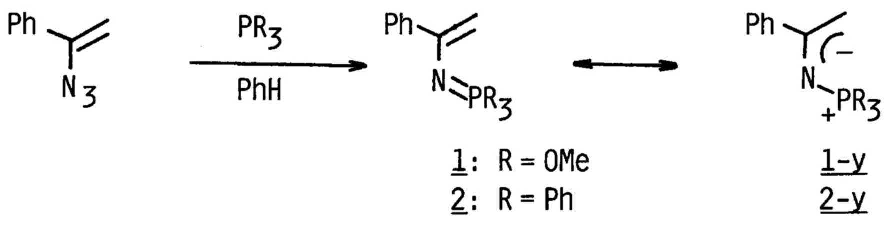
The reaction of N-vinyliminotrimethoxyphosphorane reacts with electron deficient acetylenes results in the formation of formal [4+2] cycloadducts, 1,2-λ^5-azaphosphorines 4a-c. However, N-vinyliminotriphenylphosphorane reacts with dimethyl acetylenedicarboxylate (DMAD) in a formal [2+2] manner. The product 4a or 4b also reacts with DMAD to give λ^5-phosphorine derivatives.

Synthesis and reactions of λ^3-phosphorines1,2) and λ^5-phosphorines,1-4) heterocyclic analogue of benzene containing one phosphorus atom in place of the carbon atom, have received considerable attention since G. Märkl accomplished the synthesis of 2,4,6,-triphenyl-λ^3-phosphorine.5) A few examples of 1,2-λ^5-azaphosphorine6) and 1,4-λ^5-azaphosphorine,7) both of which contain a phosphorus and a nitrogen instead of two carbons of benzene, have appeared. However, no simple synthesis and reaction of these ring systems have been examined. The 1,2-λ^5-azaphosphorine ring system is considered to have three resonance structures (A, B, and C), and it would be interested to search the main contributor to the resonance hybrid.

We report hereon a simple synthesis of 1,2-λ^5-azaphosphorine derivatives, 4a-c, and their cycloaddition reaction. Our synthetic strategy was at first to obtain the iminophosphorane bearing a vinyl group on the nitrogen atom. The N-vinyliminophosphorane, 1 or 2,8,9) which was easily hydrolyzed to give acetophenone in the presence of water, was prepared by the Staudinger reaction10) of α-azidostyrene with trimethyl phosphite or with triphenylphosphine at room temperature in a 83 or

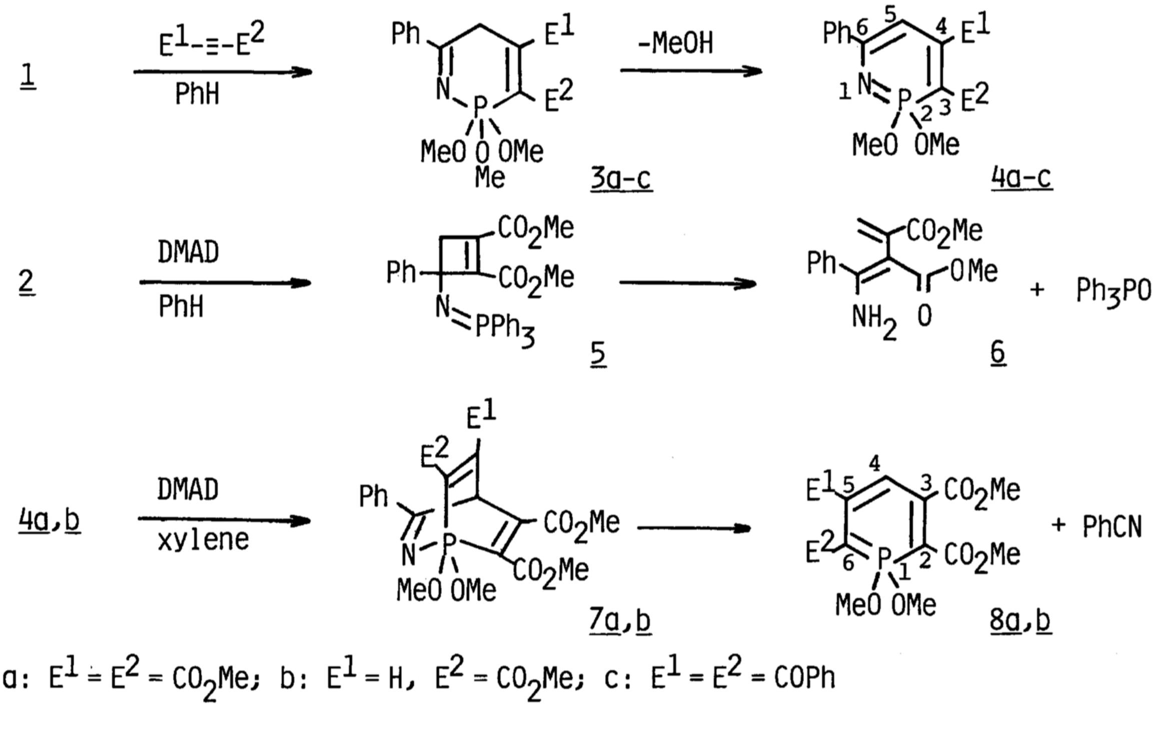




97% yield, respectively. Considering the ^{1}H-NMR spectra of 1,[9] the olefinic protons appear at relatively higer field than usual, and this tendency is increased in 2.[9] This fact may suggest an enhanced contribution of the ylide structures, 1-y and 2-y, to the resonance hybrid of N-vinyliminophosphoranes, 1 and 2.

The reaction of 1 (1 mmol) with dimethyl acetylenedicarboxylate (DMAD, 1 mmol) in benzene (2 ml) at room temperature for 24 h followed by separation through TLC afforded 4a in a 58% yield. Similarly, the reaction of 1 with methyl propiolate or dibenzoylacetylene resulted in the formation of 4b or 4c in a 57 or 17% yield. The reaction accompanied intractable tar, and the yields of 4a-c were rather low. The formation of 4a-c are explained by the formal [4+2] cycloaddition of 1 with acetylenes and subsequent elimination of methanol molecule. Regioselective formation of 4b bearing a methoxycarbonyl group at 3-position is ascribed to the intervention of ylide character for 1, anionic carbon of which would connect with β-carbon atom of methyl propiolate. Recently, synthetic utilities of iminophosphoranes, e.g. hydrolysis,[11] oxidation leading to nitro compounds,[12] and intra[13] or intermolecular[14] aza-Wittig reactions, have been pronounced. Therefore, the present reaction clarified a new aspect of the iminophosphoranes, which serve as a diene unit for the Diels-Alder type reactions. On the other hand, the iminophosphorane 2 reacted with DMAD at room temperature to result in the formation of 6 (62%) and triphenylphosphine oxide (72%). The reaciton is explained by the formal [2+2] cycloaddition[15] of 2 with DMAD and the following ring opening and hydrolysis. This behavior of 2 giving 6 seems to suggest that the diene character of 2 is reduced as compared to that of 1.

The 1,2-λ^5-azaphosphorines 4a-c also have N-vinyliminophosphorane moieties. When 4a or 4b with DMAD in xylene was heated under reflux for 48 h, the λ^5-phosphorine derivative 8a or 8b was obtained in a 58 or 60% yield respectively, along with benzonitrile which was detected by GLC analysis. A remarkable site



a: $E^1 = E^2 = CO_2Me$; b: $E^1 = H$, $E^2 = CO_2Me$; c: $E^1 = E^2 = COPh$

selectivity was observed in the [4+2] cycloaddition to give 7a,b. The following elimination of benzonitrile would give 8a,b.

The structures of 4a-c and 8a,b were determined on the basis of the ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, IR, and UV spectra.[8,16)] Especially, the ^{13}C-NMR spectra (Table 1) were instructive for characteristic in these ring system. The chemical shifts for C3 and C5 carbons in 4a-c are considerably shifted to higer field compared with that of C4, and the coupling constant J_{P-C5} is larger than J_{P-C4} in 4a-c. Similar trends were observed for 8a,b. These features have also been found for other λ^5-phosphorines[3)] and acyclic ylides.[17)] Therefore, the cyclic ylide structure C seems to be an appreciable contributor to the resonance hybrid of the 1,2-λ^5-azaphosphorine ring system.

Table 1. Some Selected ^{13}C-NMR[a)] and ^{31}P-NMR[b)] Parameters of 1,2-λ^5-Azaphosphorines 4a-c and λ^5-Phosphorines 8a,b [c)]

	4a	4b	4c	8a	8b
δ_{C2}	----	----	----	84.9	91.7
δ_{C3}	78.5	83.1	90.7	150.2	150.4
δ_{C4}	155.3	151.1	160.2	101.9	101.8
δ_{C5}	99.7	100.4	101.1	----	146.3
δ_{C6}	138.4	139.1	138.6	----	85.4
J_{P-C2}	----	----	----	148.32	146.48
J_{P-C3}	155.03	153.20	146.49	10.60	9.77
J_{P-C4}	12.81	10.38	10.98	18.31	18.31
J_{P-C5}	25.03	24.42	26.24	----	8.54
J_{P-C6}	21.97	22.58	21.97	----	143.43
J_{C4-H}	----	157.47	----	167.85	166.63
J_{C5-H}	164.80	162.96	163.57	----	159.30
^{31}P	38.1	39.4	38.3	57.2	58.5

a) Recorded in $CDCl_3$ and chemical shifts are given in ppm (δ) relative to internal Me_4Si. b) Recorded in C_6D_6 and chemical shifts are given in ppm (δ) relative to external 85% H_3PO_4 standard. c) All of the coupling constans (J) are given in Hz.

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9) For 1: bp 114 °C/ 133 Pa; ^{1}H-NMR (CCl_4) δ 3.76 (9H, d, J_{P-H}=12.1 Hz), 4.32 (1H, d, J=2.6 Hz), 4.78 (1H, d, J=2.6 Hz), 7.12-7.40 (3H, m), 7.68-7.85 (2H, m).
For 2: mp 91-94 °C; ^{1}H-NMR ($CDCl_3$) δ 3.85 (1H, d, J=2.1 Hz), 4.64 (1H, d, J=2.1 Hz), 7.10-7.95 (20H, m).

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16) 4a: mp 85-86 °C; ^{1}H-NMR (CCl_4) δ 3.63 (6H, d, J_{P-H}=12.1 Hz), 3.79 (3H, s), 3.87 (3H, s), 6.37 (1H, d, J_{P-H}=1.4 Hz), 7.30-7.57 (3H, m), 7.85-8.20 (2H, m); ^{13}C-NMR δ 51.4, 52.3, 53.5, 78.5, 99.7, 126.9, 127.0, 128.0, 130.3, 138.4, 155.3, 165.6, 169.1; IR (CCl_4) 1733, 1698 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 265 (3.96), 384 (4.34) nm.
4b: bp 130 °C (bath temp)/ 66 Pa; ^{1}H-NMR (CCl_4) δ 3.52 (6H, d, J_{P-H}=12.4 Hz), 3.71 (3H, s), 6.35 (1H, dd, J=8.0, 1.7 Hz), 7.20-7.42 (3H, m), 7.75-8.03 (2H, m), 8.09 (1H, dd, J=36.0, 8.0 Hz); ^{13}C-NMR δ 51.1, 53.1, 83.1, 100.4, 126.9, 127.0, 127.9, 129.8, 139.1, 151.1, 167.0; IR (CCl_4) 1689 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 259 (4.06), 389 (4.37) nm.
4c: mp 141.5-142.5 °C; ^{1}H-NMR ($CDCl_3$) δ 3.71 (6H, d, J_{P-H}=13.1 Hz), 6.46 (1H, d, J_{P-H}=1.1 Hz), 7.10-8.05 (15H, m); ^{13}C-NMR δ 53.7, 90.7, 101.5, 127.1, 127.4, 127.8, 127.9, 128.2, 128.6, 130.5, 131.1, 132.7, 136.0, 136.1, 138.6, 139.9, 160.2, 193.1, 196.0; IR ($CHCl_3$) 1667 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 226 (4.39), 259 (4.24), 414 (4.14) nm.
8a: mp 146-147 °C; ^{1}H-NMR ($CDCl_3$) δ 3.65 (3H, d, J_{P-H}=10.5 Hz), 3.75 (6H, s), 3.79 (6H, s), 5.60 (1H, d, J_{P-H}=2.6 Hz); ^{13}C-NMR δ 51.8, 52.4, 55.5, 84.9, 101.9, 150.2, 164.8, 168.5; IR ($CHCl_3$) 1729, 1700 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 259 (3.73), 399 (4.42) nm.
8b: bp 105 °C (bath temp)/ 133 Pa; ^{1}H-NMR ($CDCl_3$) δ 3.68 (6H, d, J_{P-H}=12.5 Hz), 3.80 (3H, s), 3.81 (3H, s), 3.83 (3H, s), 5.71 (1H, dd, J=8.9, 3.2 Hz), 8.10 (1H, dd, J=38.0, 8.9 Hz); ^{13}C-NMR δ 51.1, 51.3, 51.9, 60.0, 85.4, 91.7, 101.8, 146.3, 150.4, 164.9, 165.5, 168.9; IR ($CHCl_3$) 1740, 1681 cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 250 (3.68), 395 (4.15) nm.

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