Preparation of Novel *N*-Vinyl-, *N*-(1-Butylvinyl)-, and *N*-(1-Methyl-1-pentenyl)iminotriphenylphosphoranes and Their Reactions with α,β-Unsaturated Ketones[1)]

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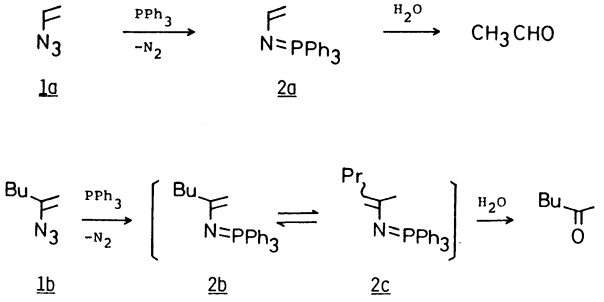
Synopsis. The novel *N*-vinyl- (**2a**) and a mixture of *N*-(1-butylvinyl)- (**2b**) and *N*-(1-methyl-1-pentenyl) iminotriphenylphosphoranes (**2c**) were prepared by the reaction of azidoethylene and 2-azido-1-hexene with triphenylphosphine, respectively. The thermal reaction of **2a**, **2b**, and **2c** with α,β-unsaturated ketones undergoes an enamine-type alkylation and the subsequent aza-Wittig reaction to give pyridine derivatives in modest yields.

Previously, we have accomplished the preparation of novel *N*-(1-phenylvinyl)iminophosphoranes by the Staudinger reaction[2)] of α-azidostyrene with trimethyl phosphite, triphenylphosphine, or tributylphosphine. These *N*-(1-phenylvinyl)iminophosphoranes seemed to provide convenient routes to 1,2-λ^5-azaphosphorines,[3)] 2-phenyl-1-azaazulenes,[4)] phenyl-substituted pyrroles,[1,5)] and phenyl-substituted pyridines.[1,6)] However, the potential value of *N*-vinyliminophosphorane bearing no substituent and alkyl substituent on vinyl groups remains unexplored. We describe here the first preparation of *N*-vinyliminotriphenylphosphorane (**2a**) and a mixture of *N*-(1-butylvinyl)- (**2b**) and *N*-(1-methyl-1-pentenyl) iminotriphenylphosphoranes (**2c**), and their reactions with α,β-unsaturated ketones to give pyridine derivatives.

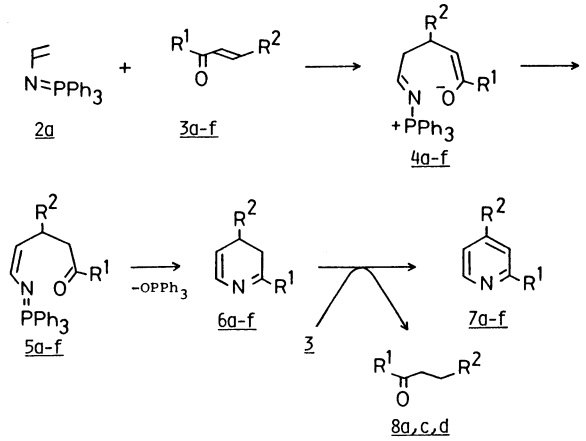
The reaction of azidoethylene (**1a**)[7)] with triphenylphosphine in anhydrous ether at 0 °C for 2 h gave crystalline *N*-vinyliminotriphenylphosphorane (**2a**) in 84% yield. The compound **2a** is unstable in moist solvent and hydrolyzed to acetaldehyde in quantitative yield (Scheme 1). Similarly, 2-azido-1-hexene (**1b**)[8)] was made to react with triphenylphosphine at room temperature for 2 h to give iminophosphoranes, which were inferred to be a mixture of *N*-(1-butylvinyl)-iminotriphenylphosphorane (**2b**) and *N*-(1-methyl-1-pentenyl)iminotriphenylphosphorane (**2c**) in a ratio of 1/2 (see Experimental). Since unstable **2b** and **2c** were not separable in pure form, no distinct physical data were obtained. However, the preparation of a mixture of **2b** and **2c** in CD_3CN and its ^1H NMR spectral study suggested several features of **2b** and **2c** (see Experimental). The initial ratio of **2b**/**2c** (1/2) changed to 1/4 after heating the mixture at 80 °C for 10 min. The ratio was fixed at 1/6 after 30 min or even after a prolonged heating at 80 °C. Thus, the thermal isomerization was suggested to occur, and the equilibrium between **2b** and **2c** is considered to lie on the side of **2c**. The tautomer **2b**, which is derived from **1b** directly, seems to be less stable than **2c**. Furthermore, the mixture of **2b** and **2c** (1/2) was hydrolyzed in moist benzene under refluxing for 10 h to give 2-hexanone in quantitative yield. Thus, the formation of **2b** and **2c** from **1b** and triphenylphosphine was assessed.



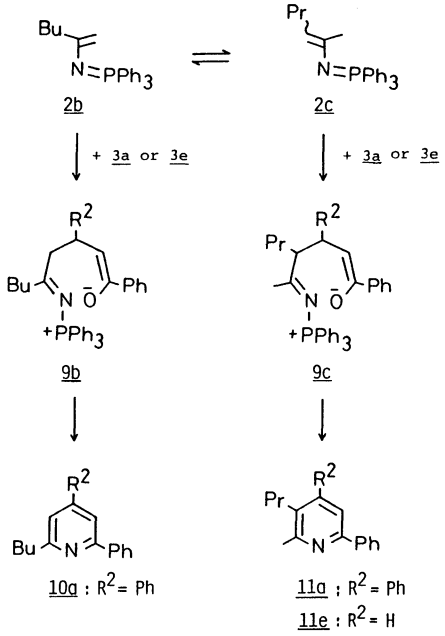
Scheme 1.

The reaction of **2a** with α,β-unsaturated ketones **3a—f** in anhydrous benzene was carried out under reflux to give pyridine derivatives **7a—f** in addition to **8a—d**. The reaction conditions and the yields of the products are summarized in Table 1. The structure of **7a—f** was unequivocally deduced from physical data (see Experimental). As previously reported,[1,6)] the results are very similar to those of *N*-(1-phenylvinyl)-iminophosphoranes with α,β-unsaturated ketones. The postulated reaction pathway for the present reaction is shown in Scheme 2. The enamine alkylation of **2a** to the β-carbon atom of **3a—f** initially occurs to give **4a—f**, followed by proton transfer to regenerate iminophosphoranes **5a—f**, which then undergo an intramolecular aza-Wittig reaction to give dihydropyridines **6a—f**. The compounds **6a—f** are dehydrogenated to give pyridines **7a—f** under the reaction conditions. The compounds **3a—d** seem also to act as a hydrogen acceptor of **6a—d** to result in the formation of **8a—d**.[6,9)]

Similarly, the reaction of a mixture of **2b** and **2c** with **3a** or **3e** in anhydrous benzene under refluxing, gave pyridines **10** and/or **11** in low yields (Scheme 3). When the reactions were carried out in toluene under refluxing, the yields of the pyridines were improved.



Scheme 2.



Scheme 3.

Table 1. Results Obtained in the Reaction of **2a** with **3a**—**f**[a)]

3	R^1	R^2	Reaction time/h	Product yield/%		Recovery of 3/%
				7	**8**	
a	Ph	Ph	48	56	15	17
b	4-Cl-C_6H_4		12	50	8	—
c	4-MeO-C_6H_4		42	28	6	57
d	Ph	Me	24	31	8	35
e	Ph	H	24	27	—	—
f	Me	H	24	25	—	—

a) The reactions were carried out in anhydrous benzene under refluxing.

Table 2. Results Obtained in the Reaction of **2b** and **2c** with **3a**, **e**

3	R^1	R^2	Reaction time/h	Solvent	Product yield/%		Recovery of 3/%
					10	**11**	
a	Ph	Ph	28	PhH	15	Trace	65
a			24	PhMe	28	8	21
e	Ph	H	28	PhH	0	30	0
e			24	PhMe	0	52	0

The structural proofs for the pyridines were obtained from their physical data (see Experimental). The results are summarized in Table 2. In the case of **3a**, the addition of both **2b** and **2c** occurs on the β-carbon atom of **3a** to give **9b** and **9c**, and the following reaction sequences (cf. Scheme 2) give pyridines **10a** and **11a**, respectively.

In conclusion, the preparations of novel *N*-vinyl- (**2a**) and *N*-(1-butylvinyl)- (**2b**), and *N*-(1-methyl-1-pentenyl) iminotriphenylphosphorane (**2c**), and their reaction with α,β-unsaturated ketones were clarified. Although preparations, properties, and synthetic applications of pyridines have also been studied,[10,11] the present results will serve as a convenient method for preparating pyridine derivatives.

Experimental

The IR spectra were recorded on a Shimadzu IR-400 spectrometer. The ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Hitachi R-24 and a R-90H spectrometer and the chemical shifts are given in ppm (δ) relative to the internal $SiMe_4$ standard. The mass spectral and high-resolution mass spectral studies were conducted using Shimadzu GCMS-QP1000 and JEOL DX-300 spectrometer. All of the melting points are uncorrected.

Preparation of *N*-Vinyliminotriphenylphosphorane (2a). A solution of azidoethylene (**1a**)[7] (480 mg, 7.0 mmol) and triphenylphosphine (1.31 g, 5.0 mmol) in dry ether (20 cm^3) was stirred for 2 h at 0 °C. The precipitated crystalline solids were filtered to give **2a** (1.27 g, 84%, based on triphenylphosphine used): mp 90 °C (decomp); ^1H NMR ($CDCl_3$) δ=3.97 (1H, ddd, J=7.4, 5.7, 1.4 Hz), 4.52 (1H, ddd, J=14.2, 1.4, 1.4 Hz), 6.69 (1H, ddd, J=14.2, 7.4, 23.2 Hz), 7.25—7.90 (15H, m); ^{13}C NMR ($CDCl_3$) δ=93.92, 129.98, 131.59, 132.43, 138.38, 142.36; IR ($CHCl_3$), 2985, 2916, 1591, 1487, 1437, 1405, 1311, 1106 cm^{-1}; HRMS Found: m/z 303.1194. Calcd for $C_{20}H_{18}NP$: M, 303.1178.

Reaction of 2a with Water. A solution of **2a** (91 mg, 0.3 mmol) in moist methanol (2 cm^3) was stirred at room temperature for 1 h. To this reaction mixture was added 2,4-dinitrophenylhydrazine (99 mg, 0.5 mmol) and a catalytic ammount of HCl, and the mixture was stirred for further 3 h. After the solvent was evaporated, the residue was separated by TLC on silica gel using benzene-AcOEt (1/1) as a developer to give 64 mg (95%) of acetaldehyde 2,4-dinitrophenylhydrazone, the structure of which was identical with that of the authentic specimen.

Preparation of *N*-(1-Butylvinyl)- (2b) and *N*-(1-Methyl-1-pentenyl)iminotriphenylphosphorane (2c). A solution of 2-azido-1-hexene (**1b**)[8] (63 mg, 0.5 mmol) and triphenylphosphine (131 mg, 0.5 mmol) in CD_3CN (0.2 cm^3) was made to react for 2 h. The ^1H NMR spectrum of the reaction mixture exhibited δ=0.7—2.4 (m), 3.39 (t, J=1.2 Hz), 3.67 (broad s), 4.08—4.54 (m), 7.1—7.8 (m). The signals at 3.39 and 3.67 are assigned to the vinyl protons of **2b**, and the signal at 4.08—4.54 is also assigned to the vinyl proton of **2c**. The ratio of **2b**/**2c** was estimated to be ca. 1/2 by the ^1H NMR spectrum. The ratio of **2b**/**2c** changed to 1/4 after heating the mixture at 80 °C for 10 min. Furthermore, by heating the mixture for 30 min, the ratio of **2b**/**2c** (1/4) changed to 1/6 and any further change was not observed after a prolonged heating.

Reaction of 2b and 2c with Water. A mixture of **2b** and **2c**, which were prepared by the reaction of **1b** (63 mg, 0.5 mmol) and triphenylphosphine (131 mg, 0.5 mmol) in benzene (2 cm^3), was made to react with water (30 mg) under refluxing for 10 h. To this reaction mixture was added 2,4-dinitrophenylhydrazine (119 mg, 0.6 mmol) in methanol (2 cm^3) containing a catalytic ammount of HCl and stirred for 5 h. The reaction mixture was then concentrated and separated by TLC on silica gel using AcOEt-hexane (1/1) as a developer to give 2-hexanone 2,4-dinitrophenylhydrazone (135 mg, 96%), which was identical with the authentic specimen.

General Procedure for the Reaction of 2a with 3a—f. A solution of **2a** (152 mg, 0.5 mmol) and **3** (0.5 mmol) in dry benzene (2 cm^3) was refluxed for a period indicated in Table 1 under nitrogen atmosphere. The reaction mixture was concentrated and the resulting residue was separated by TLC on silica gel using benzene-hexane (1/1) as a developer to give pyridine derivatives **7**, along with **3**, **8**, and triphenylphosphine oxide (60—90% based on **2a** used). The results are summarized in Table 1. The structural proofs for the pyridine derivatives **7a**—**f** were based on the following physical

data.

2,4-Diphenylpyridine (**7a**): mp 186—187 °C (from ethanol) (lit,[12] 190.5—192.5 °C); ^{1}H NMR (CCl_4) δ=7.20—7.90 (9H, m), 7.83 (1H, m), 7.95—8.20 (2H, m), 8.65 (1H, d, J=5.0 Hz).

2,4-Bis(4-chlorophenyl)pyridine (**7b**): mp 105—106 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ=7.22—7.65 (7H, m), 7.75 (1H, broad s), 7.83 (2H, d, J=8.2 Hz), 8.66 (1H, d, J=4.8 Hz); IR ($CHCl_3$), 2977, 1603, 1545, 1497, 1469, 1382, 1093, 1015, 820 cm^{-1}; MS, m/z (rel intensity), 303 (M^+, 10), 301 (M^+, 69), 299 (M^+, 100). Found: C, 67.86; H, 3.77; N, 4.57%. Calcd for $C_{17}H_{11}NCl_2$: C, 68.02; H, 3.69; N, 4.67%.

2,4-Bis(4-methoxyphenyl)pyridine (**7c**): mp 152—153 °C (from benzene-hexane); ^{1}H NMR ($CDCl_3$) δ=3.81 (6H, s), 7.01 (2H, d, J=9.3 Hz), 7.02 (2H, d, J=10.7 Hz), 7.34 (1H, dd, J=5.2, 1.7 Hz), 7.63 (2H, d, J=9.3 Hz), 7.80—7.90 (1H, m), 8.05 (2H, d, J=10.7 Hz), 8.67 (1H, d, J=5.2 Hz); IR ($CHCl_3$), 2964, 2846, 1614, 1586, 1514, 1469, 1286, 1254, 1242, 1176, 1034, 824 cm^{-1}; MS, m/z (rel intensity), 293 (M^++2, 5), 292 (M^++1, 23), 291 (M^+, 100). Found: C, 78.69; H, 5.89; N, 4.78%. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81%.

4-Methyl-2-phenylpyridine (**7d**): mp 183—184 °C (picrate) (lit,[13] 185—187 °C); ^{1}H NMR (CCl_4) δ=1.41 (3H, s), 7.02 (1H, broad d, J=5.5 Hz), 7.33—7.60 (4H, m), 7.85—8.15 (2H, m), 8.55 (1H, d, J=5.5 Hz).

2-Phenylpyridine (**7e**): mp 174—175 °C (picrate) (lit,[14] 176—177 °C); ^{1}H NMR ($CDCl_3$) δ=7.03—7.30 (1H, m), 7.32—7.52 (3H, m), 7.60—7.72 (2H, m), 7.84—8.04 (2H, m), 8.67—8.70 (1H, m).

2-Methylpyridine (**7f**): 1,2-dimethylpyridinium iodide: mp 221—222 °C (from ethanol) (lit,[15] 229—231 °C). The hydrogenated compounds **8a**, **8b**, **8c**, and **8d** are known, and were confirmed by comparison of the physical data.

General Procedure for the Reaction of 2b and 2c with 3a,e. A solution of **2b** and **2c** was prepared in situ by the reaction of **1b** (75 mg, 0.6 mmol) and triphenylphosphine (131 mg, 0.5 mmol) at room temperature for 2 h. To this solution was added **3** (0.5 mmol), and the mixture was refluxed for a period indicated in Table 1 under nitrogen atmosphere. The reaction mixture was then concentrated and the resulting residue was separated by TLC on silica gel using benzene-hexane (1/1) as a developer to give pyridine derivatives and triphenylphosphine oxide (60—90%). The results are summarized in Table 2. The structural proof for the pyridine derivatives was based on the following physical data.

2-Butyl-4,6-diphenylpyridine (**10a**): mp 163—164 °C (picrate); ^{1}H NMR (CCl_4) δ=0.98 (3H, t, J=6.0 Hz), 1.17—2.17 (4H,m), 2.87 (2H, t, J=7.0 Hz), 7.12 (2H, s), 7.24—7.69 (8H, m), 7.90—8.15 (2H, m); IR ($CHCl_3$), 2963, 2938, 2868, 1596, 1584, 1549, 1496, 1452, 1402 cm^{-1}; MS, m/z (rel intensity) 287 (M^+, 1), 245 (100). HRMS Found: m/z 287.1657. Calcd for $C_{21}H_{21}N$: M, 287.1675.

2-Methyl-4,6-diphenyl-3-propylpyridine (**11a**): mp 145—146 °C (picrate); ^{1}H NMR (CCl_4) δ=0.80 (3H, t, J=6.4 Hz), 1.10—1.70 (2H, m), 2.40—2.70 (2H, m), 2.60 (3H, s), 7.10—7.45 (9H, m), 7.80—8.00 (2H, m); IR ($CHCl_3$), 2961, 2878, 1591, 1581, 1546, 1496, 1445, 1383 cm^{-1}; MS, m/z (rel intensity), 287 (M^+, 35), 258 (100). HRMS Found: m/z287.1657. Calcd for $C_{21}H_{21}N$: M, 287.1675.

2-Methyl-6-phenyl-3-propylpyridine (**11e**): mp 108—110 °C (picrate); ^{1}H NMR (CCl_4) δ=1.00 (3H, t, J=6.6 Hz), 1.23—1.87 (2H, m), 2.57 (2H, t, J=7.6 Hz), 2.57 (3H, s),7.25—7.50 (5H, m), 7.80—8.20 (2H, m); IR ($CHCl_3$), 2959, 2934, 2874, 1587, 1565, 1461, 1447, 1385 cm^{-1}; MS, m/z (rel intensity), 211 (M^+, 25), 182 (100). HRMS Found: m/z 211.1365. Calcd for $C_{15}H_{17}N$: M, 211.1362.

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