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Formation and Decomposition of 1,2,3-Triazolines Prepared from Diphenyl Phosphorazidate (DPPA) and Enamines of Diaryl-Type Ketones[1)]

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The pyrrolidine enamine **1** of deoxybenzoin reacted with diphenyl phosphorazidate (DPPA, $(C_6H_5O)_2P(O)N_3$) to give two amidines, the 1,2-migration product **7a** and the 1,3-dipolar elimination product **8a** in a ratio of 77:23. The reaction of DPPA with the enamine **2** of benzyl 2-pyridyl ketone proceeded slightly better in the presence of boron trifluoride etherate, giving both the 1,2-migration and 1,3-dipolar elimination products **7b** and **8b**. However, the main products in the reaction of DPPA with the pyrrolidine enamine **3** of 2-phenacylpyridine were 4-phenyl-5-(2-pyridyl)-1,2,3-triazole (**11**) and diphenyl *N*-pyrrolidinophosphoramidate (**12e**). Some other 1,3-dipolar cycloadditions of enamines with organic azides were also investigated.

Keywords——enamine; phosphorus azide; diphenyl phosphorazidate; boron trifluoride etherate; 1,3-dipolar cycloaddition; 1,2-migration; 1,3-dipolar elimination; *N*-phosphorylated amidine; methylation; 1,2,3-triazoline

We have already reported[2)] a convenient three-step conversion of alkyl aryl ketones to 2-arylalkanoic acids using diphenyl phosphorazidate (DPPA, $(C_6H_5O)_2P(O)N_3$). The key step of the conversion is the 1,3-dipolar cycloaddition of DPPA to enamines of alkyl aryl ketones, followed by 1,2-aryl migration to carbon carrying electron-donating alkyl functions, with concomitant evolution of nitrogen.[2)] We now report the analogous reaction of DPPA and some other azides with enamines derived from diaryl-type ketones, involving 1,2-aryl migration to carbon carrying electron-withdrawing functions.

The pyrrolidine enamine **1**[3)] prepared from deoxybenzoin was allowed to react with DPPA in ethyl acetate as usual,[2)] giving two products **7a** and **8a**. The reaction intermediate is apparently the 1,2,3-triazoline **4a**, which is labile and gives the betaine **5a**. The amidine **7a** is formed from **5a** *via* **6a** by expulsion of nitrogen, followed by 1,2-phenyl migration (path a), as shown in Chart 1. The amidine **8a** is directly formed from **5a** by 1,3-dipolar elimination (path b).[4)] In the reaction of DPPA with the pyrrolidine enamine of propiophenone,[2b)] the ratio of 1,2-phenyl migration to 1,3-dipolar elimination was 96:4. In contrast to this, the ratio of **7a** to **8a** was found to be rather low (77:23). This may be due to the presence of the more electron-withdrawing β-phenyl function, which facilitates the cleavage of the C–C bond as compared with the β-methyl function, giving a larger amount of the elimination product **8a**. Croce and Stradi have reported[5)] that the reaction of *p*-toluenesulfonyl azide with the morpholine enamine of deoxybenzoin affords a 1:1 mixture of 1,2-migration and 1,3-dipolar elimination products. Thus, our results demonstrate the superiority of both DPPA and the pyrrolidine enamine[2b)] for promoting the 1,2-migration.

Our attention was next directed to the reaction of DPPA with the pyrrolidine enamine **2**[3)] of benzyl 2-pyridyl ketone containing a more electron-withdrawing 2-pyridyl function. Two kinds of amidines **7b** and **8b** were also formed in this case. The ratio of **7b** to **8b** was smaller than that of **7a** to **8a**. This can be explained by the smaller migratory aptitude of the 2-pyridyl function as compared with the phenyl function. To increase the ratio of the 1,2-

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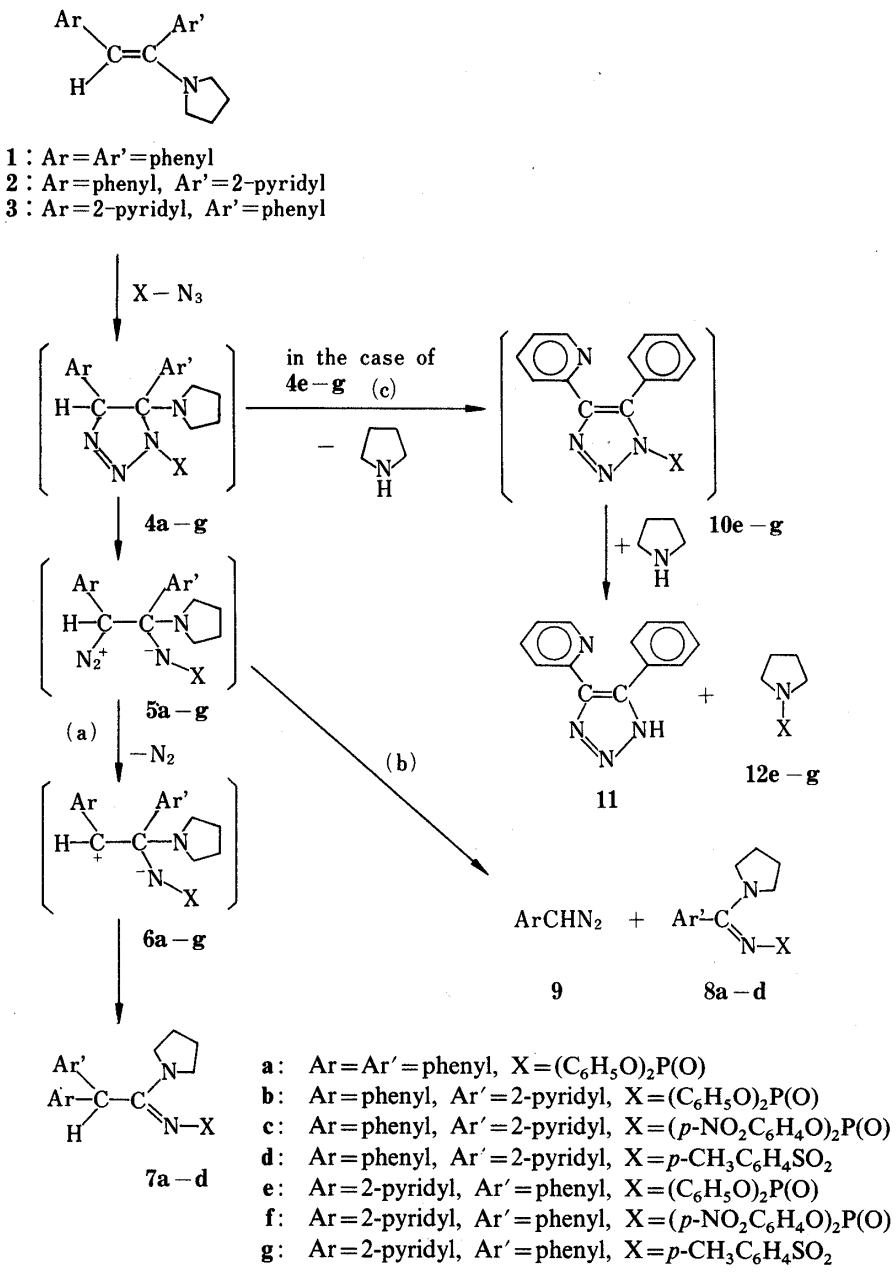

Chart 1

migration product **7b**, various reaction conditions (temperature, solvent, and additives) were extensively surveyed by the use of thin layer chromatography (TLC), as shown in Table I.

Raising the reaction temperature in ethyl acetate resulted in a decrease of **7b**, though the combined yield of **7b** and **8b** increased. Reaction solvent also played an important role, and polar solvents such as dimethylformamide and 1,2-dichloroethane were not suitable for the formation of **7b**. Addition of Lewis acids as well as organic bases slightly raised the ratio of **7b**. Among them, boron trifluoride etherate afforded the best result, though its use in excess severely decreased the combined yield of **7b** and **8b**.

Reaction of the enamine **2** with other organic azides was also investigated in tetrahydrofuran in the presence of boron trifluoride etherate. Di-*p*-nitrophenyl phosphorazidate[6] gave a similar result to DPPA, and the 1,2-migration product **7c** and the 1,3-dipolar elimination product **8c** were obtained in a ratio of 63 : 37. However, diethyl phosphorazidate,[7] diphenylphosphinic azide,[2c] and ethyl phenylthiophosphonoazidate[2c] were com-

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TABLE I. Reaction of DPPA with the Pyrrolidine Enamine **2** of Benzyl 2-Pyridyl Ketone[a]

Run	Solvent	Temp (°C)	Additive[b]	Ratio[c] **7b**:**8b**	Yield (%)[c] [**7b**+**8b**]
1	$CH_3CO_2C_2H_5$	Room temp. (24)	—	55:45	43
2	$CH_3CO_2C_2H_5$	40	—	41:59	—
3	$CH_3CO_2C_2H_5$	60	—	37:63	—
4	$CH_3CO_2C_2H_5$	Reflux (80)	—	31:69	72
5	$C_6H_5CH_3$	Room temp.	—	58:42	—
6	$HCON(CH_3)_2$	Room temp.	—	29:71	—
7	$ClCH_2CH_2Cl$	Room temp.	—	41:59	—
8	Tetrahydrofuran	Room temp.	—	56:44	48
9	Tetrahydrofuran	Room temp.	CF_3SO_3Ag	62:38	—
10	Tetrahydrofuran	Room temp.	$RhCl_3$	53:47	54
11	Tetrahydrofuran	Room temp.	$(C_2H_5)_3N$	61:39	46
12	Tetrahydrofuran	Room temp.	DBU[d]	60:40	—
13	Tetrahydrofuran	Room temp.	$BF_3\cdot(C_2H_5)_2O$[e]	53:47	36
14	Tetrahydrofuran	Room temp.	$BF_3\cdot(C_2H_5)_2O$	67:33	41
15	Tetrahydrofuran	Room temp.	$BF_3\cdot(C_2H_5)_2O$[f]	70:30	25
16	Tetrahydrofuran	Room temp.	$BF_3\cdot(C_2H_5)_2O$	65:35	59[g]
17	Tetrahydrofuran	Room temp.	$BF_3\cdot(C_2H_5)_2O$[h]	76:24	5

a) Each reaction was carried out for 12 h as described in Experimental, unless otherwise stated.
b) Unless otherwise stated, 1 eq of additive was used.
c) Determined by the use of a thin-layer chromatogram scanner.
d) Diazabicyclo[5.4.0]undecene-5.
e) 0.1 eq.
f) DPPA was added before the addition of boron trifluoride etherate.
g) The reaction time was extended to 32 h, and the products were isolated.
h) 2 eq.

pletely inactive and the starting material was recovered in the form of benzyl 2-pyridyl ketone after aqueous work-up. Since electron-poor azides are known to add particularly easily to electron-rich enamines,[8] the unreactivity of the above azides can be ascribed to the less electron-withdrawing properties of the functional groups attached at the phosphorus atom of the azides. In significant contrast to the case of DPPA, reaction of **2** with *p*-toluenesulfonyl azide resulted in the formation of the 1,3-dipolar elimination product **8d** only. This result confirms that DPPA is most suitable for promoting 1,2-aryl migration in the labile 1,2,3-triazoline intermediates.

Reaction of DPPA with the pyrrolidine enamine **3**[3] of 2-phenacylpyridine in tetrahydrofuran also afforded both the 1,2-migration and 1,3-dipolar elimination products **7b** and **8a** in a ratio of 42:58. However the main products in this reaction were 4-phenyl-5-(2-pyridyl)-1,2,3-triazole (**11**) and diphenyl *N*-pyrrolidinophosphoramidate (**12e**), which were formed by path c in Chart 1. Addition of boron trifluoride etherate decreased the formation of **11** and **12e**, but the ratio of **7b** to **8a** was almost the same. Replacement of DPPA with its *p*-nitro derivative afforded **7c** and **8f** in a ratio of 36:64, but the formation of **11** could not be observed. In contrast, the reaction of *p*-toluenesulfonyl azide with the enamine **3** afforded both the 1,2,3-triazole **11** and the pyrrolidinylamide **12g** in almost 90% yields, and only trace amounts of **7d** and **8g** could be detected. The formation of the 1,2,3-triazole derivative **11** is presumably due to the stronger acidity of hydrogen on the triazoline rings of **4e** and **4g** because of the electron-withdrawing effect of the 2-pyridyl function. Thus, elimination of pyrrolidine from **4e** and **4g** occurs to give the triazoles **10e** and **10g**, whose N–P or N–S bond is easily cleaved by the attack of pyrrolidine, giving the triazole **11** and pyrrolidinylamides

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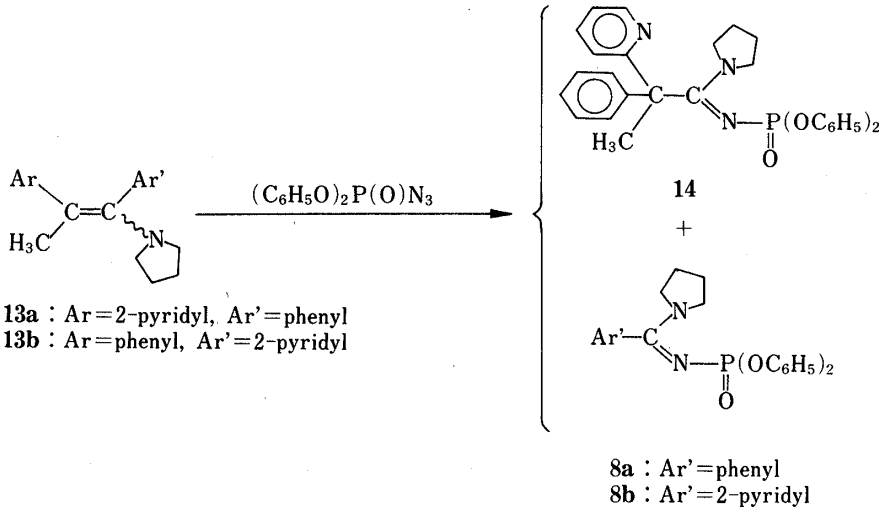

Chart 2

12e and **12g**, as shown in Chart 1. Decrease of the ratio of 1,2-migration products **7** to 1,3-dipolar elimination products **8** may be explained by the presence of the electron-withdrawing β-2-pyridyl function, which facilitates the fission of the carbon–carbon bond to give **8** preferentially.

Finally, the reactions of DPPA with methyl analogs **13** of **2** and **3** were investigated briefly (Chart 2). The enamine **13a** afforded the 1,2-migration product **14** and the 1,3-dipolar elimination product **8a** in a ratio of 37:63. The enamine **13b** also afforded **14** and **8b** in a ratio of 28:72. Addition of boron trifluoride etherate in the latter case increased the ratio to 59:41, but the combined yield of **14** and **8b** decreased.

Experimental

Melting and boiling points are uncorrected. Infrared (IR) spectra were recorded on a JASCO IRA-2 spectrophotometer (potassium bromide discs for crystals and films for oils). Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a JEOL PMX-60, MH-100, or FX-100 spectrometer with tetramethylsilane as an internal standard, in carbon tetrachloride or deuteriochloroform. Silica gel (70—230 mesh ASTM, Merck Art. 7734) and alumina (activity II-III, Merck Art. 1097) were used for column chromatography. Preparative layer chromatography (PLC) was carried out on plates (20 cm × 20 cm, 2 mm thickness) precoated with silica gel ($60F_{254}$, Merck Art. 5717). Quantitative analysis by thin layer chromatography was carried out using silica gel plates ($60F_{254}$, 0.25 mm, Merck Art. 5715) and a Shimadzu high speed TLC scanner CS-920. Each spot was detected under ultraviolet light (254 nm).

1-(1,2-Diphenylethenyl)pyrrolidine (1)[3]——A mixture of deoxybenzoin (2.94 g, 15 mmol), pyrrolidine (4.27 g, 60 mmol), and boron trifluoride etherate (213 mg, 1.5 mmol) in toluene (75 ml) was refluxed for 17 h under nitrogen using a Dean–Stark water separator with molecular sieve 4A as the dehydrating agent. The mixture was concentrated *in vacuo*, and the residue was distilled at 136—140 °C (0.08 mmHg) to give **1** (2.29 g, 61%) as a yellow oil. IR ν_{max} cm^{-1}: 1590. NMR δ: 1.6—2.0 (4H, m), 2.8—3.2 (4H, m), 5.34 (1H, s), 6.6—7.1 (5H, m), 7.19 (5H, s).

1-[2-Phenyl-1-(2-pyridyl)ethenyl]pyrrolidine (2)[3]——Prepared in 81% yield from benzyl 2-pyridyl ketone[9] using benzene in the same manner as described above, a yellow oil, bp 147—156 °C (0.5 mmHg), IR ν_{max} cm^{-1}: 1590. NMR δ: 1.47—2.17 (4H, m), 2.87—3.37 (4H, m), 5.43 (1H, s), 6.43—7.70 (8H, m), 8.65 (1H, d, J=5 Hz).

1-[1-Phenyl-2-(2-pyridyl)ethenyl]pyrrolidine (3)[3]——Prepared in 71% yield from 2-phenacylpyridine[10] using benzene in the same manner as described above, a yellow oil, bp 145—150 °C (0.045 mmHg). IR ν_{max} cm^{-1}: 1570. NMR δ: 1.34—2.08 (4H, m), 2.90—3.36 (4H, m), 5.53 (1H, s), 6.02 (1H, d, J=8 Hz), 6.59 (1H, t, J=6 Hz), 6.96 (1H, t, J=8 Hz), 7.32 (5H, s), 8.24 (1H, d, J=5 Hz).

Reaction of 1 with DPPA——DPPA (660 mg, 2.4 mmol) in ethyl acetate (6 ml) was added to **1** (499 mg, 2 mmol) in ethyl acetate (9 ml) under nitrogen. The mixture was stirred at room temperature for 1 h, at 50—55 °C for 3 h, then refluxed for 17 h. After concentration *in vacuo*, the residue was separated by silica gel (100 g) column chromatography with ethyl acetate–hexane (3:2).

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The amidine **7a** (645 mg, 47%) was obtained from the first eluate fraction. Recrystallization from ethyl acetate–petroleum benzin gave colorless needles, mp 112—114 °C. IR ν_{max} cm^{-1}: 1565, 1490, 1220, 1202, 940, 915. NMR δ: 1.44—1.92 (4H, m), 1.80—3.08 (2H, m), 3.48—3.80 (2H, m), 6.44 (1H, s), 6.9—7.6 (20H, m). *Anal.* Calcd for $C_{30}H_{29}N_2O_3P$: C, 72.57; H, 5.89; N, 5.64. Found: C, 72.64; H, 6.13; N, 5.61.

The amidine **8a** (116 mg, 14%) was obtained from the second eluate fraction, and identified by comparison with an authentic sample.[2b]

Reaction of 2 with DPPA (Table I, Run 16)——Boron trifluoride etherate (710 mg, 5 mmol) in tetrahydrofuran (1.5 ml) was gradually added to the enamine **2**, (1.25 g, 5 mmol) in tetrahydrofuran (2 ml) with ice-cooling under nitrogen. After addition of DPPA (2.75 g, 10 mmol) in tetrahydrofuran (2 ml), the mixture was stirred at room temperature for 32 h. The product ratio of **7b** to **8b** was 65 : 35 as determined by the TLC scanner. After concentration of the mixture *in vacuo*, the residue was chromatographed over alumina (20 g) with acetone–ethyl acetate–chloroform (1 : 2 : 2), then separated by silica gel column chromatography with acetone–ethyl acetate–chloroform (1 : 2 : 2).

The amidine **7b** (1.090 g, 44%) was obtained from the first eluate fraction. Recrystallization from ethyl acetate–petroleum benzin gave colorless crystals, mp 81—83 °C. IR ν_{max} cm^{-1}: 1565, 1490, 1222, 1202, 925. NMR δ: 1.57—1.97 (4H, m), 2.66—3.08 (1H, br s), 3.33—3.83 (3H, m), 6.50 (1H, s), 6.80—7.73 (18H, m), 8.50 (1H, d). *Anal.* Calcd for $C_{29}H_{28}N_3O_3P$: C, 70.01; H, 5.67; N, 8.45. Found: C, 70.23; H, 5.64; N, 8.64.

The amidine **8b** (297 mg, 15%) was obtained from the second eluate fraction. Recrystallization from ethyl acetate–petroleum benzin gave colorless crystals, mp 124—126 °C. IR ν_{max} cm^{-1}: 1565, 1482, 1202, 926. NMR δ: 1.62—2.20 (4H, m), 3.42—3.85 (4H, m), 6.82—7.46 (m), 7.07 (s) (13H), 8.32 (1H, d, J=5 Hz). *Anal.* Calcd for $C_{22}H_{22}N_3O_3P$: C, 64.81; H, 5.44; N, 10.31. Found: C, 64.80; H, 5.54; N, 10.32.

The other experimental data on the reaction of **2** with DPPA are summarized in Table I.

Reaction of 2 with Di-*p*-nitrophenyl Phosphorazidate——The reaction was carried out in the same way as the reaction of **2** with DPPA described above. The mixture was stirred at room temperature for 14 h, then the solvent was removed *in vacuo*. The residue was separated by PLC using ethyl acetate–chloroform (9 : 1).

The amidine **7c** (26%) was obtained from the fraction at *Rf* 0.40 as a yellow oil. IR ν_{max} cm^{-1}: 1563, 1520, 1342, 1215, 920. NMR δ: 1.60—2.06 (4H, m), 2.80—3.20 (1H, m), 3.30—3.80 (3H, m), 6.40 (1H, s), 6.60 (1H, d, J=8 Hz), 7.00—7.48 (10H, m), 7.78—8.28 (4H, m), 8.54 (1H, d, J=5 Hz).

The amidine **8c** (15%) was obtained from the fraction at *Rf* 0.27 as a yellow oil. IR ν_{max} cm^{-1}: 1563, 1526, 1345, 1220, 915. NMR δ: 1.58—2.30 (4H, m), 3.32—3.62 (4H, m), 6.95—8.50 (m), 7.27 (d, J=9 Hz), 8.16 (d, J=9 Hz) (11H), 8.38 (1H, d, J=5 Hz).

Reaction of 2 with *p*-Toluenesulfonyl Azide——The reaction was carried out as in the reaction of **2** with DPPA described above. The mixture was stirred at room temperature for 14 h, then the solvent was removed *in vacuo* and the residue was separated by PLC using acetone–ethyl acetate–chloroform (1 : 1 : 1) to give the amidine **8d** (82%) as colorless crystals, mp 168—169 °C (from diethyl ether–hexane). IR ν_{max} cm^{-1}: 1542, 1280, 1149, 1092. NMR δ: 1.30—2.33 (4H, m), 2.35 (3H, s), 2.93—3.33 (2H, m), 3.52—3.93 (2H, m), 6.83—8.10 (m), 7.15 (d, J=8 Hz), 7.67 (d, J=8 Hz) (7H), 8.53 (1H, d, J=5 Hz). *Anal.* Calcd for $C_{17}H_{19}N_3O_2S$: C, 61.98; H, 5.81; N, 12.76. Found: C, 62.03; H, 5.67; N, 12.79.

Reaction of 3 with DPPA——(i) Without Boron Trifluoride Etherate. DPPA (1.63 g, 5.9 mmol) in tetrahydrofuran (1 ml) was added to the enamine **3** (742 mg, 2.96 mmol) in tetrahydrofuran (2 ml) at 65 °C (bath temperature) under argon, and the mixture was stirred at 65 °C for 18 h, then concentrated *in vacuo*. The residue was chromatographed over alumina (30 g) using ethyl acetate–hexane (1 : 1), then methanol–chloroform (1 : 10). The first eluate fraction contained several products (1.238 g), which were separated as described later. The second eluate fraction afforded 4-phenyl-5-(2-pyridyl)-1,2,3-triazole (**11**, 360 mg, 55%) as pale yellow prisms from diethyl ether–petroleum benzin, mp 150—153 °C. IR ν_{max} cm^{-1}: 3600—2400, 1592, 1420, 1205, 998, 775, 692. NMR δ: 7.0—7.6, 7.6—8.0 (8H, m), 8.64 (1H, d, J=5 Hz). MS *m/e*: 222 (M^+), 193, 166, 69. *Anal.* Calcd for $C_{13}H_{10}N_4$: C, 70.26; H, 4.54; N, 25.21. Found: C, 70.01; H, 4.41; N, 25.17.

A part (0.491 g) of the first eluate fraction containing several products was separated by silica gel (30 g) column chromatography using ethyl acetate–hexane (1 : 4→1 : 0) to give four products successively: (1) 2-phenacylpyridine (14 mg, 6%); (2) diphenyl *N*-pyrrolidinophosphoramidate (**12e**, 191 mg, 54%), as a pale yellow oil, bp 220 °C (0.45 mmHg, by Kugelrohr distillation). (IR ν_{max} cm^{-1}: 1590, 1485, 1195, 925; NMR δ: 1.70—1.98 (4H, m), 3.24—3.52 (4H, m), 7.34 (10H, s); MS *m/e*: Calcd for $C_{16}H_{18}NO_3P$: 303.1024. Found: 303.1023); (3) the amidine **8a** (97 mg, 20%); (4) the amidine **7b** (87 mg, 15%).

(ii) With Boron Trifluoride Etherate. Boron trifluoride etherate (292 mg, 2.06 mmol) in tetrahydrofuran (0.7 ml) was added to the enamine **3** (515 mg, 2.06 mmol) in tetrahydrofuran (0.7 ml) with ice-methanol cooling under argon, followed by the addition of DPPA (1.132 g, 4.12 mmol). The mixture was stirred at room temperature for 12 h, at 50—60 °C for 3 h, then at 75—80 °C for 19 h. The solvent was removed *in vacuo*, and the residue was treated as above (i) to give **11** (19 mg, 4%), **8a** (17%), and **7b** (12%).

Reaction of 3 with Di-*p*-nitrophenyl Phosphorazidate——Di-*p*-nitrophenyl phosphorazidate (1.10 g, 3 mmol) was added to the enamine **3** (501 mg, 2 mmol) in ethyl acetate (1.5 ml), and the mixture was stirred at 60—65 °C for 1.5 h under nitrogen. The solvent was removed *in vacuo*, and the residue was passed through an alumina (50 g) column with

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ethyl acetate–hexane (2 : 3). The eluate was concentrated *in vacuo*, and the residue was dissolved in ethyl acetate–benzene (2 : 1, 80 ml). This solution was washed with 5% aqueous hydrochloric acid (30 ml × 3) and water (30 ml × 1), then dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was separated by silica gel (50 g) column chromatography with ethyl acetate–hexane (2 : 1) to give the amidine **8f** (141 mg, 14%) from the first eluate fraction, mp 135—136 °C (ethyl acetate–petroleum benzin). IR ν_{max} cm^{-1}: 1550, 1527, 1347, 1216, 915. NMR δ: 1.62—2.20 (4H, m), 3.14 (2H, br t), 3.64 (2H, br t), 7.18 (d, J=9 Hz), 7.41 (s) (9H), 8.16 (4H, d, J=9 Hz). *Anal.* Calcd for $C_{23}H_{21}N_2O_7P$: C, 55.65; H, 4.26; N, 11.29. Found: C, 55.84; H, 4.32; N, 11.22.

The amidine **7c** (92 mg, 8%) was obtained from the second eluate fraction.

Reaction of 3 with *p*-Toluenesulfonyl Azide——The reaction was carried out in the same way as that with di-*p*-nitrophenyl phosphorazidate. The crude residue was chromatographed on alumina (50 g) with ethyl acetate–hexane (1 : 3). The first eluate fraction was further purified by silica gel (55 g) column chromatography with ethyl acetate–hexane (1 : 6) to give 1-(*p*-toluenesulfonyl)pyrrolidine (**12 g**, 390 mg, 87%) as colorless needles, mp 123—125 °C (ethyl acetate–diethyl ether–petroleum benzin). IR ν_{max} cm^{-1}: 1591, 1490, 1330, 1160. NMR δ: 1.50—2.05 (4H, m), 2.43 (3H, s), 2.88—3.52 (4H, m), 7.32, 7.72 (4H, dd, J=8 Hz, AB type). *Anal.* Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22. Found: C, 58.76; H, 6.78; N, 6.23.

The second eluate fraction from the alumina column chromatography afforded 4-phenyl-5-(2-pyridyl)-1,2,3-triazole (**11**, 398 mg; 91%).

2-(2-Pyridyl)propiophenone[11]——Sodium hydroxide (0.126 g, 3 mmol) in water (2 ml) was added to a mixture of 2-phenacylpyridine[9] (0.296 g, 1.5 mmol), methyl iodide (0.426 g, 3 mmol), and tetrabutylammonium hydrogen sulfate (0.509 g, 1.5 mmol) in chloroform (2 ml) with ice-cooling and stirring. The mixture was stirred at room temperature for 2 h, then diluted with water (30 ml) and chloroform (30 ml). The organic layer was dried over sodium sulfate, and concentrated *in vacuo*. The residue was treated with diethyl ether and filtered. The filtrate was concentrated, and the residue was purified by silica gel column chromatography with ethyl acetate–chloroform–hexane (4 : 1 : 1), followed by Kugelrohr distillation to give 2-(2-pyridyl)propiophenone (276 mg, 87%) as a yellow oil, bp 140 °C (0.18 mmHg), IR ν_{max} cm^{-1}: 1685. NMR δ: 1.57 (3H, d, J=8 Hz), 4.93 (1H, q, J=8 Hz), 6.90—7.73 (6H, m), 7.87—8.20 (2H, m), 8.49 (1H, d, J=5 Hz). *Anal.* Calcd for $C_{14}H_{13}NO$: C, 79.60; H, 6.20; N, 6.63. Found: C, 79.59; H, 6.24; N, 6.61.

1-Phenylethyl 2-Pyridyl Ketone[11]——The reaction was carried out using benzyl 2-pyridyl ketone[8] in the same way as described for 2-(2-pyridyl)propiophenone, but the reaction time was extended to 17 h. Purification was done by alumina column chromatography with ethyl acetate–hexane (1 : 4) to give 1-phenylethyl 2-pyridyl ketone (86%) as colorless needles, mp 64.5—65 °C (petroleum benzin). IR ν_{max} cm^{-1}: 1695. NMR δ: 1.53 (3H, d, J=7 Hz), 5.50 (1H, q, J=7 Hz), 6.90—7.62 (6H, m, J=8 Hz), 7.73 (1H, dd, J=8, 2 Hz), 8.00 (1H, dd, J=8, 2 Hz), 8.60 (1H, d, J=5 Hz). *Anal.* Calcd for $C_{14}H_{13}NO$: C, 79.60; H, 6.20; N, 6.63. Found: C, 79.54; H, 6.10; N, 6.79.

1-[1-Phenyl-2-(2-pyridyl)-1-propenyl]pyrrolidine (13a)[12]——Titanium tetrachloride (3.24 g, 17 mmol) in benzene (25 ml) was added to a stirred mixture of 2-(2-pyridyl)propiophenone (2.58 g, 12 mmol) and pyrrolidine (12.15 g, 17 mmol) in benzene (60 ml) at 5—10 °C under nitrogen. The mixture was stirred at room temperature for 12 h, then titanium tetrachloride (1.62 g, 8.5 mmol) in benzene (12 ml) was added. The mixture was stirred at room temperature for 59 h, and filtered. The filtrate was concentrated *in vacuo*, and the residue was distilled at 150—160 °C (0.45 mmHg) to give the enamine **13a** (739 mg, 23%) as a yellow oil. IR ν_{max} cm^{-1}: 1580. NMR δ: 1.50—2.05 (m), 1.88 (s), 2.32 (s) (7H), 2.72 (br t, J=6 Hz), 3.15 (br t, J=5 Hz) (4H), 6.42—7.75 (m), 7.05 (s), 7.30 (s) (8H), 8.30—8.67 (1H, m). The isomeric ratio of (*E*) to (*Z*) was 37 : 63, as determined from the peak intensities at 2.72 (*E*) and 3.15 (*Z*) ppm.

1-[2-Phenyl-1-(2-pyridyl)-1-propenyl]pyrrolidine (13b)[12]——Prepared in 17% yield in the same manner as described for **13a**, a yellow oil, bp 125—133 °C (0.2 mmHg). IR ν_{max} cm^{-1}: 1580. NMR δ: 1.47—2.03 (m), 2.25 (s) (7H), 2.69 (br t, J=6 Hz), 3.1 (br t, J=6 Hz) (4H), 6.67—8.08 (m), 6.97 (s) (8H), 8.42—8.77 (1H, m). The isomeric ratio of (*E*) to (*Z*) was 48 : 52, as determined from the peak intensities at 2.69 (*E*) and 3.1 (*Z*) ppm.

Reaction of 13a with DPPA——DPPA (771 mg, 2.8 mmol) in ethyl acetate (1 ml) was added to the enamine **13a** (370 mg, 1.4 mmol) in ethyl acetate (0.5 ml) under nitrogen. The mixture was stirred at 65 °C for 11 h, and concentrated *in vacuo*. The residue was separated by silica gel (100 g) column chromatography with ethyl acetate–hexane (2 : 3) to give the amidine **8a** (259 mg, 46%) in the first eluate fraction. The second eluate fraction afforded the amidine **14** (193 mg, 27%) as a yellow oil. IR ν_{max} cm^{-1}: 1580, 1200, 920. NMR δ: 1.25—2.08 (m), 1.73 (s) (7H), 2.42—2.90 (2H, m), 3.70—4.26 (2H, m), 6.83—7.45 (m), 7.18 (s), 7.23 (s) (17H), 7.47—7.60 (1H, m), 8.53 (1H, m). MS *m/e*: Calcd for $C_{30}H_{30}N_3O_3P$: 511.2025. Found: 511.2026.

Reaction of 13b with DPPA——A mixture of the enamine **13b** (264 mg, 1 mmol) and DPPA (413 mg, 1.5 mmol) in tetrahydrofuran (1.5 ml) was stirred at room temperature for 42 h under nitrogen. The solvent was removed *in vacuo*, and a part (200 mg) of the residue (782 mg) was separated by PLC with acetone–ethyl acetate–chloroform (1 : 2 : 2) to give the amidine **14** (14 mg, 11%) from the fraction at *Rf* 0.39 and the amidine **8b** (30 mg, 29%) from the fraction at *Rf* 0.23.

A similar experiment with boron trifluoride etherate (0.142 g, 1 mmol) afforded **14** (17 mg, 7.5%) and **8b** (9 mg, 5%).

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References and Notes

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