On the Reaction of *N*-Vinyliminophosphoranes. 9.[1] The Synthesis and Reaction of *N*-(1,3,5-Cycloheptatrienyl)iminophosphoranes to Provide a Novel Route to 1-Azaazulenes

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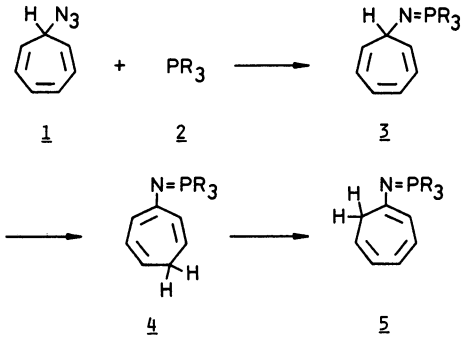
The first syntheses of *N*-(2,4,6-cycloheptatrienyl)iminophosphoranes (**3a, b**) and their thermal conversion to *N*-(1,3,5-cycloheptatrienyl)iminophosphoranes (**5a,b**) have been studied. The kinetic study of the 1,5-hydrogen migration of **3a,b** to *N*-(1,3,6-cycloheptatrienyl)iminophosphoranes (**4a,b**) has also been investigated. The reaction of **5b** with α-bromoacetophenone derivatives has provided a novel route to the 1-azaazulene ring system, albeit in low yields.

The reaction of a tertiary phosphine with an organic azide to produce an iminophosphorane after nitrogen evolution is known as the Staudinger reaction.[2] Many intermolecular[3] and intramolecular[4] Wittig-type (aza-Wittig) reactions with carbonyl compounds to construct a carbon-nitrogen double bond have been reported. However, the synthetic versatility of iminophosphoranes has still not been fully explored compared with that of methylenephosphoranes.[5] This fact can be ascribed in part to the poor variation of the substituent on the nitrogen atom of iminophosphoranes. Previously, we demonstrated the simple preparation of novel *N*-(1-phenylvinyl)iminophosphorane,[6] *N*-vinyliminotriphenylphosphorane,[7] and *N*-(1-butylvinyl)iminotriphenylphosphorane[7] by the Staudinger reaction of the corresponding organic azides with tertiary phosphines. *N*-Vinyliminophosphoranes were found to react with α-bromo ketones, α,β-unsaturated ketones, and tropone derivatives in an enamine alkylation process followed by an aza-Wittig reaction to provide a convenient route to phenyl-substituted pyrroles,[8,9] pyridines,[7,9] and 1-azaazulenes.[6,10] However, the potential value of *N*-vinyliminophosphoranes bearing cycloalkene on the nitrogen atom remains unexplored. We describe here the preparation of novel *N*-(1,3,5-cycloheptatrienyl)iminophosphoranes (**5a, b**) and their reactions with α-bromoacetophenone derivatives to give 2-aryl-1-azaazulene derivatives.

Results and Discussion

The reaction of 7-azido-1,3,5-cycloheptatriene (**1**)[11] with triphenylphosphine (**2a**) and tributylphosphine (**2b**) in dry benzene at room temperature afforded *N*-(2,4,6-cycloheptatrienyl)iminotriphenylphosphorane (**3a**) and *N*-(2,4,6-cycloheptatrienyl)iminotributylphosphorane (**2b**), respectively. Compound **3a** is a crystalline compound, which could be easily purified by recrystallization. On the other hand, compound **3b** is not stable on silica gel and it could not be purified. Thus, oily **3b** was used for further reactions. However, the structures of **3a** and **3b** were easily deduced on the basis of spectral data. The ^{13}C NMR



Scheme 1.

Table 1. ^{13}C and ^{31}P NMR Chemical Shifts (ppm) of Iminophosphoranes[a]

Compound	C1	C2	C3	C4	C5	C6	C7	Remaining signal	^{31}P[b]
3a	132.51	119.55	129.95				54.61	131.77(9.0), 131.51(95.3)	11.7
	(15.2)	(1.4)					(1.4)	130.44(2.8), 127.59(11.8)	
3b	131.29	117.72	128.40				52.38	25.08, 22.40, 22.05,[d]	23.9
	(12.7)						(2.8)	21.18, 21.79, 11.49	
5a	143.14	107.15		130.55	126.66[c]		39.55	132.18(9.7), 131.29(2.8)	3.5
	(6.2)	(13.8)		119.89	115.20		(19.3)	129.69(94.7), 128.11(11.7)	
5b	144.29	102.72		129.19	125.44[c]		39.20	25.10, 23.06, 22.66,[d]	24.8
	(9.0)	(12.4)		117.43	113.39		(20.0)	22.48, 12.26	

a) The numerical values in parentheses denote the coupling constants with ^{31}P. b) Downfield relative to external 85% H_3PO_4 standard. c) Each of the chemical shifts for C3—C6 are not assigned distinctly. d) Butyl groups appear as multiplets because of its coupling with ^{31}P.

and ^{31}P NMR spectral data are summarized in Table 1.

In general, the cycloheptatrienes undergo sequential 1,5-hydrogen migration and the equilibrium shifts to the side of the most stable isomer bearing a substituent at Cl, although the formation of other isomers has been detected. Therefore, the thermal reaction of **3a, b** is probably a useful method for the attempted preparation of *N*-(1,3,5-cycloheptatrienyl)iminophosphoranes **5a, b**. When **3a** was heated in toluene under reflux, isomer **4a** was formed at first. Progress of the reaction could be followed by ^1H NMR spectroscopy. After prolonged heating, only the desired product **5a** was obtained in 89% yield after recrystallization. Similarly, compound **3b** was isomerized in benzene under reflux for 7 h to give **5b** in good yield. The ^1H NMR spectra of **5a, b** exhibited a typical pattern of the 1-substituted cycloheptatriene. The ^{13}C NMR and ^{31}P NMR spectral data, which are summarized in Table 1, and other spectral data are in good accordance with the proposed structures, **5a, b**.

6a-c 7a-c

a: R=Me ; b: R=OMe ; c: R=Ph

Scheme 2.

A kinetic study of the rearrangement (**3a**→**4a** and **3b**→**4b**) was carried out at temperatures ranging from 68.0 °C to 99.0 °C and from 60.3 °C to 79.5 °C, respectively, to establish the mechanistic aspects. Further rearrangement of **4a, b** to **5a, b** was not observed during the kinetic studies of the early stage of the reactions. A plot of the logarithm of the concentration of unchanged **3a, b** against the reaction time was linear. The rate constants, thus obtained, are shown in Table 2. Arrhenius plots of the data for **3a** and **3b** (Table 2) provided straight lines, from which the kinetic parameters were calculated. These parameters as well as those of the thermal 1,5-hydrogen shift of 7-substituted cycloheptatrienes **6a—c** to 3-substituted cycloheptatrienes **7a—c** are summarized in Table 3.

Table 2. The First-Order Rate Constants k of **3a** and **3b**

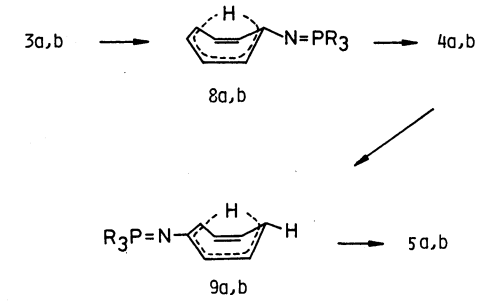
	Temp/°C	$10^5 \times k/s^{-1}$		Temp/°C	$10^5 \times k/s^{-1}$
3a	68.0	1.04	**3b**	60.3	0.96
	79.5	3.60		68.0	3.04
	86.5	9.25		76.0	6.04
	99.0	27.56		79.5	8.83

Table 3. The Kinetic Parameters of 1,5-Hydrogen Shift of 7-Substituted Cycloheptatrienes

Compound	E_a/kcal mol^{-1}	log A	$\Delta S^{\ddagger}$/cal mol^{-1}deg^{-1}
3a	26.6	12.1	−5.0[a]
3b	26.3	12.3	−6.1[a]
6a	33.25±0.19	12.6±0.2	−4.9[b]
6b	26.407	10.04	−15.0[c]
6c	27.6	10.8	−11.7[d]

a) At 80 °C. b) Ref. 12. c) Ref. 13. d) Ref. 14.

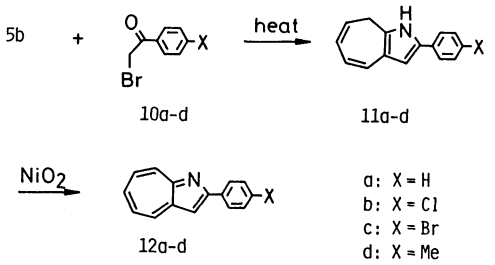
The preexponential factors obtained, $10^{12.1}$ and $10^{12.3}$ for **3a** and **3b**, respectively, correspond to the negative entropy of activation, i.e., −5.0 and −6.1 eu (at 80 °C). These values are intermediate between that of **6a**[12] and those of **6b, c**.[13,14] These facts clearly suggest that the 1,5-hydrogen shift of **3a, b** is sigmatropic in character and proceeds via a rigid transition state such as **8**. The activation energies for **3a** and **3b**



Scheme 3.

are similar to those of **6b**[13] and **6c**.[14] Thus, the steric or electronic effect of the phosphoranylideneamino group seems also to accelerate the 1,5-hydrogen shift in **3a, b**. Compounds **4a, b** further undergo a 1,5-hydrogen shift via a transition state **9**; the equilibrium are almost shifted to the side of the most stable isomers, **5a, b**.

The thermal reaction of **5a** with α-bromoacetophenone (**10a**) in benzene in the presence of triethylamine under reflux afforded no isolable products. However, compound **5b** reacted with **10a** to afford 1,8-dihydrocyclohepta[*b*]pyrrole (**11a**)[6,10] in 28% yield. Compound **11a** is not very stable, and it was dehydrogenated by NiO_2[15] in benzene to afford 2-phenyl-1-azaazulene (**12a**) in 44% yield. When a series of annelation reactions giving **11a** and the subsequent dehydrogenation by NiO_2 was carried out without rigorous purification of **11a**, compound **12a** was also obtained in 12% yield (Table 4, entry 1) (see Experimental). Similarly, reactions of **5b** with **10b—d** were carried out



10a-d 11a-d 12a-d

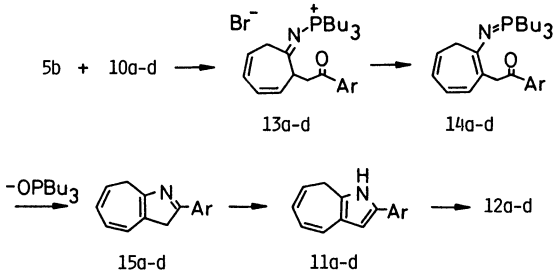
a: X=H
b: X=Cl
c: X=Br
d: X=Me

Scheme 4.

Table 4. Annelation Reaction of *N*-(1,3,5-Cycloheptatrieneyl)iminophosphorane **5b** with α-Bromoacetophenones (**10a—d**) and Subsequent Dehydrogenation

Annelation reaction[a]			Dehydrogenation[b]		
Entry	Compound **10**	Reaction time/h	Reaction time/h	Product **12**	Yield/%
1	**10a**	22	15	**12a**	12
2	**10b**	15	15	**12b**	11
3	**10c**	5	15	**12c**	8
4	**10d**	15	15	**12d**	11

a) All the reactions were carried out in benzene under refluxing. b) Reactions were carried out at room temperature.



Scheme 5.

in dry benzene under reflux to give plausible intermediates **11b—d**, which were subsequently dehydrogenated by NiO_2 to give the 2-aryl-1-azaazulene derivatives **12b—d**. The detailed reaction conditions and the yields of the products are summarized in Table 4. Product **12a**[16] is a known compound, and the other 1-azaazulenes **12b—d** were characterized on the basis of spectral data.

The plausible reaction pathways for the formation of 1-azaazulenes **12a—d** are summarized in Scheme 5. By analogy with the reaction of *N*-vinyliminophosphorane[8,9] with α-bromoketones, the initial step is the formation of a C-C bond between **5b** and **10a—d** to give intermediates **13a—d**, which undergo hydrogen migration to give **14a—d**. The intramolecular aza-Wittig reaction followed by hydrogen migration constructing the pyrrole ring gives **11a—d**. The oxidation of **11a—d** with NiO_2 results in the formation of 1-azaazulenes **12a—d**.

Thus, the desired *N*-(1,3,5-cycloheptatrienyl)iminophosphoranes **5a, b** were easily prepared, and were reacted with α-bromoacetophenones to give arylsubstituted 1-azaazulenes albeit in low yields. Further synthetic applications of the iminophosphoranes are in progress.

Experimental

The IR spectra were recorded on a Shimadzu IR-400 spectrometer. The ^1H NMR and ^{13}C NMR spectra were recorded on Hitachi R-24 and Hitachi R-90H spectrometers, and the chemical shifts are given in ppm (δ) relative to the internal $SiMe_4$ standard. The ^{31}P NMR spectra were recorded on a Hitachi R-90H spectrometer and the chemical shifts are given in ppm (δ) relative to the external 85%-H_3PO_4 standard. Mass spectral and high-resolution mass spectral studies were conducted using Shimadzu GCMS-QP1000 and JEOL DX-300 spectrometers. All the melting points were measured on a Büch apparatus and are uncorrected.

Preparation of *N*-(2,4,6-Cycloheptatrienyl)iminophosphoranes 3a, b. A solution of tropylium tetrafluoroborate (5 g, 28 mmol) and sodium azide (10 g, 154 mmol) in water (50 cm^3) was stirred for 5 min at room temperature. The reaction mixture was extracted with benzene and the benzene extract was dried over $MgSO_4$ and then concentrated to 50 cm^3. To this solution of 7-azidocycloheptatriene (**1**)[11] thus obtained was added to triphenylphosphine (**2a**) (6.5 g, 25 mmol) or tributylphosphine (**2b**) (5 g, 25 mmol) at room temperature and stirred for 2 h or 5 h. After the benzene was evaporated, the resulting residue was crystallized from benzene-hexane to give yellow crystals of **3a** (3.1 g, 89%): mp 109—110 °C (from benzene-hexane); ^1H NMR ($CDCl_3$) δ=3.00 (1H, dm, *J*=19.5 Hz), 5.50 (2H, dd, *J*=4.6, 9.2 Hz), 5.80—6.10 (2H, m), 6.52 (2H, t, *J*=2.6 Hz), 7.30—7.85 (15H, m); IR ($CHCl_3$) 3004, 1591, 1485, 1441, 1393, 1304, 1180, 1105, 908, 697 cm^{-1}; MS, *m/z* (rel intensity) 367 (M^+, 16), 261 (100). Found: C, 81.99; H, 6.19; N, 3.60%. Calcd for $C_{25}H_{22}NP$: C, 81.72; H, 6.04; N, 3.81%. In the case of **3b**, the benzene was evaporated in vacuo and the resulting oily residue was used for further reaction, because of its instability to heat and chromatography on silica gel. For **3b**: ^1H NMR ($CDCl_3$) δ=0.75—1.15 (9H, m), 1.15—1.85 (18H, m), 2.55 (1H, dm, *J*=20.5 Hz), 5.25 (2H, dd, *J*=8.5, 4.5 Hz), 5.70—6.15 (2H, m), 6.54 (2H, t, *J*=3.0 Hz); IR ($CHCl_3$) 2955, 2929, 2866, 1468, 1391, 1305, 1184, 1094 cm^{-1}. HRMS Found: *m/z* 307.2431. Calcd for $C_{19}H_{34}NP$: M, 307.2429.

Thermal Isomerization of 3a,b to *N*-(1,3,5-Cycloheptatrienyl)-iminophosphoranes 5a,b. (A) A solution of **3a** (3.5 g, 9.5 mmol) in toluene (10 cm^3) was heated under reflux for 7 h. After the toluene was evaporated in vacuo, the resulting residue was crystallized from hexane to give yellow crystals of **5a** (3.1 g, 89%): mp 131—132 °C (from EtOH); ^1H NMR ($CDCl_3$) δ=2.65 (2H, dd, *J*=7.8, 1.0 Hz), 4.90—5.40 (2H, m), 5.83—6.30 (3H, m), 7.30—7.91 (15H, m); IR ($CHCl_3$) 2995, 1574, 1496, 1441, 1328, 1174, 1107, 1026 cm^{-1}; MS, *m/z* (rel intensity) 367 (M^+, 75), 366 (100). Found: C, 81.83; H, 6.22; N, 3.60%. Calcd for $C_{25}H_{22}NP$: C, 81.72; H, 6.04; N, 3.81%.

(B) A solution of **3b** in benzene, which was prepared as described above, was heated under reflux for 7 h. After the benzene was evaporated, the resulting residue was distilled under reduced pressure to give **5b** (6.15 g, 81% based on tropylium cation used). For **5b**: bp 137 °C/11 Pa. ^1H NMR (CCl_4) δ=0.75—1.20 (9H, m), 1.20—2.10 (18H, m), 2.23 (2H, dd, *J*=7.2, 1.6 Hz), 4.80—5.15 (2H, m), 5.55—6.40 (3H, m); IR ($CHCl_3$) 2964, 2934, 2871, 1567, 1486, 1441, 1333, 1204, 1026 cm^{-1}. HRMS Found: *m/z* 307.2413. Calcd for $C_{19}H_{34}NP$: M, 307.2429.

Reaction Rate of 1,5-Hydrogen Migration of 3a, b to 4a, b. The solution of **3a** (0.5 mol dm^{-3}) in CCl_2CCl_2 was placed in six reaction tubes (5 mm in outer diameter and 30 mm long), which were fitted in the neck of a 500 cm^3 flask with six necks and a reflux condenser, which contained a suitable solvent. Six tubes were heated at the same time by vapor of boiling solvent such as dioxane (99.0 °C), trichloroethylene

(86.5 °C), benzene (79.5 °C), or hexane (68 °C). During heating, each tube was periodically withdrawn from the flask and cooled quickly with ice bath to quench the reaction. The ^{1}H NMR spectrum was measured by a Hitachi R-24 spectrometer. The concentration ratios of the isomerized product, **4a** and **3a**, were calculated from the proton area of the signal ascribed to the 7H-proton of cycloheptatriene of the corresponding compounds.

The solution of **3b** (3.0 mol dm^{-3}) in CCl_2CCl_2 with 1/6 molar equivalent amounts of anisole was placed in six reaction tubes, which were fitted in the same apparatus described above. Six tubes were heated at the same time by vapor of boiling solvent such as *i*-PrOH (79.5 °C), CCl_4 (76.0 °C), hexane (68 °C), or $CHCl_3$ (60.3 °C). The ^{1}H NMR spectrum was measured, and the concentration ratios of the remaining **3b** was determined by the proton area of the signals ascribed to the 7H-proton of **3b** and the methyl proton of anisole used as the internal standard. From this concentration ratio, the product ratio of **4b** was calculated.

The Reaction of *N*-(1,3,5-Cycloheptatrienyl)iminotributylphosphorane (5b) with α-Bromoacetophenone (10a). A solution of the iminophosphorane (**5b**) (307 mg, 1 mmol), α-bromoacetophenone (**10a**) (199 mg, 1 mmol), and triethylamine (202 mg, 2 mmol) in benzene (5 cm^3) was heated under reflux for 22 h. After the reaction was completed, the reaction mixture was chromatographed on Florisil. The fractions eluted with benzene afforded 1,8-dihydro-2-phenylcyclohepta[*b*]pyrrole (**11a**) (58 mg, 28 %), which was identified by comparison of the spectral data of the authentic specimen.[6]

General Procedure for the Reaction of *N*-(1,3,5- Cycloheptatrienyl)iminotributylphosphorane (5b) with α-Bromoacetophenones (10a—d) and Subsequent Dehydrogenation. A solution of the iminophosphorane (**5b**) (307 mg, 1 mmol), α-bromoacetophenone (**10**) (1 mmol), and triethylamine (202 mg, 2 mmol) in benzene (5 cm^3) was heated under reflux for a period indicated in Table 4. After the reaction was completed, the reaction mixture was chromatographed on Florisil. The fractions eluted with benzene was concentrated to 20 cm^3. To this solution was added NiO_2 (910 mg, 10 mmol); and the mixture was then stirred for 10—15 h at room temperature. After the reaction mixture was filtered through Celite to remove insoluble materials, the filtrate was concentrated and the resulting residue was purified by TLC on Silica gel using hexane-ethyl acetate (1/1) to give 1-azaazulene derivatives (**12**) in the yields indicated in Table 4. 2-Phenyl-1-azaazulene (**12a**): mp 148—149.5 °C (from EtOH) (lit, 157—159 °C); ^{1}H NMR ($CDCl_3$) δ=7.22—7.72 (7H, m), 8.19—8.48 (3H, m), 8.48—8.74 (1H, m); IR ($CHCl_3$) 2906, 2857, 1586, 1466, 1445, 1412, 1030 cm^{-1}; *m/z* (rel intensity) 205 (M^+, 100); UV (EtOH, log ε) 205 (4.33), 237 (4.20), 287 (4.59), 310 (4.45), 355 (4.09), 372 (4.04), 497 (3.44), 529 (3.16) nm; (EtOH-TFA, log ε) 260 (4.30), 282 (4.33), 306 (4.57), 340 (3.90), 446 (4.06) nm. 2-(4-Chrolophenyl)-1-azaazulene (**12b**): mp 165—165.9 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ=7.24—7.78 (6H, m), 8.06—8.82 (4H, m); IR ($CHCl_3$) 2985, 2955, 1602, 1464, 1437, 1413, 1087, 1012 cm^{-1}; MS, *m/z* (rel intensity) 242 (M^++1, 5), 241 (M^+, 28), 240 (M^++1, 18), 239 (M^+, 100); UV (EtOH, log ε) 205 (4.26), 237 (4.18), 287 (4.50), 312 (4.41), 356 (4.09), 372 (4.06), 496 (3.45), 527 (3.25) nm; (EtOH-TFA, log ε) 263 (4.26), 280 (4.23), 310 (4.49), 345 (3.93), 446 (4.03) nm. Found: C, 75.49; H, 4.35; N, 6.09%. Calcd for $C_{15}H_{10}NCl$: C, 75.16; H, 4.20; N, 5.84%. 2-(4-Bromophenyl)-1-azaazulene (**12c**): mp 169—171.5 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ=7.27—7.83 (6H, m), 8.02—8.73 (4H, m); IR ($CHCl_3$) 2985, 2955, 1597, 1464, 1437, 1411, 1070, 1009 cm^{-1}; MS, *m/z* (rel intensity) 286 (M^++1, 11), 285 (M, 58), 284 (M^++1, 11), 283 (M^+, 59), 204 (100); UV (EtOH, log ε) 206 (4.39), 248 (4.30), 288 (4.65), 313 (4.58), 356 (4.25), 373 (4.23), 496 (3.56), 527 (3.32) nm; (EtOH-TFA, log ε) 263 (4.43), 279 (4.36), 311 (4.63), 345 (4.09), 447 (4.20) nm. Found: C, 63.37; H, 3.59; N, 4.81%. Calcd for $C_{15}H_{10}NBr$: C, 63.40; H, 3.55; N, 4.93%. 2-(4-Methylphenyl)-1-azaazulene (**12d**): mp 146.5—147.5 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ=2.33 (3H, s), 7.09—7.64 (6H, m), 8.04—8.30 (3H, m), 8.41—8.65 (1H, m); IR ($CHCl_3$) 2990, 2940, 1615, 1467, 1438, 1413 cm^{-1}; MS *m/z* (rel intensity) 220 (M^++1, 27), 219 (M, 100); UV (EtOH, log ε) 206 (4.25), 240 (4.12), 288 (4.43), 315 (4.36), 361 (4.04), 377 (4.02), 497 (3.34), 529 (3.00) nm; (EtOH-TFA, log ε) 262 (4.27), 278 (4.16), 314 (4.43), 349 (3.82), 450 (4.05) nm. Found: C, 87.21; H, 5.85; N, 6.21%. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39%.

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References

1) Part 8. N. Kanomata and M. Nitta, *Tetrahedron Lett.*, **29**, 5957 (1988).

2) Yu. G. Gololobov, I. N. Zhmurova, and L. F. Kasukhin, *Tetrahedron*, **37**, 437 (1981).

3) J. A. Kloek and K. L. Leschinsky, *J. Org. Chem.*, **43**, 1460 (1978); O. Tsuge, S. Kanemasa, and K. Matsuda, *J. Org. Chem.*, **49**, 2688 (1984); T. Saito, M. Nakane, M. Endo, H. Yamashita, Y. Oyamada, and S. Motoki, *Chem. Lett.*, **1986**, 135; P. Molina, M. Alajarín, and A. Vidal, *Tetrahedron Lett.*, **29**, 3849 (1988).

4) P. H. Lambert, M. Vaultier, and R. Carrié, *J. Chem. Soc., Chem. Commun.*, **1982**, 1224; T. Sasaki, S. Eguchi, and T. Okano, *J. Am. Chem. Soc.*, **105**, 5912 (1983); D. M. B. Hickey, A. R. MacKenzie, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, **1984**, 776; L. Bruche, L. Garanti, and G. Zecchi, *Synthesis*, **1985**, 304; H. R. Stegmann, D. Klotz, and J. E. Weiss, *Chem. Ber.*, **118**, 4632 (1985).

5) K. B. Becker, *Tetrahedron*, **36**, 1717 (1980).

6) M. Nitta and T. Kobayashi, *Chem. Lett*, **1986**, 463.

7) Y. Iino and M. Nitta, *Bull. Chem. Soc. Jpn.*, **61**, 2235 (1988).

8) Y. Iino, T. Kobayashi, and M. Nitta, *Heterocycles*, **24**, 2437(1986).

9) T. Kobayashi, Y. Iino, and M. Nitta, *Nippon Kagaku Kaishi*, **1987**, 1237.

10) M. Nitta, Y. Iino, E. Hara, and T. Kobayashi, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 51.

11) J. J. Looker, *J. Org. Chem.*, **30**, 638 (1965).

12) K. W. Egger, *J. Am. Chem. Soc.*, **89**, 3688 (1967).

13) T. Nozoe and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **38**, 665 (1965).

14) A. P. ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 741 (1962).

15) K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).

16) Y. Sugiyama, N. Soma, and Y. Kishida, *Bull. Chem. Soc. Jpn.*, **45**, 3174 (1972).