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Thermal Rearrangements of Cyclic Amine Ylides. VIII.[1] Intramolecular Cyclization of 2-Ethynylpyridine *N*-Ylides into Indolizines and Cycl[3.2.2]azines

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Treatment of 6-unsubstituted 2-ethynyl-1-phenacylpyridinium bromides (**10a**—**c**) with 1,5-diazabicyclo[5.4.0]undec-5-ene in refluxing benzene resulted in cyclization to give the 3-benzoylindolizines (**11**) *via* the *N*-ylide intermediates **13**, whereas heating the salts **10** in refluxing acetic acid afforded the 1-benzoylindolizines (**12**). Upon similar treatment with the base, 2-ethynyl-6-methylpyridinium salts (**20a**—**c**) gave the 3-benzoyl-5-methylindolizines (**22**); in the case of the phenylacetylene compound **20c**, 2,3-diphenylcycl[3.2.2]azine (**23**) was also obtained. However, the reaction of 6-amino-2-ethynylpyridines (**27a**—**c**) with phenacyl bromide produced 5-ethynyl-1-azaindolizines (**28**), which were converted into 1-azacycl[3.2.2]azines (**29**). The mechanisms of these intramolecular cyclizations are discussed.

Keywords——2-ethynylpyridine; 2-ethynyl-1-phenacylpyridinium ylide; indolizine; 1-azaindolizine; 1-azacycl[3.2.2]azine; cycl[3.2.2]azine; intramolecular cyclization; rearrangement

Thermal sigmatropic rearrangements of cyclic allylamine *N*-ylides have been well studied[2] in connection with those of related open-chain compounds.[3] The propynylamine *N*-ylides (**1a**)[4] and *N*-oxides (**1b**)[5] and related *S*-ylides[6] are also known to undergo thermal [2,3]-sigmatropic rearrangement giving the corresponding allenic compounds **2**. These results prompted us to examine the thermal behavior of cyclic propargylic ylides, and we have already reported several new results. For example, the thermolysis of 6-ethynyl-1,2,5,6-tetrahydropyridine *N*-imides (**3**) resulted in ring expansion to give the 1,2-diazonines (**5**) *via* the allenic intermediates **4**.[7] Similar ring expansion was also observed for the cyclic sulfonium ylides having an ethynyl group at the α-position of the ring, giving rise to the corresponding three-carbon ring enlargement products such as thiocin, thionin, and thiecin derivatives.[8]

On the other hand, as for aromatic amine ylides, the intermolecular 1,3-dipolar cycloaddition[9] of azine *N*-ylides and *N*-imides to olefins or acetylenes and the intramolecular 1,5-dipolar cyclization[10] of azine *N*-vinylimides have been widely investigated. However, few such reactions of pyridinium ylides having an unsaturated substituent at the 2-position of the pyridine ring are known. Therefore, we examined the thermal behavior of 2-ethynylpyridine *N*-imides (**6**) and have shown that they undergo intramolecular cyclization to afford 3-azaindolizines (**8**) *via* the intermediates **7**.[11] We report here the thermal intramolecular cyclization of 2-ethynylpyridine *N*-ylides.[12]

The starting 2-ethynylpyridines used in the present work were prepared from the corresponding 2-bromopyridines and acetylenes according to the reported method.[13] Treatment of the 6-unsubstituted 2-ethynylpyridines (**9a**—**c**)[11] with phenacyl bromide gave the 1-phenacylpyridinium bromides (**10**), precursors of the desired pyridine *N*-ylides, in high yields. The salts **10a**—**c** were treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in refluxing benzene, resulting in cyclization to give the 3-benzoylindolizines (**11a**—**c**) in 60—70% yields. Treatment of **10** with hydroxide or alkoxide ions also afforded **11**, but in lower

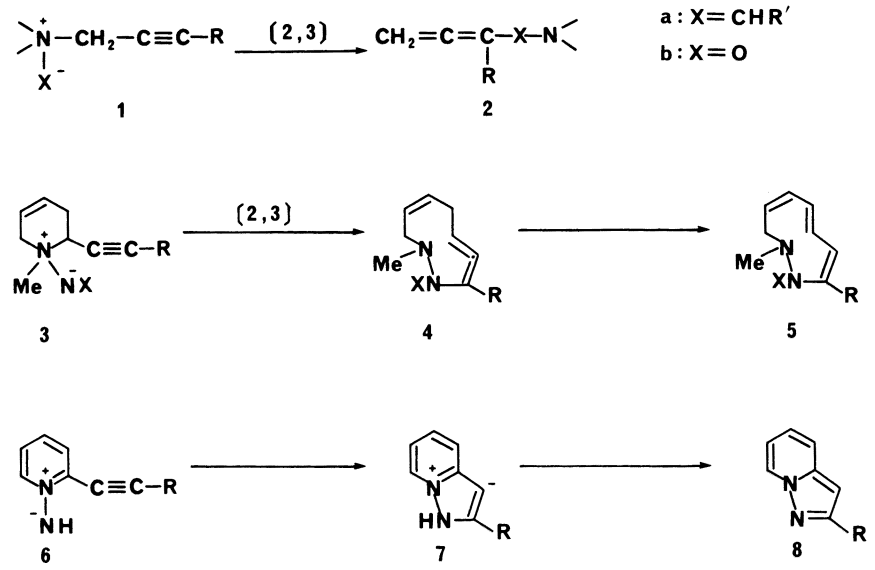

Chart 1

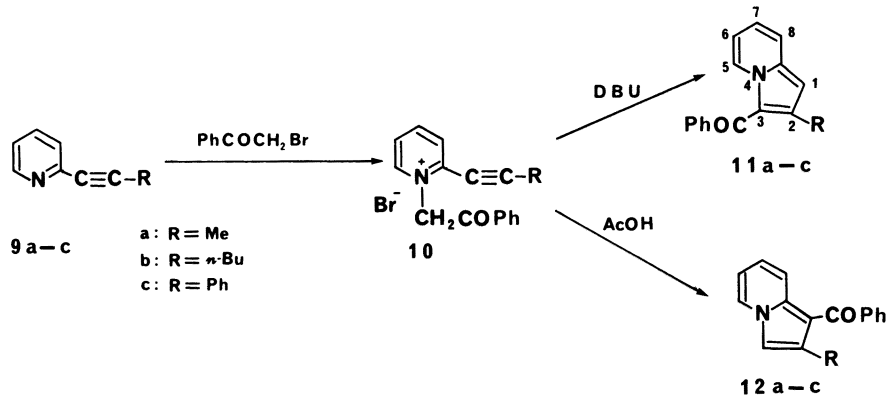

Chart 2

yields. When a polar solvent such as ethanol or dimethylformamide was used instead of benzene, the yields of **11** decreased.

It should be noted that, unexpectedly, heating the salts **10a**—**c** in refluxing acetic acid also resulted in cyclization giving rise to the 1-benzoylindolizines (**12a**—**c**) in 50—70% yields, but no 3-benzoyl isomers **11**.

The 2-phenylindolizines (**11c**[14] and **12c**[15]) are known and the other products **11a, b** and **12a, b** were characterized by spectral comparison with **11c** and **12c**. The proton nuclear magnetic resonance (^{1}H-NMR) spectra of the 3-benzoylindolizines (**11**) showed singlet signals due to 1-H at around δ 6.3, whereas those of the 1-benzoyl isomers **12** showed singlet signals assignable to 3-H at around δ 7.2. The doublet signal due to 5-H in **11** appeared at lower field (*ca.* δ 9.5) than that for **12** (*ca.* δ 8.0), probably because of the shielding effect of the 3-benzoyl group.

Possible mechanisms leading to the indolizines are shown in Chart 3, although none of the intermediates could be isolated. The base-induced reaction of **10** may proceed by initial formation of the *N*-ylides **13**, which might cyclize to give the products **11** *via* the zwitter ionic

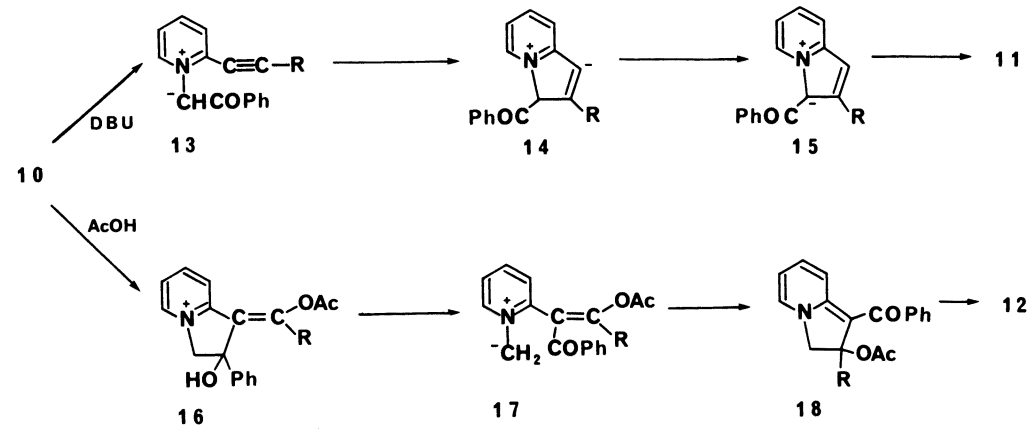

Chart 3

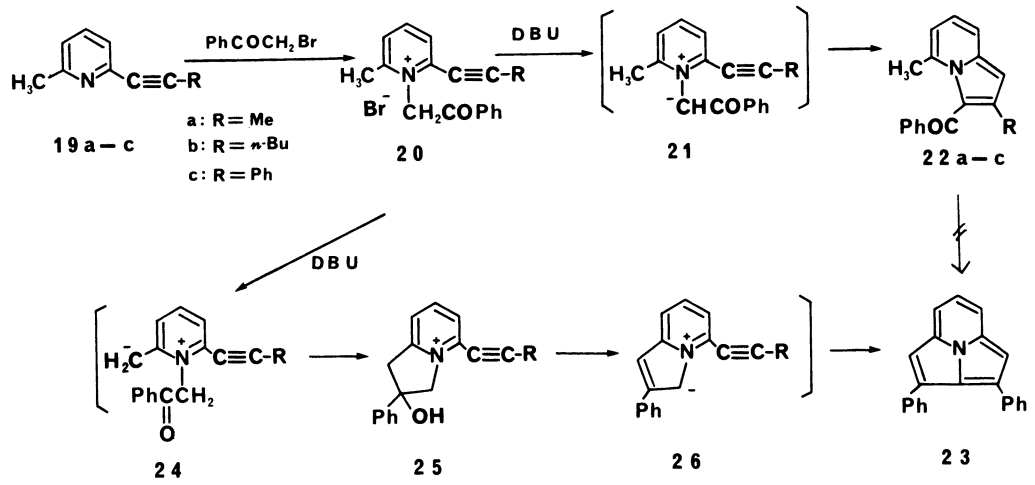

Chart 4

intermediates **14** and the cyclic *N*-ylides **15** successively. In contrast to the cases of the aliphatic amine ylides (**1** and **3**),[4-7] a concerted mechanism for the present reaction seems unlikely because of prohibitive ring strain in the five-membered cyclic allenic intermediates. This behavior is analogous to that observed for the 2-ethynylpyridine *N*-imides (**6**). On the other hand, the acid-induced reaction may proceed *via* the addition of an acetoxy anion to the triple bond to produce allenic intermediates followed by cyclization to **16**, which may give the methylides **17** by ring fission. The ylides **17** would undergo [2,3]-sigmatropic rearrangement to the bicyclic intermediates **18**, which then give the 1-benzoyl products **12** by elimination of acetic acid. In addition, when a solution of hydrochloric acid or *p*-toluenesulfonic acid in ethanol or benzene was used instead of acetic acid, the salts **10** were decomposed and gave no indolizines, indicating that acetoxy anion may play an important role in this acid-induced reaction.

Next, the 6-methylpyridinium bromides (**20a—c**), prepared from the corresponding 2-ethynyl-6-methylpyridines (**19**) and phenacyl bromide, were treated with DBU to also produce the 5-methyl-3-benzoylindolizines (**22a—c**) in 30—60% yields, probably *via* the *N*-ylides **21**. In the case of the phenylacetylene compound **20c**, 2,3-diphenylcycl[3.2.2]azine (**23**)[16] was obtained in 7% yield in addition to **22c**. However, in the cases of **20a, b**, the

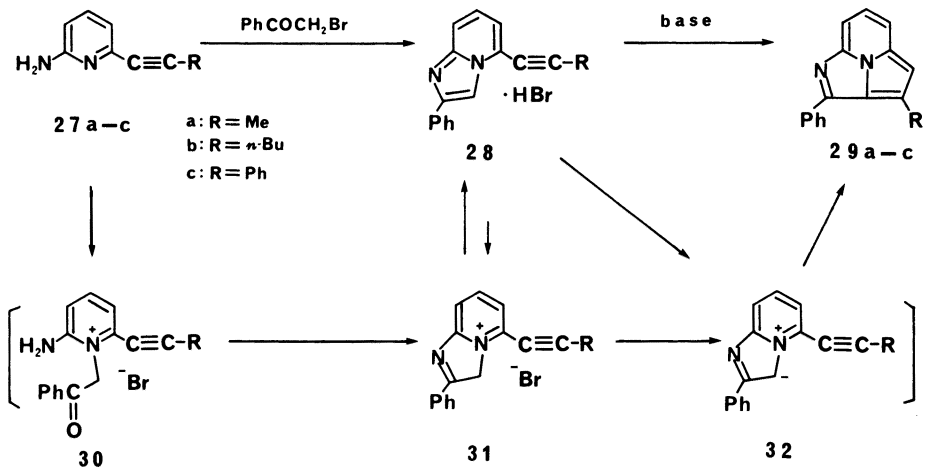

Chart 5

corresponding cyclazines could not be isolated, although the presence of very small amounts of compounds assumed to be cyclazines in product mixtures was confirmed by thin-layer chromatography and ^{1}H-NMR spectral analysis.

A possible mechanism for the formation of the cyclazine **23** is shown in Chart 4. The initial base-induced deprotonation from the methyl group to **24** may also occur in competition with the deprotonation from the phenacyl group to the ylide **21**. The intermediate **24** may cyclize to give the cyclic *N*-ylide **26** *via* **25**. The ylide **26** might further cyclize to the tricyclic product **23**, analogously to the formation of **11** from **13**. In addition, further treatment of the indolizines (**22**) with the base gave no cyclazines.

In contrast to the cases of the 6-unsubstituted pyridines (**9**) and 6-methylpyridines (**19**), treatment of 6-amino-2-ethynylpyridines (**27a—c**) with phenacyl bromide did not give the phenacylpyridinium salts **30**, but directly afforded the 5-ethynyl-2-phenyl-1-azaindolizine hydrobromides (**28a—c**) in 80—90% yields. The salts were treated with DBU in refluxing benzene to produce the 2-phenyl-1-azacycl[3.2.2]azines (**29a—c**: 70—80% yields), which were characterized by comparison with the related compounds reported.[17] These compounds **29** were also obtained by treatment of **28** with sodium carbonate in water.

The reaction of **27** with phenacyl bromide may proceed by initial formation of the phenacylpyridinium salts **30**, which are then converted to the products **28** *via* the Schiff bases **31**, although these key intermediates could not be isolated. The formation of the cyclazines (**29**) from **28** may also involve the cyclic ylide intermediates **32** formed from **28** directly or *via* **31** by the base treatment.

In conclusion, the present results provide a new route for preparing indolizines[18] and cyclazines,[19] although many synthetic methods for these heterocyclic rings are known.

Experimental

Melting points were measured on a Yanagimoto micro melting hot stage apparatus and are uncorrected. Infrared (IR) spectra were determined with a Hitachi 270-30 spectrometer and mass spectra (MS) were measured with a JEOL DX-300 instrument. ^{1}H-NMR spectra were recorded on a JEOL JNM-MH100 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard unless otherwise stated; spectral assignments were confirmed by spin-decoupling experiments. Microanalyses were carried out in the Microanalytical Laboratory of this school by Mrs. R. Igarashi.

2-Ethynyl-1-phenacylpyridinium Bromides (10a—c)——General Procedure: A solution of a 2-ethynylpyridine

(**9**:[11] 3 mmol) and phenacyl bromide (0.6 g, 3 mmol) in $CHCl_3$ (20 ml) was refluxed for 4—6 h and then evaporated to dryness *in vacuo*. The resulting solid residue was washed with ether and recrystallized from methanol–ethyl acetate to give **10** as pale yellow prisms.

10a: 0.87 g, 92% yield, mp 189—190 °C (dec.). IR (KBr): 2220 (C≡C), 1660 (C=O) cm^{-1}. *Anal.* Calcd for $C_{16}H_{14}BrNO$: C, 60.76; H, 4.43; N, 4.43. Found: C, 60.66; H, 4.34; N, 4.48.

10b: 0.83 g, 77% yield, mp 148—149 °C (dec.). IR (KBr): 2220 (C≡C), 1685 (C=O) cm^{-1}. *Anal.* Calcd for $C_{19}H_{20}BrNO$: C, 63.69; H, 5.58; N, 3.91. Found: C, 63.61; H, 5.68; N, 3.92.

10c: 0.91 g, 80% yield, mp 196—198 °C (dec.). IR (KBr): 2220 (C≡C), 1675 (C=O) cm^{-1}. *Anal.* Calcd for $C_{21}H_{16}BrNO$: C, 66.67; H, 4.23; N, 3.70. Found: C, 66.59; H, 4.27; N, 3.75.

Treatment of the Salts (10a—c) with DBU: Formation of 3-Benzoylindolizines (11a—c)——General Procedure: DBU (0.31 ml, 2 mmol) was added dropwise to a mixture of a salt (**10**: 2 mmol) and benzene (10 ml) with stirring. The mixture was refluxed for 12 h with stirring. After cooling, the mixture was washed with saturated NaCl, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane–CH_2Cl_2 (1 : 3) as an eluent to give **11**.

11a: 0.32 g, 67% yield, pale yellow viscous oil. MS *m/z*: 235 (M^+). IR (neat): 1595 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.86 (3H, s, Me), 6.26 (1H, s, 1-H), 6.74 (1H, dd, 6-H), 7.05 (1H, dd, 7-H), 7.3—7.7 (6H, m, 8- and Ph-H), 9.76 (1H, d, 5-H), $J_{5,6}=7$, $J_{6,7}=7$, $J_{7,8}=9$ Hz. *Anal.* Calcd for $C_{16}H_{13}NO$: C, 81.70; H, 5.53; N, 5.95. Found: C, 81.73; H, 5.54; N, 5.98.

11b: 0.33 g, 59% yield, pale yellow viscous oil. MS *m/z*: 277 (M^+). IR (neat): 1590 (C=O) cm^{-1}. ^{1}H-NMR δ: *n*-Bu [0.67 (3H, t, $J=7$ Hz), 0.8—1.5 (4H, m), 2.18 (2H, t, $J=8$ Hz)], 6.22 (1H, s, 1-H), 6.63 (1H, dd, 6-H), 6.92 (1H, dd, 7-H), 7.2—7.4 (6H, m, 8- and Ph-H), 9.49 (1H, d, 5-H), $J_{5,6}=7$, $J_{6,7}=7$, $J_{7,8}=8$ Hz. *Anal.* Calcd for $C_{19}H_{19}NO$: C, 82.31; H, 6.85; N, 5.05. Found: C, 82.28; H, 6.92; N, 5.07.

11c: 0.40 g, 68% yield, mp 136—138 °C (lit.[14] 137—137.5 °C). This compound was identical with an authentic sample prepared by the method of the literature,[14] in which no spectral data were described, so they are reported here. MS *m/z*: 297 (M^+). IR (KBr): 1590 (C=O) cm^{-1}. ^{1}H-NMR δ: 6.39 (1H, s, 1-H), 6.68 (1H, dd, 6-H), 6.8—7.4 (12H, m, 7-, 8-, 2-Ph-, and COPh-H), 9.59 (1H, d, 5-H), $J_{5,6}=7$, $J_{6,7}=7$ Hz.

Treatment of the Salts (10a—c) with Acetic Acid: Formation of 1-Benzoylindolizines (12a—c)——General Procedure: A solution of a salt (**10**: 1 mmol) in AcOH (10 ml) was refluxed with stirring for 12 h and then evaporated *in vacuo*. The residue was extracted with CH_2Cl_2 and the extract was washed with saturated $NaHCO_3$, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel using hexane–CH_2Cl_2 (1 : 3) as an eluent to give **12**.

12a: 115 mg, 49% yield, pale yellow viscous oil. MS *m/z*: 235 (M^+). IR (neat): 1600 (C=O) cm^{-1}. ^{1}H-NMR δ: 2.03 (3H, s, Me), 6.72 (1H, dd, 6-H), 7.09 (1H, dd, 7-H), 7.12 (1H, s, 3-H), 7.3—7.5 (5H, m, Ph-H), 7.95 (1H, d, 5-H), 8.48 (1H, d, 8-H), $J_{5,6}=7$, $J_{6,7}=7$, $J_{7,8}=9$ Hz. *Anal.* Calcd for $C_{16}H_{13}NO$: C, 81.70; H, 5.53; N, 5.95. Found: C, 81.65; H, 5.59; N, 5.86.

12b: 122 mg, 44% yield, mp 68—70 °C, pale yellow needles (from CH_2Cl_2–hexane). MS *m/z*: 277 (M^+). IR (KBr): 1610 (C=O) cm^{-1}. ^{1}H-NMR δ: *n*-Bu [0.71 (3H, t, $J=7$ Hz), 0.9—1.6 (4H, m), 2.36 (2H, t, $J=8$ Hz)], 6.76 (1H, dd, 6-H), 7.13 (1H, dd, 7-H), 7.18 (1H, s, 3-H), 7.3—7.4 (5H, m, Ph-H), 8.00 (1H, d, 5-H), 8.51 (1H, d, 8-H), $J_{5,6}=7$, $J_{6,7}=7$, $J_{7,8}=9$H. *Anal.* Calcd for $C_{19}H_{19}NO$: C, 82.31; H, 6.86; N, 5.05. Found: C, 82.19; H, 6.94; N, 5.07.

12c: 200 mg, 67% yield, mp 133—135 °C (lit.[15] mp 135—136 °C), pale yellow prisms (from CH_2Cl_2–hexane). This compound was identical with an authentic sample prepared by the method of the literature,[15] in which no spectral data were given, so they are reported here. MS *m/z*: 297 (M^+). IR (KBr): 1600 (C=O) cm^{-1}. ^{1}H-NMR δ: 6.57 (1H, dd, 6-H), 6.9—7.5 (11H, m, 7- and Ph-H), 7.14 (1H, s, 3-H), 7.81 (1H, d, 5-H), 7.90 (1H, d, 8-H), $J_{5,6}=7$, $J_{6,7}=7$, $J_{7,8}=9$ Hz.

2-Ethynyl-6-methylpyridines (19a—c)——These compounds were prepared from 2-bromo-6-methylpyridine and corresponding acetylenes, according to the procedure for the preparation of the 2-ethynylpyridines (**9**).

19a: 81% yield, pale yellow oil, bp 114—116 °C (12 mmHg). MS *m/z*: 131 (M^+). IR (neat): 2260 (C≡C) cm^{-1}. ^{1}H-NMR δ: 2.02 (3H, s, Me), 2.48 (3H, s, 6-Me), 6.99 (1H, d, 5-H), 7.13 (1H, d, 3-H), 7.44 (1H, dd, 4-H), $J_{3,4}=8$, $J_{4,5}=7$ Hz. *Anal.* Calcd for C_9H_9N: C, 82.44; H, 6.87; N, 10.68. Found: C, 82.32; H, 6.96; N, 10.71.

19b: 82% yield, pale yellow oil, bp 150—155 °C (20 mmHg). MS *m/z*: 173 (M^+). IR (neat): 2250 (C≡C) cm^{-1}. ^{1}H-NMR δ: *n*-Bu [0.92 (3H, t, $J=7$ Hz), 1.2—1.8 (4H, m), 2.2—2.8 (2H, m)], 2.48 (3H, s, 6-Me), 6.99 (1H, d, 5-H), 7.15 (1H, d, 3-H), 7.46 (1H, dd, 4-H), $J_{3,4}=8$, $J_{4,5}=7$ Hz. *Anal.* Calcd for $C_{12}H_{15}N$: C, 83.23; H, 8.67; N, 8.09. Found: C, 83.19; H, 8.68; N, 7.99.

19c: 79% yield, pale yellow oil, bp 165—168 °C (6 mmHg). MS *m/z*: 193 (M^+). IR (neat): 2250 (C≡C) cm^{-1}. ^{1}H-NMR δ: 2.49 (3H, s, 6-Me), 7.01 (1H, d, $J=7$ Hz, 5-H), 7.2—7.7 (7H, m, 3-, 4-, and Ph-H). *Anal.* Calcd for $C_{14}H_{11}N$: C, 87.04; H, 5.70; N, 7.25. Found: C, 86.94; H, 5.76; N, 7.30.

2-Ethynyl-6-methyl-1-phenacylpyridinium Bromides (20a—c)——Compounds **10a—c** (3 mmol) were treated with phenacyl bromide and worked up as described for the preparation of **10** to give **20a—c**. However, the salts **20** were too hygroscopic to be isolated, and thus were used for the following reaction without purification.

Treatment of the Salts (20a—c) with DBU: Formation of 3-Benzoyl-5-methylindolizines (22a—c) and 2,3-

Diphenylcycl[3.2.2]azine (23c)——The salts **20a—c** were treated with DBU in benzene and worked up as described for **10** to give **22a—c** and **23c**.

22a: 250 mg, 33% yield from **19a**, pale yellow viscous oil. MS *m/z*: 249 (M^+). IR (neat): 1620 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.99 (3H, s, 2-Me), 2.37 (3H, s, 5-Me), 6.37 (1H, s, 1-H), 6.61 (1H, d, 6-H), 7.03 (1H, dd, 7-H), 7.2—7.6 and 7.8—8.0 (4H, m, and 2H, m, 8- and Ph-H), $J_{6,7}=7$, $J_{7,8}=8$ Hz. *Anal.* Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.82; H, 6.08; N, 5.61.

22b: 260 mg, 30% yield from **19b**, pale yellow viscous oil. MS *m/z*: 291 (M^+). IR (neat): 1620 (C=O) cm^{-1}. ^{1}H-NMR δ: *n*-Bu [0.73 (3H, t, $J=7$ Hz), 0.9—1.6 (4H, m), 2.2—2.4 (2H, m)], 2.33 (3H, s, 5-Me), 6.45 (1H, s, 1-H), 6.60 (1H, d, 6-H), 7.04 (1H, dd, 7-H), 7.3—7.6 and 7.9—8.0 (4H, m, and 2H, m, 8- and Ph-H), $J_{6,7}=7$, $J_{7,8}=8$ Hz. *Anal.* Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.51; H, 7.27; N, 4.74.

22c: 560 mg, 61% yield from **19c**, pale yellow viscous oil. MS *m/z*: 311 (M^+). IR (neat): 1630 (C=O) cm^{-1}. ^{1}H-NMR δ: 2.26 (3H, s, 5-Me), 6.39 (1H, d, 6-H), 6.45 (1H, s, 1-H), 6.7—7.3 and 7.5—7.6 (10H, m, and 2H, m, 7-, 8-, and Ph-H), $J_{6,7}=7$ Hz. *Anal.* Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.77; H, 5.56; N, 4.29.

23c: 61 mg, 7% yield from **19c**, mp 123—124 °C, yellow prisms (from benzene–hexane). This compound was identical with an authentic sample prepared by the literature method.[16] ^{1}H-NMR δ: 6.4—6.8 (2H, m), 7.1—7.3 (7H, m), 7.4—7.8 (6H, m).

6-Amino-2-ethynylpyridines (27a—c)——These compounds were prepared from 6-amino-2-bromopyridine[20] and the corresponding acetylenes, according to the procedure for the preparation of the 2-ethynylpyridines (**9**).[11]

27a: 74% yield, mp 97—99 °C, pale yellow prisms (from ether). MS *m/z*: 132 (M^+). IR (KBr): 3340 and 3150 (NH), 2230 (C≡C) cm^{-1}. ^{1}H-NMR δ: 1.97 (3H, s, Me), 4.88 (2H, br, NH_2), 6.40 (1H, d, 5-H), 6.70 (1H, d, 3-H), 7.29 (1H, dd, 4-H), $J_{3,4}=7$, $J_{4,5}=8$ Hz. *Anal.* Calcd for $C_8H_8N_2$: C, 72.73; H, 6.06; N, 21.21. Found: C, 72.70; H, 6.16; N, 21.17.

27b: 80% yield, yellow viscous oil. MS *m/z*: 174 (M^+). IR (neat): 3470 and 3330 (NH), 2240 (C≡C) cm^{-1}. ^{1}H-NMR δ: *n*-Bu [0.89 (3H, t, $J=7$ Hz), 1.1—1.7 (4H, m), 2.33 (2H, t, $J=8$ Hz)], 5.27 (2H, br, NH_2), 6.39 (1H, d, 5-H), 6.78 (1H, d, 3-H), 7.27 (1H, dd, 4-H), $J_{3,4}=8$, $J_{4,5}=8$ Hz. *Anal.* Calcd for $C_{11}H_{14}N_2$: C, 75.86; H, 8.05; N, 16.09. Found: C, 75.77; H, 8.13; N, 16.10.

27c: 85% yield, mp 102—105 °C, yellow prisms (from ether). MS *m/z*: 194 (M^+). IR (KBr): 3470 and 3330 (NH), 2220 (C≡C) cm^{-1}. ^{1}H-NMR δ: 5.04 (2H, br, NH_2), 6.34 (1H, d, 5-H), 6.86 (1H, d, 3-H), 7.31 (1H, dd, 4-H), 7.2—7.4 and 7.5—7.7 (3H, m, and 2H, m, Ph-H), $J_{3,4}=8$, $J_{4,5}=8$ Hz. *Anal.* Calcd for $C_{13}H_{10}N_2$: C, 80.41; H, 5.15; N, 14.43. Found: C, 80.45; H, 5.31; N, 14.33.

Treatment of 27a—c with Phenacyl Bromide: Formation of 5-Ethynyl-2-phenyl-1-azaindolizine Hydrobromides (28a—c)——Compounds **27a—c** (2 mmol) were treated with phenacyl bromide and worked up as described for **10** to give **28**.

28a: 490 mg, 79% yield, mp 213—215 °C (dec.), colorless prisms. IR (KBr): 2240 (C≡C), 1640 (C=N) cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 2.37 (3H, s, Me), 7.5—7.7 and 7.9—8.1 (each 4H, m, 6-, 7-, 8-, and Ph-H), 8.72 (1H, s, 3-H). *Anal.* Calcd for $C_{16}H_{13}BrN_2$: C, 61.34; H, 4.15; N, 8.95. Found: C, 61.20; H, 4.18; N, 8.76.

28b: 550 mg, 78% yield, mp 114—116 °C (dec.), colorless prisms. IR (KBr): 2230 (C≡C), 1640 (C=N) cm^{-1}. ^{1}H-NMR (CD_3OD) δ: *n*-Bu [1.02 (3H, m), 1.4—1.9 (4H, m), 2.81 (2H, t, $J=7$ Hz)], 7.5—7.7 and 7.9—8.1 (each 4H, m, 6-, 7-, 8-, and Ph-H), 8.68 (1H, s, 3-H). *Anal.* Calcd for $C_{19}H_{19}BrN_2$: C, 64.22; H, 5.35; N, 7.88. Found: C, 63.90; H, 5.39; N, 7.70.

28c: 650 mg, 87% yield, mp 211—215 °C (dec.), colorless needles. IR (KBr): 2210 (C≡C), 1635 (C=N) cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 7.5—7.9 and 8.0—8.1 (9H, m, and 4H, m, 6-, 7-, 8-, and Ph-H), 8.76 (1H, s, 3-H). *Anal.* Calcd for $C_{21}H_{15}BrN_2$: C, 67.20; H, 4.00; N, 7.47. Found: C, 67.03; H, 4.02; N, 7.47.

Treatment of 28a—c with DBU: Formation of 2-Phenyl-1-azacycl[3.2.2]azines (29a—c)——The salts **28a—c** (1 mmol) were treated with DBU and worked up as described for the treatment of **10** with DBU to give **29**.

29a: 160 mg, 72% yield, mp 121—124 °C, pale yellow needles (from CH_2Cl_2–hexane). MS *m/z*: 232 (M^+). ^{1}H-NMR δ: 1.99 (3H, s, 3-Me), 6.7—7.0, 7.2—7.6, and 7.8—8.1 (2H, m, 4H, m, and 2H, m, 5-, 6-, 7-, and Ph-H), 7.95 (1H, s, 4-H). *Anal.* Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.74; H, 5.09; N, 12.12.

29b: 190 mg, 70% yield, pale yellow viscous oil. MS *m/z*: 274 (M^+). ^{1}H-NMR δ: 3-*n*-Bu [0.98 (3H, t, $J=7$ Hz), 1.3—1.9 (4H, m), 2.54 (2H, t, $J=8$ Hz)], 6.8—7.1, 7.2—7.6, and 7.8—8.0 (2H, m, 4H, m, and 2H, m, 5-, 6-, 7-, and Ph-H), 8.03 (1H, s, 4-H). *Anal.* Calcd for $C_{19}H_{18}N_2$: C, 83.17; H, 6.61; N, 10.21. Found: C, 83.05; H, 6.65; N, 10.08.

29c: 230 mg, 79% yield, mp 124—126 °C, pale yellow needles (from CH_2Cl–hexane). MS *m/z*: 294 (M^+). ^{1}H-NMR δ: 6.9—7.1, 7.3—7.7, and 7.4—8.1 (2H, m, 9H, m, and 2H, m, 5-, 6-, 7-, and Ph-H), 8.06 (1H, s, 4-H). *Anal.* Calcd for $C_{21}H_{14}N_2$: C, 85.69; H, 4.79; N, 9.52. Found: C, 85.61; H, 4.78; N, 9.38.

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