

Studies on Diazepines. VII.¹⁾ Syntheses of Novel 1H-1,2-Diazepines condensed with Aromatic Heterocyclic Rings

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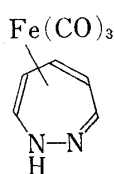
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Irradiation of the fused pyridinium ylides (6) or their dimers (7), prepared from 1,5- and 1,8-naphthyridine, thieno[2,3-*b*]- and thieno[3,2-*b*]-pyridine, and furo[2,3-*b*]-pyridine by N-amination with O-mesitylenesulfonylhydroxylamine followed by treatment with base, resulted in the formation of the corresponding fused 1H-1,2-diazepines (8), which are previously unknown bicyclic ring systems. However, a similar synthetic route from the pyrrolopyridines (10) failed to yield pyrrolodiazepines.

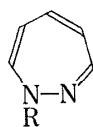
Keywords—photolysis; ring-expansion; N-ylides of fused pyridines; diazepines; 1H-1,2-pyridodiazepines; 1H-1,2-thienodiazepines; 1H-1,2-furodiazepine

Since Streith³⁾ first showed in 1968 that the photolysis of N-acyliminopyridinium ylides gives the previously unknown 1H-1,2-diazepines, the chemistry of the new ring system has been widely investigated.⁴⁻⁶⁾

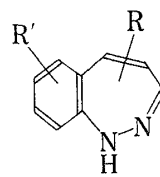
The monocyclic 1H-1,2-diazepines are 8 π -electron aza-analogs of the unstable cycloheptatrienyl anion and can be isolated only as their iron tricarbonyl complexes (1)⁵⁾ or N-substituted derivatives (2)⁶⁾ whose substituents are electron withdrawing groups such as acyl groups, as shown in Chart 1. However, we have previously reported⁷⁾ the general synthesis of the fully unsaturated 1H-1,2-benzodiazepines (3) from N-iminoquinolinium ylide dimers by irradiation. These benzodiazepines (3) are the first examples of N-unsubstituted 1H-1,2-diazepines. The stability of the benzodiazepines appears to depend on the aromaticity of the benzene ring.



1



2



3

R = COMe, CO₂R'
SO₂Ar, etc.

R, R' = H, Me, Cl, OMe,
CO₂Me, OAc, etc.

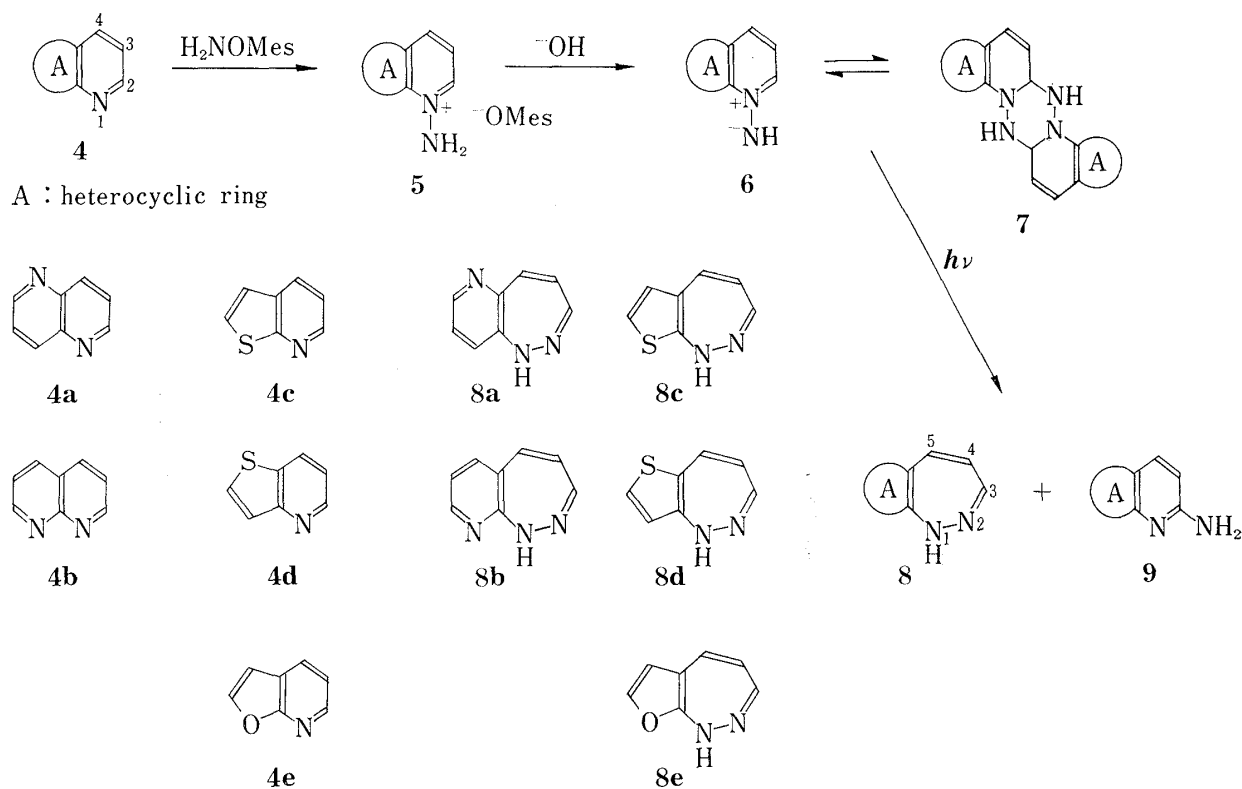
Chart 1

- 1) Part VI: T. Tsuchiya, H. Arai, H. Hasegawa, and H. Igeta, *Chem. Pharm. Bull.* (Tokyo), **26**, 2205 (1978).
- 2) Location: *Kanagawa-machi, Kanazawa*, 920-11, Japan.
- 3) J. Streith and J.M. Cassal, *Angew. Chem. Intern. Ed. Engl.*, **7**, 129 (1968).
- 4) For a review, see M. Nastasi, *Heterocycles*, **4**, 1509 (1976).
- 5) A.J. Carty, R.F. Hobson, H.A. Patel, and V. Snieckus, *J. Am. Chem. Soc.*, **95**, 6835 (1973); D.J. Harris and V. Snieckus, *J. Chem. Soc. Chem. Commun.*, **1976**, 844.
- 6) J. Streith, A. Blind, J.M. Cassal, and C. Sigwalt, *Bull. Soc. Chim. France*, **1969**, 948; T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (1970); A. Balasubramanian, J.M. McIntosh, and V. Snieckus, *ibid.*, **35**, 433 (1970); R.A. Abramovitch and T. Takaya, *ibid.*, **38**, 3311 (1973).
- 7) T. Tsuchiya, J. Kurita, H. Igeta, and V. Snieckus, *J. Chem. Soc. Chem. Commun.*, **1974**, 640; T. Tsuchiya, J. Kurita, and V. Snieckus, *J. Org. Chem.*, **42**, 1856 (1977); T. Tsuchiya and J. Kurita, *Chem. Pharm. Bull.* (Tokyo), **26**, 1896 (1978).

In connection with the above-mentioned results, we were interested in the preparation of 1,2-diazepines condensed with various aromatic heterocyclic rings. We report here the syntheses of some pyrido-, thieno-, and furo-1H-1,2-diazepines, all of which are previously unknown bicyclic ring systems.⁸⁾

The fused pyridines, 1,5- and 1,8-naphthyridine (**4a** and **4b**), thieno[2,3-*b*]- and thieno[3,2-*b*]-pyridine (**4c** and **4d**), and furo[2,3-*b*]pyridine (**4e**) were aminated with O-mesitylene-sulfonylhydroxylamine according to the method of Tamura *et al.*⁹⁾ to give the corresponding N-aminopyridinium mesitylenesulfonates (**5**) in good yields.

Treatment of the N-iminonaphthyridinium salts (**5a, b**) with potassium carbonate gave the N-iminonaphthyridinium ylide dimers (**7**) in *ca.* 65% yields, presumably *via* the ylides (**6**) by analogy with the case of N-iminoquinolinium ylides.^{7,10)} Irradiation of the dimers (**7a, b**) in methylene chloride solution containing acetic acid resulted in the formation of the corresponding pyrido-1H-1,2-diazepines (**8a, b**) in *ca.* 25% yields.



Though the thieno- and furo-pyridinium salts (**5c—e**) did not yield the corresponding dimers upon treatment with bases, treatment of these salts with potassium hydroxide in methanol, followed by irradiation of the solution presumably containing the ylides (**6**) gave the thieno[2,3-*c*]- (**8c**), thieno[3,2-*c*]- (**8d**), and furo[2,3-*c*]- (**8e**) 1H-1,2-diazepines in 70%, 65%, and 15–20% yields, respectively. Small amounts of 2-aminothienopyridines (**9c** and **9d**) and 2-aminofuro[2,3-*b*]pyridine (**9e**) were isolated in addition to the diazepines.

The ¹H nuclear magnetic resonance (NMR) spectral data of the diazepines thus obtained are consistent with the proposed structures and rule out the tautomeric 2H-, 3H-, and 5H-1,2-diazepine structures by analogy with the case of 1H-1,2-benzodiazepines.⁷⁾ Charac-

8) A part of this work has been published in a preliminary communication: T. Tsuchiya, M. Enkaku, and H. Sawanishi, *Heterocycles*, **9**, 621 (1978).

9) Y. Tamura, J. Minamikawa, and M. Ikeda, *Synthesis*, **1977**, 1; and refs. cited therein.

10) T. Okamoto, M. Hirobe, and T. Yamazaki, *Chem. Pharm. Bull.* (Tokyo), **14**, 512 (1966).

terization of the new fused diazepines (**8**) and 2-aminopyridines (**9**) by infrared (IR), ultraviolet (UV), and mass (MS) spectrometry was also carried out (see "Experimental").

Next, the pyrrolo[2,3-*b*]pyridines (**10a–c**) were also N-aminated to give the corresponding mesitylenesulfonates (**11**) in high yields. An analogous route to the pyrrolo-diazepine derivative from the salt (**11a**: R=H) failed because the ylide (**12**) formed by base treatment tautomerizes rapidly to 7-amino-7H-7-azaindole (**13**),¹¹⁾ which can be isolated almost quantitatively. Irradiation of the indole (**13**) resulted in recovery of almost all the starting material and gave no diazepine derivative. On the other hand, the salts (**11b**: R≠H) whose ylides do not undergo tautomerization were irradiated as described for the thieno- and furo-analogs to yield the corresponding diazepines (**14**); these transformations were confirmed by ¹H-NMR spectral analysis of the residue obtained by careful and rapid evaporation of the photolysate at a low temperature. However, the diazepines (**14**) gradually decomposed during separation and could not be isolated.

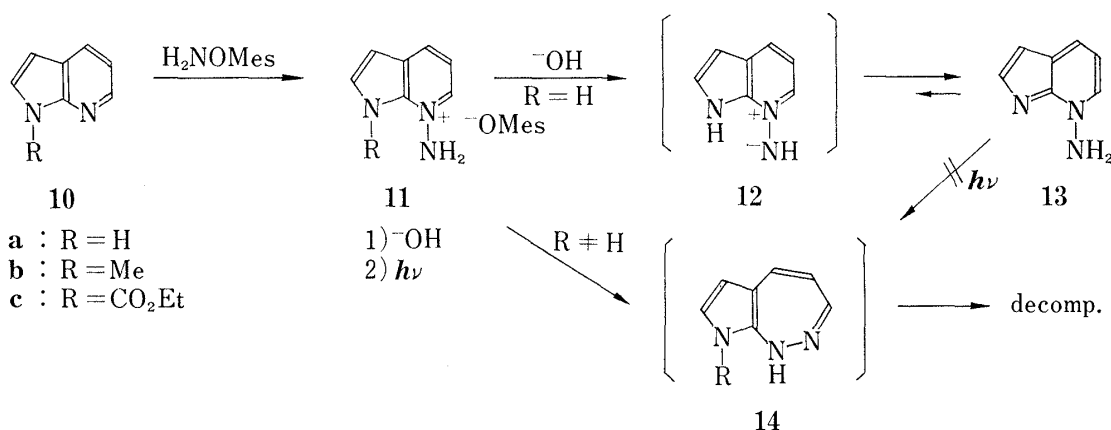


Chart 3

The N-unsubstituted diazepines (**8a, b**) condensed with a pyridine ring were isolated as stable crystals, as in the case of benzodiazepines. However, the thienodiazepines (**8c, d**) are less stable than **8a, b** but more stable than the furodiazepine (**8e**), which decomposes gradually on standing. Furthermore the diazepines (**14**) condensed with an N-substituted pyrrole ring are too unstable to be isolated. These results suggest that the stability of the 1,2-diazepines depends on the aromaticity of the heterocyclic ring condensed with the diazepines, as expected.

Experimental

Melting points were measured on a Yamato MP-21 apparatus and are uncorrected. IR spectra were determined with a JASCO IRA-2 spectrometer and MS spectra were obtained with a JEOL JMS-D100 instrument. NMR spectra were recorded on a JEOL JNM-MH100 spectrometer in CDCl₃ solution using tetramethylsilane as an internal standard unless otherwise stated, and spectral assignments were confirmed by spin-decoupling experiments and, in the case of NH protons, by exchange with D₂O. UV spectra were recorded on a Hitachi 323 spectrophotometer. Microanalyses were performed in the Microanalytical laboratory of this school by Miss R. Hamano. Photolyses were carried out under a nitrogen atmosphere using an immersion apparatus equipped with a 400 W high-pressure Hg lamp and a Pyrex filter, which was cooled internally with running water.

Materials—1,5- and 1,8-naphthyridine,¹²⁾ thieno-[2,3-*b*]- and thieno[3,2-*b*]-pyridine,¹³⁾ furo[2,3-*b*]pyri-

11) The structure of **13** was confirmed by spectral comparison with 7-methyl-7H-7-azaindole prepared from indole by the reported method (ref. 16).

12) H. Rappoport and A.D. Batcho, *J. Org. Chem.*, **28**, 1753 (1963).

13) L.H. Klemm, C.E. Klopfenstein, R. Zell, D.R. McCoy, and R.A. Klemm, *J. Org. Chem.*, **34**, 347 (1969).

dine,¹⁴) pyrrolo[2,3-*b*]pyridine,¹⁵) and 7-methylpyrrolo[2,3-*b*]pyridine¹⁶) were prepared by the reported procedures.

Preparation of N-Aminopyridinium Mesitylenesulfonates (5a—e)—General procedure: The procedure of Tamura and co-workers¹⁷) for the preparation of **5a** and **5b** was employed. A solution of O-mesitylenesulfonylhydroxylamine (1.1 mol equiv.) in CH₂Cl₂ (100—150 ml) was added dropwise to a solution of the condensed pyridine derivative (**4**: 0.05—0.1 mol) in CH₂Cl₂ (ca. 50 ml) with constant stirring at room temperature. The reaction mixture was stirred for a further 1 hr and then cooled in an ice bath. After addition of ether (200—400 ml) to the mixture, the resulting crystalline precipitates were collected and recrystallized from ethanol or ethanol-ethyl acetate to give the salt (**5**).

5a: 84% yield, mp 193—195° (brown needles).

5b: 87% yield, mp 149—152° (yellow prisms).

5c: 98% yield, mp 155—156.5° (colorless prisms). NMR (CD₃OD) δ : 7.70 (1H, d, 5-H), 7.86 (1H, dd, 3-H), 8.06 (1H, d, 6-H), 8.75 (1H, d, 4-H), 8.94 (1H, d, 2-H), $J_{2,3}=7$, $J_{3,4}=8$ Hz, -OMes [2.19 (3H, br), 2.55 (6H, br), 6.78 (2H, br)]. Anal. Calcd. for C₁₆H₁₈N₂O₃S₂: C, 54.82; H, 5.18; N, 7.99. Found: C, 54.77; H, 5.16; N, 7.93.

5d: 97% yield, mp 163—164° (colorless plates). NMR (CD₃OD) δ : 7.82 (1H, dd, 3-H), 7.98 (1H, d, 6-H), 8.60 (1H, d, 5-H), 8.90 (1H, d, 2-H), 8.93 (1H, d, 4-H), $J_{2,3}=5$, $J_{3,4}=9$ Hz, -OMes [2.20 (3H, br), 2.58 (6H, br), 6.82 (2H, br)]. Anal. Calcd. for C₁₆H₁₈N₂O₃S₂: C, 54.82; H, 5.18; N, 7.99. Found: C, 54.57; H, 5.18; N, 7.96.

5e: 78% yield, mp 153—154° (colorless plates). NMR (CD₃OD) δ : 7.31 (1H, d, 5-H), 7.71 (1H, dd, 3-H), 8.23 (1H, d, 6-H), 8.55 (1H, d, 4-H), 8.59 (1H, d, 2-H), $J_{2,3}=6$, $J_{3,4}=7$ Hz, -OMes [2.21 (3H, br), 2.58 (6H, br), 6.78 (2H, br)]. Anal. Calcd. for C₁₆H₁₈N₂O₄S: C, 57.43; H, 5.43; N, 8.38. Found: C, 57.45; H, 5.38; N, 8.27.

N-Iminonaphthyridinium Ylide Dimers (7a, b)—A solution of potassium carbonate (3.24 g, 23 mmol) in water (70 ml) was added dropwise to a solution of the N-iminonaphthyridinium salts (**5a, b**: 8 g, 23 mmol) in water (140 ml) with stirring at room temperature. After stirring for an additional 30 min in an ice bath, the resulting crystalline precipitate was collected by filtration and washed with cold water and then with several portions of methanol to give the dimers (**7a, b**), which were used in the following photolysis without further purification. Further reprecipitation with 5% aqueous potassium hydroxide solution from an aqueous 5% hydrogen chloride solution of the dimer furnished an analytical sample.

7a: 63% yield, mp 186° (decomp.). Anal. Calcd. for C₁₆H₁₄N₆: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.02; H, 4.83; N, 29.08.

7b: 65% yield, mp 169° (decomp.). Anal. Calcd. for C₁₆H₁₄N₆: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.05; H, 4.72; N, 28.85.

1H-1,2-Pyridodiazepines (8a, b)—A solution of the dimers (**7a, b**: 2 g) and acetic acid (4 g) in CH₂Cl₂ (350 ml) was irradiated for 5—6 hr. Acetic acid was removed by extraction with satd. NaHCO₃, then the reaction solution was washed with water, dried over MgSO₄, and evaporated to dryness. The resulting residue was chromatographed on alumina, eluting with CH₂Cl₂, to give the diazepines (**8a, b**), which were recrystallized from isopropyl ether (IPE)-benzene mixture.

Pyrido[3,2-*c*]-1H-1,2-diazepine (**8a**): 25% yield, mp 119—120° (red needles). MS m/e : 145 (M⁺). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3200 (NH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 232 (16000), 306 (3000). NMR δ : 6.18 (1H, dd, 4-H), 7.02 (1H, d, 5-H), 7.16 (1H, d, 3-H), 6.8—7.3 (2H, m, 7- and 8-H), 8.26 (1H, d, 6-H), 6.6 (1H, br, NH), $J_{3,4}=4$, $J_{4,5}=11$ Hz. Anal. Calcd. for C₈H₇N₃: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.18; H, 4.87; N, 28.93.

Pyrido[2,3-*c*]-1H-1,2-diazepine (**8b**): 20% yield, mp 113—114° (red prisms). MS m/e : 145 (M⁺). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3250 (NH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 234 (19000), 313 (2000). NMR δ : 5.84 (1H, dd, 4-H), 6.58 (1H, d, 5-H), 6.87 (1H, d, 7-H), 7.02 (1H, d, 3-H), 7.24 (1H, d, 6-H), 8.09 (1H, d, 8-H), 7.3 (1H, br, NH), $J_{3,4}=4$, $J_{4,5}=11$ Hz. Anal. Calcd. for C₈H₇N₃: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.06; H, 4.81; N, 28.91.

Thieno- and Furo-1H-1,2-diazepines (8c—e), and 2-Aminopyridines (9c—e)—A solution of KOH (1.12 g, 20 mmol) in MeOH (10 ml) was added dropwise to a solution of the salts (**5c, d**: 3.5 g, **5e**: 3.34 g, 10 mmol) in MeOH (350 ml) over a 30 min period under irradiation. The mixture was irradiated for ca. 1 hr longer and then concentrated *in vacuo* below 30°. The residue was extracted with ether and the extract was washed with satd. NaCl, dried over MgSO₄, and evaporated to dryness *in vacuo*. The resulting residue was chromatographed on alumina, eluting with *n*-hexane-ether, to give the diazepines (**8**) and 2-aminopyridine derivatives (**9**), successively.

Thieno[2,3-*c*]-1H-1,2-diazepine (**8c**): ca. 70% yield, mp 81—83°, red needles (from IPE). MS m/e : 150 (M⁺). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3200 (NH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 250 (11000). NMR δ : 5.98 (1H, dd, 4-H), 6.67 (1H, d, 6-H),

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15) R.R. Lorentz, B.F. Tullar, C.F. Koelsch, and S. Archer, *J. Org. Chem.*, **30**, 2531 (1965).

16) M.M. Robison and B.L. Robison, *J. Am. Chem. Soc.*, **77**, 6554 (1955).

17) Y. Tamura, Y. Miki, J. Minamikawa, and M. Ikeda, *J. Heterocyclic Chem.*, **11**, 657 (1974).

6.75 (1H, d, 7-H), 6.81 (1H, d, 5-H), 6.94 (1H, d, 3-H), 6.8 (1H, br, NH), $J_{3,4}=4$, $J_{4,5}=11$ Hz. *Anal.* Calcd. for $C_7H_6N_2S$: C, 55.98; H, 4.03; N, 18.65. Found: C, 56.01; H, 4.02; N, 18.60.

Thieno[3,2-*c*]-1H-1,2-diazepine (**8d**): 65% yield, mp 94–95°, red needles (from IPE). MS m/e : 150 (M^+). IR $\nu_{\max}^{KBr}$ cm^{-1} : 3250 (NH). UV $\lambda_{\max}^{EtOH}$ nm (ϵ): 277 (10000). NMR δ : 5.92 (1H, dd, 4-H), 6.42 (1H, d, 7-H), 6.68 (1H, d, 5-H), 6.83 (1H, d, 3-H), 7.28 (1H, d, 6-H), 6.6 (1H, br, NH), $J_{3,4}=4$, $J_{4,5}=11$ Hz. *Anal.* Calcd. for $C_7H_6N_2S$: C, 55.98; H, 4.03; N, 18.65. Found: C, 55.91; H, 4.00; N, 18.62.

Furo[2,3-*c*]-1H-1,2-diazepine (**8e**): 15–20% yield, red viscous oil. MS m/e : 134 (M^+). IR $\nu_{\max}^{EtOH}$ cm^{-1} : 3250 (NH). UV $\lambda_{\max}^{EtOH}$ nm: 255. NMR δ : 5.28 (1H, dd, 4-H), 5.70 (1H, d, 6-H), 5.99 (1H, d, 5-H), 6.46 (2H, m, 3- and 7-H), 6.4 (1H, br, NH), $J_{3,4}=4$, $J_{4,5}=11$ Hz. *Anal.* Calcd. for $C_7H_6N_2O$: C, 62.68; H, 4.51; N, 20.89. Found: C, 62.45; H, 4.51; N, 20.62.

2-Amino-thieno[2,3-*b*]pyridine (**9c**): 6% yield, mp 121.5–123°. Colorless needles (from benzene–IPE). MS m/e : 150 (M^+). IR $\nu_{\max}^{KBr}$ cm^{-1} : 3150 and 3400 (NH). UV $\lambda_{\max}^{EtOH}$ nm (ϵ): 240 (22000), 322 (6000). NMR δ : 6.48 (1H, d, 3-H), 7.09 (2H, br s, 5- and 6-H), 7.78 (1H, d, 4-H), 4.7 (1H, br NH). *Anal.* Calcd. for $C_7H_6N_2S$: C, 55.98; H, 4.03; N, 18.65. Found: C, 56.03; H, 4.02; N, 18.53.

2-Amino-thieno[3,2-*b*]pyridine (**9d**): ca. 10% yield, mp 148–149°, colorless plates (from benzene–IPE). MS m/e : 150 (M^+). IR $\nu_{\max}^{KBr}$ cm^{-1} : 3350 (NH). UV $\lambda_{\max}^{EtOH}$ nm (ϵ): 254 (14000), 328 (6000). NMR δ : 6.60 (1H, d, 3-H), 7.27 (1H, d, 6-H), 7.61 (1H, d, 5-H), 7.88 (1H, d, 4-H), 4.5 (1H, br, NH). *Anal.* Calcd. for $C_7H_6N_2S$: C, 55.98; H, 4.03; N, 18.65. Found: C, 56.01; H, 3.99; N, 18.72.

2-Amino-furo[2,3-*b*]pyridine (**10e**): 4–5% yield, red viscous oil. MS m/e : 134 (M^+). IR $\nu_{\max}^{EtOH}$ cm^{-1} : 3350 (NH). UV $\lambda_{\max}^{EtOH}$ nm: 254, 317. NMR δ : 6.41 (1H, d, 3-H), 6.56 (1H, d, 5-H), 7.37 (1H, d, 6-H), 7.61 (1H, d, 4-H), 4.5 (1H, br, NH).

7-Ethoxycarbonyl-pyrrolo[2,3-*b*]pyridine (**10c**)—A solution of pyrrolo[2,3-*b*]pyridine (**10a**: 9.44 g, 80 mmol) in dry xylene (100 ml) was added dropwise to a refluxing suspension of $NaNH_2$ (4.17 g, 104 mmol) in xylene (150 ml), and the mixture was refluxed for a further 7 hr. After cooling, a solution of ethyl chloroformate (11.25 g, 104 mmol) in xylene (30 ml) was added to the reaction mixture and the mixture was refluxed for a further 2.5 hr. The reaction mixture was extracted with dil. HCl and the extract was made alkaline with K_2CO_3 . The alkaline solution was extracted with CH_2Cl_2 and the extract was washed with water, dried, and evaporated to dryness. The residue was chromatographed on silica gel, eluting with CH_2Cl_2 , to give **10c**: 72% yield, mp 38–40°, colorless needles (from IPE). NMR δ : 1.49 and 4.60 (3H, t, and 2H, q, CO_2Et), 6.58 (1H, d, 3-H), 7.23 (1H, dd, 5-H), 7.78 (1H, d, 2-H), 7.94 (1H, d, 4-H), 8.58 (1H, d, 6-H), $J_{4,5}=8$, $J_{5,6}=4$ Hz. *Anal.* Calcd. for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.12; H, 5.39; N, 14.73.

7-Amino-pyrrolo[[2,3-*b*]pyridinium Mesitylenesulfonates (**11a–c**)—Pyrrolo[2,3-*b*]pyridine (**11a–c**: 1–2 g) was treated with O-mesitylenesulfonylhydroxylamine (1.1 mol equiv.) and the product was worked up as described for **5** to give the salts (**11**), which were recrystallized from EtOH–AcOEt mixture.

11a: 94% yield, mp 171–173°, colorless plates. IR $\nu_{\max}^{KBr}$ cm^{-1} : 3250, 3150 (NH). NMR (CD_3OD) δ : 6.84 (1H, d, 3-H), 7.42 (1H, dd, 5-H), 7.66 (1H, d, 2-H), 8.42 (1H, d, 6-H), 8.46 (1H, d, 4-H), $J_{4,5}=8$, $J_{5,6}=6$ Hz, $-OMes$ [2.20 (3H, br s), 2.57 (6H, br s), 6.77 (2H, br s)]. *Anal.* Calcd. for $C_{16}H_{16}N_3O_3S$: C, 57.64; H, 5.74; N, 12.60. Found: C, 57.60; H, 5.70; N, 12.63.

11b: 83% yield, mp 159–161°, colorless needles. NMR (CD_3OD) δ : 4.31 (3H, s, N–Me), 6.87 (1H, d, 3-H), 7.42 (1H, dd, 5-H), 7.59 (1H, d, 2-H), 8.42 (1H, d, 6-H), 8.49 (1H, d, 4-H), $J_{4,5}=8$, $J_{5,6}=6$ Hz. *Anal.* Calcd. for $C_{17}H_{21}N_3O_3S$: C, 58.77; H, 6.09; N, 12.09. Found: C, 58.71; H, 6.04; N, 12.11.

11c: 86% yield, mp 107–109°, colorless needles. NMR (CD_3OD) δ : 1.52 and 4.62 (3H, t, and 2H, q, CO_2Et), 7.03 (1H, d, 3-H), 7.73 (1H, d, 5-H), 8.03 (1H, d, 2-H), 8.55 (1H, d, 4-H), 8.59 (1H, d, 6-H), $J_{4,5}=8$, $J_{5,6}=6$ Hz. *Anal.* Calcd. for $C_{19}H_{23}N_3O_5S$: C, 56.28; H, 5.72; N, 10.36. Found: C, 55.93; H, 5.70; N, 10.18.

7-Amino-7H-7-azaindole (**13**)—A solution of the salt (**11a**: 1 g) in water (30 ml) was treated with a solution of potassium carbonate (0.6 g) in water (10 ml) with stirring at room temperature. After stirring for an additional 1 hr, the reaction mixture was extracted with CH_2Cl_2 and the extract was washed with water, dried, and concentrated. The resulting residue was recrystallized from benzene to give the indole (**13**) quantitatively: mp 148–149.5°, pale yellow needles. MS m/e : 133 (M^+). IR $\nu_{\max}^{KBr}$ cm^{-1} : 3200 (NH). UV $\lambda_{\max}^{EtOH}$ nm (ϵ): 238 (19000), 308 (10000). NMR δ : 6.68 (1H, d, 3-H), 6.81 (1H, t, 5-H), 7.80 (1H, d, 4-H), 7.84 (1H, d, 2-H), 8.06 (1H, d, 6-H), 6.5 (2H, br, NH_2), $J_{5,6}=8$, $J_{4,5}=6$ Hz. *Anal.* Calcd. for $C_7H_7N_3$: C, 63.12; H, 5.30; N, 31.55. Found: C, 63.12; H, 5.24; N, 31.33.

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