Condensation Reactions of (1*E*,3*E*)-4-Amino-3-cyano-4-methoxy-1-phenyl-2-azabutadiene and Electrocyclizations of Diazatrienes

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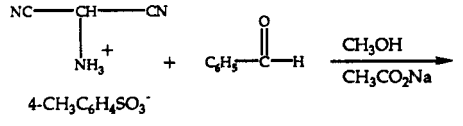
(1*E*,3*E*)-4-Amino-3-cyano-4-methoxy-1-phenyl-2-azabutadiene (**2**) reacts with 2-methoxypropene in refluxing methylbenzene in the presence of catalytic pyridinium *p*-toluenesulfonate (PPTS) to give 2-cyano-5,5-dimethyl-3-methoxy-6-phenyl-4,5-dihydro-1,4-diazabenzene (**5**). Similarly, 2-aza-1,3-butadiene **2** reacts with triethyl orthoformate and triethyl orthobenzoate to give 3-cyano-2-methoxy-5-phenyl-1,4-diazabenzene (**6**) and 2-cyano-3-methoxy-5,6-diphenyl-1,4-diazabenzene (**7**), respectively. The PPTS-catalyzed reaction of **2** with triethyl orthoacetate gives 2-cyano-3-methoxy-5-methyl-6-phenyl-1,4-diazabenzene (**8**) and 2-cyano-5-ethoxy-3-methoxy-5-methyl-6-phenyl-4,5-dihydro-1,4-diazabenzene (**9**). Phenylmethanal and (2-thienyl)methanal react with 2-aza-1,3-butadiene **2** to give 5-methoxy-2,3-diphenyl-1,4-diazabenzene (**17**) and 5-methoxy-2-phenyl-3-(2-thienyl)-1,4-diazabenzene (**18**), respectively. Diazatrienes (enediimines) are proposed as the intermediates undergoing six π-electron electrocyclizations to 1,4-diazabenzenes (dihydropyrazines, pyrazines, and pyrazinecarbonitriles).

2-Aza-1,3-dienes are valuable substrates for the construction of heterocyclic compounds and natural products syntheses by cycloaddition reactions with dienophiles.[1-8] Although a number of synthetic methods are available for the preparation of 2-aza-1,3-butadienes, many of the procedures require difficultly accessible substrates and/or tedious experimental manipulations. It has been observed that aminopropanedinitrile 4-methylbenzenesulfonate (ammoniopropanedinitrile *p*-toluenesulfonate, aminomalononitrile *p*-toluenesulfonate (tosylate), AMNT, **1**) reacts with aromatic aldehydes in methanolic sodium ethanoate via 2-azaallyl anions and/or azomethine ylides to give (1*E*,3*E*)-4-amino-1-aryl-3-cyano-4-methoxy-2-azabutadienes **2** and *trans*-3,6-diaryl-2,2,5,5-tetracyanopiperazines **3** (eq 1).[9-14] Structure **2** suggests that appropriate reactions at the amino group could lead to the relatively rare diazatrienes,[15-19] which would also be valuable building blocks to heterocycles via cycloadditions and/or electrocyclizations.



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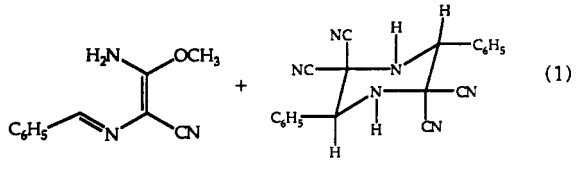
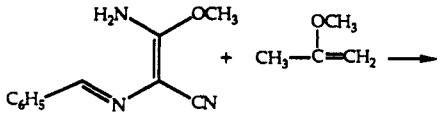


2 **3** (1)

Although preliminary experiments with **2** and dienophiles (dimethyl acetylenedicarboxylate (DMAD),[20a,b] *N*-phenylmaleimide,[20c] tetracyanoethene[20c]) were unsuccessful, it reacted with 2-methoxypropene (isopropenyl methyl ether) in refluxing methylbenzene in the presence of catalytic amounts of pyridinium *p*-toluenesulfonate (PPTS)[21] to give 2-cyano-5,5-dimethyl-3-methoxy-6-phenyl-4,5-dihydro-1,4-diazabenzene (pyrazine-2-carbonitrile, **5**, 82%, eq 2). Its structure was determined by single-crystal X-ray crystallographic analysis,[22] infrared, ultraviolet, ^{1}H NMR, and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analyses. The enol ether 2-methoxypropene is protonated on C-1 to give rise to a stable carbocation which can undergo nucleophilic addition by the nitrogen atom of the amino group in 2-aza-1,3-butadiene **2**.[23] Proton transfer from nitrogen to oxygen followed by loss of methanol affords (2*E*,4*E*,6*E*)-5-cyano-4-methoxy-1-methyl-7-phenylheptatriene (**4**), which undergoes electrocyclization followed by a 1,5-hydrogen shift

(1) Presented in part at the 13th International Congress of Heterocyclic Chemistry, Corvallis, OR, August 11, 1991.
(2) Boger, D. L.; Weinreb, S. N. *Hetero Diels–Alder Methodology In Organic Synthesis*; Academic Press: San Diego, 1987; Chapter 9.
(3) Fringuelli, F.; Taticchi, A. *Dienes in the Diels–Alder Reaction*; Wiley: New York, 1990.
(4) (a) Ciganek, E. *Org. React.* **1984**, *32*, 1. (b) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183.
(5) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63.
(6) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10.
(7) Carlson, R. G. *Ann. Rep. Med. Chem.* **1974**, *9*, 270.
(8) De Kimpe, N.; Yao, Z.-P.; Boeykens, M.; Nagy, M. *Tetrahedron Lett.* **1990**, *31*, 2771.
(9) Freeman, F.; Kim, D. S. H. L. *J. Org. Chem.* **1991**, *56*, 657.
(10) Freeman, F.; Kim, D. S. H. L. *Synthesis* **1989**, 698.
(11) Freeman, F.; Kim, D. S. H. L.; Ziller, J. W. *Acta Crystallogr. C* **1991**, *47*, 2122.
(12) Freeman, F.; Kim, D. S. H. L.; Ziller, J. W. *Acta Crystallogr. C* **1991**, *47*, 2124.
(13) Linn, W. J.; Ciganek, E. *J. Org. Chem.* **1969**, *34*, 2146.
(14) Lown, J. W.; Matsumoto, K. *Can. J. Chem.* **1972**, *50*, 534.
(15) Diazatrienes (enediimines) are intermediates in the photorearrangements of 2,3-dihydropyrazines[16] and 1,3-diazabicyclo[3.1.0]hex-3-enes.[17,18] 4,5-Di(*tert*-butyl)-1,1,1,8,8,8-hexafluoro-2,7-bis(trifluoromethyl)-3,6-diazaocta-2,4,6-triene has been isolated from the thermal cycloreversion of 5-*tert*-butyl-3,3-bis(trifluoromethyl)-2,2,2-trimethoxy-2,2-dihydro-1,4,2-oxaphosphol-4-ene.[19]
(16) (a) Beak, P.; Miesel, J. L. *J. Am. Chem. Soc.* **1967**, *89*, 2375. (b) Padwa, A.; Smolanoff, J.; Wetmore, S. I., Jr. *J. Chem. Soc., Chem. Commun.* **1972**, 409. (c) Padwa, A.; Wetmore, S. I., Jr. *J. Chem. Soc., Chem. Commun.* **1972**, 1116. (d) Arnold, D. R.; Abraitys, V. Y.; McLeod, D. *Can. J. Chem.* **1971**, *49*, 923. (e) Matsuura, T.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1724.
(17) (a) Padwa, A.; Clough, S.; Glazer, E. *J. Am. Chem. Soc.* **1970**, *92*, 1778. (b) Padwa, A.; Glazer, E. *J. Chem. Soc., Chem. Commun.* **1971**, 838. (c) Padwa, A.; Glazer, E. *J. Org. Chem.* **1973**, *38*, 284.
(18) (a) Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 1954. (b) Orahovats, A.; Heimgartner, H.; Schmid, H.; Heinzelmann, W. *Helv. Chim. Acta* **1975**, *58*, 2662.
(19) Burger, K.; Goth, H.; Einhellig, K.; Gieren, A. *Z. Naturforsch.* **1981**, *36b*, 345.
(20) (a) Gompper, R.; Heinemann, U. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 296. (b) Gompper, R.; Heinemann, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 217. (c) Caglioti, L.; Rosini, G.; Tundo, P.; Vigevani, A. *Tetrahedron Lett.* **1970**, 2349.
(21) (a) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772. (b) Anderson, R. C.; Fraser-Reid, B. *Tetrahedron Lett.* **1978**, 3233.
(22) Freeman, F.; Kim, D. S. H. L. Submitted for publication.
(23) Chwang, W. K.; Kresge, A. J.; Wiseman, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 6972.

0022-3263/92/1957-0550$03.00/0



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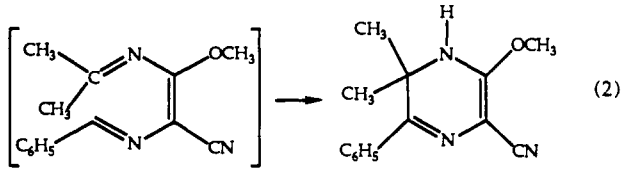
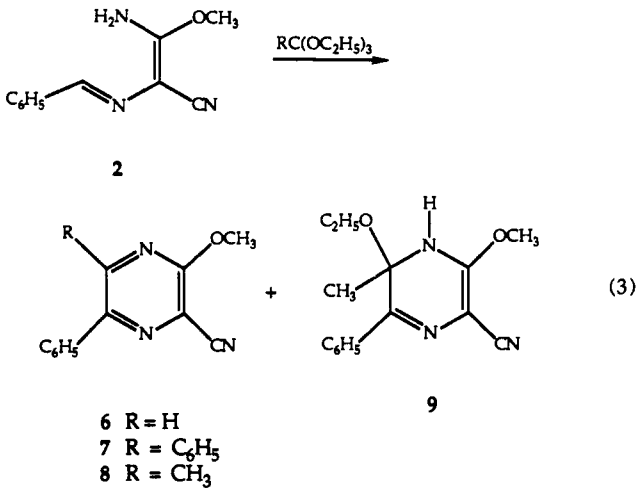


4 5 (2)

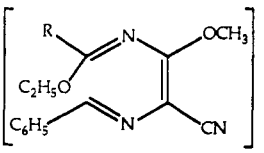
to the 4,5-dihydro-1,4-diazabenzene **5**.

2-Aza-1,3-butadiene **2** reacted with triethyl orthoformate and triethyl orthobenzoate to give 3-cyano-2-methoxy-5-phenyl-1,4-diazabenzene (pyrazine-3-carbonitrile, **6**, 91%) and 2-cyano-3-methoxy-5,6-diphenyl-1,4-diazabenzene (**7**, 54%, eq 3), respectively. This procedure gave a higher



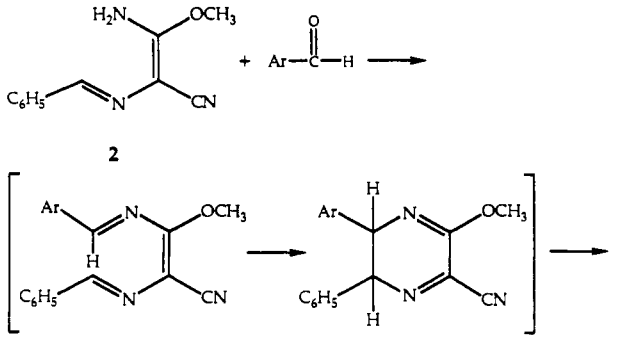
2 6 R = H; 7 R = C_6H_5; 8 R = CH_3 9 (3)

yield than the reported synthesis of pyrazine **7**.[24] The PPTS-catalyzed reaction of 2-aza-1,3-butadiene **2** with triethyl orthoacetate gave 2-cyano-3-methoxy-5-methyl-6-phenyl-1,4-diazabenzene (**8**, 43%) and its precursor 2-cyano-5-ethoxy-3-methoxy-5-methyl-6-phenyl-4,5-dihydro-1,4-diazabenzene (**9**, 35%). Single-crystal X-ray crystallographic analysis confirmed the structure of product **9**. In contrast to the 4,5-dihydropyrazine **5**, which cannot easily form the pyrazine ring structure (eq 2), compound **9** on heating with azabenzene or triethylamine afforded only 1,4-diazabenzene **8**. The intermediates for compounds **6**, **7**, and **8** are most likely the respective diazatrienes **10**, **11**, and **12**.

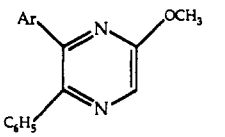


10 R = H
11 R = C_6H_5
12 R = CH_3

Phenylmethanal and 2-thienylmethanal react with 2-aza-1,3-butadiene **2** to give 5-methoxy-2,3-diphenyl-1,4-diazabenzene (**17**, 74%)[25,26] and 5-methoxy-2-phenyl-3-(2-thienyl)-1,4-diazabenzene (**18**, 62%, eq 4), respectively.



2 13 Ar = C_6H_5; 14 Ar = 2-thienyl 15 Ar = C_6H_5; 16 Ar = 2-thienyl



(4)

17 Ar = C_6H_5
18 Ar = 2-thienyl

Acid-catalyzed imine formation leads to the substituted 2,5-diaza-1,3,5-hexatrienes **13** and **14**, respectively, which undergo electrocyclization to **15** and **16**, respectively. Several plausible mechanisms may account for the formation of products **17** and **18** from **15** and **16**, respectively. Loss of hydrogen cyanide from **15** and **16** could lead to highly strained cyclic six-membered ketene imine intermediates[27-29] which may undergo 1,5-hydrogen shifts to 1,4-diazabenzenes **17** and **18**, respectively. Alternately, a series of prototropic shifts, catalyzed by the PPTS present, may lead to intermediates which can also eliminate hydrogen cyanide to form the observed **17** and **18**. A series of 1,5-hydrogen shifts in intermediates **15** and **16**, followed by elimination of hydrogen cyanide, could also lead to the respective products **17** and **18**.

The above described procedures provide novel and facile routes to 4,5-dihydro-1,4-diazabenzene and to 1,4-diazabenzene with different aromatic, alkyl, and heteroaromatic substituents at various positions of the ring, in one step from readily accessible 2-aza-1,3-butadienes[9-12] and the corresponding vinyl ether, aromatic aldehyde, heteroaromatic aldehyde, or orthoester.

Experimental Section

Melting points were determined in open capillary tubes with a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Desert Analytics Organic Microanalysis, Tucson, AZ.

High-resolution mass spectra (HRMS) were obtained with a VG 7070-HF mass spectrometer (70 eV). Chemical ionization mass spectra (CIMS, 2-methylpropane) and electron impact mass spectra (EIMS) were obtained with a Finnigan 9610 GC-EI-CI mass spectrometer with a Nova 3 data system operating at an ionization potential of 70 or 100 eV.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a General Electric Model QE 300 (300 MHz) spectrometer, and chemical shifts (δ) are reported in parts per million (ppm) relative to internal tetramethylsilane (0.00 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded on a General Electric Model QE 300 (75.5 MHz) spectrometer, and

(24) Takakazu, K.; Fumihko, N.; Ohtsuka, Y. *J. Heterocycl. Chem.* **1980**, *17*, 455.
(25) Compound **15** was previously synthesized in lower yield.[26]
(26) Nisho, T.; Kondo, M.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2497.
(27) Cyclic seven-membered ring ketene imines have been reported.[28,29]
(28) Huisgen, R. In *Advances in Cycloaddition*; Curran, D. P., Ed.; JAI Press: Greenwich, CT, 1988; Vol. 1, p 1.
(29) Chapman, O. L.; Le Roux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 285.

chemical shifts are reported in parts per million relative to the central solvent ($CDCl_3$) resonance at 77.0 ppm.

IR spectra were obtained with a Perkin-Elmer 1620 FTIR spectrophotometer, calibrated with the 1601 cm^{-1} absorption of polyphenylethene.

Ultraviolet spectra were obtained in ethanenitrile on a Shimadzu UV/VIS-160A spectrophotometer.

Analytical TLC was performed on Analtech Uniplate 10 × 20 cm (250-mm thick) silica gel GF prescored glass plates which were developed in a solvent mixture of 1:2 ethyl ethanoate/hexanes. After the solvent had risen to the top, the plates were checked under ultraviolet light and developed in a diiodine chamber to visualize the compounds.

Flash column chromatography was performed on 230–400 mesh silica gel.

(1*E*,3*E*)-4-Amino-3-cyano-4-methoxy-1-phenyl-2-azabutadiene (2) was prepared as previously described.[9,10]

2-Cyano-3-methoxy-5,5-dimethyl-6-phenyl-4,5-dihydro-1,4-diazabenzene (5). To a solution of (1*E*,3*E*)-4-amino-3-cyano-1-phenyl-2-azabutadiene (**2**, 200 mg, 1.0 mmol) in dry methylbenzene (20 mL) were added pyridinium *p*-toluenesulfonate (PPTS, 5 mg, 0.02 mmol) and 2-methoxypropene (2 mL, 1.51 g, 20.9 mmol) under a nitrogen atmosphere. The reaction solution was refluxed for 48 h, cooled, diluted with 100 mL of 1:1 ethyl ethanoate/diethyl ether solution, transferred to a separatory funnel, and washed with water (3 × 100 mL), and the layers were separated. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The residue was purified by column chromatography with 2:1 hexanes/ethyl ethanoate to give 198 mg (82.2%) of **5**, mp 168–169 °C: IR (Nujol, cm^{-1}) 3180, 2191 (C≡N), 1556 (C=N), 1530 (C=N); UV λ_{max} (log ϵ) 341 (3.74), 237.5 (4.03), 213 (3.70); ^1H NMR ($CDCl_3$) δ 1.40 (s, 6 H), 3.98 (s, 3 H), 5.97 (s, 1 H), 7.27–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.76, 55.12, 57.79, 82.26, 120.03, 127.96, 128.05, 128.71, 136.87, 151.10, 158.93; HREIMS *m/z* 241.1201 (calcd for $C_{14}H_{15}N_3O$ 241.1215).

Light yellow crystals of 4,5-dihydro-1,4-diazabenzene **5** were grown for X-ray crystallographic analysis by slow evaporation from a solution of the compound in aqueous propanone.

3-Cyano-2-methoxy-5-phenyl-1,4-diazabenzene (6). To a solution of **2** (200 mg, 1.0 mmol) in dry methylbenzene (20 mL) were added triethyl orthoformate (2 mL, 1.78 g, 12.0 mmol) and pyridinium *p*-toluenesulfonate (5 mg, 0.02 mmol) under a nitrogen atmosphere. The reaction solution was refluxed for 48 h, cooled, diluted with 100 mL of 1:1 ethyl ethanoate/diethyl ether solution, transferred to a separatory funnel, and washed with water (3 × 100 mL), and the layers were separated. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The residue was purified by column chromatography with 20:1 hexanes/ethyl ethanoate to give 192 mg (91%) of product (**6**), mp 154–155 °C: IR (Nujol, cm^{-1}) 2232 (C≡N), 1584 (C=C), 1565 (C=N), 1531 (C-N); UV λ_{max} (log ϵ) 339 (3.53), 261.5 (3.92), 216.5 (3.43); ^1H NMR ($CDCl_3$) δ 4.14 (s, 3 H), 7.26–7.94 (m, 5 H), 8.74 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.0, 114.17, 118.21, 126.30, 129.13, 129.77, 134.51, 141.58, 146.37, 160.54; HREIMS *m/z* 211.0741 (calcd for $C_{12}H_9N_3O$ 211.0545). Anal. Calcd for $C_{12}H_9N_3O$: C, 68.25; H, 4.27; N, 19.91. Found: C, 68.04; H, 4.13; N, 20.05.

2-Cyano-3-methoxy-5,6-diphenyl-1,4-diazabenzene (7) was prepared from **2** and trimethyl orthobenzoate (2 mL, 2.11 g, 11.6 mmol) as described above for the preparation of compound **6**. The residue was column chromatographed with 20:1 hexanes/ethyl ethanoate. The solvent was evaporated in vacuo, and petroleum ether (37.6–52.0 °C, 5 mL) was added dropwise to the residue to initiate crystallization. The solid was recrystallized from chloroform/petroleum ether to give 155 mg (54%) of 1,4-diazabenzene **7**, mp 168–169 °C (lit.[24] mp 165–167 °C): IR (Nujol, cm^{-1}) 2232 (C≡N), 1595 (C=C), 1579 (C=N), 1539 (C=N); UV λ_{max} (log ϵ) 348 (4.15), 261 (4.11), 223.5 (4.28); ^1H NMR ($CDCl_3$) δ 4.18 (s, 3 H), 7.25–7.50 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 54.77, 114.41, 115.65, 128.29, 128.38, 128.72, 129.46, 129.89, 136.81, 136.94, 146.26, 152.63; HREIMS *m/z* 287.1041 (calcd for $C_{18}H_{13}N_3O$ 287.1058). Anal. Calcd for $C_{18}H_{13}N_3O$: C, 75.24; H, 4.56; N, 14.63. Found: C, 75.36; H, 4.46; N, 14.69.

2-Cyano-3-methoxy-5-methyl-6-phenyl-1,4-diazabenzene (8) and 2-Cyano-5-ethoxy-3-methoxy-5-methyl-6-phenyl-4,5-dihydro-1,4-diazabenzene (9) were prepared from **2** and triethyl orthoacetate (2 mL, 1.77 g, 10.9 mmol) as described above for the preparation of compound **6**. The residue was purified by column chromatography with 20:1 hexanes/ethyl ethanoate to give 1,4-diazabenzene **8** (117 mg, 43.2%), mp 109–110 °C, and 4,5-dihydro-1,4-diazabenzene **9** (95 mg, 35%) as a thick oil. Compound **9** was converted into compound **8** quantitatively on treatment with azabenzene or triethylamine.

Compound 8: IR (Nujol, cm^{-1}) 2234 (C≡N), 1579 (C=C), 1540 (C=N); UV λ_{max} (log ϵ) 325 (3.91), 251 (4.08), 219 (3.76); ^1H NMR ($CDCl_3$) δ 2.53 (s, 3 H), 4.02 (s, 3 H), 7.35–7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.32, 54.60, 114.39, 115.04, 128.38, 128.76, 128.86, 136.66, 147.25, 153.72, 159.45; HREIMS *m/z* 225.0889 (calcd for $C_{13}H_{11}N_3O$ 225.0902). Anal. Calcd for $C_{13}H_{11}N_3O$: C, 69.33; H, 4.89; N, 18.67. Found: C, 69.33; H, 4.73; N, 18.41.

Compound 9: ^1H NMR ($CDCl_3$) δ 1.42 (t, 3 H), 2.00 (s, 3 H), 3.81 (s, 3 H), 4.42 (q, 2 H), 7.35–7.66 (m, 5 H), 8.23 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.02, 19.58, 55.11, 63.75, 91.33, 114.75, 127.19, 128.58, 129.80, 136.71, 150.74, 166.60, 167.78; HREIMS *m/z* 271.1329 (calcd for $C_{15}H_{17}N_3O_2$ 271.1321).

5-Methoxy-2,3-diphenyl-1,4-diazabenzene (17). To a solution of **2** (200 mg, 1.0 mmol) in dry methylbenzene (20 mL) were added pyridinium *p*-toluenesulfonate (5 mg, 0.02 mmol) and phenylmethanal (2 mL, 2.10 g, 19.7 mmol) under a nitrogen atmosphere. The reaction mixture was refluxed for 2 h, cooled, diluted with 100 mL of 1:1 ethyl ethanoate/diethyl ether solution, transferred to a separatory funnel, and washed with water (3 × 100 mL), and the layers were separated. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated in vacuo. The residue was column chromatographed with 20:1 hexanes/ethyl ethanoate, and the solvent was evaporated in vacuo. The product **17** was recrystallized from chloroform/petroleum ether to give 193 mg (73.6%) of 1,4-diazabenzene **17**: mp 128–129 °C (lit.[25] mp 130–131.5 °C): IR (Nujol, cm^{-1}) 1582 (C=C), 1559 (C=N), 1539 (C=N); UV λ_{max} (log ϵ) 317 (4.03), 272 (4.07), 223.5 (4.26); ^1H NMR ($CDCl_3$) δ 3.90 (s, 3 H), 7.11–7.36 (m, 10 H), 8.13 (s, 1 H); ^{13}C NMR ($CDCl_3$), δ 53.47, 127.63, 127.92, 128.03, 128.34, 129.46, 129.70, 132.44, 138.29, 138.67, 144.42, 148.06, 158.25; HREIMS *m/z* 262.1113 (calcd for $C_{17}H_{14}N_2O$ 262.1106). Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.87; H, 5.34; N, 10.69. Found: C, 77.63; H, 5.22; N, 10.74.

5-Methoxy-2-phenyl-3-(2-thienyl)-1,4-diazabenzene (18) was prepared from **2** and 2-thienylmethanal (2 mL, 2.36 g, 21 mmol) as described above for the preparation of compound **17**. The residue was column chromatographed with 20:1 hexanes/ethyl ethanoate to give a white solid which was recrystallized from chloroform/petroleum ether to give 167 mg (62%) of pyrazine **18**, mp 100–101 °C: IR (Nujol, cm^{-1}) 1560 (C=N), 1540 (C=N); UV λ_{max} (log ϵ) 297 (3.78), 229 (3.79); ^1H NMR ($CDCl_3$) δ 3.87 (s, 3 H), 6.54–7.45 (m, 8 H), 8.07 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 53.63, 126.61, 126.80, 127.26, 128.35, 128.58, 128.76, 129.10, 132.43, 138.48, 138.62, 141.94, 147.29, 157.71; HREIMS *m/z* 268.0657 (calcd for $C_{15}H_{12}N_2OS$ 268.0670). Anal. Calcd for $C_{15}H_{12}N_2OS$: C, 67.16; H, 4.48; N, 10.45. Found: C, 67.07; H, 4.35; N, 10.41.

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Supplementary Material Available: ^{13}C NMR and ^1H NMR spectra of 2-cyano-3-methoxy-5,5-dimethyl-6-phenyl-4,5-dihydro-1,4-diazabenzene (**5**) and 2-cyano-5-ethoxy-3-methoxy-5-methyl-6-phenyl-4,5-dihydro-1,4-diazabenzene (**9**) and the X-ray crystallographic results for compound **5** (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.