The Synthesis and Some Conformational Observations on the 3,10-Diazabicyclo[4.3.1]decane System

TADASHI SASAKI,* SHOJI EGUCHI, AND TSUTOMU KIRIYAMA

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464, Japan

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10-Methyl-3,10-diazabicyclo[4.3.1]decane (**7**) and its 7,9-*exo*-ethano derivative **12** were prepared by $LiAlH_4$ reduction of 10-methyl-3,10-diazabicyclo[4.3.1]decan-4-one (**3**) and its 7,9-*exo*-ethano derivative **9**, both of which were obtained by the Schmidt reaction of pseudopelletierine (**1**) and 6,8-*exo*-ethanopseudopelletierine (**8**), respectively. The same reduction of **3** afforded a stable aluminum complex, tris(10-methyl-3,10-diazabicyclo-[4.3.1]decane)aluminum hydroxide (**6**) in 76% yield, but reduction of **9** yielded no such stable complex. Treatment of **7** with 1 equiv of methylene iodide gave 10-methyl-3,10-diazatricyclo[4.3.1.$1^{3,10}$]undecanium iodide (**19**).

Recently we reported the synthesis of 9-methyl-9-azatricyclo[3.3.1.$0^{3,7}$]nonane (9-methyl-9-azanoradamantane) from pseudopelletierine (**1**) (9-methyl-9-azabicyclo[3.3.1]nonan-3-one) by the transannular C–H insertion reaction of the corresponding 3-carbene.[1] As an extension of a study on the azabicyclic and azatricyclic systems, this paper deals with the syntheses of the amines **7** and **12** from **1** and 6,8-*exo*-ethanopseudopelletierine (**8**),[2,3] respectively, and the chemical behavior and nmr spectra of these compounds and the 4-ones (**3** and **9**).

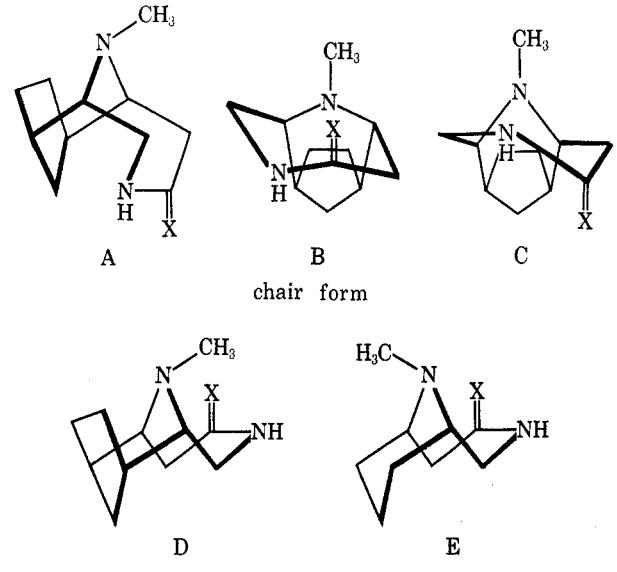
Results and Discussion

The Schmidt reaction of pseudopelletierine (**1**) proceeded smoothly to give 10-methyl-3,10-diazabicyclo-[4.3.1]decan-4-one (**3**) in high yield as reported by Paquette and Wise.[4] The Beckmann rearrangement of **1** oxime hydrochloride (**2**) with polyphosphate ester in refluxing chloroform afforded a complex mixture of unidentifiable products together with a trace of **3**. **3** gave a methiodide **4** and hydrochlorides **5a** + **5b** by routine procedures (Scheme I).

The Schmidt reaction of **8** similarly gave a lactam **9**[3] (93%). The structure was evidenced by analytical and spectral data; the nmr signal due to a C_2 equatorial proton at τ 6.20 (double d, J = 14.8 and 3.7 Hz) is similar to that of **3**, indicating a similar conformation of **9** to that of **3** as shown in Chart I. **9** gave a hydrochloride **11**, while **9** did not react with methyl iodide even on heating at 90° in a sealed tube in contrast with the facile formation of **4** from **3** and methyl iodide. Such a behavior of **9** is quite similar to that of **8** (see Scheme II); the lone electron pair on nitrogen is sterically hindered by the proximity of the exo ethano bridge. Hence, for **9** was assigned an anti orientation of the 10-methyl group against the 7,9-ethano bridge.

Reduction of the cyclic lactam **3** with lithium aluminum hydride in refluxing tetrahydrofuran afforded a

CHART I



crystalline aluminum complex **6** in 76% yield, which was characterized as tris(10-methyl-3,10-diazabicyclo-[4.3.1]decane)aluminum hydroxide on the basis of analytical and nmr data (Figure 1, **6**); the nmr signals due to three *N*-methyl protons appear in a sharp singlet at τ 7.33, indicating that **6** has a symmetrical cis form with a C_3 symmetry of the octahedral structure. Furthermore, a broad doublet (J = 9.0 Hz) at τ 8.83 was assignable to a C_8 endo proton, supporting a boat conformation of the homopiperazine ring and a chair conformation of the piperidine ring in **6**.[5] The complex **6** was very stable to alkali; treatment with 30% aqueous sodium hydroxide liberated only a trace of a free amine **7**. However, **6** afforded **7** readily by basifying the solution in hydrochloric acid.

The amine **7** was characterized as 10-methyl-3,10-diazabicyclo[4.3.1]decane on the basis of analytical, spectral, and chemical evidence; the mass spectrum had a M^+ at m/e 154 ($C_9H_{18}N_2$) and the nmr spectrum (Figure 1, **7**) had signals at τ 6.70–7.20 (m, 6, $2NCH_2$ and 2NCH), 7.38 (s, 3, NCH_3), 7.50–8.90 (m, 8, $4CH_2$), and 8.06 (s, 1, NH, disappeared on deuteration). **7** gave a dipicrate, mp 238–240°, and a hydriodide **14** of the methiodide **15** (Scheme III).

(1) (a) T. Sasaki, S. Eguchi, and T. Kiriyama, *J. Amer. Chem. Soc.*, **91**, 212 (1969); (b) T. Sasaki, S. Eguchi, and T. Kiriyama, *Tetrahedron*, **27**, 893 (1971).

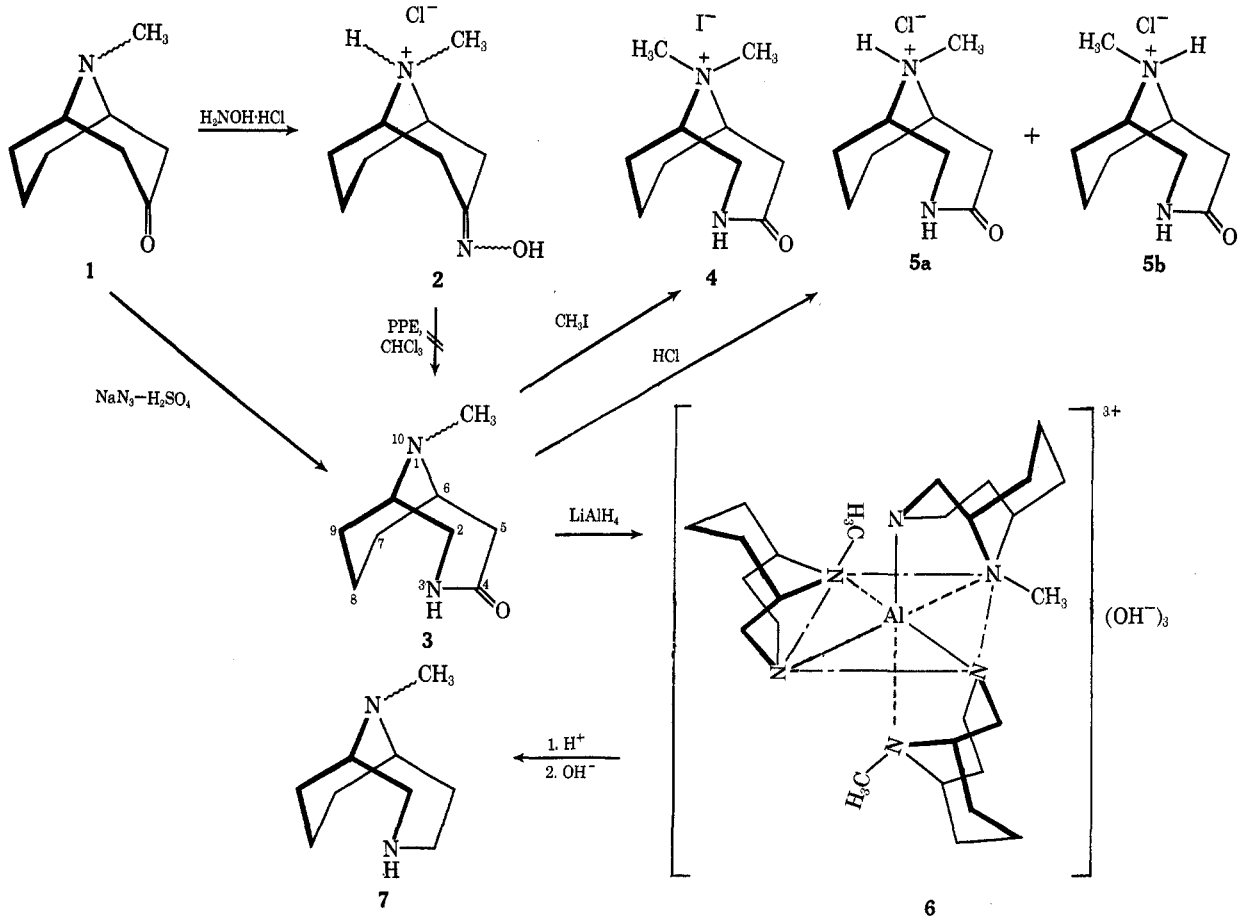
(2) L. A. Paquette and J. W. Heimaster, *J. Amer. Chem. Soc.*, **88**, 763 (1966).

(3) The ethano-bridged **8** and **9** could be named as 10-methyl-10-azatricyclo[4.3.1.$1^{6,9}$]undecan-3-one and 11-methyl-3,11-diazatricyclo[4.4.1.$1^{7,10}$]-dodecan-4-one, respectively. However, we prefer the above trivial name since the nomenclature as the tricyclic compounds can not distinguish two possible configurational isomers corresponding to the *exo*- and *endo*-ethano derivatives: *cf.* G. Ferguson, W. D. K. Macrossan, J. Martin, and W. Parker, *J. Chem. Soc. B*, 242 (1968).

(4) (a) L. A. Paquette and L. Wise, *J. Amer. Chem. Soc.*, **87**, 1561 (1965). (b) For mass spectrum of **3**, see A. M. Duffield, C. Djerassi, L. Wise, and L. A. Paquette, *J. Org. Chem.*, **31**, 1599 (1966).

(5) Appearance of this proton at such a characteristically higher field could be explained by anisotropy of the C_1–C_2 and C_6–C_5 bonds: *cf.* R. G. Foster and M. C. McIvon, *Chem. Commun.*, 280 (1967).

SCHEME I



The lithium aluminum hydride reduction of **9** gave the corresponding amine **12** as a colorless crystal. The structure was evidenced by analytical and spectral data; the nmr spectrum had signals at τ 6.68–7.25 (m, 6, $2NCH_2$ and 2NCH), 7.37 (s, 3, NCH_3), 7.46–8.30 (m, 5, C_7 H, C_9 H, 2 C_5 H, and C_8 endo H), 8.15 (s, 1, NH, disappeared on deuteration), 8.50 (broad s, 4, 7,9-ethano bridge), and 8.93 (broad double t, J = 12.5 and 6.0 Hz, 1, C_8 exo H).

The fact that no stable aluminum complex was produced in the reduction of **9** in contrast with **3** could be explained by an anti orientation of the NCH_3 to the 7,9-ethano bridge in **9**, since in this configuration **12** can not be inverted to a boat form of the homopiperazine ring, an indispensable form to produce a stable aluminum complex like **6**.

As summarized in Scheme IV, **12** did not afford a dimethiodide but a monomethyl hydriodide **21** with excess methyl iodide.

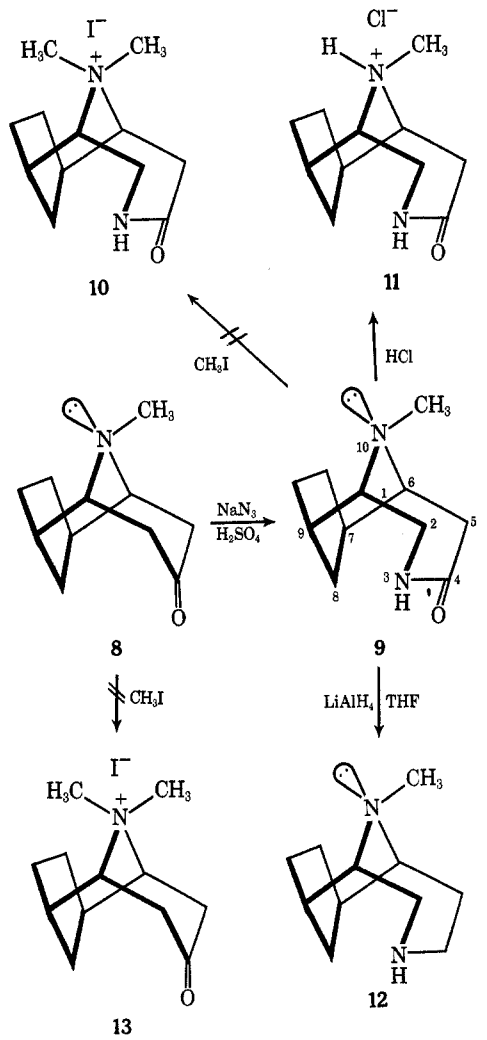
Both **7** and **12** gave the corresponding dihydrochlorides **16** and **20** with excess hydrogen chloride. However, the behavior of **7** on treatment with 1 equiv of trifluoroacetic acid was quite different from that of **12** as shown by the nmr spectra; the nmr spectrum of **7** in the presence of 1 equiv of trifluoroacetic acid had a characteristic signal at τ 8.93 in a broad doublet (J = 9.3 Hz) assignable to a C_8 endo proton of the monocation **17** with a chair–boat conformation (Figure 1, **17** and Scheme III). The whole spectral pattern of **17** was also very similar to that of **6**, supporting above assignment. Contrarily, the nmr spectrum of **12** in the presence of 1 equiv of trifluoroacetic acid had signals corresponding to just intermediate ones between the free base **12** and the dication **20**, indicating that the monocation of **12** could be interpreted as an equilibrating mixture of **22** and **23** on the nmr time scale. This fact indicates that the inversion of the homopiperazine ring in **12** is impossible because of the severe steric hindrance of the anti NCH_3 group.

The formation of a stable aluminum complex **6** and a stable monocation **17** from **7** led to the examination of a reaction of **7** with methylene iodide. Treatment of **7** with 1 equiv of methylene iodide at room temperature afforded a 3,10-methano derivative **18** which liberated easily hydrogen iodide to give 10-methyl-3,10-diazatricyclo[4.3.1.$1^{3,10}$]undecanium iodide (**19**) as a colorless crystal. The structure was determined on the basis of analytical and spectral data; in the nmr spectrum (Figure 1, **19**), appearance of a characteristic broad doublet at τ 8.83 (J = 10.2 Hz) assignable to a C_8 endo proton supported the assigned structure.

Evidently both **7** and **16** take a chair–chair conformation on the basis of the different nmr spectra from those of **6**, **17**, and **19**, all of which were concluded to take a chair–boat conformation as discussed above. A chair–chair conformation is also assignable for **12** as well as **20** and **21** by their nmr spectral patterns similar to those of **7**, **15**, and **16**. In the series of **12**, the chair–chair conformation is apparently favored because of a severe steric hindrance in a chair–boat form due to the presence of an anti N-methyl group.

In a N-methyl homopiperazine ring, there are three possible chair conformers, A, B, and C, as depicted in Chart I. An inspection of the Dreiding stereomodel

Scheme II



suggested that the B and C forms suffer from a considerable internal strain due to the bond angle deformation at C_1 and C_6, which is lacking in A form. Hence, A is the most plausible form as a chair–chair conformer of **7** and **12**. Furthermore, the lactams **3** and **9** had amide bands at 1648 and 1650 cm^{-1}, respectively, which correspond to the normally conjugated amide bands. Thus, the A form is also the most plausible for **3** and **9**, since a considerable distortion of the C_2–N_3–C_4–C_5 plane is anticipated in B and C forms, where the normal lactam character could not be expected.

Finally, a nitrogen pyramidal inversion problem is mentioned briefly on the basis of the nmr data of the hydrochlorides. The hydrochloride of **3** revealed two sharp singlets at τ 6.81 and 6.89 in *ca.* 1:2 ratio, which were assignable to *N*-methyl protons of **5a** and **5b** (Scheme I), while the hydrochloride of **9** exhibited only one singlet at τ 7.00 due to *N*-methyl protons of **11** (Scheme II). Although the nitrogen pyramidal inversion is known to require relatively small activation energy, the protonation to an amine function requires much less energy.[6] Hence, the above facts indicate the presence of the *N*-pyramidal inversion in **3** but not in **9** (at room temperature). The hydrochloride **16** exhibited only one singlet at τ 6.94 due to *N*-methyl protons (Figure 1, **16**); this could be reasonably explained by the protonation *via* a monocation like **17** rather than by the absence of the *N*-pyramidal inversion. All of these results are in good agreement with the chemical behaviors described above.

(6) (a) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Amer. Chem. Soc.*, **89**, 3761 (1967). (b) For a review on the pyramidal inversion, see A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem.*, **82**, 453 (1970).

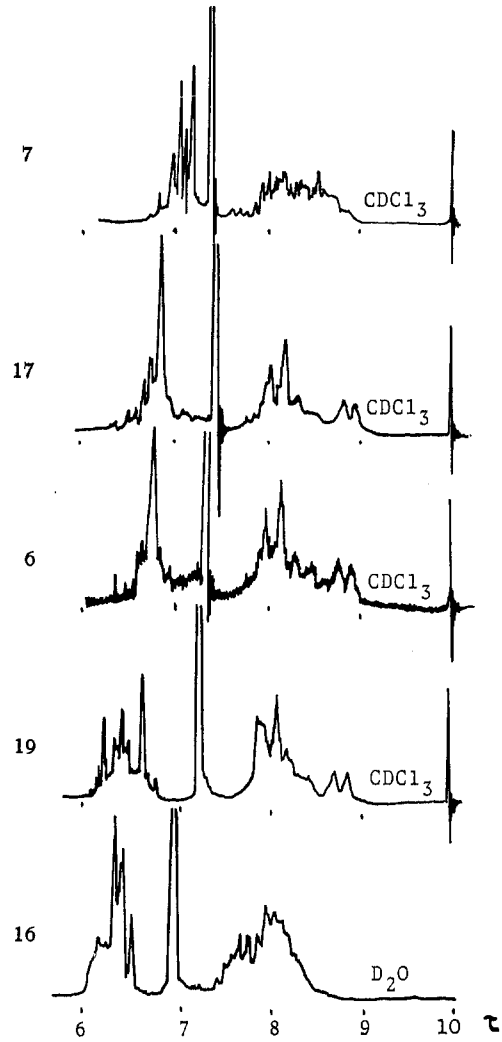


Figure 1.—The 60-MHz spectra of **7**, **17**, **6**, **19**, and **16**. All compounds except **6** were deuterated by shaking in D_2O. For **16**, $CHCl_3$ was used as an internal reference.

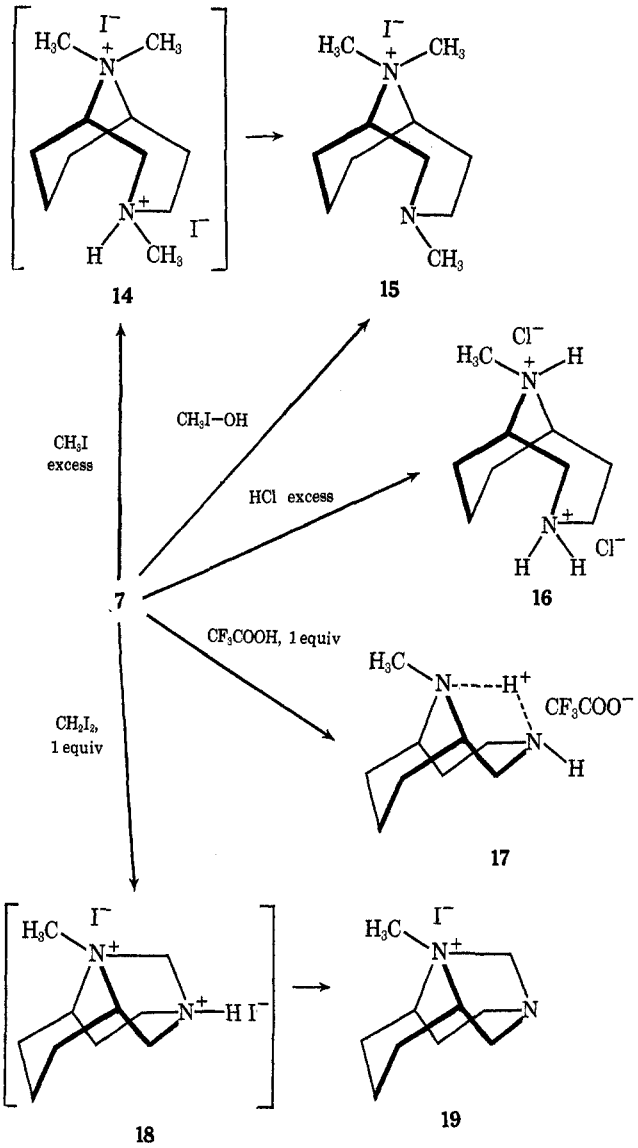
Experimental Section[7]

10-Methyl-3,10-diazabicyclo[4.3.1]decan-4-one (3).—This was prepared by the reported procedure:[4a] mp 164–166° (lit.[4a] mp 164–166°); ir (KBr) 3160, 3040, 2880, and 1648 cm^{-1}; nmr ($CDCl_3$) τ 2.56 (broad s, 1, NH, disappeared on deuteration), 6.11 (d d, 1, J = 15.0 and 4.1 Hz, C_2 eq H), 6.73–7.36 (m, 3, C_2 ax H, C_1 H, and C_6 H), 7.48 (s, 3, NCH_3), and 7.50–8.72 (m, 8, remaining protons).

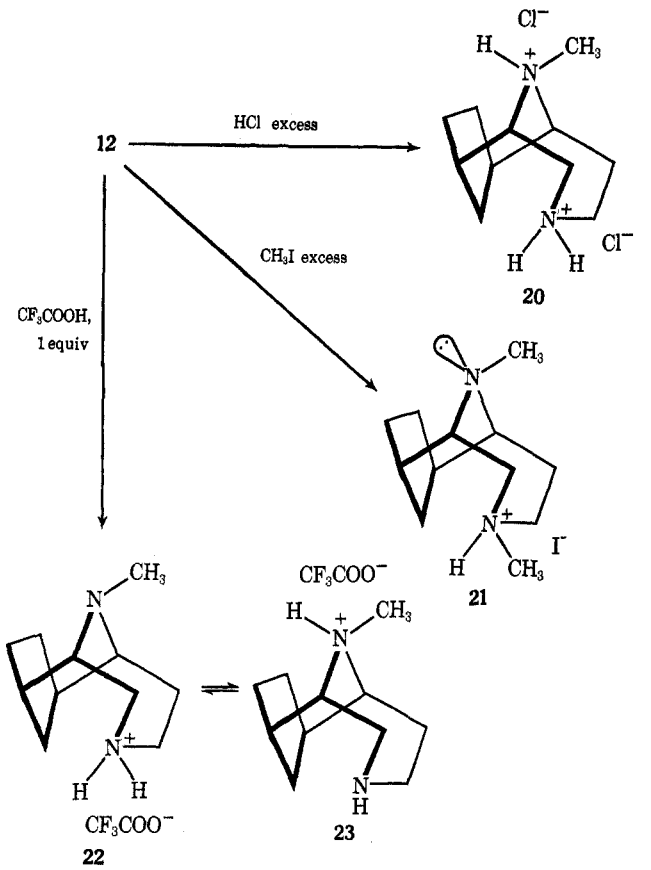
7,9-*exo*-Ethano-10-methyl-3,10-diazabicyclo[4.3.1]decan-4-one (9).[3]—The Schmidt reaction of 6,8-*exo*-ethanopseudopelletierine (**8**)[2] was carried out similarly to the preparation of **3** by using 8.95 g (50 mmol) of **8**, 20 ml of concentrated sulfuric acid, and 6.5 g (100 mmol) of sodium azide to give 8.98 g (93%) of **9**. An analytical sample was obtained by recrystallization from *n*-hexane–ethyl acetate as colorless needles: mp 154°; ir (KBr) 3240, 3160, 3020, 2925, and 1650 cm^{-1}; nmr ($CDCl_3$) τ 3.50

(7) All melting points were obtained on a hot-stage type micromelting point apparatus and are uncorrected. Nmr spectra were recorded on a JEOL JNM-C-60HL spectrometer at 60 MHz and mass spectra on a JEOL JMS-01SG mass spectrometer at 75 eV. Ir spectra were obtained with a JASCO IR-S ir spectrophotometer. Microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer.

SCHEME III



SCHEME IV



(broad s, 1, NH, disappeared on deuteration), 6.20 (d d, 1, J = 14.8 and 3.9 Hz, C_2 eq H), 6.55–7.09 (m, 3, C_2 ax H, C_1 H, and C_6 H), 7.10–7.48 (m, 2, C_5 CH_2), 7.51 (s, 3, NCH_3), 7.62–7.94 (m, 2, C_7 H and C_9 H), 8.08–8.68 (m, 5, 7,9-ethano bridge and C_8 endo H), and 8.96 (d, t, 1, J = 12 and 4.0 Hz, C_8 exo H); mass spectrum m/e 194 (M^+), 136, 122, 108, 95, and 94.

Anal. Calcd for $C_{11}H_{18}ON_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 74.15; H, 10.10; N, 15.74.

10-Methyl-3,10-diazabicyclo[4.3.1]decan-4-one Methiodide (4).—To a solution of 0.17 g (1.0 mmol) of **3** in 5 ml of ethanol was added dropwise 0.50 g (3.5 mmol) of methyl iodide, resulting in a rapid precipitation of colorless crystals, which were filtered and washed with ethanol to give **4**: mp >300°; ir (KBr) 3240, 2928, 2880, 1664, 1455, and 1360 cm^{-1}.

Anal. Calcd for $C_{10}H_{19}ON_2I$: C, 38.72; H, 6.17; N, 9.03. Found: C, 38.82; H, 5.90; N, 9.10.

10-Methyl-3,10-diazabicyclo[4.3.1]decan-4-one Hydrochloride (5a and 5b).—Into a solution of 0.17 g (1.0 mmol) of **3** in 10 ml of dry benzene was bubbled dry hydrogen chloride gas. The resulting colorless precipitates were recrystallized from ethanol to give hygroscopic needles of **5a** and **5b**: mp 229–233°; ir (KBr) 3160, 3020, 2930–2420, 1695, 1629, and 1446 cm^{-1}; nmr (D_2O) τ 5.60–6.70 (m, 5, C_2 CH_2, C_1 H, C_6 H, and C_5 H), 6.81 and 6.89 (each s, total 3, NCH_3), and 7.00–8.50 (m, 7, other protons).

Anal. Calcd for $C_9H_{17}ON_2Cl$: C, 52.81; H, 8.37; N, 13.69. Found: C, 52.63; H, 8.70; N, 13.55.

Hydrochloride 11 of 9.—This was prepared similarly as above as a very hygroscopic crystal: mp 247–249°; ir (KBr) 3200, 2930–2650, 1640, and 1482 cm^{-1}; nmr (D_2O) τ 5.84–6.84 (m, 5, C_2 CH_2, C_1 H, C_6 H, and one of C_5 CH_2), 7.00 (s, 3, NCH_3), 7.17–7.64 (m, 3, C_7 H, C_9 H, and one of C_5 CH_2), 7.64–8.42 (m, 5, 7,9-ethano bridge and C_8 endo H), and 8.73 (d t, 1, J = 12 and 4 Hz, C_8 exo H).

Anal. Calcd for $C_{11}H_{19}ON_2Cl$: C, 57.26; H, 8.30; N, 12.14. Found: C, 57.38; H, 8.44; N, 11.88.

Tris(10-methyl-3,10-diazabicyclo[4.3.1]decane)aluminum Hydroxide (6).—A mixture of 8.4 g (50 mmol) of **3** and 1.9 g (50 mmol) of lithium aluminum hydride in 100 ml of dry tetrahydrofuran was refluxed for 1 day. After cooling, the unreacted reducing agent was decomposed by adding aqueous tetrahydrofuran under ice cooling. The mixture was diluted with 500 ml of water and extracted with methylene chloride (six 50-ml portions) after addition of 50 ml of 30% aqueous sodium hydroxide. The combined extracts were dried (Na_2SO_4) and removal of the solvent afforded 7.0 g (76%) of **6** as colorless needles. An analytical sample was obtained after recrystallization from ethyl acetate: mp 180°; ir (KBr) 2620–3000, 1548, 1437, and 1153 cm^{-1}; nmr ($CDCl_3$), see Figure 1, **6**.

Anal. Calcd for $C_{27}H_{51}N_6Al(OH)_3 \cdot {}^1/_2H_2O$: C, 59.31; H, 10.14; N, 15.37. Found: C, 59.35; H, 10.22; N, 15.54.

10-Methyl-3,10-diazabicyclo[4.3.1]decane (7).—A solution of 6.5 g (0.12 mol) of **6** in 50 ml of water was acidified with 20 ml of concentrated hydrochloric acid and was heated at 90° for 10 min. The cooled solution was basified with 20% aqueous sodium hydroxide and extracted with methylene chloride (six 50-ml portions). The combined extracts were dried (Na_2SO_4) and the solvent was removed to give 5.4 g (90%) of crude **7** as a syrupy oil. An analytical sample was obtained by dry distillation under reduced pressure as a hygroscopic and sublimable solid: mp 43–46° (sealed tube); ir (KBr) 3280, 2925, and 1442 cm^{-1}; mass spectrum m/e 154 (M^+); nmr, see Figure 1, **7**.

A picrate of **7** had mp 238–240° and 253–255° dec.

Anal. Calcd for $C_{21}H_{24}O_{14}N_8$: C, 43.45; H, 4.17; N, 19.30. Found: C, 43.77; H, 3.96; N, 19.18.

7,9-*exo*-Ethano-10-methyl-3,10-diazabicyclo[4.3.1]decane (12).[3] —The lithium aluminum hydride reduction of 7.75 g (40 mmol) of **9** under the similar conditions as described on **6** and work-up gave 5.47 g (76%) of **12** as a syrupy oil, which was purified by dry distillation under reduced pressure to give **12** as a hygroscopic

and sublimable crystal: mp 66–69° (sealed tube); ir (KBr) 3360, 2860, and 1450 cm^{-1}; mass spectrum *m/e* 180 (M^+).

Anal. Calcd for $C_{23}H_{26}O_{14}N_8$: C, 45.55; H, 4.32; N, 18.48. Found: C, 45.56; H, 4.41; N, 18.39.

The hydrochloride **20** of **12** was very hydroscopic and dissolved directly in D_2O for nmr measurement: nmr τ 5.82–6.60 (m, 6, $2NCH_2$, C_1 H, and C_6 H), 6.84 (s, 3, NCH_3), and 7.10–8.71 (m, 10, other protons).

The monotrifluoroacetic acid salt (**22** and **23**) of **12** was prepared in benzene solution and after removal of the solvent, the remained mono salt was dissolved in D_2O for nmr: nmr τ 6.40–6.93 (m, 4, $2NCH_2$), 6.93–7.22 (m, 2, C_1 H and C_6 H), 7.28 (s, 3, NCH_3), 7.44–8.27 (m, 5, C_5 CH_2, C_7 H, C_9 H, and C_8 endo H), 8.39 (broad s, 4, 7,9-ethano bridge), and 8.78 (d, t, 1, J = 12 and 3.7 Hz, C_8 exo H).

10-Methyl-3,10-diazatricyclo[4.3.1.$1^{3,10}$]undecanium Iodide (19).—To a solution of 0.072 g (0.50 mmol) of **7** in 5 ml of dry benzene was added a solution of 0.134 g (0.50 mmol) of methylene iodide in 5 ml of dry benzene with stirring at room temperature. Stirring was continued for 1 hr. Removal of the solvent under reduced pressure left a brownish residue which was dissolved in ethanol and treated with Norit A to afford 0.023 g of **19** as a colorless prism: mp 182–185°; ir (KBr) 3180–2800, 1540, 1472, and 1440 cm^{-1}; nmr, see Figure 1, **19**.

Anal. Calcd for $C_{10}H_{19}N_2I$: C, 40.83; H, 6.51; N, 9.52. Found: C, 40.85; H, 6.54; N, 9.74.

3,10,10-Trimethyl-3,10-diazabicyclo[4.3.1]decanium Iodide (15).—A mixture of 0.15 g (1.0 mmol) of **7** and 0.43 g (3.0 mmol) of methyl iodide in 10 ml of dry benzene was stirred at room temperature for 30 min. Removal of the solvent and surplus methyl iodide under reduced pressure gave a hydriodide (**14**) of **15**, which on treatment with Norit A in ethanol afforded 0.12 g (38%) of **15** as prisms: mp 268–270°; ir (KBr) 3000, 2920, 2870, 1500, 1440, and 1134 cm^{-1}; nmr ($CDCl_3$) τ 5.98–6.33 (m, 4, C_1 H, C_6 H, and C_2 CH_2), 6.48 (s, 6, $N^+(CH_3)_2$), 6.60–7.30 (m, 2, C_4 CH_2), 7.42 (s, 3, NCH_3), and 7.68–9.04 (m, 8, other protons).

Anal. Calcd for $C_{11}H_{23}N_2I$: C, 42.59; H, 7.47; N, 9.03. Found: C, 42.67; H, 7.09; N, 8.96.

15 was also obtained by direct methylation of **7** with methyl iodide in the presence of sodium hydride in benzene in 18% yield.

7,9-*exo*-Ethano-3,10-dimethyl-3,10-diazabicyclo[4.3.1]decanium Iodide (21).—A mixture of 0.09 g (0.5 mmol) of **12** and 0.22 g (1.5 mmol) of methyl iodide in 10 ml of dry benzene was stirred at room temperature for 30 min. Removal of the solvent and excess methyl iodide gave a brownish residue which on treatment with Norit A in ethanol afforded 0.027 g (43%) of **21** as a colorless prism: mp 173–175°; ir (KBr) 3270, 2925, 2780, 1470, and 1341 cm^{-1}; nmr (D_2O) τ 6.10–6.95 (m, 6, C_1 H, C_6 H, C_2 CH_2, and C_4 CH_2), 7.03 and 7.12 (each s, 6, $2NCH_3$), 7.50–8.10 (m, 5, C_7 H, C_9 H, C_8 endo H, and C_5 CH_2), 8.24 (broad s, 4, 7,9-ethano bridge), and 8.43–8.90 (m, 1, C_8 exo H).

Anal. Calcd for $C_{12}H_{23}N_2I$: C, 44.73; H, 7.19; N, 8.69. Found: C, 44.44; H, 7.05; N, 8.56.

Registry No.—**4**, 3371-52-6; **5**, 29584-53-0; **6**, 29661-05-0; **7**, 29584-54-1; **7** picrate, 29584-55-2; **9**, 29577-62-6; **11**, 29577-63-7; **12**, 29577-64-8; **15**, 29584-56-3; **19**, 29584-57-4; **21**, 29577-65-9.

Studies in Nonpyridinoid Aza-Aromatic Systems. I. The Synthesis and Tautomeric Character of Cyclopenta[*b*]quinoline (Benzo[*b*][1]pyrindine)[1]

JOHN J. EISCH* AND FRANK J. GADEK

Maloney Chemical Laboratory, The Catholic University of America, Washington, D. C. 20017

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The synthesis of the tautomeric benzo[*b*][1]pyrindine (**3**) from 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**4**) has been accomplished by three routes: (a) metalation with C_6H_5Li, oxidation to the 3-hydroxy derivative, and dehydration under well-defined conditions; (b) bromination to yield the 1-bromo or 3-bromo derivative, hydrolysis, and dehydration; and (c) N-oxidation, acetoxylative reduction, and dehydration. Compound **3** is a purple liquid consisting of 67% of the 1-H, 33% of the 3-H, and 0.1% of the 4-H tautomer. The small content of the 4-H tautomer belies its important role in determining the striking color of **3** and its chemical reactivity in response to electrophiles. The physical properties of **3** are assessed in the light of existing knowledge concerning the structure of pyrindines.

Armit and Robinson first recognized the significance of the aromatic sextet[2] through a study of the indenoquinoline system, where a cationic *N*-alkylpyridinium ring is fused to a ring bearing anionic cyclopentadienyl character (**1**). Subsequent developments in the theory of aromaticity[3,4] have led chemists to recognize this pyrindine system (**1**) as a nitrogen isostere of azulene. Although the substituted tautomers and derivatives of 1,5-pyrindine (**1**) and 2,5-pyrindine (**2**) have been known for some time,[5–8] the highly labile, parent N-substituted pyrindines have been isolated or detected only relatively recently.[9,10] The unsubstituted benzopyrindines, on the other hand, have not been reported in the literature, although unsuccessful synthetic attempts leading to other valuable substituted ones have been recorded.[7,8,11,12] For none of the pyrindines has a careful study of the N–H and C–H tautomers been made, nor is much known of the chemistry of the pyrindines or their relatives. The present article reports the first synthesis of the novel, unsubstituted benzo[*b*][1]pyrindine (cyclopenta[*b*]quinoline[13]), gives the first complete spectral characterization of the tautomers of a pyrindine, and evaluates several interesting alternatives for obtaining

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