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]

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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

(1) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967, Abstracts O-180.

(2) J. W. Armit and R. Robinson, *J. Chem. Soc.*, **121**, 827 (1922); *ibid.*, **127**, 1604 (1925).

(3) E. Hückel, *Z. Physik.*, **70**, 204 (1931); *ibid.*, **76**, 628 (1932).

(4) (a) D. Ginsburg, Ed., "Non-Benzenoid Aromatic Compounds," Interscience, New York, N. Y., 1959; (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 256–304; (c) M. E. Vol'pin, *Russ. Chem. Rev.*, **29**, 129 (1960); (d) D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier, New York, N. Y., 1966.

(5) W. Borsche, *Justus Liebigs Ann. Chem.*, **377**, 120 (1910).

(6) (a) V. Prelog and S. Szpilfogel, *Helv. Chim. Acta*, **28**, 1684 (1945); (b) V. Prelog and O. Metzler, *ibid.*, **29**, 1170 (1946).

(7) M. Los and W. H. Stafford, *J. Chem. Soc.*, 1680 (1959).

(8) W. Treibs and G. Kempter, *Chem. Ber.*, **92**, 601 (1959).

(9) A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson, and A. G. Osborne, *J. Amer. Chem. Soc.*, **81**, 1255 (1959).

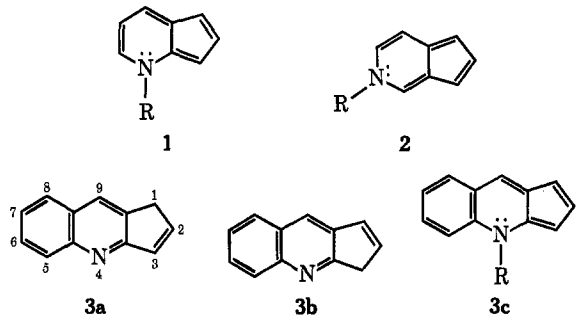
(10) (a) A. G. Anderson, Jr., and H. L. Ammon, *Tetrahedron Lett.*, 2579 (1966); (b) A. G. Anderson, Jr., and H. L. Ammon, *Tetrahedron*, **23**, 3601 (1967).

(11) W. Treibs, *Naturwissenschaften*, **49**, 37 (1962).

(12) L. E. Kholodov, I. F. Tishchenkova, and V. G. Yashunskii, *Tetrahedron Lett.*, 1535 (1970).

(13) Systematic name recommended by *Chemical Abstracts* and "Ring Index."

tautomeric cyclopenta[*b*]quinolines (**3a–c**) from their dihydro derivative (**4**). Subsequent papers will explore the chemistry of the azulenoid, aromatic system (**3c**) (R = alkyl or anion).



1 **2** **3a** **3b** **3c**

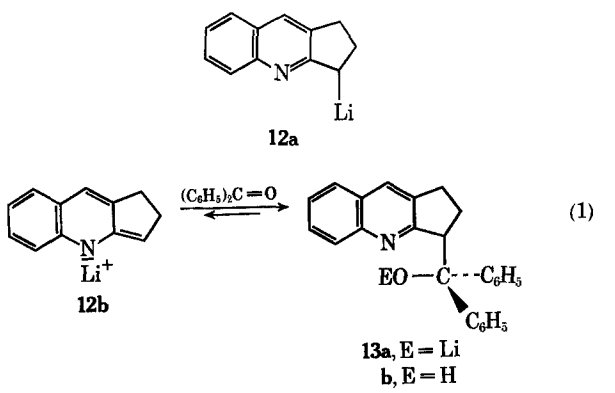
Results

Although we undertook the synthesis of a benzo derivative of 1-pyrindine (R = H) in the hope of obtaining a pyrindine of superior stability, these expectations were only partly realized. The most convenient starting material for the synthesis of **3** was the 2,3-dihydro derivative (**4**, β-quinindane) of **3a**, available from a Pfitzinger reaction between isatin and cyclopentanone and the thermal decarboxylation of the resulting 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline-9-carboxylic acid (**5**).[5] In exploring methods of introducing a double bond into the five-membered ring of **4**, bromination was attempted under both free-radical and polar conditions. In the former method, **4** reacted with *N*-bromosuccinimide in carbon tetrachloride to yield 57% of a labile, monobromo derivative **6** (mp 84–86°) that proved too unstable to be analyzed. Because of its apparent homogeneity and its hydrolysis to yield the 1-hydroxy derivative **7** of **4**, it is concluded that bromination occurred preferentially at the 1-methylene group of **4**. On the other hand, bromination of **4** with 1 equiv of bromine in a warm solution of glacial acetic acid containing anhydrous sodium acetate gave a labile monobromo derivative (**8**, mp 125–127°) that could be hydrolyzed with ethanolic–aqueous silver nitrate solution to yield the 3-hydroxy derivative **9** of **4**.[14] The identities of the 1-hydroxy (**7**) and 3-hydroxy (**9**) derivatives rest on their analytical data, their nmr spectra which support a CHOH group adjacent to an aromatic ring (exclusion of the 2-hydroxy derivative), and the independent synthesis of the 3-hydroxy derivative **9** in two well-precedented ways (*cf. infra*). These observed preferential brominations are consistent with the views that free-radical abstraction of hydrogen is more rapid at C-1 (adverse polar effect[15]) (**10**) and that bromination in acetic acid may proceed through enaminization (**11**) (Scheme I).

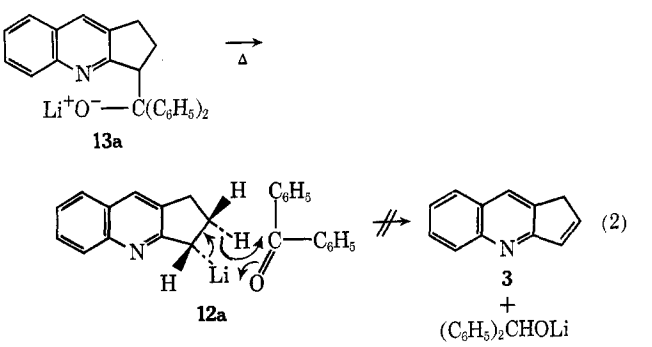
Previous mention of the monobromo derivative obtained from **4** and *N*-bromosuccinimide had assumed that it was the 3 isomer,[7] but no chemical or physical characterization was reported.

Ultimately, however, both brominations have proved impractical for the preparation of the 1- or 3-hydroxy precursors of the desired benzo[*b*][1]pyrindine (**3**). The hydrolyses of the 1-bromo and 3-bromo derivatives **6** and **8** were always overshadowed by side reactions leading to intractable gums and black solids. Even the attempt to dehydrohalogenate the 1-bromo derivative **6** directly, with sodium iodide in dimethylformamide at room temperature, led only to decomposition.

The preferential introduction of substituents at the 3 position of β-quinindane **4** could be achieved *via* its lithium salt **12**, which could be prepared in essentially quantitative yield by treating **4** with 1 equiv of phenyllithium in diethyl ether.[16] The lithium enaminate salt, presumably better formulated as a contact ion pair centered on nitrogen (**12b**), rather than as an organolithium reagent at C-3[17] (**12a**), underwent solely C-alkylation both with ketones and with methyl iodide (eq 1). The interaction of **12b** with benzophenone was shown to be reversible, for the treatment of the pure, isolated 2,3-dihydro-α,α-diphenyl-1*H*-cyclopenta[*b*]quinoline-3-methanol (**13b**) with 1 equiv of phenyllithium, forming **13a**, led to the detection of **4** and benzophenone upon hydrolytic work-up. The reversible dissociation of **13a** into its components thus limited the yield of carbinol to *ca.* 70%. The reversibility of the reaction, **12** ⇌ **13a**, was of great interest, since it was felt that the lithium salt **12** might eventually react with benzophenone in an alternative manner (eq 2), namely by hydride transfer.



12a (1) **12b** **13a**, E = Li **b**, E = H



13a **12a** (2) **3** + $(C_6H_5)_2CHOLi$

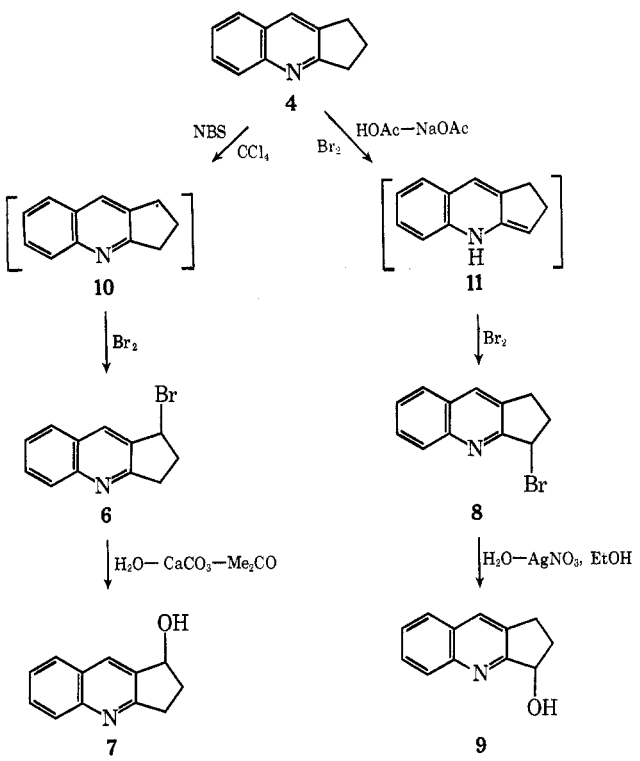
(14) J. J. Eisch and K. C. Fichter, unpublished studies.

(15) In a Hammett study of the relative reactivities of substituted toluenes toward *N*-bromosuccinimide, E. C. Kooyman, R. Van Helden, and A. F. Bickel [*Kon. Ned. Akad. Wetensch. Proc., Ser. B*, **56**, 75 (1953)] showed that bromination occurred preferentially at points of high electron availability: a plot of log reactivity *vs.* σ gave ρ of −1.55. As a specific precedent for the behavior of **4**, the behavior of 1,5-diphenyl-1-pentanone toward *N*-bromosuccinimide can be cited; attack at the methylene next to the phenyl, rather than next to the carbonyl, is observed.

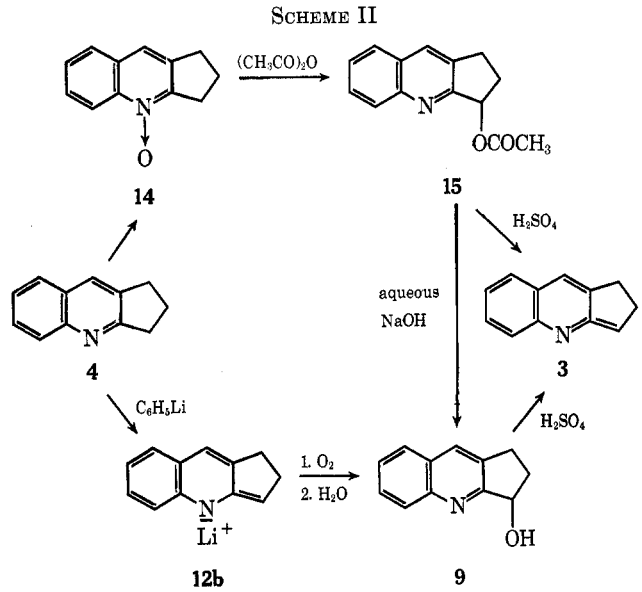
(16) K. Ziegler and H. Zeiser, *Justus Liebigs Ann. Chem.*, **485**, 174 (1931), achieved almost complete α metalation of both 2-methylpyridine and 2-methylquinoline by use of phenyllithium.

(17) *Cf.* G. Stork and S. R. Dowd, for the C-alkylation of the magnesium salts of N-substituted imines. The colors observed for **12b** and **16** fit the view that extensive charge delocalization occurs in such π systems with much charge on nitrogen. One might speculate that the failure of **12** to lose lithium hydride (eq 2) is a further indication that **12b** is a more accurate representation than **12a**.

SCHEME I



SCHEME II



The interaction of benzophenone with various alkyl Grignard reagents to yield benzhydrol and alkene[18a] suggested that the reversal of **13a** into its components might lead to the desired benzo[*b*][1]pyrindine (**3**) and benzhydrol.[18b] However, prolonged refluxing of **13a** suspended in ether or in benzene gave no indication of the formation of benhydrol or **3**.

Despite the failure of the lithium salt **12** to serve as a source of the benzo[*b*][1]pyrindine *via* hydride transfer, its treatment with molecular oxygen proved to be a convenient route to the 3-hydroxy-β-quinindane **9**, albeit in modest yield. An alternative route to this hydroxy derivative was a three-step sequence involving the N-oxidatione of β-quinindane, treatment of the resulting *N*-oxide **14** with acetic anhydride, and the saponification of the 3-acetoxy derivative **15** (Scheme II). The assignment of the structure of the hydroxy-β-quinindane as the 3 isomer is supported by the known tendency of both phenyllithium[16] and acetic anhydride[19,20] to attack the α-methylene hydrogens of their respective pyridine substrates.

The foregoing preparations of the 1-hydroxy and 3-hydroxy derivates of β-quinindane **7** and **9** now permitted attempts at their dehydration for the formation of the benzo[*b*][1]pyrindine system (**3**). Although 7-hydroxy-6,7-dihydro-1,5-pyrindine or its acetate is reported to give an 88% yield of 1,5-pyrindine by dehydration with concentrated sulfuric acid during **1** hr at 120–130°,[20] such conditions were far too severe for the dehydration or the dehydroacetoxylation of **7**, **9**, or **15**. Milder dehydration procedures, such as traces of strong acids (sulfuric or *p*-toluenesulfonic) in warm acetic acid or benzene, proved to be ineffectual and stronger acids tended to produce polymeric materials. Only by short-term exposure (3–5 min) to concentrated sulfuric acid preheated to 120° and by immediate quenching on ice could a satisfactory yield of **3** be obtained. Even with such control, only the 3-hydroxy (**9**) or the 3-acetoxy **15** derivative gave satisfactory yields of **3** (50–60%); the 1-hydroxy derivative **7** was more prone to side reactions and afforded only traces of **3**.

The benzo[*b*][1]pyrindine (β-quinindene, **3**) proved to have gratifyingly unusual properties. The compound was obtained, upon distillation, as a deep purple oil, which upon chilling crystallized to a pure white solid. The solid β-quinindene had a melting point almost identical with that of β-quinindane **4**; its ability to undergo repeated melting to a purple oil and resolidification to a white solid appears to be an example of thermochromism.[21] Although this β-quinindene could be stored unchanged under a nitrogen atmosphere below 0° for several days, exposure to oxygen and temperatures above 60° tended to promote decomposition.

The spectral properties of this benzo[*b*][1]pyrindine (**3**) showed that it was a mixture of the three tautomers, 1-H (**3a**), 3-H (**3b**), and 4-H (**3c**, R = H), in proportions varying with the physical state, temperature, time, and treatment of the sample. An infrared spectrum of the neat, supercooled purple oil displayed an N–H absorption of medium intensity at 2.9 μ; in a 10% solution in carbon tetrachloride this absorption had almost completely disappeared. The visible spectrum of a pink 1.94 *M* solution of **3** in benzene at 25° displayed one broad absorption from 470 to 540 mμ, centered at 507 mμ. The ultraviolet absorption spectrum of **3** in cyclohexane, in comparison with that of β-quinindane **4** displayed the expected bathochromic shift: absorptions for **4** at λ_{max} 237 mμ (log ε 4.58), 305 (3.75), and 319; for **3** at 246 mμ (log ε 4.67), 297 (3.90), 318 (3.87) and 332 (3.99). In a 0.01 *N* solution of hydrochloric acid in 95% ethanol the β-quinindane **4** had absorption maxima at 244 mμ (log ε 4.55) and 319 (4.05) and the β-quinindene **3** at 230 mμ (sh, log ε 5.03), 259 (4.80), 280 (sh, 4.45),

(18) (a) M. S. Kharasch and S. Weinhouse, *J. Org. Chem.*, **1**, 209 (1936); (b) *cf.* H. Gilman and C. W. Bradley, *J. Amer. Chem. Soc.*, **60**, 2335 (1938), for the ready loss of lithium hydride from organolithium compounds.

(19) (a) V. Boekelheide and W. L. Linn, *ibid.*, **76**, 1286 (1954); (b) O. H. Bullit and J. T. Maynard, *ibid.*, **76**, 1370 (1954).

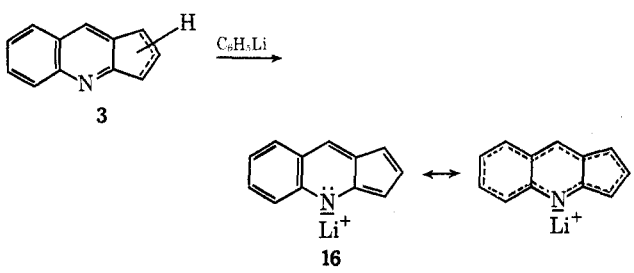
(20) M. M. Robinson, *ibid.*, **80**, 6254 (1958).

(21) J. H. Day, *Chem. Rev.*, **63**, 65 (1963).

312 (4.28), and 332 (4.30). The nmr spectrum of **3** in carbon tetrachloride (25% by weight) showed two distinct methylene signals, each having small hyperfine splittings, at δ 3.48 (A) and 3.22 (B) ppm, respectively. The areas of signals A and B were taken as measures of the ratio of 3*H*-benzo[*b*][1]pyrindine (**3b**) to 1*H*-benzo[*b*][1]pyrindine (**3a**), since the methyl group in α-picoline absorbs at a lower field (2.6 ppm) than the methyl group in β-picoline (2.2 ppm).[22] A freshly distilled sample of **3** showed in carbon tetrachloride a 3-H:1-H tautomeric ratio of 45:55; after 72 hr at 0° the ratio had changed to 33:67. This ratio (±2 parts) seems to be the thermodynamically stable mixture at 25° (*cf. infra*).

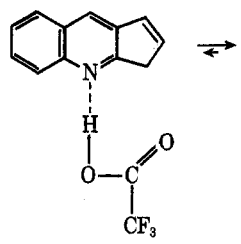
The nmr spectral data give a ready measure of the proportion of the two isomers, **3a** and **3b**, showing that **3a** is more stable than **3b** by *ca.* 450 cal. The absence of any infrared or nmr evidence for the existence of a considerable amount of 4*H*-benzo[*b*][1]pyrindine (**3c**, R = H) in moderately concentrated solutions suggests that less than 1% of **3c** was present. The presence of 0.093% of **3c** in a 1.94 *M* solution of benzo[*b*][1]pyrindine in benzene was estimated by visible spectroscopy. The assumption was made that the extinction coefficient for a corresponding band in the similar, isoelectronic 5,6-benzazulene system[23] could be used for tautomer **3c** (ϵ 316 for the 557-mμ band). Accordingly, one can estimate that tautomers **3a** and **3b** are at least 4 kcal more stable than isomer **3c**.

The proportion of the 1*H*- and 3*H*-benzo[*b*][1]pyrindine tautomers, **3a** and **3b**, was also dependent upon the chemical treatment of the sample or upon the solvent in which the nmr spectrum of tautomeric mixture **3** was recorded. Treatment of **3** with 1 equiv of phenyllithium at 0° resulted in the formation of the blood-red lithium salt **16** which, as with the lithium salt of β-quinindane **12b**, seems best formulated as an enaminate ion-pair salt. The visible spectrum of **16**, a

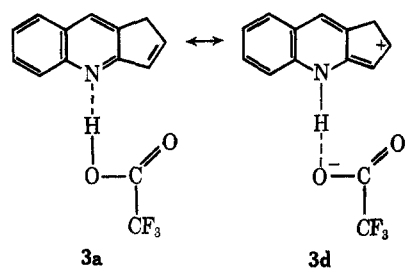


solution of which was prepared by adding 1 equiv of *n*-butyllithium in hexane to **3** dissolved in benzene, has three broad maxima at λ_{max} 468 mμ (log ϵ 2.99), 497 (3.01), and 530 (2.94). Hydrolysis of **16** after a short-term storage at 0° yielded recovered **3** having 31% of the 1-H tautomer (**3a**) and 69% of the 3-H tautomer (**3b**). Reasonable agreement between this base-equilibrated ratio and the ratio of tautomers achieved eventually by storage of **3** (*cf. supra*) verifies that the two tautomers were present in their equilibrium proportions.

The chemical shifts and the separation of methylene signals A (**3b**) and B (**3a**) were dependent upon the solvent (solvent, A, B, and A–B in ppm): neat 3.56, 3.04, and 0.52; CCl_4 (26% wt) 3.42, 3.16, and 0.26; CCl_4–NMe_3 (31% wt) 3.57, 3.42, and 0.15; CF_3COOH (52% wt) 4.24, 4.06, and 0.18; and C_6H_5Br (6% wt) 3.12, 2.86, and 0.26. Although the ratio of A:B did not change significantly in most of these solvents [typical ratio for freshly distilled sample, (45 ± 3):55], the proportion A:B in trifluoroacetic acid was 23:77. Furthermore, these methylene peaks were shifted downfield by 0.8–0.9 ppm, had lost all hint of hyperfine structure, and no longer displayed base-line separation. These observations can be interpreted to mean that protonation or hydrogen bonding of **3** by trifluoroacetic acid further favors the formation, at equilibrium, of tautomer **3a** because of available charge delocalization (**3d**). The narrowing and incipient merging of the



3b



3a **3d** (3)

methylene signals, moreover, suggested that the rate of tautomer interconversion had increased in this acidic medium. In an analogous attempt to accelerate the interconversion of tautomers **3a** and **3b**, trimethylamine was added to a CCl_4 solution of **3**. The decrease in the separation of the signals A and B (0.26 → 0.15 ppm) suggests that the rate had increased somewhat. Complete coalescence of these signals, by heating these acidic or basic solutions by or heating a solution of **3** in bromobenzene, could only be achieved under conditions (>100°) where irreversible chemical change occurred. Presumably such systems, being at once analogs of 2-vinylpyridine and cyclopentadiene, eventually undergo auto-Michael reactions,[24] as supported by the broad nmr signal in the 3.0–3.5-ppm region of decomposed material.

Discussion

A comparison of the benzo[*b*][1]pyrindines (**3a–c**, R = H) with the known 1,5-pyrindine tautomeric mixture (*i.e.*, **1**, R = H, and its tautomers) is in order. The amounts of the N–H tautomer, 0.093% for a 1.9 *M* violet solution of **3** in benzene *vs.* 0.11% for a neat orange sample of **1**,[25] are estimated by different methods, namely assumptions concerning the ultraviolet extinction coefficient of **3c** and **1** and a pK_a estimate of the basicities of the 1-H and 5-H tautomers of **1**, respectively. In the latter pK_a method no ac-

(22) E. B. Baker, *J. Chem. Phys.*, **23**, 1981 (1955).
(23) E. Heilbronner, *Helv. Chim. Acta.*, **39**, 1059 (1956).
(24) W. E. Doering and R. A. N. Weil, *J. Amer. Chem. Soc.*, **69**, 2461 (1947).
(25) C. B. Reese, *ibid.*, **84**, 3979 (1962).

count was taken of the varying amounts of the 5-H and 7-H tautomers of **1**.[25] With these limitations in mind, one can conclude that the amount of N–H tautomer for a neat sample of **3** would be greater than that of **1**, since a solution of **3** is already comparable to neat **1**. The deep purple color of melted **3** confirms this assumption. However, the nmr spectrum of **3**, even in concentrated form, gave no sign of an N–H peak ascribable to **3c** in the region of 3.6–4.7 ppm,[26] but this is not surprising in view of the small amount present. The superior sensitivity of a visible spectral estimate for this azulene-like tautomer (azalene **3c**) is also seen in the fact that even a 0.01% solution of azulene itself is highly colored.[27]

The assignment of this purple-colored component as the N–H tautomer (**3c**, R = H) was supported by the observed blood-red color of the analogous lithium salt **16** in ether–benzene and the purple color of anions of 3-substituted benzo[*b*][1]pyrindines in tetrahydrofuran.[28] Quaternizing **3** with methyl iodide and then treating the salt with sodium carbonate does give a purple species, presumably **3c** (R = CH_3).[28] With the pyrindine system there is disagreement as to whether this procedure leads to **1** (R = CH_3).[10b,25] A difficulty with this method, possibly overlooked in the pyrindine system,[10b,25,29] is that methylation occurs both on nitrogen (82%) and on the α-carbon atom (18% on C_3 in **3**).[28] C-Alkylation can most reasonably be attributed to β (C_3) electrophilic attack on the enamine tautomer **3c** (R = H).

The present nmr data on **3** demonstrate, for the first time, the relative stability of C–H tautomers of a pyrindine system. Attempts to make such a distinction based upon differences in ultraviolet absorptions were unsuccessful.[29,30] The recorded nmr spectrum of 1-pyrindine does show some slight favoring of the 5-H tautomer over the 7-H, by our visual estimation, but the significance of this spectral information has not been pointed out.[29] Moreover, no data were given on the length of time between the preparation of the pyrindine and the spectral measurement. With the benzo[*b*][1]pyrindine, the equilibrium mixture at 25° contains 67 ± 2% of the 1-H tautomer **3a**. Protic or hydrogen-bonding media, such as trifluoroacetic acid, enhance the amount of **3a** (eq 3). Furthermore, the bathochromic shift in the ultraviolet spectrum of **3**, especially in acidic solution, can be ascribed principally to the importance of polar resonance forms, such as **3d**, available to the predominant tautomer **3a**.

The visible spectra of 4H-benzo[*b*][1]pyrindine (**3c**) and its lithium salt **16** show pronounced bathochromic shifts when compared with spectra of 1-pyrindine (**1**, R = H or CH_3). Recent quantum mechanical calculations predicted that such a shift would be observed.[31] Comparison of the spectral shapes of 5,6-benzazulene[23,32] and **3c** shows that both have similar broad absorptions at >500 mμ, with **3c** peaking some 50 mμ below that of the azulene. Visible spectra of substituted benzo[*b*][1]pyrindines have been known to resemble that of 5,6-benzazulene rather closely.[7,8] The lithium salt **16** has a visible maximum only 27 mμ below that of 5,6-benzazulene, but its absorption drops more sharply above 550 mμ.

The question of the rate of interconversion of the 1-H and 3-H tautomers of **3** in acidic or basic media cannot be answered definitively. In trifluoroacetic acid the methylene signals lost both their fine structure and base-line separation. The recorded spectrum of 1-pyrindine in this medium displays such coalescence of methylene signals, although the author does not comment on its significance.[29] It would appear that the exchange of protons between the C_1 and C_3 sites in benzo[*b*][1]pyrindine and between the C_5 and C_7 sites in 1-pyrindine become significant in this medium. Analogous attempts to observe coalescence by heating **3** itself, or with triethylamine, were indicative of some accelerated proton exchange, but their success was limited by the decomposition of **3**. As with the well-studied indene system,[33,34] such proton exchange may well occur by an intramolecular route.

Although the nature of the thermal decomposition products of **3** is not completely clear, existing evidence suggests that a Michael reaction of enamine **3c** or its anion **16** occurs with the 1-H tautomer, itself a vinylic pyridine.[24] The facility of such an allylic carbanion attack on a vinylpyridine is seen in the smooth 1,4 addition of allylmagnesium bromide to *trans*-2-phenylvinylpyridine (2-stilbazole).[35]

Ongoing research is concerned with evaluating the aromatic character of the N–H tautomer of benzo[*b*][1]-pyrindine and its delocalized anion,[26] with an eye to the azulene-like character of these systems.

Experimental Section

Melting points were determined with a Thomas-Hoover "Unimelt" apparatus and are corrected. Infrared spectra were recorded of samples as potassium bromide disks, mineral oil suspensions, or solutions in pure solvents, by means of a Perkin-Elmer spectrophotometer, Model 139. Proton magnetic resonance spectra were measured with a Varian spectrometer, Model A-60, on samples dissolved as 10% solutions in pure solvents containing tetramethylsilane as an internal standard. Signals are reported using the δ scale in parts per million, followed by the integrated intensities of the proton signals and the coupling constants (J) in hertz. Ultraviolet and visible spectral data were obtained with a Cary spectrophotometer, Model 15, on samples dissolved in cyclohexane, benzene, or 95% ethanol of "spectral-grade" purity. Vpc analyses were performed on an F & M dual-column chromatograph equipped with 2-ft columns packed with 10% silicone gum rubber on firebrick. Tlc plates were prepared with silica gel, developed usually with methylene chloride and then sprayed with chromic acid solution for detection of the separated components. Elemental analyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

All preparations and reactions involving either air- and moisture-sensitive organometallic reagents or reactive heterocyclic intermediates were conducted under an atmosphere of dry, oxygen-free nitrogen. Appropriate techniques for such manipulations, including the necessary purification of solvents, have already been described.[37]

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Reagents.—The known 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline-9-carboxylic acid (**5**) was prepared in large-scale runs of 1–3 mol by adapting a published Pfitzinger reaction involving isatin and cyclopentanone in a basic medium. Although a 90% yield of crude acid **5** was obtained, the melting range (230–260°) and the subsequent decarboxylation products betrayed the presence of the 3-cyclopentidylidene derivative of **4**. The impurity presumably arose from the participation of 2-cyclopentylidenecyclopentanone, the aldol condensation product of the starting ketone, in a competing Pfitzinger reaction.[5,38]

2,3-Dihydro-1*H*-cyclopenta[*b*]quinoline (**4**) was prepared by the thermal decarboxylation of **5** at 250–300° (sand bath) and by the fractional distillation of the residue: the first main fraction, bp 106–108° (0.25 mm), was colorless **4**, which solidified on standing; the second main fraction was a yellow oil, bp 157–159° (0.70 mm), which by spectral data was thought to be the cyclopentylidene derivative of **4** (5% yield). The first fraction was dissolved in ether and the resulting solution extracted with 5% sodium hydroxide solution, washed with water, and dried over anhydrous calcium sulfate. After removal of ether the residual **4** was recrystallized from petroleum ether (bp 30–60°) to yield colorless crystals of **4**: mp 59–61° (lit.[5] 59–60°); spectral data nmr (CS_2) 1.90–2.52 (m, 2-CH_2) 2.90–3.45 (m, 1-CH_2, 3-CH_2), 7.5–8.38 (m, 5 H).

Lithium Salt of 2,3-Dihydro-1*H*-cyclopenta[*b*]quinoline (12).—To a solution of **4** (8.45 g, 50.0 mmol) in 100 ml of dry benzene were added dropwise 55 mmol of phenyllithium in 60 ml of ether, while the reagents were stirred in a bath of ice water. Upon adding the first few drops of the phenyllithium reagent, a vivid red color appeared, but this faded as the addition continued. The Gilman color test I remained negative[39] until an excess of phenyllithium had been added. The tan-colored suspension was allowed to come to room temperature over a 3-hr stirring period. Then a solution of 11.4 g (62.5 mmol) of benzophenone in 100 ml of dry benzene was added dropwise over a 45-min period. The color of the reaction mixture lightened and a noticeable exotherm occurred. After a further 2-hr stirring period, the suspension was hydrolyzed with 150 ml of saturated sodium bicarbonate solution. Usual work-up, drying of organic extract, and removal of solvent left the crude carbinol, which upon recrystallization from methylene chloride yielded 12.4 g (71%) of 2,3-dihydro-α,α-diphenyl-1*H*-cyclopenta[*b*]quinoline-3-methanol (**13b**), mp 152–154°. An analytical sample melted at 154–155.5°: ir $\lambda_{max}^{CH_2Cl_2}$ 2.95 μ (OH).

Anal. Calcd for $C_{25}H_{21}NO$: C, 85.43; H, 6.02. Found: C, 85.35; H, 6.01.

Although **13b** suffered no cleavage, *via* reverse aldol reaction, into **4** and benzophenone when chromatographed on neutral alumina with a benzene eluent, cleavage did occur during tlc on silica gel. Even during successful acid-catalyzed dehydration of **13b** to produce 2,3-dihydro-3-diphenylmethylene-1*H*-cyclopenta[*b*]quinoline, some reverse aldol cleavage was detected. This cleavage also occurred when pure **13b** was treated with 1 equiv of phenyllithium and the mixture then worked up. The demonstrated ease with which the lithium salt **12** reacts reversibly with benzophenone clearly puts a limit on the yield of isolable carbinol **13b**. Since treatment of **12** with methyl iodide gave a >90% isolated yield of the 3-methyl derivative of **4**, the formation of **12** from **4** and phenyllithium must proceed almost quantitatively.

2,3-Dihydro-3-hydroxy-1*H*-cyclopenta[*b*]quinoline (9) from 4.—According to the foregoing procedure, proportional amounts of **4** and phenyllithium in ether were used to prepare 400 mmol of the lithium salt **12** in 1000 ml of dry benzene. With cooling at −15° and vigorous stirring a stream of dry oxygen gas was bubbled through the suspension over a 4-hr period. After being stirred overnight at room temperature, the reaction suspension was hydrolyzed with 1 *N* hydrochloric acid and the liquid layers were separated from residual solids by filtration. The separated aqueous layer was made basic with 5% sodium hydroxide solution and the precipitated organic bases were taken up in ether. Drying of the ether extract, removal of solvent, and washing the residue with cyclohexane left 23 g (31%) of crude **9**. Recrystallizations from cyclohexane–petroleum ether (bp 30–60°) gave the pure 3-hydroxy derivative **9** as pale yellow cubic crystals, 9.6 g (13%), mp 128–129°. Several variations in the oxidation procedure did not improve the yield: spectral data ir $\lambda_{max}^{mineral\ oil}$ 3.10 μ (OH); nmr ($CDCl_3$) 2.50–3.2 (m, 2-CH_2, 1-OH), 3.30–3.70 (m, 1-CH_2), 5.70–6.0 (m, 3-CH).

Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.98. Found: C, 77.74; H, 6.05.

3-Acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (15).—Water (0.42 g, 24 mmol) was added to a mixture of 5.2 g (500 mmol) of acetic anhydride and 6.51 g (30 mmol) of 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline *N*-oxide (**14**).[40] After a slightly exothermic reaction had occurred, the mixture was heated on a boiling water bath for 1.5 hr. After concentrating and cooling, the solution was taken up in ether and made basic by treatment with a 5% sodium carbonate solution. The ether layer was separated, dried over anhydrous potassium carbonate, and freed of volatile solvent. Recrystallization of the residual dark oil from petroleum ether gave light yellow, rod-like clusters of the 3-acetoxy derivative **15**: mp 106–108°; 5.6 g (81%); ir λ_{neat}^{KBr} 5.70 μ; nmr ($CDCl_3$) 2.26 (s, 3 H), 2.4–3.0 (m, 2-CH_2), 3.1–3.5 (m, 1-CH_2), 6.3–6.5 (m, 3-CH_2), 7.6–8.2 (4 H), 8.3–8.5 (m, 5-CH).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.76; N, 6.10. Found: C, 73.88; H, 5.65; N, 6.20.

This compound could be saponified to yield the aforementioned 3-hydroxy derivative **9**, by heating a mixture of **15** (850 mg, 3.7 mmol), sodium hydroxide (200 mg), and water (1.8 g) on a boiling water bath for 15 min. The mixture was cooled, saturated with potassium carbonate, and extracted with several portions of chloroform. The combined chloroform extracts were passed through a short column of alumina and the resulting eluate was evaporated to dryness. Recrystallization of the residue from cyclohexane–petroleum ether (bp 30–60°) yielded 41% of pure **9**, identical by ir and nmr spectral and mixture melting point criteria with the oxidation product of the lithium salt **12**.

1*H*- (or 3*H*- or 4*H*-) Cyclopenta[*b*]quinoline (Benzo[*b*][1]-pyridine) (3).—The procedure given here had to be followed strictly, in order to obtain satisfactory yields of **3**. Other procedural variants and other methods of dehydration (trace of sulfuric acid in glacial acetic acid, 85% *o*-phosphoric acid, or *p*-toluenesulfonic acid in warm benzene[41]) proved to be unsatisfactory.

Over the course of 20 min the powdered 3-hydroxy derivative **9** (3.00 g, 16.2 mmol), or an equivalent amount of the 3-acetoxy compound **15**, was dusted into 35 ml of cooled, concentrated sulfuric acid contained in a flask equipped with a motor-driven stirrer. The orange-brown solution was immediately thereupon immersed in an oil bath maintained at 120–130°, heated for 4 min, and promptly poured over 300 g of ice. While the thawed solution was kept below 30°, a 50% aqueous solution of sodium hydroxide (150 g) was slowly added. The organic precipitate was taken up in ether and the ether extract, after extraction with water, was dried over anhydrous potassium carbonate. A trace of hydroquinone was added to the extract and the entire purification was executed promptly, in order to minimize decomposition. With very slight warming the solvent was removed with a rotary evaporator and the residual brown oil immediately distilled at reduced pressure in an apparatus previously flushed with nitrogen. The dehydration product **3** distilled over as a violet-colored oil, bp 130–132° (1.3 mm), 1.5 g (50%). This substance gradually solidified to an almost colorless substance, mp 59–61° (sealed tube), and could be stored for several weeks without apparent decomposition if kept under nitrogen below 0°. Redistillation always was accompanied by considerable losses due to thermal dimerization or polymerization (nmr examination of the residue).

A further distillation provided an analytical sample, bp 115–116° (0.5 mm), which was shipped for analysis in a sealed, nitrogen-filled ampoule: spectral data ir λ_{max}^{neat} 2.9 (distinct NH), 6.15 and 6.35 μ (aromatic C=C with conjd C=C); $\lambda_{max}^{10\%\ CCl_4}$ essentially no distinct band at 2.9 μ; nmr (CCl_4) 3.16 (s, 1, 1-CH_2), 3.42 (s, 1, 3-CH_2), 6.40–7.16 (m, 2, 1-, 2- and 3-vinyl), 7.16–8.08 (m, 5, aromatic CH) (*cf.* Results for further details, such as the variation in the integrated intensities and the peak separations of the 1- and 3-methylene signals).

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.42; N, 8.38. Found: C, 85.83; H, 5.40; N, 8.81.

The product formed a picrate readily (highest mp 215.5–217.5°, from ethanol) but the elementary analysis was not satisfactory, despite repeated attempts at purification (3.35% high on C, 1.21% low on N), nor were satisfactory derivatives ob-

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tained with chloroplantinic acid, picrolonic acid, 2,4,7-trinitrofluoren-9-one, or 1,3,5-trinitrobenzene. The presence of sensitive tautomeric components in **3** that are decomposed by acid and oxidizing agents may be at fault in these unfruitful reactions.

Lithium Salt of Cyclopenta[*b*]quinoline (Benzo[*b*][1]pyridine) (16).—The sensitivity of the cyclopenta[*b*]quinoline **3**, apparently to base-promoted autoaddition, demands that the reaction conditions described here be adhered to strictly or subsequent hydrolysis will permit no recovery of **3**.

Under a nitrogen atmosphere a solution of 1.31 g (7.86 mmol) of **3** dissolved in 50 ml of dry, degassed benzene was treated dropwise over 8 min with 7.92 mequiv of ethereal phenyllithium while stirring at 0° was maintained. Then the blood-red solution of lithium salt **15** was stirred for a further 10 min at 0° and then promptly hydrolyzed at 0° with degassed water and worked up in the usual way. Distillation gave a 28% recovery of **3**, as proved both by bp and by ir and nmr spectral data.

If the blood-red solution of **16** was allowed to stand at >20° for 1 hr and then worked up in the same manner, no **3** was obtained.

1-Bromo-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (6).—To a stirred, refluxing solution of 8.45 g (50.0 mmol) of **4** in 150 ml of carbon tetrachloride were added 8.95 g (52.0 mmol) of colorless, pure *N*-bromosuccinimide, in portions, over the course of 45 min. The resulting suspension was heated at reflux for an additional 20 min, cooled, and filtered. With a minimum of warming the filtrate was freed of solvent under reduced pressure. The resultant dark residue was extracted promptly with six 50-ml portions of hot petroleum ether (bp 30–60°) and these combined extracts were then concentrated. Cooling of the extracts deposited 7.1 g (28.5 mmol, 57%) of yellow cubic crystals of 1-bromo-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**6**), mp 84–86°. This product appeared to be homogeneous (*i.e.*, one isomer) as judged by its melting point and ir spectrum, but its sensitivity to air and to heat prevented an elemental analysis or further purification. Its identity as the 1 isomer rests upon its subsequent hydrolysis, albeit in low yield, to the 1-hydroxy derivative of **4**.

The infrared spectrum of **6** in CS_2 showed strong bands at 3.15, 3.35, 6.15, 7.2, 8.5, 10.55, 11.15, 11.7, 12.2, 12.75, 13.4, and 13.9 μ.

2,3-Dihydro-1-hydroxy-1*H*-cyclopenta[*b*]quinoline (7).—A sample of the bromo derivative **6** (6.2 g, 25 mmol), prepared as described above and dissolved in 50 ml of acetone, was stirred for 1 hr at room temperature with a slurry of 5 g of powdered calcium carbonate in 25 ml of water. The reaction suspension was filtered and the filtrate concentrated by warming under reduced pressure. The residue was extracted with ether, the ether extract dried, and the solvent removed from the extract. Several recrystallizations of this residue from a cyclohexane–petroleum ether (bp 30–60°) pair gave almost colorless needles: 1.1 g (24%) of the 1-hydroxy derivative **7**; mp 166.5–168°; a test for halogen was negative; spectral data ir (mineral oil) 3.05 μ (OH), and strong bands at 6.15, 8.75, 9.15, 9.4, 10.9, 11.75, 12.75, and 13.2 μ; nmr ($CDCl_3$) 2.15 (m, 1, 1-OH), 2.3–2.9 (m, 2, 2-CH_2), 3.0–3.3 (m, 2, 3-CH_2), 5.25–5.6 (m, 1, 1-CH), 7.6–8.1 (m, 5, arom). The assignment of the multiplet at 2.15 to the 1-hydroxyl group was made upon the basis of the disappearance of this signal when a sample of in $CDCl_3$ was shaken with deuterium oxide.

Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99. Found: C, 77.71; H, 6.22.

Dehydration of 2,3-Dihydro-1-hydroxy-1*H*-cyclopenta[*b*]quinoline (7).—The dehydration of the 1-hydroxy isomer proved to be even more sensitive to further reaction than that of the 3-hydroxy isomer and hence was impractical for the preparation of benzo[*b*][1]pyrindine. Milder dehydrating agents for brief reaction periods, dimethyl sulfoxide at reflux, oxalic acid in hot aqueous solution, or phosphorus pentoxide in refluxing xylene, gave no dehydration; longer reaction times led to further reaction. Only with conditions similar to those used with 3-hydroxy isomer was any success achieved. Thus, when a 2.0-g sample of **7** was heated with 35 ml of concentrated sulfuric acid for 4 min and then worked up as before, distillation under reduced pressure afforded only a few drops of benzo[*b*][1]pyrindine (**3**), whose identity was established by ir and nmr spectral comparison.

Mass Spectra of 2,3-Dihydro-1-hydroxy-1*H*-cyclopenta[*b*]quinoline and of 2,3-Dihydro-3-hydroxy-1*H*-cyclopenta[*b*]quinoline.—Under a pressure of 10^{-6} Torr, a source temperature of 330° and electron energies of 70 eV, the following relative abundances (selected values) of ion fragments were observed—mass (abundance relative to the base peak): 1-hydroxy isomer, 185 (100), 184 (97), 169 (7), 168 (27), 167 (37), 157 (7), 156 (37), 155 (7), 154 (10), 140 (10), 139 (10), 130 (10), 129 (17), and 128 (23); 3-hydroxy isomer, 185 (45), 184 (16), 183 (13), 169 (70), 168 (68), 167 (45), 157 (78), 156 (100), 140 (11), and 129 (45).

Registry No.—**3a**, 268-85-9; **4**, 5661-06-3; **6**, 29411-23-3; **7**, 29411-24-3; **9**, 29411-25-4; **13b**, 29520-62-5; **15**, 29411-26-5.

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