agitated with a stream of dry nitrogen. Removal of the solvents under reduced pressure and glc analysis[16] of the crude mixture showed the presence of the starting material and a major product in a *ca.* 23:77 ratio. Only traces of other volatile products were observed. Distillation of the mixture gave a fraction, bp 75–85° (bath temperature) (0.2 mm), which proved to be mainly starting material. A higher boiling fraction, bp 100–110° (bath temperature) (0.2 mm), weighing 300 mg (55%), was collected. This fraction contained essentially one component, which was identified as the 5/6-fused ethoxy ketone **19**: uv max (95% EtOH) 242 mμ (ε 10,600); ir (CCl_4) 5.91 (C=C) and 6.08 μ (C=C); nmr (CCl_4) δ 3.45 (q, 2 H, J_{AX} = 7 Hz, OCH_2CH_3), 2.9–1.6 (broad absorption, 9 H), 1.63 (broad s, 3 H, C-1 CH_3), 1.10 (t, 3 H, J = 7 Hz, OCH_2CH_3), and 0.88 (s, 3 H, C-4 CH_3). *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.72; H, 9.79.

Irradiation of **7b** under identical conditions with those described above gave **19** as the sole photoproduct.

Irradiation of 14 in Absolute Ethanol.—Dienone **14** (380 mg) in 250 ml of absolute ethanol ws irradiated under identical conditions with those described above for **8b**. Removal of the solvent under reduced pressure gave 400 mg of crude liquid which on the basis of its spectral properties appeared to be largely the unconjugated diene ester **20**. Attempted purification of the compound by preparative glc[16] led to extensive isomerization to a mixture of **20** and the corresponding cis- and trans-conjugated diene esters. However, an analytical sample of **20** could be collected from the mixture. The sample showed ir (CCl_4) 5.74 (ester C=O) and 6.06 μ (conjugated diene); nmr (CCl_4) δ 5.42 (broadened t, J = 6 Hz, 1 H, vinyl H), 4.17 (q, J = 7 Hz, 2 H, $OCHCH_3$), 2.97 (broadened d, J = 6 Hz, 2 H, O=CCH_2CH=), 1.70 (s, 3 H, CH_3C=), 1.65 (s, 3 H, CH_3C=), and 1.25 (t, 3 H, OCH_2CH_3). *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, C, 75.00; H, 9.45.

Registry No.—**7a**, 22416-99-5; **7b**, 22417-00-1; **7c**, 22417-01-2; **8a**, 22417-02-3; **8b**, 22417-03-4; **8c**, 22417-04-5; **9a**, 22417-05-6; **9b**, 33070-69-8; **10a**, 17299-55-7; **10b**, 33070-71-2; **10c**, 33070-72-3; **14**, 33070-73-4; **19**, 33065-85-9; *cis*-**20**, 33065-86-0; *trans*-**20**, 33065-87-1; 2-methylcyclopentanone, 1120-72-5.

Photocyclizations. II. Synthesis of Iminoethanophenanthridine (Seven-Membered Ring) Homologs[1]

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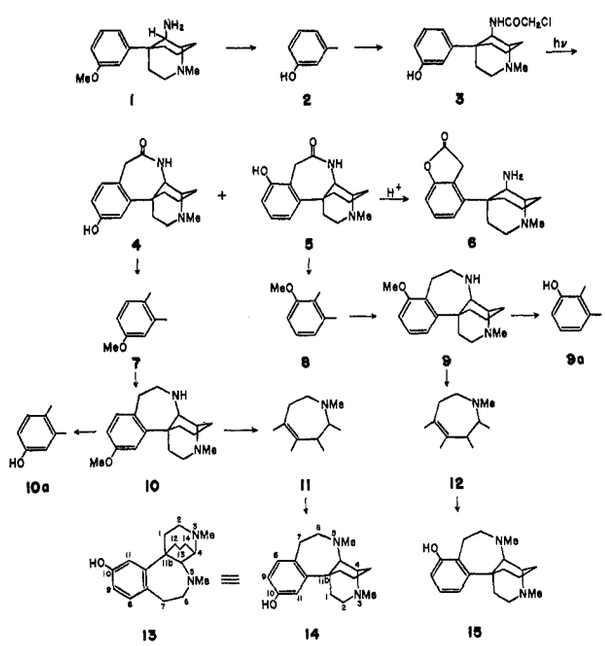
Photolysis of 9-*cis*-chloroacetamino-5-(*m*-hydroxyphenyl)-2-methyl-2-azabicyclo[3.3.1]nonane (**3**) has given both ortho and para ring closure to propanopyridobenzazepinones, **5** and **4**, whose structures were deduced from mass and nmr spectral data and by chemical evidence. The *O*-acetyl derivative of *o*-hydroxy compound **5** formed more slowly than that of **4**. Furthermore, acid treatment of **5** caused lactam ring opening with the formation of a new lactone ring (*cf.* **6**), in effect N → O acyl migration. Methylation of **4** and **5** followed by diborane reduction gave homophenanthridines **10** and **9**, respectively, which were N-methylated then O-demethylated to **14** and **15**.

In paper I of this series[2] we reported the synthesis of 4,5-dihydro-1*H*-naphth[1,8-de]azocin-2(3*H*)-one by irradiation of 1-(2-chloroacetamino)naphthalene. This communication is concerned with the photocyclization of a chloroacetamino group attached to a rigid azabicyclononane system with attack at both the ortho and para positions of a neighboring phenolic ring.[3] The results described here indicate a broadened scope and utility for this reaction especially toward the synthesis of complex heterocyclic systems.

The starting amine **1**[4] was hydrolyzed to **2** with boiling 48% hydrobromic acid. Conversion of **2** to the chloroacetamino compound **3** was effected in high yield by N,O dichloroacetylation with choroacetic anhydride in an aprotic solvent (potassium carbonate) and selective saponification.[5]

Amide **3**, irradiated in dilute aqueous solution, was completely consumed during 90 min to give two products. Preliminary mass spectral data (*m/e* 286 and 243[6] and no higher peaks) and proximate R_f values (for the sublimed mixture) in several solvent systems[7] were



(1) These compounds are named benzazepines in the Experimental Section in accord with Chemical Abstracts recommendations.

(2) H. H. Ong and E. L. May, *J. Org. Chem.*, **35**, 2544 (1970).

(3) Previously reported photocyclizations of *N*-chloroacetyl compounds (see ref 2 and papers cited therein) have included no examples of alicyclic amines. Furthermore, this appears to be the first record of closure to the ortho position in a monophenolic compound.

(4) H. H. Ong and E. L. May, *J. Heterocycl. Chem.*, **8**, 1007 (1971).

(5) Low yields of **3** (1 mol of chloroacetic anhydride) or extensive quaternization of **2** (with excess reagent) were obtained when the procedure of O. Yonemitzu, T. Tokuyama, M. Chaykovsky, and B. Witkop, *J. Amer. Chem. Soc.*, **90**, 776 (1968), was used.

(6) This is probably due mainly to loss of CH_2NCH_3, but loss of –NHCO– may also contribute; *cf.* A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **86**, 5536 (1964).

(7) Silica gel GF plates: system I, $MeNO_2$–AcOH–H_2O (90:28:12), R_f 0.41, 0.35; II, $CHCl_3$–Et_3N (5:1), R_f 0.07, 0.18, for example.

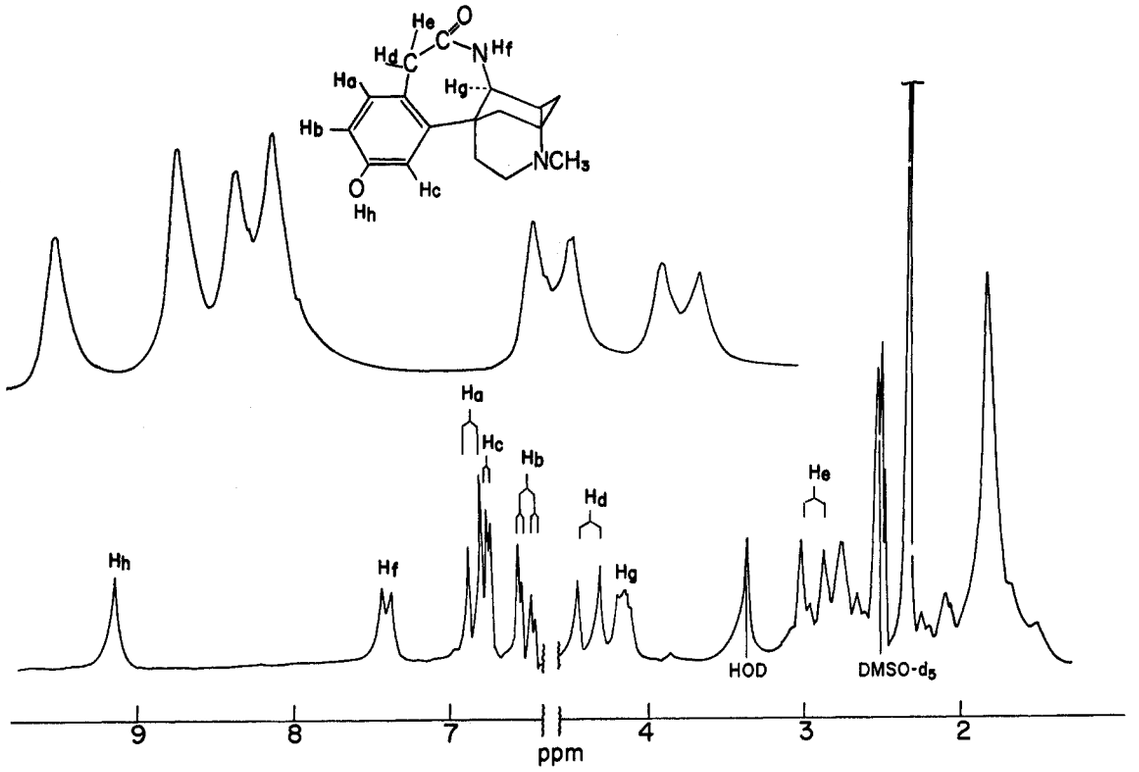
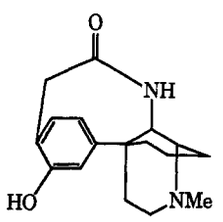


Figure 1.—Nmr spectrum of 4 measured at 100 MHz in DMSO-d_6. Multiplets arising from the aromatic protons are shown amplified and expanded (ten times) just above the main spectrum.

consistent with isomeric structures **5** and **4** (ortho and para ring closure through loss of hydrogen chloride) as the principal products.

Separation of **4** from **5** was effected by fractional crystallization in ethanol. Compound **4**, the more soluble of the two, was assigned the empirical formula $C_{17}H_{22}N_2O_2$ based on its elementary and mass spectral analyses. Its ir spectrum exhibited a carbonyl stretching frequency at 1655 cm^{-1}, expected for a medium-sized lactam, and its nmr spectrum established the site of cyclization as para to the phenolic hydroxyl group. A 100-MHz pattern of **4** taken in DMSO-d_6 (Figure 1) showed the presence of three aromatic protons: a doublet centered at δ 6.82 (J_{ab} = 8.0 Hz), a second doublet centered at δ 6.74 (J_{bc} = 2.5 Hz), and a quartet centered at δ 6.51. The splitting pattern and coupling constants are such that they are reconcilable only with structure(s) incorporating a 1,2,4-trisubstituted benzene, as in **4**. The only other possible structure consistent with the foregoing spectral data is **16**, which was ruled out on steric considerations. The nonequivalent nature of the two methylene protons adjacent to the carbonyl group (H_d at δ 4.36 and H_e at δ 2.96, doublets, $|J|$ = 14 Hz)[8] should not be too surprising in view of the rigidity and lack of symmetry of **4**. The considerable difference in chemical shift between H_d and H_e could be partly due to the anisotropic effect exerted by the nearby aromatic system; H_d is deshielded by being in or near the aromatic ring, whereas H_e is shielded by being above or under the π plane.[9,10] Effects of other magnetically anisotropic groups, such as the carbonyl double bond and the alicyclic ring, are also not to be excluded.



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Compound **4** was readily converted to its *O*-acetyl derivative, the nmr spectrum of which (100 MHz, $CDCl_3$) further confirmed the 1,2,4 pattern of the aromatic protons: two doublets at δ 7.06 (J = 8.5 Hz) and 7.02 (J = 2.4 Hz) and a quartet at δ 6.85. In addition, the phenolic proton signal at δ 9.12 vanished while a sharp singlet due to the acetyl group appeared at δ 2.44.

The less soluble photoproduct, **5**, is also assigned the empirical formula $C_{17}H_{22}N_2O_2$ on the basis of elemental analyses and mass spectral data. Its ir spectrum exhibited a carbonyl frequency of 1665 cm^{-1}, somewhat higher than the corresponding band observed with **4**. The position of ring closure was likewise established by nmr spectroscopy to be ortho to the phenolic hydroxyl group and the alicyclic substituent.

A 100-MHz spectrum of **5** taken in DMSO-d_6 showed a pseudo-AMX pattern for the three aromatic protons, each appearing as a quartet (see Figure 2), indicative of three adjacent protons each of which is coupled unevenly to two others. The "double doublet" at lowest field (δ 6.91) showed the two largest splittings (J_{ortho} = 7.6 and 8.4 Hz), and hence must be the signal from the

(8) A negative value is assumed for the geminal coupling constant.

(9) The methylene protons adjacent to the carbonyl group in 7-hydroxy-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one gave a singlet at δ 3.55; *cf.* reference in footnote 5.

(10) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 67.

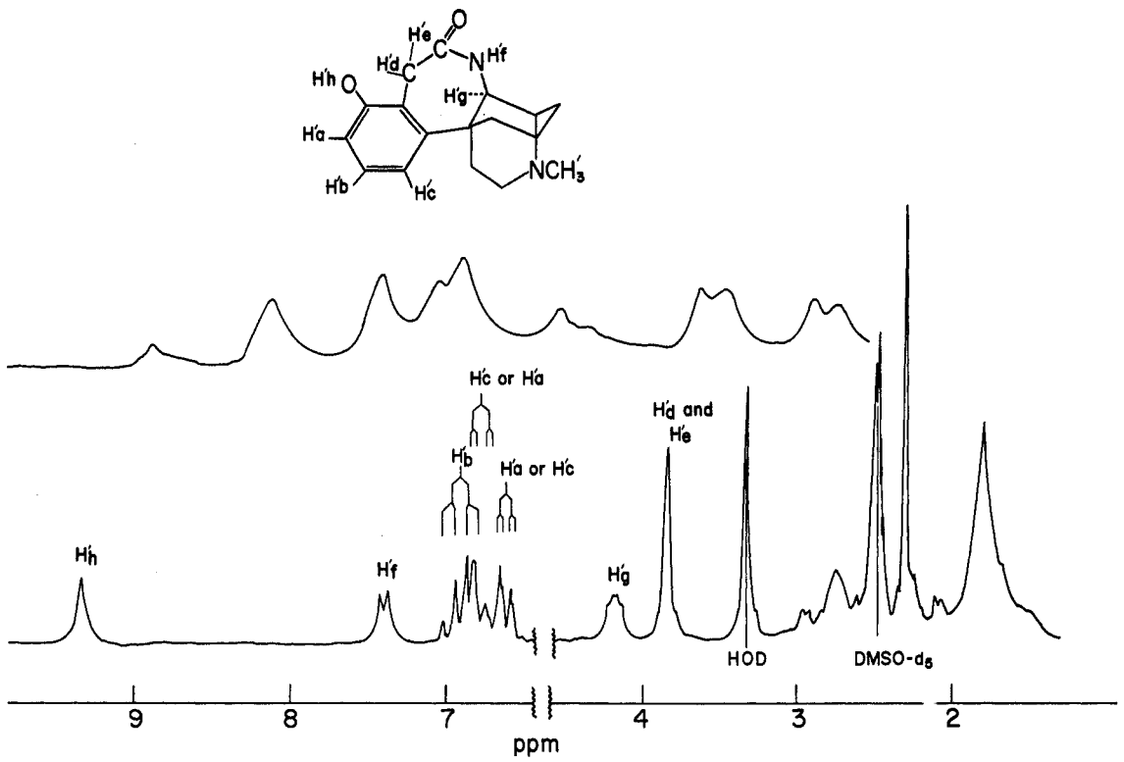

Figure 2.—Nmr spectrum of **5** measured at 100 MH_z in DMSO-d_6. Multiplets arising from the aromatic protons are shown amplified and expanded (ten times) just above the main spectrum.

middle proton, H'_b. Although it seems reasonable that the quartet at the highest field (δ 6.62) can be attributed to H'_a, an unambiguous assignment could not be made without data from the appropriate double resonance experiments. It is interesting to note that the two methylene protons, H'_d and H'_e, in **5** now coalesced to a single peak at δ 3.80; this possibly reflects a different conformation adopted (preferentially) by the seven-membered azepine ring in **5**, as compared to that in **4**, because of crowding by the ortho hydroxyl group.

Compound **5** reacted less readily with acetic anhydride to give a mono-*O*-acetyl derivative, whose nmr spectrum showed the aromatic protons in a degenerate ABX pattern, the X part (the multiplet at higher field) being attributed to the proton para[11] to the acetoxy group. A well-separated AB quartet (δ 3.92 and 3.72) was now observed for the two methylene protons in the azepine ring.

The structure of **5** was further confirmed by chemical evidence. The hydrochloride, despite its thermal stability, underwent a facile acid rearrangement to give an amino lactone, **6** (ν_{max} 1800 cm^{-1}), which can be formed only when the lactam bridge is ortho to the phenolic hydroxyl group. The presence of a primary amino group was apparent from the mass spectrum of **6**, which showed a moderate peak at *m/e* 269 and a prominent peak at *m/e* 256 due to the loss of NH_3 and $CHNH_3$, respectively, in addition to the molecular ion at *m/e* 286.[12] The *O*-acetyl derivative of **5** underwent a similar acid rearrangement to give **6** in good yield, but, under identical conditions, **4** was resistant to acid hydrolysis.

(11) D. W. Mathieson, "Nuclear Magnetic Resonance for Organic Chemists," Academic Press, London, 1967, p 184.

(12) The peaks at *m/e* 269 and 256 were totally absent in the spectrum of **5**. Peaks corresponding to $M^+ - NH_3$ and $M^+ - CHNH_3$ were also observed in the mass spectra of **1** and **2**.

Methylation of **4** with excess diazomethane gave **7** in 90% yield, along with a trace of the O,N-dimethylated product. Reduction of **7** with diborane in THF gave **10**, which was converted to **11** by reductive methylation with formaldehyde and formic acid. Refluxing **10** and **11** with 48% HBr afforded **10a** and **14**, respectively.

Compound **5** was subjected to the same reaction sequences to give **9a** and **15** *via* intermediates **8**, **9**, and **12**. The ease of reaction and the yield of each step corresponded well with those observed for photoproduct **4**.

The effect of pH on the photolysis of **3** was also studied. There was apparently no change in the course of reaction when the pH of the irradiation mixture was increased from 3 to 9. The relative as well as total yields of **4** and **5** remained virtually unchanged.

Experimental Section

All melting points were determined on a Kofler hot-stage and are uncorrected; ir spectra were recorded with a Perkin-Elmer grating spectrophotomer, model 257. Mass spectral data were obtained with a Hitachi RMR-6E double-focusing spectrometer at 80 eV, and nmr spectra were measured on a Varian HA-100 or HA-60 spectrometer using tetramethylsilane (δ 0) as internal standard.

9-*cis*-Amino-5-(*m*-hydroxyphenyl)-2-methyl-2-azabicyclo-[3.3.1]nonane (2) Dihydrodromide.—A mixture of 0.4 g (1.5 mmol) of **1**[4] and 3 ml of 48% HBr was refluxed under N_2 for 30 min. The cooled solution was concentrated *in vacuo* to give 510 mg (83%) of **2** 2HBr, mp 263–265°.

Anal. Calcd for $C_{15}H_{24}Br_2N_2O$: C, 44.14; H, 5.92; N, 6.86. Found: C, 43.86; H, 5.69; N, 6.90.

The free base was precipitated when an aqueous solution of **2** dihydrobromide was treated with 40% K_2CO_3. Recrystallization from ether–petroleum ether (bp 30–60°) gave colorless prisms: mp 164–165°; ν_{max}^{KBr} 3160, 1590 cm^{-1}; mass spectrum *m/e* 246 (M^+), 229, 216, 203 (base).

Anal. Calcd for $C_{15}H_{22}N_2O$: C, 73.16; H, 9.00; N, 11.37. Found: C, 73.29; H, 8.88; N, 11.12.

9-*cis*-Chloroacetamino-5-(*m*-hydroxyphenyl)-2-methyl-2-azabicyclo[3.3.1]nonane (3).—A solution of 320 mg (1.3 mmol) of **2** in 20 ml of $CHCl_3$ with 720 mg of anhydrous K_2CO_3 was stirred while 480 mg (2.8 mmol) of chloroacetic anhydride in 5 ml of $CHCl_3$ was added dropwise during 5–10 min. Stirring was continued for an additional 2 hr, and water was added to decompose the unreacted anhydride. The chloroform layer was separated and evaporated *in vacuo* to a sirup which by its ir spectrum (Nujol) was shown to be the dichloroacetylated derivative of **2** (1780 and 1670 cm^{-1}). NaOH (1 *N*, 10 ml) was then added to the residue to effect saponification of the ester group. After 30 min, the clear, aqueous solution was washed once with ether, acidified to pH 4 with 12 *M* HCl, and basified again with solid K_2CO_3. The precipitate was filtered (405 mg, 96%); silky needles from ether–petroleum ether, ν_{max}^{KBr} 3270, 2700, 1675 cm^{-1}. It decomposed and polymerized slowly above 120° without melting.

Anal. Calcd for $C_{17}H_{23}ClN_2O_2$: C, 63.26; H, 7.18; N, 8.68. Found: C, 63.80; H, 7.36; N, 8.78.

The hydrochloride gave (methanol–ether) microscopic granules. It darkened without melting at *ca.* 300°: nmr (D_2O, 60 MHz) δ 6.70–6.30 (m, 4, aromatic protons), 3.95 (s, 2, $ClCH_2$–), 3.00 (s, 3, $-N^+CH_3$), the remaining alicyclic protons were not resolved.

Anal. Calcd for $C_{17}H_{24}Cl_2N_2O_2$: C, 56.83; H, 6.70; N, 7.79 Found: C, 56.61; H, 6.57; N, 8.01.

Photolysis of 3. 1,2,3,4,4a,5-Hexahydro-8-hydroxy-3-methyl-4,11b-propano-11b*H*-pyrido[4,3-*a*][3]benzazepin-6(7*H*)-one (5) and 1,2,3,4,4a,5-Hexahydro-10-hydroxy-3-methyl-4,11b-propano-11b*H*-pyrido[4,3-a][3]benzazepin-6(7*H*)-one (4).—A solution of 360 mg (1 mmol) of **3** HCl in 500 ml of oxygen-free water was irradiated with a 200-W Hanovia high-pressure mercury-immersion lamp equipped with a Vycor filter. Nitrogen was bubbled through the solution during the irradiation and the quartz well was kept water-cooled. After neutralization with 152 mg (1.1 mmol) of K_2CO_3, the solution was concentrated to dryness at 30°. Trituration of the residue with water gave 256 mg (87%) of a precipitate which was approximately a 50:50 mixture of **4** and **5**, as indicated by tlc in several systems.[7] A preliminary purification of the mixed photoproducts was carried out by sublimation (10^{-4} mm) at 240°. A mass spectrum of the mixture showed the base peak (also the highest in mass number) at *m/e* 286, corresponding to molecular ion(s) of the dehydrohalogenated photoproducts.

When the photolysis of **3** was carried out in neutral (pH 7 phosphate buffer) or alkaline medium (K_2CO_3 added prior to irradiation), similar results were obtained. The relative as well as total yields of **4** and **5** were essentially unchanged.

Separation and Identification of Photoisomers (4 and 5).—The photoproducts obtained from irradiation of **3** were almost insoluble in all organic solvents, with the exception of DMSO and alcohols. In general, **5** was less soluble than **4**. A small amount of pure **5** was obtained by five recrystallizations of the sublimed mixture from a minimum of boiling ethanol. For a larger scale separation, 2 g of the sublimed mixture was dissolved in 50 ml of boiling ethanol. The solution was slightly cooled, seeded with a few crystals of pure **5**, and left undisturbed for 24 hr. The crystals which separated contained approximately 70% of **5** and 30% of **4**, and two more recrystallizations with seeding afforded 650 mg (28%) of pure **5**, colorless prisms from ethanol. The homogeneity of **5** could be shown by tlc, which revealed only one spot, R_f 0.41 in system I and 0.07 in system II;[7] it darkened without melting above 300°; ν_{max}^{KBr} 3260, 3100, 1665 cm^{-1}; mass spectrum *m/e* 286 (M^+), 243; nmr (DMSO-d_6, 100 MHz) δ 9.34 (s, 1, ArOH), 7.40 (d, 1, NHCO, J_{NHCH} = 6 Hz), 6.91 (q, 1, aromatic H, $J \cong$ 7.6 and 8.4 Hz), 6.79 (q, 1, aromatic H, $J \cong$ 1.5 and 8.4 Hz), 6.62 (q, 1, aromatic H, $J \cong$ 1.5 and 7.6 Hz), 4.15 (q, 1, –CHNHCO–), 3.80 (s, 2, $ArCH_2$–), 2.29 (s, 3, NCH_3).

Anal. Calcd for $C_{17}H_{22}N_2O_2$: C, 71.29; H, 7.74; N, 9.78. Found: C, 71.37; H, 7.97; N, 9.76.

Compound **5** gave a positive color test with ferric chloride. Its hydrochloride salt was prepared in ether; recrystallization from methanol–ether gave colorless prisms, mp >300°.

Anal. Calcd for $C_{17}H_{23}ClN_2O_2$: C, 63.26; H, 7.18; N, 8.68. Found: C, 63.06; H, 7.34; N, 8.53.

The filtrates from the recrystallizations of **5** were combined and concentrated to dryness. Two recrystallizations of the residue from a minimum of boiling methanol gave 570 mg (25%) of virtually pure **4**: fine needles; mp 285–288° dec; ν_{max}^{KBr} 3260, 1655 cm^{-1}; mass spectrum *m/e* 286 (M^+), 243; nmr (DMSO-d_6, 100 MHz) δ 9.12 (s, 1, ArOH), 7.39 (d, 1, NHCO–, J_{NHCH} = 6 Hz), 6.82 (d, 1, aromatic H, J = 8.0 Hz), 6.74 (d, 1, aromatic H, J = 2.5 Hz), 6.51 (q, 1, aromatic H, J = 2.5 and 8.0 Hz), 4.36 and 2.96 [q, 2, ArCH(H′)–, $|J|$ = 14 H], 4.15 (q, 1, –CHNHCO–), 2.32 (s, 3, NCH_3).

Anal. Calcd for $C_{17}H_{22}N_2O_2$: C, 71.29; H, 7.74; N, 9.28. Found: C, 71.44; H, 7.46; N, 9.57.

Compound **4** gave a positive phenol test with $FeCl_3$ solution. It was shown to be free of **5** by tlc in two sysems (one spot; R_f 0.35 in system I, 0.18 in system II).[7]

***O*-Acetyl Derivative of 5.**—A suspension of 100 mg (0.35 mmol) of **5** in 2 ml of acetic anhydride was warmed at 90° until a clear solution was formed (24 hr). Evaporation of the solution *in vacuo* gave an oily residue which was taken up in methylene chloride, washed with $NaHCO_3$, and dried (Na_2SO_4). Removal of the solvent gave 85 mg (74%) of a precipitate which was recrystallized from acetone to give hexagonal plates: mp 235–238°; ν_{max}^{KBr} 3230, 1770, 1680 cm^{-1}; mass spectrum *m/e* 328 (M^+), 300, 286, 285; nmr ($CDCl_3$, 100 Hz) δ 7.15–7.25 (m, 2, aromatic protons, AB part of an ABX), 6.92 (m, 1, aromatic H, X part of an ABX), 6.40 (d, 1, NHCO–, J_{NHCH} = 6 Hz), 4.26 (q, 1, –CHNH–), 3.92 and 3.70 [q, 2, ArCH(H′)–, $|J|$ = 15 Hz], 2.45 (s, 3, CH_3CO–), 2.34 (s, 3, NCH_3).

Anal. Calcd for $C_{19}H_{24}N_2O_3$: C, 69.48; H, 7.36; N, 8.53. Found: C, 69.49; H, 7.65; N, 8.83.

***O*-Acetyl Derivative of 4.**—A mixture of 120 mg (0.35 mmol) of **4** in 2 ml of acetic anhydride was kept at 90° for 2 hr, during which time a clear solution was gradually formed. After isolation as described above, 91 mg (77%) was obtained. Recrystallization from acetone–hexane gave prisms: mp 232–235° dec; ν_{max}^{Nujol} 3200, 1770, 1670 cm^{-1}; mass spectrum *m/e* 328 (M^+), 300, 286, 285; nmr ($CDCl_3$, 100 MHz) δ 7.06 (d, 1, aromatic H, J = 8.5 Hz), 7.02 (d, 1, aromatic H, J = 2.4 Hz), 6.85 (q, 1, aromatic H, J = 8.5 and 2.4 Hz), 4.39 and 3.27 [q, 2, ArCH(H′)–, $|J|$ = 15 Hz], 4.26 (q, 1, –CHNHCO–), 2.44 (s, 3, CH_3CO–), 2.35 (s, 3, NCH_3).

Anal. Calcd for $C_{19}H_{24}N_2O_3$: C, 69.48; H, 7.36; N, 8.53. Found: C, 69.68; H, 7.31; N, 8.67.

Acid Rearrangement of 5 HCl to 9-*cis*-Amino-5-(2′-oxo-2′,3′-dihydrobenzofuryl)-2-methyl-2-azabicyclo[3.3.1]nonane (6) 2HCl.—A solution of 161 mg (0.5 mmol) of **5** HCl in 4 ml of 4 *N* HCl was refluxed under N_2 for 24 hr. The course of the reaction was followed by tlc[7] which showed a gradual change from R_f 0.41 to 0.33. Evaporation of the excess acid, followed by reprecipitation from ethanol–ethyl acetate, gave 125 mg of a very hygroscopic powder. It decomposed gradually above 150–160°: ν_{max}^{Nujol} 3180, 1800 cm^{-1}; mass spectrum *m/e* 286 (M^+), 269, 256.

Anal. Calcd for $C_{17}H_{24}Cl_2N_2O_2$: N, 7.79. Found: N, 8.04.

1,2,3,4,4a,5-Hexahydro-8-methoxy-3-methyl-4,11b-propano-11b*H*-pyrido-[4,3-a][3]benzazepin-6(7*H*)-one (8).—A solution of 134 mg (0.5 mmol) of **5** in 10 ml of methanol was allowed to stand overnight with an excess of diazomethane prepared from 1.2 g of *N*-methyl-*N*′-nitrosoguanidine. Evaporation of the reaction mixture, followed by vacuum sublimation (10^{-4} mm, 170°), gave 110 mg (74%) of virtually pure **8**. Recrystallization from acetone–hexane afforded colorless plates: mp 228–231°; ν_{max}^{Nujol} 1675 cm^{-1}; mass spectrum *m/e* 300 (M^+), 257 (base).

Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.06; N, 9.32. Found: C, 71.48; H, 7.68; N, 9.25.

1,2,3,4,4a,5,6,7-Octahydro-8-methoxy-3-methyl-4,11b-propano-11b*H*-pyrido[4,3-a][3]benzazepine (9) 2HBr.—To a solution of 300 mg (1 mmol) of **8** was added 6 ml of 1 *M* borane[13] in THF and the mixture was refluxed for 4 hr. The slightly cooled solution was treated with 12 ml of 6 *N* HCl and refluxing was continued for an additional 2 hr. Evaporation *in vacuo* left a semisolid mass which was basified with 1 *N* NaOH. The liberated oil was taken up in ether, dried over K_2CO_3, and converted to 285 mg (64%) of **9** 2HBr in ether. Recrystallization from ethanol–ether gave fine needles: mp 265–268°; mass spectrum *m/e* 286 (M^+), 271, 243 (base).

Anal. Calcd for $C_{18}H_{28}Br_2N_2O$: C, 48.22; H, 6.29; N, 6.24. Found: C, 48.13; H, 6.48; N, 6.58.

1,2,3,4,4a,5,6,7-Octahydro-3-methyl-4,11b-propano-11b*H*-pyrido[4,3-*a*]-[3]benzazepin-8-ol (9a) 2HBr.—A solution of 150

(13) Purchased from Alpha Inorganics, Inc.

mg (0.52 mmol) of **9** in 3 ml of 48% HBr was refluxed under N_2 for 30 min. Evaporation of the excess acid *in vacuo* left an oily residue which was crystallized from ethanol–acetone–ether to give 191 mg (84%) of irregular prisms, mp 283–286°, mass spectrum *m/e* 272 (M^+), 229 (base).

Anal. Calcd for $C_{17}H_{26}Br_2N_2O$: C, 47.01; H, 6.03; N, 6.45. Found: C, 46.91; H, 6.26; N, 6.36.

1,2,3,4,4a,5,6,7-Octahydro-3,5-dimethyl-8-methoxy-4,11b-propano-11b*H*-pyrido[4,3-a][3]benzazepine (12) 2HBr.—A mixture of 400 mg (1.4 mmol) of **9** and 2 ml of formic acid was refluxed for 2 hr before 1.8 ml of 38% formaldehyde solution was added. Refluxing was continued for 18 hr. Evaporation of the mixture *in vacuo*, followed by basification with 1 *N* NaOH, afforded 390 mg of **12** as a viscous oil. It was converted to its dihydrobromide in anhydrous ether, yield 605 mg (93%). Recrystallization from 90% ethanol–ether gave colorless rods, mp 275–277°, mass spectrum *m/e* 300 (M^+), 285, 270, 269, 257 (base).

Anal. Calcd for $C_{19}H_{30}Br_2N_2O$: C, 49.36; H, 6.54; N, 6.06. Found: C, 49.20; H, 6.69; N, 6.28.

1,2,3,4,4a,5,6,7-Octahydro-3,5-dimethyl-4,11b-propano-11b*H*-pyrido[4,3-a]-[3]benzazepin-8-ol (15) 2HBr.—A mixture of 320 mg (0.7 mmol) of **12**·2HBr in 3 ml of 48% HBr was refluxed under N_2 for 30 min. Evaporation *in vacuo* left a crystalline residue which was recrystallized from 90% ethanol–ether to give 300 mg (96%) of **15** 2HBr, mp 230–235° dec, *m/e* 286 (M^+), 243 (base).

Anal. Calcd for $C_{18}H_{28}Br_2N_2O$: C, 48.22; H, 6.29; N, 6.24. Found: C, 48.31; H, 6.54; N, 6.08.

1,2,3,4,4a,5-Hexahydro-10-methoxy-3-methyl-4,11b-propano-11b*H*-pyrido-[4,3-a][3]benzazepin-6(7*H*)-one (7).—A solution of 240 mg (0.84 mmol) of **4** in 50 ml of methanol was methylated with an excess of diazomethane in the same manner as described for **5**. The course of reaction was followed by tlc (system I) which showed a gradual disappearance of the spot at R_f 0.35 while a new spot emerged at R_f 0.56. Evaporation of the solution followed by sublimation (10^{-4} mm, 180°) gave 223 mg (88%) of **7**, rectangular plates from acetone: mp 246–249° dec; ν_{max}^{Nujol} 3200, 1675 cm^{-1}; *m/e* 300 (M^+), 257 (base).

Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.06; N, 9.32. Found: C, 72.22; H, 7.86; N, 9.55.

1,2,3,4,4a,5,6,7-Octahydro-10-methoxy-3-methyl-4,11b-propano-11b*H*-pyrido[4,3-a][3]befinazepine (10) 2HBr.—A solution of 240 mg (0.8 mmol) of **7** in 50 ml of THF was reduced with 5 ml of 1 *M* borane in THF. After 4 hr, the mixture was treated with 12 ml of 6 *N* HCl and refluxing was continued for an additional 2 hr. Evaporation of the mixture *in vacuo* left an oily residue which was basified with 2 *N* NaOH and extracted with ether. After drying briefly over K_2CO_3, the amine was converted to **10** 2HBr by passing through anhydrous HBr, yield 225 mg (63%). Recrystallization from 90% ethanol–ether gave irregular prisms, mp 269–272°, mass spectrum *m/e* 286 (M^+), 271, 243 (base).

Anal. Calcd for $C_{18}H_{28}Br_2N_2O$: C, 48.22; H, 6.29; N, 6.24. Found: C, 47.98; H, 6.52; N, 6.18.

1,2,3,4,4a,5,6,7-Octahydro-3-methyl-4,11b-propano-11b*H*-pyrido[4,3-a][3]benzazepin-10-ol (10a) 2HBr.—A mixture of 224 mg (0.5 mmol) of **10**·2HBr in 4 ml of 48% HBr was refluxed for 30 min. Evaporation of the excess acid *in vacuo* left a sirup which, upon trituration with acetone, crystallized to yield 196 mg (90%) of **10a**·2HBr. Recrystallization from 95% ethanol–ether gave fine needles, mp 279–282° dec, mass spectrum *m/e* 272 (M^+), 229 (base).

Anal. Calcd for $C_{17}H_{26}Br_2N_2O$: C, 47.02; H, 6.03; N, 6.45. Found: C, 47.26; H, 6.32; N, 6.31.

1,2,3,4,4a,5,6,7-Octahydro-3,5-dimethyl-10-methoxy-4,11b-propano-11b*H*-pyrido[4,3-a][3]benzazepine (11) 2HBr.—Compound **10**, 286 mg (1 mmol, purified through its dihydrobromide), was methylated with formic acid (90%) and formalin in the same manner as described for **9** to give 431 mg (93%) of **11** 2HBr, mp 243–246° dec, prisms from 90% ethanol–ether, mass spectrum *m/e* 300 (M^+), 285, 270, 269, 257 (base).

Anal. Calcd for $C_{19}H_{30}Br_2N_2O$: C, 49.36; H, 6.54; N, 6.06. Found: C, 49.44; H, 6.61; N, 6.25.

1,2,3,4,4a,5,6,7-Octahydro-3,5-dimethyl-4,11b-propano-11b*H*-pyrido-[4,3-a][3]benzazepin-10-ol (14) 2HBr.—A mixture of 462 mg (1 mmol) of **11**·2HBr in 3 ml of 48% HBr was refluxed gently for 1 hr. Evaporation of the excess acid *in vacuo* left an oily residue which crystallized upon trituration with acetone, yield 350 mg (78%). Recrystallization from 80% ethanol–ether gave elongated plates, mp 238–241° dec, mass spectrum *m/e* 286 (M^+), 243 (base).

Anal. Calcd for $C_{18}H_{28}Br_2N_2O$: C, 48.22; H, 6.29; N, 6.24. Found: C, 48.20; H, 6.53; N, 6.39.

When the refluxing time was prolonged to more than 1 hr, extensive decomposition and polymerization took place.

Registry No.—**2**, 32969-96-3; 2 diHBr, 32969-97-4; **3**, 32969-98-5; **3** HCl, 33068-03-0; **4**, 33020-81-4; **4** *O*-acetyl derivative, 33020-82-5; **5**, 33068-04-1; **5** HCl, 33020-83-6; **5** *O*-acetyl derivative, 33020-84-7; **6** diHCl, 33068-05-2; **7**, 33020-85-8; **8**, 33020-86-9; **9** diHBr, 33020-87-0; **9a** diHBr, 33020-88-1; **10** diHBr, 33020-89-2; **10a** diHBr, 33020-90-5; **11** diHBr, 33020-91-6; **12** diHBr, 33020-92-7, **14** diHBr, 33020-93-8; **15** diHBr, 33020-89-2.