to 40° for 3 hr and poured over ice. After neutralization with ammonium hydroxide, the organic material was extracted twice with 200 ml of chloroform. The organic layer was washed twice with 200 ml of water, dried (Na_2SO_4), evaporated, and taken up in 100 ml of ether. This solution was treated with charcoal, heated, and washed thoroughly with ether through 40 g of Florisil. On concentration at reduced pressure and crystallization, 7.37 g (41%) of tan needles, mp 88–89.5°, was obtained. The mother liquor yielded another 1.05 g of less pure material. Recrystallization of the first crop from ether afforded **7c**: mp 88.5–90°; ir ($CHCl_3$) 1526, 1345 cm^{-1}; uv max (2-propanol) 228 mμ (ε 51400), 277 (4450), sh 311–314 (5000), 324–325 (6400); nmr (DMSO) 2.52 (s, 3, 7-CH_3), 2.67 (s, 3, 2-CH_3), 3.94 (s, 3-OCH_3), 7.55, 7.96 (AB, 2, J = 8.5 Hz, $H_{3,4}$), 8.06 (s, 1, H_8); mass spectrum m/e 232 (M^+). *Anal.* Calcd for $C_{12}H_{12}N_2O_3$ (232.23): C, 62.06; H, 5.21; N, 12.06. Found: C, 61.83; H, 5.34; N, 11.97.

6-Hydroxy-2,7-dimethyl-5-nitroquinoline (2). Method A.—To a solution of 32.0 g (184.8 mmol) of **7b** in 100 ml of concentrated sulfuric acid, stirred in an ice bath, a solution of 20.4 g (200 mmol) of potassium nitrate in 50 ml of concentrated sulfuric acid was added dropwise within 30 min. The reaction mixture was stirred for 2 hr in an ice bath and then for 2 hr at room temperature. The reaction mixture was poured over ice, neutralized with ammonium hydroxide, and extracted with 1.5 l. of chloroform. The organic layer was washed twice with 500 ml of water, dried (Na_2SO_4), washed thoroughly with chloroform through 100 g of Florisil, and finally concentrated to 300 ml to yield 33.8 g of **2**, mp 177–178.5°, as small plates. From the mother liquor another 2.95 g, mp 178°, was obtained; the total yield was 36.75 g (91.5%). This material was identical by mixture melting point, tlc, and spectra with the material isolated from the base treatment of **1c**.

Method B.—A mixture of 0.5 g (2.15 mmol) of **7c** and 15 ml of 40% hydrobromic acid was heated at reflux for 3 hr (oil bath temperature 150°), then was poured over ice, neutralized with ammonium hydroxide, and extracted twice with 200 ml of chloroform. The combined chloroform layers were washed with 100 ml of water, dried (Na_2SO_4), and concentrated at reduced pressure. The residue was crystallized from ethanol and gave 0.39 g (83%) of **2**, yellow needles, mp 177–178.5°.

5-Amino-6-hydroxy-2,7-dimethylquinoline.—A solution of 4.36 g (2.0 mmol) of **2**, in 50 ml of concentrated hydrochloric acid was warmed together with 20 g of stannous chloride dihydrate on a steam bath until the solution became colorless. This mixture was neutralized with sodium carbonate and extracted with 500 ml of chloroform. The emulsion which formed was filtered through Celite. The chloroform layer was separated, dried (Na_2SO_4), and concentrated to yield 250 mg (6.6%) of a brownish powder: mp 231–233°; ir (KBr) 3400, 3350, 3260, 2700–2500 cm^{-1}; mass spectrum m/e 188 (M^+). *Anal.* Calcd for $C_{11}H_{12}N_2O$ (188.22): C, 70.18; H, 6.43; N, 14.88. Found: C, 70.23; H, 6.45; N, 15.02.

5-Acetamido-6-acetoxy-2,7-dimethylquinoline.—A solution of 150 mg (0.8 mmol) of 5-amino-6-hydroxy-2,7-dimethylquinoline and 5 ml of acetic anhydride was warmed on the steam bath for 10 min. After cooling, ether was added and the crystals, which were separated by filtration, were washed with ether to yield 180 mg (83%): mp 239.5–240°; ir (KBr) 3275, 1750, 1658 cm^{-1}; nmr (DMSO) 2.16 (s, 3, 7-CH_3), 2.33 (s, 6, 2CH_3C=O), 2.66 (s, 3, 2-CH_3), 7.37, 8.07 (AB, 2, J_{ortho} = 8 Hz, $H_{3,4}$) 7.80 (s, 1, H_8), 9.80 (s, 1, NH); mass spectrum m/e 272 (M^+). *Anal.* Calcd for $C_{15}H_{16}N_2O_3$ (272.29): C, 66.16; H, 5.92; N, 10.29. Found: C, 66.11; H, 5.99; N, 10.29.

2,4,7-Trimethoxyloxazolo[4,5-*f*]quinoline (8).—Pyrolysis of 100 mg (0.37 mmol) of 5-acetamido-6-acetoxy-2,7-dimethylquinoline in a metal bath at 250° resulted in the evolution of acetic acid. After 5 min, the reaction was finished and the crude semicrystalline oil was dissolved in an ether–methylene chloride mixture and washed with methylene chloride through 0.5 g of Florisil. The almost colorless solution was concentrated under reduced pressure. The crude residue crystallized from ether to give 35 mg (45%) of **8**: mp 134–134.5°; nmr ($CDCl_3$) δ 2.64, 2.70, 2.71 (s, 9, 3CH_3) 7.32, 8.55 (AB, 2, J_{ortho} = 8.5 Hz, $H_{3,4}$), 7.71 (s, 1, H_8); mass spectrum m/e 212 (M^+). *Anal.* Calcd for $C_{13}H_{12}N_2O$ (212.24): C, 73.56; H, 5.70; N, 13.20. Found: C, 73.76; H, 5.72; H, 13.27.

Registry No.—**1a**, 25999-31-9; **1b** sodium salt, 31478-24-7; **1c** sodium salt, 31478-25-8; **2**, 31504-47-9; **3**, 31478-26-9; **4**, 31478-27-0; **5a** sodium salt, 31478-28-1; **7a**, 31478-29-2; **7a** picrate, 31478-30-5; **7b**, 31478-31-6; **7c**, 31478-32-7; **8**, 31478-33-8; 5-amino-6-hydroxy-2,7-dimethylquinoline, 31478-34-9; 5-acetamido-6-acetoxy-2,7-dimethylquinoline, 31478-35-0.

Acknowledgment.—We are indebted to the Physical Chemistry Department, Hoffmann-La Roche Inc., Nutley, N. J., under the supervision of Dr. P. Bommer, for the analytical and spectral data.

The Decahydro-1*H*-dibenzo[*a*,*h*]quinolizine System

GLENN C. MORRISON,* WIACZESLAW A. CETENKO, AND JOHN SHAVEL, JR.

Department of Organic Chemistry, Warner-Lambert Research Institute, Morris Plains, New Jersey 07950

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Having obtained the four isomers of the inside yohimbane system,[1] we turned our attention to their benzene analogs. When 3,4-dimethoxyphenethylamine and 2-formylcyclohexaneacetic acid were heated in acetic acid for a short time the open unsaturated lactam **1** was obtained. Longer heating of either the starting materials or lactam **1** resulted in cyclization to give lactam **2** as the predominant product, lactam **3** as the secondary product, and lactam **4** in trace yield. The lactams were reduced to the corresponding bases **8**, **10**, and **6**, respectively.

In the indole series the main product of the condensation had been the trans-anti isomer. However, the indole lactams may have been formed by a Pictet–Spengler cyclization followed by lactamization thus favoring a different isomer than in this case, where lactamization is the first step.

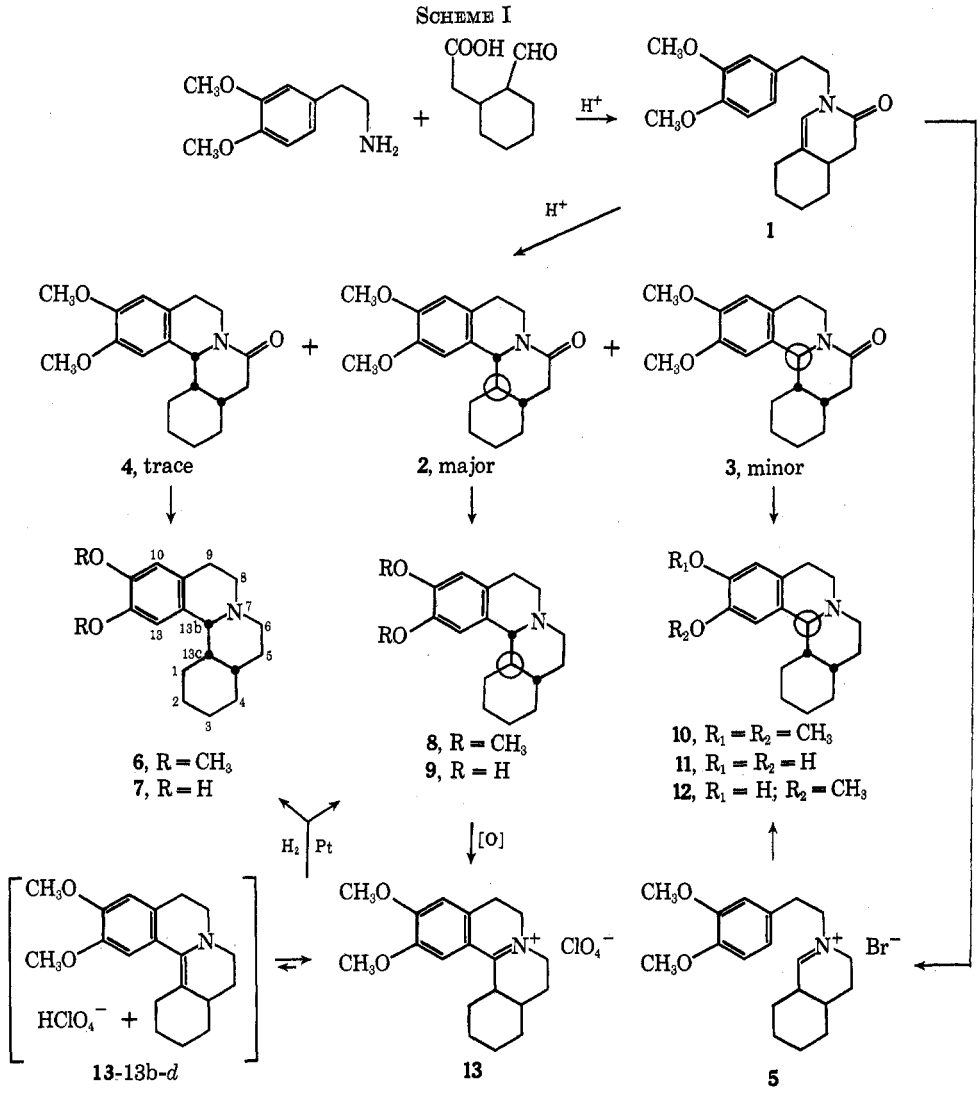
The uncyclized lactam **1** was reduced to the enamine **5** which on acid treatment undergoes hydrolysis of one methoxyl group and cyclization to the base **12**. The three dimethoxy bases **6**, **8**, and **10** were hydrolyzed to their corresponding dihydroxy derivatives **7**, **9**, and **11**. Further hydrolysis of **12** afforded the dihydroxy compound **11**, whose stereochemistry corresponds to the secondary product of the condensation reaction.

Having three isomers in hand we attempted to obtain the final one by the scheme which had produced the two isomers not obtained from the condensation in the indole series. Base **8** was oxidized to the dehydro compound **13**. Hydrogenation of **13** with platinum in alcohol gave back isomer **8** as the principal product along with isomer **6** and a small amount of isomer **10**. Sodium borohydride reduction gave essentially the same result. Zinc–acid reduction afforded a mixture containing a larger amount of isomer **10** (Scheme I).

The main difference between the indole and benzene series, other than the electronic nature of the two aromatic systems, is the steric relation of the hydrogens at C-1 to the adjacent hydrogen of the aromatic system. In the indole cis series we have shown that the syn

(1) G. C. Morrison, W. A. Cetenko, and J. Shavel, Jr., *J. Org. Chem.*, **32**, 2768 (1967).

SCHEME I



isomer is predominantly in the conformation which has a trans quinolizidine, and the anti isomer is a mixture of the three possible conformations. In these conformations the steric factor is relatively unimportant since the distance between the closest hydrogens at C-1 and the indole NH is over 2 Å. This is supported experimentally by the fact that on going from the indole NH to NCH_3 series there was little or no effect on the conformation make-up. Therefore in the cis benzene series the conformations of the isomers should be the same as for their corresponding indole isomer, since the distance between the hydrogen at C-1 and the adjacent aromatic hydrogen is reduced only 0.4 Å. The infrared spectrum of **10** shows no Bohlmann bands. The nmr spectrum displays a signal at 3.8 ppm for one hydrogen (buried under the methoxyl) and a methylene envelope with a half-width of 9 cps. This data corresponds perfectly to that for the cis-anti isomer in the indole series. Isomer **6** shows Bohlmann bands of moderate intensity, no signal in the 3.2–4.5-ppm region, disappearance of a singlet at 3.15 ppm (W_H = 7 cps) in the C-13b-*d* derivative, and a methylene envelope half-width of 32 cps. Again this corresponds to the cis-syn data in the indole series.

In the trans indole series the distance between the closest hydrogen at C-1 and the indole NH is 1.3 Å in both the trans-syn isomer and the favored trans quinolizidine conformation of the trans-anti isomer. The cis quinolizidine conformation of the trans-anti isomer has no serious steric interaction. In both isomers insertion of a *N*-methyl group reduces this distance to approximately zero and results in a shift to the cis quinolizidine conformation for the anti isomer and to the ring D boat conformation for the syn isomer. In the benzene series the distance between the hydrogen at C-1 and the adjacent aromatic hydrogen is 0.9 Å. This increased steric interaction may or may not affect the conformational preferences; therefore, both conformations of the trans-anti isomer must be considered and possibly even the boat conformation for the trans-syn isomer.

The spectral data for **8** are no Bohlmann bands, no signal in the 3.5–4.5-ppm region, and a methylene envelope half-width of 40 cps. The methylene envelope data are further support for the assignment of a trans C–D ring fusion. The remaining nmr and infrared data are in conflict on the basis of the classical interpretations: no Bohlmann bands for cis quinolizidine[2] and no signal above 3.8 for trans quinolizidine.[3] The only documented exception to the Bohlmann rule is that of Meyers.[4] However, the dividing line of 3.8 ppm for

(2) F. Bohlmann, *Chem. Ber.*, **91**, 2157 (1958).
(3) M. Uskokovic, H. Bruderer, C. von Planta, T. Williams, and A. Brossi, *J. Amer. Chem. Soc.*, **86**, 3364 (1964).
(4) J. C. Sircar and A. I. Meyers, *J. Org. Chem.*, **32**, 1248 (1967).

cis and trans quinolizidines is at best an approximation since long-range shielding effects are certain to have an effect on this position. For example, we have shown that in the case of trans-anti *N*-methyl inside yohimban, which exists in a cis quinolizidine conformation (most likely exclusively), the quinolizidine crotch hydrogen resonates at 3.65 ppm. On going from cis-anti *N*-methyl inside yohimban to the cis-anti benzene series there should be no change in conformation. However, the chemical shift of the crotch hydrogen is −0.2 ppm. Applying this correction the expected position of the cis quinolizidine conformation of the trans-anti isomer should be 3.45 ppm.

A close examination of the methylene envelope of **8** suggests a poorly resolved doublet at 3.4 ppm (peak separation of 5 cps) which corresponds well to the calculated position. To support the assignment of this pattern to the crotch hydrogen of **8** we have carried out the reduction of the dehydro compound **13** with sodium borodeuteride. The main product isolated was **6** deuterated at C-13b. By thin layer chromatography a small sample of C-13b deuterated **8** was obtained in reasonable purity. Although the nmr spectrum of this material was poorly resolved, it was essentially the same as the spectrum of **6** except for the lack of the doublet at 3.4 ppm. The splitting pattern of **8** is typical of 180° coupling rather than 60° coupling;[1] therefore, we have assigned **8** as the trans-anti isomer in the cis quinolizidine conformation. The fact that we were unable to obtain the cis-syn isomer by any of our procedures is probably due to its lower thermodynamic stability in the benzene series.

Experimental Section[5]

The melting points were determined using a Thomas-Hoover apparatus which had been calibrated against known standards. The infrared spectra were recorded with a Baird Model 455 instrument on chloroform solutions. The nmr spectra were determined with a Varian Associates A-60 spectrometer on deuteriochloroform solutions unless noted.

2-(3,4-Dimethoxyphenethyl)-4,4a,5,6,7,8-hexahydro-3(2*H*)-isoquinolone (1).—A solution of 67 g of homoveratrylamine and 63 g of 2-formycyclohexaneacetic acid[1] in 440 ml of acetic acid was refluxed for 2.5 hr. The acetic acid was removed *in vacuo*. The residue was treated with 200 ml of 10% sodium hydroxide solution and 1.5 l. of methylene chloride. The methylene chloride layer was washed with water and dried over sodium sulfate, and the solvent was removed. The residue was digested with 400 ml of ethyl acetate and allowed to cool. The mixture was filtered and the ethyl acetate solution was evaporated to dryness. The residue was chromatographed on 2.5 kg of basic alumina. Elution with benzene–methylene chloride 1:1 gave, after recrystallization from Skellysolve B, 18.1 g (28%) of a crystalline solid, mp 91–92°.

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 7.99; N, 4.44. Found: C, 72.63; H, 8.07; N, 4.47.

***trans-anti-*, *cis-anti-*, and *cis-syn*-1,2,3,4,4a,5,8,9,13b,13c-Decahydro-11,12-dimethoxy-6*H*-dibenzo[*a*,*h*]quinolizin-6-ones (2, 3, and 4).**—A solution of 163 g of homoveratrylamine and 162 g of 2-formylcyclohexaneacetic acid in 1.1 l. of acetic acid was refluxed for 24 hr. The acetic acid was removed *in vacuo*. The residue was treated with 1 l. of 10% sodium carbonate solution and 2.7 l. of methylene chloride. The methylene chloride layer was washed with water and dried with sodium sulfate, and the solvent was removed. The residue, after crystallization from 3.8 l. of ethyl acetate, afforded 158 g (56%) of a solid, mp 168–170°. Recrystallization from ethyl acetate gave an analytical sample of the trans-anti isomer **2**, mp 170–171°.

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 7.99; N, 4.44. Found: C, 72.58; H, 8.03; N, 4.71.

Concentration of the mother liquor to 600 ml gave a second crop, 104 g, mp 134–140°, which was chromatographed on 4.0 kg of alumina. Elution of the column with methylene chloride gave, after recrystallization from Skellysolve B, 18 g (6%) of the cis-anti isomer **3**, mp 146–147°.

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 7.99; N, 4.44. Found: C, 72.45; H, 7.94; N, 4.49.

The mother liquor from the crystallization was evaporated to dryness and the residue was chromatographed on 1.2 g of alumina. Elution with benzene–methylene chloride 1:1 gave, after recrystallization from ethyl acetate, 0.05 g (0.02%) of the cis-syn isomer **4**, mp 152–155°.

2-(3,4-Dimethoxyphenethyl)-3,4,4a,5,6,7,8,8a-octahydroisoquinolinium Bromide (5).—To a solution of 10.2 g of lithium aluminum hydride in 800 ml of ether was added a solution of 17.8 g of **1** in 1.4 l. of ether. The solution was refluxed for 3 hr and allowed to stand for 20 hr. The excess hydride was destroyed by the dropwise addition of water and the mixture was filtered. On acidification of the ethereal solution with hydrogen bromide there was deposited a solid which, after recrystallization from acetonitrile, afforded 9.3 g (43%) of solid, mp 192–194°. Further recrystallization gave an analytical sample, mp 195–196°.

Anal. Calcd for $C_{19}H_{28}BrNO_2$: C, 59.69; H, 7.38; N, 3.66. Found: C, 59.63; H, 7.26; N, 3.94.

***trans-anti*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine (8).**—To a solution of 18 g of lithium aluminum hydride in 750 ml of tetrahydrofuran was added a solution of 110 g of **2** in 2.4 l. of tetrahydrofuran and the resulting solution was refluxed for 5 hr. The excess hydride was destroyed by the dropwise addition of water and the mixture was filtered. The tetrahydrofuran solution was stripped to dryness. Recrystallization of the residue from Skellysolve B gave 91 g (86%) of a solid, mp 101–102°.

Anal. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.96; H, 9.06; N, 4.57.

***cis-syn*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine (6).**—Reduction of 30 mg of **4** by the procedure used for the trans-anti isomer gave a solid. Thin layer chromatography on silica gel using a 1:1 benzene–ethyl acetate system in an ammonia atmosphere showed that this sample was identical with that obtained from the reduction of 1,2,3,4,4a,5,6,8,9,13c-decahydro-11,12-dimethoxydibenzo[*a*,*h*]-quinolizinium perchlorate.

***cis-anti*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine (10).**—Reduction of 9.9 g of **3** by the procedure used for the trans-anti isomer gave, after recrystallization from Skellysolve B, 6.9 g (75%) of a solid, mp 118.5–119°. Further recrystallization gave an analytical sample, mp 119–120°.

Anal. Calcd for $C_{18}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.82; H, 9.11; N, 4.57.

***cis-anti*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11-hydroxy-12-methoxy-1*H*-dibenzo[*a*,*h*]quinolizine (12).**—A solution of 6.5 g of **5** in 6 *N* hydrochloric acid was refluxed for 6 hr. The pH of the reaction mixture was adjusted to 9 with 40% sodium hydroxide solution, and the mixture was extracted with ether. The ethereal solution was washed with water and dried over sodium sulfate and the solvent was removed. Crystallization of the residue from benzene gave 0.6 g (12%) of solid, mp 134–135°.

Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.42; H, 8.91; N, 4.43.

***trans-anti*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11,12-dihydroxy-1*H*-dibenzo[*a*,*h*]quinolizine (9).**—A solution of 2.0 g of **8** in 55 ml of hydrobromic acid was refluxed for 6 hr in a nitrogen atmosphere. The reaction mixture was neutralized to pH 8.5 with dilute ammonium hydroxide and extracted with methylene chloride. The methylene chloride layer was washed with water and dried over sodium sulfate, and the solvent was removed. Recrystallization of the residue from ethyl acetate gave 0.92 g (50%) of a solid, mp 223–224°.

Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.62; H, 8.53; N, 4.97.

***cis-anti*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11,12-dihydroxy-1*H*-dibenzo[*a*,*h*]quinolizine Hydrobromide (11). Method A.**—A solution of 8.0 g of **10** in 200 ml of hydrobromic acid was refluxed for 6 hr. On standing there was deposited a solid which,

(5) The authors are indebted to Mr. A. Lewis and his associates, to Dr. C. Greenough for the spectral data, and to Mrs. U. Zeek for analytical determinations.

after recrystallization from ethanol, afforded 7.4 g (79%) of a solid, mp 288–290°.

Anal. Calcd for $C_{17}H_{23}NO_2 \cdot HBr$: C, 57.63; H, 6.83; N, 3.95. Found: C, 57.52; H, 6.89; N, 3.94.

Method B.—A solution of 0.10 g of **12** in 15 ml of hydrobromic acid was refluxed for 6 hr. On standing, there was deposited 0.11 g of a crystalline solid, mp 288–290°. This sample was shown to be identical with that obtained in method A by the method of mixture melting point.

***cis-syn*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11,12-dihydroxy-1*H*-dibenzo[*a*,*h*]quinolizine Hydrobromide (7).**—A solution of 7.0 g of **6** in 175 ml of hydrobromic acid was refluxed for 8 hr. On standing there was deposited a solid which on recrystallization from ethanol afforded 6.9 g (84%) of a solid, mp 329–331°.

Anal. Calcd for $C_{17}H_{23}N_2O_2 \cdot HBr$: C, 57.63; H, 6.83; N, 3.95. Found: C, 57.43; H, 6.76; N, 3.97.

1,2,3,4,4a,5,6,8,9,13c-Decahydro-11,12-dimethoxydibenzo[*a*,*h*]quinolizinium Perchlorate (13).—To a solution of 50 g of **8** in 1 l. of 5% acetic acid was added a solution of 530 g of mercuric acetate in 1.5 l. of 5% acetic acid. After the addition had been completed the solution was heated at 95° for 3 hr with stirring. The hot reaction mixture was saturated with hydrogen sulfide and filtered. Treatment of the filtrate with perchloric acid gave, after recrystallization from methanol, 44 g (66%) of a solid, mp 180–182°. Further recrystallization gave an analytical sample, mp 187–188°.

Anal. Calcd for $C_{19}H_{25}NO_2 \cdot HClO_4$: C, 57.07; H, 6.55; N, 3.50. Found: C, 56.83; H, 6.56; N, 3.78.

Hydrogenation of 1,2,3,4,4a,5,6,8,9,13c-Decahydro-11,12-dimethoxydibenzo[*a*,*h*]quinolizinium Perchlorate (13).—To a solution of 30 g of **13** in 60 ml of water and 800 ml of ethanol was added 3.0 g of platinium oxide and the mixture was hydrogenated at atmospheric pressure. Uptake ceased after the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration. After removal of the solvent the residue was treated with 300 ml of 10% sodium hydroxide solution and 2.3 l. of ether. The ether layer was washed with water and dried over sodium sulfate and the solvent was removed. The residue was chromatographed on 600 g of alumina. Elution of the column with benzene gave 6.0 g (27%) of *cis-syn*-2,3,4,4a,5,6,8,9,13b,13c-decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine (**6**), mp 120–122°.

Anal. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.70; H, 9.01; N, 4.73.

Elution of the column with chloroform–methanol gave 5.4 g of material which contained mostly trans-anti-2,3,4,4a,5,6,8,9,13b,13c-decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine (**8**) as shown by thin layer chromatography.

Preparation of the C-13b-*d* Derivatives of *cis-syn*- and *trans-anti*-2,3,4,4a,5,6,8,9,13b,13c-Decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine.—To a solution of 4.9 g of **13** in 45 ml of deuterium oxide was added 1.8 g of sodium borodeuteride over a 10-min interval. The reaction mixture was extracted with methylene chloride. The methylene chloride layer was dried over sodium sulfate and the solvent was removed. The residue (4.9 g) was chromatographed on 160 g of alumina. Elution of the column with benzene gave 1.7 g of *cis-syn*-2,3,4,4a,5,6,8,9,13b,13c-decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine-13b-*d*, mp 121–122°.

Anal. Calcd for $C_{19}DH_{26}NO_2$: C, 75.45; H, 9.33; N, 4.63. Found: C, 75.59; H, 9.37; N, 4.39.

Elution of the column with 1% methanol in ether gave 0.6 g which was rechromatographed on 40 g of alumina. Elution with methylene chloride gave 0.31 g which was subjected to preparative thin layer chromatography on silica gel. The plates were developed with ethyl acetate–benzene (1:1). The desired zone was removed from the plate and extracted with methylene chloride. The methylene chloride was removed and the residue dissolved in Skellysolve B. On standing there was deposited 0.06 g of a *trans-anti*-2,3,4,4a,5,6,8,9,13b,13c-decahydro-11,12-dimethoxy-1*H*-dibenzo[*a*,*h*]quinolizine-13b-*d*, mp 95–98°.

Registry No.—**1**, 31446-56-7; **2**, 31446-57-8; **3**, 31446-58-9; **4**, 31446-59-0; **5**, 31446-60-3; **6**, 31446-61-4; **7**, 31446-62-5; **8**, 31446-63-6; **9**, 31446-64-7; **10**, 31446-65-8; **11**, 31446-66-9; **12**, 31446-67-0; **13**, 31446-68-1; **13**-13b-*d* (cis-syn,) 31446-69-2; **13**-13b-*d* (trans-anti), 31446-70-5.

Preparation of Amidines from *gem*-Dichloroaziridines[1,2]

MARCUS K. MEILAHN,* LARRY L. AUGENSTEIN, AND JAMES L. MCMANAMAN

Department of Chemistry, University of Northern Colorado, Greeley, Colorado 80631

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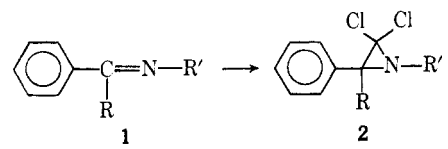
The first preparation of a *gem*-dichloroaziridine was reported by Fields and Sandri in 1959.[3] They synthesized 1,3-diphenyl-2,2-dichloroaziridine (**2a**) by the addition of dichlorocarbene, generated by the reaction of chloroform with sodium methoxide, to benzylidene-



1 **2**

aniline (**1a**). A number of other methods have been used to generate the dichlorocarbene in this reaction and the methods are summarized in Table I. The new

TABLE I

gem-DICHLOROAZIRIDINES[a]

Imine	R	R′	Aziridine	Yield, %	Method[b]	Ref
1a	Hydrogen	Phenyl	**2a**	55	A	3
				80	B	*c*
				61	C	*d*
				68, 91[e]	D	*f*
1b	Phenyl	Phenyl	**2b**	*g*	D	*h*
1c	Hydrogen	1-Naphthyl	**2c**	39	A	*i*
				44	B	*i*
1d	Phenyl	Benzyl	**2d**	65[i]	A	*i*
				7	B	*i*
1e	Ethyl	Phenyl	**2e**	56	A	*i*
				52	B	*i*
1f	Ethyl	1-Naphthyl	**2f**	68	A	*i*
				31	B	*i*

[a] This table also contains the other reported *gem*-dichloroaziridine systems. [b] The reaction of sodium methoxide with chloroform (A), ethyl trichloroacetate (B), hexachloroacetone (C), and the reaction of potassium *tert*-butoxide with chloroform (D). [c] J. A. Deyrup and R. B. Greenwald, *J. Amer. Chem. Soc.*, **87**, 4538 (1965). [d] P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **25**, 1431 (1960). [e] Yields reported for R′ = *p*-chlorophenyl and *p*-methoxyphenyl, respectively. [f] A. G. Cook and E. K. Fields, *ibid.*, **27**, 3686 (1962). [g] Not reported. [h] J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 321 (1965). [i] This report. [j] This yield was obtained in one run; typical yields for this reaction were *ca.* 4%.

alkyl- and aryl-substituted *gem*-dichloroaziridines reported in Table I were prepared by two of these methods. Although the yields are comparable for the two methods, the aziridines were more readily purified from the reaction which employed chloroform as the carbene source.

Hydrolysis.—The hydrolysis of 1,3-diphenyl-2,2-dichloroaziridines (**2a**) has been reported to afford α-chloro-α-phenylacetamide (**4a**) in quantitative

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(3) E. K. Fields and S. M. Sandri, *Chem. Ind. (London)*, 1216 (1959).