

chloride 0.80 in acetone-water (4:1), 0.58 in butanol-5*N* acetic acid (7:3) (absorption in all cases). Ultraviolet absorption spectra in methanol,  $\lambda_{\max}$  238  $m\mu$  ( $\epsilon$  12,100), 312 ( $\epsilon$  7,200); in 0.1*N* hydrochloric acid the spectra is essentially the same as methanol.

*Anal.* Calcd. for  $C_8H_8N_4O$  (176.2): C, 54.5; H, 4.6; N, 31.8. Found: C, 54.5; H, 4.8; N, 31.6.

*Method 2.* 3-Formamido-5-methylpyrazine-2-(*N*-methyl)-carboxamide (VIII) (100 mg., 0.52 mmole) was heated on a steam bath for 8 hr. in a solution of 5 ml. of pyridine and 1 ml. of water. After the solution stood at room temperature overnight the crystals were collected; yield 40 mg. (44%). The infrared spectra of this product and that obtained by method 1 were identical.

*Method 3.* Compound VIII (100 mg., 0.52 mmole) was warmed on a steam bath in 10 ml. of 5% sodium bicarbonate solution until solution was complete (4-5 min). The crystals were filtered off after standing 2 days at room temperature, yield 54 mg. (59%). The infrared spectrum of this material was identical to spectra of the products obtained by methods 1 and 2.

*3-Formamido-5-methylpyrazine-2-(N-methyl)carboxamide (VIII). Method 1.* 3-Amino-5-methylpyrazine-2-(*N*-methyl)-carboxamide (1.0 g., 6.0 mmoles) was dissolved in a solution containing 5 ml. of formic acid and 10 ml. of acetic anhydride and warmed on a steam bath for several minutes to initiate the reaction. After standing at room temperature for a few minutes, crystals separated; yield 0.75 g. (71%), m.p. 225-231° (resolidifies to give crystals which do not melt below 300° indicating ring closure to VII).  $R_f$  0.84 in butanol-5*N* acetic acid (7:3), 0.87 in acetone-water (4:1) (dull purple fluorescence), tailed spot between VII and IX in 3% ammonium chloride. Ultraviolet absorption spectra in methanol,  $\lambda_{\max}$  256  $m\mu$  ( $\epsilon$  19,000), 316  $m\mu$  ( $\epsilon$  7,480).

*Anal.* Calcd. for  $C_8H_{10}N_4O_2$  (194.2): C, 49.5; H, 5.2; N, 28.9. Found: C, 49.2; H, 5.4; N, 29.2.

*Method 2.* 3,7-Dimethyl-4(3H)-pteridinone (0.50 g., 2.8 mmoles) was refluxed for 12 hr. in 30 ml. of a pyridine-water (5:1) solution. On cooling 0.33 g. of starting material was filtered off and the filtrate was taken to dryness *in vacuo*. This was extracted with 30 ml. of water and filtered from the

insoluble residue; yield 106 mg., m.p. 226.5-230°. Recrystallization from 10 ml. of 50% ethanol yielded 50 mg., m.p. 232-235°. This material was identical to that prepared by Method 1 as shown by infrared spectra, mixed melting point, and paper chromatography.

When this formyl compound (VIII) or 3,7-dimethyl-4-(3H)-pteridinone (VII) was refluxed for 1 min. in 1*N* sodium hydroxide, they were converted to 3-amino-5-methyl-2-pyrazinoic acid (V) and 3-amino-5-methylpyrazine-2-(*N*-methyl)carboxamide (IX) as shown by chromatography in 3% ammonium chloride 0.5% sodium carbonate and acetone-water (4:1). By heating for 1 min. on a steam bath in 0.1*N* sodium hydroxide a third yellow-green fluorescent product was formed which traveled side-by-side with compound X in the three above-mentioned solvent systems. This compound (X) was slowly hydrolyzed to the acid (V) on standing in 0.1*N* sodium hydroxide at room temperature.

*3-Formamido-5-methylpyrazine-2-carboxylic acid (X).* One gram of 3-amino-5-methylpyrazine-2-carboxylic acid was added to a solution of 5 ml. of formic acid in 10 ml. of acetic anhydride and warmed on the steam bath for a few minutes to initiate the reaction. After standing at room temperature for 5 min. the solution was refluxed for 30 min., then treated with Norit and filtered. Twenty milliliters of anhydrous ether was added to the filtrate. This solution was protected with a tube of Drierite and allowed to stand for several hours at room temperature, then chilled overnight. The product was collected and dried; yield 0.45 g. (38%), m.p. 184-185° dec.  $R_f$  0.82 in 3% ammonium chloride 0.84 in 0.5% sodium carbonate, 0.64 in acetone-water (4:1) (yellow-green fluorescence). Ultraviolet absorption spectra in methanol,  $\lambda_{\max}$  252  $m\mu$  ( $\epsilon$  15,500), 311  $m\mu$  ( $\epsilon$  6,920).

*Anal.* Calcd. for  $C_7H_7N_3O_3$  (181.2): C, 46.4; H, 3.9; N, 23.2. Found: C, 46.6; H, 4.2; N, 23.4.

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

## Benzacridines. V.<sup>1</sup> Dibenz[a,c]acridine and 1,4-Dimethylbenz[c]acridine

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Application of the  $\alpha$ -dehydrobromination-rearrangement reaction previously reported for 6-bromo-5,5-dimethyl-5,6-dihydrobenz[c]acridine has led to a new synthesis of dibenz[a,c]acridine. Several other possible conditions for carrying out this transformation have been investigated. A new benz[c]acridine, namely, 1,4-dimethylbenz[c]acridine, is reported.

The initial paper in this series<sup>2</sup> reported a new pathway to benz[c]acridine derivatives substituted in the five and six positions. These positions, which involve the carbon atoms of the "K-region" for this ring system, provide interesting derivatives for further studies of chemical carcinogenesis.<sup>3</sup> It was also of importance to find further examples of the " $\alpha$ -dehydrobromination-rearrangement" of 6-bromo-5,5-dimethyl-5,6-dihydrobenz[c]acridine

(VIII) that led to the isolation of 5,6-dimethylbenz[c]acridine (XI) in high yield.

Condensation of 4,4-tetramethylene-1-tetralone (I) with *o*-nitrobenzaldehyde was carried out in the presence of acetic acid and sulfuric acid providing 2-(*o*-nitrobenzal)-4,4-tetramethylene-1-tetralone (II) in 84% yield. Reduction of the ketone II with iron and acetic acid followed by direct cycliza-

(1) For paper IV, see N. H. Cromwell and J. C. David, *J. Am. Chem. Soc.*, **82**, 2046 (1960).

(2) V. L. Bell and N. H. Cromwell, *J. Org. Chem.*, **23**, 789 (1958).

(3) See (a) C. A. Coulson, *Advances in Cancer Research*, Academic Press, Inc., New York, N. Y., 1953, Vol. I, pp. 1-56 and (b) A. Lacassagne, N. P. Buu-Hoi, R. Daudel, and F. Zajdela, *Advances in Cancer Research*, Academic Press, Inc., New York, N. Y., 1956, Vol. IV, pp. 316-369.

tion of the intermediate aminoketone with hydrochloric acid produced 5,5-tetramethylene-5,6-dihydrobenz[*c*]acridine (IV) in 83% over-all yield. Reaction of the tetralone I with isatin under basic conditions afforded a 75% yield of 7-carboxy-5,5-tetramethylene-5,6-dihydrobenz[*c*]acridine (III). Thermal decarboxylation of the acid III also gave the dihydrobenz[*c*]acridine IV. The unstable bromide V, obtained by treatment of IV with *N*-bromosuccinimide in carbon tetrachloride, was directly heated at 170° affording the hydrobromide of 5,6,7,8-tetrahydrodibenz[*a,c*]acridine (VI). The over-all yield of VI from the dihydrobenz[*c*]acridine IV was 76%. As expected, the ultraviolet absorption spectra of III and IV closely resemble those obtained for 5,6-dihydrobenz[*c*]acridines while VI provided a spectrum very similar to that observed for 5,6-dimethylbenz[*c*]acridine.<sup>2</sup> Dehydrogenation of the tetrahydro compound VI produced dibenz[*a,c*]acridine (VII) that was shown to be identical with an authentic sample prepared from phenanthraquinone and *o*-nitrobenzyl chloride. This conversion provides additional evidence for the structure of the products obtained from thermal dehydrobromination-rearrangement of the bromides V and VIII.

Various other conditions for carrying out the conversion of the bromide VIII to 5,6-dimethylbenz[*c*]acridine have been attempted affording lower yields of the desired product compared to those obtained by direct thermal decomposition. Heating of the bromide VIII with pyridine provided only a 20% yield of 5,6-dimethylbenz[*c*]acridine (XI). Treatment of the bromide VIII with  $\gamma$ -picoline at room temperature for an extended period gave the stable  $\gamma$ -picolinium bromide IX in 89% yield. At approximately the same temperature observed for the decomposition of the bromide VIII the salt IX evolves  $\gamma$ -picoline and the neutralized residue afforded a 58% yield of 5,6-dimethylbenz[*c*]acridine. A quantitative yield of silver bromide was isolated from the reaction of VIII with silver nitrate in dry acetonitrile. After hydrolysis and neutralization of the reaction mixture the major product (49%), probably obtained by hydrolysis of the nitrate, was 6-hydroxy-5,5-dimethyl-5,6-dihydrobenz[*c*]acridine (X) while only a 20% yield of 5,6-dimethylbenz[*c*]acridine was isolated.

Previously reported carcinogenic testing of the mono- and dimethylbenz[*c*]acridines indicated that activity was largely dependent on the presence of a substituent at the seven position.<sup>8b</sup> Since the known methylbenz[*c*]acridines did not include methyl substitutions at the one and four positions, 1,4-dimethylbenz[*c*]acridine (XV) was synthesized from the readily available 5,8-dimethyl-1-tetralone (XII). Condensation of the tetralone XII with *o*-nitrobenzaldehyde produced 2-(*o*-nitrobenzal)-5,8-dimethyl-1-tetralone (XIII) which upon reduction

with iron and acetic acid and cyclization in the presence of hydrochloric acid yielded 1,4-dimethyl-5,6-dihydrobenz[*c*]acridine (XIV). Dehydrogenation of XIV with palladium-charcoal provided 1,4-dimethylbenz[*c*]acridine (XV).

#### EXPERIMENTAL<sup>4</sup>

*4,4-Tetramethylene-1-tetralone* (I). Cyclization of 2.80 g. of 4-phenyl-4,4-tetramethylenebutyric acid,<sup>5</sup> prepared by the method of Arnold, was accomplished by heating on a steam bath for 25 min. with 10 ml. of polyphosphoric acid. The cooled reaction mixture was poured on ice and, after the addition of ether and benzene, the organic layer was washed with water and sodium carbonate solution and dried over anhydrous sodium sulfate. After concentration the solution was passed through an alumina column and the benzene eluates were concentrated under reduced pressure to constant weight providing 2.30 g. (90%) of 4,4-tetramethylene-1-tetralone (I),  $n_D^{25}$  1.5720, reported<sup>5</sup>  $n_D^{25}$  1.5732.

*2-(o-Nitrobenzal)-4,4-tetramethylene-1-tetralone* (II). A solution of 1.80 g. (0.0090 mole) of 4,4-tetramethylene-1-tetralone (I) and 1.36 g. (0.0090 mole) of *o*-nitrobenzaldehyde in 2.3 ml. of sulfuric acid and 14 ml. of acetic acid was allowed to stand at room temperature for 5 days. The crystals that had formed were collected by filtration and washed with methanol providing 2.25 g. of 2-(*o*-nitrobenzal)-4,4-tetramethylene-1-tetralone (II), m.p. 121–123°. The solid obtained by addition of water to the filtrate was dissolved in ethyl acetate, treated with Norite, and allowed to crystallize affording an additional 0.27 g. of II, m.p. 123–124°, making the total yield 2.52 g. (84%). An analytical sample, m.p. 125–125.5°,  $\lambda_{\max}$  276 m $\mu$  ( $\epsilon$  19,200), was prepared by crystallization from ethyl acetate.

*Anal.* Calcd. for  $C_{21}H_{19}NO_3$ : C, 75.65; H, 5.74; N, 4.20. Found: C, 75.84; H, 5.63; N, 4.02.

*7-Carboxy-5,5-tetramethylene-5,6-dihydrobenz[*c*]acridine* (III). A mixture of 0.50 g. (0.0025 mole) of 4,4-tetramethylene-1-tetralone, 0.40 g. (0.0025 mole) of isatin, 0.52 g. of potassium hydroxide, 0.8 ml. of methanol, and 0.5 ml. of water was refluxed for 11 hr. The reaction mixture was diluted with water and acidified to bromophenol blue with hydrochloric acid. The resulting solid was collected, washed with water, and crystallized from ethyl acetate providing 0.62 g. (75%) of 7-carboxy-5,5-tetramethylene-5,6-dihydrobenz[*c*]acridine (III), m.p. 210.5–213°. Recrystallization from ethyl acetate yielded an analytical sample, m.p. 211.5–213°,  $\lambda_{\max}$  209, 214, 226, 260 sh, 267, 300, 316, 331, 346 m $\mu$  ( $\epsilon \times 10^{-4}$ , 4.05, 3.89, 2.48, 2.94, 3.65, 0.82, 0.87, 1.13, 1.29).

*Anal.* Calcd. for  $C_{22}H_{19}NO_3$ : C, 80.22; H, 5.81; N, 4.25. Found: C, 79.70; H, 5.88; N, 4.02.

*5,5-Tetramethylene-5,6-dihydrobenz[*c*]acridine* (IV). Powdered electrolytic iron, 1.3 g., was added in small portions to a solution of 2.80 g. (0.0084 mole) of 2-(*o*-nitrobenzal)-4,4-tetramethylene-1-tetralone (II) dissolved in 35 ml. of acetic acid and 4 ml. of water and heated on a steam bath. The reaction mixture was heated for an additional 15 min., cooled, and treated with a solution of 35 g. of potassium hydroxide in 200 ml. of water. The resulting suspension was extracted with four 150-ml. portions of ether. The ether extracts were washed with water and after concentration the residue was heated on a steam bath for 0.5 hr. with 5 ml. of concd. hydrochloric acid and 30 ml. of ethanol. After dilution with water the reaction mixture was neutralized with sodium carbonate solution and the solid that formed was collected and washed with water. A benzene solution of this

(4) Ultraviolet spectral determinations were made at about 25° with a Cary recording spectrophotometer, model 11 MS, using 95% ethanol unless otherwise specified.

(5) R. T. Arnold, J. S. Buckley, and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 3153 (1950).

material was passed through a column of basic alumina and crystallization of the concentrated benzene eluates from methanol afforded 2.00 g. (83%) or 5,5-tetramethylene-5,6-dihydrobenz[*c*]acridine (IV), m.p. 162–165°. Preparation of an analytical sample was accomplished by crystallization from methanol and ethyl acetate giving colorless needles, m.p. 165–166°,  $\lambda_{\max}$  211, 215, 226 sh, 259 sh, 267, 299, 317, 332, 346 m $\mu$  ( $\epsilon \times 10^{-4}$ , 4.22, 4.13, 3.00, 2.96, 3.63, 0.85, 0.87, 1.26, 1.47).

*Anal.* Calcd. for  $C_{21}H_{13}N$ : C, 88.38; H, 6.71; N, 4.91. Found: C, 88.23; H, 6.59; N, 5.00.

*Thermal decarboxylation of 7-carboxy-5,5-tetramethylene-5,6-dihydrobenz[*c*]acridine (III).* Decarboxylation of 0.95 g. of the acid III was accomplished by heating for 1.5 hr. at 240°. The crude product was dissolved in benzene and extraction with sodium hydroxide solution led to the recovery of 0.15 g. of starting material. The dried benzene solution was passed through an alumina column and the concentrated benzene eluates were crystallized from methanol providing 0.35 g. (50%) of 5,5-tetramethylene-5,6-dihydrobenz[*c*]acridine (IV), m.p. 162–164°. This compound was shown to be identical with the preparation obtained *via* 2-(*o*-nitrobenzal)-4,4-tetramethylene-1-tetralone (II) by a mixture melting point determination.

*5,6,7,8-Tetrahydrodibenz[*a,c*]acridine (VI).* A solution of 1.42 g. (0.0045 mole) of 5,5-tetramethylene-5,6-dihydrobenz[*c*]acridine (IV) in 25 ml. of carbon tetrachloride was refluxed 45 min. with 0.98 g. (0.0056 mole) of *N*-bromosuccinimide and a trace of benzoyl peroxide. The reaction mixture was cooled, diluted with ether, and washed with sodium carbonate solution. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated at room temperature under reduced pressure. The resulting unstable yellow solid was heated for 10 min. at 170° under a nitrogen atmosphere. The red colored solid produced was heated with sodium hydroxide solution and benzene. The benzene solution was washed with water, dried by azeotropic distillation, and passed through a column of basic alumina. Concentration of the benzene eluates and crystallization of the residue from ethyl acetate produced 1.07 g. (76%) of 5,6,7,8-tetrahydrodibenz[*a,c*]acridine (VI), m.p. 193–196°. Recrystallization from ethyl acetate yielded an analytical sample as yellow needles, m.p. 196–197°,  $\lambda_{\max}$  223, 235 sh, 270 sh, 277, 292, 321, 337, 352, 369, 387 m $\mu$  ( $\epsilon \times 10^{-4}$ , 3.62, 2.72, 4.61, 5.39, 5.14, 0.57, 0.62, 0.65, 0.70, 0.58).

*Anal.* Calcd. for  $C_{22}H_{17}N$ : C, 89.01; H, 6.05. Found: C, 88.87; H, 6.20.

*Dibenz[*a,c*]acridine (VII).* Following the procedure of Austin<sup>6</sup> phenanthraquinone was allowed to react with *o*-nitrobenzyl chloride in the presence of stannous chloride, concentrated hydrochloric acid, and methanol. Purification of the crude product was accomplished by chromatography in benzene on basic alumina followed by concentration of the benzene eluates providing dibenz[*a,c*]acridine in 50% yield as pale yellow needles, m.p. 204–205°, reported m.p. 205°,  $\lambda_{\max}$  257, 272, 282, 304, 338, 354, 372 m $\mu$  ( $\epsilon \times 10^{-4}$ , 6.08, 6.49, 8.14, 1.04, 0.70, 1.16, 1.35).

*Dehydrogenation of 5,6,7,8-tetrahydrodibenz[*a,c*]acridine (VI).* Dehydrogenation of 0.08 g. of 5,6,7,8-tetrahydrodibenz[*a,c*]acridine (VI) was carried out in the presence of 10% palladium-charcoal under a nitrogen atmosphere for 10 min. at 300°. The crude product was dissolved in benzene, treated with Norite, and allowed to crystallize yielding 0.02 g. (25%) of dibenz[*a,c*]acridine (VII), m.p. 199–202°, mixture melting point determination with the dibenz[*a,c*]acridine prepared above and comparison of ultraviolet spectra showed the two compounds to be identical.

*Reactions of 6-bromo-5,5-dimethyl-5,6-dihydrobenz[*c*]acridine (VIII).* A. *5,5-Dimethyl-5,6-dihydrobenz[*c*]acridine 6-( $\gamma$ -picolinium bromide) (IX).* A solution of 1.95 g. (0.0058 mole) of 6-bromo-5,5-dimethyl-5,6-dihydrobenz[*c*]acridine (VIII)<sup>2</sup>

in 10 ml. of  $\gamma$ -picoline was allowed to stand at room temperature for 9 days. The crystals that had formed were collected and washed with acetone affording 2.20 g. (89%) of 5,5-dimethyl-5,6-dihydrobenz[*c*]acridine 6-( $\gamma$ -picolinium bromide) (IX). Recrystallization from isopropyl alcohol-ether yielded an analytical sample, m.p. 165–185° dec.,  $\lambda_{\max}$  in methanol 213, 223 sh, 266, 302, 316, 330, 345 m $\mu$  ( $\epsilon \times 10^{-4}$ , 4.18, 3.21, 4.16, 0.85, 0.85, 0.94, 0.87).

*Anal.* Calcd. for  $C_{26}H_{22}N_2Br$ : C, 69.60; H, 5.37; N, 6.50; Br, 18.53. Found: C, 68.96; H, 5.27; N, 6.50; Br, 18.56.

B. *Reaction with pyridine.* A solution of 2.0 g. of the bromo compound VIII in 20 ml. of dry pyridine was heated on a steam bath for 4 hr. Water was added and the precipitated solid was collected, dissolved in acetone, and treated with Norite. Addition of water gave 0.3 g. (20%) of yellow crystals shown by a mixture melting point determination to be 5,6-dimethylbenz[*c*]acridine (XI).<sup>2</sup>

C. *Reaction with silver nitrate in acetonitrile.* To a solution of 2.0 g. (0.0059 mole) of the bromo compound VIII in 40 ml. of warm, dry acetonitrile 1.02 g. (0.0059 mole) of silver nitrate dissolved in 10 ml. of acetonitrile was added dropwise. The reaction mixture was filtered hot, removing the theoretical amount of silver bromide. The filtrate was neutralized with sodium carbonate solution and the precipitated crystals were filtered from the warm mixture yielding 0.30 g. (20%) of 5,6-dimethylbenz[*c*]acridine. Upon addition of water and cooling, the mother liquor gave 0.80 g. (49%) of 5,5-dimethyl-6-hydroxy-5,6-dihydrobenz[*c*]acridine (X).<sup>2</sup> The products were identified by mixture melting point determinations with authentic samples.

*Thermal decomposition of 5,5-dimethyl-5,6-dihydrobenz[*c*]acridine 6-( $\gamma$ -picolinium bromide) (IX).* A 1.00-g. sample of the salt IX was heated for 15 min. at 165–185°. As the decomposition proceeded, the solid became red in color and the evolution of  $\gamma$ -picoline was observed. After cooling, the residue was dissolved in hot dioxane and neutralized with sodium carbonate solution. A dry benzene solution of the solid obtained was passed through an alumina column and the concentrated eluates yielded, after crystallization from benzene-methanol, 0.35 g. (58%) of 5,6-dimethylbenz[*c*]acridine, m.p. 161–163°. A mixture melting point determination with a sample obtained by heating 6-bromo-5,5-dimethyl-5,6-dihydrobenz[*c*]acridine<sup>2</sup> demonstrated the compounds to be identical.

*5,8-Dimethyl-1-tetralone (XII).* Preparation of this tetralone was accomplished by modification of the procedure used by Barnett.<sup>7</sup> During a period of 1 hr. 300 g. of aluminum chloride was added to a mixture of 106 g. (1.0 mole) of *p*-xylene, 98 g. (0.98 mole) of succinic anhydride and 375 ml. of methylene chloride. Hydrolysis and extraction of the reaction mixture in the usual manner provided a quantitative yield of crude acidic material. Direct reduction of 100 g. of keto acid using the Wolff-Kishner method was carried out with 65 g. of potassium hydroxide, 54 ml. of 95% hydrazine, and 525 ml. of diethylene glycol. The crude  $\gamma$ -(*p*-xylyl)-butyric acid, obtained in quantitative yield, was cyclized with polyphosphoric acid in the usual manner and chromatography on alumina in benzene followed by crystallization of the eluates from petroleum ether at about –30° gave a 60% yield of 5,8-dimethyl-1-tetralone (XII), m.p. 32–33.5°, reported m.p. 33°.

*2-(*o*-Nitrobenzal)-5,8-dimethyl-1-tetralone (XIII).* After a mixture of 8.70 g. (0.05 mole) of 5,8-dimethyl-1-tetralone, 7.50 g. (0.05 mole) of *o*-nitrobenzaldehyde, 10 ml. of sulfuric acid, and 60 ml. of acetic acid was allowed to stand for 40 hr., the crystals that had formed were collected and washed with a small amount of acetic acid and methanol. Recrystallization from benzene-petroleum ether (b.p. 30–60°) afforded 7.35 g. (48%) of 2-(*o*-nitrobenzal)-5,8-dimethyl-1-tetralone (XIII), m.p. 133–134.5°. An analytical sample,

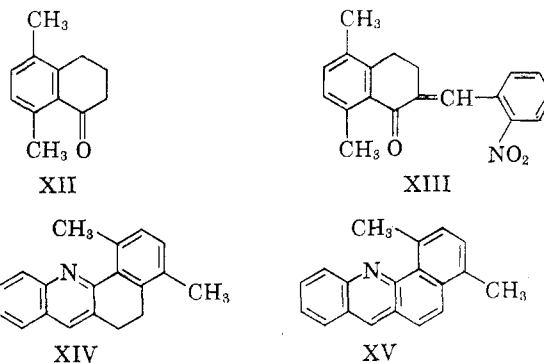
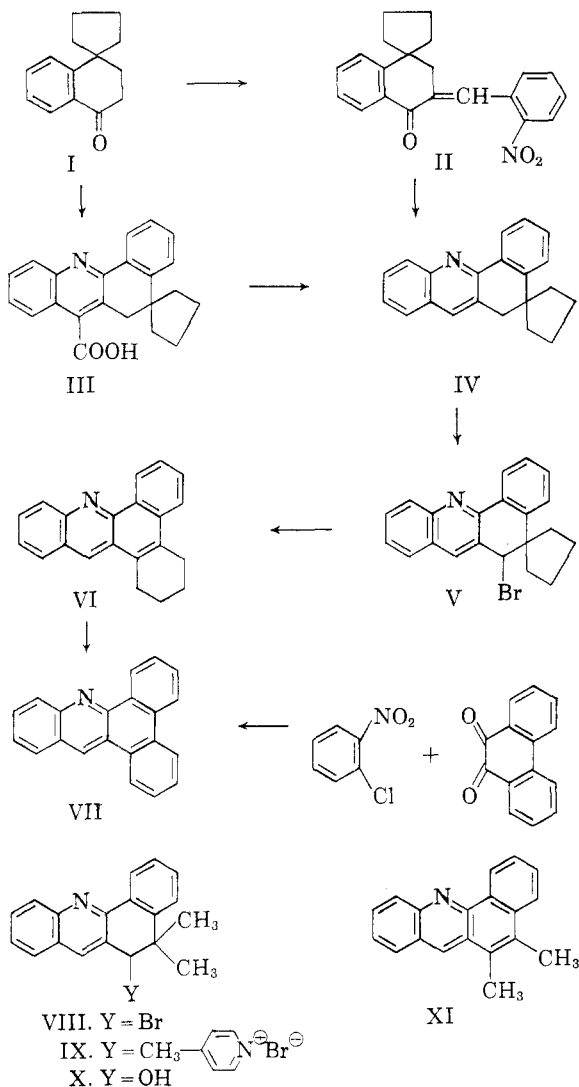
(6) P. C. Austin, *J. Chem. Soc.*, 1765 (1908).

(7) E. de Barry Barnett and F. G. Sanders, *J. Chem. Soc.*, 434 (1933).

m.p. 133.5–134.5°,  $\lambda_{\max}$  273 m $\mu$  ( $\epsilon$ , 24,400), was prepared by crystallization from methanol and benzene.

Anal. Calcd. for  $C_{19}H_{17}NO_3$ : C, 74.25; H, 5.58; N, 4.56. Found: C, 74.54; H, 5.72; N, 4.39.

1,4-Dimethyl-5,6-dihydrobenz[c]acridine (XIV). As described for the ketone II, 4.64 g. (0.015 mole) of 2-(*o*-nitrobenzal)-5,8-dimethyl-1-tetralone (XIII) was reduced with iron powder and cyclized in the presence of hydrochloric



acid producing, after chromatography and crystallization from methanol, 3.05 g. (78%) of 1,4-dimethyl-5,6-dihydrobenz[c]acridine (XIV), m.p. 96.5–98°. Recrystallization from methanol provided an analytical sample, m.p. 102–102.5°,  $\lambda_{\max}$  220, 258 sh, 266, 312, 327, 342 m $\mu$  ( $\epsilon \times 10^{-4}$ , 4.50, 2.64, 3.36, 0.88, 1.17, 1.38).

Anal. Calcd. for  $C_{19}H_{17}N$ : C, 88.00; H, 6.60; N, 5.40. Found: C, 88.16; H, 6.61; N, 5.13.

1,4-Dimethylbenz[c]acridine (XV). Dehydrogenation of 2.0 g. of 1,4-dimethyl-5,6-dihydrobenz[c]acridine (XIV) was carried out at 210–220° in the presence of 10% palladium-charcoal. This provided, after dissolving in benzene and passage through an alumina column followed by crystallization from ethyl acetate, 0.50 g. (25%) of 1,4-dimethylbenz[c]acridine (XV), m.p. 108–110°. Recrystallization from ethyl acetate yielded an analytical sample, m.p. 110–111°,  $\lambda_{\max}$  229, 244, 272 sh, 277 sh, 280, 338, 356, 373, 391 m $\mu$  ( $\epsilon \times 10^{-4}$ , 4.95, 4.51, 8.70, 9.20, 9.50, 0.68, 0.62, 0.96, 1.33).

Anal. Calcd. for  $C_{19}H_{15}N$ : C, 88.68; H, 5.88; N, 5.44. Found: C, 88.85; H, 5.82; N, 5.32.

A picrate was prepared in the usual manner and after crystallization from acetone melted with decomposition at 181–183°,  $\lambda_{\max}$  226, 242, 280, 342, 356, 372, 392 m $\mu$  ( $\epsilon \times 10^{-4}$ , 3.19, 2.86, 4.52, 0.80, 1.02, 1.07, 0.78).

Anal. Calcd. for  $C_{25}H_{18}N_4O_7$ : C, 61.73; H, 3.73; N, 11.52. Found: C, 61.90; H, 3.91; N, 11.24.

For the purpose of comparison the ultraviolet spectrum of 5,6-dimethylbenz[c]acridine picrate<sup>2</sup> was determined,  $\lambda_{\max}$  223, 236 sh, 271 sh, 278, 293, 340 sh, 356, 370, 388 sh, m $\mu$  ( $\epsilon \times 10^{-4}$ , 4.14, 3.22, 3.58, 4.22, 4.04, 0.74, 1.08, 1.00, 0.60).

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