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Syntheses of Benzo[b]- and Benzo[j]phenanthridines (I)

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The isomeric lactams benzo[b]phenanthridine-5(6H)-one and benzo[j]phenanthridine-6(5H)-one were obtained in equal yields by Schmidt reaction on 11H-benzo[b]fluoren-11-one (44% total) or by Beckmann reaction on 11H-benzo[b]fluoren-11-one oxime (22% total). Reduction of the lactams with lithium aluminum hydride gave the 5,6-dihydrobenzo[b]- and -[j]phenanthridines. Dehydrogenation of these dihydro derivatives produced the parent aromatic heterocycles benzo[b]- and benzo[j]phenanthridine in best overall yields of 20% and 12%, respectively. A few substituted benzophenanthridines were also prepared. Assignment of structures was based on ultraviolet, infrared, and n.m.r. spectra of the dihydro derivatives as well as on separate unequivocal synthesis of the isomeric benzophenanthridines.

According to a theory promulgated largely by the Pullmans (3) carcinogenicity in polynuclear aromatic hydrocarbons can often-times be correlated with chemical structure, whereby a combination of high chemical reactivity at the K-region (toward an electrophilic cellular receiver) with low chemical reactivity at the L-region fosters carcinogenic properties. Particularly since a nitrogen atom represents a center of high electron availability in an aromatic azacyclic molecule, it has been of interest to prepare such heterocyclic compounds for comparative biological testing. Many studies have been made with angular benzacridines (4), where a nitrogen atom is located in the L-region. However, few such heterocycles with a nitrogen atom in the K-region have yet been synthesized (5). The present paper concerns the synthesis (in quantities sufficiently large for biological testing) of benzo[b]- and benzo[j]phenanthridines (XIII and XIV, respectively), the two simplest analogs of benz[a]anthracene containing a nitrogen atom in the K-region.

Transformations carried out are shown in Scheme I. Thus, Schmidt reaction of 11H-benzo[b]fluoren-11-one (I) occurred readily at 100° in trichloroacetic acid as solvent to give a mixture of amides from which was separated, by sublimation and recrystallization, equal yields (22%) of benzo[b]phenanthridine-5(6H)-one (V), m.p. 305° and benzo[j]phenanthridine-6(5H)-one (VI), m.p. 355°. Beckmann rearrangement of 11H-benzo[b]fluoren-11-one oxime (II) also occurred with polyphosphoric acid at 175° to give the same lactams, again in about equal, but lower, yields (11%). If the generally accepted strictly *trans* stereochemistry of Beckmann rearrangement (6) applies here it would mean that oxime II consists of both *syn* and *anti* isomers. In fact, the narrow melting range (1°) of II and the relative yields of the isomeric lactams would then imply that II is a 1:1 molecular complex of these geometric forms. *A priori* one would expect oximation of I to produce approximately equal amounts of the isomers on the basis of both closely similar steric and electronic effects of the benzo and naphtho moieties in the

molecule. This latter consideration applied to the proposed mechanistic pathway for the Schmidt reaction (7) allows rationalization of equal yields of lactams therefrom (8). Treatment of II with *p*-toluenesulfonyl chloride gave a quantitative yield of crude oxime tosylate (III). Since recrystallization of the tosylate raised the melting point 38°, it may be that both geometric isomers were present in the crude product.

Treatment of the benzophenanthridones with excess lithium aluminum hydride in refluxing dioxane gave the corresponding crystalline 5,6-dihydrobenzophenanthridines (C₁₇H₁₃N), IX and X, in excellent yields. That the heterocyclic ring *b* was the one actually reduced in each case was apparent from the presence of an N-H stretching band in the infrared spectrum as well as of a broad absorption band for NH at $\delta = ca. 3.7$ and a sharp singlet for one CH₂ group at $ca. 4.4$ p.p.m. in the n.m.r. spectrum. Dehydrogenation of these derivatives to the parent aromatic azacyclic compounds, benzo[b]phenanthridine (XIII, m.p. 202°), and benzo[j]phenanthridine (XIV, m.p. 143°), respectively, was effected in good yield by means of 30% palladium-charcoal in refluxing decahydronaphthalene. The overall yields from I using the Schmidt reaction for the first step, were 20% for XIII and 12% for XIV.

Alternative, less attractive pathways from VI to XIV *via* the isolable, reasonably stable 6-chlorobenzo[j]phenanthridine (XI) were also explored. Thus, treatment of lactam VI with phosphorus oxychloride in the presence of a small amount of dimethylaniline furnished the chloro compound in 87% yield, but the subsequent action of lithium aluminum hydride in effecting replacement of Cl by H to form XIV directly or the action of Raney nickel and hydrogen in ethanolic hydroxide in effecting hydrogenation-hydrogenolysis to form X proceeded in only mediocre yield. Nucleophilic displacement of Cl by OC₂H₅ did occur, however, to produce 6-ethoxybenzo[j]phenanthridine (VII, 91% yield).

In the [b]-series, on the other hand, the corresponding 5-chlorobenzo[b]phenanthridine (IV) was ob-

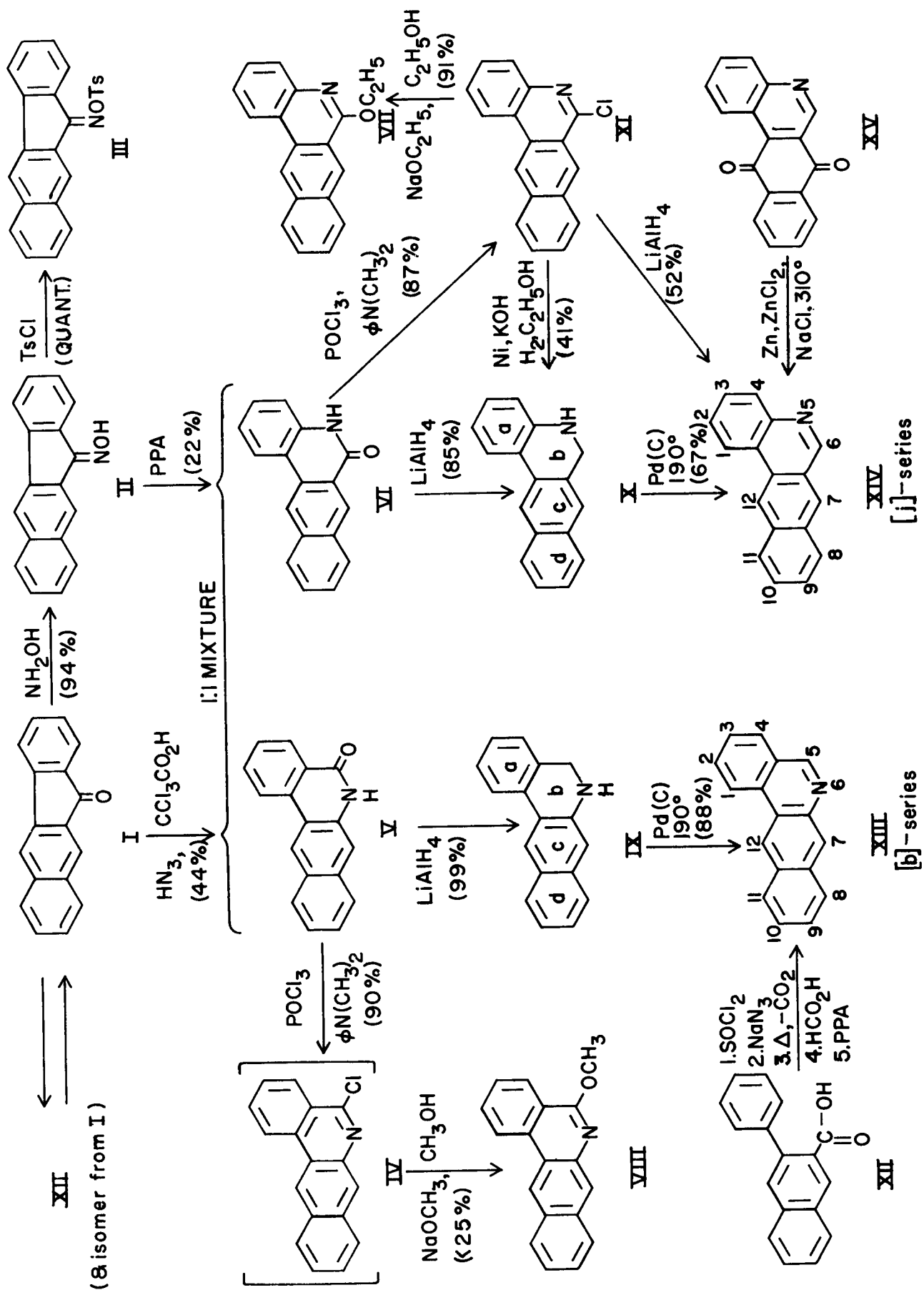


TABLE I
Ultraviolet Absorption Maxima for Benzo[b]- and Benzo[j]phenanthridines and Derivatives (a).

| Compound (b) | Solvent | λ max m μ | Log ϵ | λ max m μ | Log ϵ | λ max m μ | Log ϵ | λ max m μ | Log ϵ | λ max m μ | Log ϵ | λ max m μ | Log ϵ |
|---------------------------|--------------|--------------------------|----------------|--------------------------|----------------|--------------------------|----------------|--------------------------|----------------|--------------------------|----------------|--------------------------|----------------|
| V (c) | EtOH (d) | 227 | 4.48 | 261 | 4.69 | 270 | 4.69 | (317) | 3.92 | 358 | 3.62 | 374 | 3.75 |
| | | 221 | 4.56 | 262 | 4.81 | 271 | 4.88 | 327 (f) | 3.84 | 358 | 3.60 | 375 | 3.48 |
| VI | EtOH (d) | 234 | 4.38 | 268 | 4.70 | (302) | 4.01 | 316 | 3.99 | | | | |
| | | 220 | 4.60 | 245 | 4.70 | | | | | | | | |
| IX (g) | EtOH-HCl (h) | 254 | 4.61 | 264 | 4.68 | (290) | 4.11 | 298 | 4.20 | 332 | 3.87 | 356 | 3.86 |
| | | 255 | 4.66 | 264 | 4.74 | (290) | 4.14 | 298 | 4.21 | 309 | 4.17 | | |
| X (g) | EtOH-HCl (h) | 218 | 4.49 | 256 | 4.62 | (264) | 4.57 | 274 | 4.61 | 264 | 4.69 | 297 | 4.56 |
| | | | | 338 | 3.80 | 352 | 3.72 | | | | | | |
| XIV | EtOH (i) | 219 | 4.47 | 231 | 4.49 | 253 | 4.51 | (271) | 4.63 | 280 | 4.80 | (289) | 4.67 |
| | | | | 321 | 3.77 | 336 | 3.87 | 368 | 3.41 | 388 | 3.36 | | |
| Benz[a] anthracene (k) | EtOH (i) | 223 | 4.36 | 228 | 4.33 | 237 | 4.54 | 277 | 4.78 | 287 | 4.90 | 300 | 3.93 |
| | | (316) | 3.72 | 327 | 3.80 | 342 | 3.82 | 358 | 3.64 | 373 | 2.88 | | |
| XIII | EtOH-HCl (h) | (219) | 4.39 | 252 | 4.64 | 256 | 4.64 | 272 | 3.98 | (284) | 4.31 | 297 | 4.46 |
| | | | | (341) | 3.60 | 356 | 3.85 | 372 | 3.98 | 285 | 4.54 | 293 | 4.57 |
| XIV | EtOH-HCl (h) | 220 | 4.38 | 246 | 4.42 | 346 | 3.85 | 363 | 3.88 | | | | |
| | | | | (334) | 3.70 | | | | | | | | |

(a) Data in parentheses are for shoulders, not true maxima. (b) For sets of compounds placed together in a brace, data for corresponding maxima (as adjusted from observations on the total spectral curves) are placed in the same column. (c) The spectrum of V was identical with that of a sample of benzo[b]phenanthridine-5(6H)-one prepared by Professor Walter J. Gensler and Nancy Wang by a method to be described by them. (d) Only minor changes occurred in the spectrum when a solvent of 0.01 M sodium hydroxide in 95% ethanol was used. (e) Also absorption at (245, 4.57). (f) Also absorption at (288, 4.20). (g) Compare with spectrum of 2-phenylanthracene: 250, 4.70; 286, 4.04 (see footnote k). Z. J. Vejdelek and B. Kakac [Col. Czech. Chem. Communications, 20, 571 (1965)] reported the ultraviolet spectrum for a dihydrobenz[*a*]anthracene of unproved structure. Although they believed their compound was the 5,6-dihydro derivative, this seems doubtful, especially since its spectrum was markedly different from that of our amine salts. (h) Solvent 0.01 M hydrochloric acid in 95% ethanol. (i) Spectral features below 310 m μ . (j) Spectral features above 310 m μ . (k) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, 1951.

tained in only impure form since it reacted rather readily with water and ethanol. However, treatment of this crude intermediate with methanolic sodium methoxide did give a low yield of 5-methoxybenzo[b]phenanthridine (VIII).

The ultraviolet absorption maxima of many of these compounds are listed in Table I. As expected, the spectra of the isomeric benzophenanthridines resemble one another and the spectrum of benz[a]anthracene to a considerable degree. Many similarities are likewise found in the spectra of the isomeric benzophenanthridinium chlorides (formed in ethanolic hydrochloric acid), as well as in the spectra of the isomeric benzophenanthridones. The spectra of the two dihydrobenzophenanthridines are grossly different when measured in neutral solution. However, they are essentially superimposable when measured in ethanolic hydrochloric acid (as is to be expected if protonation occurs on the non-bonding electron-pairs of the nitrogen atoms), in which case they have a shape closely similar to that of 2-phenylnaphthalene but with more fine structure (consistent with greater rigidity in the molecule) and a bathochromic shift of the whole curve by 12-15 μ (corresponding effectively to two alkyl substituents present on the phenylnaphthalene chromophore). The ultraviolet spectra thus were consistent with the general structural assignments but did not allow clear identification of the [b]- and the [j]-series.

Part of this latter goal was accomplished by Clar reduction (by means of a mixture of zinc dust, sodium chloride, and zinc chloride at 310°) of the known benzo[j]phenanthridine-7,12-dione (XV) (9) to the parent benzo[j]phenanthridine, identical (as based on melting point and spectral criteria) with the 143° benzophenanthridine obtained by way of the Schmidt reaction. But this structural assignment appeared to be in conflict with the work of Brown, Hey and Rees (10), who reported the synthesis of benzo[b]phenanthridine of melting point 146-147° by a method involving cyclization of 3-phenyl-2-formamidonaphthalene, formed from the key intermediate 3-phenyl-2-naphthoic acid (XII), reported m.p. 166° (10,11) and 174° (12). In our hands repetition of the method of Brown *et al.* for the synthesis of XII by treatment of 3-carboethoxy-2-naphthyldiazonium borofluoride with copper and benzene gave, instead, 2,2'-binaphthyl-3,3'-dicarboxylic acid, m.p. 293°, and an unidentified acidic product of constant melting range 136-146°. Alkali fusion of ketone I, according to the procedure of Baddar *et al.* (12), and crystallization of the mixed acidic products led to a fraction (B) of constant melting point, 145-147°, assigned the structure XII on the basis of the fact that it could be reconverted (by treatment with concentrated sulfuric acid at room temperature) to I (identified by m.p., mixture m.p., and infrared spectrum) in >60% yield (13). Treatment of B by the successive steps shown for XII \rightarrow XIII in Scheme I (essentially following the procedure of Brown *et al.*) (10) gave benzo[b]phenanthridine of m.p. 199-200.5°, identical as based on mixture melting point and ultraviolet

spectra with the 202° isomer obtained by way of the Schmidt reaction.

Finally, confirmation of our structural assignments for the [b]- and the [j]-series was obtained on the basis of comparison of predicted and observed differences in the n.m.r. spectra of the dihydrobenzophenanthridines, IX and X. First, it is apparent that the location of the nitrogen atom in ring *b* (*cf.* Scheme I) will scarcely alter the frequencies of absorption of the protons on the most distant ring *d*. On the other hand, on the bases of the known relative chemical shifts (as compared to benzene as a standard) for the benzenoid hydrogens in *N*-methyl-aniline (shift to higher field: 0.80 for *o*-H, 0.30 for *m*-H, and 0.57 for *p*-H, in p.p.m.) and in benzylamine (shift to higher field: 0.03 for each H) (14) one would expect differences in the frequencies of absorption of the protons on the *a* and *c* rings in the two dihydro isomers. Thus, absorptions for the protons on the *a* ring of X should occur at higher field (smaller δ -value) from those on the *a* ring of IX, while those on the *c* ring of X should occur at lower field from the corresponding ones of IX - with a larger difference observable between the frequencies of the protons at position 7 than at position 12. For one isomer (assigned structure IX) sharp singlets occurred at $\delta = 6.91$ (1 proton, assigned to C₇) and 8.18 (1 proton, assigned to C₁₂) while multiple absorption peaks (8-9 protons) covered the range from 7.0-8.1 p.p.m. For the other isomer (assigned structure X) two strong peaks occurred at 7.50 and 7.55 (*ca.* 2 protons, presumably including one at C₇) and a sharp singlet occurred at 8.14 p.p.m. (1 proton, assigned to C₁₂). Multiple absorption peaks also covered the ranges from 6.5-7.5 (4-5 protons) and 7.6-8.1 p.p.m. (3 protons). The general patterns of the two spectra in the range 7.6-8.1 were nearly identical as would be expected if absorption there resulted from some of the protons in ring *d*. Correspondingly, and consistent with expectations, absorptions in the range from 6.5 to *ca.* 7.5 in the latter compound would arise from protons in ring *a*. By the chemical transformations previously described, the compound thus assigned structure IX was found to be in the same series as the 305° benzophenanthridone and the 202° benzophenanthridine, while the compound thus assigned structure X was found to be in the same series as the 355° benzophenanthridone and the 143° benzophenanthridine.

EXPERIMENTAL (15)

Schmidt Reaction on I.

To a heated (100°), stirred mixture (protected from atmospheric moisture) of 230 g. of trichloroacetic acid and 5 ml. of concentrated sulfuric acid first was added 7.5 g. (0.033 mole) of 11H-benzo[b]-fluoren-11-one (16) and then (portionwise, over a period of 70 min.) 2.8 g. (0.043 mole) of sodium azide. Gas was evolved from the black solution and a black tarry material precipitated. After 4 more hr. of heating and stirring, the hot reaction mixture was poured into a vigorously stirred mixture of 250 g. of ice and 250 ml. of water. A red, flocculent precipitate (which coagulated to a dark brown tar) resulted. The tar was separated, washed with water, and crystallized.

from ethanol, yield 7.05 g. (87%) of brown crystalline mixed amides, m.p. 255-267°. Sublimation at 250° and 0.3 mm. followed by recrystallization from dimethylformamide (2-3 g./100 ml.) gave 1.7 g. (21%) of benzo[j]phenanthridine-6(5H)-one (VI), m.p. 350-354°; obtained as fine, light red needles, m.p. 354-356°, on recrystallization from the same solvent.

Anal. Calcd. for $C_{17}H_{11}NO$: C, 83.24; H, 4.52; N, 5.71. Found: C, 83.05; H, 4.54; N, 5.90.

Concentration of the dimethylformamide mother liquid to ca. 1/3 of the original volume gave 1.85 g. (23%) of impure, isomeric benzo[b]phenanthridine-5(6H)-one (V), m.p. 278-280°; obtained as fine, yellow needles, m.p. 304.5-306°, on repeated recrystallization from the same solvent.

Anal. Found: C, 82.94; H, 4.74; N, 5.93.

Similar yields were obtained on runs using up to 33 g. of starting ketone.

Beckmann Rearrangement of II.

A stirred mixture of 6.6 g. of 11H-benzo[b]fluoren-11-one oxime (16) (m.p. 232-233°) and 240 g. of polyphosphoric acid was heated (over a period of 1.5 hr.) to 170-180°, at which temperature it was maintained for 3 hr. Dilution of the cold (ice-salt bath) resultant mixture with 80 ml. of water gave a brown precipitate which was separated, washed with water, dried, and refluxed with 500 ml. of ethanol for 30 min. The insoluble portion was sublimed and recrystallized in the aforementioned manner to give 0.88 g. (13%) of VI, m.p. >345°, and 0.64 g. (9%) of crude V, m.p. 278-282°.

11H-Benzo[b]fluoren-11-one Oxime Tosylate (III).

To a cold (0°) solution of 5 g. of 11H-benzo[b]fluoren-11-one oxime in 1 l. of absolute acetone was added 12.5 ml. of 8% aqueous sodium hydroxide solution and then 4.4 g. of *p*-toluenesulfonyl chloride. The precipitated sodium chloride was removed by filtration. Evaporation of the filtrate gave 8.1 g. of yellow crystals (m.p. 161-165°) which were recrystallized from ethanol and then from benzene to give a yellow powder, m.p. 202-203°.

Anal. Calcd. for $C_{24}H_{17}NO_3S$: C, 72.16; H, 4.29; N, 3.51; S, 8.03. Found: C, 72.52; H, 4.50; N, 3.62; S, 8.05.

6-Chlorobenzo[j]phenanthridine (XI).

A mixture of 1.7 g. of benzo[j]phenanthridine-6(5H)-one (m.p. 350-354°), 20 ml. of phosphorus oxychloride, and 0.5 ml. of dimethylaniline was stirred and refluxed for 4 hr. Removal of volatile components *in vacuo* left a residue which was washed with ice-cold water and dried, yield 1.6 g. (87%) of red crystals, m.p. 179.5-181.5°; obtained as bright yellow needles, m.p. 185-185.5°, on repeated recrystallization from ethanol; λ max (EtOH) 218 m μ (log ϵ , 4.59), 232 (4.50), 272s (4.76), 281 (4.80), 303 (3.93), 322 (3.77), 337 (3.87), 352 (3.77), 370 (3.45), 387 (3.41).

Anal. Calcd. for $C_{17}H_{10}NCl$: C, 77.42; H, 3.82; N, 5.31; Cl, 13.45. Found: C, 77.51; H, 3.97; N, 5.36; Cl, 13.38.

6-Ethoxybenzo[j]phenanthridine (VII).

A solution of 6.1 g. of preceding chloro compound (m.p. 179.5-183.5°) in ethanolic sodium ethoxide (prepared from 7.7 g. of sodium and 400 ml. of absolute ethanol) was refluxed for 12 hr. From the cooling solution was deposited 5.75 g. (91%) of crystals, m.p. 112-113°; converted to needles, m.p. 112.5-113°, on repeated recrystallization from ethanol; λ max (EtOH) 220 m μ (log ϵ , 4.61), 229s (4.51), 272 (4.88), 280s (4.63), 289 (4.46), 304 (3.69), 334 (3.78), 346s (3.71), 355 (3.72), 373 (3.59); n.m.r. absorptions at δ = 1.53 (triplet, methyl group, J = 7.5 c.p.s.), 4.71 (quartet, methylene group, J = 7.5 c.p.s.), 5.8-8.5 (complex, aromatic protons), and ca. 8.75 (overlapping singlets for protons on C₇ and C₁₂?) p.p.m.

Anal. Calcd. for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13; O, 2.86. Found: C, 83.54; H, 5.58; N, 5.24; O, 2.82.

5-Methoxybenzo[b]phenanthridine (VIII).

5-Chlorobenzo[b]phenanthridine (6.25 g., m.p. 111-115°) was prepared from benzo[b]phenanthridine-5(6H)-one (6.45 g., m.p. 278-284°) in the manner used for the chloro compound in the [j] series. Attempts to purify further the chloro derivative by recrystallization from 95% or from absolute ethanol led to solvolysis. A solution of the crude chloro compound in methanolic sodium methoxide (prepared from 10.4 g. of sodium and 600 ml. of absolute methanol) was refluxed for 12 hr., concentrated to 200 ml., diluted with 300 ml. of water, and extracted repeatedly with benzene. Evaporation of the dried benzene extract gave a viscous, dark brown tar which was chromatographed on Alcoa F-20 alumina using cyclohexane and benzene. The first fraction of effluent contained 2.1 g. of oily crystals which were triturated with methanol and recrystallized several times from ethanol to give fine needles, m.p. 87.5-89°.

Anal. Calcd. for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40; O, 1.18.

11.97. Found: C, 82.94; H, 4.85; N, 5.38; O, 1.73.

5,6-Dihydrobenzo[j]phenanthridine (X). (a) From VI.

To a warm (40-50°) suspension of 3.5 g. (0.014 mole) of benzo[j]phenanthridine-6(5H)-one in 1 l. of purified dioxane (17) in an atmosphere of nitrogen was added portionwise 1.2 g. (0.032 mole) of lithium aluminum hydride. As the reaction proceeded, the amide dissolved to give first an intense green solution and then an intense red one which was strongly fluorescent. The mixture was refluxed for 4 hr., cooled, and treated successively with 1 ml. of water, 1 ml. of 20% aqueous sodium hydroxide, and 1 ml. of water. The precipitate was separated and washed with hot dioxane. Combined dioxane solutions were dried (sodium sulfate) and distilled to leave a residue of 2.8 g. (85%) of product, m.p. 161.5-165.5°; converted to yellow leaflets, m.p. 178.5-180°, on repeated recrystallization from ethanol.

Anal. Calcd. for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.09; H, 5.82; N, 5.84.

(b) From 6-Chlorobenzo[j]phenanthridine (XI).

A solution of 1 g. of 6-chlorobenzo[j]phenanthridine in 250 ml. of absolute ethanol containing 1 g. of potassium hydroxide was agitated with ca. 1.2 g. of freshly prepared Raney nickel (18) at room temperature in hydrogen gas at 3 atm. pressure for 18 hr. The residue from filtration of the mixture and evaporation of the filtrate was crystallized from ethanol to give 359 mg. (41%) of bright yellow crystals, m.p. 160-162°, raised to 178.5-180° (undepressed on admixture with compound from method a) on recrystallization.

Benzo[j]phenanthridine (XIV). (a) By Dehydrogenation of X.

A stirred mixture of 3 g. of 5,6-dihydrobenzo[j]phenanthridine (m.p. 123-132°), 2.5 g. of 30% palladium-charcoal, and 250 ml. of decahydronaphthalene was refluxed and stirred for 48 hr. The catalyst was removed by filtration and washed with hot benzene. Distillation of the combined organic solvents *in vacuo* left 2 g. (67%) of yellow product, m.p. 130-133°; converted to bright yellow needles, m.p. 141.5-143°, on recrystallization from 50% ethanol and then from petroleum ether; n.m.r. absorptions at δ = 7.2-8.2 (complex, 7 protons), 8.27 (singlet; 1 proton, perhaps on C₇), 8.35-8.65 (multiplet, 1 proton), 8.75 (singlet; 1 proton, probably on C₁₂), 9.22 p.p.m. (singlet; 1 proton, on C₆).

Anal. Calcd. for $C_{17}H_{11}N$: C, 89.05; H, 4.84; N, 6.11. Found: C, 89.19; H, 4.90; N, 5.78.

(b) From the Chloro Derivative (XI).

Using method (a) for preparation of 5,6-dihydrobenzo[j]phenanthridine there resulted 1.65 g. of deep red residue from 1.8 g. of 6-chlorobenzo[j]phenanthridine and 0.95 g. of lithium aluminum hydride. A benzene solution of this residue was chromatographed on alumina to give 0.82 g. (52%) of XIV, m.p. 127-133°, identified after further purification by direct comparison with product from dehydrogenation.

(c) From Benzo[j]phenanthridine-7,12-dione (XV).

An intimate mixture of 0.91 g. of benzo[j]phenanthridine-7,12-dione (9), 0.91 g. of zinc dust (Mallinckrodt anal. reagent), 0.91 g. of sodium chloride, and 5 g. of anhydrous zinc chloride was heated at 310° for 30 min. with occasional stirring. The cooled mixture was treated with 10 ml. of 20% hydrochloric acid. The insoluble portion was washed with 10 ml. of 30% aqueous sodium hydroxide, dried, and sublimed at 210° and 0.5 mm. The bright yellow sublimate (0.13 g.) was recrystallized (with filtration of the solution) twice from petroleum ether (30-60°) to give colorless crystals, m.p. 142-143°, identical with product from (a) as based on mixture m.p. (141.5-143°), ultraviolet spectra in ethanol and in ethanolic hydrochloric acid, and n.m.r. spectrum.

N-Methylbenzo[j]phenanthridine-6(5H)-one.

A solution of 210 mg. of benzo[j]phenanthridine in 6 ml. of methyl iodide was refluxed for 1 hr. The orange residue from evaporation of solvent was warmed for 30 min. with a mixture of 10 ml. of dioxane, 10 ml. of water, 0.3 g. of sodium hydroxide, and 0.46 g. of potassium ferricyanide. The cooled mixture was diluted with 30 ml. of water and filtered to give 207 mg. (87%) of precipitate, m.p. 169-170.5°, converted to cream-colored, fine needles on recrystallization first from ethanol and then from petroleum ether (30-60°) m.p. 180-181°. [Brown, Hey, and Rees (10) reported the formation of colorless needles, m.p. 174-175°, from similar treatment of their "2,3-benzophenanthridine" .]

Anal. Calcd. for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.60; H, 5.14; N, 5.45.

5,6-Dihydrobenzo[b]phenanthridine (IX).

Reduction of 3 g. of benzo[b]phenanthridine-5(6H)-one (m.p. 282-

291^o) with lithium aluminum hydride according to the preceding method for the isomeric benzophenanthridone gave 2.8 g. (99%) of crude product; converted to yellow prisms, m.p. 178-179.5^o (depressed 18^o on admixture with analytically pure X), on recrystallization from ethanol.

Anal. Calcd. for C₁₇H₁₃N: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.17; H, 5.88; N, 6.13.

3-Phenyl-2-naphthoic Acid (XII).

Alkali fusion of 11H-benzo[b]fluoren-11-one (I) was conducted according to the method of Baddar *et al.* (12) except that the product from the acetic acid mother liquor was recrystallized twice from glacial acetic acid and then several times from petroleum ether (60-90^o) to give white crystals of XII, m.p. 145-147^o.

When 102 mg. of this product was allowed to stand with 10 ml. of concentrated sulfuric acid for 2 hr. at room temperature and then poured on ice there resulted 66 mg. of bright yellow crystals, m.p. 149.5-150.5^o (after one recrystallization from ethanol), undepressed on admixture with I. Its infrared spectrum was identical with that of I.

Benzo[b]phenanthridine (XIII). (a) By Dehydrogenation of IX.

Dehydrogenation of 5,6-dihydrobenzo[b]phenanthridine by means of palladium-charcoal was conducted as for the previously described isomer, except that the mixture was refluxed for only 12 hr., 88% yield of XIII, m.p. 175-179^o; converted to yellow-tan needles, m.p. 200.5-202.5^o, on repeated recrystallization from ethanol; n.m.r. absorptions at $\delta = 7.1-8.65$ (complex, 8 protons) 8.70 (singlet; 1 proton, probably on C₇ or C₁₂), 8.95 (singlet; 1 proton, probably on C₁₂ or C₇), 9.24 p.p.m. (broad peak; 1 proton, on C₆).

Anal. Calcd. for C₁₇H₁₁N: C, 89.05; H, 4.84; N, 6.11. Found: C, 88.84; H, 5.08; N, 6.22.

(b) From XII.

Without isolating intermediates but following the reported procedure of Brown, Hey, and Rees (10) (see Scheme I) 1 g. of 3-phenyl-2-naphthoic acid (XII) was converted to a benzophenanthridine, yield 70 mg. of crude product (8% overall), m.p. 162-174^o. Two recrystallizations from petroleum ether (30-60^o) accompanied by removal by filtration of some insoluble material gave XIII, m.p. 199-200.5^o. A mixture melting point with product (m.p. 199-200.5^o) from (a) showed no depression. Products from (a) and (b) showed identical ultraviolet spectra when measured in ethanol or in ethanolic hydrochloric acid.

2,2'-Binaphthyl-3,3'-dicarboxylic Acid.

3-Amino-2-naphthoic acid (m.p. 214-215.5^o, dec., Aldrich Chemical Co., Milwaukee, Wis., reported m.p. 214^o) was converted to the ethyl ester (m.p. 114-115.5^o, reported 115-115.5^o) according to the procedure of Möhlau (19) and then to the diazonium borofluoride (m.p. 147-149^o, reported m.p. 140-142^o) according to the procedure of Brown, Hey, and Rees (10). Decomposition of 10 g. of the borofluoride and hydrolysis of the resultant product (10) gave 6.1 g. of acidic product, m.p. 98-101^o, which was fractionated into nearly equal quantities of cyclohexane-soluble and cyclohexane-insoluble (m.p. 278-280^o) portions. Repetitive recrystallization from petroleum ether of the cyclohexane-soluble portion gave a product of constant m.p. 136-146^o, not further investigated. Three recrystallizations from ether of the cyclohexane-insoluble portion and drying at 0.1 mm. and 22^o for 20 hr. gave white crystals of 2,2'-binaphthyl-3,3'-dicarboxylic acid hemietherate, m.p. 292-293^o (lit. (20) m.p. 298-299^o, as colorless needles from alcohol).

Anal. Calcd. for C₂₂H₁₄O₄·1/2C₄H₁₀O: C, 75.97; H, 5.05; neut. equiv., 189.7. Found: C, 75.81; H, 5.05; neut. equiv., 185.

The analytical sample was dried further *in vacuo* at 100^o for a few hours to expel the solvent of crystallization.

Anal. Calcd. for C₂₂H₁₄O₄: C, 77.18; H, 4.12. Found: C, 77.60; H, 4.26.

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