The recorded m. p.[16] for methyl lithocholate are 125–126, 125–127 and 130°. By acetylation with acetic anhydride in pyridine and recrystallization from methanol the methyl 3α-acetoxycholanate was obtained, m. p. 129–130°. The recorded m. p. are 128–130 and 129–131°.[19]

Saponification of Ethyl 3α-Hydroxy-7,12-diketocholanate Diethylenemercaptol.—One gram of the mercaptol was saponified in the manner described for dehydrocholic acid ethyl ester triethylenemercaptol. After recrystallization from methanol 3α-hydroxy-7,12-diketocholanic acid diethylenemercaptol melted at 230–231° (Kofler block); yield 0.89 g. (94%).

Anal. Calcd. for $C_{28}H_{44}O_3S_4$: S, 23.04. Found: S, 23.07; rotation for 21.0 mg. was $\alpha^{27}D$ +0.74 ± 0.03°; $[\alpha]^{27}D$ +69.6 ± 3°.

Estrone Acetate Ethylenemercaptol.—28.5 mg. of estrone acetate and 100 mg. of ethanedithiol were treated in the manner described for dehydrocholic acid ethyl ester. After recrystallization from acetone the mercaptol melted at 141.5–142°, yield 35 mg. (94%).

Anal. Calcd. for $C_{22}H_{18}O_2S_2$: S, 16.44. Found: S, 16.14; rotation for 16.9 mg. was $\alpha^{27}D$ +0.17 ± 0.02°; $[\alpha]^{27}D$ +20.2 ± 2°.

Summary

1. The following compounds have been prepared and characterized: 4-cholesten-3-one dibenzylmercaptol, 4-cholesten-3-one ethylenemercaptol, dehydrocholic acid 3-diphenylmercaptol, dehydrocholic acid ethyl ester 3-diethylmercaptol, dehydrocholic acid 3,7,12-triethylenemercaptol and its ethyl ester, 3α-hydroxy-7,12-diketocholanic acid and its ethyl ester, estrone acetate 17-ethylenemercaptol.

2. The constitution has been proved by hydrogenolitic desulfuration with Raney nickel.

3. Ethanedithiol condenses with the keto group at the carbon atoms 3, 7, 12 and 17 of the steroid skeleton, while monothiols only react with that at the carbon atom 3.

4. The desulfuration of mercaptols represents a convenient method for preparative reduction of ketosteroids.

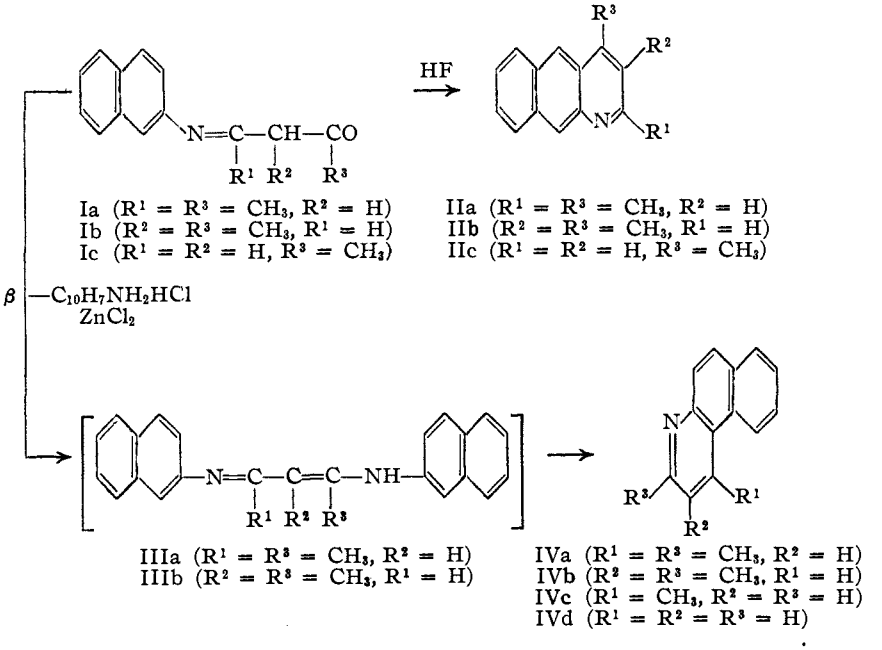
SÃO PAULO, BRASIL RECEIVED JUNE 15, 1946

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Cyclization Studies in the Benzoquinoline and Naphthoquinoline Series. II

BY WILLIAM S. JOHNSON, EUGENE WOROCH AND FREDERICK J. MATHEWS[1]

In the first communication of this series[2] it was shown that 4-(2-naphthylimino)-pentanone-2, Ia, is cyclized by hydrogen fluoride in almost quantitative yield to 2,4-dimethylbenzo[*g*]quinoline, IIa. This exclusive preference for linear cyclization into the 3- rather than into the 1-position—even though the latter was unhindered—not only was quite unexpected[3] but was, to our knowlege, without precedent. In the present work we are reporting the results of some further studies of this type of cyclization as well as some investigations on directing the cyclization into the 1-position.



Ia (R^1 = R^3 = CH_3, R^2 = H)
Ib (R^2 = R^3 = CH_3, R^1 = H)
Ic (R^1 = R^2 = H, R^3 = CH_3)

IIa (R^1 = R^3 = CH_3, R^2 = H)
IIb (R^2 = R^3 = CH_3, R^1 = H)
IIc (R^1 = R^2 = H, R^3 = CH_3)

IIIa (R^1 = R^3 = CH_3, R^2 = H)
IIIb (R^2 = R^3 = CH_3, R^1 = H)

IVa (R^1 = R^3 = CH_3, R^2 = H)
IVb (R^2 = R^3 = CH_3, R^1 = H)
IVc (R^1 = CH_3, R^2 = R^3 = H)
IVd (R^1 = R^2 = R^3 = H)

Angular cyclization of Ia has now been realized to give the previously known[4] 1,3-dimethylbenzo[*f*]quinoline, IVa. The method of ring closure involved heating the anil Ia in alcoholic solution with β-naphthylamine hydrochloride and zinc chloride according to the procedure of Petrow.[5] Since the reaction appears to involve the anilino anil IIIa as an intermediate it may be considered a modification of König's quinoline synthesis.[6] This angular cyclization of Ia suggests that the ring closure of 3-(2-naphthyl

(1) Present address: Department of Chemistry, Kent State University, Kent, Ohio.

(2) Johnson and Mathews, THIS JOURNAL, 66, 210 (1944).

(3) See footnote 7 of ref. 2.

(4) Reed, *J. prakt. Chem.*, [2] 35, 298 (1887).

(5) Petrow, *J. Chem. Soc.*, 693 (1942).

(6) König, *Ber.*, 56, 1853 (1923).

iminomethyl)-butanone-2, Ib, by this method gave, as presumed by Petrow, the product (IVb) of angular cyclization. Confirmatory evidence for the structure IVb is now furnished by the ultraviolet absorption spectrum which is characteristic of benzo[*f*]quinolines (Fig. 1).

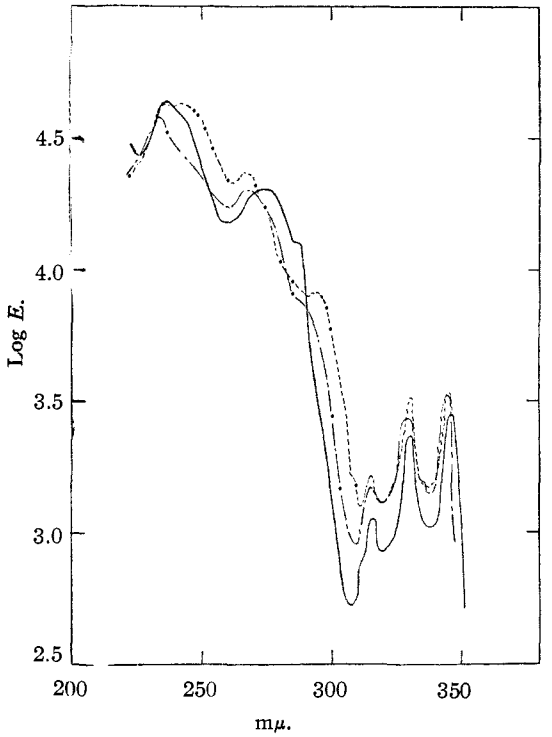


Fig. 1.— ——2,3-Dimethylbenzo[*f*]quinoline IVb; - - - 1,3-dimethylbenzo[*f*]quinoline IVa; — - — - — benzo[*f*]-quinoline IVd.

The anil Ib proved to be less susceptible than Ia to cyclization with hydrogen fluoride; however, by carrying out the reaction under pressure at elevated temperature it was found possible to effect cyclization in over 80% yield. The product was different from that obtained by the zinc chloride-catalyzed method; and that it was 3,4-dimethylbenzo[g]quinoline, IIb, formed by linear cyclization, follows from its characteristic absorption spectrum (Fig. 2) and intense yellow color of its hydrochloride. Further evidence for the generality of linear cyclization of anils like Ia and Ib with hydrogen fluoride was supplied by a study of the ring closure of 1-(2-naphthylimino)-butanone-3, Ic. This anil also was resistant to cyclization and, in addition, the product was sensitive to the acid reagent so that the conditions for the reaction were critical. The best yield (43%) of material of good purity was obtained after six hours at 100°. That the product was the linear benzolepidine IIc was shown by the characteristic absorption spectrum (Fig. 2) and color of its hydrochloride. The melting point, 84.5–85°, moreover, is

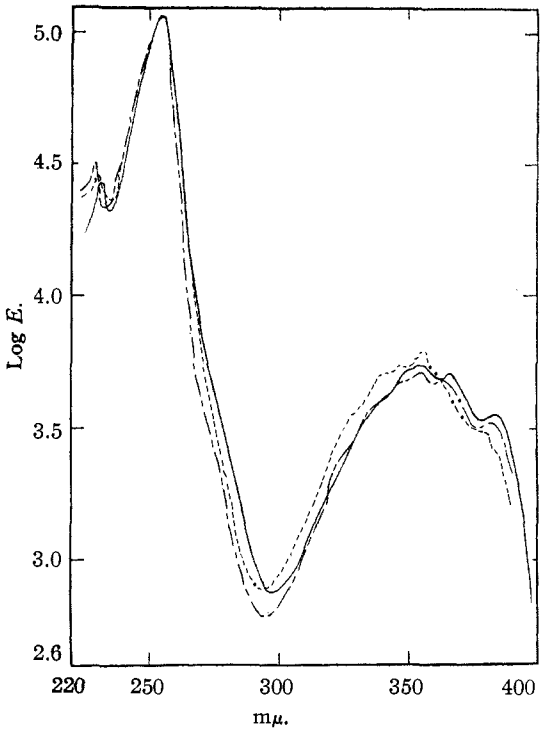
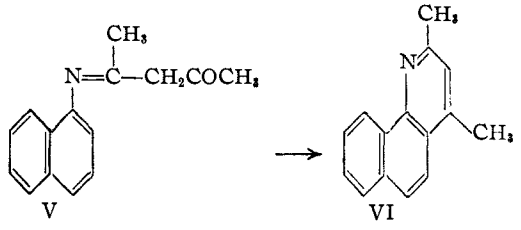


Fig. 2.— - - - - 2,4-Dimethylbenzo[g]quinoline IIa —— 3,4-dimethylbenzo[g]quinoline IIb; — - — - — 4-methylbenzo[g]quinoline IIc.

not in agreement with that (94–95°) reported for the angular isomer VIc.[7]

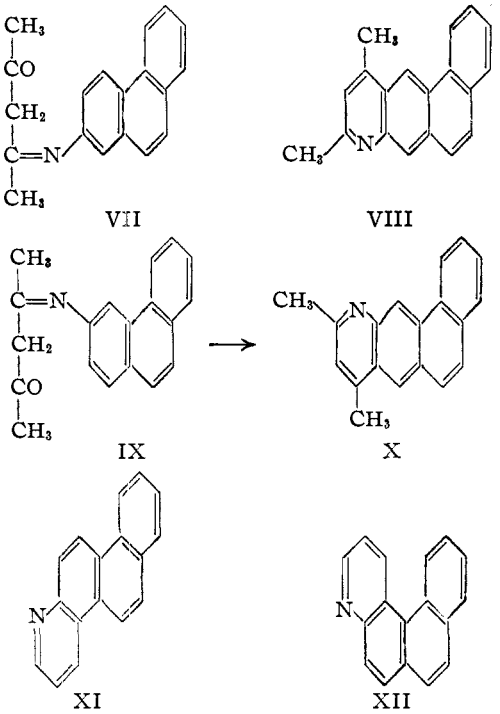


The abnormal preference for cyclization into the 3- rather than the 1-position of the naphthalene nucleus observed with the anils Ia, Ib and Ic and hydrogen fluoride, suggests that the anil side-chain (under the influence of the acid catalyst) acts as a deactivating group. Since the 1-position of the naphthalene nucleus is more affected than the 3-position by a substituent in the 2-position—presumably due to the greater proportion of double bond character between carbons 1 and 2 than between 2 and 3[8]—it would be expected that a deactivating group at 2- might render the 3-position more reactive than the 1-position toward substitution. Some independent evidence in support of the deactivating effect of the anil side-chain is afforded by a comparison of the behavior of the isomeric anils Ia and V which differ only in the point

(7) Kaslow and Sommer, THIS JOURNAL, **68**, 644 (1946).

(8) Fieser, Gilman's "Organic Chemistry," vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 117; Pauling, *ibid.*, Vol. II, p. 1943.

of attachment of the side-chain. The former is cyclized practically quantitatively with hydrogen fluoride at room temperature while the latter is not cyclized at all under these conditions, but requires more drastic treatment. Since both cyclizations involve substitution at a β-position of the naphthalene nucleus it would seem reasonable to attribute this difference in reactivity to a deactivating effect of the anil side-chain. The fact that the Skraup and the König quinoline syntheses give angular cyclization with β-naphthylamines may be attributed to the likelihood that intermediate anilino anils like IIa are involved. As suggested by Sidgwick[9] this affords the opportunity for cyclization either into a nucleus substituted by an imino group or into one substituted by an amino group. Since the latter may have an activating influence, the ring closes not into the original nucleus, but into the activated 1-position of the second nucleus, thus explaining the apparent reversal of the position of the substituents on the side-chain.



On the basis of the above considerations it would be expected that the anils VII and IX would undergo linear cyclization with hydrogen fluoride, because of the apparent lack of double bond character between carbons 2 and 3 of the phenanthrene nucleus.[8,10] The anils VII and IX were formed easily in 90 and 89% yields, respectively, from 2- and 3-phenanthrylamine and acetylacetone. Treatment with hydrogen fluoride at room temperature effected cyclization in 94 and 92% yields. The absorption spectra of the two products were found to be almost identical, and resembled closely the spectrum of 1,2-benzanthracene (Fig. 3). The hydrochlorides of the

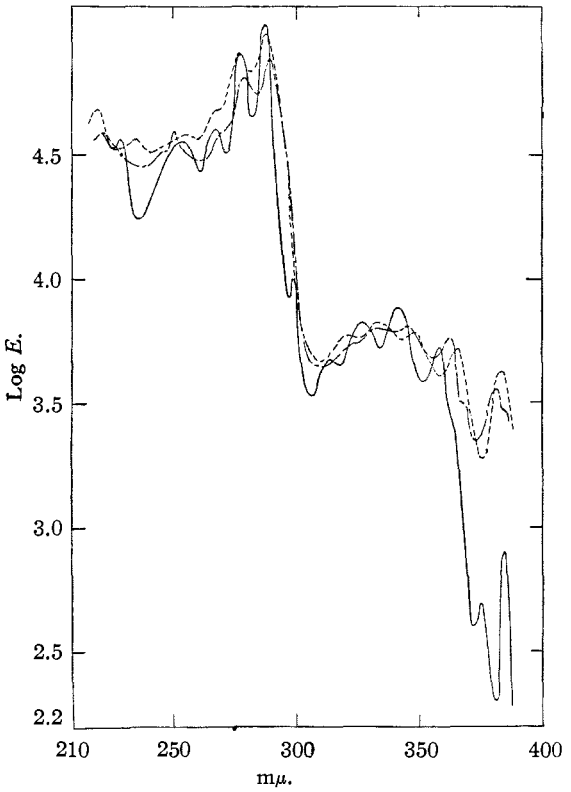


Fig. 3.— —— 1,2-Benzanthracene; - - - - 8,10-dimethylnaphtho[2,1-*g*]quinoline X; — — — — 9,11-dimethylnaphtho[1,2-*g*]quinoline VIII.

bases, moreover, exhibited the intense yellow color characteristic of the linear products.[2] Since the Skraup reaction with 2- and 3-phenanthrylamine has been shown to give exclusively the angular naphthoquinolines XI and XII,[11] the absorption spectra (Figs. 4 and 5) of these bases were obtained for comparison and were found to be quite different from those of the bases obtained by the cyclization of the anils VII and IX. In view of all considerations it therefore seems reasonably certain that the latter bases have the linear structure VIII and X. It is interesting to compare the absorption spectra of naphtho[2,1-*f*]quinoline (XI) with that of chrysene (Fig. 4), and of naphtho[1,2-*f*]quinoline (XII) with that of 3,4-benzphenanthrene[12] (Fig. 5).

The two 1,2-benzanthracene analogs VIII and X are being tested for carcinogenic properties by

(9) Taylor and Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1942, p. 545.

(10) This situation is not entirely analogous to that already discussed in the naphthalene series, because there seems to be less resistance to linear cyclization into the phenanthrene than into the naphthalene nucleus. For example, γ-2-phenanthrylbutyric acid can be cyclized in either direction: Fieser and Johnson, THIS JOURNAL, **61**, 1647 (1939). It is interesting to note that hydrogen fluoride effects linear ring closure of this acid.

(11) Mosettig and Krueger, *J. Org. Chem.*, **3**, 317 (1938).

(12) Mayneord and Roe, *Proc. Roy. Soc.* (London), **158A**, 634 (1937).

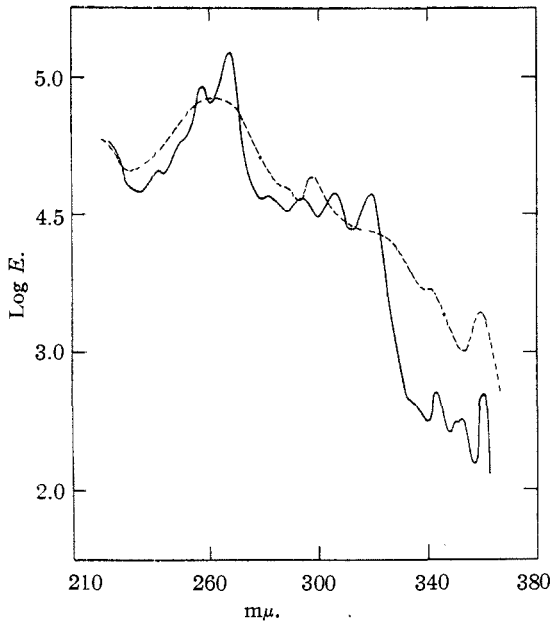


Fig. 4.— - - - - Naphtho[2,1-*f*]quinoline XI; — chrysene

Dr. Harold M. Rusch of the McArdle Memorial Laboratory, Madison, Wisconsin.

Acknowledgment.—The authors wish to thank Dr. R. Norman Jones for furnishing the absorption curves of 1,2-benzanthracene and of chrysene appearing in Figs. 3 and 4.

Experimental[13]

Cyclization of 4-(2-Naphthylimino)-pentanone-2 (Ia) by the Zinc Chloride-Catalyzed Method.—The method used was a modification of the general procedure of Petrow.[5] A solution of the anil Ia[2] (4.5 g.), 3.6 g. of β-naphthylamine hydrochloride and 2.7 g. of zinc chloride in 40 cc. of ethanol was boiled under reflux for twelve hours. The alcohol was removed in a current of air, and 150 cc. of 3% hydrochloric acid added to the pasty mass. After heating on the steam-bath for one hour (to hydrolyze any unreacted anil) the solution was made alkaline with ammonium hydroxide and extracted with ether. The residue obtained on evaporation of the ether was heated at 100° for one hour with 10 cc. of acetic anhydride and 0.5 g. of sodium acetate in order to acetylate any β-naphthylamine. The excess acetic anhydride was removed, and the residue was taken up in ether and washed with dilute hydrochloric acid. The acid solutions which contained the tertiary amine were made alkaline with ammonium hydroxide and extracted with ether. Evaporation of the dried ether solution afforded 2.0 g. of yellow crystals, m. p. 95–120° with softening at 82°. Crystallization (Norit) from dilute alcohol gave 1.35 g. (33% yield) of 1,3-dimethylbenzo[*f*]quinoline (IVa), m. p. 125.5–127.5°. A sample after evaporative distillation at reduced pressure (high vacuum pump) was obtained as colorless crystals, m. p. 126–127.5°, undepressed on admixture with a specimen of IVa (m. p. 125–127°) prepared by the Doebner-Miller reaction.[4]

3-(2-Naphthyliminomethyl)-butanone-2 (Ib) has been prepared in unspecified yield by Petrow using equivalent amounts of formyl ketone and amine. In the present work 17.83 g. of dry β-naphthylamine hydrochloride and 13.03 g. of sodioformylbutanone-2—as isolated directly from the sodium methoxide-catalyzed condensation of ethyl methyl ketone with ethyl formate (see the preparation of sodioformylacetone below)—were boiled under reflux for ten minutes with 150 cc. of methanol. Upon addition of 200 cc. of water the precipitated sodium chloride dissolved, and the crude anil Ib separated as a yellow solid; yield 19.7 g. (88%); m. p. 140–145°. Recrystallization from ethanol gave 11.7 g. (52% yield) of yellow needles, m. p. 166–167.5°. A sample evaporatively distilled and twice recrystallized from ethanol was obtained as pale yellow needles melting at 171–172° (reported,[5] 171–172° cor.).

(13) All melting points are corrected unless otherwise specified.

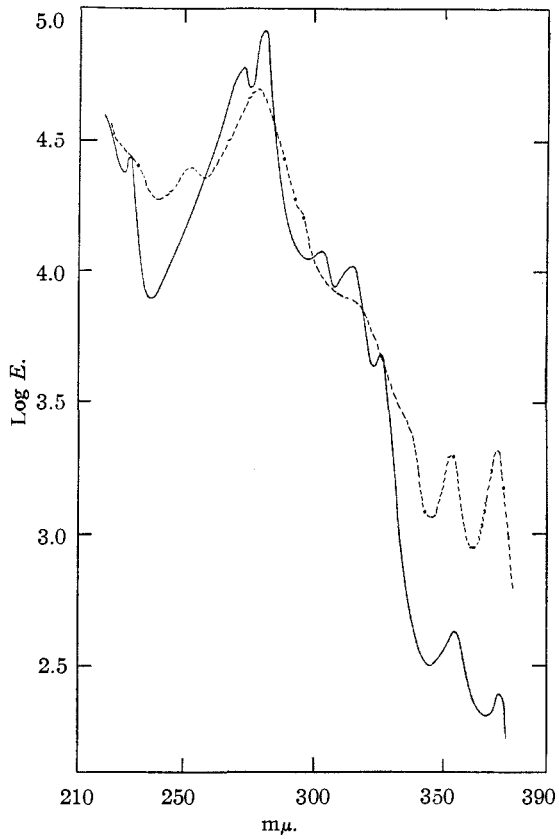


Fig. 5.— —— 3,4-Benzphenanthrene[12]; - - - - naphtho-[1,2-*f*]-quinoline XII.

Cyclization of 3-(2-Naphthyliminomethyl)-butanone-2 (Ib). (*a*) *By the Zinc Chloride-Catalyzed Method.*—The procedure described above for the cyclization of Ia was employed. Thus from 2.0 g. of the anil Ib, 1.59 g. of β-naphthylamine hydrochloride and 1.2 g. of zinc chloride in 40 cc. of ethanol, there was obtained 1.29 g. (70% yield) of crude 2,3-dimethylbenzo[*f*]quinoline (IVb), m. p. about 110–120°. Crystallization from acetone gave 0.90 g. (49% yield) of colorless prisms, m. p. 122–125°. Recrystallization twice from acetone-petroleum ether (b. p. 60–68°) raised the m. p. to 124–125° (reported,[5] 124–125°).

(*b*) *With Hydrogen Fluoride.*—A copper vessel was charged with 2.00 g. of the anil Ib (m. p. 162–166°) and about 50 cc. of anhydrous hydrogen fluoride. The copper vessel was then enclosed in a steel bomb of the type used for high pressure hydrogenation. After heating for nineteen hours in a steam-heated oil-bath, the bomb was chilled (ice-salt bath), opened, and the hydrogen fluoride removed in a current of air. The residue was treated with a saturated solution of sodium carbonate, and extracted with chloroform. The residue obtained on evaporation of the chloroform was crystallized from ligroin (b. p. 90–100°) giving 1.48 g. (80% yield) of yellow needles, m. p. 137.5–139.5°. An additional 0.12 g., m. p. 127.5–135°, and 0.10 g., m. p. 125–132°, were isolated

from the mother liquors. Analytically pure **3,4-dimethylbenzo[g]quinoline** (IIb) was obtained by repeated recrystallization from ligroin (b. p. 90–100°); yellow needles, m. p. 139.5–140° with softening at 137°. On dissolving in dilute hydrochloric acid an intense yellow color developed.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32. Found: C, 86.51; H, 5.97.

The **picrate** crystallized from nitromethane in the form of small, yellow needles, melting with decomposition at 270–271° (uncor.) in an evacuated tube introduced at 255°.

Anal. Calcd. for $C_{21}H_{16}O_7N_4$: C, 57.80; H, 3.70. Found: C, 57.48; H, 3.99.

Sodioformylacetone.—The condensation of ethyl formate with acetone in the presence of sodium ethoxide is reported to give this substance in 46% yield.[14] We have found that the reaction is improved by the use of sodium methoxide in place of ethoxide, and a procedure has been developed whereby the apparent yield of sodioformylacetone is 91%.

A mixture of 3.27 g. (0.061 mole) of powdered alcohol-free sodium methoxide,[15] 4.56 g. (0.061 mole) of ethyl formate, 3.58 g. (0.062 mole) of dry acetone and 150 cc. of dry ether was placed in a flask which was evacuated and filled with nitrogen. After shaking for ten minutes the straw-colored mixture was allowed to stand for fifteen hours at room temperature. The powdery precipitate of sodioformylacetone was separated by suction filtration, washed with ether and dried over potassium hydroxide in a vacuum desiccator; yield 6.03 g. It can be stored easily in a tightly stoppered bottle. When benzene was used in place of ether as a solvent, the mixture became gelatinous and was difficult to filter.

1-(2-Naphthylimino)-butanone-3 (Ic).—A mixture of 12.96 g. of sodioformylacetone and 17.16 g. of β-naphthylamine hydrochloride was heated under reflux in 400 cc. of methanol for fifteen minutes. The dark solution was treated with Norit and filtered. From the filtrate there was obtained by concentration and crystallization a total of 14.03 g. (70% yield) of light tan needles, m. p. 134–140°. Recrystallization from ethyl acetate–ligroin (b. p. 90–100°) gave 8.54 g. (43% yield) of yellow needles, m. p. 138–139°. A sample was sublimed at reduced pressure and recrystallized from ethyl acetate–petroleum ether (b. p. 90–100°), giving pale-yellow plates, m. p. 138.5–139°.

Anal. Calcd. for $C_{14}H_{13}ON$: C, 79.59; H, 6.20. Found: C, 79.20; H, 6.21.

4-Methylbenzo[g]quinoline (6,7-Benzolepidine) (IIc). (*a*) *From Pure Anil Ic.*—The best of eight experiments in which the cyclization time and temperature were varied is reported below.

Two grams of 1-(2-naphthylimino)-butanone-3 (m. p. 137.5–139°) was treated in a bomb with about 50 cc. of hydrogen fluoride as described above for the anil Ib, except that the heating period was shortened to six hours. After the chloroform extraction, the solvent was removed leaving a brown oily residue. It was possible to isolate the cyclized material either by evaporative distillation at reduced pressure followed by recrystallization from benzene–ligroin or by acetylation followed by extraction with dilute hydrochloric aicd (as described above under the zinc chloride-catalyzed cyclizations). Chromatographic adsorption, however, proved to be the best method of effecting a good separation of pure material. The above residue was dissolved in benzene, and a portion of the solvent was distilled off in order to remove traces of water and chloroform. The dark solution was then passed through a 1 by 30 cm. column of activated alumina (−80 mesh). Development of the chromatogram with benzene gave seven distinct fractions from which the desired one was selected by extrusion of the column and streaking the outside with a fine camel's hair brush dipped in 5% hydrochloric acid. A brilliant yellow color clearly indicated the fraction containing the linear base. Elution with benzene–methanol gave a yellow solution which on concentration afforded 0.65 g. of bright yellow needles, m. p. 84–85° and, on further concentration, an additional 0.13 g. of material melting at 81–83° was obtained, making the total yield 43%. A sample twice recrystallized from petroleum ether (b. p. 60–68°) was obtained as yellow needles, m. p. 84.5–85°, which gave the characteristic intense yellow color with dilute hydrochloric acid.

Anal. Calcd. for $C_{14}H_{11}N$: C, 87.01; H, 5.74. Found: C, 86.79; H, 5.80.

The **picrate** crystallized from nitromethane as small orange-yellow needles, melting with decomposition at 264–266° (uncor.) in an evacuated tube when introduced at 250°.

Anal. Calcd. for $C_{20}H_{14}O_7N_4$: C, 56.87; H, 3.34. Found: C, 56.50; H, 3.23.

Experiments in which the cyclization time was increased appreciably afforded crude products which were quite tarry and from which the pure base was not isolated in good yield.

(*b*) *From Crude Anil Ic.*—A mixture of 10.8 g. of sodioformylacetone and 13.4 g. of β-naphthylamine hydrochloride was heated for fifteen minutes with 250 cc. of methanol, and the mixture was poured over 200 g. of ice. The crude anil which separated amounted to 14.8 g. (94% yield), m. p. 124–133°. Two grams of this material was cyclized according to the procedure described above; yield 0.34 g. (19%) of yellow needles, m. p. 83–84.5°. A cyclization was performed in the same way except that the bomb was allowed to stand at room temperature for five weeks. The yield of material melting at 81–83° was 0.45 g. (25%).

Cyclization of 4-(1-Naphthylimino)-pentanone-2 with Hydrogen Fluoride.—Several attempts to effect cyclization under the conditions used successfully with the 2-naphthylimino isomer,[2] gave only α-naphthylamine, produced by hydrolysis of the anil.

A 1.00-g. sample of the anil was treated with about 50 cc. of hydrogen fluoride, and heated in a bomb at 100° for one hour. The product was isolated in the usual way (see procedures above), and was heated for one hour with 10 cc. of acetic anhydride. The hydrochloric acid-soluble material from this treatment amounted to 0.52 g. of dark brown oily solid. Crystallization from 60–80° ligroin (Norit) gave 0.12 g. of almost colorless needles of 2,4-dimethylbenzo[*h*]quinoline, m. p. 51–52°; not depressed on admixture with a specimen prepared by sulfuric acid cyclization (m. p. 50.5–51°).[2] An additional 0.29 g. of the base, m. p. 47–49°, was obtained from the mother liquors by evaporative distillation at 120° (0.7 mm.), making the total yield 44%.

The **2- and 3-phenanthrylamines** were prepared by the Beckmann rearrangement of the oximes of 2- and 3-acetylphenanthrene.[16] The acetylation of phenanthrene proceeded as described by Mosettig and van de Kamp.[17] It was found important to use phenanthrene of good purity[18] and not to decrease the volume of nitrobenzene appreciably. The rearrangement of the oximes was carried out according to the procedure of Bachmann and Boatner.[16a] The yield of 2-phenanthrylamine from oxime melting at 194–198.5° was 78%. When 3-acetylphenanthrene was treated in ethanol with hydroxylamine hydrochloride and pyridine, apparently an unfavorable mixture of stereoisomeric oximes was produced, for the Beckmann rearrangement gave only a 36% yield of 3-phenanthrylamine.

4-(2-Phenanthrylimino)-pentanone-2 (VII).—A mixture of 1.00 g. of 2-phenanthrylamine (m. p. 84–85°),

(14) Claisen and Stylos, *Ber.*, **21**, 1144 (1888).

(15) Prepared by heating at 200° under reduced pressure (high vacuum pump).

(16) (a) Bachmann and Boatner, THIS JOURNAL, **58**, 2097 (1936); (b) Mosettig and Krueger, *J. Org. Chem.*, **3**, 317 (1938).

(17) Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

(18) Technical phenanthrene was purified according to Bachmann, *ibid.*, **57**, 555 (1935).

0.80 g. of acetylacetone and 2 g. of powdered Drierite was heated on the steam-bath for three to four hours. Elution with ether followed by crystallization from benzene–petroleum ether (b. p. 40–60°) gave 1.11 g. of pale orange needles, m. p. 118–120°. An additional 0.18 g. of material, m. p. 117–119°, was obtained from the mother liquor, making the total yield 90%. A sample purified for analysis by repeated recrystallization from the same solvent pair was obtained as yellow plates, m. p. 120.5–121°.

Anal. Calcd. for $C_{19}H_{17}ON$: C, 82.88; H, 6.22. Found: C, 82.82; H, 6.41.

4-(3-Phenanthrylimino)-pentanone-2 (IX) was prepared from 3-phenanthrylamine (m. p. 82–84°) exactly as described above except that double quantities were used. The first crop of product amounted to 2.46 g. of yellow prisms, m. p. 123–124°; the second crop, 0.09 g., m. p. 120–122°. The total yield thus was 2.55 g. or 89%. The analytical sample was obtained as pale yellow prisms, m. p. 124–125°.

Anal. Calcd. for $C_{19}H_{17}ON$: C, 82.88; H, 6.22. Found: C, 82.82; H, 6.00.

9,11-Dimethylnaphtho[1,2-*g*]quinoline (VIII).—To 1.00 g. of the anil VII (m. p. 118–120°) in a platinum can was added about 50 cc. of anhydrous hydrogen fluoride. After standing overnight at room temperature the reagent had largely evaporated, and the residue was neutralized with 10% sodium carbonate solution. The base was extracted with benzene, and after drying the benzene solution was concentrated. On cooling 0.78 g. of yellow prisms separated, m. p. 210–210.5°. An additional 0.10 g., m. p. 209–210°, was obtained by further concentrating the mother liquor, making the total yield 94%. A sample purified by repeated recrystallization from benzene was obtained as pale yellow needles, m. p. 211–212°.

Anal. Calcd. for $C_{19}H_{15}N$: C, 88.68; H, 5.88. Found: C, 89.08; H, 5.87.

The **picrate** crystallized from nitromethane as small, yellow needles, melting with decomposition at 288–289° (uncor.) in an evacuated tube introduced at 275°.

Anal. Calcd. for $C_{25}H_{18}O_7N_4$: C, 61.73; H, 3.73. Found: C, 62.13; H, 3.82.

8,10-Dimethylnaphtho[2,1-*g*]quinoline (X) was prepared from the anil IX (m. p. 123–124°) exactly as described in the preceding experiment. The first crop of product amounted to 0.55 g. of small yellow needles, m. p. 134–135°; the second crop, 0.31 g., m. p. 133–135°. The analytical sample was obtained as small, yellow needles, m. p. 135–136°.

Anal. Calcd. for $C_{19}H_{15}N$: C, 88.68; H, 5.88. Found: C, 88.57; H, 5.90.

The **picrate** crystallized from nitromethane in the form of small, yellow needles, melting with decomposition at 305–307° (uncor.) in an evacuated tube introduced at 290°.

Anal. Calcd. for $C_{25}H_{18}O_7N_4$: C, 61.73; H, 3.73. Found: C, 61.77; H, 3.58.

Both of the above naphthoquinolines VIII and X exhibited a blue fluorescence in dilute ethanol solution, and gave an intense yellow color with dilute hydrochloric acid.

The **absorption spectra** were determined on a Beckman ultraviolet spectrophotometer, and optically void ethanol was employed as the solvent. The analytical samples described in the present and in a previous paper were used. Naphtho[2,1-*f*]quinoline (XI) and naphtho[1,2-*f*]quinoline (XII) were prepared by the procedure of Mosettig and Krueger.[11] The former was purified by recrystallization from toluene; colorless leaflets; m. p. 229–230° (reported,[11] 226–227°). XII was purified by chromatographic adsorption on alumina followed by recrystallization from benzene–petroleum ether (b. p. 40–60°); yellow needles; m. p. 106–107° (reported,[11] 106–107°).

The principal absorption maxima are given below. The wave lengths are in ångström units, and the intensity (log *E*) is given in parentheses after each wave length.

1,3-Dimethylbenzo[*f*]quinoline (IVa.).—2355 (4.63), 2410 (4.63), 2660 (4.37), 3935 (3.91), 3150 (3.22), 3300 (3.51), 3450 (3.53). **Benzo[*f*]quinoline.**—2335 (4.58), 2670 (4.30), 3150 (3.17), 3290 (3.43), 3440 (3.53). **2,3-Dimethylbenzo[*f*]quinoline** (IVb).—2355 (4.64), 2740 (4.31), 3160 (3.05), 3300 (3.37), 3460 (3.44). **2,4-Dimethylbenzo[*g*]quinoline** (IIa).—2295 (4.45), 2545 (5.07), 3555 (3.79). **4-Methylbenzo[*g*]quinoline** (IIc).—2280 (4.49), 2535 (5.07), 3550 (3.72), 3630 (3.69), 3820 (3.52). **3,4-Dimethylbenzo[*g*]quinoline** (IIb).—2310 (4.43), 2545 (5.07), 3555 (3.74), 3655 (3.72), 3835 (3.55). **8,10-Dimethylnaphtho[2,1-*g*]quinoline** (X).—2195 (4.68), 2775 (4.91), 2885 (4.98), 3330 (3.82), 3480 (3.78), 3660 (3.72), 3845 (3.63). **9,11-Dimethylnaphtho[1,2-*g*]quinoline** (VIII).—2220 (4.58), 2505 (4.59), 2790 (4.81), 2890 (4.88), 3325 (3.80), 3455 (3.81), 3625 (3.76), 3820 (3.56). **Naphtho[1,2-*f*]quinoline** (XII) 2525 (4.39), 2785 (4.69), 3530 (3.31), 3710, (3.32). **Naphtho[2,1-*f*]quinoline** (XI).—2620 (4.86), 2975 (4.27), 3590 (3.29).

Summary

Further studies of the cyclization of anils derived from β-naphthylamine and β-diketones indicate that hydrogen fluoride generally induces linear rather than the expected angular cyclization. The latter type of orientation is realized, however, when the cyclization is effected with zinc chloride and β-naphthylamine hydrochloride. The mechanisms of these two strikingly different types of ring closures are discussed.

The linear cyclization with hydrogen fluoride is observed also with anils derived from 2- and 3-phenanthrylamine. This behavior is consistent with the theoretical considerations.

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