destroyed before acidification, a quantitative yield of 8-methoxy-5-tetralincarboxylic acid II was obtained.

Preparation of 8-Methoxy-5-bromoacetyltetralin (VII).—To a solution of 6.5 g. of ketone (I) dissolved in 100 cc. of glacial acetic acid there was added 5.1 g. of bromine dissolved in 25 cc. of acetic acid. After standing for twelve hours the solution was poured into ice-water and the precipitate was collected on a filter; weight 4.5 g.; m. p. 73–74° after recrystallization from aqueous acetic acid.

Anal. Calcd. for $C_{13}H_{15}O_2Br$: C, 55.1; H, 5.3. Found: C, 55.15; H, 5.51.

8-Methoxy-5-acetoxyacetyltetralin (VIII).—Two grams of the aforementioned bromoketone (VII), 2 g. of fused potassium acetate and 15 cc. of ethanol were refluxed for five hours. After cooling the solution, the potassium bromide was collected on a filter and the filtrate was poured into ice-water. The precipitate was dried and recrystallized first from petroleum ether (90–100°) and finally from dilute alcohol; m. p. 91–92°; yield 90%.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.7; H, 6.87. Found: C, 68.88; H, 6.79.

This compound reduced Fehling solution but could not be hydrolyzed to give a pure compound.

Summary

1. It has been shown that methyl esters may be obtained directly as products of the haloform reaction.

2. These esters probably result from the action of methanol on the trihalomethyl ketones which are intermediates in this reaction.

MINNEAPOLIS, MINNESOTA RECEIVED SEPTEMBER 25, 1943

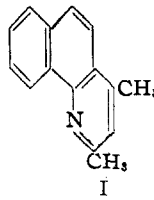
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Cyclization Studies in the Benzoquinoline Series

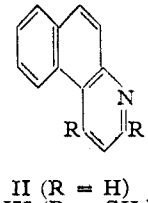
BY WILLIAM S. JOHNSON AND FREDERICK J. MATHEWS[1]

The Doebner–Miller type of quinoline synthesis[2a] with paraldehyde, acetone and β-naphthylamine gives a benzoquinoline derivative, $C_{15}H_{13}N$, m. p. 126–127°.[3] In contrast the quinoline synthesis of Combes[4] is reported to give with β-naphthylamine and acetylacetone a benzoquinoline of the same molecular formula, but m. p. 66–67°.[5] Both syntheses are known to be quite general for the production of quinoline derivatives. Thus from α-naphthylamine the Doebner–Miller and Combes' methods give bases[3,5] which are shown in the present work to be identical (formula I). The discrepancy regarding the benzoquinolines derived from β-naphthylamine presents a problem in proof of structures which is considered in this communication.

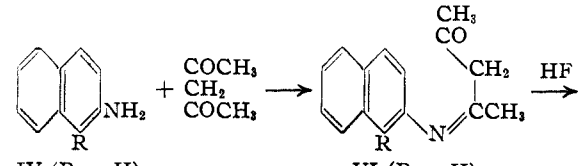
Previous studies suggest a similarity in mechanism—particularly at the cyclization step—between the Doebner–Miller and Skraup syntheses.[2] Since the latter is known[6] to give the angular base, benzo[f]quinoline (II) from β-naphthylamine, it would seem reasonable for Reed's 127° base to be 1,3-dimethylbenzo[f]quinoline (III). If the 127° base is III, the base reported by Combes could be 2,4-dimethylbenzo[g]quinoline (VIII) arising from the alternate—and indeed unexpected[7]—linear cyclization into the 3-position of the naphthalene nucleus. That these postulates are correct is shown below.



I

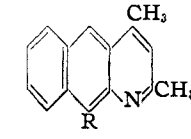


II (R = H)
III (R = CH_3)



IV (R = H)
V (R = CH_3)

VI (R = H)
VII (R = CH_3)



VIII (R = H)
IX (R = CH_3)

When the anil VI, which could be obtained in excellent yield from β-naphthylamine and acetylacetone, was treated with warm concentrated sulfuric acid according to the procedure of Combes,[5] only a small yield (4%) of basic material, m. p. 128.5–129° cor. (pure), was obtained. This substance proved to be identical with material which was prepared by the procedure of Reed.[3] The main product of the reaction was the monosulfonic acid (91% yield) of the expected base of Combes. The sulfonic acid (position of acid group unknown) could be hydrolyzed with dilute sulfuric acid at 220° to give the desired benzoquinoline. It was found, however, that under

(1) Present address: Röhm and Haas, Philadelphia, Pa.

(2) (a) Sidgwick, "Organic Chemistry of Nitrogen," Oxford University Press, 2nd ed., 1937, pp. 546–547; (b) *idem.*, pp. 544–546.

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

(4) Hollins, "Synthesis of Nitrogen Ring Compounds," D. Van Nostrand Company, New York, N. Y., 1924, pp. 266–270.

(5) Combes, *Compt. rend.*, **106**, 1536 (1888).

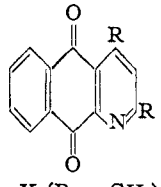
(6) Skraup and Cobenzl, *Monatsh.*, **4**, 436 (1883).

(7) There is a general tendency for 2,1-cyclization to occur in the naphthalene nucleus. In the case of the Skraup reaction, for example, this tendency is so strong that a methyl group at position-1 prevents the reaction while a bromine atom or a nitro group is displaced to give 2,1 instead of 2,3 cyclization [Lellmann and Schmidt, *Ber.*, **20**, 3154 (1887); Marckwald, *Ann.*, **274**, 331 (1893); **279**, 1 (1894)].

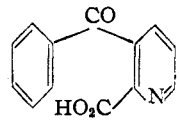
considerably milder cyclization conditions (two minutes below 60° instead of one-half hour at 100°) the sulfonation reaction could be largely eliminated and the base was produced directly from VI in yields up to 83%. The pure substance melted at 93–93.8° cor.[8] The balance of the material consisted of a small amount of the higher-melting isomer and of the sulfonic acid already mentioned. When the anil (VI) was treated with hydrogen fluoride,[9] the pure cyclized material (VIII) was produced in superior yield (96%) and to the exclusion of the angular isomer (III).[10]

It is noteworthy that hydrogen fluoride failed to cyclize the isomeric anil derived from α-naphthylamine.

In an effort to establish the structure, the 93° base was oxidized with potassium dichromate in acetic acid. A quinone (X) was produced which resembled anthraquinone in that it gave a deep colored vat with alkaline hydrosulfite and on reductive acetylation formed a crystalline hydroquinone diacetate. A number of attempts were



X (R = CH_3)
XI (R = H)



XII

made to cleave the quinone by alkali fusion,[11] but only intractable decomposition products were obtained. Acid permanganate, however, oxidized X rapidly in the cold to give a good yield of phthalic acid, the isolation of which, to be true, did not constitute a proof of structure. This facile oxidation, however, is in striking contrast to the behavior of anthraquinone, which is relatively stable. That the reactivity of the new quinone is due to the linear heterocyclic structure X was shown by an examination of the parent substance XI prepared by the unambiguous cyclization[12] of 3-benzoylpicolinic acid (XII).[13] This quinone closely resembled the one in question, responding comparably in the vat test, and in the easy oxidation to phthalic acid.

Evidence for the structures of the two benzoquinolines derived from β-naphthylamine also was supplied by a study of their absorption spectra. That of the 93° base is convincingly similar to that of anthracene (Fig. 1), while the absorption

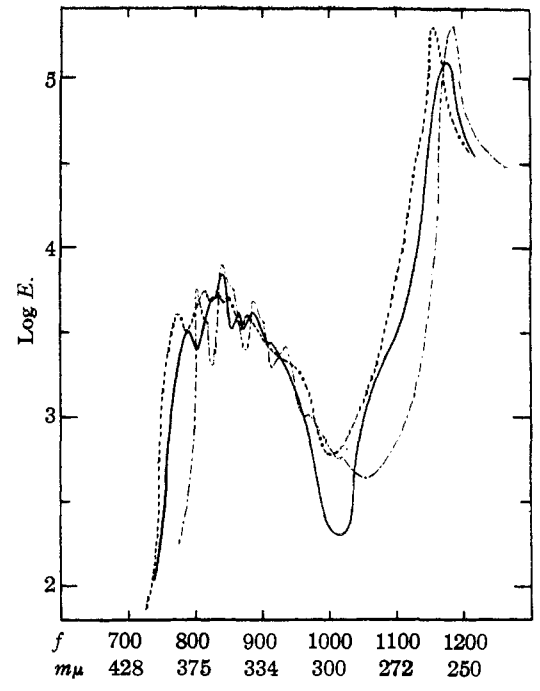


Fig. 1.— ——— 2,4-Dimethylbenzo[g]quinoline (VIII); - - - - - 2,4,10-trimethylbenzo[g]quinoline (IX); — - — - anthracene.

of the 127° isomer resembles that of phenanthrene (Fig. 2). Even more striking is the comparison of the absorption of the latter base with that of

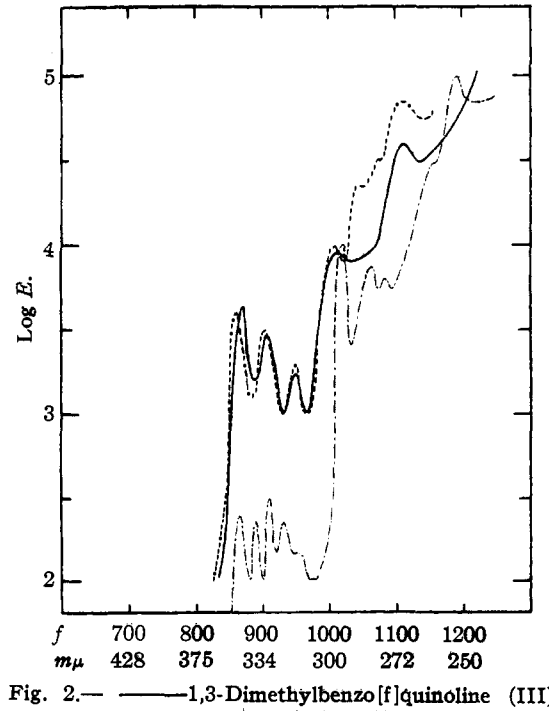


Fig. 2.— ———1,3-Dimethylbenzo[f]quinoline (III); - - - - 2,4-dimethylbenzo[h]quinoline (I); — - — - phenanthrene.

(8) Our first preparations of Combes' base melted sharply at 74.5–75.5° cor. During the progress of the work some of this material changed into the polymorph, m. p. 93–93.8° cor., and since this occurrence only the latter has been encountered.

(9) Fieser and Hershberg, THIS JOURNAL, 61, 1272 (1939).

(10) An apparent tendency for hydrogen fluoride to favor linear cyclization of a different type has been noted previously by Fieser and Johnson, THIS JOURNAL, 61, 1647 (1939); Fieser and Daudt, *ibid.*, 63, 782 (1941), and Fieser and Heymann, *ibid.*, 63, 2333 (1941).

(11) *Cf.* Cason and Fieser, *ibid.*, 62, 2681 (1940).

(12) Philips, *Ber.*, 28, 1658 (1895).

(13) Kirpal, *Monatsh.*, 31, 295 (1911).

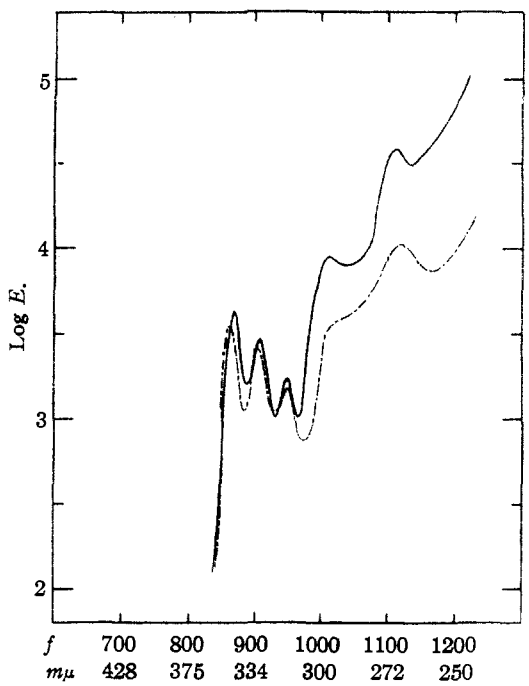
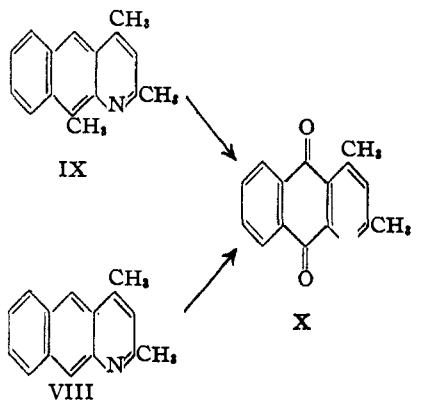


Fig. 3.— ——— 1,3-Dimethylbenzo[f]quinoline (III); — - — - — benzo[f]quinoline (II).

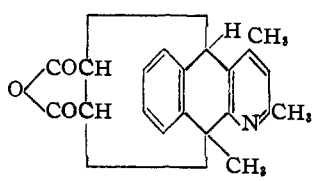
Skraup's benzo[f]quinoline (II)[14] (Fig. 3); the principal maxima appear at almost identical wave lengths. The absorption spectrum of 2,4-dimethylbenzo[h]quinoline (I) is included in Fig. 2 and bears a close relationship to those of the other angular analogs.

Further evidence for the structure of the 93° base was afforded by a study of the homolog 2,4,10-trimethylbenzo[g]quinoline (IX). This base was prepared in excellent yield by the condensation of 1-methyl-2-naphthylamine (V) with acetylacetone followed by hydrogen fluoride cyclization of the resulting anil (VII). Since the α-position of the naphthalene nucleus was blocked by the methyl group, only linear cyclization was possible, and, therefore, the product of ring closure must have the structure IX. Oxidation of this substance with potassium dichromate in propionic acid solution yielded a quinone (X) which was identical with the one obtained from the 93° base. The structure of the 93° base, therefore, is conclusively established (formula VIII). The loss of the 10-methyl group on oxidation is compatible with the anthracene-like structure of IX.[15]

The two linear bases (VIII and IX) had comparable properties: with hydrochloric acid they were converted into bright yellow hydrochlorides and when warmed with concentrated sulfuric acid they readily yielded monosulfonic acids. This is in distinct contrast to the behavior of the angular



bases which have colorless hydrochlorides and are sulfonated only under more drastic conditions.[8] This relative susceptibility of the linear and angular bases to sulfonation is reminiscent of the respective behavior of anthracene and phenanthrene. The new linear base (IX) also resembled anthracene in the reaction with maleic anhydride to form an addition product, probably XIII.[16]



XIII

The dimethyl base (VIII) also reacted readily with maleic anhydride, but the product was intractable. The angular bases, however, failed to react at all under the same conditions. The two linear bases were also closely comparable in respect to their absorption spectra (Fig. 1). A definite bathochromic shift may be noted in the maxima of the trimethyl derivative. This effect of the 10-methyl group is consistent with the observation that *meso* substituents exert such shifts in the absorption spectra of benzanthracene derivatives.[17]

Experimental Part[18]

4-(2-Naphthylimino)-pentanone-2 (VI).—The method of Combes[5] was modified by the introduction of Drierite into the reaction mixture. A mixture of 5.0 g. of β-naphthylamine, 6 cc. of acetylacetone and 10 g. of Drierite was heated on the steam-bath for three to four hours. The crude product obtained on elution with ether amounted to 7.55 g. (96% yield based on the amine), m. p. 89–96° with previous softening. One recrystallization from benzene–petroleum ether gave 6.5 g. (83% yield) of pure material, m. p. 98–99°. An additional 0.25 g., m. p. 96–98°, was obtained from the filtrate. A sample prepared for analysis formed tan flat needles and rods from ligroin, m. p. 98.5–99°.

Anal. Calcd. for $C_{15}H_{15}ON$: C, 79.97; H, 6.71. Found: C, 79.98; H, 6.66.

2,4-Dimethylbenzo[g]quinoline-x-sulfonic Acid.—A solution of 5.0 g. of the above anil (VI) in 25 cc. of concen-

(14) Structure known (see ref. 6).

(15) *Cf.* the oxidative degradation of *meso* alkylanthracenes to 9,10-anthraquinone; Barnett, "Anthracene and Anthraquinone," D. Van Nostrand Co., New York, N. Y., 1921, p. 20.

(16) *Cf.* the well-known addition of maleic anhydride to anthracene.

(17) R. N. Jones, THIS JOURNAL, 62, 148 (1940).

(18) Unless otherwise stated all melting points are corrected.

trated sulfuric acid was heated on the steam-bath for one-half hour, cooled, and poured onto ice. The mixture was made alkaline, and a small amount (0.20 g.) of the angular 1,3-dimethylbenzo[f]quinoline (III) was obtained, m. p. 120–125°. Twice recrystallized from ligroin (90–100°) it melted at 128.5–129°, and showed no depression when mixed with an authentic specimen of the base prepared by the procedure of Reed.[5] Acidification of the alkaline solution yielded 5.8 g. (91%) of the yellow sulfonic acid of the linear base. It crystallized in small rods when a solution of the ammonium salt in dilute alcohol was boiled gently. The acid chars without melting when heated on a spatula; however, it is probably identical with the substance described by Combes[6] as shown by analysis.

Anal. Calcd. for $C_{15}H_{13}O_3NS$: C, 62.71; H, 4.56. Found: C, 62.94; H, 4.60.

2,4-Dimethylbenzo[g]quinoline (VIII): (a) By Hydrolysis of the Sulfonic Acid.—A suspension of 0.5 g. of the above sulfonic acid in 20 cc. of 10% (by volume) sulfuric acid was heated in a sealed tube at 220° for six hours. The mixture was made alkaline, and extracted with ether which gave 0.25 g. (70% yield) of the base, m. p. 63–70°. Once recrystallized from petroleum ether (60–68°) it melted at 71–72° (low-melting modification; see ref. 8). After the high-melting form was encountered in some later preparations, this material on recrystallization melted at 92–93°. Reaction temperatures above 220° caused considerable loss by charring while lower temperatures failed to effect complete hydrolysis.

(b) **Cyclization with Sulfuric Acid.**—The conditions for ring closure by this method appear to be very critical; it was not always possible to obtain yields as high as in the following experiment. To 85 cc. of chilled (2°) concentrated sulfuric acid was added with swirling 25.5 g. of 4-(2-naphthylimino)-pentanone-2 (VI). Better results were obtained when this operation did not exceed three minutes. The solution was then swirled in a flask at 60° (water-bath) for two minutes, cooled in an ice-bath and poured onto ice (300 g.). The insoluble yellow sulfate of the cyclized product was decomposed by making the mixture alkaline, and the base was taken up in ether. After treatment with Norit and drying, the ether was evaporated and the residue crystallized from ligroin (90–100°). This gave 19.6 g. (83.5% yield) of 2,4-dimethylbenzo[g]quinoline, m. p. 85–91° (high-melting form) with softening at 73°. One recrystallization gave 16.8 g. (71.5% yield) of material melting at 92–93°.

Evaporation of the filtrate from the first crystallization of VIII deposited a mixture of crystals from which could be separated mechanically about 0.5 g. (2% yield) of colorless clusters of needles, m. p. 121–125°, which consisted mainly of the angular isomer III; after two recrystallizations (90–100° ligroin) the m. p. was 128.5–129°, not depressed on mixing with authentic 1,3-dimethylbenzo-[f]quinoline. Attempts to cyclize the anil with dilute sulfuric acid resulted in hydrolysis.

(c) **Ring Closure with Hydrogen Fluoride.**—To 13.4 g. of the anil (VI) in a platinum vessel was added approximately 300 cc. of anhydrous hydrogen fluoride. After standing overnight at room temperature the residue was treated with 10% potassium carbonate solution, extracted with ether, treated with Norit, filtered, shaken with saturated salt solution and dried over anhydrous sodium sulfate. Evaporation of the ether yielded 11.75 g. (96%) of light tan crystals, m. p. 91–92.5°, not depressed on mixing with samples obtained by methods (a) and (b).

A sample of 2,4-dimethylbenzo[g]quinoline was purified for analysis by evaporative distillation at 130–140° (1 mm.). Recrystallization from acetone–ligroin gave colorless prismatic needles, m. p. 93–93.8°. Dilute solutions of the base exhibit a strong blue fluorescence. In dilute hydrochloric acid it gives an intense yellow solution of the salt.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32. Found: C, 87.05; H, 6.47.

2,4-Dimethylbenzo[g]quinoline hydrochloride was prepared by passing dry hydrogen chloride into an ether solution of the base. The salt on recrystallization from alcohol formed bright yellow microscopic crystals, m. p. 324–325° (dec.) (uncor.).

Anal. Calcd. for $C_{15}H_{14}ClN$: C, 73.91; H, 5.79 Found: C, 73.95; H, 5.76.

2,4-Dimethylbenzo[g]quinoline picrate was formed in alcohol and recrystallized from bromobenzene. It formed glistening yellow needles, m. p. about 271–273° (dec.) with previous darkening (introduced in bath at 250°).

Anal. Calcd. for $C_{21}H_{16}O_7N_4$: C, 57.80; H, 3.70. Found: C, 57.87; H, 3.46.

Reaction of 2,4-Dimethylbenzo[g]quinoline and Maleic Anhydride.—A solution of 0.4 g. of 2,4-dimethylbenzo(g)-quinoline and 1.5 g. of freshly distilled maleic anhydride in 10 cc. of benzene was allowed to stand for several hours at room temperature. The dark red precipitate amounted to 0.9 g. (air-dried), m. p. about 110–130° (dec.). All attempts to purify this material met with failure, apparently due to decomposition. This product may be the maleic anhydride addition compound by analogy to the homologous substance XIII which has been isolated in a pure state (described below).

2,4-Dimethylbenzo[g]quinoline-5,10-quinone (X).—A mixture of 16.3 g. of 2,4-dimethylbenzo[g]quinoline, 450 cc. of glacial acetic acid, 30 cc. of water and 23.5 g. of powdered potassium dichromate was boiled under reflux for one and one-quarter hours. The solution was cooled, poured into 500 cc. of saturated salt solution (to prevent emulsions) and extracted with benzene. Evaporation gave 8.9 g. (48% yield) of orange crystals of the quinone, m. p. 210.5–213.5° (dec.). A sample purified by sublimation at 180–190° (1 mm.) and recrystallization from benzene formed light orange needles, m. p. 215–216° (dec.). The quinone is photosensitive, turning bright red upon exposure to daylight for about two hours. It dissolves in alkaline sodium hydrosulfite solution to give a deep purple vat.

Anal. Calcd. for $C_{15}H_{11}O_2N$: C, 75.94; H, 4.67. Found: C, 75.80; H, 4.57.

5,10-Diacetoxy-2,4-dimethylbenzo[g]quinoline.—When the quinone (X) was treated by the customary procedure for reductive acetylation with zinc-dust, acetic anhydride and sodium acetate, only intractable oils were obtained. When sulfuric acid was used in place of the sodium acetate, the reduced diacetate was obtained.

To a solution of 0.50 g. of the quinone (X) in 15 cc. of acetic anhydride was added 0.4 cc. of concentrated sulfuric acid and 2 g. of zinc-dust. The pale orange solution presently turned bright yellow (due to the salt of the reduced diacetate; *cf.* the color of the hydrochloride of the base VIII), and was heated for one hour on the steam-bath. The filtered and cooled solution was poured onto ice, made alkaline, and extracted with benzene. The organic layer was extracted with a 3% solution of sodium hydrosulfite in 5% sodium hydroxide until all the quinone was removed as followed by the color of the vat, treated with Norit, and evaporated. The residue was sublimed at 165–180° (3 mm.) and recrystallized from benzene–ligroin (90–100°) to give yellow needles, m. p. 198–199°; yield 0.25 g. (37%). 5,10-Diacetoxy-2,4-dimethylbenzo[g]quinoline forms bright yellow solutions with dilute mineral acids, and does not give a vat test. It is relatively stable to light, but decomposes on long standing.

Anal. Calcd. for $C_{19}H_{17}O_4N$: C, 70.57; H, 5.30. Found: C, 70.68; H, 5.18.

Oxidation of 2,4-Dimethylbenzo[g]quinoline-5,10-quinone.—To a solution of 0.100 g. of the quinone (X) in 10 cc. of 20% (by volume) sulfuric acid was added dropwise a saturated solution of potassium permanganate until the latter was decolorized only slowly. The manganese dioxide was decomposed with sodium bisulfite and the solution extracted with ether. Evaporation of the dried ether layer gave 0.055 g. of almost colorless material m. p. 170–175°. Sublimation gave 0.025 g. of phthalic anhydride, m. p. 121–128°. After purification it melted at 126–128° and on mixing did not depress the m. p. of an authentic

specimen. The free acid had the m. p. 190–192°, not depressed on mixing with authentic phthalic acid. The neutral equivalent was 84.5 (calcd. 83.1).

Oxidation of Benzo[g]quinoline-5,10-quinone.—Benzo[g]quinoline-5,10-quinone (XI) was prepared from 3-benzoylpicolinic acid (XII) by the action of sulfuric acid.[12] The picolinic acid was obtained by the Friedel and Crafts reaction of quinolinic anhydride and benzene.[13] The quinone which was obtained in 6% yield was sublimed at 170–190° (1 mm.) and recrystallized from toluene. It formed pale greenish-yellow needles, m. p. 279–280° (uncor.) (literature[12] m. p. 280°), and gave a brilliant purple vat with alkaline sodium hydrosulfite solution.

For the oxidation of the quinone (50 mg.) the procedure already described for the oxidation of the dimethyl homolog (X) was used. The reaction proceeded similarly in every respect, and phthalic acid (25 mg.) was likewise isolated.

1-Methyl-2-naphthylamine (V) has been prepared previously[19] in 50% yield by the Bucherer reaction on 1-methyl-2-naphthol. In the present work the yield was improved considerably.

A mixture of 7.8 g. of 1-methyl-2-naphthol[20] (m. p. 107–109°), 10 g. of sodium bisulfite, 40 cc. of concentrated ammonium hydroxide solution, and 10 cc. of water was heated in a sealed Pyrex tube at 200 to 205° for forty-eight hours. The mixture was then diluted with water, made strongly alkaline with sodium hydroxide and extracted with ether. If the ether layer was evaporated, the residue could not be purified satisfactorily by recrystallization since an apparently homogeneous substance, m. p. 91–93° contaminated the product. This contaminant was shown to consist of a molecular complex of amine and unchanged naphthol which could not be separated with alkali. The amine could be liberated as the hydrochloride by treating an ether solution of the complex with dry hydrogen chloride. Thus it was found expedient to apply this treatment to the original dried ether layer. The amine hydrochloride was filtered, washed with ether, dissolved in hot water and decomposed with sodium hydroxide. The liberated amine was extracted with ether and dried. Evaporation of the solvent gave a crude product m. p. 46–50°; yield 7.2 g. or 93%. Once recrystallized from petroleum ether (60–68°) it formed a colorless product, m. p. 49–50° (literature[19] m. p. 50–51°), amounting to 5.5 g. (71% yield).

4-(1-Methyl-2-naphthylimino)-pentanone-2 (VII).—The procedure already described for the homolog VI was used, except that a large excess of acetylacetone was employed since the ketone is more accessible than the amine in this case. From 14.0 g. of 1-methyl-2-naphthylamine (m. p. 49–50°) and 20 cc. of acetylacetone with 28 g. of Drierite, there was obtained 22.0 g. of crude anil (VII), m. p. 87–92°. Recrystallization from ligroin (90–100°) gave 15.2 g. of material, m. p. 92–93.5°, and a second crop amounting to 3.2 g., m. p. 90–92°; thus the yield of pure anil was 87%. A sample twice recrystallized from petroleum ether (60–68°) formed light tan prisms, m. p. 93–94.8°.

Anal. Calcd. for $C_{16}H_{17}ON$: C, 80.31; H, 7.16. Found: C, 80.37; H, 7.21.

2,4,10-Trimethylbenzo[g]quinoline (IX).—The cyclization of the above anil (VII) was carried out according to both procedures (b) and (c) for the preparation of 2,4-dimethylbenzo[g]quinoline already described. The sulfuric acid method (b) gave good yields (up to 93%) of the cyclized base, but suffered from the same type of uncertainty already mentioned in the case of the lower homolog. Consistently excellent yields of the new quinoline derivative were realized when the hydrogen fluoride method (c) was employed. Thus from 5.0 g. of 4-(1-methyl-2-naphthylimino)-pentanone-2 (m. p. 91–93°) was obtained 4.42 g. (96% yield) of 2,4,10-trimethylbenzo[g]-quinoline, m. p. 122–125°. Material purified by evaporative distillation at 130–140° (1 mm.) and recrystallization from acetone–petroleum ether formed colorless prisms, m. p. 126.2–127°. Like the lower homolog its solutions exhibit a strong fluorescence, and with dilute hydrochloric acid it gives a bright yellow salt.

Anal. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83. Found: C, 86.75; H, 6.71.

2,4,10-Trimethylbenzo[g]quinoline hydrochloride was prepared as described above for the homologous substance. The orange-yellow salt crystallized from alcohol in microscopic crystals, m. p. 295–296° (dec.) (uncor.).

Anal. Calcd. for $C_{16}H_{16}ClN$: C, 74.55; H, 6.26. Found: C, 74.75; H, 6.02.

2,4,10-Trimethylbenzo[g]quinoline picrate crystallized in yellow rods from the solvent pair nitromethane–tetrachloroethane. The m. p. was 253–255° (dec.) with previous darkening (introduced in bath at 240°).

Anal. Calcd. for $C_{22}H_{18}O_7N_4$: C, 58.66; H, 4.03. Found: C, 58.72; H, 4.16.

2,4,10-Trimethylbenzo[g]quinoline-x-sulfonic acid was prepared according to the procedure already described for the homolog. From 15.0 g. of the anil (VII) was obtained 17.4 g. (92% yield) of the acid. On slow hydrolysis of the ammonium salt the pure acid crystallized in small orange-yellow rods. It is hygroscopic, and more soluble than the lower homolog.

Anal. Calcd. for $C_{16}H_{15}O_3NS$: C, 63.77; H, 5.02. Found: C, 63.41; H, 4.98.

Reaction of 2,4,10-Trimethylbenzo[g]quinoline with Maleic Anhydride.—A solution of 0.30 g. of the base and 0.75 g. of freshly distilled maleic anhydride in 6 cc. of benzene was boiled under reflux for six hours. After cooling the solution was diluted with 15 cc. of benzene, dry hydrogen chloride passed in, and the precipitated hydrochloride filtered. This product was colorless, indicating that the addition was complete (*cf.* the intense yellow color of the salt of the starting base). The adduct was regenerated by boiling for ten minutes with acetone and powdered sodium acetate, filtering and evaporating the solvent; yield 0.33 g. The residue was purified by recrystallization from ether (poor recovery). It formed colorless microscopic crystals, m. p. 203.5–204.5°. Attempts to prepare the dibasic acid in a pure state were discouraged by difficulties attributable to the amphoteric nature of the substance.

Anal. Calcd. for $C_{20}H_{17}O_3N$: C, 75.22; H, 5.37. Found: C, 74.90; H, 5.26.

When the angular bases (I and III) were submitted to the reaction conditions above they were recovered unchanged.

Potassium Dichromate Oxidation of 2,4,10-Trimethylbenzo[g]quinoline.—A solution of 2.0 g. of the benzoquinoline and 5.4 g. of potassium dichromate in 40 cc. of propionic acid and 5 cc. of water was boiled under reflux for two hours. The cooled, green solution was poured into 300 cc. of water and extracted with benzene. The quinone was extracted from the benzene solution with a 1 to 1 mixture of 5% sodium hydrosulfite and 10% sodium hydroxide solution. The quinone was regenerated from the purple vat by passing air through the aqueous solution for several hours. Thus was obtained 0.1 g. (about 5% of the theoretical) of crude quinone, m. p. 180–195°. The reduced diacetate was prepared by the procedure already described. Sublimation and recrystallization gave material, m. p. 196–198°, identical in appearance with the reduced diacetate obtained from 2,4-dimethylbenzo[g]quinoline quinone. A mixture of the two samples showed no m. p. depression.

2,4-Dimethylbenzo[h]quinoline (I) was prepared from α-naphthylamine and acetylacetone according to previous procedures.[5,21] The use of Drierite (see above) was found to increase the yield (99%) of the anil which we were not able to obtain homogeneous. Fusion of the material occurred over a wide range below 100° even after several recrystallizations (*cf.* v. Braun, *et al.*,[21] who give the m. p.

(19) Scholl and Neuberger, *Monatsh.*, **33**, 507 (1912); Shimomura and Cohen, *J. Chem. Soc.*, 740 (1921).

(20) Robinson and Weygand, *J. Chem. Soc.*, 386 (1941).

(21) v. Braun, Gmelin and Petzold, *Ber.*, **57**, 382 (1924).

165°). The crude anil, however, could be cyclized with sulfuric acid in good yields (80–90%). The benzoquinoline twice recrystallized from petroleum ether (40–60°) formed colorless needles, m. p. 51.5–53°. Material of the same m. p. was obtained laboriously in about 2% yield using the procedure of Reed.[3] The mixed m. p. showed no depression. It was surprising to find that hydrogen fluoride failed to cyclize noticeably 4-(1-naphthylimino)-pentanone-2; hydrolysis to α-naphthylamine took place instead.

Absorption Spectra.—A Hilger quartz spectrograph equipped with a Hilger photometer was used in conjunction with a hydrogen discharge tube as the light source. Ethanol, specially dried over magnesium ethoxide[22] and distilled in an all-glass apparatus, was used as the solvent.

The analytical samples of the benzoquinolines were used. Benzo[f]quinoline (Eastman Kodak Company) was recrystallized from 60–68° petroleum ether, m. p. 90.5–91.5°. Anthracene was sublimed and recrystallized from chloroform and ethanol, m. p. 214.5–215.5°. A pure sample of phenanthrene was prepared by dehydrogenation of pure 9,10-dihydrophenanthrene[23] over 30% palladium-charcoal,[24] followed by recrystallization from ethanol, m. p. 98–99°.

The linear compounds were determined at four concentrations: *M*/4000, *M*/10,000, *M*/40,000 and *M*/200,000. For anthracene a determination was made also at *M*/400,000. The angular substances were determined at *M*/2000, *M*/10,000, *M*/50,000 and *M*/200,000. In the figures the abscissas are plotted in fresnel (*f*) units in accordance with the suggestion of Brode.[25] The log *E* values observed for anthracene and phenanthrene do not check those of Capper and Marsh,[26] but in the case of anthracene are in agreement with those of Heertjes and Waterman.[27]

The principal maxima are given below. The wave lengths are in ångström units, the intensity in log *E* (in parentheses), and * indicates inflections.

Anthracene.—3740 (3.75), 3700* (3.55), 3560 (3.9), 3505* (3.75), 3375 (3.70), 3340* (3.58), 3200 (3.43), 3090 (3.05), 2940 (2.75), 2530 (5.30).

2,4-Dimethylbenzo[g]quinoline.—3800 (3.45), 3640 (3.70), 3575 (3.85), 3470 (3.62), 3380 (3.62), 3290 (3.45). 2565 (5.10).

2,4,10-Trimethylbenzo[g]quinoline.—3870 (3.6), 3695 (3.75), 3600 (3.7), 3530 (3.7), 3420 (3.6), 2590 (5.3).

Phenanthrene.—3460 (2.4), 3375 (2.24), 3290 (2.5), 3220 (2.34), 3150 (2.18), 3080 (2.00), 2935 (4.00), 2815 (3.88), 2760 (3.80), 2600 (4.48), 2525 (5.00).

2,4-Dimethylbenzo[h]quinoline.—3480 (3.6), 3310 (3.50), 3160 (3.30), 2980 (4.00), 2870 (4.35), 2790 (4.50), 2700 (4.85).

1,3-Dimethylbenzo[f]quinoline.—3450 (3.65), 3300 (3.48), 3160 (3.24), 2970 (3.95), 2700 (4.60).

Benzo[f]quinoline.—3470 (3.54), 3310 (3.41), 3160 (3.18), 2900* (3.57), 2665 (4.06).

Summary

The preparation and proof of structure of some benzoquinoline derivatives is considered. Particular attention is given to the cyclization of the anil from β-naphthylamine and acetylacetone, which, surprisingly, takes place so as to give a linear benzoquinoline. The latter represents a class of compounds about which little has been known. Some of the properties of this type of substance are considered.

(22) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, 2nd ed. Part II, 1941, p. 359.

(23) Fieser and Johnson, THIS JOURNAL, **61**, 168 (1939).

(24) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

(25) W. Brode, "Chemical Spectroscopy," John Wiley and Sons, New York, N. Y., 1939, p. 191.

(26) Capper and Marsh, *J. Chem. Soc.*, 724 (1926).

(27) Heertjes and Waterman, *Bull. soc. chim.*, [5] **7**, 187 (1940).

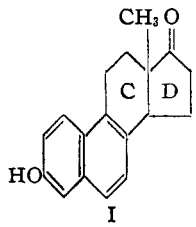
MADISON, WISCONSIN RECEIVED AUGUST 2, 1943

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

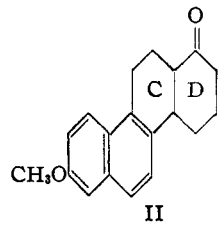
Introduction of the Angular Methyl Group. II.[1] *cis-* and *trans*-8-Methylhydrindanone-1[2]

BY WILLIAM S. JOHNSON

The purpose of this communication is to describe a method for converting decalone-1 (III) into the angularly methylated hydrindanones (IX and X). This process affords a means of arriving at the structure defined by rings C and D (compare formula I) of a number of the steroid hormones, and obviously serves as a model synthesis for the preparation of hormones of the equilenin (I) type from chrysene derivatives like II.[3]



I



II

Considerable attention already has been devoted to 8-methylhydrindanone-1[4–11] but with one exception[11] all of the syntheses have led to one and the same isomer of this compound which, however, can exist in two racemic forms described by *cis* (IX) and *trans* (X) fusion of the rings. The present synthesis affords a means of obtaining each of these diastereoisomers, which is fortunate particularly in view of the fact that the ring C/D

(1) For the first paper of this series see Johnson, THIS JOURNAL, **65**, 1317 (1943).

(2) This work was assisted in part by a grant from the Wisconsin Alumni Research Foundation.

(3) The unsaturated progenitor (double bond in ring D) of compound II is available by the Robinson-Schlittler synthesis; Robinson and Thompson, *J. Chem. Soc.*, 1739 (1939).

(4) Chuang, Tien and Ma, *Ber.*, **69**, 1494 (1936).

(5) Kon, Linstead and Simons, *J. Chem. Soc.*, 814 (1937).

(6) Linstead, Millidge and Walpole, *ibid.*, 1140 (1937).

(7) Robinson and Walker, *ibid.*, 1160 (1937).

(8) Elliott and Linstead, *ibid.*, 660 (1938).

(9) Burnop and Linstead, *ibid.*, 720 (1940).

(10) Nenitzescu and Przemetzky, *Ber.*, **74B**, 676 (1941).

(11) Bachmann and Kushner, THIS JOURNAL, **65**, 1963 (1943).