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The Synthesis and some Reactions of 2,3-Substituted 1-Phenylbenzo[*f*]quinoline (1)

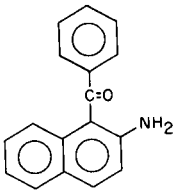
Tze-Lock Chan and Jan Hamer

Department of Chemistry, Tulane University

A series of 2,3-substituted 1-phenylbenzo[*f*]quinolines was synthesized by the Friedlander condensation of 1-benzoyl-2-naphthylamine with β-keto esters. Some chemical transformations of these compounds and the preparation of 13*H*-benzo[*f*]indeno[2,1-*c*]quinoline-13-one and its 9-methyl derivative are described.

In the course of our studies directed toward the synthesis of azahelicenes, it was desirable to explore reaction pathways possibly leading to the model dibenzo-[*a*,*k*]phenanthridine via benzo[*f*]quinoline intermediates. As a result, the synthesis and reactions of a number of 1-phenylbenzo[*f*]quinolines possessing a handle for cyclization on the 2-position have been investigated. We have found that these compounds can be conveniently prepared by employing the Friedlander condensation of 1-benzoyl-2-naphthylamine (I) with esters containing activated methylene groups. With diethyl malonate, ethyl acetoacetate and ethyl benzoylacetate, the 1-phenylbenzo[*f*]quinolin-3-ols obtained under the classical conditions for the Friedlander synthesis (2) are analogous to the carbostyrils from *o*-aminobenzophenone (3). Acid-catalyzed condensation (4) of I and ethyl acetoacetate yielded the expected 1-phenyl-2-carboethoxy-3-methylbenzo[*f*]quinoline (XIII).

When compound I was heated in the presence of a large excess of diethyl malonate at 165-175° two ring closure products were isolated in small yields. Based on nmr, infrared and elemental analysis, structures assigned to these products were 1-phenyl-2-carboethoxybenzo[*f*]-quinolin-3-ol (II) and 2-(1-phenyl-3-hydroxy-2-benzo[*f*]-quinolylamido)-1-benzoylnaphthalene (III). At reaction temperatures higher than 180°, III was formed exclusively. On the other hand, the uncyclized 2-carboethoxyacetamido-1-benzoylnaphthalene (IV), the intermediate for II, was isolated at 125-130°.

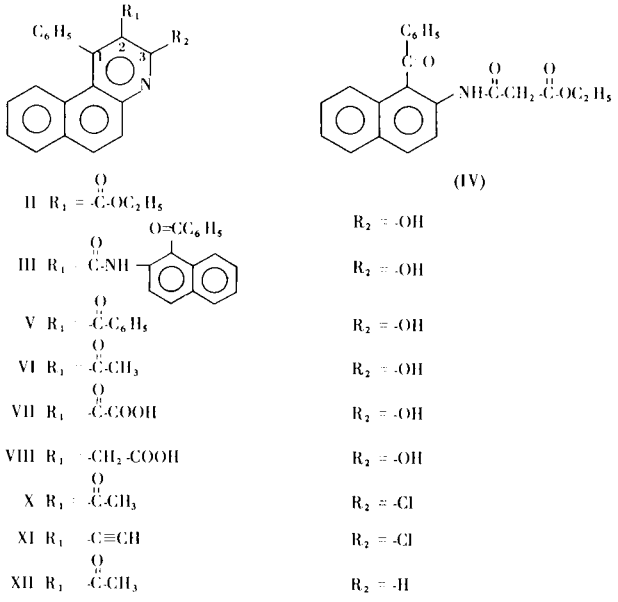


I

At 160-175°, ethyl benzoylacetate and ethyl acetoacetate were found to condense readily with I to give, respectively, 1-phenyl-2-benzoylbenzo[*f*]quinolin-3-ol (V) and 1-phenyl-2-acetylbenzo[*f*]quinolin-3-ol (VI). As observed in the *o*-aminobenzophenone system (3), these reactions proceeded through the eliminations of one molecule each of ethanol and water. The factors which influence the modes of cyclization in the Friedlander-type condensations have been discussed in detail (5).

It was hoped that VI could be used for the preparation of a hydroxy derivative of dibenzo[*a*,*k*]phenanthridine. The projected synthesis involved the transformation of the acetyl group into an acetic acid moiety either before or after the removal of the 3-hydroxyl group, followed by a cyclodehydration. For this purpose, VI was oxidized by selenium dioxide in boiling dioxane to give 1-phenyl-3-hydroxy-2-benzo[*f*]quinolineglyoxylic acid (VII) (6). Reduction of VII with red phosphorus and constant-boiling hydroiodic acid yielded 1-phenyl-3-hydroxy-2-benzo[*f*]quinolineacetic acid (VIII), which was also ob-

CHART I

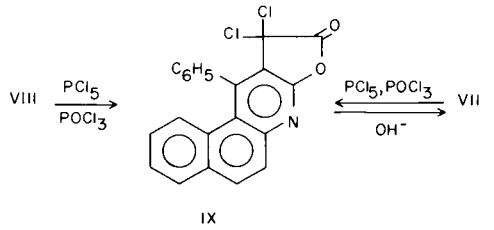


tained in very low yield from the Willgerodt reaction of VI. Attempted cyclization of VIII in sulfuric acid, polyphosphoric acid and trifluoroacetic anhydride at different temperatures were unsuccessful. In all cases, either recovered starting material or tar was isolated.

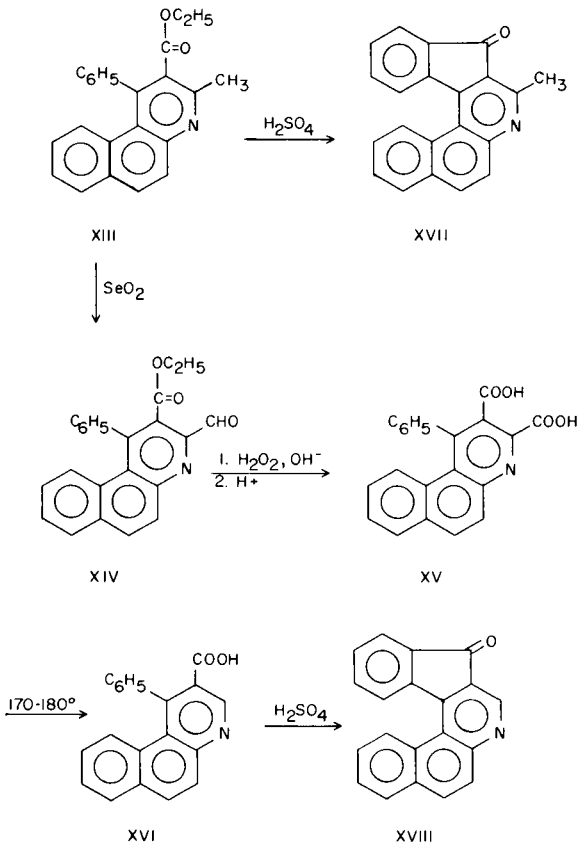
Attempts to replace the hydroxyl group in VIII by a chlorine atom with refluxing phosphorus oxychloride or with phenylphosphonic dichloride at 170-180° gave unchanged starting material. However, treatment with a mixture of phosphorus pentachloride and phosphorous oxychloride resulted in lactonization of the acid and hydroxyl groups accompanied by the chlorination of the methylene protons giving α,α-dichloro-1-phenyl-3-hydroxy-2-benzo[*f*]quinolineacetic acid γ-lactone (IX). Both spectral and chemical evidence (Scheme I) are compatible with the assigned structure. The absence of infrared absorption assignable to an N-H or carboxylic acid group coupled with the presence of a strained carbonyl peak at 5.51 μ support the lactone structure. The nmr spectrum of this compound showed only the presence of aromatic protons. Basic hydrolysis of IX gave VII. Further structural proof is demonstrated by the formation of IX when VII was subjected to the same chlorination conditions. The observed lactonization of VII and VIII indicates that the acid chloride formed reacted with the tautomeric 3-hydroxyl group before the latter could be replaced by chlorine.

Replacement of the hydroxyl group in VI by chlorine proceeded smoothly with phenylphosphonic dichloride at 170° giving the expected 1-phenyl-2-acetyl-3-chlorobenzo-[*f*]quinoline (X). However, in boiling phosphorus oxychloride containing a catalytic amount of *N*,*N*-dimethylaniline, VI was found to give mainly 1-phenyl-2-ethynyl-3-chlorobenzo[*f*]quinoline (XI) together with a small amount of X. Spectral data confirm the structure of XI. Infrared spectrum of XI displayed a strong C≡C-H peak at 3.04 μ, a weak C≡C peak at 4.75 μ and showed no carbonyl absorption. The nmr spectrum exhibit a multiplet at 2.03-3.04 τ and a sharp singlet at 6.07 τ in the respective ratio of 11:1. The observed conversion of the acetyl group in VI into an ethynyl group is in effect the reversed reaction of the hydration of an acetylene. Although carbonyl compounds can be transformed into acetylenes via the dichloro intermediates by reactions with phosphorus

SCHEME I



SCHEME II



pentachloride, dehydration under the above described conditions does not appear to be general. We noted the formation of a small amount of 4-phenyl-3-ethynyl-2-chloroquinoline from the known 4-phenyl-3-acetylquinolin-2-ol (3) but found acetophenones to be unaffected. It was further noted that the dehydration of the acetyl moiety in VI occurred before the 3-hydroxyl group was replaced by chlorine. In a separate run, X (prepared by the phenylphosphonic dichloride method) was recovered unchanged.

Catalytic hydrogenolysis of X gave a low yield of 1-phenyl-2-acetylbenzo[*f*]quinoline (XII) and an unidentified substance. The action of selenium dioxide on XII resulted in the formation of a dark amorphous mixture from which a pure compound could not be isolated.

The discovery by Fehnel (4) that acid-catalyzed Friedlander condensations of *o*-aminobenzophenone gave exclusively the "normal" products led us to the examination of the reaction of I with ethyl acetoacetate under these conditions. A good yield of 1-phenyl-2-carboethoxy-3-methyl-benzo[f]quinoline (XIII) was indeed obtained in boiling acetic acid containing a catalytic amount of concentrated sulfuric acid. Compound XIII was subsequently used for the syntheses of 13*H*-benzo[*f*]indeno-[2,1-*c*]quinoline-13-one (XVIII) and its 8-methyl derivative (XVII), as outlined in Scheme II. Heating XIII in concentrated sulfuric acid afforded a moderate yield of the cyclic ketone XVII. Selenium oxidation of XIII gave 1-phenyl-2-carboethoxy-3-formylbenzo[*f*]quinoline (XIV).

Treatment of this aldehyde with either alkaline hydrogen peroxide or silver oxide gave 1-phenylbenzo[*f*]-quinoline-2,3-dicarboxylic acid (XV) which was selectively decarboxylated to the mono-acid (XVI). Cyclization of XVI to XVIII was effected by concentrated sulfuric acid at 100°.

A number of attempts were made to convert XVIII into dibenzo[*a*,*k*]phenanthridine without success. For example, two routes were tried to transform the carbonyl function in XVIII into a hydroxymethyl group for ring expansion. In one of them, methoxymethylenetriphenylphosphorane generated in methanol failed to condense with XVIII. In the other, the ketone was reduced by sodium borohydride to an enantiomeric hydroxy mixture which reacted with hydrobromic acid to give the corresponding bromo compounds, but the latter did not react with triphenylphosphine under a variety of conditions.

EXPERIMENTAL

Melting points were determined with a Fisher-Johns hot stage and are uncorrected. Nmr spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as internal standard. The chemical shifts are recorded in τ values. Infrared data were obtained on a Beckman IR-8 infrared spectrophotometer using potassium bromide pellets. Only certain absorptions are given (in microns). Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee.

Reaction of 1-Benzoyl-2-naphthylamine (7) and Diethyl Malonate.

To a solution of 20 ml. of diphenyl ether and 20 ml. (0.13 mole) of diethyl malonate preheated to 165-175° was added 4.0 g. (0.016 mole) of 1-benzoyl-2-naphthylamine over a period of 0.5 hour. The mixture was held at the same temperature range for an additional period of 1 hour. The solvent and excess of diethyl malonate were removed by distillation under reduced pressure. The residue was extracted with two 100 ml. portions of boiling carbon tetrachloride and the insoluble solid was collected by filtration. The fraction soluble in carbon tetrachloride was recrystallized once from ethanol-water and twice from pyridine-water to give 0.7 g. (12%) of 1-phenyl-2-carboethoxybenzo[*f*]quinolin-3-ol (II), m.p. 269-270°. The infrared spectrum of this compound showed carbonyl absorptions at 5.89 and 6.16 μ; nmr spectrum (TFA), aromatic protons at 1.41-2.70 (11.6 H), methylene group at 5.69 (quartet, 2H) and methyl group at 9.02 (triplet, 3H) τ.

Anal. Calcd. for $C_{22}H_{17}NO_3$: C, 76.95; H, 4.99; N, 4.08. Found: C, 76.95; H, 4.99; N, 4.07.

One recrystallization of the carbon tetrachloride insoluble fraction from pyridine-ethanol afforded 1.3 g. (30%) of 2-(1-phenyl-3-hydroxy-2-benzo[*f*]quinolylamido)-1-benzoylnaphthalene (III), m.p. >300°, (see below).

When the same amounts of 1-benzoyl-2-naphthylamine and diethyl malonate were heated at 180-185° for 1 hour in the absence of diphenyl ether, 3.9 g. (90%) of III was obtained which crystallized in the cooled reaction mixture. The infrared spectrum of this compound showed unresolved broad carbonyl absorption at 5.99-6.20 and >N-H absorption at 3.05 μ; nmr spectrum (TFA), >N-H group at 1.09 (broad, 1H) and aromatic protons at 1.63-2.77 (22H) τ. Three recrystallizations of the crude product from a pyridine-ethanol mixture furnished the analytical sample.

Anal. Calcd. for $C_{37}H_{24}N_2O_3$: C, 81.60; H, 4.44; N, 5.14. Found: C, 81.35; H, 4.43; N, 5.00.

When the reaction with the same amounts of the starting material was carried out in the absence of diphenyl ether at 125-130° for 3 hours, 3.7 g. of a crude product mixture, m.p. 100-130°, was obtained by allowing a solution of the reaction mixture in 20 ml. of ether and 150 ml. of ligroin (b.p. 90-120°) to crystallize at −10° for a period of 24 hours. Two recrystallizations of this material from methylcyclohexane afforded 2.6 g. (45%) of 2-carboethoxyacetamido-1-benzoylnaphthalene (IV), m.p. 108-110°. The remaining components were not identified. The infrared spectrum of IV showed > N-H absorption at 3.07 and and carbonyl absorptions at 5.81 and 6.05 μ; nmr spectrum (TFA), > N-H at 0.39 (singlet, 1H), aromatic protons at 1.84-2.67 (11.5 H), methylene adjacent to methyl at 5.74 (quartet, 2H), methylene between two carbonyls at 6.34 (singlet, 2H) and methyl at 8.74 (triplet, 3 H) τ. Further recrystallization from methylcyclohexane provided the analytical sample, m.p. 111-112°.

Anal. Calcd. for $C_{22}H_{19}NO_4$: C, 73.13; H, 5.26; N, 3.89. Found: C, 72.94; H, 5.34; N, 4.00.

1-Phenyl-2-benzoylbenzo[*f*]quinolin-3-ol (V).

A mixture of 3.0 g. (0.012 mole) of 1-benzoyl-2-naphthylamine and 20 ml. of ethyl benzoylacetate was heated at 170-175° for 2 hours. The resulting mixture was poured into 150 ml. of boiling methanol. The product crystallized on cooling to give 2.8 g. (62%) of white needles, m.p. > 300°. The analytical sample was prepared by further recrystallizations from ethanol. The infrared

spectrum of this compound showed broad carbonyl absorption centered at 6.21 μ; nmr spectrum (TFA) indicated only aromatic protons.

Anal. (8) Calcd. for $C_{26}H_{17}NO_2$: C, 83.18; H, 4.56; N, 3.73; mol. wt., 375.4. Found: C, 82.55; H, 4.74; N, 3.77; mol. wt. 374.

1-Phenyl-2-acetylbenzo[*f*]quinolin-3-ol (VI).

A mixture of 5.0 g. (0.02 mole) of 1-benzoyl-2-naphthylamine and 20 ml. of ethyl acetoacetate was heated at 160-165° for 1.5 hours. Boiling ethanol was added to the reaction mixture until solution was achieved. The product crystallized at room temperature to give 5.5 g. (88%) of white needles, m.p. 288-289°. The infrared spectrum showed carbonyl absorptions at 5.92 and 6.20 μ; nmr spectrum (TFA), aromatic protons at 1.46-2.68 (11 H) and methyl group at 7.80 (singlet, 3 H) τ.

Anal. Calcd. for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47. Found: C, 80.62; H, 5.00; N, 4.38.

1-Phenyl-3-hydroxy-2-benzo[*f*]quinolineglyoxylic Acid (VII).

To the solution of 15.0 g. (0.048 mole) of VI in 500 ml. of refluxing dioxane was added in portions 15.0 g. (0.14 mole) of selenium dioxide in 20 ml. of water over 0.5 hours. The mixture was refluxed for 15 hours. After removal of the solvent, the dark residue was washed with approximately 300 ml. of water and extracted with 300 ml. of 10% aqueous potassium hydroxide solution. Elemental selenium was removed by filtration. The alkaline filtrate was acidified with concentrated hydrochloric acid to give 14.9 g. of the crude product, m.p. 253-258° dec. Repeated recrystallizations from an ethanol-water mixture gave fluffy yellow needles, m.p. 260-261° dec. The infrared spectrum showed broad carboxylic acid absorption at 3.33-3.53 and carbonyl absorptions at 5.90, 6.15 and 6.23 μ; nmr spectrum (TFA) indicated only aromatic protons.

Anal. Calcd. for $C_{21}H_{13}NO_4$: C, 73.46; H, 3.82; N, 4.08. Found: C, 73.74; H, 4.08; N, 4.29.

1-Phenyl-3-hydroxy-2-benzo[*f*]quinolineacetic Acid (VIII).

A mixture of 8.0 g. (0.023 mole) of VII, 6.0 g. of red phosphorus and 35 ml. of constant-boiling hydroiodic acid was refluxed for 5 hours. The hot reaction mixture was filtered. The filtrate was added to approximately 200 ml. of water to precipitate the organic acid. One recrystallization from methanol afforded 4.6 g. (60%) of light-yellow crystals, m.p. 296-299°. An analytical sample, m.p. 298-300°, was obtained by further recrystallization. The infrared spectrum showed broad carboxylic acid absorption at 3.35-3.54 μ; nmr spectrum (TFA), aromatic protons at 1.60-2.70 (11H) and methylene group at 6.08 (singlet, 2H) τ.

Anal. Calcd. for $C_{21}H_{15}NO_3$: C, 76.58; H, 4.59; N, 4.25. Found: C, 76.42; H, 4.48; N, 4.32.

The acid was also obtained in 8% yield from the Willgerodt reaction of VI with morpholine and sulfur followed by basic hydrolysis in ethanol. The presence of excess sulfur complicated the purification of the product.

α,α-Dichloro-1-phenyl-3-hydroxy-2-benzo[*f*]quinolineacetic Acid Lactone (IX).

A mixture of 0.6 g. (1.8 mmole) of pure VIII, 1.0 g. phosphorus pentachloride and 10 ml. of phosphorus oxychloride was heated to reflux for 3 hours. Excess phosphorus oxychloride dark-brown residue was decomposed with ice-water. The yellow solid collected was washed with 100 ml. of warm acetone to remove a small amount of tarry substance. The acetone insoluble solid was recrystallized from fresh acetone to give 0.4 g. (58%) pale-yellow needles, m.p. 268-270°. Further recrystallization did not change the melting point. The infrared spectrum of IX showed carbonyl absorption at 5.51 μ; the nmr spectrum (TFA) indicated only the presence of aromatic protons.

Anal. Calcd. for $C_{21}H_{11}Cl_2NO_2$: C, 66.33; H, 2.92; N, 3.68; Cl, 18.65. Found: C, 66.10; H, 3.08; N, 3.66; Cl, 18.75.

Under the same reaction conditions, this lactone was also obtained in 55% yield from VII. The products from both reactions were identical in respect to melting point, mixed melting point and infrared spectrum.

Hydrolysis of IX.

To the suspension of 0.3 g. (0.79 mmole) of IX in 25 ml. of boiling ethanol was added approximately 20 ml. of 5% aqueous potassium carbonate solution. The mixture was refluxed for a period of one hour after which 10 drops of 10% aqueous potassium hydroxide solution was added. Heating was continued for about two minutes until a clear solution was observed. The mixture was poured into a beaker and most of the ethanol was removed by means of a stream of cool air. The alkaline solution was treated with activated charcoal, filtered and acidified with concentrated hydrochloric acid to give 0.1 g. (37%) of VII. The organic acid obtained was identical in respect to melting point and infrared spectrum with an authentic sample prepared as described above.

1-Phenyl-2-acetyl-3-chlorobenzo[*f*]quinoline (X).

A mixture of 10.0 g. (0.032 mole) of VI and 35 ml. of phenylphosphonic dichloride was heated at 165-175° for 0.5 hours. The resulting dark solution was cooled and poured into 300 ml. of ice-water containing 15 ml. of concentrated ammonium hydroxide. Additional base was added in small portions during the decomposition to maintain a weakly basic medium. After 2 hours the mixture was repeatedly extracted with chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate. The crude product obtained after removal of solvent was recrystallized from methanol to give 8.1 g. (73%) of a white solid, m.p. 168-169°. The infrared spectrum exhibited carbonyl absorption at 5.90 μ; nmr (deuteriochloroform), aromatic protons at 2.10-3.10 (11 H), methyl at 7.91 (singlet, 3H) τ.

Anal. Calcd. for $C_{21}H_{14}ClNO$: C, 76.05; H, 4.22; N, 4.22; Cl, 10.70. Found: C, 75.95; H, 4.37; N, 4.14; Cl, 10.55.

Chlorination of VI with Phosphorus Oxychloride.

A mixture of 3.1 g. (0.01 mole) of VI, 25 ml. of phosphorus oxychloride and 0.5 ml. of *N,N*-dimethylaniline was refluxed for 4 hours. After the volatile reagents were removed by vacuum distillation, the syrupy residue was decomposed in ice-water while ammonium hydroxide was added to maintain a slightly basic medium. The yellow precipitate was collected, washed with water and dried in a desiccator over-night. This material was extracted with 250 ml. of acetone, a small amount of insoluble material being discarded. The crude product obtained after removal of acetone was recrystallized twice from benzene-methanol to give 1.5 g. (47%) of 1-phenyl-2-ethynyl-3-chlorobenzo[*f*]quinoline (XI) as almost white needles, m.p. 179-181°. The infrared spectrum showed strong C≡C-H peak at 3.04, weak C≡C absorption at 4.75 μ; nmr (deuteriochloroform), aromatic protons at 2.03-3.04 (11 H). acetylenic proton at 6.07 (sharp singlet, 1 H) τ.

Anal. (8) Calcd. for $C_{21}H_{12}ClN$: C, 80.38; H, 3.80; N, 4.46; Cl, 11.23; mol. wt. 313.7. Found: C, 80.90, 79.32; H, 3.99, 3.99; N, 4.56, 4.50; Cl, 11.86; mol. wt. 318.

Evaporation of the benzene-methanol mother liquors above followed by recrystallization from methanol gave 0.4 g. (12%) of X.

Catalytic Hydrogenation of X.

A mixture of 4.0 g. (0.012 mole) of X, 100 ml. of methanol, 150 ml. of dimethylformamide, 1 g. of potassium hydroxide and 0.5 g. of 5% palladium-charcoal was agitated at an initial hydrogen pressure of 30 psi for 2 hours. The catalyst was removed by filtration and the filtrate was concentrated to about 100 ml. The crude product mixture, precipitated by addition of 300 ml. of water, was collected and dried. This material was separated into two fractions in chloroform. The solid material insoluble in chloroform was recrystallized from ethyl acetate to give 0.9 g. of an unidentified compound, m.p. 253-256°. The chloroform-soluble fraction was recrystallized twice from hexane affording 1.0 g. (27%) of 1-phenyl-2-acetylbenzo[*f*]quinoline (XII) as white needles, m.p. 140-142°. The infrared spectrum of XII showed carbonyl absorption at 5.92 μ; nmr (deuteriochloroform) aromatic protons of benzene rings at 2.03-3.03 (11 H), ring proton adjacent to nitrogen at 1.09 (singlet, 1H) and methyl group at 8.13 (singlet, 3H) τ.

Anal. Calcd. for $C_{21}H_{15}NO$: C, 84.82; H, 5.09; N, 4.71. Found: C, 84.70; H, 5.23; N, 4.60.

1-Phenyl-2-carboethoxy-3-methylbenzo[*f*]quinoline (XIII).

A solution of 37.1 g. (0.15 mole) of 1-benzoyl-2-naphthylamine and 20.8 g. (0.16 mole) of ethyl acetoacetate in 150 ml. of glacial acetic acid containing 0.5 ml. of concentrated sulfuric acid was refluxed for 2 hours. The reaction mixture was cooled and poured onto ice. Concentrated ammonium hydroxide was then added slowly until the mixture became basic to litmus. The gummy substance was stirred in an ice-bath until a solid precipitate was formed. The crude product was recrystallized from aqueous ethanol to give 36.3 g. (71%) of cream-colored needles, m.p. 101-102°. The infrared spectrum indicated carbonyl absorption at 5.88 μ; nmr (deuteriochloroform), aromatic protons at 2.03-3.05 (11 H), methylene of ethyl at 5.98 (quartet, 2H), methyl of ethyl at 9.04 (triplet, 3 H) and 3-methyl group at 7.22 (singlet, 3 H) τ.

Anal. Calcd. for $C_{23}H_{19}NO_2$: C, 80.91; H, 5.61; N, 4.10. Found: C, 80.94; H, 5.70; N, 4.11.

8-Methyl-13*H*-benzo[*f*]indeno[2,1-*c*]quinoline-13one (XVII).

A solution of 3.0 g. (9 mmoles) of XIII in 25 ml. of concentrated sulfuric acid was heated in a steam-bath for 2 hours. The resulting brown solution was cooled, poured onto ice and basified with concentrated ammonium hydroxide. The crude product was recrystallized once each from acetone-water and benzene-hexane to give 1.7 g. (66%) of fluffy orange needles, m.p. 166-168°. The infrared spectrum showed carbonyl absorption at 5.95 μ; nmr (deuteriochloroform), aromatic protons at 1.15-2.80 (10 H) and methyl at 7.05 (3 H) τ.

Anal. Calcd. for $C_{21}H_{13}NO$: C, 85.40; H, 4.44; N, 4.74. Found: C, 85.25; C, 4.24; N, 4.62.

1-Phenyl-2-carboethoxy-3-formylbenzo[*f*]quinoline (XIV).

A mixture of 20.0 g. (0.059 mole) of XIII, 10.0 g. (0.09 mole) of selenium dioxide and 75 ml. of glacial acetic acid was refluxed for 2 hours. The resulting mixture was filtered hot to remove elemental selenium. The aldehyde crystallized on cooling. Two recrystallizations from ethanol including treatment with decolorizing carbon afforded 14.5 g. (69%) of an almost white solid, m.p. 171-174°. The infrared spectrum showed broad carbonyl absorption at 5.85-5.93; nmr (deuteriochloroform), aromatic protons at 1.92-2.95 (11 H), aldehydic proton at -0.30 (singlet, 1 H); methylene at 5.82 (quartet, 2 H) and methyl at 8.90 (triplet, 3 H).

The analytical sample was prepared by column chromatography, m.p. 173-175°.

Anal. Calcd. for $C_{23}H_{17}NO_3$: C, 77.73; H, 4.82; N, 3.94. Found: C, 77.64; H, 4.96; N, 3.88.

1-Phenylbenzo[*f*]quinoline-2,3-dicarboxylic Acid (XV).

A mixture of 16.0 g. (0.045 mole) of XIV, 400 ml. of 10% sodium hydroxide and 30 ml. of 30% hydrogen peroxide was heated cautiously with stirring in a steam-bath. Once the vigorous reaction began, the mixture was withdrawn from the steam-bath and allowed to stand at room temperature until the foaming subsided. Heating was resumed for an additional period of 4 hours during which the sodium salt gradually precipitated out. The mixture was cooled to about 45° and concentrated hydrochloric acid was added until most of the solid dissolved. The resulting suspension was filtered warm and the insoluble material was washed with 250 ml. of hot water. The organic acid was precipitated by acidifying the cool alkaline filtrate with hydrochloric acid. It was recrystallized from acetone-water to give 11.3 g. (73%) of almost white needles. The material melted slowly at 150-160°, re-solidified upon further heating and finally melted at 270-273°. Compound XV could also be prepared in somewhat lower yield by oxidizing XIV in a solution of silver nitrate and sodium hydroxide at 50°. The infrared spectrum of XV showed broad carboxylic acid absorption at 3.27-3.50 and broad carbonyl group at 5.88 μ. The nmr spectrum, measured in THF at the region 0-5 τ, indicated acid protons at 1.10 (unresolved broad peak, 2 H) and aromatic protons at 1.90-2.98 (11 H) τ.

Anal. (9) Calcd. for $C_{21}H_{13}NO_4$: C, 73.47; H, 3.81; N, 4.08. Found: C, 74.88; H, 4.07; N, 4.17.

1-Phenylbenzo[*f*]quinoline-2-carboxylic Acid (XVI).

This acid was prepared in quantitative yield by heating XV alone at 170-180° for 3 hours. The product obtained had m.p. at 270-273° and because of its insolubility in organic solvents, it was used in the next step without further purification.

13*H*-Benzo[*f*]indeno[2,1-*c*]quinoline-13-one (XVIII).

A solution of 16.8 g. (0.053 mole) of XVI in 75 ml. of concentrated sulfuric acid was heated in a steam-bath for 4 hours. The resulting brown syrup was cooled, poured onto ice and basified with concentrated ammonium hydroxide. The orange solid was collected, dried and extracted with 300 ml. of chloroform. After removal of solvent, the residue was recrystallized from acetone-methanol to give 9.3 g. (59%) of yellow needles, m.p. 203-205°. The infrared spectrum indicated carbonyl absorption at 5.94 μ; nmr (deuteriochloroform) phenylic protons at 1.12-2.64 (10 H) and proton adjacent to nitrogen at 0.95 (singlet, 1 H) τ.

Anal. Calcd. for $C_{20}H_{11}NO$: C, 85.40; H, 3.90; N, 4.98. Found: C, 85.54; H, 4.07; N, 4.87.

REFERENCES

(1) This work was supported in part by Grant GM 11644 from the National Institutes of Health.

(2) For a review of the Friedlander synthesis, see R. C. Elderfield, "Heterocyclic Compounds," Vol. 4, R. C. Elderfield, ed., John Wiley and Sons, Inc., New York, New York, 1950, pp. 45-47, 209.

(3) W. Borsche and F. Sinn, *Ann. Chem.*, 538 283 (1939).

(4) For examples of acid-catalyzed Friedlander condensation

of *o*-aminobenzophenone, see (a) E. A. Fehnel, *J. Org. Chem.*, 31, 2899 (1966); (b) E. A. Fehnel and D. E. Cohn, *ibid.*, 31, 3852 (1966).

(5) E. A. Fehnel, J. A. Dryrup and M. B. Davidson, *ibid.*, 23, 1996 (1958).

(6) Selenium dioxide oxidation of o-acetylbiphenyl was reported to give 9,10-phenanthrenequinone. See, R. C. Fuson and R. L. Talbott, *ibid.*, 26, 2764 (1961).

In the present work, only the benzoquinolineglyoxylic acid was isolated even when the oxidation was carried out with a limited amount of selenium dioxide under a nitrogen atmosphere.

(7) M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, 73, 436 (1951).

(8) A better value could not be obtained after repeated analyses.

(9) A better value could not be obtained after repeated analyses. Contamination with the monocarboxylic acid XVI appears to occur.

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