EXPERIMENTAL

4,7-Phenanthroline. All of the operations in this synthesis were carried out in a well ventilated hood and behind a safety shield. A 12-l. flask equipped with a sealed stirrer and a 400-mm. jacket Allihin condenser is charged with 170 g. *N,N'*-diacetyl-*p*-phenylenediamine, 800 g. 96% sulfuric acid, 200 g. glycerol, 150 g. nitrobenzene, and 84 g. ferrous sulfate heptahydrate. The flask is heated with stirring until the heat of reaction is sufficient to maintain the mixture at steady reflux. After the reaction subsides the mixture is refluxed for 2 hr., diluted with 2 l. of water, and the excess nitrobenzene steam distilled. The strongly acid solution is treated twice with Norite and filtered while hot through an asbestos mat. The liquid is cooled and made basic with ammonium hydroxide. The crude phenanthroline is precipitated as a black, semicrystalline mass which is filtered and dried. The crude product is sewed into a cloth sack and extracted with ligroin (b.p. 66–75°) in a Soxhlet extractor to give 120 g. (75%) of white, crystalline 4,7-phenanthroline, m.p. 173°.

3-(p-Tolyl)-4,7-phenanthroline. A solution of 50 ml. anhydrous ethyl ether and 4.3 g. (0.025 mole) of freshly distilled *p*-bromotoluene is added very slowly from a dropping funnel to a stirred suspension of 0.4 g. (0.057 g.-atom) of finely chopped lithium ribbon in 100 ml. of anhydrous ether. The reaction is vigorous and the lithium is consumed in 1 hr. The *p*-tolyl lithium reagent thus formed is added dropwise to a stirred solution of 4.7 g. (0.025 M) of 4,7-phenanthroline in 50 ml. thiophene-free benzene. Initially a red complex is formed which after standing 24 hr. fades to orange. The suspension is shaken in a separatory funnel with 200 ml. water which causes the precipitate to pass into the ether-benzene phase. Evaporation of the solvent leaves the yellow dihydrophenanthroline which vigorously dehydrogenates upon the addition of 6*N* hydrochloric acid to 3-(*p*-tolyl)-4,7-phenanthroline. Two recrystallizations from anisole gave 5.3 g. (80%) of buff needles, m.p. 181°.

Anal. Calcd. for $C_{19}H_{14}N_2$: N, 10.36. Found: N, 10.49, 10.48.

The other products listed in the tables were prepared by the same procedure using the appropriate aryllithium reagent. The aryl bromides were distilled just prior to use and the reactions were run under oxygen-free nitrogen. The benzo[*f*]quinoline was prepared as previously described.[16]

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, INDIANA UNIVERSITY]

Nitration of 3-Phenylquinoline[1,2]

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Mononitration of 3-phenylquinoline gave as the only isolatable product, 3-(*p*-nitrophenyl)quinoline. Further nitration gave two products; the main dinitro compound was proven to be 5-nitro-3-(*p*-nitrophenyl)quinoline. The structure of this substance was proven by synthesis. A modified Skraup reaction using α-methylacrolein diacetate gave 3-methylquinoline which on nitration resulted in 5- and 8-nitro-3-methylquinoline. The former was oxidized to 5-nitro-3-quinolinecarboxylic acid which was converted to 5-nitro-3-aminoquinoline by way of the azide and urethan. Coupling 5-nitro-3-quinolinediazo hydroxide with dimethylamine gave the corresponding dimethyltriazeno compound which upon decomposition in benzene, produced 5-nitro-3-phenylquinoline. Nitration of the latter gave 5-nitro-3-(*p*-nitrophenyl)quinoline. The synthesis of many other quinoline compounds related to this work is described.

It has been reported by Koenigs and Nef[4] that the nitration of 4-phenylquinoline gave about 60% *p*-nitrophenyl-, 30% *m*-nitrophenyl- and 5% of the *o*-nitrophenyl-quinoline. These were called α-, β-, and γ-nitro compounds. LeFevre and Mathur[5] found that nitration of 2-phenylquinoline gave about 60% *p*-nitro- and 30% of the *m*-nitro-phenyl quinoline. The latter authors also reported a quantitative yield of 2-(*m*-nitrophenyl)quinolinium methosulfate by the nitration of 2-phenylquinolinium methosulfate. Similar ratios of meta and para substitution have been reported by Forsyth and Pyman[6] for the nitration of 2-phenyl- and 4-phenylpyridine. The meta substitution is explained on the basis of ammonium salt formation while the para orientation is explained by attack on the dissociated molecule. The similarity of behavior in the 2-phenyl- and 4-phenyl-quinoline and -pyridine may be attributed to resonance through the vinylogous position in the pyridine ring. A much smaller amount of meta substitution occurred on nitration[7] of 2-benzyl- and 4-benzylpyridine. However, on the basis of vinylogy, it was quite surprising not to

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have meta substitution occurring in the nitration of 2-styrylpyridine.[8] Since it has been reported[6] that 3-phenylpyridine gave no meta nitration product, it was of interest to determine whether or not similar behavior might be shown by 3-phenylquinoline. It was also of interest to determine whether introduction of a second nitro group would occur in the phenyl group or in the quinoline portion of the molecule.

Of the several methods reported[9a-e] for the preparation of 3-phenylquinoline, the best one with respect to yield and the number of steps involved is the Pfitzinger reaction between isatin and phenylpyruvic acid.[9d] This gave consistently a yield of 68–70% of 3-phenyl-2,4-quinolinedicarboxylic acid which on decarboxylation gave 70–75% of purified 3-phenylquinoline. The preparation of β-phenylpyruvic acid by the acid hydrolysis of ethyl ethoxalylphenylacetate[10] according to the procedure of Wislicenus[11] proved to be much easier than the benzalazlactone method.[12]

The treatment of 3-phenylquinoline in sulfuric acid with one equivalent of concentrated nitric acid gave consistently a 78–80% yield of crude nitration product which on recrystallization yielded 64–68% of a pure mononitro compound. Some 3-phenylquinoline was always recovered. The *p*-nitrophenyl orientation was shown by oxidation of the mononitro compound from which only *p*-nitrobenzoic acid was isolated. It was not possible to show the presence of other nitrophenylquinolines; one can only say that the major product was 3-(*p*-nitrophenyl)-quinoline. The direct approach to the synthesis of 3-(*p*-nitrophenyl)quinoline from *p*-nitrophenylpyruvic acid by the Pfitzinger reaction failed. Only brown resinous polymer-like material was obtained. Another confirmatory structure proof was obtained by conversion of the mononitro compound to the *N*-oxide and this was rearranged in boiling acetic anhydride to 3-(*p*-nitrophenyl)carbostyril which had been reported by Pschorr.[13]

The nitration of 3-(*p*-nitrophenyl)quinoline in sulfuric acid with one equivalent of nitric acid gave two dinitro compounds, I and II. The lower melting compound, I, was obtained in a 63–65% yield and the higher melting isomer, II, was generally about a 10% yield. No other pure dinitro compounds could be isolated. Proof that in both I and II, the second nitro group was in the quinoline portion of the molecule came through oxidation studies. Both substances gave *p*-nitrobenzoic acid. All attempts at oxidation to isolate a nitroanthranilic acid were unsuccessful; either the unchanged dinitrophenylquinoline and *p*-nitrobenzoic acid or only *p*-nitrobenzoic acid were isolated. Even oxidation attempts with the carbostyril derived from I did not yield an anthranilic acid.

One obvious synthetic route to the structure proof is through the nitroisatins. 7-Nitroisatin was prepared according to the procedure of Buchman,[14] but it would not undergo the Pfitzinger reaction with phenylpyruvic acid. Another method involved the use of chloroisatins; 4- and 6-chloroisatin[15,16] were subjected to the Pfitzinger reaction with phenylpyruvic acid to yield 5- and 7-chloro-3-phenyl-2,4-quinolinedicarboxylic acids which were decarboxylated to the corresponding 5- and 7-chloro-3-phenylquinoline. Nitration of 5-chloro-3-phenylquinoline gave 5-chloro-3-(*p*-nitrophenyl)-quinoline. However, attempted reduction of one nitro group in I using sodium sulfide was not successful since a pure mononitro monoamino phenylquinoline could not be isolated. Thus, structure proof through use of the chloro compound was not possible.

On the assumption that perhaps I might be 5-nitro-3-(*p*-nitrophenyl)quinoline, proof of structure through synthetic means from a 5-nitroquinoline was attempted. 3-Methylquinoline was prepared according to the procedure of Untermohlen[17] and this was nitrated to give a 78% yield of mixed nitro-3-methylquinolines which were separated by means of the nitrate salts. One nitration product proved to be 8-nitro-3-methylquinoline[18] and the other one was shown to be the 5-nitro compound. Oxidation of this substance to the nitro-3-quinolinecarboxylic acid and then decarboxylation, gave 5-nitroquinoline. Conversion of 5-nitro-3-quinolinecarboxylic acid to the axide through the acid chloride and decomposition of the azide in ethyl alcohol gave the urethan which was hydrolyzed easily to 5-nitro-3-aminoquinoline. The Hofmann hypohalite method for preparing the 3-amino compound was not satisfactory. Also, the azide could not be prepared satisfactorily from 5-nitro-3-quinolinecarbohydrazide. When 5-nitro-3-aminoquinoline was diazotized then coupled with dimethylamine and the 5-nitro-3-(dimethyltriazeno)quinoline decomposed in benzene, 5-nitro-3-phenylquinoline was obtained. Direct decomposition of the diazohydroxide compound in benzene with alkali, did not give any isolatable 5-nitro-3-phenylquinoline. Nitration of

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5-nitro-3-phenylquinoline gave a dinitro compound which did not depress the melting point of I.

EXPERIMENTAL[19]

3-Phenyl-2,4-quinolinedicarboxylic acid. Ethyl phenylethoxalylacetate[10] was hydrolyzed according to the method of Wislicenus.[11] The ester (0.4 mole) was heated under gentle refluxing with 1.25 l. of 10% sulfuric acid for 24 hr. The aqueous layer was separated from the oil and it was allowed to stand in a refrigerator for a day then the precipitated phenylpyruvic acid was removed by filtration. The oily layer, which had been separated, was subjected to further hydrolysis to yield an additional quantity of phenylpyruvic acid. The yield was 45–55%.

A stirred solution of 35.5 g. (0.216 mole) of phenylpyruvic acid and 32.1 g. (0.218 mole) of isatin in 190 ml. of 15% sodium hydroxide was heated gently for 3 hr. The hot solution was filtered and the cold filtrate was acidified with 2*N* hydrochloric acid. The brown colored granular solid was collected on a filter and was washed with water. The solid was shaken with 600 ml. of saturated sodium bicarbonate solution, filtered to remove the isatin, and the filtrate was acidified with hydrochloric acid. The yield of 3-phenyl-2,4-quinolinedicarboxylic acid was 43.7 g. (68%). The isatin recovered was 13.8 g.

3-Phenylquinoline. A stirred mixture of 1250 ml. of paraffin oil, 254 g. (0.86 mole) of 3-phenyl-2,4-quinolinedicarboxylic acid and 87 g. of copper bronze was heated to 280° at a rate (4 hr.) so as to prevent excessive frothing. When there was no further evolution of gas, the solution was cooled to room temperature, the oil was diluted with 800 ml. of dry ether, the solution was filtered to remove the copper, and the latter was washed with 300 ml. of dry ether. Dry hydrogen chloride was bubbled into the paraffin oil–ether solution until no further precipitate was formed. The white solid was collected by filtration and washed with two 150-ml. portions of dry ether. The hydrochloride was treated with 10% ammonia solution, the solution extracted twice with ether and the latter was dried with magnesium sulfate. After removal of the ether, the substance was distilled at 165–168° (1.5–2 mm.) yielding 207 g. (71%) of a pale yellow liquid which solidified when it cooled. The 3-phenylquinoline was recrystallized from hexane to yield fine white needles, m.p. 51–52°. This value has been reported by Adams.[9e]

7-Chloro-3-phenylcinchoninic acid. A solution of 2.8 g. (0.015 mole) of 6-chloroisatin[15] and 2.6 g. (0.016 mole) of phenylpyruvic acid in 40 ml. of 15% sodium hydroxide solution was heated for 2 hr. At the end of the time, the hot solution was filtered and the filtrate was acidified with hydrochloric acid. The solid was dissolved in sodium bicarbonate solution, then reprecipitated with dilute hydrochloric acid to yield 4.4 g. of 7-chloro-3-phenyl-2,4-quinolinedicarboxylic acid. The dicarboxylic acid was heated for 5–8 min. in boiling nitrobenzene. After the solution cooled, it was diluted with ether, the solid was collected on a filter and it was washed with two 25-ml. portions of ether. The yield was 3.7 g. (85%), m.p. 286–288°. After recrystallization from nitromethane, the substance melted at 287.5–288.5°.

Anal. Calcd. for $C_{16}H_{10}ClNO_2$: Cl, 12.52. Found: Cl, 12.72.

5-Chloro-3-phenyl-2,4-quinolinedicarboxylic acid. A solution of 1.84 g. (0.01 mole) of 4-chloroisatin[15] and 1.8 g. (0.011 mole) of phenylpyruvic acid in 39 ml. of 15% sodium hydroxide was refluxed for 2 hr. The hot solution was filtered, the filtrate was acidified with dilute hydrochloric acid and solid was collected on a filter. After solution in dilute sodium bicarbonate and reprecipitation with acid, the yield of the dicarboxylic acid was 2.45 g. (75%). It was recrystallized from benzene-ethanol (9:1), giving needles which melted at 189–190°.

Anal. Calcd. for $C_{17}H_{10}ClNO_4$: Cl, 10.84. Found: Cl, 10.87.

7-Chloro-3-phenylquinoline and 5-chloro-3-phenylquinoline were prepared by decarboxylation of the corresponding 2,4-quinolinedicarboxylic acid in paraffin oil in exactly the same procedure as used for the preparation of 3-phenylquinoline.

5-Chloro-3-phenylquinoline. Recrystallized from methanol as light yellow needles, m.p. 112–113°.

Anal. Calcd. for $C_{15}H_{10}ClN$: Cl, 14.82. Found: Cl, 15.20.

7-Chloro-3-phenylquinoline. Recrystallized from dilute ethyl alcohol as short needles, m.p. 111–112°.

Anal. Calcd. for $C_{15}H_{10}ClN$: Cl, 14.82. Found: Cl, 14.89.

Nitration of 3-phenylquinoline. Concentrated sulfuric acid (110 ml. was cooled to 0° and stirred while 20.5 g. (0.1 mole) of 3-phenylquinoline were added portion-wise. After the substance was dissolved the solution was cooled to −10° and a cold solution of 6.5 ml. of concentrated nitric acid in 25 ml. of concentrated sulfuric acid was added dropwise, with stirring, over a period of 3 hr. The nitration mixture was poured onto 750 ml. of ice and water, then it was neutralized with concentrated ammonia water (400 ml.). The solid was collected by filtration, washed, and dried. The yield was 23 g. The solid was refluxed with 700 ml. of benzene, filtered to remove insoluble material, and the solution was concentrated to about 400 ml. by distillation. After several recrystallizations and concentration of the mother liquors to about one-half the volume to obtain further solid for recrystallization, 16 g. (64%) of dark yellow needles were obtained which melted at 178–179°.

Anal. Calcd. for $C_{15}H_{10}N_2O_2$: N, 11.20. Found: N, 11.15.

Three grams of the nitro compound was added to a solution of 200 ml. of 10% sulfuric acid and 10 g. of potassium permanganate. The solution was refluxed for 30 min. After cooling, the permanganate was destroyed with sodium bisulfite and the decolorized solution was filtered. The solid was washed with water and recrystallized from dilute (1:1) ethyl alcohol. The substance melted at 236–237°; a mixed melting point determination with authentic *p*-nitrobenzoic acid gave no depression. The benzanilide was prepared and it showed no melting point depression with authentic *p*-nitrobenzanilide, m.p. 211–212°.

3-(p-Nitrophenyl)quinolinium methiodide. Five grams of 3-(*p*-nitrophenyl)quinoline was heated under reflux for several hours with 10 g. of methyl iodide. The crude methiodide was recrystallized twice from ethyl alcohol, m.p. 247–249°.

Anal. Calcd. for $C_{16}H_{13}IN_2O_3$: N, 7.14. Found: N, 7.29.

1-Benzyl-3-(p-nitrophenyl)quinolinium chloride. 3-(*p*-Nitrophenyl)quinoline (0.5 g.) in 15 ml. of benzyl chloride was heated for 3 hr., then cooled, filtered, and washed with ether. Two recrystallizations from 50 ml. of a 1:1 solution of methyl alcohol–ethyl acetate gave a substance melting at 242–243°.

Anal. Calcd. for $C_{22}H_{17}ClN_2O_2$: N, 7.43. Found: N, 7.53.

1-Benzyl-3-phenylquinolinium chloride. This was prepared exactly as described for the *p*-nitrophenyl compound except that 5 ml. of benzyl chloride were used. It was recrystallized from absolute ethanol–ethyl acetate solution, m.p. 235–236°.

Anal. Calcd. for $C_{22}H_{18}ClN$: Cl, 10.70. Found: Cl, 10.85.

3-(p-Nitrophenyl)quinolinium picrate. The picrate was prepared by standard procedure; recrystallized from ethyl alcohol, the substance melted at 230.5–231.5°.

Anal. Calcd. for $C_{21}H_{13}N_5O_9$: N, 14.61. Found: N, 14.62.

1-Methyl-3-(p-nitrophenyl)-2-quinolone. To a stirred suspension of 5 g. (0.013 mole) of 3-(*p*-nitrophenyl)quinolinium methiodide in 300 ml. of water at 0° was added simultaneously over a 20-min. period, a solution of 13.2 g. (0.04 mole) of potassium ferricyanide in 75 ml. of water and 3.2 g. (0.08 mole) of sodium hydroxide in 50 ml. of water. The cold solution was stirred for 3 hr. The solid was collected, dried, and

(19) Microanalyses performed by Miss Joanna Dickey of this department.

recrystallized twice from ethyl alcohol to yield 1.5 g. (42%) of yellow needles which melted at 225–226°.

Anal. Calcd. for $C_{16}H_{12}N_2O_3$: N, 10.00. Found: N, 10.28.

1-Methyl-3-phenyl-2-quinolone. This substance was prepared from 10 g. (0.029 mole) of 3-phenylquinolinium methiodide[9c] as described for the *p*-nitrophenyl compound. Recrystallized from dilute ethyl alcohol and twice from ligroin (63–90°) gave a 28% yield of white prisms, m.p. 140–141°.

Anal Calcd. for $C_{16}H_{13}NO$: N, 5.96. Found: N, 6.13.

3-(p-Nitrophenyl)quinoline-1-oxide. A solution of 9.8 g. (0.04 mole) of 3-(*p*-nitrophenyl)quinoline in 60 ml. of glacial acetic acid and 12 ml. (0.15 mole) of 30% hydrogen peroxide was warmed at 65–70° for 3 hr. The solution was concentrated in vacuum, then treated with 200 ml. of saturated sodium carbonate solution and the warm aqueous suspension was extracted with three 200-ml. portions of chloroform. After drying, the chloroform solution was concentrated to 150 ml., then cooled, and the solid was collected. Further concentration gave a second portion of solid. The crude substance (3.5 g.) was recrystallized five times from benzene to yield 2.6 g. (25%) of white needles which melted at 258.5–259.5°.

Anal. Calcd. for $C_{15}H_{10}N_2O_3$: N, 10.53. Found: N, 10.44.

3-Phenylquinoline-1-oxide. This was prepared exactly as described above for 3-(*p*-nitrophenyl)quinoline-1-oxide, using 12.5 g. (0.06 mole) of 3-phenylquinoline. After extraction with two 200-ml. portions of chloroform, drying and concentration of the chloroform in vacuum to 50 ml., the solution was diluted with 100 ml. of ligroin (63–90°) then the solid collected on a filter. The solution was concentrated in vacuum again, then hot ligroin added to the hot solution until cloudiness developed. The yield of white granular material was 6 g. (38%); m.p. 117–120°. Recrystallization from benzene hexane (1:1) gave white prisms which melted at 123–124°.

Anal. Calcd. for $C_{15}H_{11}NO$: N, 6.33. Found: N, 6.45.

3-(p-Nitrophenyl)carbostyril. A solution of 1.5 g. 3-(*p*-nitrophenyl)quinoline-1-oxide in 30 ml. of acetic anhydride was refluxed for 3 hr. After cooling, the solid was collected by filtration and recrystallized from 85% acetic acid. A yield of 1 g. of white granular material, m.p. 320–321°, was obtained.

Anal. Calcd. for $C_{15}H_{10}N_2O_3$: N, 10.53; C, 67.67; H, 3.76. Found: N, 10.78; C, 67.68; H, 4.11.

3-Phenylcarbostyril. This was prepared from 2.1 g. of 3-phenylquinoline-1-oxide as described above for 3-(*p*-nitrophenyl)carbostyril. The yield was 1.1 g. (44%), m.p. 227–229°. Recrystallized from benzene, the substance melted at 231–232°.

Anal. Calcd. for $C_{15}H_{11}NO$: N, 6.33. Found: N, 6.27.

2-Chloro-3-(p-nitrophenyl)quinoline. 3-(*p*-Nitrophenyl)-carbostyril (0.8 g.) was refluxed for 30 min. with 7 ml. of phosphoryl trichloride, then the solution was poured onto excess ammonia water and ice. The white solid was collected and was recrystallized twice from ethyl alcohol to yield 0.6 g. of white needles, m.p. 152–153°.

Anal. Calcd. for $C_{15}H_9ClN_2O_2$: Cl, 12.48. Found: Cl, 12.79.

3-(p-Aminophenyl)quinoline. To a cold stirred solution of 5.9 g. of stannous chloride dihydrate in 15 ml. of concentrated hydrochloric acid was added 1.9 g. of 3-(*p*-nitrophenyl)quinoline. After remaining at room temperature for 1.5 hr., the solution was heated to 85–90° then it was cooled and neutralized with concentrated ammonia water. The solid was collected, then it was warmed with 10% sodium hydroxide solution and the solution was filtered. The dried solid weighed 1.1 g. and melted at 173–175°. After recrystallization from benzene, the melting point of the substance was raised to 175.5–177°.

Anal. Calcd. for $C_{15}H_{12}N_2$: N, 12.72. Found: N, 12.54.

The *acetyl* derivative was prepared and recrystallized from benzene, m.p. 188–189°.

Anal. Calcd. for $C_{17}H_{14}N_2O$: N, 10.68. Found: N, 10.67.

The *benzoyl* derivative: recrystallized from benzene, m.p. 203–204°.

Anal. Calcd. for $C_{22}H_{16}N_2O$: N, 8.61. Found: N, 8.74.

3-(p-Hydroxyphenyl)quinoline. One gram of 3-(*p*-aminophenyl)quinoline was warmed with 8 ml. of 40% sulfuric acid, then the solution was cooled to 0° and 0.35 g. of sodium nitrite in 2 ml. of water was added dropwise. After five minutes, the diazonium salt solution was added slowly to 20 ml. of boiling 40% sulfuric acid. After boiling for 3–5 min. the solution was cooled, poured onto ice, and neutralized with ammonia water. After collecting the solid, it was dried and recrystallized, with decolorization, from benzene. The yield of fine yellow needles was 0.15 g., m.p. 224.5–226°.

Anal. Calcd. for $C_{15}H_{11}NO$: N, 6.33. Found: N, 6.40.

Nitration of 3-(p-nitrophenyl)quinoline. To a stirred solution of 9.5 g. (0.038 mole) of 3-(*p*-nitrophenyl)quinoline in 55 ml. of concentrated sulfuric acid at −10° was added dropwise a solution of 2.6 ml. (0.04 mole) of concentrated nitric acid in 13 ml. of concentrated sulfuric acid. The addition was carried out over a 2-hr. period. After the nitration mixture stood at room temperature for a short time, it was poured onto 300 ml. of ice and water and the solution was neutralized with concentrated ammonia water. The solid was collected, dried, and refluxed with 2 liters of benzene. After the insoluble material was removed by filtration the benzene solution was concentrated to 700 ml. and allowed to cool. The dark yellow granular solid was collected and recrystallized from benzene to yield 0.8 g. of a substance II, which melted at 288.5–289.5°.

Anal. Calcd. for $C_{15}H_9N_3O_4$: N, 14.24. Found: N, 14.05.

The mother liquor, from which the above high melting dinitro compound II had separated, was concentrated to a small volume and the solid which separated was collected and recrystallized from one liter of 3:2 absolute ethyl alcohol–benzene solution. After removal of the light yellow solid, the filtrate was concentrated to about 500 ml. and the solid was collected by filtration. The combined solids were recrystallized from 3:1 ethyl alcohol–benzene solution and from absolute ethyl alcohol to yield 6.8 g. (57% of yellow colored needles (I) which melted at 224.5–226.5°.

Anal. Calcd. for $C_{15}H_9N_3O_4$: N, 14.24. Found: N, 14.00.

Oxidation of 3 g. of the dinitro compound (I) by refluxing in 100 ml. of 30% sulfuric acid containing 6 g. of chromic anhydride for five hours resulted in the recovery of 1.65 g. of the dinitro compound and 0.25 g. of a carboxylic acid which did not depress the melting point of an authentic sample of *p*-nitrobenzoic acid.

5-Nitro-3-(p-nitrophenyl)quinolinium methiodide. 5-Nitro-3-(*p*-nitrophenyl)quinoline (0.25 g.) was heated on a steam bath for one hour with 10 g. of methyl sulfate. The cold solution was diluted with 50 ml. of ether and the white precipitate was collected on a filter. The solid was warmed with 50 ml. of saturated potassium iodide solution, cooled, and the red crystalline methiodide was recrystallized from absolute ethyl alcohol. The yield was 0.2 g. (54%), m.p. 234–235.5°.

Anal. Calcd. for $C_{16}H_{12}IN_3O_4$: N, 9.61. Found: N, 9.26.

5-Nitro-3-(p-nitrophenyl)quinoline-1-oxide. This was prepared from 3 g. of 5-nitro-3-(*p*-nitrophenyl)quinoline according to the method described for 3-(*p*-nitrophenyl)quinoline. The substance was recrystallized from 50% acetic acid and twice from absolute ethanol. The yield was 1.75 g. (50%), m.p. 263–265°.

Anal. Calcd. for $C_{15}H_9N_3O_5$: N, 13.50. Found: N, 13.70.

5-Nitro-3-(p-nitrophenyl)carbostyril. This substance was prepared from 1.25 g. of the above *N*-oxide according to the method for 3-(*p*-nitrophenyl)carbostyril. The yield of crude white solid was 0.9 g. (72%), m.p. 365–367°. The melting point was raised to 366–367° by recrystallization from glacial acetic acid.

Anal. Calcd. for $C_{15}H_9N_3O_5$: N, 13.50. Found: N, 13.90.

2-Chloro-5-nitro-3-(p-nitrophenyl)quinoline. Two-tenths gram of the above carbostyril was refluxed with 4 ml. of phosphoryl trichloride for one hour, then it was poured onto flaked ice and neutralized with ammonia water. The solid was collected and recrystallized twice from 95% ethyl alcohol to yield 0.12 g. of white short needles, m.p. 214–215°.

Anal. Calcd. for $C_{15}H_8ClN_3O_4$: Cl, 10.78. Found: Cl, 11.15.

5-Amino-3-(p-aminophenyl)quinoline. To a stirred solution of 18 g. (0.08 mole) of stannous chloride dihydrate in 20 ml. of concentrated hydrochloric acid at 5°, was added portionwise 3 g. of 5-nitro-3-(*p*-nitrophenyl)quinoline. After addition the solution was cooled, then it was made alkaline with sodium hydroxide. The solid was collected and recrystallized four times from dilute ethyl alcohol to yield 0.7 g. of tan needles, m.p. 127.5–129.5°.

Anal. Calcd. for $C_{15}H_{13}N_3$: N, 17.86. Found: N, 17.21.

3-Methylquinoline. α-Methylacrolein diacetate was prepared from purified α-methylacrolein[20] according to a procedure described in patent literature.[21] 3-Methylquinoline was prepared from methacrolein diacetate according to the general procedure of Untermohlen[17a] but using the specific procedure described in Organic Reactions[17b] for the preparation of 3-ethylquinoline. The yield was 52%.

Nitration of 3-methylquinoline. A solution of 17.5 ml. (0.272 mole) of concentrated nitric acid in sulfuric acid was added dropwise to a stirred solution of 39 g. (0.272 mole) of 3-methylquinoline dissolved in 207 ml. of concentrated sulfuric acid. The temperature was maintained at 10° and the addition was carried out over a period of seven hours. After the nitration mixture warmed to 0°, it was poured onto 500 ml. of ice and water and then it was neutralized with concentrated ammonia water. The precipitate was removed by filtration, washed thoroughly, and was dried in air. The yield was 40 g. (78%) and the material melted at 68–82°. The solid was dissolved in 800 ml. of hot 10% nitric acid and the solution was allowed to cool. The white crystalline nitrate salt was removed by filtration and the solid was washed with cold dilute nitric acid. The filtrate was concentrated to one-half the volume and the solution was cooled finally in a freezing mixture. The solid was collected as previously described. The combined fractions were dissolved in warm water and the solution was neutralized with concentrated ammonia water. The yellow solid was collected on a filter, washed, and dried in air. The yield was 26 g. (51%), m.p. 106–107°. The 5-nitro-3-methylquinoline was recrystallized from hexane, giving light yellow needles; the melting point was not changed.

Anal. Calcd. for $C_{10}H_8N_2O_2$: N, 14.90. Found: N, 14.75.

Nitrate salt. Recrystallized from water, m.p. 164.5–165.5°.

Anal. Calcd. for $C_{10}H_9N_3O_5$: N, 16.73. Found: N, 16.47.

The nitric acid mother liquor from the separation of 5-nitro-3-methylquinolinium nitrate was neutralized with concentrated alkali. The deep yellow solid was collected on a filter, washed, and dried. The yield was 13 g. (26%), m.p. 95–99°. After four recrystallizations from hexane, the substance melted at 109.5–111°. The reported[18] melting point for 8-nitro-3-methylquinoline is 110°.

5-Nitro-3-quinolinecarboxylic acid. To a stirred refluxing solution of 10 g. (0.053 mole) of 5-nitro-3-methylquinoline and 0.7 g. of manganese dioxide in 300 ml. of 30% sulfuric acid solution, was added dropwise a solution of 20 g. (0.2 mole) of chromium trioxide in 100 ml. of 39% sulfuric acid. After refluxing for 3 hr., the hot solution was filtered through a sintered glass funnel and the filtrate was poured into 2 liters of water. After the solution remained in a refrigerator for a day, the long colorless needles were collected on a filter, washed, and finally dried in a vacuum. The yield was 3.2 g., m.p. 274–278° (dec.). The substance was recrystallized from nitromethane and the solid was refluxed with diethyl ether to remove any of the recrystallization solvent. The substance melted at 279–281° (dec.). No further change in melting point could be obtained.

Anal. Calcd. for $C_{10}H_6N_2O_4$: N, 12.84. Found: N, 12.83.

The acidic filtrate was neutralized with concentrated ammonia water to a *p*H 4–5 and after standing for several hours, the precipitate was collected. The dried solid weighed 5.3 g. The substance was shaken with dilute sodium bicarbonate and the insoluble portion removed by filtration. The recovered 5-nitro-3-methylquinoline weighed 4.25 g. (42.5%) and melted at 103–104°. Neutralization of the sodium bicarbonate filtrate with hydrochloric acid gave an additional 0.7 g. of the carboxylic acid which brought the combined yield to 3.9 g. (34%).

Decarboxylation of 5-nitro-3-quinolinecarboxylic acid. To a solution 0.3 g. of silver nitrate in 25 ml. of water was added a solution of 0.35 g. of 5-nitro-3-quinolinecarboxylic acid in 100 ml. of ethyl alcohol then the solution was heated for 5 min. The alcohol removed by distillation, an equal volume of water was added and the silver salt removed by filtration. The dried solid was placed in a vacuum sublimation apparatus and heated at 0.5 mm. at 285° for several hours. The sublimate melted at 65–67°; after recrystallization from hexane, it melted at 68.5–70°. A mixed melting point determination with authentic 5-nitroquinoline (m.p. 70–71°) gave a m.p. 69.5–70.5°.

Ethyl 5-nitro-3-quinolinecarboxylate. A solution of 2.9 g. (0.013 mole) of 5-nitro-3-quinolinecarboxylic acid in 25 ml. of thionyl chloride was refluxed for 2 hr. The excess thionyl chloride was removed by distillation and the residue was refluxed for 15 min. with 40 ml. of absolute ethyl alcohol. After most of the alcohol had been removed by distillation, the solution was diluted somewhat with water and neutralized carefully with dilute alkali. The yield of the ester was 2.9 g. (90%), m.p. 101.5–102°. It was recrystallized from hexane, without change in the melting point, giving clear, pale yellow needles.

Anal. Calcd. for $C_{12}H_{10}N_2O_4$: N, 11.38. Found: N, 11.35.

Methyl 5-nitro-3-quinolinecarboxylate was recrystallized from hexane and from ethyl alcohol, m.p. 135.5–136.5°.

Anal. Calcd. for $C_{11}H_8N_2O_4$: N, 12.07. Found: N, 11.92.

5-Nitro-3-quinolinecarboxamide. The acid chloride was prepared from 2 g. of the carboxylic acid as described above, and after removal of the excess thionyl chloride, the residue was treated with concentrated ammonia water containing ice. The precipitate was collected, dried, and recrystallized from ethyl alcohol. The substance melted at 258.5–259°.

Anal. Calcd. for $C_{10}H_7N_3O_3$: N, 19.35. Found: N, 19.20.

5-Nitro-3-quinolinecarbonyl azide. A solution of 3 g. (0.014 mole) of 5-nitro-3-quinolinecarboxylic acid in 20 ml. of thionyl chloride was refluxed for two hours, after which the thionyl chloride was removed, leaving a solid residue. The residue was refluxed with 70 ml. of dry acetone until the solid had disintegrated into a fine suspension. The cold acetone suspension was added portionwise at 5–10° to a solution of 3.6 g. (0.056 mole) of sodium azide in 15 ml. of water. After standing at 10° for 15 min., the solution was diluted with 200 ml. of water and ice and after 20 min. the solid was collected upon a filter, washed, and finally dried in a vacuum desiccator. The substance melted at 125–126°; the yield was 1.96 g. (58%). Attempts at recrystallization gave inconsistent results. In recrystallization, the azide was dissolved in a solvent such as benzene at room temperature, then hexane was added and the solution cooled to a low temperature. However, a sample was not obtained which gave an analysis close to the theoretical value. On the average, about 20% of the 5-nitro-3-quinolinecarboxylic acid could be recovered from the aqueous acetone filtrate.

Anal. Calcd. for $C_{10}H_5N_5O_3$: N, 28.81. Found: N, 26.63.

Ethyl 5-nitro-3-quinolylurethan. A solution of 1.2 g. (0.005 mole) of 5-nitro-3-quinolinecarbonyl azide in 50 ml. of absolute alcohol was refluxed for one hour, after which the volume was reduced to one-half by distillation, and 50 ml. of water was added. The solution was concentrated and diluted with water, and the precipitated solid was collected. The dried substance was recrystallized from a 2:1 hexane-

(20) We are grateful for a generous supply provided by the Shell Development Co., Emeryville, Calif.

(21) J. H. Brant and F. R. Conklin, U. S. Patent **2,393,740** [*Chem. Abstr.*, **40**, 3127 (1946)].

benzene solution. The yield of fine yellow needles was 1.1 g. (85%), m.p. 141–142°.

Anal. Calcd. for $C_{12}H_{11}N_3O_4$: N, 16.09. Found: N, 16.14.

5-Nitro-3-aminoquinoline. One gram (0.004 mole) of ethyl 5-nitro-3-quinolylurethan was refluxed with 50 ml. of 6*N* hydrochloric acid for 8 hr. and the volume reduced to one-half by distillation. The solution was allowed to cool on ice, after which the white solid was removed by filtration and the hydrochloride decomposed with sodium carbonate solution. The solid was collected, dried, and refluxed for 2 hr. with a solution of 9 ml. of acetic anhydride in 50 ml. of benzene. About one-half of the solvent was removed by distillation, the solution was cooled in ice water, and the solid was collected by filtration. The yield of crude 5-nitro-3-acetamidoquinoline was 1 g. (88%), m.p. 195–199°. The acetamido derivative was refluxed for one hour with 50 ml. of 20% hydrochloric acid and the solution was concentrated. When the solution cooled, the hydrochloride was collected by filtration. The substance was treated with sodium carbonate solution to liberate the amine which was recrystallized first from benzene, and then from water. The yield of bright red granular solid, m.p. 184.5–185° was 0.54 g. (70%).

Anal. Calcd. for $C_9H_7N_3O_2$: N, 22.22. Found: N, 22.32.

5-Nitro-3-acetamidoquinoline was purified by recrystallization from benzene. The substance melted at 202.5–203.5°.

Anal. Calcd. for $C_{11}H_9N_3O_3$: N, 18.18. Found: N, 18.14.

5-Nitro-3-phenylquinoline. 5-Nitro-3-aminoquinoline (1.1 g., 0.006 mole) was dissolved in 80 ml. of hot 28% hydrochloric acid. The solution was cooled rapidly to 0° and it was diazotized by the dropwise addition of 0.44 g. of sodium nitrite in 5 ml. of water. After the solution remained at 0° for a short time, 0.4 g. of urea was added. The cold diazonium salt solution was allowed to drip into a cold stirred solution of 10 ml. of 25% dimethylamine and 38 g. of sodium carbonate in 150 ml. of ice water. The temperature was held at 8–12°. After stirring for 30 min., the olive green solid was removed by filtration, washed, and dried in a vacuum. The yield of crude 1-(5-nitro-3-quinolyl)-3,3-dimethyltriazene, m.p. 103–105°, was 1.27 g. (90%).

A 200-ml. three-necked flask was fitted with a mechanical stirrer, dropping funnel, and a reflux condenser to which was attached a bubble counter. A solution of 1.27 g. of the dry crude triazene in 50 ml. of benzene was poured into the flask and the stirred solution was heated to boiling while 1.5 g. of toluenesulfonic acid in 30 ml. of benzene was added dropwise over a 20-min. period. The solution was refluxed until there seemed to be no further evolution of nitrogen. The benzene solution was washed with 100 ml. of 5% sodium hydroxide solution, then with water, and it was dried over sodium sulfate. After removal of the solvent, the residue was sublimed by heating it at 180° under 1–2 mm. pressure. A yield of 0.45 g. (35%) of pale yellow needles, m.p. 125–130°, was obtained. After a recrystallization from dilute ethyl alcohol and from hexane, the melting point was elevated to 156–156.5°.

Anal. Calcd. for $C_{15}H_{10}N_2O_2$: N, 11.20. Found: N, 11.56.

The *methiodide* was prepared by refluxing 5-nitro-3-phenylquinoline with methyl iodide and recrystallizing the substance from ethyl alcohol, m.p. 237–238°.

Anal. Calcd. for $C_{16}H_{13}IN_2O_2$: N, 7.14. Found: N, 7.07.

Nitration of 5-nitro-3-phenylquinoline. Nitration of 0.1 g. of this substance and isolation was carried out exactly like the procedure used for 3-(*p*-nitrophenyl)quinoline, using proportional amounts of reagents. A yield of 0.07 g. (58%) of product, m.p. 198–212°, was obtained. The substance was recrystallized from ethyl alcohol and from benzene–hexane to give fine yellow needles, m.p. 224.5–226°. A mixed melting point determination with the dinitro compound I showed no depression.

5-Chloro-3-(p-nitrophenyl)quinoline. Two-tenths gram of 5-chloro-3-phenylquinoline was nitrated and the product isolated by exactly the same procedure as for the previous nitrations. The crude nitration product was recrystallized from methanol-hexane solution and from absolute ethanol, giving slightly yellow needles, m.p. 183–184°. Oxidation of a sample yielded *p*-nitrobenzoic acid.

Anal. Calcd. for $C_{15}H_9ClN_2O_2$: Cl, 12.44. Found: Cl, 12.21.

The *methiodide* was obtained as fine yellow needles by refluxing 5-chloro-3-(*p*-nitrophenyl)quinoline with methyl iodide and recrystallization of the product from absolute ethanol, m.p. 247–249°.

Anal. Calcd. for $C_{16}H_{12}ClIN_2O_2$: N, 6.56. Found: N, 6.49.

BLOOMINGTON, IND.

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Effect of Amines on Hydrogenolysis of Alkylphenols

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It has been demonstrated that the hydrogenolysis of alkyl phenols over nickel-on-kieselguhr catalyst can be inhibited by organic amines, although the latter do not prevent hydrogenation of the benzene ring. The data obtained support the hypothesis that both acidic sites and hydrogenation sites are present on the nickel catalyst.

In the hydrogenation of unsaturated alcohols with nickel catalysts both hydrogenation of the unsaturated double bonds and hydrogenolysis of the hydroxyl groups can occur. Recently Pines, *et al*[1] have proposed a carbonium ion mechanism for the hydrogenolysis reaction involving acidic sites on the catalyst. Pines reported that if the sites active for hydrogenation are poisoned with sulfur, only hydrogenolysis occurs. If both pyridine and a sulfur-containing compound are present in the charge, no reaction occurs. According to Pines' hypothesis, the pyridine poisons the acidic catalyst sites responsible for hydrogenolysis.

In order to obtain further evidence for acidic sites in addition to hydrogenation sites on nickel catalysts, the effect of organic bases on the hydrogenolysis of the hydroxyl group in alkylphenols was studied. The hydrogenation of phenol and cresols with a nickel catalyst yields the correspond-

(1) H. Pines, M. Shamaiengan, and W. S. Postl, *J. Am. Chem. Soc.*, **77**, 5099 (1955).