colored vanillic acid, whereas sulfur dioxide gave a white product in all cases.

Reaction of Vanillin with Fused Potassium Hydroxide above 240°.—The same apparatus was used. A mixture of 165 g. of potassium hydroxide and 20 g. of water was heated to 225° and with vigorous stirring was treated with 60 g. of vanillin in small portions at such a rate as to keep the resulting vigorous reaction from effervescing out of the crucible and to maintain the temperature at 225°. Vanillin addition required approximately twenty minutes. The temperature was maintained at 225° for another five minutes, at which time all effervescence had ceased. A sample dissolved in water and acidified with hydrochloric acid gave only crystals of vanillic acid melting sharply at 207–208°. The mixture was heated to 240° for five minutes, which caused the fused mass to become more fluid. A sample at this point indicated only vanillic acid. No test for protocatechuic acid could be obtained by the very sensitive ferric chloride reaction. The temperature was then raised to 245-250°, at which temperature effervescence again took place. After five minutes at 250°, a sample no longer gave a precipitate of vanillic acid when dissolved in water and acidified with hydrochloric acid. The fusion mixture was allowed to cool somewhat and was dissolved in 600 ml. of water. The alkaline solution was acidified with 6 *N* hydrochloric acid, giving an effervescent yellow solution which, upon standing, deposited colorless crystals. The crystals were filtered, washed with water, and dried at 105° to yield 36 g. (59%) of protocatechuic acid melting at 199-200° and not depressing the melting point of a mixture with authentic protocatechuic acid. Saturation of the acid filtrate with sodium chloride and extraction with ether yielded an additional 24 g. (40%) of protocatechuic acid melting at 195–200°.

This experiment was repeated, the temperature being maintained just below 245° for thirty minutes. At that point no protocatechuic acid could be found. Raising the temperature to 245° caused reaction to set in and the temperature to rise to 255°. The mixture was worked up as above to yield 99% protocatechuic acid.

Summary

Caustic fusion of vanillin below 240–245° results in very high yields of vanillic acid free from protocatechuic acid. Fusion of vanillin above 240–245° yields protocatechuic acid free from vanillic acid. The critical demethylation temperature varies somewhat with the alkali–vanillin ratio. Reaction of vanillin with strong alkali solution at elevated temperatures does not yield either of the acids.

APPLETON, WISCONSIN

RECEIVED JULY 12, 1946

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

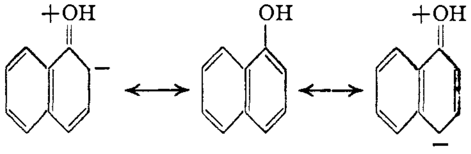
Absorption Spectra of Heterocyclic Compounds. I. Quinolinols and Isoquinolinols[1]

BY GALEN W. EWING[1a] AND EDGAR A. STECK

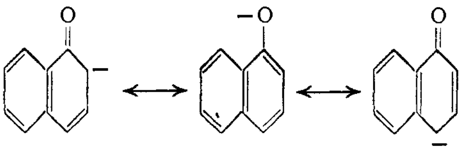
An examination of the literature shows that very few of the simple derivatives of quinoline and isoquinoline have been studied from the standpoint of their absorption spectra. It seems desirable, both from theoretical considerations and with the object of discovering criteria for the identification of isomers, to investigate the spectroscopic properties of various isomeric series differing from one member to the next only in the position of the substituent groups. The present paper deals with the mono-hydroxy derivatives[2] of quinoline and isoquinoline. A subsequent paper is planned to consider the monoamino derivatives.

It is convenient for present purposes to classify the quinolinols and isoquinolinols into three groups—those which bear formal analogy to (1) α-naphthol, (2) β-naphthol, and (3) those which can be written as derivatives of 2- and 4-pyridones.

I. α-Naphthol Analogs.—In the prototype of this class, α-naphthol itself (II), the absorption of light by a neutral solution is largely due to contributing structures such as I and III which resonate with II. The contribution to resonance of these forms, however, is relatively slight, since their formation involves the separation of charges and hence is not favored. However in basic solution where the phenol is completely ionized, V, the formation of the corresponding quinonoidal forms IV and VI is much more probable, and hence contribute more strongly to the resonance. Since these quinonoidal forms absorb light more strongly than the purely aromatic forms, a bathochromic shift is expected in passing from neutral to basic solution. That this is borne out by experiment can be seen from Fig. 1.



I II III



IV V VI

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(1) Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, N. J., April 11, 1946.

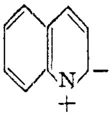
(1a) Present address: Department of Chemistry, Union College, Schenectady, New York.

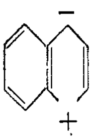
(2) The following spectra have been reported, though many with insufficient precision according to modern standards: *2-Quinolinol*—(a) Hartley and Dobbie, *J. Chem. Soc.*, **75**, 640 (1899); (b) Morton and Rogers, *ibid.*, **127**, 2698 (1925); (c) Ley and Specker, *Ber.*, **72**, 192 (1939); (d) Morton and Stubbs, *J. Chem. Soc.*, 1321 (1939); *6-Quinolinol*—(e) Dobbie and Fox, *ibid.*, **101**, 77 (1912); *8-Quinolinol*—(f) Dabrowski and Marchlewski, *Bull. int. acad. polon. sci. lett., Cl. sci. math. nat.*, **A**, 479 (1935); (g) Bednarczyk and Marchlewski, *ibid.*, **A**, 187 (1937); (h) Kiss, Bacskai and Csokan, *J. prakt. Chem.*, [2] **160**, 1 (1942).

Further evidence for this formulation is the resemblance between the absorption of α-naphthol in basic solution and that of a neutral solution of 1,4-naphthoquinone,[3] with an absorption maximum at 332 mμ ($\epsilon = 3100$).

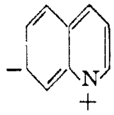
Quinoline differs from the naphthols in that its spectrum shows a bathochromic shift when one passes from neutral to acid solution rather than to basic. Quinoline in neutral solution may be formulated as a resonance hybrid between many structures of which VII to XI are representative. The contributions of polar structure, such as VIII to XI, are less important than of non-polar VII on account of the separation of charges which is involved in their formation. In acid solution, however, quinoline takes up a proton to form the positively charged quinolinium ion. This ion can be assigned resonance structures such as XII to XVI which correspond in bond structures to VII to IX, respectively.

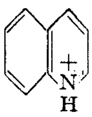

VII

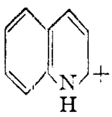

VIII

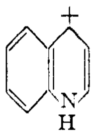

IX

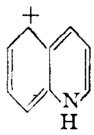

X

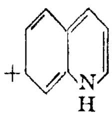

XI


XII


XIII


XIV


XV


XVI

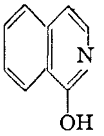
The positive charge may be thought of as wandering around the molecule to any of several of the carbon atoms. As this does not necessitate a separation of charges, these forms are relatively strong contributors to the resonance, and hence a bathochromic shift occurs upon acidification. Similar reasoning may be applied to the spectra of isoquinoline. The spectra of quinoline[4] and isoquinoline[5] are shown in Figs. 2 and 3.

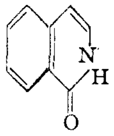
The spectra of 5-isoquinolinol (Fig. 4) and of 5- and 8-quinolinols (Figs. 5 and 6) show bathochromic shifts in both acid and basic solutions relative to neutral alcohol, thus combining the effects characteristic of naphthol and quinoline types. In the case of 8-quinolinol it was expected that hydrogen bridging between the oxygen and nitrogen atoms might reduce the absorption somewhat in neutral solution by its stabilizing action on a resonance form which is not a major contributor to absorption. To test this point spectra were determined on the methyl ether (Fig. 7). The shift in basic solution is eliminated, as would be expected, but in neutral as well as in acid solution the curves are nearly identical with those of the quinolinol itself. Hence no hydrogen bonding is detected by this method.

II. β-Naphthol Analogs.—β-Naphthol differs from its isomer in that its spectrum shows three distinct regions of absorption rather than only two (Fig. 8). The effect of change of solvent is similar, however.

The spectra of 3-, 6- and 7-quinolinols and of 7-isoquinolinol are shown in Figs. 9 to 12. Each shows bathochromic shifts in both acid and basic solutions as expected of phenolic quinolines.

III. Quinolones and Isoquinolones.—Those quinoline and isoquinoline derivatives which have the hydroxyl substituted in the pyridine ring in the α- or γ-positions relative to the nitrogen may be written as ketonic compounds. The absorption spectra may be used as a criterion to determine in a given case whether the keto or enol form correctly expresses the structure. For example, in the case of 1-hydroxyisoquinoline, XVII or XVIII (Fig. 13), the spectra are essentially identical in alcohol, dilute acid and dilute base. The absence of a bathochromic shift in basic solution is evidence of absence of a phenolic hydroxyl, whereas the lack of a similar shift in acid solution indicates that the nitrogen is saturated and hence cannot make a greater contribution to resonance structures after taking up a proton.


XVII


XVIII

It was thought that a tautomeric shift toward the phenolic structure might be found if the solution were made sufficiently basic, so a spectrum was run in a 10% sodium hydroxide solution (Fig. 13). It was found that the second maximum was shifted from 276 to 298 mμ wave length, but that the third maximum (325 mμ) was not appreciably affected. In the truly phenolic isomers considered previously both maxima were shifted by considerable amounts. The complete cause of this observation is not immediately evident, but tentatively it may be taken to indicate increased phenolic properties in highly basic solution. This interpretation is further upheld by the spectra of 2-methyl-1-isoquinolone (Fig. 14) which resemble closely those of 1-isoquinolone, except that there is no shift in 10% alkaline solution.

Very similar spectra are shown by 2-quinolone (Fig. 15).

In the case of 4-quinolone (Fig. 16), similarly, no bathochromic shifts are observed in either acid or basic solution, including in this case the spectrum in 50% sodium hydroxide. The spectrum

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(3) Anderson and Roedel, THIS JOURNAL, **67**, 955 (1945); Hodgson and Hathway, *Trans. Faraday Soc.*, **41**, 120 (1945).

(4) Spectra of quinoline have been reported by (a) Fischer, "Die physik. Chem. in der gerichtl. Med. u. d. Toxikol." (1925); quoted by "International Critical Tables," Vol. 5, McGraw-Hill, New York, N. Y., 1925, p. 363; (b) Hunter, Qureshy and Samuel, *J. Chem. Soc.*, 1576 (1936). The wave lengths of the maxima given by these authors agree with ours, but the curves differ somewhat in shape.

(5) Spectra of isoquinoline have been reported by (a) Fischer and Steiner, *Compt. rend.*, **175**, 882 (1922); (b) Steiner, *ibid.*, **176**, 244 (1923); (c) Pruckner and Witkop, *Ann.*, **554**, 134 (1943).

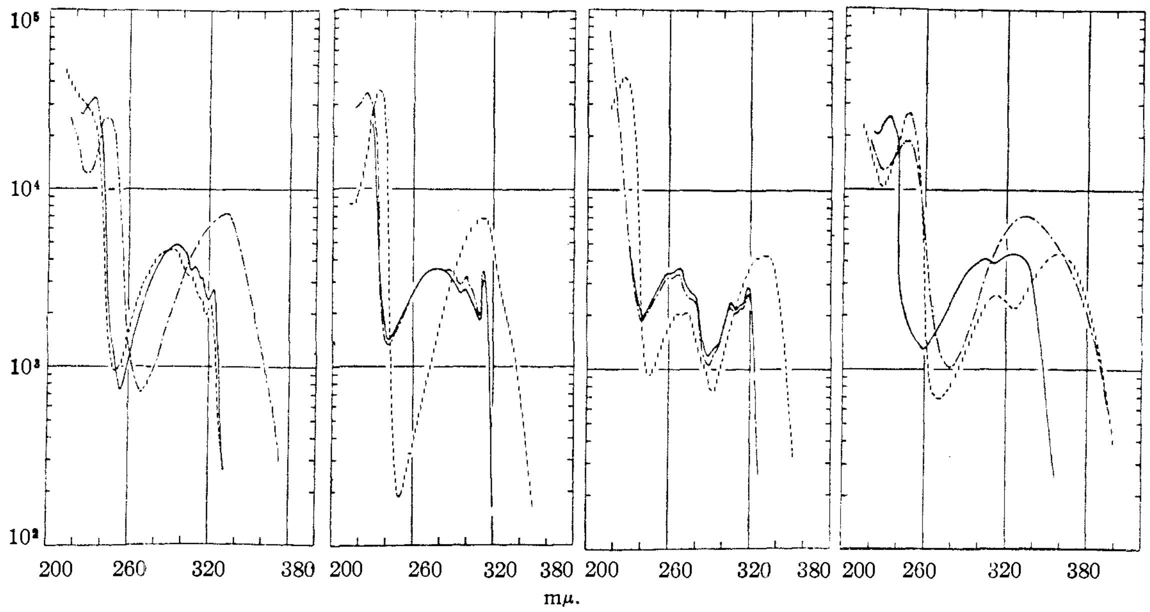


Fig. 1.—α-Naphthol. Fig. 2.—Quinoline. Fig. 3.—Isoquinoline. Fig. 4.—5-Isoquinolinol.

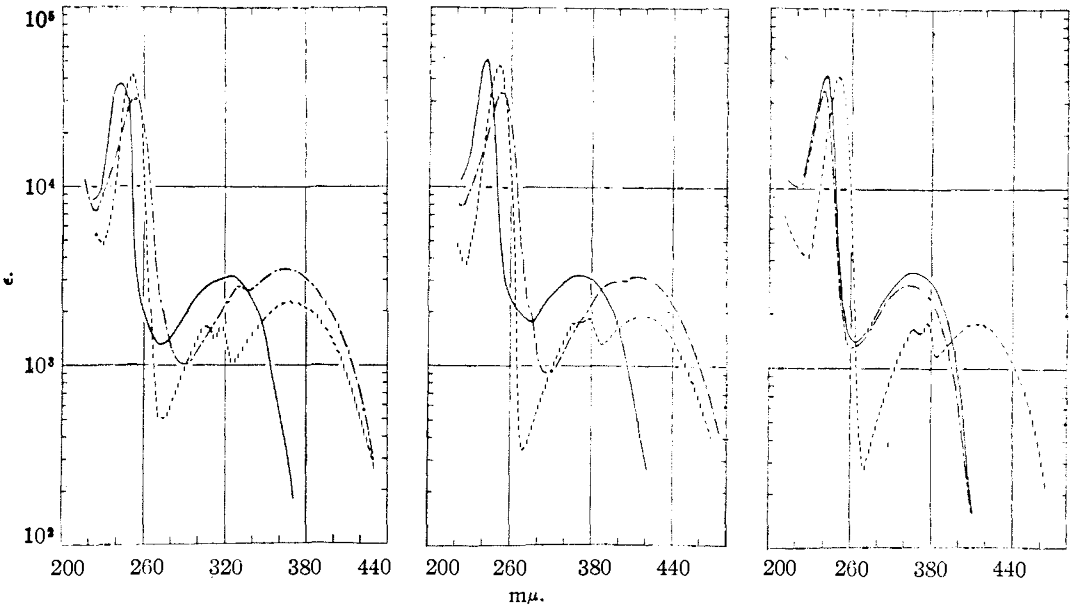
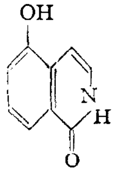


Fig. 5.—5-Quinolinol. Fig. 6.—8-Quinolinol. Fig. 7.—8-Quinolyl methyl ether.

Spectra of substances related to α-naphthol. Solvents, ——— 95% ethanol, - - - - N/100 hydrochloric acid, - - — N/100 sodium hydroxide.

of 4-quinolone in alcoholic solution shows an unexplained splitting of the near ultraviolet maximum into two peaks, at wave lengths 318 and 330 mμ. It was thought that this might be a specific solvent effect, but an additional curve run in aqueous phosphate buffer at pH 7 showed the same bifurcation. A similar effect has been observed in 3-methyl-4-quinolone (Fig. 17), 2-methyl-4-quinolone (Fig. 18), and in several other substituted 4-quinolones. 4-Methoxyquinoline (Fig. 19) does not share this peculiarity.

To test our interpretations, we may consider the spectra of 1,5-dihydroxyisoquinoline (Fig. 20). This compound would be expected to possess the structure XIX, 5-hydroxy-1-isoquinolone.



XIX

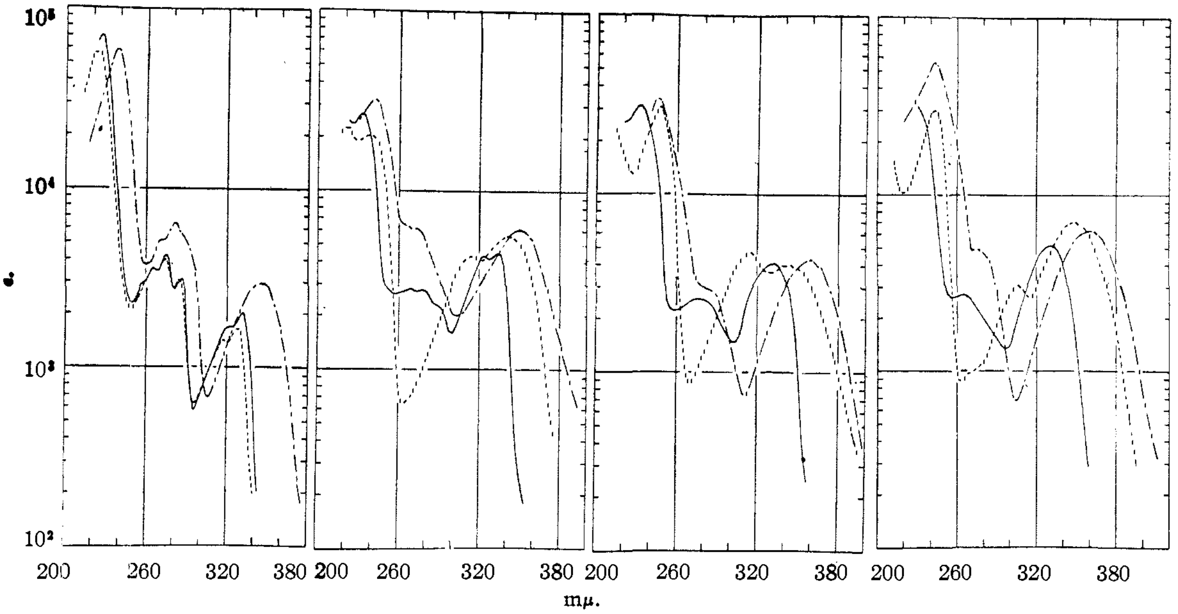


Fig. 8.—β-Naphthol. Fig. 9.—3-Quinolinol. Fig. 10.—6-Quinolinol. Fig. 11.—7-Quinolinol.

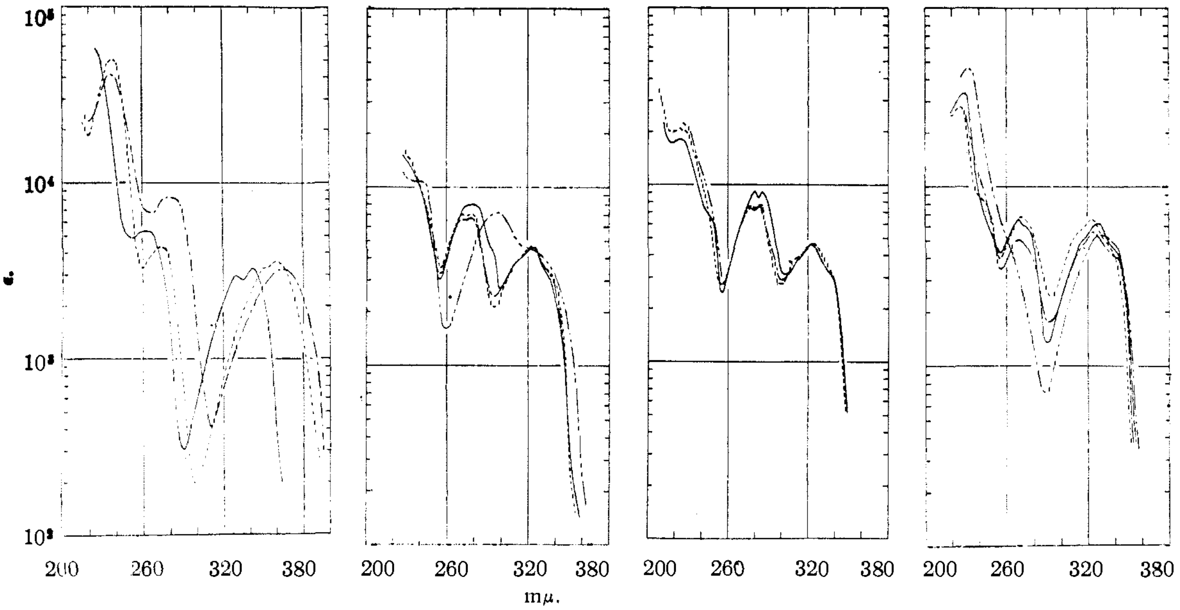


Fig. 12.—7-Isoquinolinol. Fig. 13.—1-Isoquinolone. Fig. 14.—2-Methyl-1-isoquinolone. Fig. 15.—2-Quinolone.

Spectra of substances related to β-naphthol. Solvents, —— 95% ethanol, - - - - N/100 hydrochloric acid, — - — N/100 sodium hydroxide, — - - — 10% sodium hydroxide, (in Fig. 16, — - - —, aqueous buffer, pH 7).

Thus it should show a bathochromic shift in base due to the phenolic group in position 5, but no shift in acid, since the nitrogen is saturated. These conclusions are borne out by the observed spectra.

IV. Pyridinols.—The spectrum of pyridine has been reported in various solvents.[6] It appears that no shift is observed in the wave length of maximum absorption on passing from neutral to acidic solution. In looking for such a shift to correspond to that observed in quinoline

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(6) (a) Hantzch, *Ber.*, **44**, 1783 (1911), finds a shift from the spectrum of the hydrochloride to that of the free base in the case of quinoline but not in pyridine; (b) Marchlewski and Pizlo, *Bull. intern. acad. polon., Cl. sci. math. nat.*, **A**, 22 (1934); quoted and curves reproduced in Landolt-Börnstein, "Tabellen," 5th ed., 3rd supp., p. 1416. Pyridine was examined in water, alcohol, chloroform, and ether solutions and the hydrochloride in water, alcohol and other solvents.

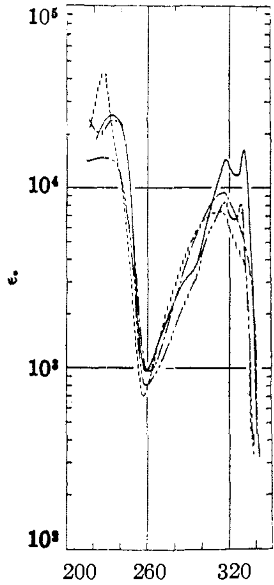

Fig. 16.—4-Quinolone.

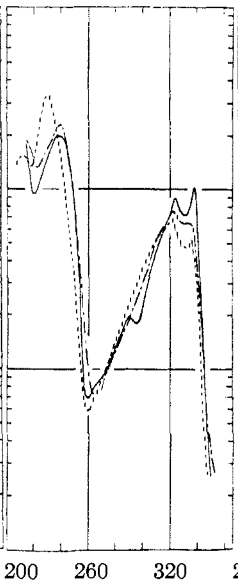

Fig. 17.—3-Methyl-4-quinolone.

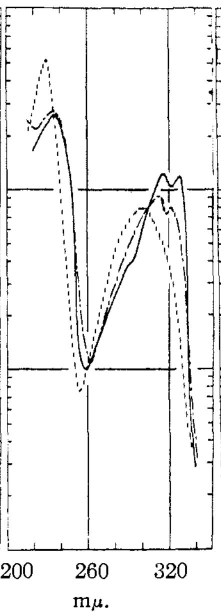

Fig. 18.—2-Methyl-4-quinolone.

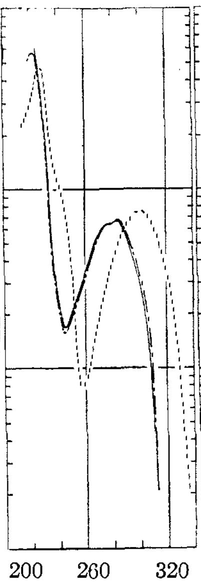

Fig. 19.—4-Quinolylmethyl ether.

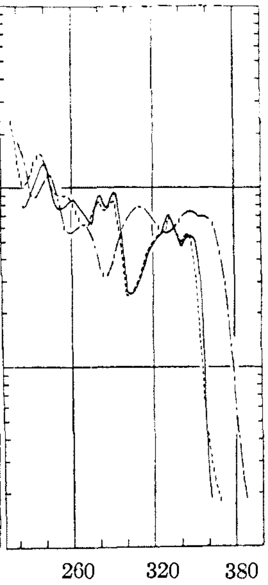

Fig. 20.—5-Hydroxyisoquinolone-1.

and isoquinoline, the spectra of pyridine in alcohol and aqueous acid and alkali were determined, and found in essential agreement with the results of the Polish workers.[6b] The absence of the shift in acid solution is unexplained.

The spectra of all three pyridinols have been reported.[7] The 3-isomer shows distinct bathochromic shifts in both acid and basic solution, relative to its absorption in neutral alcohol,[7c] and thus behaves like 3-quinolinol.

The spectra of 2-pyridone were reported by Specker and Gawrosch[7c] in neutral and basic solutions. We have determined it also in aqueous acid solution, *p*H 2. Our results and those of Specker and Gawrosch are given in Table I.

TABLE I

ABSORPTION SPECTRA OF 2-PYRIDONE

Solvent	First maximum λ, mμ	ε	Second maximum λ, mμ	ε
Methanol	227	10,000	297	6300
0.1 *N* sodium methylate	230	10,000	295	6300
0.01 *N* HCl, aq.	225	6,900	295	5700

There is essentially no change in spectrum with changing *p*H, in agreement with our observations on 2-quinolone.

The spectrum of 4-pyridone was reported by Specker and Gawrosch,[6c] and has been repeated by us with concordant results. Both acid and basic solutions show an unexplained hypsochromic shift relative to the absorption in neutral alcohol.

Discussion

A critical examination of the literature leads to no doubt about the phenolic nature of those quinolinols and isoquinolinols in which the hydroxyl is substituted in the benzenoid ring, also including 3-quinolinol. The 8- and 6-quinolinols have received much more detailed study than any of the others, but in every case where the following phenolic reactions have been attempted, positive results have been obtained, to wit—(a) ferric chloride gives colors[8-10]; (b) reactions of the Kolbe type with carbon dioxide and sodium carbonate give the corresponding phenol carboxylic acids[9]; (c) the Reimer–Tiemann reaction with chloroform in the presence of sodium hydroxide gives substituted aldehydes[9,11-13]; (d) the Lederer–Manasse reaction with formaldehyde in the presence of alkali gives substituted carbinols or diarylmethanes[14-16]; (e) the Borsche–Berkhout modification of the Lederer–Manasse reaction using sulfuric acid as the condensing agent gives cyclic methylene ethers or diarylmethanes[16,17]; (f) the Bucherer reaction can be used to form aminoquinolines from the corresponding hydroxy compounds[18]; (g) coupling reactions take place

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[7] (a) Riegel and Reinhard, THIS JOURNAL, **48**, 1334 (1926); (b) Stiller, Keresztesy and Stevens, *ibid.*, **61**, 1237 (1939); (c) Specker and Gawrosch, *Ber.*, **75**, 1338 (1942).

[8] Riemerschmid, *ibid.*, **16**, 721 (1883).

[9] Lippmann and Fleissner, *ibid.*, **19**, 2467 (1886).

[10] Mills and Watson, *J. Chem. Soc.*, **97**, 753 (1910).

[11] Sen and Ray, *J. Ind. Chem. Soc.*, **9**, 178 (1932).

[12] Bobranski, *J. prakt. Chem.*, [2] **134**, 141 (1932).

[13] Kochanska and Bobranski, *Ber.*, **69**, 1807 (1936).

[14] Manasse, *ibid.*, **27**, 2409 (1894); **35**, 3844 (1902).

[15] Cohn, *J. prakt. Chem.*, [2] **83**, 499 (1911).

[16] Monti and Verona, *Gazz. chim. ital.*, **62**, 878 (1932).

[17] Schüller, *J. prakt. Chem.*, [2] **88**, 180 (1913).

[18] Woroshtzow and Kogan, *Ber.*, **65**, 142 (1932).

TABLE II

PRODUCTS OF REACTIONS OF QUINOLONES

Reaction	2-Quinolone	4-Quinolone	2-Methyl-4-quinolone
Dil. alkali + RX	—NR + —OR[a,b]	—OR (+ —NR)[k,l]	—NR[r]
Concd. alkali + RX	—OR + —NR[c,d]	—OR[k,l]	....
Ag salt + RX	—OR[a,b]	—OR[l]	....
Diazomethane	—OCH_3[e]	—OCH_3[m]	....
Catalytic hydrogenation	3,4-Dihydro[f]	No reaction[f]	No reaction[f]
Borsche-Berkhout	Cyclic ethers[g,h,i]	Cyclic ethers (low yield)[n]	Cyclic ethers (better yield)[n]
Benzoyl chloride	....	4-Cl derivs.[o]	....
Reimer-Tiemann	....	Aldehyde[p] (alc. NaOH)	Aldehyde[p] (aq. NaOH)
Ferric chloride	Brownish color	Red color[q]	Yellow-red[s]
Temp. for isomerization, —OR to —NR	250°[j]	>300°[l]	....

[a] Friedländer and Weinberg, *Ber.*, **15**, 1421 (1882); **18**, 1528 (1885). [b] Friedländer and Müller, *ibid.*, **20**, 2009 (1887). [c] Friedländer and Ostermaier, *ibid.*, **14**, 1916 (1881). [d] Bogert and May, THIS JOURNAL, **31**, 507 (1909). [e] Meyer, *Monatsh.*, **26**, 1316 (1905). [f] Reference 21. [g] Experiment carried out on 4-methyl-2-quinolone. [h] Reference 16. [i] Monti and Dinelli, *Gazz. chim. ital.*, **66**, 732 (1936). [j] Meyer and Beer, *Monatsh.*, **34**, 1178 (1913). [k] Wenzel, *ibid.*, **15**, 465 (1894). [l] Meyer, *ibid.*, **27**, 262 (1906). [m] Meyer, *ibid.*, **27**, 988 (1906). [n] Monti, Cirelli and Romano, *Gazz. chim. ital.*, **66**, 42 (1936). [o] Ellinger and Reiser, *Ber.*, **42**, 3337 (1909). [p] Bobranski, *ibid.*, **69**, 1113 (1936). [q] Greshof, *Rec. trav. chim.*, **19**, 360 (1900). [r] Knorr and Antrick, *Ber.*, **17**, 2870 (1884). [s] Conrad and Limpach, *ibid.*, **20**, 947, 949 (1887); Limpach, *ibid.*, **64**, 969 (1931).

readily with diazonium compounds[19,20]; (h) in every case catalytic hydrogenation gives the 1,2,3,4-tetrahydro derivative.[2]

In the cases of the quinolone types, however, the picture is not as clear; under some conditions phenolic properties are evident, though other tests show the structures to be ketonic or lactamic in nature. In Table II are summarized pertinent reactions of α- and γ-quinolones. From these data, one may conclude that the 4-quinolone is more phenolic in nature than its 2-methyl derivative and than 2-quinolone. However, even the latter compound shows some degree of phenolic properties especially in the presence of concentrated alkali, when it can react with alkyl halides to give principally the alkoxy derivatives.

Thus similar conclusions are possible from chemical evidence as well as from the spectroscopic data.

Experimental Part

Absorption Spectra.—All spectra were determined with a Beckman Quartz Spectrophotometer, Model DU, Serial No. D-377.[22] The spectral band width isolated[23] for each density reading was within the range of approximately 0.9 to 3.5 mμ. Density readings were never further apart than 5 mμ intervals, while in regions of special interest the interval was reduced to 2 mμ and in the immediate neighborhood of maxima and minima to 1 mμ. The individual points are not shown on the graphs since they are so numerous as to detract from clarity. The absorption cells were of silica; the thickness of each was 1.000 ± 0.002 cm. The concentrations employed varied with the degree of absorption, but were mostly within the range 10 to 35 mg. per liter. In every case the reference liquid used as a blank was from the same batch of solvent used to dissolve the sample.

The molecular extinction coefficients, ε, were calculated by the equation

$$\epsilon = (M/ct) \log_{10}(I_0/I)$$

where M is the molecular weight of the solute, c its concentration in grams per liter of solution, t the thickness of the absorption cell in cm., I_0 the intensity of the incident light, and I that of the light transmitted by the solution.

Solvents. (**a**) **Alcohol.**—The alcohol used was 95% grain alcohol, U. S. P., which was found by test to be perfectly satisfactory for this purpose. (**b**) **Acid and Base.**—Hundredth normal solutions of reagent grade hydrochloric acid and of sodium or potassium hydroxides were used unless otherwise noted. (**c**) **Neutral Buffer.**—The buffer used for the neutral solution of the 4-quinolone was prepared from a capsule of material marketed under the name "pHydrion buffers." This is a phosphate buffer.

Compounds.—Unless otherwise stated, commercial samples of the required compounds were purified by the usual methods until the physical constants corresponded with the values given in the literature.

3-Pyridinol and **3-, 4-, 5-, 6-,** and **7-quinolinols** were obtained from Dr. Cavallito[21] of these Laboratories, and if necessary resublimed *in vacuo* to constant melting point.

1-Isoquinolone was prepared according to the directions of Chichibabin and Oparina,[24] in which isoquinoline was aminated with sodamide (60% conversion) then the 1-amino derivative diazotized and hydrolyzed (60% yield). Colorless needles were crystallized from benzene, m. p. 210.5–211° (reported,[24] 210°; 209-210°[25]).

2-Methyl-1-isoquinolone was prepared from isoquinoline as described by Fisher and Hamer.[26] The product, which was obtained in 50% yield, crystallized from hexane in the form of nacreous plates, m. p. 55.5-56° (reported,[26] 38°). *Anal.* Calcd. for $C_{10}H_9ON$: C, 75.50; H, 5.70; N, 8.81. Found: C, 75.36; H, 5.49; N, 8.76.

The 5- and 7-isoquinolinols and **1,5-isoquinolindiol** were obtained through the courtesy of Dr. R. B. Woodward[27] of Harvard University.

2-Methyl-4-quinolone was prepared by the Conrad-Limpach synthesis,[28] employing Dowtherm A as a diluent in the cyclization (*cf.* ref.[29]). Crystallization from water, followed by drying at 100° under a pressure of 0.5 mm., gave white prismatic needles, m. p. 234-234.5° (reported,[28] 230-231°).

3-Methyl-4-quinolone was available from earlier work.[30]

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(19) Mathéus, *Ber.*, **21**, 1642, 1886 (1888).

(20) Woroshtzow and Kogan, *ibid.*, **63**, 2354 (1930).

(21) Cavallito and Haskell, THIS JOURNAL, **66**, 1166 (1944).

(22) Manufactured by the National Technical Laboratories, Pasadena, California. See Cary and Beckman, *J. Opt. Soc. Am.*, **31**, 682 (1941).

(23) For the significance of this see Hogness, Zscheile and Sidwell, *J. Phys. Chem.*, **41**, 379 (1937).

(24) Chichibabin and Oparina, *J. Russ. Phys.-Chem. Soc.*, **50**, 548 (1920).

(25) Wibaut and Haaijman, *Rec. trav. chim.*, **62**, 466 (1943).

(26) Fisher and Hamer, *J. Chem. Soc.*, 1907 (1934).

(27) Woodward and Doering, THIS JOURNAL, **67**, 860 (1945).

(28) Reference [s] in Table II.

(29) Steck, Hallock and Holland, THIS JOURNAL, **68**, 380 (1946).

(30) Steck, Hallock and Holland, *ibid.*, **68**, 129 (1946).

4-Quinolyl methyl ether was prepared from the 4-chloro compound[31] and resublimed: m. p. 39–39.5° (reported, 41°). The **hydrochloride** crystallized from absolute alcohol–ether in the form of white needles, m. p. 171° (reported,[32] 164–166°, dec.).

Anal. Calcd. for $C_{10}H_9NO\cdot HCl$: N, 7.16. Found: N, 7.06.

The **picrate** separated from alcoholic solution in the form of bright yellow needles, m. p. 199–199.2°, dec. (reported,[31] 203°). The **styphnate** crystallized as golden yellow needles from alcohol, m. p. 219–219.5°, dec.

Anal. Calcd. for $C_{10}H_9NO\cdot C_6H_3N_2O_8$: N, 13.87. Found: N, 13.84.

8-Quinolyl methyl ether was prepared by the method of Kaufmann and Rothlin.[33] The distilled product (b. p. 95–98° at 0.1 mm. pressure) was thrice crystallized from petroleum ether giving white prisms, m. p. 45–45.5° (reported,[33] 46–47°). The **picrate** was obtained from alcohol as fine yellow needles, m. p. 162.5–163° (reported,[34] 143°, dec.).

Anal. Calcd. for $C_{10}H_9NO\cdot C_6H_3N_3O_7$: N, 14.44. Found: N, 14.64.

It was observed that upon standing in the presence of air many of the hydroxy compounds, especially in basic solution, turned dark slowly. The naphthols were the worst offenders but several of the heterocyclic materials showed a similar effect in lesser degree. To determine the possible effect of such visible darkening upon the spectrum, an aging test was run upon α-naphthol as an example of these compounds. The spectrum reported in Fig. 1 was determined on a fresh solution which showed no darkening. Another solution was prepared of approximately 0.5% α-naphthol (highly purified) in 0.01 N sodium hydroxide. By the time the crystals had dissolved completely the liquid had assumed a light straw color. The spectrum was run immediately and after standing for various intervals in normal laboratory illumination. It was found that the color deepened very markedly, becoming almost black. By the end of sixty-nine hours the 333 mμ maximum had not changed appreciably in height, but by four hundred eighty-three hours it had dropped by some 30%. The absorption in the lower visible region had, of course, increased, but without showing any marked selectivity. No sign of the maxima of 1,4-naphthoquinone at 405 and 425 mμ[3] were observed. All the spectra reported in this paper were run on fresh solutions, and it is thought that this darkening can have had but negligible effect on them.

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Summary

1. Ultraviolet absorption spectra have been determined for all the isomeric hydroxyquinolines and several hydroxyisoquinolines.

2. Spectrophotometric evidence is in general in agreement with chemical evidence in the assignment of phenolic structure to all hydroxyquinolines and -isoquinolines except where the substituent is in the α- or γ-position relative to the ring nitrogen. These isomers are predominantly ketonic (or lactamic) in nature.

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[31] Backeberg, *J. Chem. Soc.*, 619 (1933).

[32] Reference *m* in Table II.

[33] Kaufmann and Rothlin, *Ber.*, **49**, 581 (1916).

[34] Fränkel and Grauer, *ibid.*, **46**, 2551 (1913).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. XII. Vapor Phase Addition to Certain Deactivated or Condensed Aromatic Rings[1,1a]

BY READE Y. TOMPSON,[2] PAUL TARRANT[3] AND LUCIUS A. BIGELOW

Several years ago it was reported from this Laboratory[4] that the vapor phase fluorination of benzene yielded C_6F_{12}, C_6HF_{11} and C_6F_{10}, together with small amounts of $C_{12}F_{22}$, and several acyclic saturated fluorocarbons of lower molecular weight, but no trace of any aromatic substitution products. These results were explained upon the assumption that the attack of fluorine on the aromatic nucleus proceeds first by addition, then by substitution, and finally by degradation, in which all the reactions take place by atomic mechanisms, and may or may not be accompanied by polymerization.

More recently some preliminary experiments made in this Laboratory by A. R. Gilbert[5] and dealing with the fluorination of a relatively unreactive aromatic ring made it seem particularly desirable at this time to obtain further information about the earlier stages of such reactions, presumably by studying the fluorination of either highly deactivated or condensed aromatic rings, eventually under the mildest practicable operating conditions. Accordingly, we are presenting here the results of a study of the vapor phase fluorination of 4-chloro-1,3-bis-(trifluoromethyl)-benzene (I), later referred to as the 4-chloro compound, benzotrifluoride, and 1-methylnaphthalene. While the findings, which are not as yet complete, do not constitute a total solution of the problem, they do represent a distinct advance in our knowledge of the mechanism by which elementary fluorine reacts with aromatic rings.

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[4] Paper XI, Fukuhara and Bigelow, THIS JOURNAL, **63**, 2792 (1941).

[5] A. R. Gilbert, Master's Thesis, Duke University, 1943.