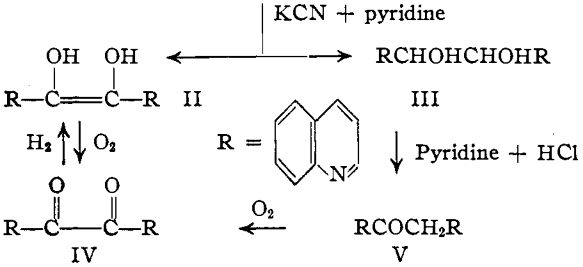
[CONTRIBUTION NO. 87 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Benzoin Condensation of Quinaldehyde

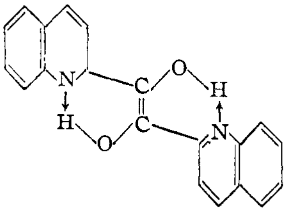
BY C. A. BUEHLER AND JAMES O. HARRIS[1]

In the benzoin condensation of quinaldehyde (I) none of the expected benzoin, but instead the isomeric 1,2-di-2-quinolyl-1,2-ethenediol (II) and its reduction product, 1,2-di-2-quinolyl-1,2-ethanediol (III) were obtained, the amounts varying with the experimental conditions employed.



The enediol II is a black to dark purple crystalline solid with a metallic luster, m. p. 232–233° (dec.). The stability is such that there is no appreciable change in appearance or melting point after six months storage at room temperature. It affects Tollens reagent, is oxidized by sodium 2,6-dichlorobenzeneoneindophenol, forms a dibenzoate, m. p. 236°, and in bubbling air through a dioxane solution gives a faintly yellow benzil (IV), m. p. 271–272°, in agreement with Brown and Hammick's value[2] of 266–267°, but not with Linsker and Evans' value[3] of 175°. Reduction of the benzil with hydrogen at low pressure in the presence of Adams platinum catalyst produces the original enediol.

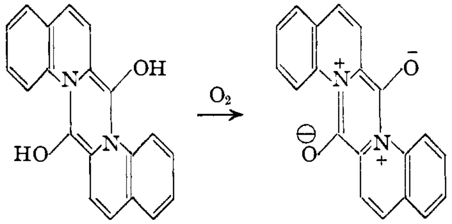
The above tests correspond to those found by Fuson[4] for aromatic enediols in which the moderate stability was attributed to conjugation and steric hindrance. To account for the greater stability of the N-heterocyclic enediols a new factor, that of chelation, is probably in operation. On this basis we are proposing tentatively the formula IIa for the new type of enediol



IIa

The high degree of conjugation, its compact, symmetrical nature, the fact that its model is planar, and the possibility of charged resonating forms account for its intense color. This chelated formula receives additional support from the fact that the usual infrared absorption band[5] for the hydroxyl group is missing (probably shifted into the region of Nujol C–H).

These views are at variance with those of Brown and Hammick[2] who did not isolate the enediol herein described, but who obtained and studied analogous compounds from isoquinoline-1-aldehyde and 3-methylquinoline-2-aldehyde. Since these products were oxidized readily to benzils similar to the benzil produced directly from quinaldehyde, these investigators have suggested the formula IIb for the enediol based largely on the *meso*-ionic formula[6] IVa for the benzil (resonating forms are shown).



IIb IVa

Brown and Hammick eliminated the normal structure IV for the benzil because of its high melting point (in comparison to Linsker and Evans' benzil[3] which Brown and Hammick also obtained), its low solubility and its lack of "properties associated with carbon–carbon double bonds, hydroxyl groups or carbonyl groups." We are unable to subscribe to this view since our benzil forms a *p*-nitrophenylhydrazone, a *p*-nitrophenylosazone, a quinoxaline and its infrared absorption spectrum has the characteristic carbonyl bond at 1696 cm.$^{-1}$. Under the circumstances it seems desirable to study the two benzils more thoroughly before abandoning the conventional formula IV for the product of this investigation.

The glycol III was originally thought to be the benzoin, but this supposition was ruled out from its analysis and that of the dibenzoate, and its infrared absorption spectrum which gave a characteristic hydroxyl band at 3110 cm.$^{-1}$ and no carbonyl band. Its reactions, other than the dibenzoate formation, gave unexpected results. With hydroxylamine hydrochloride in a mixture of ethanol and pyridine, a pinacol rearrangement

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[1] Monsanto Chemical Company, Nitro, West Virginia.

[2] B. R. Brown and D. Ll. Hammick, *Nature*, **164**, 831 (1949); *J. Chem. Soc.*, 628 (1950).

[3] F. Linsker and R. L. Evans, THIS JOURNAL, **68**, 948 (1946).

[4] R. C. Fuson and co-workers, *ibid.*, **61**, 975, 2010 (1939).

[5] We are indebted to Dr. Wilson M. Whaley of this Laboratory for the determination and interpretation of all the infrared spectra obtained from Nujol mulls of the compounds.

[6] W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, 307 (1949).

occurred leading to the oxime of desoxyquinaldoin. Pyridine and hydrogen chloride alone gave desoxyquinaldoin (V). Hydroxylamine hydrochloride in a mixture of aqueous sodium hydroxide and dioxane yielded quinaldoxime while *p*-nitrophenylhydrazine in acetic acid solution produced quinaldehyde *p*-nitrophenylhydrazone. Apparently in the last two reactions the reagents oxidize the glycol to the benzoin which by reversion leads to the original aldehyde. It was not possible to convert the enediol to the glycol or the enediol dibenzoate to the glycol dibenzoate by catalytic reduction at low pressure in the presence of Adams platinum catalyst.

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Experimental[7]

Quinaldehyde (I).—This compound was prepared by the method of Kaplan,[8] 60 g. of quinaldine giving 27 g. (41%) of aldehyde, m. p. 69–70° (Henze[9] gives 71°).

1,2-Di-2-quinolyl-1,2-ethenediol (II).—To a solution of 26 g. of aldehyde in 300 ml. of 50% aqueous ethanol was added a solution of 2 g. of potassium cyanide in 5 ml. of water. The solution turned red and a dark brown solid separated immediately. This mixture was stirred for a few minutes and then heated at reflux temperature for about 30 minutes. After cooling, the enediol was filtered and washed first with water, then with several ml. of methanol and finally with a like amount of ether. Upon drying at 100°, 23.5 g. (90%) of black to dark purple metallic crystals, m. p. 230–231° (dec.) was obtained. Purification by crystallization from pyridine or dioxane elevated the melting point to 232–233° (dec.). The compound produces a silver mirror with Tollens reagent and destroys the color of sodium 2,6-dichlorobenzeneoneindophenol.

The enediol may also be produced by the hydrogenation of quinaldil with hydrogen at low pressure in the presence of Adams platinum catalyst. Further hydrogenation under these conditions does not occur.

Anal. Calcd. for $C_{20}H_{14}N_2O_2$: C, 76.43; H, 4.46; N, 8.92. Found: C, 76.55, 76.76; H, 4.28, 4.49; N, 9.58, 9.30.

The dibenzoate prepared in, and crystallized from, pyridine as white crystals, m. p. 236°.

Anal. Calcd. for $C_{34}H_{22}N_2O_4$: N, 5.36. Found: N, 5.50, 5.28.

Quinaldil (IV).—A solution of 3 g. of the enediol in 300 ml. of dioxane was heated to boiling and air was passed through the solution. When the dark brown color had changed to a light yellow, the solution was cooled and diluted with water; yellow crystals, 2.5 g. (83%), m. p. 266–268°. Purification by crystallization from pyridine elevated the melting point to 271–272°. (Linsker and Evans[2] give 175°; Brown and Hammick,[3] 266–267°.)

Anal. Calcd. for $C_{20}H_{12}N_2O_2$: C, 76.92; H, 3.84; N, 8.97. Found: C, 76.84, 76.68; H, 3.74, 3.68; N, 9.21, 9.29.

The *p*-nitrophenylhydrazone was prepared by dissolving 0.5 g. of the benzil and 0.25 g. of *p*-nitrophenylhydrazine in 25 ml. of boiling acetic acid, after which the *p*-nitrophenylhydrazone separated almost immediately from solution; yield 0.7 g., m. p. 260°. Three crystallizations from acetic acid elevated the melting point to 261–262°.

Anal. Calcd. for $C_{26}H_{17}N_5O_3$: N, 15.65. Found: N, 15.76, 15.51.

The *p*-nitrophenylosazone was prepared by dissolving 0.1 g. of the above *p*-nitrophenylhydrazone and 0.1 g. of *p*-nitrophenylhydrazine in 10 ml. of boiling pyridine and refluxing until precipitation appeared to be complete. The solid osazone after being washed with methanol, ether and acetic acid and then dried melted at 332–333°.

Anal. Calcd. for $C_{32}H_{22}N_8O_4$: N, 19.24. Found: N, 19.01, 19.07.

The quinoxaline was formed when 0.5 g. of quinaldil was boiled in a solution of 0.2 g. of *o*-phenylenediamine in 20 ml. of acetic acid for one hour. The cooled solution was poured in 100 ml. of water and the resulting emulsion was destroyed by adding 20% sodium hydroxide solution. The impure solid in solution in ethanol was heated with Norit A, after which cooling and dilution with water gave 0.5 g., m. p. 180–181°. Further purification by crystallization from an ethanol-water solution led to a melting point of 187°.

Anal. Calcd. for $C_{26}H_{16}N_4$: C, 81.23; H, 4.19. Found: C, 81.19, 81.25; H, 4.35, 4.39.

1,2-Di-2-quinolyl-1,2-ethanediol (III).—Many attempts were made to find a satisfactory method to prepare this compound. In the best method discovered the aldehyde, 2 g., dissolved in 20 ml. of pyridine, was diluted with 400 ml. of water and then while stirring a small amount of potassium cyanide was added. Almost immediately the solution became milky and then turned slightly yellow. By heating on a steam-cone, precipitation was completed and the yellow to brown solid was filtered and washed first with water and then with methanol. The crude product was leached with 50-ml. portions of carbon tetrachloride until the brown color of the enediol was removed. The white crystals remaining were crystallized from pyridine to give 0.8 g. (40%) of crystals, m. p. 214–215° (dec.). Further purification by crystallization from pyridine elevated the melting point to 218° (dec.).

Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 76.06, 75.89; H, 4.86, 4.99; N, 9.02, 8.74.

The dibenzoate prepared in pyridine and crystallized from ethyl acetate was a white solid, m. p. 225–226°.

Anal. Calcd. for $C_{34}H_{24}N_2O_4$: C, 77.84; H, 4.61; N, 5.34. Found: C, 77.79, 77.77; H, 4.61, 4.74; N, 5.52, 5.37.

Cleavage led to the formation of **quinaldoxime** when 0.3 g. of the glycol was refluxed for one hour in a mixture of 1 g. of hydroxylamine hydrochloride in 6 ml. of water, 4 ml. of sodium hydroxide solution and 20 ml. of dioxane. After the solution had been cooled and filtered, the filtrate was reduced to half its former volume in a current of air and water was added until precipitation was complete. About 0.15 g. of white solid was obtained. Crystallization several times from benzene, using Norit A the first time, gave well-formed needles, m. p. 190–191° (Kwartler and Lindwall[10] give 188–189°). A mixed melting point with the oxime prepared directly from quinaldehyde showed no depression.

Anal. Calcd. for $C_{10}H_8N_2O$: C, 69.75; H, 4.68. Found: C, 69.54, 69.54; H, 4.67, 4.63.

Cleavage likewise resulted in the formation of **quinaldehyde *p*-nitrophenylhydrazone** when 0.3 g. of the glycol, 0.3 g. of *p*-nitrophenylhydrazine and 15 ml. of acetic acid were refluxed for about 10 minutes. The solid, which separated on cooling, amounted to 0.2 g. after two crystallizations from acetic acid and melted at 251–253°. There was no depression in melting point when mixed with a specimen prepared directly from quinaldehyde.

Anal. Calcd. for $C_{15}H_{12}N_2O_2$: C, 65.74; H, 4.14. Found: C, 65.47, 65.77; H, 4.23, 4.16.

Desoxyquinaldoin Oxime.—A second oxime from the glycol was obtained as follows: A solution of 0.3 g. of the

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[7] All m. p.'s, which are uncorrected, were obtained using an aluminum melting point block.

[8] H. Kaplan, This Journal, **63**, 2655 (1941).

[9] M. Henze, *Ber.*, **67**, 750 (1934).

[10] C. E. Kwartler and H. G. Lindwall, This Journal, **59**, 524 (1937).

glycol in a mixture of 12 ml. of absolute ethanol, 15 ml. of pyridine and 0.4 g. of hydroxylamine hydrochloride was refluxed for 1 hour and 40 minutes, after which the volume was reduced to about 10 ml. The addition of water until precipitation was complete gave 0.3 g. of a white solid. Crystallization twice from ethanol and once from ethanol-water yielded the pure oxime, m. p. 209–210° (dec.).

Anal. Calcd. for $C_{20}H_{15}N_3O$: C, 76.65; H, 4.82. Found: C, 76.74, 76.66; H, 5.25, 5.22.

Desoxyquinaldoin (V).—The glycol, 0.5 g., in 20 ml. of pyridine in which a small amount of hydrogen chloride had been dissolved was refluxed for 30 minutes, cooled and poured into 250 ml. of dilute ammonium hydroxide solution. The yellow to orange precipitate when dried weighed 0.4 g., m. p. 218°. Three crystallizations from carbon tetrachloride elevated the melting point to 221°.

Anal. Calcd. for $C_{20}H_{14}N_2O$: C, 80.52; H, 4.82: N, 9.36. Found: C, 80.62, 80.35; H, 4.78, 4.58; N, 9.54, 9.45.

The desoxyquinaldoin yielded an **oxime** when treated with hydroxylamine hydrochloride in absolute ethanol and pyridine. The white crystals, m. p. 208–209° (dec.), melted unchanged when mixed with the second oxime obtained from the glycol as described above.

Anal. Calcd. for $C_{20}H_{15}N_3O$: C, 76.65; H, 4.82. Found: C, 76.62, 76.49; H, 4.84, 4.74.

The desoxyquinaldoin in a mixture of dioxane and pyridine oxidized to **quinaldil**, m. p. 271–272°, when air was passed through the solution for 24 hours. This compound melted unchanged when mixed with the quinaldil obtained by the oxidation of the enediol.

Anal. Calcd. for $C_{20}H_{12}N_2O_2$: C, 76.92; H, 3.84. Found: C, 76.34, 76.64; H, 3.80, 3.98.

Summary

The benzoin condensation of quinaldehyde produces 1,2-di-2-quinolyl-1,2-ethenediol and its reduction product, 1,2-di-2-quinolyl-1,2-ethanediol.

A chelated ring formula is proposed to account for the high stability of the enediol.

The validity of Brown and Hammick's formula for the quinaldil obtained on the oxidation of 1,2-di-2-quinolyl-1,2-ethenediol is questioned since the compound responds to physical and chemical tests indicating the presence of the carbonyl group.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OKLAHOMA]

Ketimines. II. Diaryl Type[1]

BY P. L. PICKARD AND D. J. VAUGHAN[2]

The stability of *t*-butyl *o*-tolyl ketimine to hydrolysis[3] suggested that diaryl ketimines substituted in the *o,o'*-positions might also be stable. In view of the ease with which the alkyl-aryl ketimines were prepared, the synthesis of diaryl ketimines seemed feasible.

The synthesis of the six isomeric ditolyl ketimines has shown the hypothesis of stability to hydrolysis to be incorrect. All ketimines hydrolyzed slowly in 6 *N* hydrochloric acid. The only reaction products isolated during preparation were unsubstituted ketimines, even when 150% excess aryl halide was used in the preparation of the Grignard reagent. The products distilled cleanly, leaving no high-boiling residues. When the ratio of aryl halide to nitrile was 1:1, traces of unreacted nitrile were recovered, due to incomplete formation of Grignard reagent,[4] undoubtedly. The yield of ketimine was not lowered appreciably, however, and the reaction mixture was more easily worked up because of the smaller amount of inorganic material present.

Hydrolysis experiments failed to answer the question of relative stability of the *o,o'*-ditolyl ketimine as compared to its isomers. All the compounds were sufficiently stable to prevent complete hydrolysis to ketone in acid solution over a 4-hour period, but the amount of ketimine hydrolyzed was practically the same in each case.

Reduction of the ketimines to the corresponding primary amines was easily accomplished over prereduced Adams catalyst at atmospheric pressure. Relative reduction rates, as indicated in the experimental portion, were calculated by plotting volume of hydrogen absorbed against time. While hydrolysis experiments failed to show any inhibitory effect of the *o*-tolyl group, hydrogenation data indicates a very definite decrease in rate due to this group.

Absorption spectra were determined in alcoholic solution. The spectra of imines and ketones were found to be similar. With the exception of the di-*p*-tolyl compounds, an arrangement of compounds in order of increasing wave length of maximum absorption is the same for the two types of compounds. Absorption of amines was different from that observed for the other compounds. This was expected because of the elimination of conjugation of the aromatic nuclei with groups in the side chain. Data on the spectra obtained are shown in Figs. 1–3.

Experimental

Preparation of Ketimines.—The procedure previously reported[3] was used. The ratio of aryl halide to aryl nitrile was varied in each case from 3:1 to 1:1 with no appreciable change in the amount of ketimine recovered.

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(1) This work was done under a contract with the Office of Naval Research.

(2) Based on a portion of a thesis presented by D. J. Vaughan in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Oklahoma.

(3) Pickard and Vaughan, THIS JOURNAL, **72**, 876 (1950).

(4) H. Gilman, *ibid.*, **51**, 1576 (1929), reports the maximum yields of *o*-, *m*- and *p*-tolylmagnesium bromide as 92.7, 88 and 86%, respectively.