thermodynamic, spectral and dielectric data that the potential curve for the proton in the F–H–F$^-$ ion has a single minimum at the midpoint.

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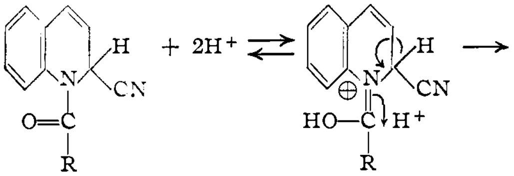
Mechanism of the Acid Catalyzed Formation of Aldehydes from Reissert Compounds

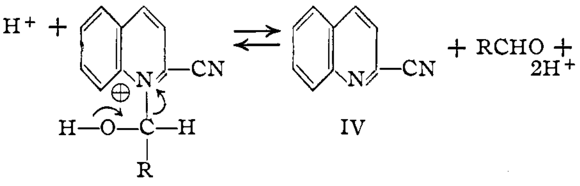
By William E. McEwen and Robert N. Hazlett

A general method for the preparation of an aldehyde from an acid chloride is first to convert the acid chloride to a Reissert compound, a 1-acyl-2-cyano-1,2-dihydroquinoline (I), by reaction with quinoline and aqueous potassium cyanide solution,[1,2,3] by reaction with quinoline and potassium cyanide in liquid sulfur dioxide[4] or by reaction with quinoline and liquid hydrogen cyanide in anhydrous benzene[5,6]; then to convert the Reissert compound to an aldehyde plus quinaldic acid by reaction with concentrated hydrochloric acid. The mechanism of the latter reaction is the subject of this investigation.

We propose that the first step in this reaction is the coördination of a proton with the amide oxygen of the Reissert compound (I) giving the conjugate acid (II).[7] By simultaneous loss of a proton from the 2-position of the quinoline ring and gain of a proton by the original carbonyl carbon atom, the complex (III) is formed, which then dissociates to an aldehyde and quinaldonitrile (IV). Under the conditions of the reaction the quinaldonitrile is hydrolyzed to quinaldic acid.[8] Doubtless an important driving force in the reaction is the gain in resonance energy attendant on conversion of the dihydroquinoline to a completely aromatic system.



I II



III IV

Evidence in support of the proposed mechanism has been obtained by a reaction of 1-benzoyl-2-cyano-1,2-dihydroquinoline (V) with hydrochloric acid in the presence of an excess of *p*-chlorobenzaldehyde. In addition to quinaldic acid and benzaldehyde, a significant quantity of *p*'-chlorobenzoin quinaldate (XI) was formed. Also the isomeric ester, *p*-chlorobenzoin quinaldate (XII) was obtained by reaction of 1-(*p*-chlorobenzoyl)-2-cyano-1,2-dihydroquinoline (VI) with hydrochloric acid in the presence of an excess of benzaldehyde.[9] The mechanism proposed earlier accounts for the formation of these esters assuming that the conjugate acids of the *p*-chlorobenzaldehyde (VII) and benzaldehyde (VIII) compete with the proton in the acceptance of an electron pair to form a new bond with the original carbonyl carbon atom of the Reissert compound, thus forming the complex (IX).[10]

Three schemes can be proposed as to how the esters XI and XII are obtained from the complex (IX): (1) The complex (IX) dissociates to quinaldonitrile and the free chlorobenzoin, which then undergo an acid catalyzed condensation to the ester by way of an imino ether. (2) The quinaldonitrile formed by dissociation of IX first undergoes hydrolysis to quinaldic acid, which is then esterified by reaction with the chlorobenzoin. (3) The complex IX gives the ester (XI or XII) via an intramolecular cyclization to the imino ether complex (X).[11] The first two possibilities were disproved when it was found that neither quinaldo-

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[1] Reissert, *Ber.*, **38**, 1603 (1905); **38**, 3415 (1905).

[2] Sugasawa and Tsuda, *J. Pharm. Soc. Japan*, **56**, 557 (1936).

[3] Rupe, Paltzer and Engel, *Helv. Chim. Acta*, **20**, 209 (1937); Rupe and Frey, *ibid.*, **22**, 673 (1939); Gassmann and Rupe, *ibid.*, **22**, 1241 (1939).

[4] Woodward, This Journal, **62**, 1626 (1940).

[5] Grosheintz and Fischer, *ibid.*, **63**, 2021 (1941).

[6] Buchanan, Cook and Loudon, *J. Chem. Soc.*, 325 (1944).

[7] Another important contributing resonance structure is one in which the oxygen atom bears the formal positive charge; *cf.*, Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 181.

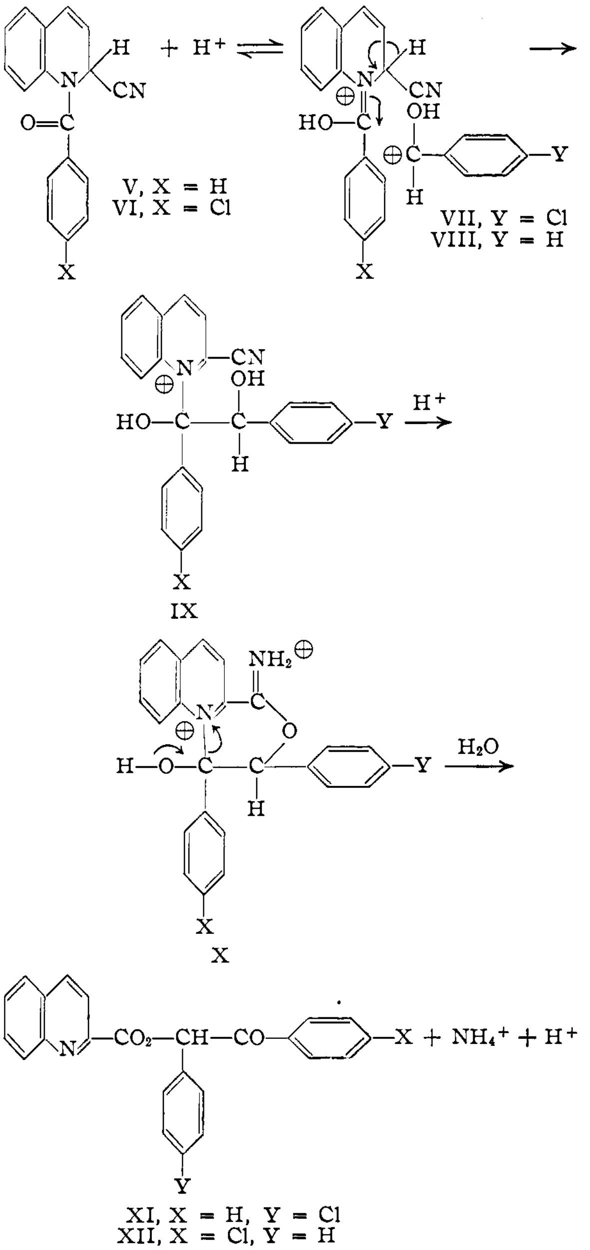
[8] There is little probability that the cyano group is hydrolyzed to a carboxyl group prior to aldehyde formation. Woodward and Kornfeld [This Journal, **70**, 2508 (1948)] have found that 1-benzoyl-2-carbomethoxy-3-acetyl-1,2-dihydroquinoline on treatment with hydrochloric acid at room temperature gives 1-benzoyl-3-acetyl-1,2-dihydroquinoline-2-carboxylic acid, and on treatment with hydrochloric acid at 100° gives benzoic acid and an unidentified oil. No benzaldehyde is formed.

[9] Reissert obtained a trace of benzoin quinaldate on reaction of 1-benzoyl-2-cyano-1,2-dihydroquinoline with hydrochloric acid.[1] The quantity of the ester was significantly increased by adding an excess of benzaldehyde at the start of the reaction.

[10] There is some degree of analogy between this reaction and the benzoin condensation. The intermediate IX is similar to one of the intermediate products of the benzoin condensation, $C_6H_5C(OH)(CN)CH(O^{\ominus})C_6H_5$, and the intermediate III might be termed a "vinylog" of an aldehyde cyanohydrin; *cf.* Luder and Zuffanti, "Electronic Theory of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 148.

[11] A fourth alternative, that the cyano group of V or VI is hydrolyzed to a carboxyl group prior to formation of a complex similar to IX, is excluded for the reason indicated in reference 8.

nitrile nor quinaldic acid reacts with benzoin under the conditions of the Reissert reaction.


V, X = H
VI, X = Cl

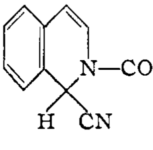
VII, Y = Cl
VIII, Y = H

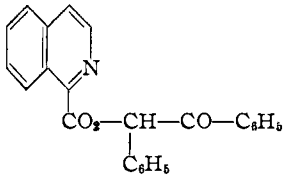
IX

X

XI, X = H, Y = Cl
XII, X = Cl, Y = H

More direct evidence favoring mechanism (3) was obtained by carrying out a competition reaction involving 1-(*p*-chlorobenzoyl)-2-cyano-1,2-dihydroquinoline (VI), 1-cyano-2-benzoyl-1,2-dihydroisoquinoline[12] (XIII), an excess of benzaldehyde and hydrochloric acid. The only products isolated from the reaction mixture, other than benzaldehyde, *p*-chlorobenzaldehyde, quinaldic acid and isoquinaldic acid, were *p*-chlorobenzoin quinaldate (XII), benzoin isoquinaldate (XIV), a small amount of free benzoin and a yellow product, $C_{34}H_{23}N_3O$. Since the latter three products were also obtained on reaction of the isoquinoline Reissert compound (XIII) itself with an excess of benzaldehyde and hydrochloric acid, it would seem that each of the Reissert compounds reacted in its own individual manner. The fact that no products corresponding to benzoin quinaldate or *p*-chlorobenzoin isoquinaldate were obtained further excludes the possibility of the esters having been formed *via* the free benzoins and further supports the concept of an intramolecular process starting from the complex (IX).


XIII


XIV

Difficulty was experienced in proving the exact structures of the isomeric esters XI and XII. Both gave quinaldic acid and a mixture of *p*- and *p'*-chlorobenzoin on alkaline hydrolysis.[13] Reaction of quinaldoyl chloride with the chlorobenzoins gave intractable oils. The esters were quite resistant to hydrolysis by aqueous sulfuric acid (3–12 *N*), and use of drastic conditions led to deep-seated decomposition. The esters would not undergo a Schmidt reaction under a variety of conditions. Reaction with phenylmagnesium bromide in ether solution also failed to take place. Finally, the ester obtained from reaction of 1-(*p*-chlorobenzoyl)-2-cyano-1,2-dihydroquinoline) (VI), excess benzaldehyde and hydrochloric acid was treated with one equivalent of hydroxylamine hydrochloride plus one equivalent of sodium acetate in alcohol solution. Unfortunately no crystalline oxime could be obtained, but treatment of the gummy reaction product with benzenesulfonyl chloride in dilute alkali solution led to the isolation of benzaldehyde (as the 2,4-dinitrophenylhydrazone) and *p*-chlorobenzonitrile. Since these are the products which would be anticipated from a Beckmann cleavage of *p*-chlorobenzoin oxime, this was considered as fair evidence in support of the assigned structure, namely, *p*-chlorobenzoin quinaldate (XII).[14]

Since benzoin isoquinaldate (XIV) was new to the literature its structure was proved by alkaline hydrolysis to benzoin and isoquinaldic acid. The structure of the yellow product, $C_{34}H_{23}N_3O$, obtained from acid treatment of the isoquinoline Reissert compound (XIII) is at present under investigation.

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[12] Reissert had previously shown that XIII gave benzaldehyde and isoquinaldic acid on reaction with hydrochloric acid.[1]

[13] The base catalyzed isomerization of an unsymmetrical benzoin is a well known reaction. *Cf.* Ide and Buck, "The Synthesis of Benzoins," pp. 269–304, in Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948.

[14] Ide and Buck, ref. 13. We could find no record in the literature of a Beckmann reaction involving an α-keto ester oxime.

Experimental[15]

1-(*p*-Chlorobenzoyl)-2-cyano-1,2-dihydroquinoline (VI).—To a mixture of 30.0 g. of potassium cyanide, 200 cc. of water and 28.2 g. of Skraup quinoline was added, in small portions with vigorous shaking and ice cooling, 45.0 g. of *p*-chlorobenzoyl chloride in the course of two hours. A precipitate of hard, pale yellow pellets was filtered, washed with water, 5% sodium bicarbonate solution and 5% hydrochloric acid. The dried, crushed product was exhaustively extracted with ether. The ether insoluble portion consisted of *p*-chlorobenzoic anhydride.

The ether extract, dried over anhydrous magnesium sulfate, gave a residue of pale amber oil which solidified on standing. Crystallization from ethanol afforded 16.7 g. (26%) of 1-(*p*-chlorobenzoyl)-2-cyano-1,2-dihydroquinoline (VI),[16] colorless prisms, m.p. 142–144°.

Anal. Calcd. for $C_{17}H_{11}ON_2Cl$: C, 69.27; H, 3.76; N, 9.51; Cl, 12.03. Found: C, 69.32, 69.35; H, 3.77, 3.63; N, 9.45; Cl, 11.73.

Reaction of 1-(*p*-Chlorobenzoyl)-2-cyano-1,2-dihydroquinoline (VI), Benzaldehyde and Hydrochloric Acid.—To a mixture of 10.0 g. of the dihydroquinoline and 20.0 g. of benzaldehyde was added dropwise, with mechanical stirring and ice cooling, 50 cc. of concentrated hydrochloric acid in the course of twenty minutes. The mixture was then allowed to stand at room temperature for an additional twenty-two hours with intermittent stirring. A bright yellow sludge, which had precipitated after adding the first few drops of hydrochloric acid, gradually dissolved. The mixture was diluted with water, partially neutralized with 10% sodium hydroxide solution (ice cooling), completely neutralized with saturated sodium bicarbonate solution, and steam distilled. The residual aqueous layer was decanted from some non-volatile, pale yellow solid, which was then washed with a small amount of hot absolute ethanol. There remained a colorless residue of 3.80 g. (28%) of *p*-chlorobenzoin quinaldate (XII), m. p. 170–172°. Several crystallizations from absolute ethanol, in which the substance is sparingly soluble, gave small, colorless prisms, m. p. 173–174°. The substance is poorly soluble in dilute hydrochloric acid.

Anal. Calcd. for $C_{24}H_{16}O_3NCl$: C, 71.73; H, 4.01; N, 3.49; Cl, 8.82. Found: C, 72.16, 71.83; H, 3.92, 4.15; N, 3.58, 3.57; Cl, 8.35, 8.45.

Alkaline Hydrolysis of the 173–174° Melting Product.—A solution of 2.0 g. of sodium carbonate in 20 cc. of water was added to a suspension of 1.71 g. of the product, m. p. 173–174°, in 15 cc. of ethanol, and the mixture was heated on the steam-bath for an hour, almost all solid material going into solution. After addition of 65 cc. of water, the resulting turbid solution was extracted with ether. Evaporation of the ether solution, dried over anhydrous magnesium sulfate, gave an impure solid. A fractional crystallization from 95% ethanol afforded 0.35 g. (33%) of *p'*-chlorobenzoin, m. p. 110–112°, as the least soluble component. A mixed m. p. with an authentic sample of *p'*-chlorobenzoin[17] showed no depression.

The alcohol mother liquors afforded 0.28 g. of lower melting material. By careful seeding of an ethanol solution of this material, a small amount of pure *p*-chlorobenzoin, m. p. 88–89°, was obtained. A mixed m. p. with an authentic sample of *p*-chlorobenzoin[17] showed no depression.

The aqueous carbonate solution was made faintly acidic with acetic acid, mixed with a saturated solution of copper acetate and heated on the steam-bath. A blue-green precipitate which formed was filtered, washed with distilled water and then decomposed by means of hydrogen sulfide. The copper sulfide was filtered and washed with hot water. Evaporation of the combined filtrate and wash afforded 0.40 g. (54%) of quinaldic acid, m. p. 154–155.5°. A mixed m. p. with an authentic sample of quinaldic acid showed no depression.

1-Benzoyl-2-cyano-1,2-dihydroquinoline (V).—The compound was prepared by the method of Rupe, Paltzer and Engel,[3] small colorless needles from alcohol, m. p. 154–155°.

Anal. Calcd. for $C_{17}H_{12}ON_2$: C, 78.41; H, 4.65; N, 10.79. Found: C, 78.67, 78.42; H, 4.33, 4.72; N, 11.06, 11.04.

Reaction of 1-Benzoyl-2-cyano-1,2-dihydroquinoline (V), *p*-Chlorobenzaldehyde and Hydrochloric Acid.—To an intimate mixture of 20.0 g. of the dihydroquinoline and 20.0 g. of *p*-chlorobenzaldehyde was added 100 cc. of concentrated hydrochloric acid in the course of ninety minutes, with ice cooling and mechanical stirring. The mixture was allowed to stand for an additional twenty-two hours with intermittent stirring. Most of the organic material went into solution, but some oil and some solid material remained undissolved. An aqueous solution containing 48.0 g. of sodium hydroxide was added to the mixture with ice cooling. The resulting faintly alkaline mixture was extracted with ether, and a trace of red solid insoluble in either layer was removed by filtration. The ether solution was washed with 5% sodium bicarbonate solution and then with 10% hydrochloric acid. The ether solution was then agitated vigorously with saturated sodium bisulfite solution for several minutes. A fairly large quantity of solid bisulfite addition compound precipitated and was removed by filtration.

Evaporation of the ether solution, dried over anhydrous magnesium sulfate, afforded about 5 cc. of pale orange liquid, which solidified, for the most part, on cooling. Crystallization from alcohol afforded 3.70 g. (12%) of *p'*-chlorobenzoin quinaldate (XI), small colorless needles, m. p. 150–151°.

Anal. Calcd. for $C_{24}H_{16}O_3NCl$: C, 71.73; H, 4.01; N, 3.49; Cl, 8.82. Found: C, 72.00, 71.95; H, 3.90, 3.88; N, 3.60, 3.56; Cl, 8.49, 8.45.

The alcohol mother liquor afforded 0.50 g. of benzoin quinaldate, m. p. 163–165°.[1] A mixed m. p. with an authentic sample of benzoin quinaldate showed no depression.

Benzoin Quinaldate.—A solution of 0.25 g. of benzoin and 0.30 g. of quinaldoyl chloride[18] in 3 cc. of dry pyridine was heated to boiling, and the red solution was then poured into water and partially neutralized with hydrochloric acid. A red solid which precipitated was twice crystallized from absolute ethanol (Norit). Tiny colorless prisms were obtained, m. p. 164–165°, 0.05 g.

Alkaline Hydrolysis of the 150–151° Melting Product.—Using the same procedure as for the 173–174° melting product, the same products in substantially the same yields were obtained.

Reaction of Benzoin, Quinaldic Acid and Hydrochloric Acid.—A mixture of 0.50 g. of benzoin, 0.40 g. of quinaldic acid and 8 cc. of concentrated hydrochloric acid was kept at room temperature, with intermittent stirring, for twenty-four hours. On working up the reaction mixture the benzoin was recovered unchanged in quantitative yield.

Reaction of Benzoin, Quinaldonitrile and Hydrochloric Acid.—A mixture of 0.20 g. of benzoin, 0.20 g. of quinaldonitrile[19] and 6 cc. of concentrated hydrochloric acid was allowed to stand at room temperature for twenty-four hours. The benzoin was recovered unchanged. Reaction also failed to take place in 1:1 dioxane–hydrochloric acid.

Proof of Structure of the 173–174° Melting Product.—To a suspension of 2.12 g. of the ester, m. p. 173–174°, in

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(15) All m. p.'s are corrected. Analyses by Oakwold Laboratories, Alexandria, Va.

(16) Grosheintz and Fischer[6] obtained VI in 77% of the theoretical yield by reaction of quinoline, *p*-chlorobenzoyl chloride and liquid hydrogen cyanide in dry benzene.

(17) Weissberger, Strasser, Mainz and Schwarze, *Ann.*, **478**, 112 (1930). Although these authors reported a m. p. of 110–111° for *p'*-chlorobenzoin, the product obtained by us according to their procedure had a m. p. of 114–115°, after two crystallizations from ethanol. A m. p. of 116–117° has been reported by Jenkins, THIS JOURNAL, **56**, 682 (1934).

(18) Beshorn and Ibele, *Ber.*, **39**, 2330 (1906).

(19) Kaufmann and Dandliker, *ibid.*, **46**, 2924 (1913).

100 cc. of absolute ethanol was added 0.74 g. of hydroxylamine hydrochloride and 0.87 g. of sodium acetate. The mixture was kept at room temperature for three hours, heated under reflux for two hours, and then kept at room temperature for an additional twelve hours. The alcohol was evaporated at reduced pressure, and 10 cc. of 10% hydrochloric acid was added to the residue. The resulting mixture was extracted with ether, and the ether solution washed with sodium bicarbonate solution. Evaporation of the ether solution, dried over anhydrous sodium sulfate, left a residue of pale yellow, intractable gum. This was suspended in 10 cc. of 10% sodium hydroxide solution, and 1 cc. of benzenesulfonyl chloride was added dropwise with shaking. Heat was evolved, and a strong isonitrile odor became apparent. The mixture was shaken for forty-five minutes, then extracted with ether. Acidification of the basic aqueous solution gave no precipitate of organic acid. The ether solution was washed with dilute hydrochloric acid (no organic base was obtained on making the acid solution basic), dried over anhydrous sodium sulfate and evaporated. The residual red oil was dissolved in alcohol and mixed with 25 cc. of 2,4-dinitrophenylhydrazine reagent.[20] An orange solid was obtained at room temperature, which, crystallized from ethyl acetate, afforded 0.54 g. (36% based on the ester) of benzaldehyde 2,4-dinitrophenylhydrazone, m. p. 235–236°. A mixed m. p. with an authentic sample of benzaldehyde 2,4-dinitrophenylhydrazone showed no depression. In another run the benzaldehyde was identified by conversion to the phenylhydrazone, m. p. 156–158°.

The alcohol mother liquor of the 2,4-dinitrophenylhydrazine reagent was concentrated, mixed with 10% hydrochloric acid and extracted with ether. The ether solution was dried over anhydrous sodium sulfate, treated with Norit and evaporated. There remained 0.20 g. (28%) of *p*-chlorobenzonitrile, m. p. 89–91°. On alkaline hydrolysis of the nitrile, ammonia was evolved, and acidification of the solution gave 0.18 g. of *p*-chlorobenzoic acid, m. p. 240–241°. A mixed m. p. with an authentic sample of *p*-chlorobenzoic acid showed no depression.

Reaction of 1-Cyano-2-benzoyl-1,2-dihydroisoquinoline, Benzaldehyde and Hydrochloric Acid.—To a mixture of 10.0 g. of 1-cyano-2-benzoyl-1,2-dihydroisoquinoline (XIII), m. p. 126–127°, prepared by the method of Rupe and Frey,[3] and 15.0 g. of benzaldehyde was added 50 cc. of concentrated hydrochloric acid in the course of one hour, with ice cooling and mechanical stirring. A bright orange color developed on addition of the first few drops of acid. The mixture was allowed to stand, with intermittent stirring, for an additional twenty-four hours, then diluted with water, partially neutralized with sodium hydroxide solution (ice cooling) and completely neutralized with sodium bicarbonate solution. The mixture was steam distilled, leaving behind a mass of viscous red liquid, which was taken up in ether, dried over anhydrous magnesium sulfate and treated with Norit. Evaporation of the ether left a red oil, which was dissolved in methyl alcohol and treated with Norit three times. Evaporation of the methyl alcohol gave a red, solid mass. A fractional crystallization of this solid from absolute ethanol afforded 1.34 g. (9.5%) of benzoin isoquinaldate (XIV), small, colorless prisms, m. p. 152.8–153.0° (dec.).

Anal. Calcd. for $C_{24}H_{17}NO_3$: C, 78.44; H, 4.67; N, 3.82. Found: C, 78.83, 78.80; H, 4.92, 4.93; N, 4.02, 4.14.

The second product of the fractional crystallization was a substance previously reported by Reissert,[1] pale yellow needles, m. p. 124–125°, 2.88 g.

Anal. Calcd. for $C_{34}H_{23}N_3O$: C, 83.39; H, 4.73; N, 8.61. Found: C, 83.01, 83.17; H, 4.45, 4.85; N, 9.10, 8.75.

The ethanol mother liquor was concentrated, mixed with 50 cc. of concentrated hydrochloric acid and extracted with ether. Evaporation of the ether solution, dried over anhydrous magnesium sulfate, afforded 0.30 g. (3.7%) of benzoin, m. p. 133–134°. A mixed m. p. with an authentic sample of benzoin showed no depression.

Alkaline Hydrolysis of the Benzoin Isoquinaldate.—On subjecting 0.31 g. of the ester, m. p. 152.8–153.0°, to alkaline hydrolysis, using the same procedure as for the chlorobenzoin quinaldates, there was obtained 0.15 g. (84%) of benzoin and 0.12 g. (82%) of isoquinaldic acid, m. p. 160–161°. A mixed m. p. with an authentic sample of isoquinaldic acid showed no depression.

Reaction of 1-(*p*-Chlorobenzoyl)-2-cyano-1,2-dihydroquinoline (VI), 1-Cyano-2-benzoyl-1,2-dihydroisoquinoline (XIII), Benzaldehyde and Hydrochloric Acid.—To a mixture of 5.00 g. of 1-(*p*-chlorobenzoyl)-2-cyano-1,2-dihydroquinoline, 10.00 g. of 1-cyano-2-benzoyl-1,2-dihydroisoquinoline and 30.0 g. of benzaldehyde was added in the course of twenty minutes 70 cc. of concentrated hydrochloric acid, with ice cooling and mechanical stirring. The mixture was allowed to stand for twenty-four hours with intermittent stirring. The strongly acid mixture was extracted with ether (ice cooling). A yellow solid, insoluble in either layer, was kept with the hydrochloric acid solution. The ether solution, yellow and fluorescent, was washed with sodium bicarbonate solution, exhaustively extracted with saturated sodium bisulfite solution, then washed with water. Evaporation of the ether solution, dried over anhydrous magnesium sulfate, afforded 0.47 g. of benzoin, m. p. 133–134°.

The original strongly acid solution plus yellow solid was diluted with a fivefold quantity of water, more yellow solid precipitating. The mixture was extracted with ether, but much of the solid material remained undissolved. This solid was washed with a small amount of ethanol, and there remained 1.01 g. of *p*-chlorobenzoin quinaldate (XII), m. p. 172–174°. The orange ether solution was dried over anhydrous magnesium sulfate, treated with Norit and evaporated. A red oil which remained finally solidified. A fractional crystalization of this solid from absolute ethanol afforded an additional 0.48 g. of *p*-chlorobenzoin quinaldate, m. p. 172–174°; 1.30 g. of benzoin isoquinaldate (XIV), m. p. 152–153°; and 3.19 g. of the yellow compound, $C_{34}H_{23}N_3O$, m. p. 124–125°. All these substances gave no depression in mixed m. p. tests with authentic samples.

Summary

A mechanism has been proposed for the acid catalyzed formation of aldehydes from Reissert compounds. Evidence in support of this mechanism has been obtained by the reaction of 1-benzoyl-2-cyano-1,2-dihydroquinoline with an excess of *p*-chlorobenzaldehyde and hydrochloric acid, *p'*-chlorobenzoin quinaldate being obtained; and of 1-(*p*-chlorobenzoyl)-2-cyano-1,2-dihydroquinoline with an excess of benzaldehyde and hydrochloric acid, *p*-chlorobenzoin quinaldate being obtained. A unique feature of the ester formation, an intramolecular process starting from an intermediate product of the reaction, has been deduced from the experimental facts.

LAWRENCE, KANSAS

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(20) Shriner and Fuson, "The Systematic Identification of Organic Compounds," 3d ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.