Methanol (150 ml.) and 2 g. of potassium hydroxide in excess of that required for neutralization were added. The reaction mixture was refluxed gently for two hours, cooled and then acidified with concentrated hydrochloric acid. The white solid (2.9 g., 86% yield) which separated melted at 199–200°, after recrystallization from ethanol. The product was soluble in dilute aqueous alkali and gave a greenish-yellow color with alcoholic ferric chloride.

Anal. Calcd. for $C_{14}H_{15}NO_2$: N, 6.11. Found: N, 5.96.

N-Methyl-N-(2-acetoxy-1-naphthylmethyl)-acetamide.—A solution of 2.9 g. of VI (0.013 mole) in 12 ml. of acetic anhydride was heated for eight hours at 100–110°. The white solid (3.1 g., 90% yield) obtained by neutralizing the reaction mixture with an excess of aqueous sodium bicarbonate melted at 123–125°, after recrystallization from methanol-water.

Anal. Calcd. for $C_{16}H_{17}NO_3$: N, 5.16. Found: N, 5.13.

N-Benzyl-N-(2-hydroxy-1-naphthylmethyl)-acetamide (IX).—Eight grams of IV in 25 ml. of acetic anhydride was heated at 130° for 12 hours. During the course of the reaction air was passed over the solution and into a solution of 2,4-dinitrophenylhydrazine. The product (m.p. 165–166°) did not depress the m.p. of formaldehyde 2,4-dinitrophenylhydrazone (m.p. 166°). The reaction mixture was concentrated to 15 ml. under reduced pressure and 100 ml. of methanol containing 4 g. of potassium hydroxide added. This solution was warmed (55°) for three hours and poured into 400 ml. of water. The solid (3.3 g., 37% yield) which separated upon acidification with hydrochloric acid melted at 169–170°, after recrystallization from ethanol.

Anal. Calcd. for $C_{20}H_{19}NO_2$: N, 4.59. Found: N, 4.51.

Alkaline Hydrolysis of II.—Three grams of II was heated under reflux for 30 minutes in 30 ml. of water containing 4 g. of potassium hydroxide. After this time the odor of methylamine was not detectable. The reaction mixture was diluted with 200 ml. of water and acidified with hydrochloric acid. The resulting white crystalline product (2.4 g.) melted at 202–203°, after recrystallization from methanol, and did not depress the m.p. of bis-(2-hydroxy-1-naphthyl)-methane (m.p. 202–203°, lit. m.p. 200°[19]).

3,4-Dihydro-3-cyclohexyl-2H-naphth[2.1-e]-*m*-oxazine.—To a solution of 9.9 g. of cyclohexylamine (0.1 mole) in 100 ml. of methanol was added with cooling 15 ml. of 37% aqueous formaldehyde (0.20 mole) in 100 ml. of methanol. The solution was cooled to −5° and added quickly to a cold solution of 14.4 g. of 1-naphthol (0.1 mole) in 100 ml. of methanol. After 10 minutes at 0°, a large crop of crystals had formed and the reaction mixture stood at room temperature for one hour. The white crystalline solid (18.0 g., 67% yield) obtained upon cooling and filtration melted at 83–87°. Heating in methanol or acetone resulted in decomposition but the product could be recrystallized by dissolving it in acetone at 25° and cooling the solution in an acetone–Dry Ice-bath; m.p. 86–88°.

Anal. Calcd. for $C_{18}H_{21}NO$: N, 5.24. Found: N, 5.16.

2-Cyclohexylaminomethyl-1-naphthol Hydrochloride.—A mixture of 11.2 g. of 3,4-dihydro-3-cyclohexyl-2H-naphth-[2.1-e]-*m*-oxazine (0.042 mole) and 5.0 ml. of concentrated hydrochloric acid in 50 ml. of ethanol was boiled for five minutes and then cooled. The resulting crystalline product (8.03 g.) was removed by filtration; m.p. 171–174° (dec.), after recrystallization from ethanol. An additional 1.48 g. was obtained from the mother liquor; yield 79%.

Anal. Calcd. for $C_{17}H_{22}ClNO$: Cl, 12.15. Found: Cl, 12.08.

2-Piperidinomethyl-1-naphthol.—A mixture of 1.2 g. (0.004 mole) of 2-cyclohexylaminomethyl-1-naphthol hydrochloride and 1.74 g. of piperidine (0.02 mole) was heated at 100–110° for 30 minutes. Upon addition of 10 ml. of methanol and cooling 0.70 g. of product was obtained; m.p. 133–134°, after recrystallization from methanol; yield 71%. The product did not depress the m.p. of 2-piperidinomethyl-1-naphthol (m.p. 133–134°, lit. m.p. 133–134°[20] and 137[7]).

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[19] K. Fries and H. Hubner, *Ber.*, **39**, 439 (1906).

[20] K. Auwers and A. Dombrowski, *Ann.*, **344**, 280 (1906).

SALT LAKE CITY, UTAH

RECEIVED SEPTEMBER 4, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KANSAS]

Formation of Aldehydes from Partially Hydrogenated N-Acyl-Pyridine, -Quinoline and -Isoquinoline Derivatives

BY WILLIAM E. MCEWEN, ROBERT H. TERSS AND I. WESLEY ELLIOTT

RECEIVED JANUARY 28, 1952

Two dihydro-Reissert compounds have been prepared and shown to give aldehydes on treatment with a mineral acid, but in poor yields compared to the parent compounds. A condensation of benzoyl chloride, dimethylaniline and quinoline gave 1-benzoyl-2-(*p*-dimethylaminophenyl)-1,2-dihydroquinoline (VI), but, in contrast to the corresponding pyridine reaction, this product did not dissociate to benzaldehyde and 2-(*p*-dimethylaminophenyl)-quinoline (VII), even under acidic conditions.

In previous papers[1,2] a mechanism was proposed for the acid-catalyzed formation of aldehydes from Reissert compounds, 1-acyl-1,2-dihydroquinaldonitriles and 2-acyl-1,2-dihydroisoquinaldonitriles, and evidence in support of that mechanism was presented. Since quinaldic acid and isoquinaldic acid are also major products in these reactions, these being derived from the initially formed quinaldonitrile and isoquinaldonitrile, it was suggested that the gain in resonance energy in going from the dihydro-compound to the completely aromatic compound might be an important driving force in this type of reaction. As a possible experimental evaluation of this idea, we have prepared two dihydro-Reissert compounds and have studied their behavior toward a mineral acid.

The addition of one mole of hydrogen to 1-benzoyl-1,2-dihydroquinaldonitrile (IA) afforded 1-benzoyl-1,2,3,4-tetrahydroquinaldonitrile (IIA) in 69% yield. In like manner, 1-benzoyl-6-methoxy-1,2-dihydroquinaldonitrile (IB) gave 1-benzoyl-6-methoxy-1,2,3,4-tetrahydroquinaldonitrile (IIB) in 62% yield. An attempted reduction of 2-benzoyl-1,2-dihydroisoquinaldonitrile, however, failed to give the anticipated 2-benzoyl-1,2,3,4-tetrahydroisoquinaldonitrile. About half the starting material was recovered, and some intractable substance was formed. Evidently the initial product of reduction is hydrogenated further at a faster rate than the isoquinoline Reissert compound itself.

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[1] W. E. McEwen and R. N. Hazlett, THIS JOURNAL, **71**, 1949 (1949).

[2] W. E. McEwen, J. V. Kindall, R. N. Hazlett and R. H. Glazier, *ibid.*, **73**, 4591 (1951).

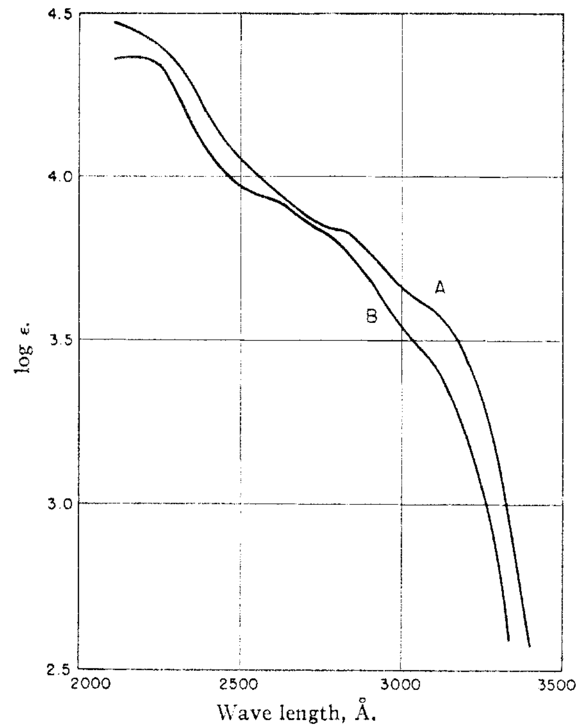
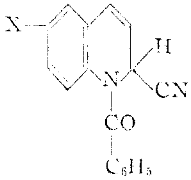
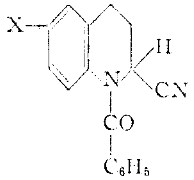


Fig. 1.—Ultraviolet absorption spectra in ethanol of: A, 1-benzoyl-1,2-dihydroquinaldonitrile (IA); B, 1-benzoyl-1,2,3,4-tetrahydroquinaldonitrile (IIA).

The ultraviolet absorption spectra of IA and IIA are shown in Fig. 1. The more highly conjugated IA absorbs at a slightly greater wave length over the whole absorption region.



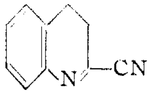
IA, X = H
IB, X = OCH_3



IIA, X = H
IIB, X = OCH_3

Each of the four compounds, IA, IB, IIA and IIB, was allowed to react with a hydrochloric acid solution of 2,4-dinitrophenylhydrazine until completion of the reaction. The yields of benzaldehyde-2,4-dinitrophenylhydrazone varied as follows: from IA, 87%; IIA, 40%; IB, 98%; IIB, 38%. In each case the benzoyldihydroquinaldonitrile gave about twice the yield of benzaldehyde as the benzoyltetrahydroquinaldonitrile. Evidently some side reaction, probably hydrolysis of the nitrile or amide group, competes favorably with aldehyde formation in the case of the benzoyltetrahydroquinaldonitriles.

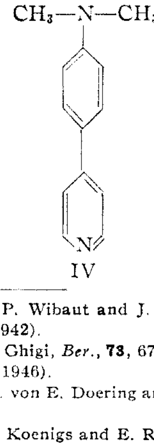
These results indicate that the magnitude of the gain in resonance energy on going from the reactants to the products does indeed play an important role in determining the yield of the aldehyde formed, but that this effect is not a necessary condition for the reaction to occur, at least in part. Whereas there is a large gain in resonance energy in going from 1-benzoyl-1,2-dihydroquinaldonitrile (IA), for example, to benzaldehyde plus quinaldonitrile, which is subsequently hydrolyzed to quinaldic acid, there is probably little gain in resonance energy in going from 1-benzoyl-1,2,3,4-tetrahydroquinaldonitrile (IIA) to benzaldehyde and the hypothetical intermediate, 3,4-dihydroquinaldonitrile (III). Actually, we were unable to isolate III; evidently it is subsequently hydrolyzed and either oxidized or dehydrogenated to quinaldic acid, the product actually isolated in this case too. The 2,4-dinitrophenylhydrazine used in these reactions does not effect the formation of benzaldehyde, since all four compounds give benzaldehyde with hydrochloric acid alone. The nitro compound, however, might help bring about the oxidation of the initially formed III.



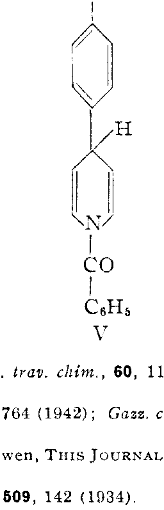
III

The formation of an aldehyde from a partially hydrogenated N-acyl-pyridine, -quinoline or -isoquinoline derivative appears to be a fairly general reaction. Wibaut and Arens[3] have reported the formation of acetaldehyde in the reduction of 1,4-diacetyl-1,4-dihydropyridine to 4-ethylpyridine by means of zinc dust and an acetic acid, acetic anhydride solution. Ghigi[4] has detected acetaldehyde as a by-product in the conversion of 1-acetoxy-2-(1′-acetyl-1′,4′-dihydro-4′-pyridyl)-acenaphthylene[5] to 1-acetoxy-2-(4′-pyridyl)-acenaphthylene in pyridine, acetic anhydride solution. Koenigs and Ruppelt[6] obtained benzaldehyde plus 4-(*p*-dimethylaminophenyl)-pyridine (IV) in the reaction between benzoyl chloride, pyridine and dimethylaniline, catalyzed by "Naturkupfer C."

In a vain attempt to gain some insight into the mechanism of these reactions, we have reinvestigated a portion of the work of Koenigs and Ruppelt. Although IV was obtained from the reaction of pyridine, benzoyl chloride and dimethylaniline at room temperature, without the use of a copper catalyst, the hypothetical intermediate, 1-benzoyl-4-(*p*-dimethylaminophenyl)-1,4-dihydropyridine (V) could not be isolated. Benzaldehyde was formed directly in the reaction mixture together with IV and did not result as a consequence of the isolation procedure. The rate of formation of V, the prob-



IV



V

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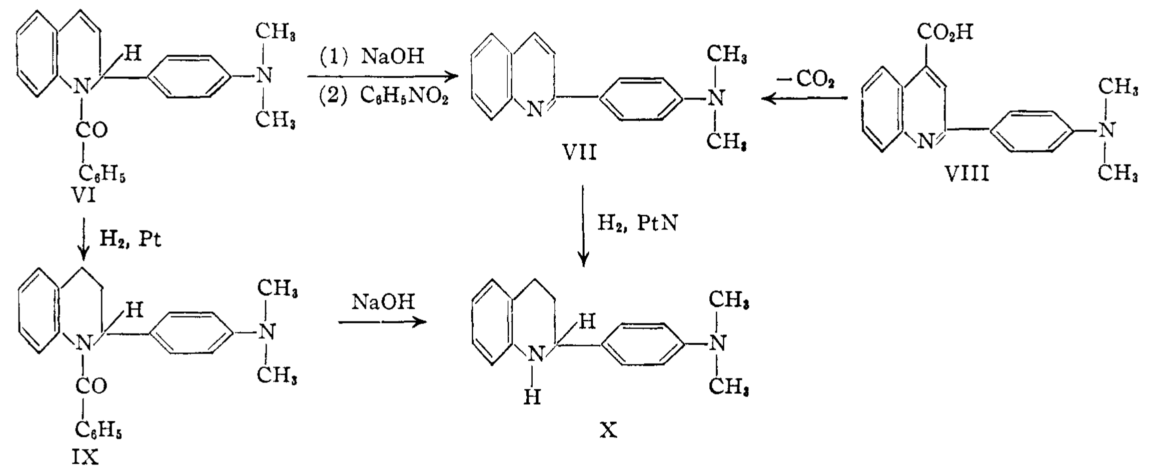
[3] J. P. Wibaut and J. F. Arens, *Rec. trav. chim.*, **60**, 119 (1941); **61**, 59 (1942).

[4] E. Ghigi, *Ber.*, **73**, 677 (1940); **75**, 764 (1942); *Gazz. chim. ital.*, **76**, 352 (1946).

[5] W. von E. Doering and W. E. McEwen, THIS JOURNAL, **73**, 2104 (1951).

[6] E. Koenigs and E. Ruppelt, *Ann.*, **509**, 142 (1934).



able intermediate, is evidently slow compared to the rate of its dissociation to benzaldehyde and IV.

An extension of the above reaction to quinoline, benzoyl chloride and dimethylaniline gave 1-benzoyl-2-(*p*-dimethylaminophenyl)-1,2-dihydroquinoline (VI),[7] its structure being proved as follows: Alkaline hydrolysis of VI gave benzoic acid, and, after treatment of the amine fraction with nitrobenzene or picric acid, 2-(*p*-dimethylaminophenyl)-quinoline (VII). An authentic specimen of VII was obtained by decarboxylation of 2-(*p*-dimethylaminophenyl)-quinoline-4-carboxylic acid (VIII), which was prepared by a Döbner synthesis.[8]

Catalytic addition of one mole of hydrogen to VI gave 1-benzoyl-2-(*p*-dimethylaminophenyl)-1,2,3,4-tetrahydroquinoline (IX). Alkaline hydrolysis of IX gave benzoic acid and 2-(*p*-dimethylaminophenyl)-1,2,3,4-tetrahydroquinoline (X). Catalytic addition of two moles of hydrogen to VII in an acidic medium also gave X.

All attempts to obtain benzaldehyde from VI failed. Treatment with hot 9 *M* sulfuric acid gave benzoic acid, and reactions with 2,4-dinitrophenylhydrazine reagent and either concentrated hydrochloric acid or Lucas reagent also failed to give benzaldehyde. Other than as a possible manifestation of either a steric effect or the greater intrinsic stability of dihydroquinolines compared to dihydropyridines, it is difficult to account for the contrasting behavior of the pyridine and quinoline systems.

Whereas the few reactions in the literature support the contention that acylpyridinium salts are attacked by nucleophilic reagents at the 4-position,[5] the evidence of Reissert compounds and the above described condensation product (VI) suggests that acylquinolinium salts are attacked by bases at the 2-position. We are investigating further reactions designed to test these generalizations.

Experimental[9]

1-Benzoyl-1,2,3,4-tetrahydroquinaldonitrile (IIA).—A suspension of 1.00 g. of 1-benzoyl-1,2-dihydroquinaldonitrile (IA)[10] and 0.10 g. of platinum oxide catalyst in 150 cc. of 95% ethanol was hydrogenated at atmospheric pressure and room temperature until the theoretical volume of hydrogen corresponding to one molar equivalent had been absorbed. The solution was filtered and the filtrate concentrated. A colorless, crystalline precipitate of 0.70 g. (69%) of 1-benzoyl-1,2,3,4-tetrahydroquinaldonitrile (IIA) was collected, m.p. 124–127°. Two recrystallizations from ethanol raised the m.p. to 134–135°.

Anal. Calcd. for $C_{17}H_{14}ON_2$: C, 77.84; H, 5.34; N, 10.68. Found: C, 77.81; H, 5.16; N, 10.6.

1-Benzoyl-6-methoxy-1,2,3,4-tetrahydroquinaldonitrile (IIB).—A suspension of 1.00 g. of 1-benzoyl-6-methoxy-1,2-dihydroquinaldonitrile (IB)[11] and 0.10 g. of platinum oxide catalyst in 100 cc. of 95% ethanol was allowed to absorb one molar equivalent of hydrogen at atmospheric pressure and room temperature. After filtration and concentration of the filtrate, there was obtained 0.62 g. (62%) of crystalline 1-benzoyl-6-methoxy-1,2,3,4-tetrahydroquinaldonitrile (IIB), m.p. 134–137°. Completely purified material melted at 141–142°.

Anal. Calcd. for $C_{18}H_{16}O_2N_2$: C, 73.95; H, 5.52; N, 9.59. Found: C, 74.21, 74.16; H, 5.62, 5.69; N, 10.01, 10.12.

Formation of Benzaldehyde-2,4-dinitrophenylhydrazone from 1-Benzoyl-1,2,3,4-tetrahydroquinaldonitrile (IIA).—A mixture of 5.00 g. (0.019 mole) of 1-benzoyl-1,2,3,4-tetrahydroquinaldonitrile (IIA), 3.80 g. (0.019 mole) of 2,4-dinitrophenylhydrazine and 110 cc. of concentrated hydrochloric acid was heated on the steam-bath for half an hour, then allowed to stand at room temperature for 48 hours. An additional 400 cc. of water was added, the mixture heated on the steam-bath, and an insoluble orange precipitate filtered and washed with hot water. There remained 2.20 g. (40%) of benzaldehyde-2,4-dinitrophenylhydrazone, m.p. 237–239°.

The filtrate was made basic with sodium bicarbonate solution and the precipitate of 2,4-dinitrophenylhydrazine removed. The alkaline filtrate was made faintly acidic with acetic acid and added to a hot solution of copper sulfate. A blue-green precipitate which formed was washed with water, then suspended in distilled water and decomposed with hydrogen sulfide. The copper sulfide was filtered and the filtrate evaporated to dryness. There remained 0.80 g. of crude material, m.p. 142–145°. One crystallization from water gave quinaldic acid, m.p. 155–156° (dec.), also in admixture with an authentic specimen of the acid.

Formation of Benzaldehyde-2,4-dinitrophenylhydrazone from IA, IB and IIB.—Treated in the manner described above for 1-benzoyl-1,2,3,4-tetrahydroquinaldonitrile (IIA), there was obtained from 1-benzoyl-1,2-dihydroquinaldonitrile (IA) an 87% yield of benzaldehyde-2,4-dinitrophenylhydrazone; from 1-benzoyl-6-methoxy-1,2-dihydroquinaldonitrile (IB), 98%; from 1-benzoyl-6-methoxy-1,2,3,4-tetrahydroquinaldonitrile (IIB), 38%.

Reaction of Pyridine, Benzoyl Chloride and Dimethylaniline. A. At Room Temperature.—A mixture of 28.1 g.

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[7] Our evidence does not exclude the isomeric structure, 1-benzoyl-2-(*p*-dimethylaminophenyl)-1,4-dihydroquinoline.

[8] H. Gilman, J. L. Towle and S. M. Spatz (THIS JOURNAL, **68**, 2017 (1946)) reported the formation of VII by the addition of *p*-dimethylaminophenyllithium to quinoline, but based the structure on analogy with other similar reactions rather than providing an independent proof.

[9] Analyses by Weiler and Strauss, Oxford, England, and Oakwold Laboratories, Alexandria, Virginia. All m.p.'s are corrected.

[10] H. Rupe, R. Paltzer and K. Engel, *Helv. Chim. Acta*, **20**, 20 (1937).

[11] A. Gassmann and H. Rupe, *ibid.*, **22**, 1241 (1939).

(0.20 mole) of freshly distilled benzoyl chloride, 23.7 g. (0.30 mole) of pyridine, distilled from anhydrous barium oxide, and 19.4 g. (0.16 mole) of purified[12] dimethylaniline was kept at room temperature in a tightly stoppered flask for seven weeks. The violet colored solid mixture which resulted was washed with dry ether, leaving an insoluble red salt. This was crystallized from 95% ethanol, whereupon 7.30 g. (19.4%) of 4-(*p*-dimethylaminophenyl)-pyridine hydrochloride was obtained, orange plates, m.p. 219.0–220.5° when the temperature was raised at the rate of 2° per minute; reported[6] 220°.

The ether wash solution was evaporated and the residue steam distilled. There remained in the distilling flask a tan residue which was crystallized from a 10:1 mixture of ethanol and chloroform, yielding 0.90 g. (2.8%) of colorless leaflets of 4-(*p*-dimethylaminophenyl)-pyridine (IV), m.p. 235.4–236.4°; reported[6] 234°.

B. At 100°.—A mixture of 0.20 mole of benzoyl chloride, 0.20 mole of pyridine and 0.16 mole of dimethylaniline in a tightly stoppered flask was heated on the steam-bath for six days. From the brown solid which resulted there was obtained a 27.4% combined yield of IV and its hydrochloride, obtained as described above.

The ether wash solution was evaporated and the residue steam distilled. There was an odor of benzaldehyde in the distillate. The distillate was extracted with ether, and the ether solution washed with dilute hydrochloric acid, then sodium bicarbonate solution. Evaporation of the ether solution, dried over anhydrous magnesium sulfate, left an oil which gave 0.40 g. of benzaldehyde-2,4-dinitrophenylhydrazone on reaction with 2,4-dinitrophenylhydrazine in the usual way.

Reaction of Quinoline, Benzoyl Chloride and Dimethylaniline.—To a solution containing 49.2 g. (0.35 mole) of benzoyl chloride and 90.5 g. (0.70 mole) of dry, synthetic quinoline was added 42.6 g. (0.35 mole) of dimethylaniline. All reagents were freshly distilled. A deep red color developed almost immediately and a solid formed. After eight hours in a tightly stoppered flask at room temperature, the reaction mixture was almost completely solid. At the end of three days the red-orange solid was broken up with the aid of 75 cc. of 50% ethanol, then made basic with sodium carbonate solution. A gummy tan solid was filtered off. An oily organic layer was separated from the filtrate and steam distilled, leaving a residue of more tan solid. The combined solid material was crystallized, first from aqueous pyridine, then absolute ethanol. There was obtained 50.3 g. (40.5%) of colorless needles of 1-benzoyl-2-(*p*-dimethylaminophenyl) - 1,2 - dihydroquinoline (VI), m.p. 183.4–184.4°.

Anal. Calcd. for $C_{24}H_{22}ON_2$: C, 81.32; H, 6.26; N, 7.91. Found: C, 81.36; H, 6.20; N, 8.14.

VI is very soluble in warm pyridine, moderately soluble in warm benzene and ethanol, insoluble in ether and water.

Alkaline Hydrolysis of 1-Benzoyl-2-(*p*-dimethylaminophenyl)-1,2-dihydroquinoline (VI).—A mixture of 2.00 g. (0.00565 mole) of 1-benzoyl-2-(*p*-dimethylaminophenyl)-1,2-dihydroquinoline (VI), 8.0 g. of sodium hydroxide and 30 cc. of 70% ethanol was refluxed for two hours. An equal volume of water was added and the ethanol distilled. The mixture was worked up in two different ways:

A.—The mixture was extracted with ether, and the ether solution dried over anhydrous potassium carbonate. Evaporation of the ether afforded 1.40 g. of gummy yellow solid. This was crystallized from ethanol, 0.26 g. (17%) of 2-(*p*-dimethylaminophenyl)-quinoline (VII) being obtained, yellow needles, m.p. 165–170°. Completely purified material melted at 176.4–177.0°. A mixed m.p. test with an authentic sample of the compound (see below) showed no depression. Gilman, Towle and Spatz[8] reported a m.p. of 173–175° for the compound prepared by the addition of *p*-dimethylaminophenyllithium to quinoline.

Anal. Calcd. for $C_{17}H_{16}ON_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.63; H, 6.43; N, 11.92.

The ethanol mother liquor was mixed with ethanolic picric acid and heated to boiling. From the deep red solution was obtained 0.86 g. (31%) of the picrate of 2-(*p*-dimethylaminophenyl)-quinoline, m.p. 219–220° after recrystallization from ethanol; reported[8] 219°.

Acidification of the alkaline solution, followed by ether extraction, afforded 0.54 g. (78%) of benzoic acid.

B.—The mixture was extracted with benzene. About 10 cc. of nitrobenzene was added and the solution heated on the steam-bath for an hour, the solution turning red. The benzene solution was extracted with 10% hydrochloric acid, and the acid solution was made basic with sodium hydroxide solution. The yellow solid which precipitated was extracted with benzene. Evaporation of the benzene left a yellow solid, which was fractionally crystallized from absolute ethanol. Altogether, 0.70 g. (47%) of 2-(*p*-dimethylaminophenyl)-quinoline (VII) was obtained.

2-(*p*-Dimethylaminophenyl)-quinoline-4-carboxylic Acid (VIII).—The following procedure was modeled after the one described for the preparation of 2-(*p*-diethylaminophenyl)-quinoline-4-carboxylic acid.[13]

A mixture of 35.2 g. (0.236 mole) of *p*-dimethylaminobenzaldehyde, 23.0 g. (0.246 mole) of aniline, freshly distilled from zinc dust, and 250 cc. of absolute ethanol containing 8 drops of concentrated sulfuric acid, was refluxed on the steam-bath for one hour, the mixture protected by a Drierite tube. There was slowly added, with mechanical stirring and mild refluxing, a solution of 24.1 g. (0.274 mole) of freshly prepared pyruvic acid[14] in 100 cc. of absolute ethanol. The resulting dark red mixture was refluxed for 20 hours, then 100 cc. of solvent was removed by distillation. A dark red solid which precipitated was collected and washed with ether. There remained 21.0 g. (30.4%) of 2-(*p*-dimethylaminophenyl) - quinoline - 4 - carboxylic acid (VIII), which began to sinter and darken at 218°. Three recrystallizations from absolute ethanol raised the m.p. to 221–223.5° (dec.). The material was dissolved in dilute sodium carbonate solution, filtered to remove some dark, insoluble material and the yellow filtrate made faintly acidic (red solution) with acetic acid. A tan precipitate which formed was collected and washed with water. Two recrystallizations from absolute ethanol gave VIII as orange crystals, m.p. 222.4–223.0° (dec.) when the temperature was raised at the rate of 2° per minute.[15]

Anal. Calcd. for $C_{18}H_{16}O_2N_2$: N, 9.58. Found: N, 9.71, 9.60.

2-(*p*-Dimethylaminophenyl)-quinoline (VII).—A solution of 0.95 g. of 2-(*p*-dimethylaminophenyl)-quinoline-4-carboxylic acid (VIII) in 6 cc. of quinoline was heated at 225° (oil-bath temperature) under nitrogen for 30 minutes. After addition of 0.50 g. of copper–bronze powder, the mixture was refluxed an additional 15 minutes. The quinoline was steam distilled, leaving a green residue. This was washed with water, then crystallized from absolute ethanol, giving 0.48 g. (57%) of crude 2-(*p*-dimethylaminophenyl)-quinoline (VII), greenish-yellow needles. Recrystallization, first from benzene–ligroin (Norit), then twice from absolute ethanol, gave 0.42 g. (50%) of yellow needles of VII, m.p. 175.8–176.8°.

Failure of 2-Chloroquinoline to Condense with Dimethylaniline in the Presence of Benzoyl Chloride.—Reaction of equimolar quantities of the three reagents, either at room temperature or at 100°, gave no VII. The starting materials were recovered.

Catalytic Reduction of 1-Benzoyl-2-(*p*-dimethylaminophenyl)-1,2-dihydroquinoline (VI).—A suspension of 2.00 g. of 1-benzoyl-2-(*p*-dimethylaminophenyl)-1,2-dihydroquinoline (VI) and 0.12 g. of platinum oxide catalyst in 70 cc. of absolute ethanol was hydrogenated at atmospheric pressure until the theoretical volume of hydrogen corresponding to the saturation of one double bond had been absorbed. The mixture was heated to boiling and filtered. Pale yellow needles of 1-benzoyl-2-(*p*-dimethylaminophenyl)-1,2,3,4-tetrahydroquinoline (IX) crystallized, 1.70 g. (84%), m.p. 162–165°. After two additional recrystallizations from absolute ethanol, the m.p. was raised to 168–169°.

Anal. Calcd. for $C_{24}H_{24}NO_2$: C, 80.86; H, 6.79; N, 7.86. Found: C, 80.98; H, 6.88; N, 7.98.

Alkaline Hydrolysis of 1-Benzoyl-2-(*p*-dimethylaminophenyl)-1,2,3,4-tetrahydroquinoline (IX).—A mixture of

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[12] Commercial dimethylaniline was refluxed with acetic anhydride for six hours, then fractionated through a 35-cm. packed column.

[13] R. F. Brown, T. L. Jacobs and S. Winstein, *et al.*, THIS JOURNAL, **68**, 2705 (1946).

[14] J. W. Howard and W. A. Fraser, "Organic Syntheses," 2nd ed., Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 475.

[15] R. Cuisa and R. Luzzatto (*Gazz. chim. ital.*, **44**, I, 64 (1914)) report VIII as ruby-red crystals of m.p. 192° (dec.).

1.45 g. of 1-benzoyl-2-(*p*-dimethylaminophenyl)-1,2,3,4-tetrahydroquinoline (IX) and 5.0 g. of sodium hydroxide in 40 cc. of 70% ethanol was refluxed for 15 hours, most of the suspended material going into solution. An equal volume of water was added, and the ethanol distilled. The mixture was extracted with ether and the ether solution dried over anhydrous potassium carbonate. After distillation of the ether, the residue was crystallized from absolute ethanol, colorless rosettes of 2-(*p*-dimethylaminophenyl)-1,2,3,4-tetrahydroquinoline (X) being obtained, 0.83 g. (76%), m.p. 100–103°. Completely purified material melted at 107.5–108.5°, also in admixture with an authentic sample of the compound (see below).

Anal. Calcd. for $C_{17}H_{20}ON_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.99; H, 8.09; N, 11.52.

Acidification of the basic layer, followed by ether extraction, afforded 0.46 g. (92%) of benzoic acid.

Catalytic Reduction of 2-(*p*-Dimethylaminophenyl)-quinoline (VII).—A suspension of 1.00 g. of 2-(*p*-dimethylaminophenyl)-quinoline (VII) and 0.10 g. of platinum oxide catalyst in 65 cc. of absolute ethanol containing 10 cc. of glacial acetic acid was hydrogenated at atmospheric pressure until the theoretical volume of hydrogen corresponding to the reduction of two double bonds had been absorbed. The suspended material went into solution during the reduction. The solution was filtered, made alkaline with sodium hydroxide solution, and the ethanol was distilled *in vacuo*. The residue was taken up in ether and dried over Drierite. On evaporation of the ether, 0.80 g. of solid remained, m.p. 100–103°. On crystallization from absolute ethanol, 0.54 g. (53%) of 2-(*p*-dimethylaminophenyl)-1,2,3,4-tetrahydroquinoline (X), colorless needles, m.p. 103–105°, was obtained. An additional recrystallization gave material of m.p. 107–108°.

Acid Hydrolysis of 1-Benzoyl-2-(*p*-dimethylaminophenyl)-1,2-dihydroquinoline (VI).—A solution of 5.00 g. of VI in 150 cc. of 9 *M* sulfuric acid was steam distilled. Benzoic acid began to appear in the distillate almost immediately. Altogether, 1.60 g. (93%) of benzoic acid was collected. There was no evidence of benzaldehyde.

The acid solution remaining in the distilling flask was made basic by the addition of sodium hydroxide solution. A red solid precipitated, 4.40 g. It resisted all attempts at purification.

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Isolation and Properties of a Series of Crystalline Oligosaccharides from Xylan[1,2]

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A polymer homologous series of crystalline oligosaccharides composed only of D-xylose units has been isolated and characterized. The series extends from the dimer to the hexamer inclusive. Members of the series have been obtained through partial acid hydrolysis of the xylan from corncob holocellulose. Evidence suggests that these oligosaccharides are linear chains composed of β-D-xylopyranoside units linked 1 → 4.

A homologous series of oligosaccharides identified and described as xylobiose, xylotriose, xylotetraose, xylopentaose and xylohexaose has now been isolated in crystalline form. These represent the first obtained crystalline oligosaccharides which are composed only of pentose sugar units. They also represent the second crystalline homologous series of oligosaccharides to be isolated. The first oligosaccharide series examined in detail was that obtained by the graded hydrolysis or acetolysis of cellulose.[3]

Conclusive evidence is submitted that the ring structure and configuration of the members of the new homologous series are the same as those of the cellulose series. The latter differ quantitatively by having a projecting $-CH_2OH$ group on each ring. A comparison of the properties of the two homologous series might yield significant data on the influence of the primary alcohol group on the molecular behavior of polysaccharides.

Preparation of the oligosaccharides in the present homologous series is accomplished by applying the Whistler and Durso charcoal chromatographic procedure[4] to a mixture of oligosaccharides obtained by the partial hydrolysis of xylan derived from corncob holocellulose. Kuhn[5] has calculated the yields of various fragments to be expected on the partial depolymerization of a uniform polymer. Using these data as rough approximations in the case of xylan it might be presumed that a maximum yield of disaccharide would be obtained by stopping the hydrolysis at two-thirds completion, and a maximum yield of trisaccharide could be expected by stopping the hydrolysis at one-half completion. When this is done, good yields of xylobiose and xylotriose are obtained.[6] Besides these two sugars there are present in the hydrolysis mixture other fragments of the xylan molecule and these are also separable by the charcoal chromatographic procedure. The entire series of oligosaccharides up to and including the hexasaccharide are thus prepared and are found to crystallize rather easily.

Each of the xyloöligosaccharides possesses a sharp melting point and produces a crystalline pattern on examination with X-rays. Comparison of the X-ray patterns, however, suggests that a slight decrease in the degree of crystallinity may occur with increase in molecular weight of the oligosaccharide. Each successive higher member of the series produces a pattern with fewer lines. Thus, while xylobiose produces twenty easily recognized lines on a flat film 5 cm. distant, xylohexaose produces but six lines. Although none of the patterns examined here have a detectable amorphous halo, it might be expected that at some higher molecular weight amorphous material would be present in sufficient extent to be evident by a

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(1) Journal Paper No. 593 of the Purdue Agricultural Experiment Station.

(2) Paper presented before the XIIth International Congress of Pure and Applied Chemistry, New York, September, 1951.

(3) L. Zechmeister and G. Tóth, *Ber.*, **64B**, 854 (1931); R. Willstätter and L. Zechmeister, *ibid.*, **46**, 2401 (1913); E. E. Dickey and M. L. Wolfrom, THIS JOURNAL, **71**, 825 (1949).

(4) R. L. Whistler and D. F. Durso, THIS JOURNAL, **72**, 677 (1950).

(5) W. Kuhn, *Ber.*, **63B**, 1503 (1930).

(6) R. L. Whistler and C. C. Tu, THIS JOURNAL, **73**, 1389 (1951).