TABLE I

β-DERIVATIVES OF α-NITRO-β-(6-IODO-3-NITROPHENYL)-ETHANE

Substance	M. p., °C.	Formula	Analyses, % Calcd. C	H	Found C	H
Anilino	115–116	$C_{14}H_{12}IN_3O_4$	40.7	2.9	41.3	2.8
o-Toluidino	168–170	$C_{15}H_{14}IN_3O_4$	42.2	3.3	42.5	3.5
m-Toluidino	113–114	$C_{15}H_{14}IN_3O_4$	42.2	3.3	42.7	3.4
p-Toluidino	130–132	$C_{15}H_{14}IN_3O_4$	42.2	3.3	42.7	3.5
o-Anisidino[a]	146–148	$C_{15}H_{14}IN_3O_5$	40.6	3.2	40.9	3.2
m-Anisidino	140–142	$C_{15}H_{14}IN_3O_5$	40.6	3.2	41.1	3.2
p-Anisidino	123–124	$C_{15}H_{14}IN_3O_5$	40.6	3.2	40.9	3.4
Phenylhydrazine	142–144	$C_{14}H_{13}IN_4O_4$	39.3	3.0	40.2	3.0
β-Naphthylhydrazine	143–144	$C_{18}H_{15}IN_4O_4$	45.2	3.1	. .	3.3
Hydroxylamine	103–105	$C_8H_8IN_3O_5$	27.2	2.3	27.6	2.5
Semicarbazide	187–188	$C_9H_{10}IN_5O_5$	27.3	2.5	27.8	2.5

[a] Both *o*- and *m*-anisidine also react readily with nitrochloronitrostyrene.

α,α'-Di-(6-iodo-3-nitrophenyl)-β,β'-dinitro-diethylamine.—A dry benzene solution of the iodostyrene saturated with ammonia was allowed to evaporate spontaneously to a small bulk. The product, recrystallized from benzene, separated in clusters of nearly colorless needles, m. p. 113–114° with foaming.

Anal. Calcd. for $C_{16}H_{13}I_2N_5O_8$: C, 29.2; H, 2.0. Found: C, 29.7; H, 2.1.

Summary

3-Nitro-6-iodonitrostyrene has been prepared and its additive capacity examined with certain organic bases. It is in this respect the most active nitrostyrene so far studied.

MEDFORD, MASS. RECEIVED OCTOBER 9, 1939

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Condensation of Butyraldehyde and Aniline

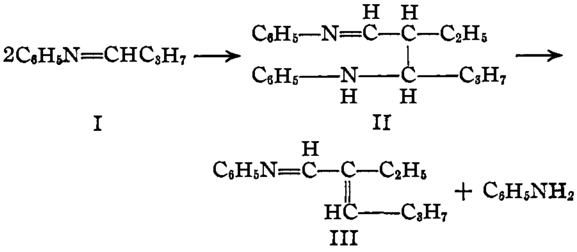
BY M. S. KHARASCH, ISADORE RICHLIN AND FRANK R. MAYO

Introduction

Two general types of structure have been suggested for the dimeric Schiff bases, the cyclic structure by Ingold and Piggott,[1] and the aldol-type structure by Miller and Plöchl.[2] The weight of chemical evidence is in favor of the latter. The work of Eibner is particularly convincing.[3] Our research has been concerned with the determination of the structure of the compounds formed by the condensation of *n*-butyraldehyde and aniline in neutral and in acid media.

Discussion of Results

Two products have thus far been isolated from the reaction of aniline and *n*-butyraldehyde in neutral media: one, a monomeric Schiff base (as the hydrogen cyanide addition product), by Rampini, and the other, its dimer, by Williams.[4] We have found that in the presence of even small amounts of acid, a yellow oil is formed during the condensation. The same oil is formed by treating the crystalline dimer with small amounts of organic acids or by allowing the dimer preparation to stand for several days. In the latter case, the catalyst is the butyric acid formed by atmospheric oxidation, since a similar preparation, carried out in an evacuated bomb-tube, will not produce the oil unless acid had been previously added. Rampini noted this oil but did not investigate it; his failure to obtain the dimer was due to his using aldehyde containing acid. It has been shown by us that this oil is the anil of α-ethyl-β-propylacrolein, formed as follows



$$\underset{\text{I}}{2C_6H_5N{=}CHC_3H_7} \longrightarrow \underset{\text{II}}{\begin{array}{l} C_6H_5{-}N{=}\overset{H}{C}{-}\overset{H}{C}{-}C_2H_5 \\ \qquad\qquad\quad | \\ C_6H_5{-}\underset{H}{N}{-}\underset{H}{C}{-}C_3H_7 \end{array}} \longrightarrow$$

$$\underset{\text{III}}{\begin{array}{l} C_6H_5N{=}\overset{H}{C}{-}C{-}C_2H_5 \\ \qquad\qquad\ \, \| \\ \qquad\quad\ HC{-}C_3H_7 \end{array}} + C_6H_5NH_2$$

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(1) Ingold and Piggott, *J. Chem. Soc.*, **121**, 2793 (1922); **123**, 2745 (1923).

(2) Miller and Plöchl, *Ber.*, **25**, 2020 (1892).

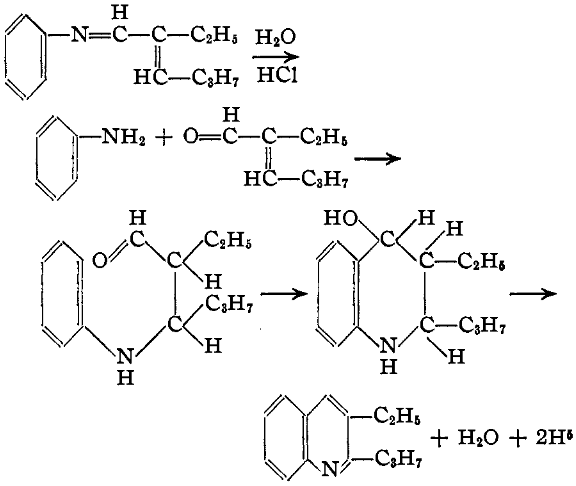
(3) Eibner, *Ann.*, **318**, 58 (1901); **328**, 121 (1903); **329**, 210 (1903).

(4) Rampini, *Ber.*, **25**, 2038 (1892); Williams, U. S. Patent 1,908,093, May 9, 1933; *C. A.*, **27**, 3854 (1933).

The structure, III, for the oil has been confirmed in several ways. Synthetically, we have prepared the same compound from aniline and α-ethyl-β-propylacrolein. Analytically, we have recovered benzanilide and acetanilide in good yields by treating the oil with benzoyl chloride and acetyl chloride, respectively; and we have prepared the 2,4-dinitrophenylhydrazone and semicarbazone of α-ethyl-β-propylacrolein by the use of the hydrazine and semicarbazide. Molecular weight determinations and elementary analyses are consistent with the molecular formula proposed.

The production of the oil of above structure seems to require that II be the structure of the dimer. This is in accord with the work of Miller, Plöchl and Eibner.[2,3] Catalytic reduction of the dimer indicates that one mole of hydrogen is taken up per mole of dimer to form a diamine. The diamine character of the reduction product is shown by its forming a dihydrochloride and a diacetyl derivative. Furthermore, the dimer exhibits properties which one would expect from a compound so closely related, in structure and in formation, to aldol. Both the elimination of aniline to form the oil (analogous to the formation of crotonaldehyde from aldol), the low boiling point (below that of the oil) and the range of the boiling point (about 50°) are indications of dissociation. Cryoscopic molecular weight determinations in triphenylmethane agree with those calculated for the dimer, while in camphor, at a temperature higher by 80°, they indicate 40–50% depolymerization.

The Condensation in the Presence of Acid.—The most general syntheses of the quinoline compounds are those in which a primary aromatic amine is condensed with an aldehyde or ketone in the presence of a mineral acid.[5] We have considered the action of concentrated hydrochloric acid on: (a) mixtures of *n*-butyraldehyde and aniline, (b) the dimer, (c) a mixture of α-ethyl-β-propylacrolein and aniline and (d) the anil of α-ethyl-β-propylacrolein. We have obtained in each instance 2-propyl-3-ethylquinoline. We believe that the formation of the quinoline from α-ethyl-β-propylacrolein anil, which at first glance seems remarkable, may best be explained as follows



Thus, the anil must be hydrolyzed so that aniline can add to the carbon-to-carbon double bond. The subsequent reaction[5] and the hydroxytetrahydroquinoline intermediate[7] in the crotonaldehyde-aniline reaction have been described previously.

Experimental Part

The Preparation of Butylidene Aniline Dimer.—Aniline, freshly distilled from zinc dust *in vacuo*, and freshly distilled *n*-butyraldehyde are mixed in equimolar proportions. The immediate separation of water and the evolution of heat require constant stirring and cooling under the water-tap. The flask is stoppered and allowed to stand for eighteen to twenty-four hours, by which time the reaction mixture is an almost solid mass of the crystalline dimer. This is crystallized from alcohol. The purest material in the best yields is obtained by taking the utmost precautions to avoid the presence of acid; this is accomplished by adding to the reaction mixture a small amount of aqueous sodium carbonate, and by adding the same to the crystallization media. Yields up to 78% of the product melting at 92.5° are obtained.

Anal. Calcd. for $C_{20}H_{26}N_2$: C, 81.61; H, 8.88; N, 9.51. Found: C, 81.49, 81.75; H, 8.88, 8.89; N, 9.41, 9.64.

Molecular Weight Determinations.—The average of ten molecular weight determinations in triphenylmethane by Rast's method[8] at two different concentrations is 281.4 (±12), compared with the value of 294.4 calculated for the dimer. The same determinations carried out in camphor, m. p. 176.7–176.9°, give values from 176 (5% solution) to 251 (10% solution) for the dimer, indicating dissociation. The low boiling point, 130–180° at 25 mm., and its range indicate dissociation. If water and acid be excluded, up to 75% of pure crystallized material may be recovered from a vacuum distillation of the crystals.

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[5] For references to the Skraup and Doebner-Miller syntheses, see Sidgwick, "The Organic Chemistry of Nitrogen," Oxford, 1937, pp. 544 ff.

[6] The hydrogen here indicated is found to reduce the monomeric Schiff base present to N-*n*-butylaniline (see experimental part).

[7] Edwards, Garrod and Jones, *J. Chem. Soc.*, **101**, 1376 (1912).

[8] Rast, *Ber.*, **55B**, 1051 (1922).

Hydrogenation of the Dimer.—By the use of a nickel catalyst[9] and hydrogen at 100 atmospheres pressure, the dimer is hydrogenated quantitatively. In the hydrogenation, one mole of dimer takes up one mole of hydrogen. The hydrogenated material is a heavy, viscous oil of boiling point 240–245° at 20 mm. A diacetyl compound is formed which has a melting point of 131°.

Anal. Calcd. for 1,3-diacetanilido-2-ethylhexane, $C_{24}H_{31}N_2O_2$: N, 7.24. Found: N, 7.47.

Anil of α-Ethyl-β-propylacrolein.—In the presence of small amounts of acid, as when old butyraldehyde is used, or as when as little as 0.03 mole % of acetic or butyric acid is added to the reaction mixture, the product from the condensation of butyraldehyde and aniline is a yellow oil of boiling point 146–148° at 15 mm. The crystalline dimer may or may not precipitate during the course of the reaction. Similarly, if an acid-free preparation is allowed to stand in air for several days, the oil is formed. The crystals are stable for much longer periods of time when the reaction is carried out in tubes from which the air is carefully evacuated. That acid and not air is responsible for the instability of the crystals is shown by their rapid decomposition in the presence of acid and absence of air. Analyses show that the oil differs from the crystalline dimer by one molecule of aniline per mole.

Anal. Calcd. for $C_{14}H_{19}N$: C, 83.47; H, 9.57; N, 6.96. Found: C, 83.64; H, 9.40; N, 6.95, 6.97.

A series of ten concordant determinations, some in triphenylmethane by Rast's method and some in freezing benzene by Beckmann's cryoscopic method gave an average value of 208.4 (±15) compared with the calculated value of 201.3 for $C_{14}H_{19}N$.

Treatment of the oil in benzene with excess benzoyl chloride at room temperature gives a 93% yield of benzanilide. Treatment of the oil with excess acetyl chloride in hot pyridine gives a 60% yield of acetanilide. The identities of these compounds were confirmed by melting points and mixed melting points with known samples.

The use of 2,4-dinitrophenylhydrazine–sulfuric acid reagent according to the directions of Ferrante and Bloom results in the production, either from the oil or from α-ethyl-β-propylacrolein, of the 2,4-dinitrophenylhydrazone of the latter.[10] In either case, the yield is 83%. The melting point of both substances is 119–120°, and mixed melting points demonstrate their identity. Similarly, a hot aqueous solution of semicarbazide hydrochloride reacts with either the oil or with α-ethyl-β-propylacrolein to give the known[11] semicarbazone of melting point 132°. The yield from the oil is 60% and the identity of the semicarbazone with that from the known aldehyde is shown by mixed melting point.

Synthesis of the Anil of α-Ethyl-β-propylacrolein from Aniline and α-Ethyl-β-propylacrolein.—α-Ethyl-β-propylacrolein is prepared from butyraldehyde in 58% yield by the method of Raupenstrauch.[12] It boils at 171–172° at 747 mm. When equimolar quantities of aniline and the acrolein are mixed, reaction takes place within five minutes as shown by the separation of water. After standing for two days, distillation of the mixture gives 70% yield of a product of boiling point 146–148° at 15 mm. Reactions of this compound with benzoyl chloride, acetyl chloride, semicarbazide hydrochloride and 2,4-dinitrophenylhydrazine give the same derivatives as those obtained from similar reactions with the oil from aniline and butyraldehyde.

Preparation of 3-Ethyl-2-propylquinoline.—We have used as a reference material the 3-ethyl-2-propylquinoline formed by the method of Kahn and purified through the picrate by the method of Spady.[13] Our product boils at 182–184° at 23 mm. The boiling point recorded by Kahn was 290–292° at atmospheric pressure. We have also obtained the material by the action of concentrated hydrochloric acid on butylidene aniline dimer and the anil of α-ethyl-β-propylacrolein. In each case the reaction proceeded for twenty to twenty-four hours at room temperature and 0.05 mole of aldehyde or its equivalent was used. The experiments are summarized in Table I.

TABLE I

PREPARATION OF 3-ETHYL-2-PROPYLQUINOLINE

Form of reactants	Moles of HCl per mole aniline[a]	Yield of 3-ethyl-2-propylquinoline, %[d]
Aldehyde and amine[b,c]	0.1	20
Aldehyde and amine	.5	58
Aldehyde and amine	1.0	79
Aldehyde and amine	1.5	60
Aldehyde and amine	2.0	56
Aldehyde and amine	5.0	54
Butylidene aniline dimer	1.0	50
α-Ethyl-β-propylacrolein	2.0	10
Anil of α-ethyl-β-propylacrolein	2.0	15
Aniline and the anil of α-ethyl-β-propylacrolein	1.0	20

[a] The hydrochloric acid used was concentrated aqueous reagent, approximately 12 *N*. The use of both anhydrous hydrogen chloride and of the concentrated acid diluted 20:1 gave poorer yields. [b] The aldehyde and amine were present in proportions of 2:1, in accordance with the directions of Kahn, although the reaction requires only 3:2 proportions. It was found, however, that the use of 3:2 proportions did not vary the yield significantly. [c] The best yields are obtained when the aldehyde and amine are first mixed and the hydrochloric acid then added. Adding the hydrochloric acid over a period of either five minutes or thirty minutes gave the same results. [d] Calculated on the basis: $3C_3H_7CHO + 2C_6H_5NH_2 \rightarrow C_{14}H_{17}N + C_6H_5NHC_4H_9 + 3H_2O$.

Identification and Determination of 3-Ethyl-2-propylquinoline.—The quinoline, either pure or in a mixture, was diluted with about one-third its volume of 95% alcohol. It was then treated with an excess of saturated alcoholic picric acid. The picrate precipitated immediately. After crystallization from alcohol the picrate melts at 161–163°. Since 3-ethyl-2-propylquinoline is the only quinoline formed, we have been able to use this as a quantitative method.[14] Analyses of mixtures containing 0 to 4 parts by weight of aniline to 3-ethyl-2-propylquinoline have yielded 98–100% of the theoretical picrate. In general, better

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[9] Covert, Connor and Adkins, THIS JOURNAL, **54**, 1651 (1932).

[10] Ferrante and Bloom, *Am. J. Pharm.*, **105**, 381 (1933).

[11] Weizmann and Garrard, *J. Chem. Soc.*, **117**, 324 (1920).

[12] Raupenstrauch, *Monatsh.*, **8**, 112 (1887).

[13] Kahn, *Ber.*, **18**, 3361 (1885); Spady, *ibid.*, **18**, 3373 (1885).

[14] *Cf.* Schöpf and Lehmann, *Ann.*, **497**, 16 (1932).

results are obtained if the quinoline fraction is separated from the tars by distillation before the determination.

By-products of the 3-Ethyl-2-propylquinoline Preparation.—The reaction mixture of the Doebner–Miller synthesis, when distilled, gives, besides the water and unchanged reagents (all of which distill below 120° at 15 mm.), two rather well-defined fractions. The first, b. p. 120–200°, consists of N-*n*-butylaniline and 3-ethyl-2-propylquinoline; the second, b. p. over 200° at 15 mm., is made up of tarry materials which may contain tetra- and di-hydro-quinolines (whose homologs have been previously reported as being present in other Doebner–Miller syntheses) and complicated polymerization products. We have confirmed the presence of N-butylaniline (67% of the yield predicted on basis of ethylpropylquinoline formed) as a by-product by the formation of its hydrochloride, m. p. 112–114° (recorded, 114°),[15] and N-butyl-N-phenyl-N′-α-naphthylurea, m. p. 277°. The hydrochloride gave neutral equivalents of 181, 182 and 185, compared with a calculated value of 185. The naphthylurea, a new compound, was prepared by the method of French and Wirtel,[16] and it has the same m. p. as that formed from known N-butylaniline. A mixed melting point showed no depression.

Anal. Calcd. for the N-butyl-N-phenyl-N′-α-naphthylurea, $C_{21}H_{22}N_2O$: N, 8.80. Found: N, 9.03.

In attempting to form the methiodide of 3-ethyl-2-propylquinoline of melting point 172°, described by Kahn,[13] we were able to isolate a material of this melting point. This compound, however, was unstable and gave neutral equivalents on titration with alkali varying from 320 to 381 (theoretical for the hydriodide is 341), showing that it was not a quaternary salt. When we attempted to form the methiodide from highly purified quinoline (through the picrate as above described), the material formed had a m. p. 160–165° and was not titratable with alkali. This is probably the true quaternary methiodide.

Anal. Calcd. for 3-ethyl-2-propylquinoline methiodide, $C_{15}H_{20}NI$: I, 37.28. Calcd. for 3-ethyl-2-propylquinoline hydriodide, $C_{14}H_{18}NI$: I, 38.63. Found (by Fajans' method): I, 37.11.

That the compound described by Kahn was probably the quinoline hydriodide was shown by its formation on passing anhydrous hydrogen iodide through a low-boiling ligroin solution of the pure quinoline. The melting point of this hydriodide was 171–172° and the material was titratable with base. A mixed melting point with the material originally isolated from treatment with methyl iodide was 169–171°.

Summary

1. The condensation of butyraldehyde and aniline in acid and neutral media has been studied.

2. The structure of the dimer of butylidene aniline has been established as well as that of the compound formed from it by the loss of aniline.

3. 3-Ethyl-2-propylquinoline has been prepared in several ways. A mechanism has been suggested for the Doebner–Miller synthesis.

4. The following new compounds have been prepared: the anil of α-ethyl-β-propylacrolein, 1,3-diphenylamino-2-ethylhexane, its diacetyl derivative, α-ethyl-β-propylacrolein-2,4-dinitrophenylhydrazone, N-butyl-N-phenyl-N′-α-naphthylurea, and 3-ethyl-2-propylquinoline hydriodide and methiodide.

CHICAGO, ILLINOIS RECEIVED OCTOBER 16, 1939

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(15) Braun and Murjahn, *Ber.*, **59**, 1202 (1926).

(16) French and Wirtel, THIS JOURNAL, **48**, 1736 (1926).

[CONTRIBUTION FROM THE MENDENHALL LABORATORY OF PHYSICS, OHIO STATE UNIVERSITY]

Spectroscopic Evidence for Hydrogen Bonds: SH, NH and NH_2 Compounds

BY WALTER GORDY[1] AND SPENCER C. STANFORD[2]

Introduction

The hydrogen bond theory,[3] which asserts that under certain conditions a proton may form a bond, or bridge, between two electronegative atoms such as N or O, was proposed by Latimer and Rodebush[4] in 1920. Earlier isolated cases of this type of bonding had been recognized.[5] The wide occurrence of hydrogen bonds, however, has just begun to be realized, largely through measurements of infra-red absorption spectra. The importance of these bridges is evidenced by the fact that chelation, and association between like and unlike molecules, resulting from hydrogen bonds, in turn cause appreciable variations in boiling points, freezing points, viscosities, dielectric constants, heats of mixing and of vaporization, vapor pressures, etc., of many compounds in the liquid and solid states as well as in solution. These bonds also play an important role in the determination of protein structure.[6]

Infrared spectroscopy is particularly well suited

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(1) Department of Physics, Mary Hardin-Baylor College, Belton, Texas.

(2) Department of Chemistry, The College of Wooster, Wooster, Ohio.

(3) For a very able discussion of the nature of the hydrogen bond, see L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, Chap. IX.

(4) W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1419 (1920).

(5) T. S. Moore and T. F. Winmill, *J. Chem. Soc.*, **101**, 1635 (1912); P. Pfeiffer, *Ann.*, **398**, 137 (1913).

(6) Mirsky and Pauling, *Proc. Nat. Acad. Sci.*, **22**, 439 (1936).