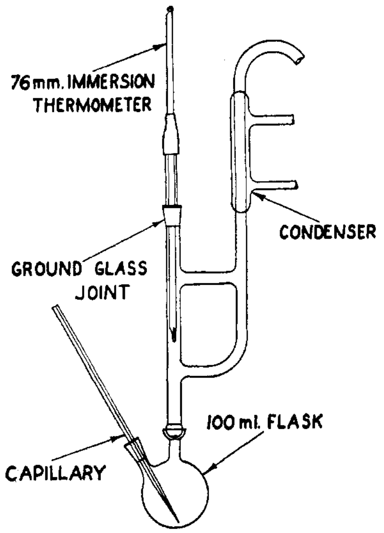


Fig. 1.—Special boiling liquid manometer.

ability of presence of an undetermined amount of isomeric compounds. Samples for physical constants were taken after two rectifications following the initial distillation and thus probably represent more nearly the correct constants for the isomer indicated than is illustrated from the rectification curves.

Figure 2 indicates three fractions, presumably close boiling decyl-*o*-cresol isomers. The largest fraction was re-rectified for physical constants data on the predominant isomer, postulated to be the 2-methyl-4-(2-decyl)-phenol.

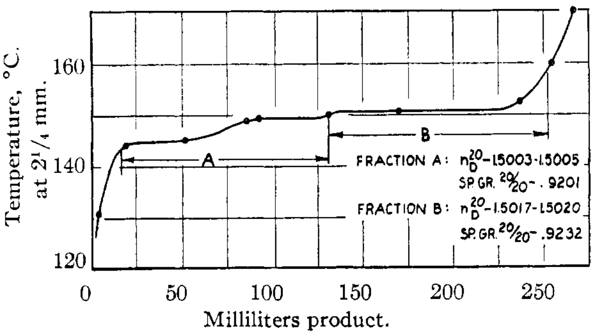


Fig. 2.—Rectification curve for alkylation of *o*-cresol with decyl alcohol.

The alkylations of *o*-cresol with 2-octanol and with 1-octanol resulted in identical C-alkyl products for the main compound as evidenced by their rectification curves and the physical constants of the products. (The solid quaternary ammonium salts prepared from their chloromethyl derivatives gave identical melting points and that of the mixture was not depressed.) The rearrangement of the carbon skeleton to give identical compounds as major product from primary and secondary alcohols may follow the olefin rearrangement[6a,b] cited previously or a carbonium ion mechanism.

[6] (a) A. W. Francis, *Chem. Revs.*, **42**, 111 (1948); (b) R. Huston and I. Kaye, THIS JOURNAL, **64**, 1577 (1942).

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

Condensation of Naphthols with Formaldehyde and Primary Amines[1]

BY W. J. BURKE, MARTIN J. KOLBEZEN[2] AND C. WAYNE STEPHENS[3]

Condensation of 2-naphthol with formaldehyde and representative aliphatic and alicyclic primary amines resulted in 2,3-dihydro-2-substituted-1H-naphth[1.2-e]-*m*-oxazines or N,N-bis-(2-hydroxy-1-naphthylmethyl)-amines depending upon reaction conditions. The naphthoxazines were readily split by acid to yield the corresponding 1-substituted-aminomethyl-2-naphthols. Typical reactions of these compounds were investigated. Related studies were made with 1-naphthol.

Study of the condensation of representative phenols with formaldehyde and primary aliphatic amines indicates that the substituent ortho to the phenolic hydroxyl group plays an important role in determining the course of the reaction.[4] In view of this and the known peculiarities of the naphthols, the investigation has been extended to include this class of related compounds.

The condensation of naphthols with formaldehyde and secondary amines has been studied in several laboratories.[5–9] Reaction of piperidine and formaldehyde with 1- and 2-naphthol has been shown to result in the introduction of a piperidinomethyl group into the 1-position of 2-naphthol and into the 2-position of 1-naphthol. Preformed methylene-bis-amines can be used in place of formaldehyde and secondary amines in the reaction with 2-naphthol.[10] The mechanism of the reaction of 2-naphthol with both N-methylolamines and methylene-bis-amines has been studied by Lieberman and Wagner.[11]

In the present work reaction of 2-naphthol with formaldehyde and methylamine in a molar ratio of 1:2:1, respectively, in methanol solution at 60° was found to result in a 98% yield of 2,3-dihydro-2-methyl-1H-naphth[1.2-e]-*m*-oxazine (I). Benzyl-, cyclohexyl- and *n*-butylamine gave similar results. Upon treatment of I with hot aqueous hydrochloric acid, formaldehyde was liberated and the hydrochloride of 1-methylaminomethyl-2-naphthol (V) formed. Condensation of V with formaldehyde in the presence of base brought about reconversion to I.

[1] Presented in part before the Organic Division of the American Chemical Society in Chicago in September, 1950.

[2] Wallace MacFarlane Fellow, 1948–1949, and University of Utah Research Committee Fellow, 1949–1950.

[3] University of Utah Research Committee Fellow, 1951.

[4] W. J. Burke, R. P. Smith and Carl Weatherbee, THIS JOURNAL, **74**, 602 (1952).

[5] F. Bayer and Company, German Patent 89,979; *Chem. Zentr.*, **68**, **I**, 576 (1897).

[6] J. Decombe, *Compt. rend.*, **197**, 258 (1933).

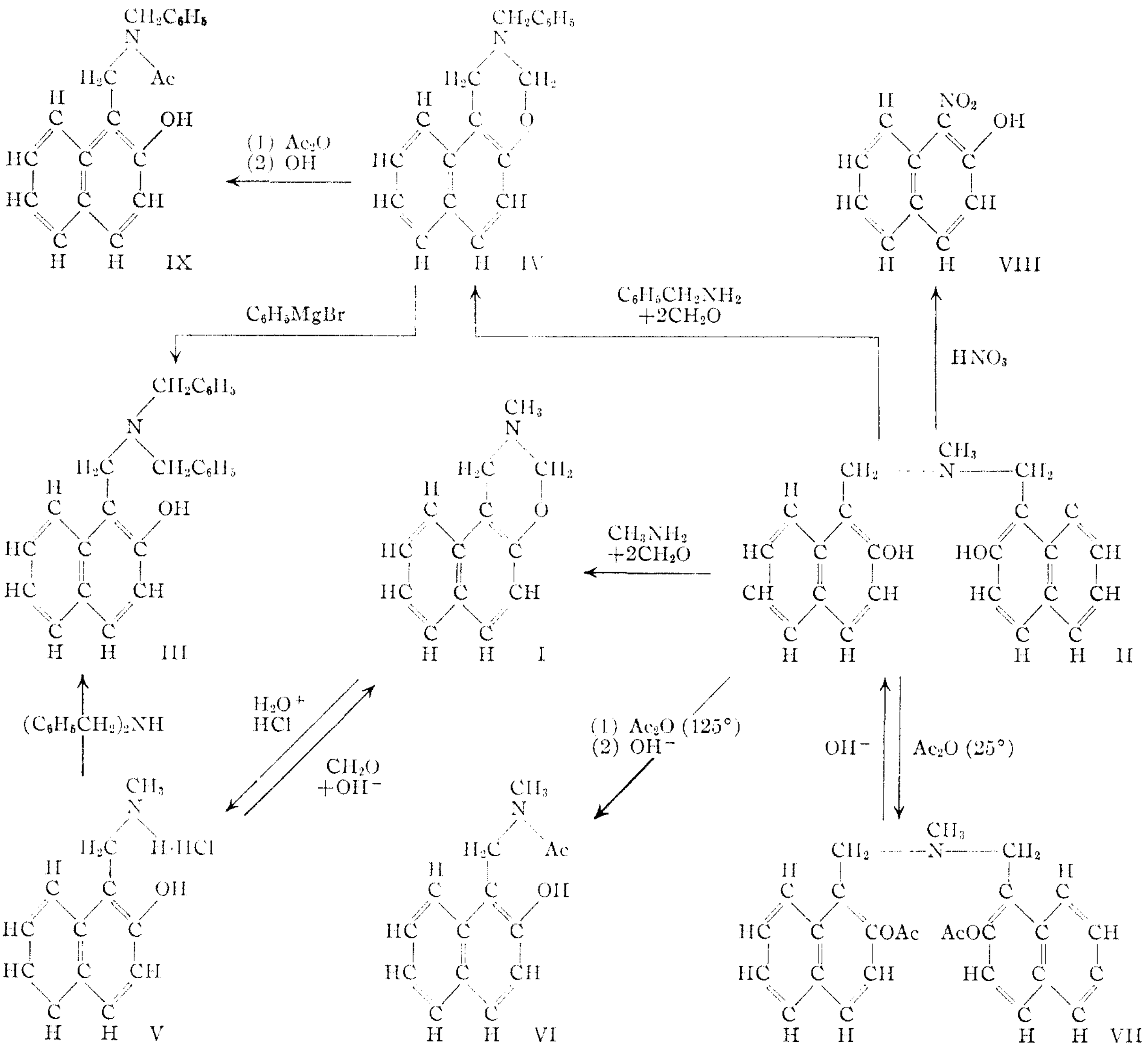
[7] W. T. Caldwell and T. R. Thompson, THIS JOURNAL, **61**, 2354 (1939).

[8] H. A. Bruson, U. S. Patent 2,040,039 (1936).

[9] H. R. Snyder and J. H. Brewster, THIS JOURNAL, **70**, 4230 (1948).

[10] J. R. Feldman and E. C. Wagner, *J. Org. Chem.*, **7**, 31 (1942).

[11] S. V. Lieberman and E. C. Wagner, *ibid.*, **14**, 1001 (1949).



Reaction of N-ethoxymethylmorpholine with an arylmagnesium halide has been shown[12] to result in the replacement of the alkoxy group with an aryl radical. In a related type of reaction, IV reacted with phenylmagnesium bromide to form III. This and the transformation of V to III by treatment with dibenzylamine and the ease of interconversion of I and V support the naphthoxazine structure assigned to I. The fact that a condensation product was not obtained when bis-(2-hydroxy-1-naphthyl)-methane was heated with formaldehyde and benzylamine points to the participation of the 1-position of 2-naphthol in the condensations studied. This is consistent with earlier work[7] which showed that 1-methyl-2-naphthol did not react with formaldehyde and piperidine. Hot acetic anhydride ruptured the oxazine ring of IV with the resulting liberation of formaldehyde. Treatment of the reaction mixture with alkali under mild conditions gave rise to N-benzyl-N-(2-hydroxy-1-naphthylmethyl)-acetamide (IX).

When the molar ratio of 2-naphthol, formaldehyde and methylamine was 2:2:1, respectively, condensation occurred at 25° in methanol to give a 91% yield of N,N-bis-(2-hydroxy-1-naphthylmethyl)-methylamine (II). Similar results were obtained with cyclohexylamine and *n*-butylamine. With benzylamine, however, the only product isolated (86% yield, based on amine) was the corresponding naphthoxazine (IV).

Nitric acid at 0° degraded II to 1-nitro-2-naphthol (VIII) while at 25° the product was 1,6-dinitro-2-naphthol. The conversion of II to IV by reaction with N,N-dimethylolbenzylamine involves both amine interchange and naphthoxazine formation. At room temperature II reacted with acetic anhydride to form the diacetate (VII), which upon alkaline hydrolysis was reconverted to II. A Zerewitinoff determination on II indicated the presence of two active hydrogens in the molecule. These results are consistent with the structure designated for II. Treatment with acetic anhydride at 125° followed by saponification resulted in the conversion of II to VI. The action of hot alkali solution brought about the degradation of II to bis-(2-hydroxy-1-naphthyl)-methane.

Temperature was found to be an important factor in determining the course of the reaction of 2-naphthol with formaldehyde and methylamine in

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(12) J. P. Mason and M. Zief, This Journal, 62, 1450 (1940).

proportions calculated for naphthoxazine formation. While I was obtained almost quantitatively at 60°, the product at a reaction temperature of 0° represented only a 20% yield of I along with a 79% yield of II, based on 2-naphthol. In contrast, replacement of methylamine with benzyl- or cyclohexylamine at 0°, resulted in the isolation of only the expected corresponding naphthoxazines and in yields in excess of 84%. Reaction temperature was also important in the condensation of cyclohexylamine with formaldehyde and 2-naphthol in a 1:2:2 molar ratio, respectively. At 0° an 86% yield of the expected N,N-bis-(2-hydroxy-1-naphthylmethyl)-cyclohexylamine was obtained. However, when the reaction was run at 60°, the only product isolated was 2,3-dihydro-2-cyclohexyl-1H-naphth[1.2-e]-*m*-oxazine (55% yield).

Efforts to prepare V directly by condensation of equimolar quantities of 2-naphthol, formaldehyde and methylamine at room temperature resulted in the formation of II in 82% yield, based on 2-naphthol. An analogous result was obtained with cyclohexylamine. This behavior is in marked contrast with results obtained when 2-naphthol is replaced with a substituted phenol. In such cases 2- or 4-alkylaminomethylphenols are readily obtained.[13-16]

Condensation of 1-naphthol with formaldehyde and cyclohexylamine in a molar ratio of 1:2:1, respectively, at −5° gave a 67% yield of 3,4-dihydro-3-cyclohexyl-2H-naphth[2.1-e]-*m*-oxazine. At higher temperatures there was a marked tendency toward polymer formation. This possibly results from the fact that 1-naphthol has two formaldehyde reactive nuclear positions, while 2-naphthol has only one. Upon treatment with hydrochloric acid the oxazine yielded formaldehyde and 2-cyclohexylaminomethyl-1-naphthol hydrochloride. Reaction of the hydrochloride with an excess of piperidine resulted in the formation of 2-piperidinomethyl-1-naphthol.[7] This indicates that the 2- rather than the 4-position of 1-naphthol was involved in the condensation with formaldehyde and cyclohexylamine.

Acknowledgment.—The financial assistance given by the Research Corporation is gratefully acknowledged.

Experimental

Naphthoxazines from 2-Naphthol.—A general procedure (A) for the preparation of these compounds follows.

A. **2,3-Dihydro-2-methyl-1H-naphth[1.2-e]-*m*-oxazine (I).**—To a cooled solution of 12.4 g. of 25% aqueous methylamine (0.10 mole) in 60 ml. of methanol was added 18.5 ml. of 37% aqueous formaldehyde (0.24 mole) in 40 ml. of methanol and 14.4 g. of 2-naphthol (0.10 mole) in 50 ml. of methanol. After 1.5 hours of gentle refluxing, the reaction mixture was poured into 400 ml. of cold water. The resulting product (19.6 g., 98% yield) melted at 67–68° after recrystallization from methanol.

Anal. Calcd. for $C_{13}H_{13}NO$: N, 7.03. Found: N, 6.95.

The hydrochloride was obtained in essentially quantitative yield by treating a cold acetone solution of the naphthoxazine with an equivalent quantity of concentrated hydrochloric acid; m.p. 185–187° (dec.).

Anal. Calcd. for $C_{13}H_{14}ClNO$: Cl, 15.04. Found: Cl, 14.98.

B. **2,3-Dihydro-2-benzyl-1H-naphth[1.2-e]-*m*-oxazine (IV).**—The white prisms melted at 126–127° after recrystallization from ethyl acetate; yield 99.5%.

Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.88; H, 6.23; N, 5.09. Found: C, 82.58; H, 6.12; N, 5.03.

The hydrochloride melted at 169–170° (dec.).

Anal. Calcd. for $C_{19}H_{18}ClNO$: Cl, 11.37. Found: Cl, 11.28.

C. **2,3-Dihydro-2-butyl-1H-naphth[1.2-e]-*m*-oxazine Hydrochloride.**—The product was isolated and characterized as the hydrochloride since the free base was an oil which tended to decompose upon distillation; m.p. 138–140°; yield 87%.

Anal. Calcd. for $C_{16}H_{20}ClNO$: Cl, 12.76. Found: Cl, 12.64.

D. **2,3-Dihydro-2-cyclohexyl-1H-naphth[1.2-e]-*m*-oxazine Hydrochloride.**—The free base was an oil. The product was isolated as the hydrochloride in essentially quantitative yield; m.p. 178–179° (dec.).

Anal. Calcd. for $C_{18}H_{22}ClNO$: Cl, 11.67. Found: Cl, 11.62.

1-Alkylaminomethyl-2-naphthol Hydrochlorides.—A general procedure useful in the preparation of compounds of this type from the corresponding naphthoxazines is given in (A).

A. **1-Cyclohexylaminomethyl-2-naphthol Hydrochloride.**—A solution of 4 g. of 2,3-dihydro-2-cyclohexyl-1H-naphth-[1.2-e]-*m*-oxazine hydrochloride (0.013 mole) and 1.0 ml. of concentrated aqueous hydrochloric acid in 60 ml. of 85% aqueous propanol-1 was distilled until a negative test for formaldehyde in the distillate was obtained with 2,4-dinitrophenylhydrazine. During the course of the distillation (25 minutes) 25 ml. of propanol-1 was added. After the distillation was interrupted, 60 ml. of acetone was added to the reaction mixture, which at that time had a volume of 20 ml. Upon cooling and filtration 3.65 g. of the product (93% yield) was obtained; m.p. 192–193° (dec.), after recrystallization from ethanol.

Anal. Calcd. for $C_{17}H_{22}ClNO$: Cl, 12.15. Found: Cl, 12.24.

B. **1-Benzylaminomethyl-2-naphthol Hydrochloride.**—This product was recrystallized from methanol; m.p. 170–172°, yield 86%.

Anal. Calcd. for $C_{18}H_{18}ClNO$: Cl, 11.83. Found: Cl, 11.79.

C. **1-Butylaminomethyl-2-naphthol Hydrochloride.**—This product was recrystallized from 50% aqueous methanol; m.p. 143–145°, yield 60%.

Anal. Calcd. for $C_{15}H_{20}ClNO$: Cl, 13.34. Found: Cl, 13.21:

D. **1-Methylaminomethyl-2-naphthol Hydrochloride (V).**—This product was recrystallized from ethanol; m.p. 202–204° (dec.), yield 94%.

Anal. Calcd. for $C_{12}H_{14}ClNO$: Cl, 15.85. Found: Cl, 15.72.

N,N-Bis-(2-hydroxy-1-naphthylmethyl)-amines.—A general procedure for the synthesis of these compounds is given in (A) below.

A. **N,N-Bis-(2-hydroxy-1-naphthylmethyl)-methylamine (II).**—To a solution of 28.8 g. of 2-naphthol (0.20 mole) and 15 ml. of 37% aqueous formaldehyde (0.20 mole) in 75 ml. of methanol was added dropwise 12.4 g. of 25% aqueous methylamine (0.10 mole) in 50 ml. of methanol. After 24 hours at room temperature the resulting solid (31.2 g., 91% yield) was removed by filtration, washed with methanol, and recrystallized from dimethylformamide–methanol (1:3 by volume); m.p. 147–148°. The product was only slightly soluble in most of the usual organic solvents but dissolved readily in dimethylformamide or pyridine.

Anal. Calcd. for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.17; N, 4.08; active hydrogen, 2.0. Found: C, 80.00; H, 6.50; N, 4.02; active hydrogen (Zerewitinoff), 2.02, 2.04.

The hydrochloride was prepared by warming a methanol suspension of the amine in the presence of an excess of concentrated hydrochloric acid. After recrystallization from methanol the compound melted at 142–144° and contained one molecule of methanol of crystallization.

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(13) H. A. Bruson, THIS JOURNAL, **58**, 1741 (1936).

(14) J. H. Burckhalter, F. H. Tendick, E. M. Jones, W. F. Holcomb and A. L. Rawlins, *ibid.*, **70**, 1363 (1948).

(15) W. J. Burke, *ibid.*, **71**, 609 (1949).

(16) W. J. Burke and Carl Weatherbee, *ibid.*, **72**, 4691 (1950).

Anal. Calcd. for $C_{28}H_{22}ClNO_2 \cdot CH_3OH$: Cl, 8.61. Found: Cl, 8.47.

After drying at 95° (2 mm.) for three hours the hydrochloride melted at 148–151° (dec.).

Anal. Calcd. for $C_{23}H_{22}ClNO_2$: Cl, 9.33. Found: Cl, 9.32.

B. **N,N-Bis-(2-hydroxy-1-naphthylmethyl)-butylamine.**—The white prisms melted at 137–138° after recrystallization from dimethylformamide–methanol (1:5 by volume); yield 64%.

Anal. Calcd. for $C_{26}H_{27}NO_2$: C, 81.00; H, 7.06; N, 3.63. Found: C, 81.05; H, 7.12; N, 3.60.

The **hydrochloride** melted at 135–137° (dec.) after recrystallization from methanol–water.

Anal. Calcd. for $C_{26}H_{28}ClNO_2$: Cl, 8.40. Found: Cl, 8.51.

C. **N,N-Bis-(2-hydroxy-1-naphthylmethyl)-cyclohexylamine.**—This product was prepared at 0°; m.p. 120–122°, after washing with methanol; yield 86%.

Anal. Calcd. for $C_{28}H_{29}NO_2$: C, 81.72; H, 7.10; N, 3.40. Found: C, 82.01; H, 6.91; N, 3.24.

The **hydrochloride** melted at 172–174°, after recrystallization from methanol.

Anal. Calcd. for $C_{28}H_{30}ClNO_2$: Cl, 7.92. Found: Cl, 7.97.

D. **Attempted Synthesis of N,N-Bis-(2-hydroxy-1-naphthylmethyl)-benzylamine.**—When 10.7 g. of benzylamine (0.10 mole) was used in place of methylamine in (A) above, the only product (23.8 g.) isolated melted at 126–127°, after recrystallization from ethyl acetate, and did not depress the m.p. of 2,3-dihydro-2-benzyl-1H-naphth[1.2-e]-*m*-oxazine (IV, m.p. 126–127°); yield 86%.

Condensation of Equimolar Quantities of 2-Naphthol, Formaldehyde and Primary Amines. A. Reaction with Methylamine.—Methylamine (12.4 g. of a 25% aqueous solution; 0.1 mole) was added portionwise with cooling to 50 ml. of methanol containing 7.5 ml. of 37% aqueous formaldehyde (0.1 mole). A solution of 14.4 g. of 2-naphthol (0.1 mole) in 50 ml. of methanol was added and the reaction mixture kept at 25° for two days. Upon cooling and filtration 14.1 g. of crystalline material (82% yield) was obtained; m.p. 146–147°, after recrystallization from methanol–dimethylformamide (3:1 by volume). The product did not depress the m.p. of N,N-bis-(2-hydroxy-1-naphthylmethyl)-methylamine (II, m.p. 147–148°).

B. **Reaction with Cyclohexylamine.**—Use of 9.9 g. of cyclohexylamine (0.1 mole) in place of methylamine in (A) resulted in the separation of 12.2 g. (59% yield) of material melting at 120–122°. The hydrochloride of this product melted at 171–174°. These m.p. data are in agreement with those reported above for N,N-bis-(2-hydroxy-1-naphthylmethyl)-cyclohexylamine and its hydrochloride.

Effect of Reaction Temperature in Condensations Involving 2-Naphthol and Formaldehyde. A. With Methylamine.—Condensation of methylamine, formaldehyde and 2-naphthol in a 1:2:1 molar ratio, respectively, in methanol solution was shown above to give I in 98% yield at 60°. When the condensation was run in the same manner except at 0° for two days the solid product (13.6 g.) was removed by filtration and washed thoroughly with methanol. The product melted at 146–147° after recrystallization from methanol–dimethylformamide, and did not depress the m.p. of II (m.p. 147–148°); yield 79%. Removal of solvent from the reaction mixture filtrate gave a white crystalline solid, which after recrystallization from methanol melted at 67–68° and did not depress the m.p. of I (m.p. 67–68°); yield 20%. At a reaction temperature of 25° for two days the yield of I was 58% accompanied by 39% of II. The yields were all based on the 2-naphthol available.

This temperature effect was not noted when either cyclohexylamine or benzylamine was used in place of methylamine either at 0 or at 25°. The expected naphthoxazines were the only products isolated and in all cases in yields in excess of 84%.

B. **With Cyclohexylamine.**—Reaction of cyclohexylamine with 2-naphthol and formaldehyde in a 1:2:2 molar ratio gave an 86% yield of N,N-bis-(2-hydroxy-1-naphthylmethyl)-cyclohexylamine at 0°. When the reaction was run at 60° and the solvent removed under reduced pressure, the only product isolated, after treatment of the residue with concentrated hydrochloric acid in acetone, melted at 179° and did not depress the m.p. of 2,3-dihydro-2-cyclohexyl-1H-naphth[1.2-e]-*m*-oxazine hydrochloride (m.p. 178–179° dec.); yield 55%.

1-Dibenzylaminomethyl-2-naphthol (III): A. Reaction of IV with Phenylmagnesium Bromide.—Upon addition of a large excess of phenylmagnesium bromide to 1.0 g. of IV in anhydrous ether, a white solid precipitated. The product in 15 ml. of ethanol was treated with 3 ml. of concentrated hydrochloric acid. The solid which separated upon cooling was neutralized with alcoholic potassium hydroxide. Addition of water to the alcoholic solution resulted in a white crystalline product, which was recrystallized from ethanol; m.p. 115–117°, yield 0.1 g. (8%). The product did not depress the m.p. of 1-dibenzylaminomethyl-2-naphthol[11] (III, m.p. 115–117°).

Anal. Calcd. for $C_{25}H_{23}NO$: N, 3.95. Found: N, 3.93.

B. **Reaction of V with Dibenzylamine.**—A reaction mixture containing 3 g. of V (0.013 mole), 8.0 g. of dibenzylamine (0.04 mole) and 40 ml. of ethanol was heated under reflux for 1.5 hours. The solid (1.27 g.) obtained upon cooling and filtration melted at 115–116°. The m.p. of this product was not depressed by admixture with a sample of 1-dibenzylaminomethyl-2-naphthol (III). An additional 1.67 g. of product was obtained from the mother liquor; yield 62%.

Reaction of II with N,N-Dimethylolamines. A. Conversion of II to I.—A mixture of 3 g. of II (0.0088 mole), 12.4 g. of aqueous 25% methylamine (0.01 mole) and 15 ml. of 37% aqueous formaldehyde (0.20 mole) in 100 ml. of methanol was heated under gentle reflux for 1.5 hours. The white crystalline product (3.4 g., 98% yield) which formed upon cooling and addition of 100 ml. of water melted at 67–68°, after recrystallization from methanol. It did not depress the m.p. of 2,3-dihydro-2-methyl-1H-naphth[1.2-e]-*m*-oxazine (I, m.p. 67–68°), prepared as described above.

B. **Conversion of II to IV.**—Replacement of methylamine in (A) above with 10.7 g. of benzylamine (0.1 mole) resulted in 4.7 g. (97% yield) of white crystalline material which melted at 126–127°, after recrystallization from ethyl acetate. The m.p. of the product was not lowered by mixing it with 2,3-dihydro-2-benzyl-1H-naphth[1.2-e]-*m*-oxazine (IV, m.p. 126–127°), prepared directly from 2-naphthol, formaldehyde and benzylamine.

Reaction of II with Nitric Acid. A. 1-Nitro-2-naphthol.—To a solution of 5.8 g. of II (0.017 mole) in 70 ml. of acetic acid at 0° was added 2.3 ml. of aqueous nitric acid (0.032 mole). After five minutes at 0° water (200 ml.) was added. The resulting yellow solid (2.7 g., 42% yield) was removed by filtration and recrystallized from ethanol–water; m.p. 102–103°. The product did not depress the m.p. of 1-nitro-2-naphthol (m.p. 102–103°). Fierz-David and Ischer[17] reported a m.p. of 102° for this compound.

B. **1,6-Dinitro-2-naphthol.**—Two grams of II (0.0058 mole) in 25 ml. of acetic acid was treated with 4 ml. of nitric acid (0.047 mole). After two days at 25°, 50 ml. of water was added. The yellow crystalline product (1.7 g., 63% yield) obtained upon cooling and filtration melted at 193–194°, after recrystallization from ethanol. The product did not depress the m.p. of a sample of 1,6-dinitro-2-naphthol (m.p. 193–194°, lit.[18] m.p. 194°).

N,N-Bis-(2-acetoxy-1-naphthylmethyl)-methylamine (VII).—A solution of 3.43 g. of II (0.01 mole) was treated with 10 g. of acetic anhydride (0.10 mole) in 20 ml. of pyridine at room temperature. After two weeks the reaction mixture was poured into 200 ml. of water and solid sodium bicarbonate added until effervescence ceased. The solid (4.3 g., 100% yield) obtained by filtration melted at 158–160° after recrystallization from ethanol.

Anal. Calcd. for $C_{27}H_{25}NO_4$: C, 75.86; H, 5.90; N, 3.28. Found: C, 75.77; H, 6.44; N, 3.26.

Hydrolysis of the above ester in 2% potassium hydroxide in methanol at 25° for three hours gave a product melting at 147–148°. The product did not depress the m.p. of II (147–148°).

N-Methyl-N-(2-hydroxy-1-naphthylmethyl)-acetamide (VI).—Five grams of II (0.0145 mole) in 30 ml. of acetic anhydride (0.32 mole) was heated at 125° for eight hours.

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[17] H. E. Fierz-David and Ischer, *Helv. Chim. Acta*, **21**, 664 (1938).

[18] C. Graebe and A. Drews, *Ber.*, **17**, 1170 (1884).

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).

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

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

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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).