(1 mm.), $n^{25}D$ 1.5056. Spectral examination indicated that the material was not homogeneous. The infrared spectrum had carbonyl absorptions at 5.81 and 5.87 μ. In 95% ethanol the material had $\lambda_{max.}$ 267 mμ. The isomeric ester obtained by heating the above material at 150° for four hours[14] absorbed at 5.87 μ in the infrared with only slight absorption at 5.81 μ and had $\lambda_{max.}$ 276 mμ. The XIII thus was contaminated with the thermally rearranged ester.

A mixture of the impure XIII (5.6 g., 0.034 mole) and 3.29 g. (0.034 mole) of sublimed maleic anhydride was kept overnight at 25°. The mixture was initially liquid but gradually became solid. The solid was triturated with pentane to remove unreacted ester, filtered and then heated at 50° (0.3 mm.) to remove maleic anhydride. The product (6.1 g., 69%) melted at 120–125°. Several recrystallizations from ethyl acetate–hexane raised the melting point to 138–139°.

Anal. Calcd.: C, 64.12; H, 5.38. Found: C, 64.54; H, 5.63.

The unreacted ester recovered from the pentane washings had a carbonyl absorption at 5.87 μ but none at 5.81 μ and had $\lambda_{max.}$ 277 mμ with no evidence of a shoulder at 267 mμ.

Treatment of Ethyl Norcaradiene Carboxylate (XIII) and Cycloheptatriene with Maleic Anhydride at 5°.—One gram (0.00616 mole) of impure XIII was mixed with 0.66 g. (0.00673 mole) of sublimed maleic anhydride and kept at 5° for 24 hours. The adduct was isolated as before giving 0.89 g. of crude material, m.p. 133–137.5°. Since the ester used was 69% ethyl norcaradiene carboxylate this is equivalent to an 80% yield of adduct.

When 1 g. (0.01085 mole) of cycloheptatriene was treated with 1.2 g. (0.0122 mole) of maleic anhydride under similar conditions, 89% of the maleic anhydride (m.p. 50–52°) was recovered. Only a trace of material sublimed at 100° (0.3 mm.) and a small amount of non-volatile residue remained behind.

EVANSTON, ILLINOIS

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

Reaction of 2-Naphthol with Formaldehyde and 2-Naphthylamine. Isolation of 1-(2-Naphthylaminomethyl)-2-naphthol

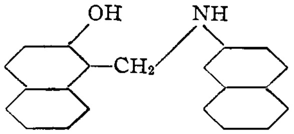
BY W. J. BURKE, LEO G. ADAMS, K. CHADWICK MURDOCK AND SVEN H. RUETMAN

RECEIVED JUNE 23, 1955

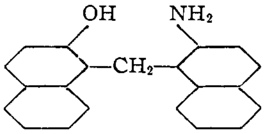
Further investigation of the reaction of 2-naphthol with formaldehyde and 2-naphthylamine resulted in the isolation of 1-(2-naphthylaminomethyl)-2-naphthol, which has been postulated as the precursor of the several products derived from this system. Two new compounds, 2,3-dihydro-2-(2-naphthyl)-1H-naphth[1,2-*e*]-*m*-oxazine and 1-(2-methyleneimino-1-naphthylmethyl)-2-naphthol were also obtained. The interrelationships of the products were studied.

The condensation of equimolar quantities of 2-naphthol with formaldehyde and 2-naphthylamine in refluxing toluene was reported by Hardman[1] to yield 1-(2-naphthylaminomethyl)-2-naphthol (I). Shortly afterward, Corley and Blout in a detailed study[2] of this condensation showed that in refluxing benzene the resulting product was not I but the isomeric 1-(2-amino-1-naphthylmethyl)-2-naphthol II.[2a] These investigators prepared I by reduction of the Schiff base III from 2-hydroxy-1-naphthaldehyde and 2-naphthylamine and demonstrated that I was readily convertible to II by heating in benzene.[2b] When the condensation was effected in toluene or xylene, good yields of 1,2,7,8-dibenzacridine and Morgan's base (a molecular compound of 1,2,7,8-dibenzacridine and its 9,10-dihydro derivative) were isolated along with only traces of II.[2c] Morgan's base, 1-methyl-2-naphthol and 1,2,7,8-dibenzacridine were formed when II was heated to its melting point.[2a]

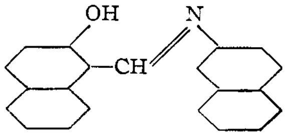
Corley and Blout proposed a sequence of reactions involving I as the initial product of the condensation of 2-naphthol with formaldehyde and 2-naphthylamine to explain the relationship of the several compounds formed.[2c] They were not able to isolate I from the condensation reaction and suggested that I was an intermediate in the formation of II. They stated that the temperature necessary for reaction to occur, as evidenced by the evolution of water (*ca.* 80°), was also sufficient for isomerization to II.[2b]



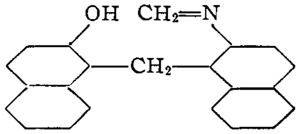
I



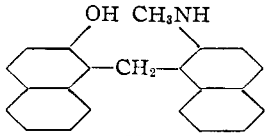
II



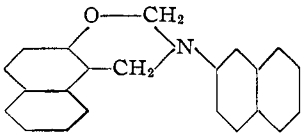
III



IV



V



VI

In connection with related work[3] it was observed that aniline and certain of its ring substituted derivatives reacted readily with formaldehyde and 2-naphthol in a molar ratio of 1:2:1 at 5° to form 2,3-dihydro-2-aryl-1H-naphth[1,2-*e*]-*m*-oxazines. These results suggested the feasibility of investigating the reaction of 2-naphthol with formaldehyde and 2-naphthylamine under conditions which might permit the isolation of I should it actually be a condensation product. Reaction of equimolar quantities of these reagents in methanol at 2° for seven days resulted in a 63% yield of I. When the condensation was effected at 25° for seven days, a 9% yield of I was obtained along with a 23% yield of II and an orange crystalline

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[1] A. F. Hardman, U. S. Patent 2,411,427 (1946).

[2] (a) R. S. Corley and E. R. Blout, THIS JOURNAL, **69**, 755 (1947); (b) R. S. Corley and E. R. Blout, *ibid.*, **69**, 761 (1947); (c) E. R. Blout and R. S. Corley, *ibid.*, **69**, 763 (1947).

[3] W. J. Burke, K. C. Murdock and G. Ec, *ibid.*, **76**, 1677 (1954).

product (47% yield), which was identified as 1-(2-methyleneimino-1-naphthylmethyl)-2-naphthol (IV).

The direct synthesis of I was confirmed by a comparison of the resulting product with that obtained by reduction of the azomethine, III. Both products and a mixture of the two melted at 128°, resolidified and remelted at 190–191°. Refluxing each in benzene gave isomerization products having the same melting and mixed melting points (198°). Ultraviolet absorption spectrum studies on samples of I from the two sources indicated the identity of the products. Acetylation of samples of I from the alternate syntheses gave the same N,O-diacetyl derivative, as indicated by melting and mixed melting point determinations. Similar results were obtained when the acetylated products were converted to the N-acetyl derivative.

Infrared absorption spectra studies and melting point behavior indicated that the orange product formed in the direct synthesis of I at 25° was identical with the Schiff base IV prepared from II and formaldehyde in 80% yield. The absorption maxima at 2.98 and 6.08 μ shown by IV are characteristic of hydroxyl and azomethine groups, respectively. Catalytic hydrogenation of IV at room temperature yielded 1-(2-methylamino-1-naphthylmethyl)-2-naphthol (V). A 70% yield of II was obtained from a slurry of I in methanol kept two weeks at room temperature. This along with the isolation of I, II and IV from the reaction of equimolar quantities of 2-naphthol, formaldehyde and 2-naphthylamine at 25° suggested that I and II were possible intermediates in the synthesis of IV in this condensation.

Reaction of I with formaldehyde in refluxing methanol gave a 65% yield of 2,3-dihydro-2-(2-naphthyl)-1H-naphth[1,2-*e*]-*m*-oxazine (VI). This demonstrated that ring closure proceeded more rapidly than isomerization of I to II under these conditions. The reaction also occurred at 5° but the yield of VI was lower (24%). VI also was prepared directly at room temperature in 64% yield by condensation of 2-naphthol, formaldehyde and 2-naphthylamine in the calculated proportions. No indication of the isomerization of VI in refluxing benzene was noted.

Acidic hydrolysis of VI gave an almost quantitative yield of formaldehyde, isolated as the 2,4-dinitrophenylhydrazone, along with a 70% yield II, which presumably resulted from the isomerization of I. The absence of a band in the neighborhood of 3.0 μ in the infrared spectrum of VI and a negative ferric chloride test for this product provided additional indication of the naphthoxazine structure assigned. Under the conditions used in the ferric chloride test, II gave an immediate deep violet coloration.

Acknowledgment.—We wish to thank the Research Corporation for the financial assistance provided by a Frederick Gardner Cottrell Grant.

Experimental

1-(2-Naphthylaminomethyl)-2-naphthol (I).—2-Naphthol (7.2 g., 0.05 mole) dissolved in 20 ml. of methanol and 1.5 g. of paraformaldehyde (0.05 mole) dissolved in 5 ml. of methanol containing 0.01 g. of potassium hydroxide were added to 60 ml. of warm methanol containing 7.2 g. of 2-naphthylamine (0.05 mole). The reaction mixture was cooled to 2° and kept at that temperature for seven days. At the end of this time a slight orange deposit had started to form on the crystalline material which separated. The crystalline material (9.5 g., 63% yield) was removed by filtration and washed with 25 ml. of cold methanol. The product was recrystallized by dissolving it in 150 ml. of acetone at room temperature, adding 750 ml. of petroleum ether, and cooling. The compound melted in a bath at 128°, resolidified and melted again at 190–191°. I prepared by the reduction of the Schiff base III,[2b] and a mixture of this product with that prepared directly as described above showed the same melting point behavior.[4] The ultraviolet absorption spectra of samples of I prepared by the alternate syntheses were essentially identical: $\lambda_{\max}^{\mathrm{EtOH}}$ (log E) 229 mμ (4.96), 279 mμ (4.20), 335 mμ (3.87).

1-(2-Amino-1-naphthylmethyl)-2-naphthol (II). **Isomerization of I in Benzene.**—A solution of 0.5 g. of I, prepared directly from 2-naphthol as described above, in 10 ml. of benzene was refluxed for 30 minutes. The fine white needles (0.4 g.) which separated were washed with hot benzene: m.p. 197–198° dec., lit. m.p. 195.5–196.5°.[2b]

I prepared by reduction of III was treated in the same manner; m.p. 198–199°. The mixed m.p. of the two products was 198–199°.

Isomerization of I in Methanol.—One gram of I prepared directly from 2-naphthol was added to 25 ml. of methanol. The mixture was stirred occasionally over a 14-day period at 28–30°. The solid (0.7 g.) was removed by filtration and washed with 50 ml. of benzene; m.p. 197–198°.

N,O-Diacetyl Derivative of I.—Two grams of I, prepared directly from 2-naphthol, was treated with a mixture of 10 ml. of pyridine and 5 ml. of acetic anhydride at 0–5° for three hours. The resulting white crystalline product (86% yield) melted at 188–189° after recrystallization from *n*-butyl alcohol; lit. m.p. 188–189°.[2b] I, prepared from III by reduction, was acetylated in the same manner; m.p. and mixed m.p. of the two products, 188–189°.

N-Acetyl Derivative of I.—One gram of each of the above acetylation products of I were treated with 10% alcoholic potassium hydroxide at 0° for 12 hours. In each case the product melted at 183–184°, after recrystallization from ethanol; lit. m.p. 182–183°.[2b] The mixed m.p. was 183–184°.

Reaction of 2-Naphthol with Formaldehyde and 2-Naphthylamine at 25°.—A solution of 0.1 molar quantities of 2-naphthol, paraformaldehyde and 2-naphthylamine in 165 ml. of methanol containing 2 drops of 10% potassium hydroxide in methanol was kept at 25° for seven days. The resulting mixture of orange and white crystals was removed by filtration and triturated with 145 ml. of acetone at 25°. The insoluble orange crystals (6.5 g.) obtained by filtration melted at 217.5–219°, after recrystallization from 1-butanol. The m.p. was not depressed by admixture with IV prepared from II and formaldehyde as described below. The acetone filtrate was evaporated to dryness at room temperature. The resulting solid was extracted successively with three 150-ml. portions of benzene and one 60-ml. portion of methanol. The white crystalline product (6.5 g.) which was not dissolved melted at 198–199° after recrystallization from acetone–ligroin at room temperature and did not depress the m.p. of II prepared by the isomerization of I in benzene. The benzene and methanol extracts were evaporated to dryness at room temperature in the hood and the residue treated with 85 ml. of acetone. An additional 0.8 g. of IV was obtained by filtration. Addition of 190 ml. of petroleum ether to the acetone filtrate followed by cooling resulted in the deposition of 1.0 g. of white crystalline product which melted at 128–130°, resolidified and melted again at 191–192°. A mixture of this product and I prepared directly at 2° as described above showed the same m.p. behavior. An additional 1.8 g. of I was obtained from the mother liquor.

An additional 0.5 g. of II along with 2.4 g. of 2-naphthol (m.p. and mixed m.p. with an authentic specimen 120–122°; lit. m.p. 122°)[5] and 1.6 g. of 2-naphthylamine (m.p. and

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(4) Corley and Blout[2b] reported melting in a bath at 128°, resolidification and melting at 196° for I prepared by the reduction of the Schiff base III.

(5) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 272.

mixed m.p. with an authentic specimen 109–110°; lit. m.p. 112°)[6] were obtained from the methanol filtrate of the reaction mixture. The yields of I, II and IV based on formaldehyde, were 9, 23 and 47%, respectively.

1-(2-Methyleneimino-1-naphthylmethyl)-2-naphthol (IV).—To a refluxing solution of 1.8 g. of 1-(2-amino-1-naphthylmethyl)-2-naphthol (0.006 mole) in 100 ml. of methanol was added 0.5 g. of paraformaldehyde (0.016 mole) in 10 ml. of methanol containing 0.01 g. of potassium hydroxide. After two hours at reflux, 75 ml. of methanol was removed by distillation. The orange crystals (1.5 g.) obtained by filtration of the chilled residue were washed with 5 ml. of methanol; yield 80%, m.p. 218–219°, after recrystallization from *n*-propyl alcohol; $\lambda_{\max}^{\text{Nujol}}$ 2.98, 6.08, 7.80, 7.95, 12.15, 12.35, 13.17 and 13.30 μ.

Anal. Calcd. for $C_{22}H_{17}NO$: C, 84.86; H, 5.51. Found: C, 84.62; H, 5.43.

Similar results were obtained when II (0.7 g.), prepared by isomerization of I in methanol at room temperature, was treated with 0.5 g. of paraformaldehyde for one week at room temperature in 75 ml. of methanol containing two drops of 10% potassium hydroxide in methanol; yield 0.57 g. (78%), m.p. and mixed m.p. with above product 216.5–218°.

1-(2-Methylamino-1-naphthylmethyl)-2-naphthol (V).—IV (1.5 g.) was hydrogenated with agitation in 250 ml. of ethyl acetate containing 0.09 g. of Adams platinum oxide catalyst at 27° for three hours with an initial hydrogen pressure of 38 p.s.i. The catalyst was removed from the pale yellow solution which was concentrated under reduced pressure to a volume of 50 ml. The pale yellow crystals which deposited were recrystallized from ethyl acetate–acetone; m.p. 191–192°.

Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; active H, 2.00. Found: C, 84.88; H, 6.06; active H, 2.04 (Zerewitinoff).

2,3-Dihydro-2-(2-naphthyl)-1H-naphth[1,2-*e*]-*m*-oxazine (VI). (A) **Preparation from I.**—A solution of 3.0 g. of I (0.01 mole) in 100 ml. of methanol containing 3.0 g. of paraformaldehyde (0.1 mole) and 4 drops of 10% alcoholic potassium hydroxide was heated under reflux for 30 minutes. The white needles (1.3 g.) which separated after two days at room temperature were removed by filtration and washed with methanol; an additional 0.7 g. of product was obtained from the mother liquor; total yield 64%; m.p. 75–76°, after recrystallization from ethyl acetate–methanol; $\lambda_{\max}^{\text{Nujol}}$ 6.15, 6.28, 8.18, 8.60, 9.50, 10.00, 10.75, 11.87, 12.37, 13.00 and 13.5 μ.

Anal. Calcd. for $C_{22}H_{17}NO$: C, 84.86; H, 5.51. Found: C, 84.68; H, 5.62.

A 24% yield of VI (m.p. and mixed m.p. with above product was 75–76°) was obtained when the condensation of I with formaldehyde was effected at room temperature for six days.

(B) **Direct Synthesis.**—Methanol (75 ml. total volume) solutions of 2-naphthol (7.2 g., 0.05 mole), paraformaldehyde (4.0 g., 0.133 mole) and 2-naphthylamine (7.2 g., 0.05 mole) were combined at room temperature. The heavy oil which separated after the reaction mixture was kept at room temperature overnight partially crystallized upon standing. The oil obtained by filtration from the white needles (4.2 g.) was dissolved in 15 ml. of warm ethyl acetate and 20 ml. of methanol was added. An additional 5.7 g. of product was obtained from this solution; total yield 64%, m.p. 75–76°, after recrystallization from ethyl acetate–methanol. The m.p. was not depressed by admixture with the product prepared from I as described above.

Anal. Calcd. for $C_{22}H_{17}NO$: N, 4.50. Found: N, 4.42, 4.45.

A benzene (3 ml.) solution containing 0.4 g. of VI was refluxed for 30 minutes. The benzene was removed under reduced pressure and the residue recrystallized from ethyl acetate–methanol; m.p. and mixed m.p. with above product 75–76°; recovery, 0.333 g. (83%). No color change was observed when a solution of ferric chloride in absolute ether was added to solution of VI in ethyl acetate. Under the same test conditions, replacement of VI with II resulted in the immediate formation of a deep violet color.

Acid Hydrolysis of 2,3-Dihydro-2-naphthyl-1*H*-naphth-[1,2-*e*]-*m*-oxazine (VI).—To a solution of 1.98 g. of 2,4-dinitrophenylhydrazine in a mixture of 80 ml. of ethanol, 8 ml. of concentrated hydrochloric acid and 18 ml. of water was added 3.1 g. of VI. The mixture was stirred for 40 minutes in a closed system. VI slowly dissolved with the simultaneous separation of fluffy yellow crystals. After 24 hours at room temperature, the yellow precipitate (2.0 g., 95% yield) was removed by filtration; m.p. 164–165.5°, after recrystallization from ethanol to which a small amount of ethyl acetate was added; the m.p. was not depressed when the product was mixed with an authentic specimen of formaldehyde 2,4-dinitrophenylhydrazone (m.p. 165–166°). The reaction mixture filtrate was carefully adjusted to a *p*H of 7 with aqueous potassium hydroxide. The light brown solid (0.5 g.) which separated was removed by filtration and washed thoroughly with water; m.p. 198–200°, after recrystallization from benzene. The m.p. was not depressed when the product was mixed with II (m.p. 198–199°). The neutral filtrate was diluted with an equal volume of water and extracted with a total of 300 ml. of ether. The ether solution was dried over sodium sulfate. The residue obtained upon removal of ether was dissolved in hot benzene. Upon cooling 1.1 g. of white crystals was obtained; an additional 0.5 g. of product was obtained from the mother liquor. The products were combined and recrystallized from cold acetone and petroleum ether; m.p. 200°. The product did not depress the m.p. of a sample of II (m.p. 198–199°); combined yield of II, 70%.

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[6] Ref. 5, p. 240.