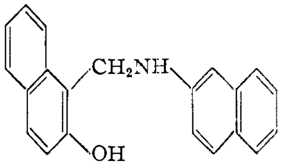
[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

The Reaction of β-Naphthol, β-Naphthylamine and Formaldehyde. II. 1-(2′-Naphthylaminomethyl)-2-naphthol and its Isomerization to 2′-Amino-2-hydroxy-1,1′-dinaphthylmethane

BY RICHARD S. CORLEY AND ELKAN R. BLOUT

Investigation of the Mannich base, 1-(2′-naphthylaminomethyl)-2-naphthol (I), whose N-acetyl derivative has been described,[1] showed that it had an apparent melting point of 196° (dec.) and did not give a mixed melting point depression with the isomeric 2-amino-2′-hydroxy-1,1′-dinaphthylmethane (II).[1] Further examination disclosed, as seen below, that the substance conformed to the structure (I) and that it readily isomerized to the dinaphthylmethane (II) on heating above *ca.* 80°.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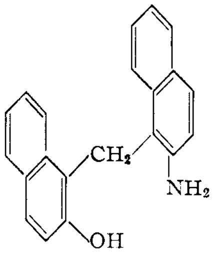
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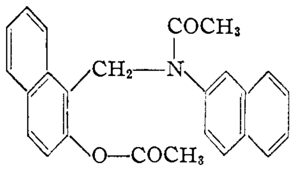
The Mannich base (I) was prepared in good yield by catalytic hydrogenation of the Schiff base[2] which had been obtained by reaction of 2-hydroxy-1-naphthaldehyde with β-naphthylamine. Although the melting point was 196° (dec.) by the usual method, when fresh samples were immersed in a bath maintained at selected temperatures, the material was found to melt at 128° and above. It solidified immediately after melting and melted again at 196° (dec.). Below 128° the compound sintered or melted incompletely and then solidified. Another point of difference from the dinaphthylmethane (II) was that the Mannich base showed an appreciably higher solubility in the common organic solvents.

Proof that the Mannich base (I) was in fact not identical with the dinaphthylmethane (II) was afforded by acetylation of the former to give the N,O-diacetyl derivative (III), which gave a mixed melting point depression with the diacetyl derivative of the dinaphthylmethane[1] prepared under identical conditions. The diacetyl derivative (III) was also obtained by acetylation of the N-acetyl derivative of the Mannich base and transformed back to it by treatment with alkali. Further characterization was provided by preparation of three additional derivatives. The O-methyl Schiff base (IV), prepared from 2-methoxy-1-naphthaldehyde[3] and β-naphthylamine, was hydrogenated to yield the O-methyl derivative (V). Acetylation of the latter gave the N-acetyl-O-methyl derivative (VI), which was also obtained by methylation of the N-acetyl derivative. Treatment of the O-methyl derivative (V) with benzenesulfonyl chloride in cold pyridine gave the N-benzene-sulfonyl-O-methyl derivative (VII), which did not show acidic properties. This reaction confirmed the presence of the *secondary* amino group. Each of these derivatives gave mixed melting point depressions with the corresponding derivatives of the dinaphthylmethane (II).[1] The comparison is summarized in Table I.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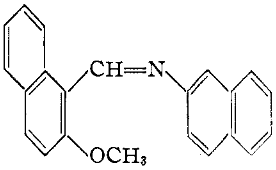
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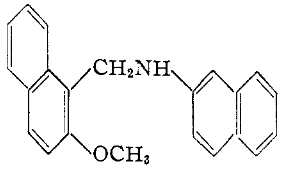
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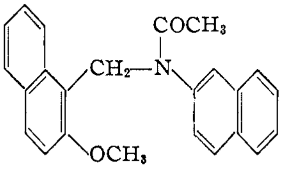
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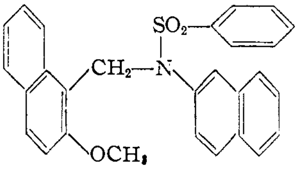
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TABLE I

MELTING POINTS

Deriv.	Of Mannich base (I), °C. m. p. 128°, 196° (dec.) see text	Of dinaphthylmethane (II) m. p. 196° (dec.)
N-Acetyl	183[1]	248
N,O-Diacetyl	189	203
O-Methyl	114	134
N-Acetyl-O-methyl	130	218
N-Benzenesulfonyl-O-methyl	176	148

Boiling the Mannich base (I) in benzene for a short time resulted in conversion to the dinaphthylmethane (II). The isomerization was demonstrated by the convenient test of acetylation of the product in cold pyridine which reaction gave the N,O-diacetyl derivative of the dinaphthylmethane. Isomerization did not occur to any appreciable extent in boiling ether, as evidenced

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(1) Corley and Blout, THIS JOURNAL, **69**, 755 (1947).

(2) Bartsch, *Ber.*, **36**, 1975 (1903).

(3) Barger and Starling, *J. Chem. Soc.*, **99**, 2301 (1911).

by the same test. In view of the extraordinary ease of this isomerization, it may well be that analogous compounds assigned such Mannich base structures are in fact the isomeric diarylmethanes.[4] The derivatives of the Mannich base (I) do not isomerize under any such mild conditions, as shown by their stability at their melting points and by crystallization without change from such a high boiling solvent as *n*-butanol.

The role of the Mannich base (I) in the reaction of β-naphthol, β-naphthylamine and formaldehyde is not known with certainty. We have not succeeded in isolating it (or a derivative) from the reaction, due, no doubt, to the fact that the temperature necessary for the reaction to occur as evidenced by evolution of water (*ca.* 80°) is also sufficient for the isomerization. However, since many Mannich bases are formed with great ease,[5] there is a strong probability that the Mannich base (I) is the initial intermediate formed in the reaction sequence and the precursor of 2-amino-2′-hydroxy-1,1′-dinaphthylmethane (II).[6]

Experimental[7]

1-(2′-Naphthylaminomethyl)-2-naphthol (I).—Five grams of the Schiff base prepared from 2-hydroxy-1-naphthaldehyde and β-naphthylamine[2] was dissolved in 150 cc. of ethyl acetate, 0.25 g. of Adams platinum oxide catalyst added, and the mixture hydrogenated at 40 lb. pressure and at room temperature. The theoretical amount of hydrogen was taken up in twenty minutes, the original deep orange color of the solution changing to a very light yellow. After filtration of the platinum, the solvent was removed under vacuum in the cold. The residue after washing twice with cold benzene yielded 4.77 g. (95%) of light cream colored needles of the Mannich base (I). For analysis this material was crystallized twice by dissolving in 100 cc. of benzene at room temperature, filtering, and adding gradually, with slow stirring, 350 cc. of hexane. This procedure gave an 80% recovery of colorless needles of pure (I), m. p. 196° (dec.) by the usual method. Mixed with the dinaphthylmethane (II)[1] it showed no depression. When fresh samples were immersed in a bath maintained at temperatures of 128° or above the material melted, then immediately solidified and melted at 196° (dec.).

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.23; H, 5.72. Found: C, 83.82; H, 5.70.

The compound was soluble in alcoholic alkali from which it was recovered unchanged on neutralization, and was considerably more soluble in the common organic solvents than the dinaphthylmethane (II). It formed a hydrochloride, by addition of hydrogen chloride in ether solution, as a colorless microcrystalline powder, m. p. 266–271° (dec.).

N,O-Diacetyl-1-(2′-naphthylaminomethyl)-2-naphthol (III).—A solution of 2.00 g. of the Mannich base (I) in 10 cc. of pure pyridine was cooled in an ice-bath to 5° or below, 5 cc. of cold acetic anhydride added dropwise and the mixture let stand in the cold for two to three hours. The product was precipitated by addition of water, collected, washed thoroughly with water, with two small portions of cold methanol, and dried to yield 2.40 g. (94%) of a colorless powder of the N,O-diacetyl derivative (III), m. p. 186–188°. The m. p. was depressed upon admixture with the N,O-diacetyl derivative of the dinaphthylmethane[1] and with the N-acetyl derivative of the Mannich base.[1] For analysis the compound was crystallized five times from *n*-butanol to give pure (III), small, colorless, rectangular prisms, m. p. 188.0–189.0°.

Anal. Calcd. for $C_{25}H_{21}NO_3$: C, 78.30; H, 5.52. Found: C, 78.26; H, 5.91.

Acetylation of 0.1 g. of the N-acetyl derivative of the Mannich base[1] in the same manner gave a nearly quantitative yield of the diacetyl derivative (III), m. p. and mixed m. p. 187–188°. The O-acetyl group of the diacetyl compound (III) was readily hydrolyzed by solution in warm alcoholic alkali to give the N-acetyl derivative, m. p. and mixed m. p. 182–183°.

O-Methyl Schiff Base (IV).—To a solution of 4.20 g. of 2-methoxy-1-naphthaldehyde (prepared according to Barger and Starling[3]) in 20 cc. of hot methanol was added 3.20 g. of β-naphthylamine in 20 cc. of methanol, and the mixture boiled gently for fifteen minutes. On cooling, there was obtained 6.60 g. (96%) of impure product. One crystallization from *n*-butanol gave 5.70 g. (87%) of yellow needles of the O-methyl Schiff base (IV), m. p. 122–123°. For hydrogenation this was purified by chromatography on alumina in benzene solution, eluting with benzene–ether from a very small amount of a brown contaminant. For analysis this was crystallized four times from *n*-butanol to give pure (IV), canary yellow needles, m. p. 122.5–123.5°.

Anal. Calcd. for $C_{22}H_{17}NO$: C, 84.84; H, 5.50. Found: C, 84.68; H, 5.70.

O-Methyl-1-(2′-naphthylaminomethyl)-2-naphthol (V).—A solution of 5.00 g. of the O-methyl Schiff base (IV) in 150 cc. of ethyl acetate plus 1 cc. of acetic acid was hydrogenated at 45 lb. and at room temperature with 0.1 g. of Adams catalyst. The reduction was complete in fifteen minutes. Filtration of the catalyst and removal of solvent *in vacuo* at 40° gave a light yellow crystalline residue which was crystallized from ether to give 3.72 g. (74%) of nearly colorless needles of the O-methyl ether (V), m. p. 111–112°. A further 1.06 g. (20%) of good material was obtained from the mother liquor by precipitation of the hydrochloride followed by treatment with alkali. For analysis the compound was crystallized four times from benzene–hexane to give pure (V), colorless needles in radial clusters, m. p. 112.5–113.5°, mixed m. p. with the O-methyl derivative of the dinaphthylmethane[1] 98–103°.

Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11. Found: C, 84.23; H, 6.00.

The compound gave a hydrochloride, by leading hydrogen chloride into a solution of the base in ether, a colorless powder, m. p. 173–174° (slight dec.).

N-Acetyl-O-methyl-1-(2′-naphthylaminomethyl)-2-naphthol (VI).—To 3.40 g. of the O-methyl ether (V) in 20 cc. of acetone was added the calculated amount of acetic anhydride (1.3 cc.) and the solution boiled down nearly to dryness. Crystallization of the residue from *n*-butanol gave 3.50 g. (96%) of the N-acetyl-O-methyl derivative (VI), m. p. 128–129°, mixed m. p. with the N-acetyl-O-methyl derivative of the dinaphthylmethane[1] 118–124°. For analysis the compound was crystallized five times from *n*-butanol to give pure (VI), small colorless blocks, m. p. 128.9–129.6°. (The m. p. depends somewhat on the rate of heating. This sample was immersed at 126° and heated at a rate of 1° per twenty seconds.)

Anal. Calcd. for $C_{24}H_{21}NO_2$: C, 81.12; H, 5.96. Found: C, 81.00; H, 6.36.

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(4) See, for example, Emmerich, *Ann.*, **241**, 343 (1887); Philpott and Jones, *J. Chem. Soc.*, 337 (1938).

(5) Blicke, "The Mannich Reaction," in "Organic Reactions," John Wiley and Sons, New York, N. Y., 1942, Vol. I, p. 303.

(6) The isomerization mechanism might involve fission of the Mannich base (I) into two fragments, 1-methylene-2-keto-1,2-dihydronaphthalene, and β-naphthylamine, followed by recombination to give the dinaphthylmethane (II). This scheme would account for the other products which have been isolated from the isomerization reaction or from the preparation of the dinaphthylmethane: namely, 1-methyl-2-naphthol, β-naphthylamine, and bis-(2-hydroxy-1-naphthyl)-methane.

(7) All melting points are corrected. Elementary analyses are by Dr. Carl Tiedcke.

The N-acetyl-O-methyl derivative was also obtained in nearly quantitative yield by methylation of the N-acetyl derivative with dimethyl sulfate in alcoholic alkali.

N-Benzenesulfonyl-O-methyl-1-(2'-naphthylaminomethyl)-2-naphthol (VII).—To a solution of 1.20 g. of the O-methyl ether (V) in 5 cc. of pyridine was added 0.75 cc. of benzenesulfonyl chloride and the solution let stand for one-half hour. The crude product was precipitated by addition of water, washed well and dried to give 1.65 g. of a bright yellow powder. The crude material was effectively decolorized by passing a benzene solution through a short column of alumina, eluting with a little benzene-ether. On concentration there was obtained 1.55 g. (89%) of colorless crystals of the Hinsberg product (VII), m. p. 174–175°, mixed m. p. with the N-benzenesulfonyl-O-methyl derivative of the dinaphthylmethane[1] 138–152°. For analysis the material was crystallized five times from acetone to give pure (VII), colorless prisms, m. p. 175.4–176.1°. The compound was unaffected by aqueous or alcoholic alkali and was recovered unchanged. It gave a qualitative test for sulfur.

Anal. Calcd. for $C_{28}H_{23}NO_3S$: C, 74.15; H, 5.11. Found: C, 74.41; H, 5.33.

Isomerization of the Mannich Base (I) in Boiling Benzene.—A solution of 0.25 g. of the Mannich base (I) in 20 cc. of benzene was boiled for one-half hour, and the excess solvent blown off by a stream of air. The initial very light yellow color of the solution had not changed. The residue was acetylated in cold pyridine, as described above, to give 0.28 g. (88%) of the N,O-diacetyl derivative of the dinaphthylmethane,[1] m. p. and mixed m. p. 201.5–202.5°. Similar treatment of another sample with boiling ether did not cause isomerization, since on acetylation a nearly quantitative yield of the N,O-diacetyl derivative of the Mannich base (III) was obtained, m. p. and mixed m. p. 187–188°.

Summary

1-(2'-Naphthylaminomethyl)-2-naphthol has been synthesized and its structure confirmed by its reactions. On heating to above *ca.* 80° it readily isomerizes to the isomeric 2-amino-2'-hydroxy-1,1'-dinaphthylmethane.

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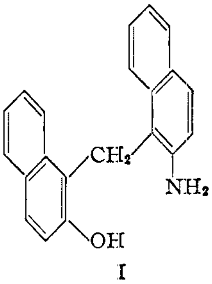
[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

The Reaction of β-Naphthol, β-Naphthylamine and Formaldehyde. III. The Dibenzacridine Products

BY ELKAN R. BLOUT AND RICHARD S. CORLEY

As has been demonstrated,[1a] the reaction of β-naphthol, β-naphthylamine and formaldehyde[2] at moderate temperatures yields 2-amino-2'-hydroxy-1,1'-dinaphthylmethane (I). The Mannich base, 1-(2'-naphthylaminomethyl)-2-naphthol (II)[1b] readily isomerizes under the conditions of the reaction to the dinaphthylmethane (I) and hence may well be the initial intermediate in the reaction sequence. The dinaphthylmethane (I) cyclizes with loss of water and hydrogen to yield 1,2,7,8-dibenzacridine bases and other products.



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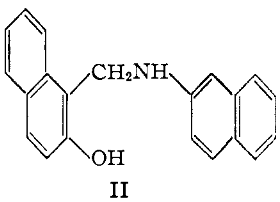
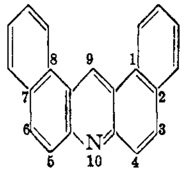


II

The preparation and properties of two of these bases, 1,2,7,8-dibenzacridine (III)[3] and Morgan's base have been investigated and are recorded in the literature.[4] Dibenzacridine (III) is described as light yellow needles or plates, m. p. 216° (uncor.), stable to oxidation by air. It gives a yellow hydrochloride. The structure of dibenzacridine is apparent from its preparation from β-substituted naphthols and naphthylamines. Morgan's base is described as orange needles, m. p. 248°[4g] (other sources give 225 to 236° uncor.[4b,d]). It is reported to give a green hydrochloride which is converted on standing to dibenzacridine hydrochloride. The structure or composition of Morgan's base remained unknown, although various speculations were made,[4d,g] which were formulations of one dibenzacridine molecule (III) with one of dihydrodibenzacridine, to correspond with its analysis for $C_{42}H_{28}N_2$. These formulations agree with the fact that Morgan's base must be connected with dibenzacridine in some oxidation–



III

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(1) (a) Paper I, Corley and Blout, THIS JOURNAL, **69**, 755 (1947); (b) Paper II, Corley and Blout, *ibid.*, 761 (1947).

(2) Ullmann and Fetvadjian, *Ber.*, **36**, 1029 (1903).

(3) Since it is the only dibenzacridine to which reference need be made in this paper, the term dibenzacridine alone will be used to denote 1,2,7,8-dibenzacridine.

(4) (a) Reed, *J. prakt. Chem.*, [2] **35**, 398 (1887); (b) Morgan, *J. Chem. Soc.*, **73**, 549 (1898); (c) Strohbach, *Ber.*, **34**, 4146 (1901); (d) Möhlau and Hasse, *ibid.*, **35**, 4164 (1902); (e) Senier and Goodwin, *J. Chem. Soc.*, **81**, 280 (1902); (f) ref. (2); (g) Senier and Austin, *ibid.*, **89**, 1387 (1906); (h) Austin, *ibid.*, **93**, 1761 (1908); see also ref. (1).