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.

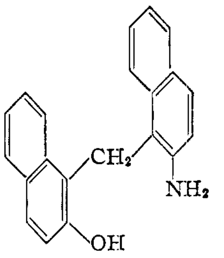
CAMBRIDGE 39, MASSACHUSETTS RECEIVED JULY 27, 1946

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

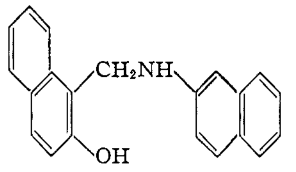
The Reaction of β-Naphthol, β-Naphthylamine and Formaldehyde. III. The Dibenzacridine Products

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.

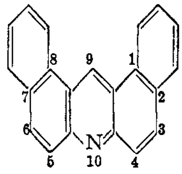


I



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).

reduction scheme. This is shown by the facile oxidation of Morgan's base to dibenzacridine with nitrous acid,[4d,g] with bromine,[4g] or simply by repeated crystallization from acetone or acetic acid,[4b] and the reduction of dibenzacridine to Morgan's base with sodium and amyl alcohol.[4b] However, no compound was ever isolated that corresponded to the postulated reduction stage, the dihydrodibenzacridine. We have found that Morgan's base is a molecular compound of dibenzacridine and 9,10-dihydrodibenzacridine (IV) and have isolated the latter compound.

The reaction of β-naphthol, β-naphthylamine and formaldehyde when carried out in boiling toluene or xylene gave only traces of the dinaphthylmethane (I), and good yields of a mixture of Morgan's base and 9,10-dihydrodibenzacridine (IV). When the reaction was carried out without solvent at 180–230° (the conditions used by Ullmann and Fetvadjian[2]), there was obtained Morgan's base in good yield, smaller amounts of dibenzacridine (III), 1-methyl-2-naphthol, and traces of 9,10-dihydrodibenzacridine (IV). At 250° the same reaction gave in good yields, and as the only product present in appreciable quantity, the molecular compound of dibenzacridine and 1-methyl-2-naphthol.

Dibenzacridine (III) was obtained in a pure condition, initially, by fractional crystallization and chromatographic adsorption on alumina of the products from the reaction at 200–220°. The best method, however, was found to be reaction at 250°, followed by isolation from the molecular compound by extraction of the 1-methyl-2-naphthol with aqueous alkali. Simple crystallization then sufficed for ordinary purification, although chromatography was still necessary for material of highest purity. The composition of the molecular compound was proved by separation of the naphthol with alkali and identification of the two components by direct comparisons with authentic samples. A phase diagram shows that a stable molecular compound, m. p. 167°, is formed, composed of one molecule of dibenzacridine and one of 1-methyl-2-naphthol (Fig. 1).

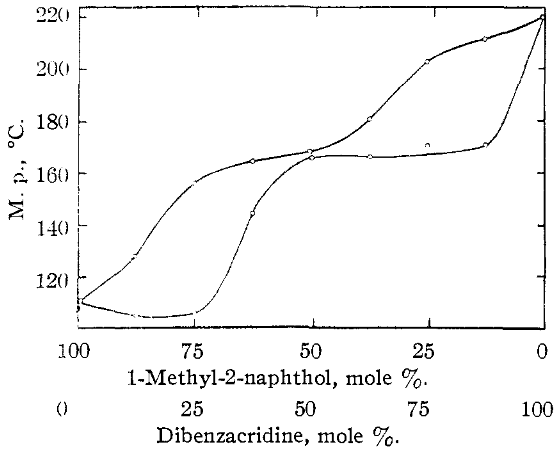

Fig. 1.—Phase diagram of 1-methyl-2-naphthol and dibenzacridine.

As a model for the reduction of dibenzacridine, the reduction of acridine with zinc dust and hydrochloric acid[5] was repeated and found to give a high yield of the colorless, non-basic 9,10-dihydroacridine. This dihydro compound is relatively stable, but reverts slowly on standing to acridine. By acetylation of the dihydro compound, or reductive acetylation of acridine, there was obtained N-acetyl-9,10-dihydroacridine, which apparently has not been previously reported. Application of this acidic reduction to dibenzacridine gave Morgan's base as an intermediate product and small yields of two *compounds*, fine yellow needles, m. p. 183°, and colorless prisms, m. p. 153°. The 183° compound had a light violet fluorescence in solution, formed a yellow hydrochloride, was stable to oxidation by air, and gave dibenzacridine (III) on oxidation with permanganate in acetone. The analysis corresponded to a compound with an empirical formula $C_{21}H_{15}N$ and thus is probably a stable isomeric dihydrodibenzacridine. The 153° compound had a brilliant blue fluorescence in the solid state and in solution, did not form a hydrochloride, and was relatively stable to oxidation by air. Analytical figures agree with empirical formulae of $C_{21}H_{19-21}N$. The positions of two of the hydrogens are undoubtedly (9, 10) in the dibenzacridine skeleton, since the compound does not show basic properties. These two compounds were not further characterized since they do not bear directly on the present study.

A polarographic reduction of dibenzacridine in acidified ethanol[6] showed reduction in two separate steps of half-wave potentials −0.46 v. and −0.69 v. *vs.* the standard calomel electrode, which is analogous to the reduction of 9-phenylacridine in two steps of −0.61 v. and −0.72 v. *vs.* the S.C.E.,[7] and the two electron reduction of acridine.[8] Catalytic reduction of dibenzacridine gave first Morgan's base with uptake of one atomic equivalent of hydrogen, then continued with the uptake of a second atomic equivalent to give a good yield of 9,10-dihydrodibenzacridine in the form of light yellow leaflets. However, the facile air oxidation of moist 9,10-dihydrodibenzacridine

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(5) Bernthsen and Bender, *Ber.*, **16**, 1972 (1883).

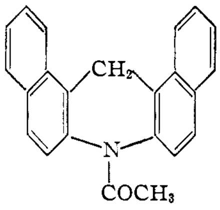
(6) This result was obtained for us by the courtesy of Drs. Melvin Fields and Robert Dryer. We hope to report in a later paper some interesting anomalies in the diffusion currents of dibenzacridine and the application of polarography to the study of Morgan's base.

(7) Lingane, Swain and Fields, This Journal, **65**, 1348 (1943).

(8) Breyer, Buchanan and Duewell, *J. Chem. Soc.*, 360 (1944). Breyer, *et al.*, ascribe the anomalies of the first step diffusion currents to a complex of acridine with a monohydroacridine radical, which differs from the interpretation of Lingane, *et al.* (*q. v.*). A molecular compound of acridine and 9,10-dihydroacridine is not stable under ordinary conditions as shown by a mixed melting point phase diagram, but its presence is probably indicated by the formation of a strong yellow color in the melts (unpublished work of this Laboratory). That it is not stable is probably a consequence of the relatively small stabilization by resonance as compared to phenazine, dihydrophenazine or Morgan's base (see text).

made its isolation in pure condition difficult. A patent[9] describes the preparation of 9,10-dihydrodibenzacridine by heating bis-(2-hydroxy-1-naphthyl)-methane with ammonia at 180° and crystallization of the reaction mixture from alcohol. We repeated this reaction, but, as might be expected in view of the instability of the dihydro product, obtained only a mixture of Morgan's base and dibenzacridine (III). Pure 9,10-dihydrodibenzacridine (IV) when in the dry state, and if kept away from light, is stable for several months at least, although slow oxidation to Morgan's base does occur. It exhibits a violet-blue fluorescence in solution and does not form a hydrochloride (*cf.* diphenylamine, 9,10-dihydroacridine, etc.). It gave Morgan's base in quantitative yield by simply boiling for a few hours in an inert solvent such as xylene, or by chromatographic adsorption on alumina. Treatment with an oxidizing agent (such as bromine or nitrous acid) gave a high yield of dibenzacridine. That it was not isolated from the decomposition products of the dinaphthylmethane (I)[1a] is undoubtedly due to its instability at such a high temperature. It is without doubt formed and is the precursor of Morgan's base in the reaction sequence.

The structure of 9, 10-dihydrodibenzacridine is apparent from the above transformations, by the close analogy of its ready dehydrogenation to the dehydrogenation of other *meso* substituted dihydro aromatic compounds (notably 9,10-dihydroacridine and 9,10-dihydroanthracene), and finally by the fact that it was found to yield N-acetyl-9,10-dihydrodibenzacridine (V) on acetylation under reducing conditions. The acetyl derivative (V) was also obtained by reductive acetylation of dibenzacridine or Morgan's base. It was isolated as colorless needles, m. p. 207°, stable in air, but which gradually reverted to Morgan's base in a solution exposed to light (see Fig. 5).



V

Morgan's base was most readily obtained by crystallization from benzene of the products of the reaction without solvent at 180–220°. The composition of Morgan's base was demonstrated by its preparation from equimolecular quantities of 9,10-dihydrodibenzacridine and dibenzacridine, and the phase diagram (Fig. 2) to be an equimolecular combination of these two compounds.

The ultraviolet absorption spectra of the model compounds, acridine, 9,10-dihydroacridine and N-acetyl-9,10-dihydroacridine, were determined (Fig. 3). The curve for acridine agrees with that given in the literature.[10] The values for 9,10-dihydroacridine ($\lambda_{max.}$ 289 mμ, log ε 4.14) show the expected agreement with those of its electronic analog, diphenylamine ($\lambda_{max.}$ 287 mμ, log ε 4.56).[11]

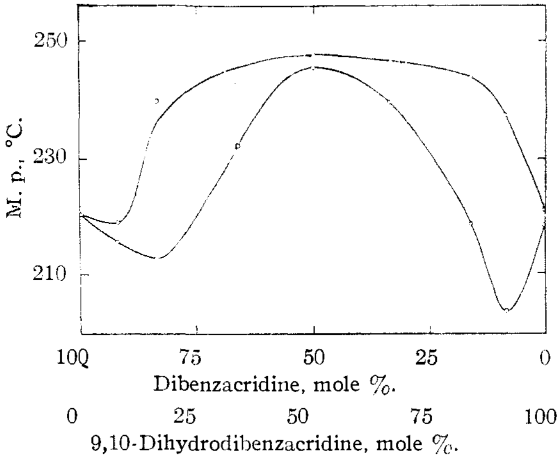


Fig. 2.—Phase diagram of dibenzacridine and 9,10-dihydrodibenzacridine.

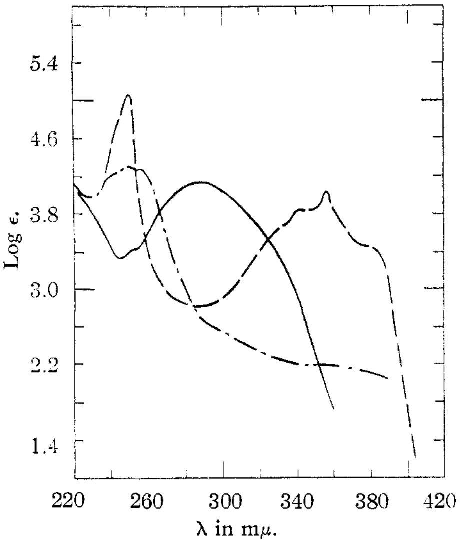


Fig. 3.—(a) ———— 9,10-Dihydroacridine; (b) —·—·—·- N-acetyl-9,10-dihydroacridine; (c) — — — acridine.

The spectra of dibenzacridine and its acidic reduction products, the 183° x,x-dihydrodibenzacridine and the 153° compound, are shown in Fig. 4. Note that the curve for the 183° compound differs appreciably from that of dibenzacridine *only* in its peak at 250 mμ, and that the middle peak of the 153° compound ($\lambda_{max.}$ 289 mμ) coincides with that of diphenylamine (see above). The spectrum of

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(9) Erich Lehmann, U. S. Patent 2,242,585 (1941); *Chem. Abs.*, **35**, P5648 (1941).

(10) Craig and Short, *J. Chem. Soc.*, 419 (1945); *cf.* Radulescu and Ostrogowich, *Ber.*, **64**, 2233 (1931), and Charlampowiczowna and Marchlewksi, *Bull. intern. l'acad. polon. sci., Classe sci. math. nat. A.*, 376 (1930).

(11) Castille, *Bull. classe sci. Acad. roy. Belg.*, **12**, 498 (1926).

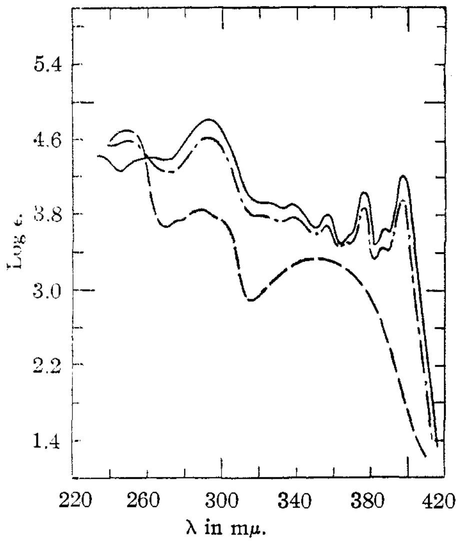

Fig. 4.—(a) ——— Dibenzacridine; (b) —·—·—·— x,x-dihydrodibenzacridine; (c)— — — — 153° compound.

N-acetyl-9,10-dihydrodibenzacridine was determined immediately after making up and after the solution had stood for different lengths of time in diffuse daylight (Fig. 5). These curves demonstrate the gradual conversion of the compound to Morgan's base or dibenzacridine (*cf.* Figs. 4 and 6). The spectra of Morgan's base and 9,10-dihydrodibenzacridine are shown in Fig. 6 in comparison with the curve calculated for Morgan's base assuming complete dissociation at these high dilutions (10^{-4}, 10^{-5} *M*). This curve was calculated by adding, at each wave length, one-half the molecular extinction coefficients of the components of the molecular compound, dibenzacridine (III) and 9,10-dihydrodibenzacridine (IV), and plotting the sum in terms of log ϵ. The agreement of the calculated and the observed curves means that complete dissociation does indeed occur on dilution (*cf.* Möhlau and Haase's values of 218 and 221 for the molecular weight of Morgan's base by the ebullioscopic method[4d]). This same phenomenon has been observed for other molecular compounds by absorption spectra[12] and by other methods.[13] While proof of the bond structure of Morgan's base must await detailed physical measurements, the facts of its dissociation as demonstrated by absorption spectra and its color are good evidence for its formulation according to the modern theory of molecular compounds promulgated chiefly by Weiss.[14] Attention should also be drawn to the analogous *blue* molecular compounds of phenazines and dihydrophenazines.[15]

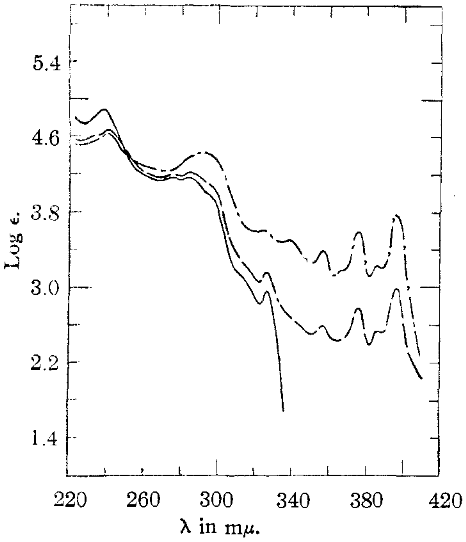

Fig. 5.—N-acetyl-9,10-dihydrodibenzacridine: (a) —— three hours' standing; (b) — — — — six days' standing; (c) —·—·—·— seventeen days' standing.

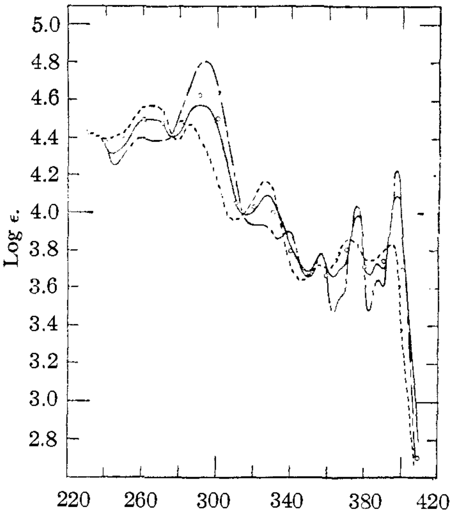

Fig. 6.—(a) ——— Morgan's base; (b) ---------- 9,10-dihydrodibenzacridine; (c) —·—·— dibenzacridine; (d) o o o o o o o calcd. curve for Morgan's base (see text).

The formation of molecular compounds from such compounds as aromatic amines and hydrocarbons on the one hand, and quinones and nitro compounds on the other, may be ascribed to a complex, essentially ionic, molecule formed by a reversible, one electron transfer from the former (donor, A) to the latter (acceptor, B) according to the net reaction: $A + B \rightleftarrows [A]^{+}: [B]^{-}$.

Application of this concept to Morgan's base gives as the initial product the complex ion-radical (VI *a* and *b*) formed by a one electron transfer from the donor, 9,10-dihydrodibenzacridine, to the acceptor molecule, dibenzacridine. The two ion-radicals are pictured as held together, plane to plane, by the electrostatic charges distributed, in each case, by resonance throughout the planar

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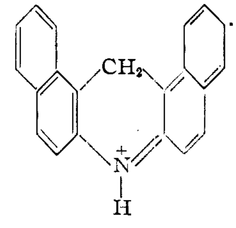
(12) Hunter, Querishy and Samuel, *J. Chem. Soc.*, 1576 (1936).

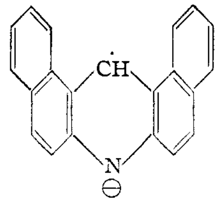
(13) Sudborough, *ibid.*, **79**, 522 (1901); Hibbert and Sudborough, *ibid.*, **83**, 1334 (1904).

(14) J. Weiss, *et al.*, *ibid.*, 245 (1942); 462 (1943); 464 (1944).

(15) Clemo and McIlwain, *ibid.*, 1991 (1934); 738 (1935).

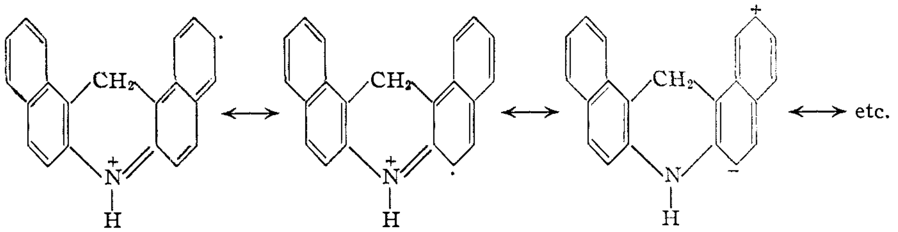


VIa

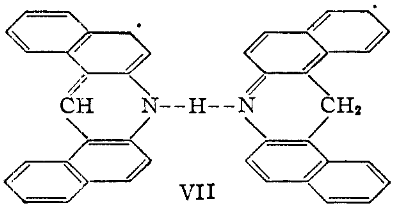


VIb

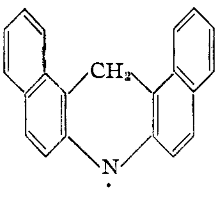
molecules (illustrated for VI). This high resonance energy presumably accounts for the stability of the complex (as is true also of the forms below). As Weiss has pointed out for analogous cases, other forms may be present. In this case we might have hydrogen bonding between two radicals (VII), or semiquinone radicals (VIIIa and b) formed by disproportionation of (VII) or directly from (VI). The actual amounts of each of these forms of the molecular compound (VI, VII and VIII) present in the over-all equilibrium would be dependent upon the external environment.



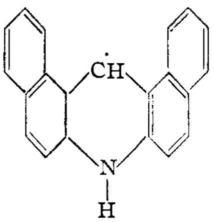
VIa



VII



VIIIa



VIIIb

With the elucidation of the composition of Morgan's base, each step in the reaction sequence is complete. The course of the reaction of β-naphthol, β-naphthylamine and formaldehyde is then as follows: β-naphthol, β-naphthylamine, formaldehyde → [1-(2′-naphthylaminomethyl)-2-naphthol(II)] → 2-amino-2′-hydroxy-1,1′-dinaphthylmethane (I) → 9,10-dihydrodibenzacridine (IV) → Morgan's base [molecular compound of (III) and (IV)] → dibenzacridine (III).

Acknowledgment.—The authors wish to make acknowledgment for this group of papers to Dr. R. B. Woodward for many helpful suggestions, to Mr. W. A. Davis and Miss Adelaide Sutton for the determinations of the absorption spectra, and to Miss Esther Polson, who kindly plotted all of the curves. We are indebted to Mr. W. F. Amon, Jr., Mr. R. M. Gofstein, Mr. V. Georgian and Dr. C. D. West whose earlier work in this Laboratory provided the basis for this study, and especially to Mr. Claude Valle, Jr., who has given us great help in much of the preparative work.

Experimental[16]

(A) Reaction of β-Naphthol, β-Naphthylamine and Formaldehyde. Reaction in Solvent.—A mixture of 28.8 g. (0.2 mole) of β-naphthol, 28.6 g. (0.2 mole) of β-naphthylamine and 7.0 g. (0.23 mole) of paraformaldehyde in 800 cc. of dry xylene was placed in a flask fitted with a "take-off" condenser and a mechanical stirrer, and the air displaced by a stream of nitrogen. The solution was refluxed gently for two hours, removing water (*ca.* 6 cc.) during this time by azeotropic distillation with 300 cc. of xylene. On cooling, the clear, light orange solution deposited in two crops 41.6 g. (74%) of a mixture of 9,10-dihydrodibenzacridine (IV) and Morgan's base. The same reaction in toluene gave in two crops on cooling 43.9 g. of product from which 4.2 g. (7%) of the dinaphthylmethane (I) was separated by extraction with cold alcoholic alkali. The residue weighed 38.7 g. (69%) and was a mixture of Morgan's base and 9,10-dihydrodibenzacridine.

(B) Reaction without Solvent.—When the reaction was carried out by fusion of equimolecular quantities of β-naphthol, β-naphthylamine and a small excess of paraformaldehyde at 180–230° according to Ullmann and Fetvadjian,[2] there was obtained on fractional crystallization from benzene or toluene 30–35% of the less soluble Morgan's base as orange needles, m. p. *ca.* 235–245°, and 10–20% of dibenzacridine (III) as yellow leaflets, m. p. 216–217°. By extraction with aqueous alkali of the toluene mother liquors of several runs there was isolated an average of 6.2% of 1-methyl-2-naphthol, m. p. and mixed m. p. 109–110°.

The same reaction was carried out at 250–260°, using 9.00 g. (0.30 mole) of paraformaldehyde, 28.8 g. of β-naphthol and 28.6 g. of β-naphthylamine, and gave after crystallization from toluene 36.2 g. (65% by weight) of bright yellow prisms of the molecular compound of 1-methyl-2-naphthol and dibenzacridine, m. p. 167°, which remained unchanged in melting point or appearance after several crystallizations from toluene. The molecular compound (86 g.) was powdered and boiled with 300 cc. of 10% sodium hydroxide solution. As soon as the color of the powder had changed to a pale yellow it was filtered off, washed twice with 50 cc. of 5% alkali, and then with water. After crystallization from benzene the residue gave 53 g. (62%) of dibenzacridine (III), m. p. 219–220°, identical with that obtained above. The aqueous filtrate was acidified and the precipitated material crystallized from benzene–hexane to give 29 g. (34%) of colorless needles of 1-methyl-2-naphthol, m. p. 110°, and m. p. 110.1–110.4° after three further crystallizations. The identity of the naphthol was proven by preparation of its picrate (from equimolecular amounts of the naphthol and picric acid in

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(16) All melting points are fully corrected except where indicated. Analyses by Dr. Carl Tiedcke.

benzene), red needles, m. p. 160–162°, and mixed melting point.[17]

Dibenzacridine (III).—The pure compound was obtained by chromatographic adsorption on alumina. A solution in benzene of the material obtained from the reaction at 180–230° or from the molecular compound of dibenzacridine and 1-methyl-2-naphthol was run through a short column of commercial grade alumina, which left behind the orange-brown impurities in a strongly adsorbed band at the top. The light yellow, fluorescent band was removed by extrusion and sectioning of the column (or by elution with 20:1 benzene–methanol) and gave on crystallization a 95% recovery of nearly colorless, very pale yellow leaflets of dibenzacridine (III), m. p. 220.4–221.1°. As noted by Senier and Goodwin,[4e] it darkens slightly on exposure to light. Dibenzacridine hydrochloride was obtained as deep yellow, small leaflets, m. p. 346–348° (uncor., dec.). Dibenzacridine picrate was isolated as small, hair-like, bright yellow needles, m. p. 332–334° (uncor.). It was insoluble in the common organic solvents, but could be crystallized from nitrobenzene.

9,10-Dihydroacridine and N-Acetyl-9,10-dihydroacridine.—9,10-Dihydroacridine[5] was purified by repeated crystallization from methanol to give the pure compound, colorless, flat needles, m. p. 172.2–173.1° (sealed under hydrogen). Exposed to air it had m. p. 169.6–172.4°, with some oxidation to acridine as shown by development of a yellow color in the melt. The reduction proceeded in two stages, with intermediate precipitation of a bright yellow powder perhaps a hydrochloride of a molecular compound of acridine and dihydroacridine, *cf.* ref. (8).

N-Acetyl-9,10-dihydroacridine was prepared by refluxing 9,10-dihydroacridine for twelve hours in excess acetic anhydride or by refluxing acridine for the same length of time with acetic anhydride, acetic acid and zinc dust. The product was precipitated by addition of water to the filtered reaction solution and purified by repeated crystallization from methanol to yield the pure compound, colorless, sparkling prisms, m. p. 151.6–152.2°. The yield varied from 78 to 84%. For analysis it was dried for five hours *in vacuo* at 80°.

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.66; H, 5.87. Found: C, 80.98; H, 6.03.

Acidic Reduction of Dibenzacridine (III).—Finely powdered dibenzacridine (one part) was placed with *ca.* thirty parts of concd. hydrochloric acid in a flask fitted with an efficient mechanical stirrer, one or two drops of lauryl alcohol added to reduce foaming, and *ca.* eight parts of zinc dust added in small portions over a period of two to three hours, during which time the mixture was kept at 80–90°. The reduction went in two steps as shown by the disappearance in a short time of the yellow dibenzacridine hydrochloride and formation of the green hydrochloride of Morgan's base which then gradually disappeared as the reaction proceeded. One reduction was stopped at the intermediate stage, filtered, the green hydrochloride decomposed with alkali and the product crystallized from benzene to give orange needles of Morgan's base, m. p. and mixed m. p. 238–244°. When the reduction was complete, as shown by disappearance of the green coloration, the mixture was cooled, filtered, and washed with water. The residue was dried and the organic products separated from zinc dust by extraction with benzene. Fractional crystallization from benzene–acetone–hexane gave fine yellow needles of the **183° x,x-dihydrodibenzacridine**, m. p. 182.2–183.0°. It had a light violet fluorescence in solution under ultraviolet light and gave a yellow hydrochloride with hydrogen chloride in ether. Treatment in acetone with permanganate gave a quantitative yield of dibenzacridine.

Anal. Calcd. for $C_{21}H_{15}N$: C, 89.66; H, 5.37. Found: C, 89.57; H, 5.45.

The mother liquors on combination and concentration gave the **153° compound**, colorless, refractive rectangular prisms, m. p. 151.0–152.6°. It exhibited a brilliant blue fluorescence in the solid state or in solution and did not form a hydrochloride.

Anal. Calcd. for $C_{21}H_{19}N$: C, 88.38; H, 6.71. Calcd. for $C_{21}H_{21}N$: C, 87.76; H, 7.36. Found: C, 87.42; H, 7.12.

The reduction gave variable results and it was not possible in all instances to isolate the 153° compound. The yield of the 183° compound was *ca.* 16% and of the 153° compound, *ca.* 6% (average of nine runs). In one run, by extraction of the zinc residue with hexane instead of benzene, the two compounds were isolated together in the form of a molecular compound, bright yellow blocks with a characteristic green fluorescence, m. p. 147–149.5°. This complex was unchanged on another crystallization from hexane, but gradually on repeated crystallization, or immediatelly on crystallization from acetone or benzene, it separated into its components.

Catalytic Reduction of Dibenzacridine (III).—A suspension of 0.100 g. of Adams platinum oxide catalyst in 150 cc. of ethyl acetate was reduced at room temperature and atmospheric pressure. When the reduction of the catalyst was complete, 1.00 g. of powdered dibenzacridine was added and warmed to give a concd. solution. Shaking was resumed and in one hour the reduction was complete, with absorption of 87 cc. of hydrogen (calcd. for one mole uptake: 86.5 cc. at 25.0°, 771 mm.). Morgan's base crystallized out midway during the hydrogenation as a suspension of fine orange needles, then disappeared to give a very light yellow solution (it is considerably less soluble than dibenzacridine or dihydrodibenzacridine). The hydrogen was displaced by carbon dioxide, the solution filtered and evaporated *in vacuo* under carbon dioxide to give a light yellow residue which yielded on rapid crystallization from ether 0.48 g. (48%) of light yellow leaflets of 9,10-dihydrodibenzacridine (IV), m. p. 218–220° (sealed under nitrogen).

A graph of hydrogen absorbed *vs.* time showed no change in rate of hydrogenation corresponding to the halfway point. However, when the reduction was repeated, stopped at the point of one atomic equivalent of hydrogen uptake, and worked up in the same manner, there was obtained a quantitative yield of Morgan's base, m. p. and mixed m. p. 241–245°. Conversely, a catalytic reduction of Morgan's base gave absorption of one atomic equivalent of hydrogen and a good yield of 9,10-dihydrodibenzacridine (IV) identical with that obtained above.

9,10-Dihydrodibenzacridine (IV).—Larger amounts of the dihydro compound were most readily obtained from the mixture with Morgan's base resulting from the reaction in xylene. Extraction of 20 g. of this mixture with three 75-cc. portions of boiling, peroxide-free ether gave on concentration 3.8 g. (19%) of nearly pure (IV), m. p. 218–220° (sealed under nitrogen). It was necessary to work with speed and to disregard mechanical losses. It was found best to conduct the extraction, filtration and concentration in an atmosphere of ether vapor (by keeping the solutions always boiling) rather than to attempt to work under nitrogen or carbon dioxide using complicated equipment. Unnecessary handling and exposure to heat and air resulted in formation of considerable amounts of contaminating Morgan's base. For analysis the product was crystallized five times from benzene, with the same precautions, and dried for five hours *in vacuo* at 50° to give very light yellow leaflets of pure 9,10-dihydrodibenzacridine (IV), m. p. 214–215° (in air, dec., with formation of Morgan's base) and m. p. 219.0–221.2° (sealed under nitrogen). It had a light violet-blue fluorescence in solution, did not form a hydrochloride, and was identical with the product isolated from the catalytic reductions of dibenzacridine and Morgan's base.

Anal. Calcd. for $C_{21}H_{15}N$: C, 89.66; H, 5.37. Found: C, 89.42; H, 5.54.

Chromatographic adsorption on alumina of 200 mg. of the dihydro compound in benzene solution gave 195 mg. (97.5%) of Morgan's base, m. p. and mixed m. p. 232–

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[17] Cornforth, Cornforth and Robinson, *J. Chem. Soc.*, 682 (1942).

242°. A solution of 500 mg. of the dihydro compound in xylene was boiled for two hours and deposited on cooling 435 mg. (87%) of Morgan's base. A solution of the dihydro compound in acetic acid gave dibenzacridine (III) on addition of excess bromine, nitrous acid, or on boiling for one hour, with intermediate formation of a dark green color due to salts of Morgan's base. The dihydro compound is, however, comparatively stable in the dry state. A sample kept for four months in the dark was found to have m. p. 210–215°, which corresponds to only a small amount of oxidation (see Fig. 2).

Reaction of 10 g. of bis-(2-hydroxy-1-naphthyl)-methane with ammonia according to the directions of Lehmann[9] gave on crystallization from benzene 3.3 g. (33%) of Morgan's base and 2.7 g. (27%) of dibenzacridine (III). No appreciable quantities of 9,10-dihydrodibenzacridine were observed at any point in the isolation procedure.

N-Acetyl-9,10-dihydrodibenzacridine (V).—A mixture of 10 g. of dibenzacridine (III), 500 cc. of acetic anhydride, 100 g. of zinc dust and 50 cc. of acetic acid was gently boiled for two days in a flask provided with a reflux condenser and protected by a tube of drying agent. The solvents were distilled off *in vacuo* and the residue extracted with 500 cc. of benzene. The brown solution was decolorized by passing it slowly through a one-inch layer of alumina in a suction funnel and gave on concentration to 100 cc. an addition of an equal quantity of hot hexane 4.07 g. (35%) of nearly colorless, small needles of the N-acetyl derivative, m. p. 202–205°. Similar reductive acetylation of 9,10-dihydrodibenzacridine (IV) and of Morgan's base gave somewhat lower yields of the same product. For analysis the compound was crystallized six times from benzene–hexane and dried *in vacuo* to give pure (V), small, colorless, sparkling needles, m. p. 205.4–206.8°. Solutions of the compound showed no fluorescence.

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.41; H, 5.38; N, 4.33. Found: C, 84.99; H, 5.34; N, 4.63.

Morgan's Base (Molecular Compound of Dibenzacridine and 9,10-Dihydrodibenzacridine).—Morgan's base isolated from the reaction with and without solvent, from the reduction of dibenzacridine, or from the oxidation of 9,10-dihydrodibenzacridine crystallized from benzene or toluene in clumps of slender orange needles, but its m. p. varied considerably (low, 232–240°; high, 246–248°) dependent on the particular conditions of the crystallization. The pure base was obtained by mixing concentrated solutions in hot benzene of equimolecular quantities of dibenzacridine (III) (0.126 g.) and 9,10-dihydrodibenzacridine (IV) (0.127 g.). The very light yellow color of the separate solutions turned deep yellow immediately on admixture, and on touching the wall of the flask with a rod, characteristic orange needles of Morgan's base rapidly crystallized out, yield 0.192 g. (76%), m. p. 241.5–246.5° (in air), m. p. 248.2–249.0° (sealed under nitrogen). The mother liquor yielded on concentration a second crop 47 mg. (18.5%) of slightly less pure Morgan's base.

Anal. Calcd. for $C_{42}H_{28}N_2$: C, 89.97; H, 5.03. Found: C, 90.25; H, 4.94.

The base was less soluble than dibenzacridine or 9,10-dihydrodibenzacridine in the common organic solvents. Solutions of the base showed a marked diminution of color on dilution or heating and had a violet fluorescence. The base formed with mineral acids deep green salts which oxidized rapidly in solution to salts of dibenzacridine (III), but which converted only very slowly on standing in the dry state. The pronounced instability of solutions of the molecular compound or its salts as compared to the dry materials is due to dissociation into its components and consequent rapid oxidation of the 9,10-dihydrodibenzacridine (IV). In the case of the hydrochloride this reversible dissociation and the concomitant irreversible oxidation were shown by alternately heating and cooling a solution of the salt in ethanol. At first the solution was a pale greenish-yellow when hot and a deep emerald green when cold, but after three or four of these cycles the green coloration had disappeared to give a lemon yellow solution of dibenzacridine hydrochloride from which dibenzacridine was isolated by treatment with alkali. Morgan's base hydrochloride was prepared with least contamination with dibenzacridine hydrochloride by heating 9,10-dihydrodibenzacridine with alcoholic hydrochloric acid. The non-basic dihydro compound was at first unaffected, then slowly dissolved to give a greenish-yellow solution which became dark green on cooling and deposited a quantitative yield of fine, dark green needles of Morgan's base hydrochloride, did not melt but converted rapidly without melting at 185° and above to dibenzacridine hydrochloride. Addition of picric acid to a solution of Morgan's base gave an orange precipitate which converted on heating over 200°, or on attempted crystallization from nitrobenzene, to the yellow picrate of dibenzacridine. Morgan's base gave a quantitative yield of dibenzacridine by treatment of a hot solution in acetic acid with bromine, with nitrous acid, or by boiling the solution for several hours.

Phase Diagrams and Absorption Spectra.—The data for both of the mixed melting point phase diagrams were obtained in the same manner. The pure compounds were weighed into small tubes, fused in an oil-bath under nitrogen, the melt cooled, powdered and the melting point taken in a capillary sealed under nitrogen.

The ultraviolet absorption spectra were determined on a Beckman quartz spectrophotometer, model DU, using a 1-cm. quartz cell and a hydrogen discharge tube as the ultraviolet source. The solvent used throughout was 95% ethanol except in the case of 9,10-dihydrodibenzacridine where ether was used to help prevent oxidation.

Summary

The reaction of β-naphthol, β-naphthylamine and formaldehyde is shown to give 9,10-dihydrodibenzacridine which is also obtained by reduction of two other products of the reaction, dibenzacridine and Morgan's base. Morgan's base is demonstrated to be a molecular compound of 9,10-dihydrodibenzacridine and dibenzacridine and its structure is formulated according to modern theory. The complete reaction sequence is shown to be: β-naphthol, β-naphthylamine, formaldehyde → [1-(2′-naphthylaminomethyl)-2-naphthol] → 2-amino-2′-hydroxy-1,1′-dinaphthylmethane → 9,10-dihydrodibenzacridine → Morgan's base (molecular compound of dibenzacridine and 9,10-dihydrodibenzacridine) → dibenzacridine.

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