Studies of Acenaphthene Derivatives. XI.[1] The Reaction of Acenaphthenequinone with Aliphatic Amines

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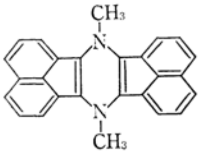
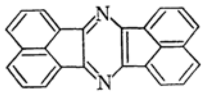
In an earlier paper[2] dealing with the reaction between acenaphthenequinone (I) and ammonia, it was shown that the structure of red crystals (II) is neither acenaphthenequinonimide anhydride[3] nor acenaphthazine,[4] but acenaphtho [1, 2-b] isoimidazole-2-spiro - 2' - acenaphthenone.

It had been shown by Rule and Thompson[5] that the reaction of I with aqueous methylamine at 100°C in a sealed tube afforded brown needles (III) (m. p. over 360°C); for these *N, N'* - dimethyldihydroacenaphthazine (IIIa) was assumed on the basis of the nitrogen value and the structure of acenaphthazine (IIIb) suggested by Schönberg and Nedzati[4] for II.



(IIIa)



(IIIb)

Since Rule and Thompson's assumption of the structure of IIIa is incorrect, however, it is doubtful whether the structure of III is IIIa or not.

It was also found that naphthalimide was formed, even if the reaction of I with ammonia was carried out under mild conditions. Accordingly, I may be expected to result easily in the formation of the corresponding naphthalimide derivative by an aliphatic amine with a higher basicity than that of ammonia. However, little information is available regarding the formation of *N*-methylnaphthalimide by the reaction of I with methylamine.

The present paper deals with the results of a reexamination of the structure of III and of the reaction of I with methyl-, ethyl- and benzylamine.

Results and Discussion

The reaction of I with 30% aqueous methylamine at 100°C in a sealed tube according to the Rule and Thompson procedure afforded yellow needles (III), m. p. over 400°C, and *N*-methylnaphthalimide (IV) in low yields due to the formation of a resinous material.

The elemental analytical data on III were in agreement with the formula $C_{24}H_{12}N_2$, whose infrared spectrum did not reveal any bands ascribed to the aliphatic C–H and N–H bonds. As Fig. 1 shows, its ultraviolet spectrum is

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[1] Part X: O. Tsuge and M. Tashiro, The Reports of the Research Institute of Science and Industry (Seisan Kagaku Kenkyusyo Hōkoku), Kyushu University, No. 36, 1 (1963).

[2] O. Tsuge and M. Tashiro, This Bulletin, **36**, 970 (1963).

[3] C. Graebe and E. Gfeller, *Ann.*, **276**, 1 (1893).

[4] A. Schönberg and F. Nedzati, *Ber.*, **54**, 238 (1921).

[5] H. G. Rule and S. B. Thompson, *J. Chem. Soc.*, **1937**, 1761.

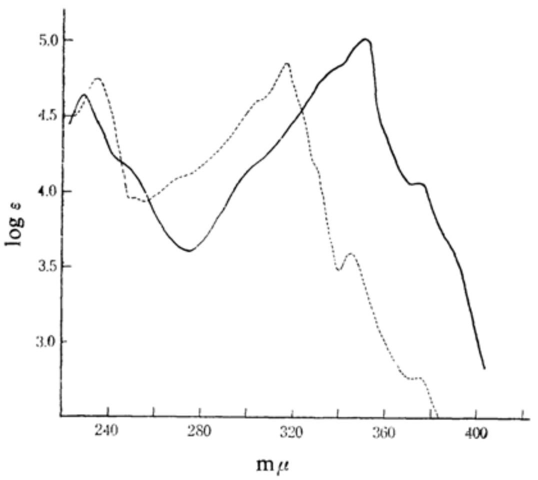

Fig. 1. UV spectra of IIIb and acenaphtho[1,2-b]quinoxaline in dioxane.
—— IIIb
---- Acenaphtho[1,2-b]quinoxaline

very similar to that of the known compound, acenaphtho[1,2-b]quinoxaline.⁶⁾ In addition, the oxidation of III with sodium dichromate in boiling glacial acetic acid resulted in the recovery of III, so it might be considered that III has a stable structure for the oxidation.

These observations are accommodated much better by the structure of acenaphthazine (IIIb) than by IIIa. The mechanism of the formation of IIIb will be discussed below.

On the other hand, IV was identical with an authentic sample prepared by the reaction of naphthalic anhydride and methylamine.⁷⁾

In treatment at room temperature for a long period, IV was formed as the main product, along with a small amount of IIIb.

In view of the fact that IIIb was obtained in the reaction of I with methylamine, it may well be doubted whether or not IIIb can be formed in the reaction of other amines than methylamine with two hydrogen atoms on the α-carbon atom. If IIIb is formed in the reaction with such amines, the structure of IIIb for III is more probable.

In the case of the reaction of I with 70% aqueous ethylamine at 80°C for 15 min., as had been expected, IIIb and *N*-ethylnaphthalimide (V) were obtained in yields of 17.5 and 42.5% respectively. V was proved, by the admixed melting point and by the infrared spectrum, to be identical with an authentic sample prepared by the reaction of naphthalic anhydride and ethylamine.⁷⁾

In the reaction of I with 40% aqueous benzylamine or 100% benzylamine, also, IIIb and *N*-benzylnaphthalimide (VI) were formed in low yields as a result of the formation of a resinous material. Although the reported melting point of VI was 95—96°C,⁸⁾ the VI which was obtained by the reaction and by the condensation of potassium naphthalimide and benzyl bromide melted at 195—195.5°C.

Furthermore, benzaldehyde was isolated and and identified as the 2,4-dinitrophenylhydrazone in the reaction with benzylamine. This fact suggests the mechanism of the formation of IIIb in the reaction of I with an amine having two hydrogen atoms on the α-carbon atom.

The formation of IIIb may be as shown in Chart I. That is, *N*-alkylacenaphthenequinonimine (VII), the product of I and one equivalent of amine, rearranges to the Schiff base (VIII). The subsequent hydrolysis of the Schiff base would yield the aldehyde and 1,2-aminoacenaphthenole (IX). The self-condensation of IX leads to the formation of dihydroacenaphthazine (X), which easily dehydrogenates to IIIb.

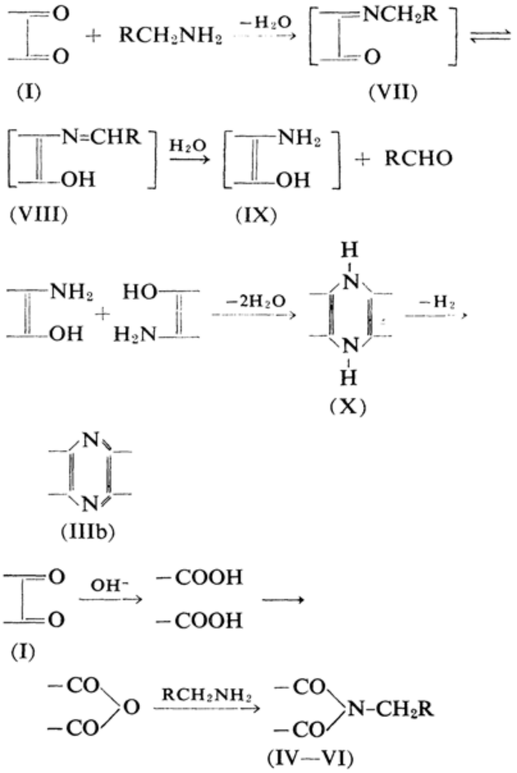

Chart 1.

In the reaction of I with ammonia, acenaphthenequinone monoimine corresponding to

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6) This compound was prepared by the condensation of I and *o*-phenylenediamine. (G. Ampola and V. Recchi, *Atti R. Accad. dei Lincei Roma* [5], **8**, 209; *Chem. Zentr.*, **1899**, **II**, 338.)

7) G. F. Jaubert, *Ber.*, **28**, 360 (1895).

8) S. M. A. Devereux, S. N. J. M. and H. B. Donahoe, *J. Org. Chem.*, **25**, 457 (1960).

VII was isolated.[2] Since the monoimine can not be rearranged to the corresponding Schiff base, it might be considered that the self-condensation of the monoimine resulted in the formation of the isoimidazole derivative mentioned above.

On the other hand, *N*-alkylnaphthalimide is assumed to be formed through naphthalic acid and naphthalic anhydride, as has been shown in a previous paper.[2]

Experimental[9]

The Reaction of I with Aqueous Methylamine. —*a) By the Rule and Thompson Procedure.*—A mixture of 2.0 g. of I and 5 ml. of 30% aqueous methylamine was heated in a sealed tube at 100°C for 6 hr. After it had cooled, the mixture was poured into water and the resinous precipitate was collected; then this was extracted with 100 ml. of methanol, leaving 0.5 g. (28%) of brown crystals, m. p. over 360°C. Recrystallization from nitrobenzene or sublimation afforded acenaphthazine (IIIb) as yellow needles, m. p. over 400°C.

Found: C, 87.79; H, 3.83; N, 8.57. Calcd. for $C_{24}H_{12}N_2$: C, 87.78; H, 3.68; N, 8.53%.

UV $\lambda_{max}^{\text{Dioxane}}$ mμ (log ε): 228.5 (4.64), 348 (5.03).

After the extract had been evaporated, there remained a resinous material, which was then dissolved in benzene and chromatographed on alumina. From the benzene eluate, *N*-methylnaphthalimide (IV) was obtained in the form of colorless needles (Found: C, 74.16; H, 4.32; N, 6.56%). Yield, 0.15 g. (6.3%); m. p. 205°C (lit.[7] m. p. 205°C). This compound was identical with the authentic sample prepared from naphthalic anhydride and methylamine.

b) At Room Temperaure.—A suspension of 2.0 g. of I in 20 ml. of 30% aqueous methylamine was stirred in a closed vessel at room temperature for 24 hr. During this time the mixture turned brown. After the reaction mixture had been poured into water, the precipitate was collected, washed with water, dried, and extracted with 50 ml. of hot ethanol, leaving 0.5 g. (28%) of brown crystals, m. p. over 360°C. Recrystallization from nitrobenzene gave yellow needles whose infrared spectrum was superimposable with that of IIIb.

After the ethanol extract had cooled, filtration afforded 1.4 g. (60.3%) of colorless needles, m. p. 195—198°C. Recrystallization from ethanol gave colorless needles, m. p. 205°C, which were proved, by the admixed melting point and infrared spectrum, to be identical with IV.

The Reaction of I with Aqueous Ethylamine.—A solution of 2.0 g. of I in 20 ml. of 70% aqueous ethylamine was heated at 80°C for 15 min. The color of the solution turned from green to reddish brown within a few minutes. The reaction mixture was then poured into water, and the precipitate collected, washed with water, dried, and extracted with 200 ml. of ether. The ether-extract was evaporated to give 1.05 g. (42.5%) of pale brown crystals, m. p. 140—145°C. Recrystallization from ethanol afforded pale yellow prisms, m. p. 154—155°C (lit.[8] m. p. 154°C. This compound was found to be identical with the *N*-ethylnaphthalimide (V) which was prepared from naphthalic anhydride and ethylamine.

The ether-insoluble residue was washed with hot benzene, leaving 0.63 g. (17.5%) of brown crystals, m. p. over 360°C. Recrystallization from nitrobenzene or sublimation afforded yellow needles which were identical with IIIb. The benzene-washing was then evaporated, leaving a resinous material which was not investigated further.

The Reaction of I with Benzylamine.—*a) With a 40% Aqueous Solution.*—When a solution of 2.0 g. of I in 20 ml. of 40% aqueous benzylamine was heated at 80°C for 1 hr., similar phenomena were observed. The reaction mixture was poured into water to precipitate a brown resinous substance. The precipitate was then collected, washed with water, dried and extracted with ether, leaving brown crystals. The ether-insoluble brown crystals were washed with 100 ml. of hot benzene, leaving 0.2 g. (7.2%) of brown crystals, m. p. over 360°C. Recrystallization from nitrobenzene afforded yellow needles whose infrared spectrum was superimposable on that of IIIb.

The benzene-washings was evaporated to leave 0.8 g. (25.8%) of pale brown crystals. Recrystallization from isopropyl alcohol afforded pale yellow needles m. p. 195—195.5°C.

Found: C, 79.47; H, 4.59; N, 4.91. Calcd. for $C_{19}H_{13}O_2N$: C, 79.43; H, 4.56; N, 4.88%.

This compound was identical with the *N*-benzylnaphthalimide prepared from potassium naphthalimide and benzyl bromide.

Although a reddish violet resinous material was obtained from the ether-washings, it was not investigated further.

b) With 100% Benzylamine.—A mixture of 2.0 g. of I and 4 ml. of benzylamine was heated at 80°C for 1 hr. After the mixture had been cooled, filtration afforded a brown precipitate which, on being washed with hot benzene, left 0.4 g. (14.3%) of brown crystals, m. p. over 360°C. Recrystallization from nitrobenzene afforded yellow needles which were identical with IIIb. The combined solution of the filtrate and the benzene-washings was then dried over sodium sulfate and chromatographed on alumina. To the first fraction of the red benzene eluate, a solution of 0.1 g. of 2, 4-dinitrophenylhydrazine in ethanol and then one drop of concentrated hydrochloric acid were added. The resultant solution was heated on a water bath for 30 min. and then cooled. Filtration gave orange crystals (50 mg.), m. p. 235°C, which were proved, by the admixed melting point and by the infrared spectrum, to be identical with benzaldehyde-2, 4-dinitrophenylhydrazone.

From the next fraction of the benzene eluate, *N*-benzylnaphthalimide (VI) was obtained as pale brown crystals. Yield, 0.4 g. (17.9%); m. p. 190—193°C. Recrystallization from isopropyl alcohol afforded pale yellow needles, m. p. 195—195.5°C. Although a resinous material was obtained from the other fractions of the benzene-ethanol eluate, it was not investigated.

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[9] All melting points are uncorrected.

N-Benzylnaphthalimide.8) — A mixture of 0.5 g. of potassium naphthalimide, which had been prepared from naphthalimide and potassium hydroxide according to the method of Mattocks and Hutchinson,10) and 0.4 g. of benzyl bromide in 10 ml. of dimethylformamide was heated on a water bath for 1 hr. After the reaction mixture had been poured into water, filtration gave 0.55 g. (86.7%) of pale yellow crystals, m. p. 189—192°C. Recrystallization from isopropyl alcohol afforded pale yellow needles, m. p. 195—195.5°C (lit.8) 95—96°C).

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10) A. M. Mattocks and O. S. Hutchinson, *J. Am. Chem. Soc.*, **70**, 3474 (1948).