Attempts to prepare this compound by chlorination of the corresponding oxime with chlorine or nitrosyl chloride were unsuccessful.

Registry No.—*anti*-**1**, 35623-67-7; *anti*-**2**, 35623-68-8; *anti*-**3**, 35623-69-9; *anti*-**4**, 35623-70-2; *anti*-**5**, 35623-71-3; *anti*-**6**, 35623-72-4; *anti*-**7**, 35623-73-5; *anti*-**8**, 35623-74-6.

A Reexamination of the Reactions of 1,2-Diaminonaphthalene with Ethyl Acetoacetate and Crotonic Acid[1-3]

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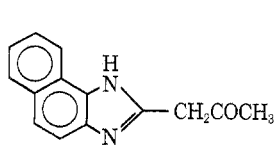
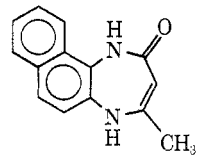
The direct condensation of 1,2-diaminonaphthalene with ethyl acetoacetate in boiling xylene has been reported[4] to give a mixture of the two isomeric products, 2-acetonylnaphthimidazole (**1**) and the dihydrodiazepinone **2**. Structure **2**, rather than the alternate cyclization possibility **3**, was assigned because, upon reduction, the product gave material isomeric with that obtained from the reaction of the naphthalenediamine with crotonic acid.[4] However, the structure of the crotonic acid product was not established with certainty and, therefore, structure **2** has remained open to question.[5] Furthermore, there is now reason in the literature[6,7] to suspect that **1** is an erroneous assignment. A recent reinvestigation in our laboratory of the reactions of 1,2-diaminonaphthalene with ethyl acetoacetate and crotonic acid has revealed that all of the previous structural assignments for the reaction products are indeed incorrect.



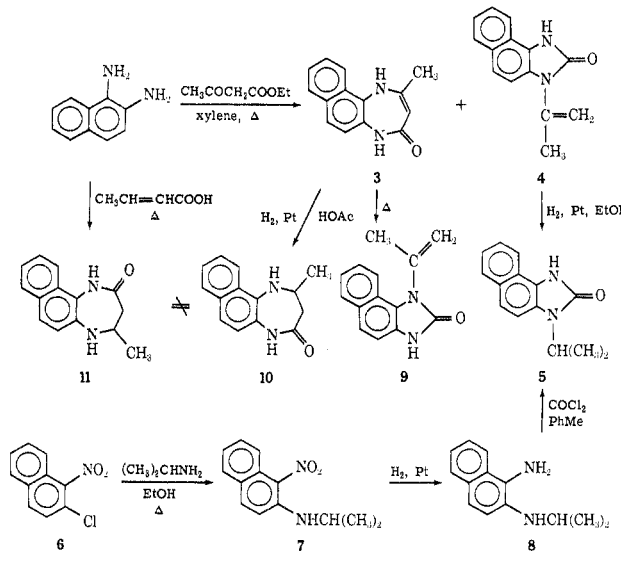
1



2

The structures of the various products involved in this study are shown in Scheme I. The lower melting product from the reaction of the diamine with ethyl acetoacetate, previously thought to be **1**, was found to be an isopropenylimidazolone on the basis of its ir spectrum (λ_{max}^{KCl} 5.85 μ) and nmr spectrum ($CDCl_3$) (methyl signal at δ 2.48 and two vinyl proton quartets at 5.53 and 5.65 ppm). Assignment of structure **4** to this material followed from the observation that, upon reduction, it afforded a product identical with a sample of 1,2-dihydro-3-isopropyl-3*H*-naphth[1,2-*d*]imidazol-2-one (**5**) prepared by unambiguous synthesis (**6** → **7** → **8** → **5**). The isomeric product from the condensation reaction (reported[4] mp 228°) had mp 228° when first isolated but this was raised to 246° upon purification. The nmr spectrum in various solvents showed, in addition to the aromatic ring protons, a methyl singlet, a methylene singlet, and a broad downfield NH signal, a pattern similar to that of other acetoacetic ester diazepinone products.[7-11]

SCHEME I



Often, but not always, the reaction of an *o*-diamine with a β-keto ester in boiling hydrocarbon solvent gives rise to a mixture of a diazepinone and an isomeric alkenylimidazolone.[6-8,10-14] The imidazolone product is now known to arise in these reactions *via* thermal rearrangement of the diazepinone.[7] Based upon previous experience,[7,8,10,11] the presence of **4** in the naphthalenediamine–ethyl acetoacetate reaction mixture suggested that the diazepine product was **2**. However, all attempts to convert the diazepinone into **4** either by fusion[7] or under conditions of base catalysis[6,9] were unsuccessful. Thermal rearrangement of the diazepinone, under stronger conditions than normally required for this reaction, afforded instead an isomeric isopropenylimidazolone, mp 222°, the nmr spectrum ($CDCl_3$) of which showed the methyl quartet 0.18 ppm upfield from that of **4** and the two vinyl quartets at δ 5.43 and 5.60 ppm. This information identified the rearranged material as **9** and, since C–N bonds are not disrupted during the ring contraction process,[7] the

(1) This investigation was supported in part by Research Grant C6516 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service.

(2) This is part 4 of the series, "Application of a Thermal Rearrangement Reaction to Questions of Structure of Condensed Dihydrodiazepinones." For part 3, see M. Israel, L. C. Jones, and M. M. Joullié, *J. Heterocycl. Chem.*, **8**, 1015 (1971).

(3) A brief account of part of this work has appeared: M. Israel, L. C. Jones, and E. C. Zoll, Abstracts of Papers, Third International Congress of Heterocyclic Chemistry, Sendai, Japan, Aug 1971, p 550.

(4) W. Ried and W. Höhne, *Chem. Ber.*, **87**, 1801 (1954).

(5) The lack of certainty of Ried and Höhne's structure assignments has been noted by J. A. Moore in "Heterocyclic Compounds," Vol. 9, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1967, pp 319 and 327.

(6) J. Davoll, *J. Chem. Soc.*, 308 (1960).

(7) M. Israel, L. C. Jones, and E. J. Modest, *Tetrahedron Lett.*, 4811 (1968).

(8) M. Israel, L. C. Jones, and E. J. Modest, *J. Heterocycl. Chem.*, **4**, 659 (1967).

(9) M. Israel, S. K. Tinter, D. H. Trites, and E. J. Modest, *ibid.*, **7**, 1029 (1970).

(10) M. Israel and L. C. Jones, *ibid.*, **8**, 797 (1971).

(11) Unpublished results from these laboratories.

(12) A. Rossi, A. Hunger, J. Kebrle, and K. Hoffmann, *Helv. Chim. Acta*, **43**, 1298 (1960).

(13) A. Rossi, A. Hunger, J. Kebrle, and K. Hoffmann, *ibid.*, **43**, 1046 (1960).

(14) R. Barchet and K. W. Merz, *Tetrahedron Lett.*, 2239 (1964).

diazepinone product must be **3**.[15] The nmr spectrum of **9**, as compared to that of **4**, can be accounted for by anisotropic shielding of the alkenyl protons by the bay proton on the naphthalene nucleus.

Careful examination of the reaction mixture and subsequent mother liquors from crystallizations failed to reveal the presence of any **2**. Interruption of the boiling xylene reaction in the hope of isolating **2** or other intermediates was unsuccessful. Condensation reactions carried out at lower temperatures also failed to give **2**; a similar product distribution of **3** and **4** was obtained in boiling toluene as solvent and in boiling benzene essentially no reaction occurred. We believe that the formation of **3** and **4** in this reaction can best be explained by considering that both diazepinone products **2** and **3** were initially formed. **3**, which was found to be resistant to thermal rearrangement, was not further affected by the reaction conditions. However, **2**, because of an apparently very low energy barrier for ring contraction, must have been converted immediately and quantitatively into **4**. Attempts to prepare **2** by an independent route in order to study its rearrangement unfortunately failed to give the desired product.

Catalytic reduction of **3** in acetic acid[4] afforded the tetrahydrodiazepinone **10**, mp 209°. This material was similar to but not identical with the tetrahydrodiazepinone, mp 229–230°, prepared by fusion of 1,2-diaminonaphthalene with crotonic acid, according to the procedure of Ried and Höhne.[4] The crotonic acid product is, therefore, correctly identified as **11**, and not **10** as previously suggested.[4]

Experimental Section[16]

1,5-Dihydro-2-methyl-4*H*-naphth[1,2-*b*][1,4]diazepin-4-one (3).—Prepared according to the procedure of Ried and Höhne,[4] this material was previously described as **2**. It formed white crystals from xylene: mp 246°; nmr (C_5D_5N) δ 2.43 (3 H, s), 3.28 (2 H, s), and 7.42–7.70 ppm (6 H, multiple aromatic peaks); uv $\lambda_{max}^{ethanol}$ 243 nm (ϵ 55,700), 294 (7100), 308 (6900), 323 (4500), and 337 (4800). The presence of **2** in the reaction mixture could not be observed by spectral or tlc studies.

1,2-Dihydro-3-isopropenyl-3*H*-naphth[1,2-*d*]imidazol-2-one (4).—The ether-soluble product from the reaction of 1,2-diaminonaphthalene and ethyl acetoacetate by the Ried and Höhne procedure,[4] this material was erroneously reported to be **1**. It formed white crystals from cyclohexane: mp 198°; nmr ($CDCl_3$) (time averaged)[17] δ 2.48 (3 H, fine splitting), 5.53 (1 H, q, J = 6 Hz), and 5.65 ppm (1 H, q, J = 6 Hz); ir λ_{max}^{KCl} 5.85 μ.

2-Isopropylamino-1-nitronaphthalene (7).—2-Chloro-1-nitronaphthalene (**6**) was prepared from 2-amino-1-nitronaphthalene essentially according to the procedure of Hodgson and Leigh;[18] in place of steam distillation, the product was purified by crystallization from ligroin (bp 95–110°). A solution of 3.2 g of **6** and 32 g of isopropylamine in 70 ml of absolute ethanol was heated at 100° for 6 hr in a stainless steel bomb. The red reaction solution was taken to dryness and the residue was washed with water to remove isopropylamine hydrochloride. The water-insoluble product was crystallized once from benzene–petroleum ether (bp 60–90°) and once from cyclohexane to give 3.5 g (100%) of **7**, mp 104–105°.

Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.83; H, 6.08; N, 12.17. Found: C, 67.82; H, 5.81; N, 11.89.

1-Amino-2-isopropylaminonaphthalene (8).—A solution of **7** (350 mg) in 50 ml of absolute ethanol was shaken under hydrogen in the presence of 200 mg of 5% palladium on charcoal on a Parr apparatus for 30 min. The catalyst was separated and the filtrate was evaporated to dryness. The residue was crystallized from ligroin to give white crystals of **8**, yield 130 mg (42%), mp 102–103°.

Anal. Calcd for $C_{13}H_{16}N_2$: C, 78.00; H, 7.99; N, 13.99. Found: C, 78.28; H, 7.97; N, 14.02.

1,2-Dihydro-3-isopropyl-3*H*-naphth[1,2-*d*]imidazol-2-one (5). Method A. Cyclization of 8.—Phosgene was passed into 30 ml of xylene for 30 min at room temperature and to this solution was added, in small portions with stirring, 300 mg of **8**. Phosgene was again bubbled into the solution (15 min), following which the reaction mixture was warmed at 60° for 5 hr. After overnight standing, the clear, pale yellow solution was evaporated to dryness under reduced pressure and the residue was crystallized several times from cyclohexane to give 330 mg (97%) of white crystals: mp 200–201°; ir λ_{max}^{KCl} 5.90 μ; uv $\lambda_{max}^{ethanol}$ 246 nm (ϵ 67,300), 293 (3800), 305 (3500), and 340 (4000); nmr ($CDCl_3$) δ 1.66 (6 H, d, J = 7 Hz), 4.98 (1 H, m, J = 28 Hz), and 7.27–8.23 ppm (6 H, multiple aromatic peaks).

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.30; H, 6.25; N, 12.38. Found: C, 74.45; H, 6.33; N, 12.28.

Method B. Reduction of 4.—A solution of 125 mg of **4** in 40 ml of absolute ethanol was shaken overnight under hydrogen in the presence of 60 mg of platinum oxide. The catalyst was separated and the ethanolic filtrate was evaporated to give a brown oil, which was dissolved in hot cyclohexane. After treatment with charcoal, the solution was reduced to 10 ml and the white precipitate was collected and crystallized twice from cyclohexane to give material identical in all respects with that obtained by method A.

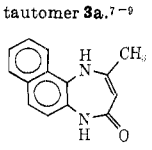
2,3-Dihydro-1-isopropenyl-1*H*-naphth[1,2-*d*]imidazol-2-one (9).—A 100-mg sample of **3** in a small test tube was heated at 250° for 3 hr in the absence of solvent. Upon cooling, the solidified mass was treated with warm (60°) benzene and the insoluble material (mostly unchanged **3**) was separated. Addition of petroleum ether to the benzene solution gave an off-white precipitate. This material was crystallized several times from benzene–petroleum ether to give 32 mg (32%) of **9** as small white crystals: mp 222°; ir λ_{max}^{KCl} 5.88 μ; nmr ($CDCl_3$) δ 2.30 (3 H, fine splitting), 5.43 (1 H, q, J = 6 Hz), and 5.60 ppm (1 H, q, J = 6 Hz).

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.40; N, 12.49. Found: C, 75.17; H, 5.47; N, 12.62.

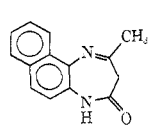
Registry No.—**3**, 35624-19-2; **4**, 35624-20-5; **5**, 35624-21-6; **7**, 35624-22-7; **8**, 35624-23-8; **9**, 35624-24-9; **11**, 35624-25-0; 1,2-diaminonaphthalene, 938-25-0; ethyl acetoacetate, 141-97-9; crotonic acid, 3724-65-0.

Acknowledgment.—We thank Mrs. Lynne C. Jones and Mrs. Marilyn A. Whitesell for technical assistance at different times during this work.

(15) Solutions of **3** in chloroform, pyridine, and dimethyl sulfoxide are bright yellow and the nmr spectrum is consistent with structure **3b**. However, the diazepinone, a white solid, probably exists in the solid state in the form of the leuco tautomer **3a**.[7-9]



3a



3b

(16) Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(17) The time-averaged spectrum was obtained by means of a Japan Electron Optics Laboratory Co. Model JRA-1 Spectrum Accumulator interfaced with a Varian Associates Model A-60 spectrometer.

(18) H. H. Hodgson and E. Leigh, *J. Chem. Soc.*, 1352 (1937).

Trifluoromethanesulfonyl Azide. Its Reaction with Alkyl Amines to Form Alkyl Azides

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p-Toluenesulfonyl azide is a widely used reagent for the transfer of the diazo group to active methylene