Summary

1. Both 4- and 4′-aminobiphenyl-2-carboxylic acids have been isolated from the alkaline cleavage of 2-aminofluorenone in diphenyl ether.

2. Proof of the structure of these compounds resolves an anomaly in the literature.

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Preparation of 2-Phenylnaphth[1,2]imidazole and 2-Methylnaphth[1,2]imidazole

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The isolation of two isomeric forms of 2-phenylnaphth[1,2]imidazole was reported by Galimberti in 1933.[1] The so-called isomers were prepared by reducing N-(2-nitro-1-naphthyl)-benzamide and N-(1-nitro-2-naphthyl)-benzamide, respectively, with zinc and hydrochloric acid. The melting points of the resulting naphthimidazoles, 214 and 296°, appeared to indicate that the two compounds were not identical.

In view of the considerable amount of evidence in favor of the active tautomeric character of the imidazole ring system, the isolation of stable isomeric forms should be of interest. It seemed desirable, therefore, to repeat Galimberti's work using carefully prepared intermediates. At the same time it was decided to prepare 2-phenylnaphth[1,2]imidazole in a neutral non-aqueous medium. If identical results are obtained from both methods then any specific effects which might be attributed to the media would be eliminated. The second method consisted of heating dry N-(2-amino-1-naphthyl)-benzamide and N-(1-amino-2-naphthyl)-benzamide, respectively, in an atmosphere of nitrogen.

N-(2-Nitro-1-naphthyl)-benzamide and N-(1-nitro-2-naphthyl)-benzamide were converted into 2-phenylnaphth[1,2]imidazole by reduction with zinc and hydrochloric acid. The corresponding amino compounds were converted into 2-phenylnaphth[1,2]imidazole by heating in a nitrogen atmosphere. Analyses, melting points, and mixed melting points indicated that the 2-phenylnaphth[1,2]imidazoles obtained from the four starting compounds were identical. Similarly, the 2-methylnaphth[1,2]imidazoles prepared from N-(2-amino-1-naphthyl)-acetamide and N-(1-amino-2-naphthyl)-acetamide proved to be identical. In view of these results it would appear that Galimberti's claim to have isolated two isomeric forms of 2-phenylnaphth[1,2]imidazole is not correct.

Both N-(1-amino-2-naphthyl)-benzamide and 2-phenylnaphth[1,2]imidazole melt at 217–218°. The same behavior was noted for N-(1-amino-2-naphthyl)-acetamide and 2-methylnaphth[1,2]-imidazole, both melting at 170.5–171.5°. It is probable that the 1-amino derivatives are converted into the corresponding naphthimidazoles during the melting point determinations, thus accounting for these observations. It is not clear, however, why the 2-amino derivatives do not behave similarly.

Experimental

N-(2-Nitro-1-naphthyl)-acetamide and N-(2-Nitro-1-naphthyl)-benzamide.—2-Nitro-1-naphthol was converted into 2-nitro-1-naphthylamine by a modification of the method described by Hodgson and Kilner.[2] Best results were obtained by heating the mixture of 2-nitro-1-naphthol, ammonium carbonate, and ammonium hydroxide for six hours at 130–140° in an autoclave. The crude 2-nitro-1-naphthylamine was recrystallized from dilute alcohol, yield 50–60%, m. p. 144° cor.

N-(2-Nitro-1-naphthyl)acetamide was prepared from 2-nitro-1-naphthylamine by treatment with acetic anhydride to which a drop of concentrated sulfuric acid had been added. The crude product was recrystallized from alcohol, yield 90%, m. p. 199° cor.[3]

N-(2-Nitro-1-naphthyl)-benzamide could not be prepared by any of the usual methods of acylation. The following procedure was finally adopted. Seven grams (0.037 mole) of 2-nitro-1-naphthylamine, 4.8 cc. (0.0415 mole) of benzoyl chloride and 3.2 cc. (0.0415 mole) of pyridine were dissolved in 150 cc. of dry xylene and refluxed for six hours. On cooling, a small amount of unchanged 2-nitro-1-naphthylamine separated as an oil which solidified on further cooling. The xylene solution was decanted and allowed to stand overnight during which time the benzoyl derivative separated. The product was recrystallized from xylene, yield 68%, m. p. 197–198° cor.[4]

Anal. Calcd. for $C_{17}H_{12}N_2O_3$: N, 9.59. Found: N, 9.54.

N-(1-Nitro-2-naphthyl)-acetamide and N-(1-Nitro-2-naphthyl)-benzamide.—N-2-Naphthylacetamide was converted into N-(1-nitro-2-naphthyl)-acetamide by nitration in glacial acetic acid[5]; yield 53%, m. p. 123–124° cor.

The acetyl derivative was hydrolyzed to 1-nitro-2-naphthylamine by treatment with alcoholic potassium hydroxide[6]; yield 91%, m. p. 125.5° cor.

N-(1-Nitro-2-naphthyl)-benzamide was prepared by the following procedure: 1-nitro-2-naphthylamine (32.5 g., 0.17 mole) was dissolved in 200 cc. of dry acetone and 13.9 cc. (0.17 mole) of pyridine and 19.9 cc. (0.17 mole) of benzoyl chloride added. After standing for two days the mixture was cooled and filtered. The filtrate was refluxed for several hours and on cooling more of the benzoyl derivative was obtained. The product was recrystallized from acetone and water, yield 33%, m. p. 170–171° cor. Unchanged 1-nitro-2-naphthylamine may be recovered by diluting the original filtrate with water.

N-(2-Amino-1-naphthyl)-acetamide.—Five grams (0.022 mole) of N-(2-nitro-1-naphthyl)-acetamide was dis-

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(1) Galimberti, *Gazz. chim. ital.*, **63**, 96 (1933).

(2) Hodgson and Kilner, *J. Chem. Soc.*, **129**, 7 (1926).

(3) Lellman and Remy, *Ber.*, **19**, 796 (1886).

(4) Worms [*ibid.*, **15**, 1815 (1881)] reported m. p. 174°.

(5) "Organic Syntheses," **13**, 72 (1933).

(6) Liebermann and Jacobsen, *Ann.* **211**, 36 (1892).

solved in 300 cc. of dry alcohol and hydrogenated in the presence of palladium.[7] The solution was filtered and the catalyst washed with 100 cc. of hot alcohol. The filtrate and washings were evaporated under reduced pressure and the product recrystallized from alcohol, yield 92%, m. p. 215–217° cor.

N-(2-Amino-1-naphthyl)-benzamide.—N-(2-Nitro-1-naphthyl)-benzamide (3.3 g.) was dissolved in 500 cc. of dry alcohol, hydrogenated and the amino compound isolated and purified as described above, yield 50%, m. p. 215–217° cor.

N-(1-Amino-2-naphthyl)-acetamide.—Ten grams of N-(1-nitro-2-naphthyl)-acetamide was dissolved in 200 cc. of dry alcohol, hydrogenated and treated as above. The amino compound was obtained as colorless needles, yield 75%, m. p. 170.5° cor.

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.97; H, 6.04; N, 13.99. Found: C, 72.04; H, 6.22; N, 14.10.

N-(1-Amino-2-naphthyl)-benzamide.—Four grams of N-(1-nitro-2-naphthyl)-benzamide was dissolved in 500 cc. of dry alcohol, hydrogenated and treated as above. The pure product was obtained as colorless needles, yield 58%, m. p. 217–218° cor.

Anal. Calcd. for $C_{17}H_{14}N_2O$: C, 77.83; H, 5.38; N, 10.68. Found: C, 77.66; H, 5.50; N, 10.69.

2-Methylnaphth[1,2]imidazole from N-(2-Amino-1-naphthyl)-acetamide.—N-(2-Amino-1-naphthyl)-acetamide (2.48 g.) was heated slowly to 225° in an atmosphere of nitrogen and kept at this temperature for twenty minutes. After cooling, the residue was recrystallized from xylene and petroleum ether and finally from benzene, yield 97%, m. p. 170.5–171.5° cor.

Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.37. Found: C, 79.16; H, 5.64; N, 15.33.

2-Methylnaphth[1,2]imidazole from N-(1-Amino-2-naphthyl)-acetamide.—This preparation was carried out as described above, yield 91%, m. p. 170.5–171.5° cor.

Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.37. Found: C, 79.02; H, 5.70; N, 15.54.

A mixed melting point determination on the two samples of 2-methyl-naphthimidazole showed no depression (170.5–171.5°).

2-Phenylnaphth[1,2]imidazole from N-(2-Nitro-1-naphthyl)-benzamide.—One gram of N-(2-nitro-1-naphthyl)-benzamide was dissolved in 100 cc. of ethyl alcohol. Zinc (0.7 g.) and 7 cc. of concentrated hydrochloric acid were slowly added and the mixture heated on a steam-bath. The almost colorless solution was filtered into one liter of water. The amorphous precipitate obtained in this manner changed to short needles when warmed for a short time on a steam-bath. The crude product was recrystallized from dilute acetone with the aid of Norite, yield 0.8 g. (71.8%). The final product proved to be a monohydrate of 2-phenylnaphthimidazole. The water of hydration was determined by heating a sample to constant weight at 100° (5 mm.).

Anal. Calcd. for $C_{17}H_{12}N_2 \cdot H_2O$: H_2O, 8.86. Found: H_2O, 8.85.

The anhydrous compound melted at 217–218°.

Anal. Calcd. for $C_{17}H_{12}N_2$: C, 83.57; H, 4.92; N, 11.47. Found: C, 83.46; H, 5.01; N, 11.37.

2-Phenylnaphth[1,2]imidazole from N-(1-Nitro-2-naphthyl)-benzamide.—The preparation was carried out as described above; yield of monohydrate, 0.7 g. (62.8%).

Anal. Calcd. for $C_{17}H_{12}N_2 \cdot H_2O$: H_2O, 8.86. Found: H_2O, 8.86.

The anhydrous product melted at 217–218° cor.

Anal. Calcd. for $C_{17}H_{12}N_2$: C, 83.57; H, 4.92; N, 11.47. Found: C, 83.45; H, 5.04; N, 11.31.

Mixed melting point determinations with the two samples of 2-phenylnaphthimidazole showed no depression (217–218°).

2-Phenylnaphth[1,2]imidazole from N-(2-Amino-1-naphthyl)-benzamide.—Samples of 1.5 g. of N-(2-amino-1-naphthyl)-benzamide were slowly heated to 225° in an atmosphere of nitrogen. After six hours the mixture was cooled, the sublimate and residue combined and recrystallized from acetone with the aid of Norite, yield 88–92%, m. p. 217–218° cor. Mixed melting point determinations with the products obtained from the reduction of N-(2-nitro-1-naphthyl)-benzamide and N-(1-nitro-2-naphthyl)-benzamide showed no depression (217–218°).

Anal. Calcd. for $C_{17}H_{12}N_2$: C, 83.57; H, 4.92; N, 11.47. Found: C, 83.50; H, 5.05; N, 11.34.

2-Phenylnaphth[1,2]imidazole from N-(1-Amino-2-naphthyl)-benzamide.—Ring closure was effected as described above, yield 80–90%, m. p. 217–218° cor. Mixed melting point determinations with the other samples of 2-phenylnaphthimidazole showed no depression (217–218°).

Anal. Calcd. for $C_{17}H_{12}N_2$: C, 83.57; H, 4.92; N, 11.47. Found: C, 83.41; H, 4.94; N, 11.40.

Summary

1. Galimberti's claim that two isomeric forms of 2-phenylnaphth[1,2]imidazole are obtained by the reduction of N-(2-nitro-1-naphthyl)-benzamide and N-(1-nitro-2-naphthyl)-benzamide could not be confirmed.

2. Preparations of 2-phenylnaphth[1,2]imidazole from N-(2-amino-1-naphthyl)-benzamide and N-(1-amino-2-naphthyl)-benzamide also failed to yield two isomeric forms.

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(7) The apparatus used was similar to that described by Schaefer [*Ind. Eng. Chem., Anal. Ed.*, **2**, 115 (1930)] and the stock solution of palladium chloride was prepared according to Hartung [THIS JOURNAL, **50**, 3370 (1928)]. Due to the adsorption of the product on charcoal, 20-mesh pumice was used as a support for the palladium. Three-tenths of a gram of palladium was used for 3 g. of pumice.