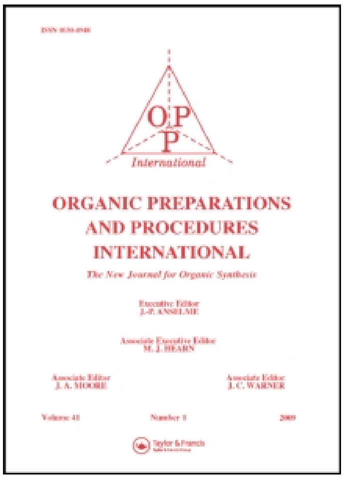

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HOFFMAN REACTION OF 1-PHENYLNAPHTHALENE-2,3-DICARBOXIMIDE

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HOFFMAN REACTION OF 1-PHENYLNAPHTHALENE-2,3-DICARBOXIMIDE

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(06/19/84)

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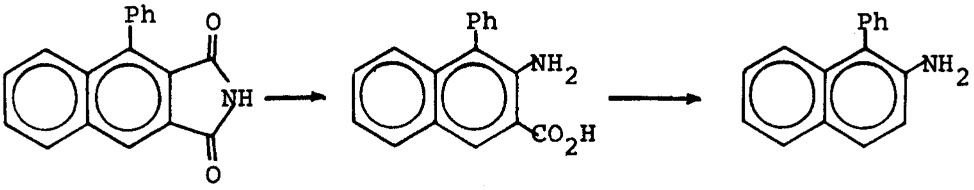
The report[1] that 1-amino-3,4-benzofluorenone, a possible precursor of β-benzanthrone quinoline could not be made by a Hofmann reaction on 1-carboxamide-3,4-benzofluorenone suggested the present study of the Hofmann reaction of 1-phenylnaphthalene-2,3-dicarboximide(I). Of the two amino acids which are possible as products in this reaction, only 1-phenyl-3-amino-2-naphthoic acid is suitable for the preparation of the desired quinoline; the product actually formed was 1-phenyl-2-amino-3-naphthoic acid(II) whose structure was established on the basis of its spectral data and decarboxylation to 1-phenyl-2-naphthylamine.[2]



I II III

EXPERIMENTAL SECTION

Melting points are uncorrected. NMR spectra were recorded with either Perkin-Elmer R12 or JEOL QF90 Pulse FT spectrometers. Mass spectrum was determined with a Hewlett-Packard 5285-B GCSM. IR and UV spectra were obtained with a Varian Cary 219 spectrophotometer and Beckmann IR-20A spectrometer respectively.

1-Phenyl-2-amino-3-naphthoic Acid(II).- 1-Phenylnaphthalene-2,3-dicarboximide(I)[3] (16.2 g 0.059 mole) was dissolved in 0.3M potassium hydroxide (300 ml) by heating and the resulting solution was cooled to 0° and treated with 0.06 mole of potassium hypobromite (from 9.6 g of bromine in a solution of 16.8 g of potassium hydroxide in 60 ml of water) in 120 ml of water. The solution was stirred at 0° for 1 hr, allowed to come to room temperature and then heated to 80°. Cooling the resulting solution was followed by the addition of conc. hydrochloric acid to pH 9 and acetic acid to pH 6.5-7 at which time gas evolution had ceased. The solution was stirred for 12 hrs and the yellow solid formed was collected and dried. Extraction with carbon tetrachloride using a Soxhlet extractor gave 8.5 g (51%) of a yellow solid which after crystallization from ethyl acetate melted at 246-253°. Further purification by sublimation under reduced pressure followed by crystallization from ethyl acetate gave a sample melting at 254-258°;

IR(KBr): 3520, 3400(NH_2), 3090(broad, OH), 1670(C=O), 700(C_6H_5) cm^{-1}; NMR($DMSO-D_6$): δ 9.12(s, 1H, 4-H), 8.42-7.46(m, 9H, aromatic) ppm: CMR($DMSO-D_6$): δ 169.66(C=O); MS m/e (rel. abund.): 263(M^+, 38.7), 218(M^+-COOH, 21.8), 217($C_{16}H_{12}N$, 100), 216($C_{16}H_{11}N$, 25.8), 190($C_{15}H_{10}$, 12.0), 189($C_{15}H_9$, 32.2), 94(C_7H_{10}, 14.2).

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32

Found: C, 77.26; H, 4.82; N, 5.23

1-Phenyl-2-naphthylamine(III).- 1-Phenyl-2-amino-3-naphthoic acid(II) (0.9 g, 3.4 mmoles), copper bronze (0.1 g) and quinoline (10 ml) were heated with stirring. Evolution of carbon dioxide started at 150° and the temperature of the mixture was raised slowly and held at 214° for 0.5 hr at which time the gas evolution ceased; only 50 ml of CO_2 were collected. An additional 0.2 g of copper bronze was added to the reaction mixture and the temperature was held at 215° for 15 min until the gas evolution ceased. A total volume of 70 ml (91.43%) of carbon dioxide was collected. The resulting dark mixture was filtered and the filtrate was washed with concentrated ammonium hydroxide (10 ml) and twice with water (10 ml). Steam distillation removed the quinoline and gave a tarry mass which was dissolved in hot methanol and treated with Norite (1.5 g). Filtration followed by removal of the methanol gave a tar which was extracted with hexane using a Soxhlet extractor. Concentration of the orange hexane extract to 50 ml gave an orange solid (0.7 g) which after five crystallizations from hexane gave a greyish white solid melting at 92-94°, mixture mp. 92-94° with an authentic sample.[2] The IR and UV spectra were identical to Sadtler IR 16494 and Sadtler UV 5159.

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