ether (b.p. 90–100°), and removal of solvent left an oil (8 g.) which was dissolved in 100 ml. of ethanol and treated with a solution of 11 g. of picric acid in 200 ml. of ethanol. The alcoholic solution was heated to boiling, and the insoluble picrate was separated by filtration. Crystallization from acetone yielded 5.9 g. of picrate, m.p. 210–211°. This product was refluxed with 13 ml. of water, 15 ml. of concentrated hydrochloric acid, and 50 ml. of benzene until solution was complete. The aqueous layer was then separated, extracted five times with hot benzene, and made alkaline with sodium hydroxide solution. Extraction with ether and crystallization from petroleum ether (b.p. 60–70°) yielded 2 g. of 7-phenylquinoline, m.p. 59–60°.

Anal. Calc'd for $C_{15}H_{11}N$: C, 87.78; H, 5.40. Found: C, 88.05; H, 5.78.

No attempt was made to isolate the picrate of 5-phenylquinoline from the picrate filtrate.

CHEMISTRY DEPARTMENT
TEMPLE UNIVERSITY
PHILADELPHIA 22, PENNA.

4-Nitrofluorene-5-carboxylic Acid

ELIZABETH K. WEISBURGER

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It has been demonstrated by Moore and Huntress[1] that nitration of fluorenone-4-carboxylic acid leads to substitution of the nitro group mostly in the 7 position and to a lesser extent in the 5 position. In a recent paper we have shown that the main product in the nitration of fluorene-4-carboxylic acid is 2-nitrofluorene-5-carboxylic acid.[2]

During the process of preparing a large quantity of the latter compound, several hundred grams of fluorene-4-carboxylic acid was nitrated. After removal of the main product, the mother liquors from the nitration afforded material with a melting point a few degrees higher than the melting point of 2-nitrofluorene-5-carboxylic acid. However, examination of the infrared and ultraviolet absorption spectra showed it to be an entirely different compound. By analogy with the findings of Moore and Huntress[1] and our own observations[2] this substance was suspected to be 4-nitrofluorene-5-carboxylic acid. This assumption was confirmed by oxidation of the material to a bright yellow compound with a melting point identical to that reported for 4-nitrofluorenone-5-carboxylic acid.[1]

A Schmidt reaction on 4-nitrofluorene-5-carboxylic acid produced a dark red low-melting nitro amine which had a greater solubility and different ultraviolet and infrared spectra than the isomeric 2-nitro-5-aminofluorene.[2] Deamination of this nitroamine gave 4-nitrofluorene,[3] thus definitely proving the structures of 4-amino-5-nitrofluorene and of 4-nitrofluorene-5-carboxylic acid.

Reduction of 4-amino-5-nitrofluorene to 4,5-diaminofluorene was best effected by catalytic hydrogenation. The use of various chemical reducing agents gave very low yields of the pure diamine.

EXPERIMENTAL

Microanalyses by Mr. Robert Koegel and staff. The ultraviolet absorption spectra were determined on a Cary instrument using 5×10^{-5} *molar* solutions in ethanol. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, using the solid potassium bromide disk method. All spectra were determined by Mr. P. H. Grantham.

4-Nitrofluorene-5-carboxylic acid (I). Fluorene-4-carboxylic acid was nitrated in six 50-g. batches as was described previously.[2] After removal of the 2-nitrofluorene-5-carboxylic acid, wt. 180 g., the mother liquor from the nitration was poured into water. A dark yellow precipitate mixed with some red oil formed. After standing overnight the oil had solidified. The precipitate, m.p. 255°, weighed 147 g. It was crystallized from acetic acid-water (2:1) to give 71 g. of I, m.p. 285°, or a 19% yield. A further crystallization from ethanol raised the m.p. to 292°. Nitration of 10–20 g. batches of fluorene-4-carboxylic acid gave better yields of 2-nitrofluorene-5-carboxylic acid and only 8% yields of I. The ultraviolet absorption spectrum in ethanol showed maxima at 250 (ϵ 19,300) and 335 mμ (ϵ 7,600) and minima at 233.5 (ϵ 14,160) and 289 mμ (ϵ 3,700).

Anal. Calc'd for $C_{14}H_9NO_4$: C, 65.88; H, 3.55; N, 5.49. Found: C, 65.43; H, 3.91; N, 5.33.

Oxidation of I. A solution of 1 g. of chromic trioxide in 3 ml. of dilute acetic acid was added to a solution of 0.2 g. of I in 40 ml. of acetic acid and was refluxed for 2 hours. The product obtained melted at 232–233°. After crystallization from ethanol the bright yellow needles had m.p. 232.5–233.5°. Moore and Huntress[1] reported m.p. 232–233° for 4-nitrofluorenone-5-carboxylic acid.

4-Amino-5-nitrofluorene (II). A Schmidt reaction on I, according to the procedure used for the isomer,[2] gave the crude dark red amine, m.p. 96°, in a 67% yield. Purification by chromatography on alumina and crystallization from ethanol (2 g./25 ml.) or benzene (2 g./5 ml.) yielded red needles, m.p. 100–101°. The spectrum had maxima at 259 (ϵ 12,300) and 319 mμ (ϵ 5,000) with minima at 255 (ϵ 12,200) and 308 mμ (ϵ 4,800) and an inflection point at 235 mμ (ϵ 18,000).

Anal. Calc'd for $C_{13}H_{10}N_2O_2$: C, 69.01; H, 4.46; N, 12.39. Found: C, 69.38; H, 4.62; N, 12.05.

The *acetyl derivative* of II formed yellow plates, m.p. 229–230°. Its spectrum showed maxima at 259 (ϵ 16,000) and 317 mμ (ϵ 4,400) with minima at 243.5 (ϵ 14,000) and 292 mμ (ϵ 3,900).

Anal. Calc'd for $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.28; H, 4.62; N, 10.62.

Deamination of II. The amine (0.45 g.) was dissolved in 10 ml. of acetic acid. After the addition of 10 ml. of 18 *N* sulfuric acid, the mixture was cooled to 10°. Diazotization was effected by adding 0.16 g. of sodium nitrite in 2 ml. of water and stirring for 0.5 hour. Then 15 ml. of cold hypophosphorous acid was added and the mixture was stirred in the cold overnight. The precipitate obtained was extracted with hot benzene and the benzene solution was percolated through an alumina column. Evaporation of the eluate gave 100 mg. of 4-nitrofluorene, m.p. 69–71°. Crystallization from cyclohexane yielded light tan needles, m.p. 73–74°, shown to be authentic 4-nitrofluorene by mixture m.p. and infrared spectrum.

4,5-Diaminofluorene (III). A solution of 2 g. of II in 50 ml. of ethanol was hydrogenated for 1 hour at room temperature under 50 lbs. pressure, using 50 mg. of platinum

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(1) Moore and Huntress, *J. Am. Chem. Soc.*, **49**, 1324 (1927).

(2) Weisburger and Weisburger, *J. Org. Chem.*, **20**, 1396 (1955).

(3) Weisburger, Weisburger, and Morris, *J. Am. Chem. Soc.*, **74**, 4540 (1952).

oxide catalyst. The crude diamine weighed 1.6 g. and had m.p. 134–135°. Two crystallizations from 50% ethanol gave 1.3 g. of shiny plates, m.p. 138–139°. The spectrum showed maxima at 226 (ϵ 29,800), 281 (ϵ 8,610), and 327 mμ (ϵ 5,270) and minima at 261 (ϵ 4,810), and 300 mμ (ϵ 3,400) with a shoulder at 239 mμ (ϵ 20,500).

Anal. Calc'd for $C_{13}H_{12}N_2$: C, 79.55; H, 6.26; N, 14.28. Found: C, 79.23; H, 6.26; N, 14.13.

4,5-Di(acetylamino)fluorene was prepared by acetylation of III with acetic anhydride in benzene. It crystallized from ethanol as white fluffy needles, m.p. 273°. The spectrum had maxima at 221 (ϵ 72,100), 243 (ϵ 46,700) and 275 mμ (ϵ 33,200) with minima at 241 (ϵ 46,300) and 260 mμ (ϵ 26,400).

Anal. Calc'd for $C_{17}H_{16}N_2O_2$: N, 10.00. Found: N, 9.68.

LABORATORY OF BIOCHEMISTRY
NATIONAL CANCER INSTITUTE
NATIONAL INSTITUTES OF HEALTH
BETHESDA 14, MARYLAND

The Preparation of 4-Amino-2-phenyl-2-butanol

RICHARD C. MANSFIELD AND CLAUDE J. SCHMIDLE

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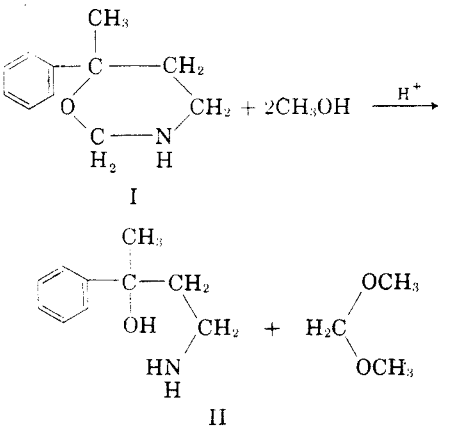
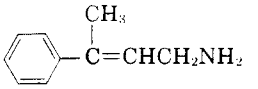
The preparation of 6-methyl-6-phenyltetrahydro-1,3-oxazine (I) from α-methylstyrene, formaldehyde, and ammonium chloride has been reported.[1,2] During investigations of this reaction involving the methanolysis previously described,[2] it was observed that prolongation or repetition of the methanol treatment resulted in cleavage of the oxazine ring. When 6-methyl-6-phenyltetrahydro-1,3-oxazine (I) was heated with one equivalent of hydrochloric acid and excess methanol[3] there was obtained 82% of 4-amino-2-phenyl-2-butanol (II). The reaction involves cleavage of the oxazine ring and elimination of formaldehyde by its conversion to methylal.

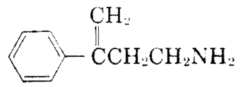

I

II

Other examples of the degradation of tetrahydro-1,3-oxazines have been reported by Urbanski and co-workers.[4,5] These investigators successfully cleaved and eliminated formaldehyde from 5-nitro-5-ethyltetrahydro-1,3-oxazine and 5-nitro-5-alkyl-3-benzyltetrahydro-1,3-oxazines using hydrochloric acid alone or diluted with alcohol. The corresponding amino alkanols were obtained. Cleavage of 6-methyl-6-aryltetrahydro-1,3-oxazines by hydrochloric acid alone, however, does not give the corresponding 3-amino alkanols. Ring closure takes place instead, to give the corresponding 4-aryl-4-piperidinols and 4-aryl-1,2,3,6-tetrahydropyridines.[2,6]

Dehydration of 4-amino-2-phenyl-2-butanol (II) to 3-phenyl-2-butenylamine (III) has been carried out using either hydrochloric acid or polyphosphoric acid. The structure of III was established by quantitative hydrogenation to 3-phenylbutylamine, which has been prepared previously by Tsukervanik and Grebenyuk[7] from β-phenylbutyronitrile, and by its spectra. The ultraviolet spectrum showed strong styrene-like conjugation. The alternative structure (IIIa) was eliminated by the infrared spectrum which showed only weak absorption in the region of olefinic hydrogen wagging (~ 890 cm.$^{-1}$) and C=C stretching (~ 1625 cm.$^{-1}$). Further support for III was provided by methyl group absorption at ~1370 cm.$^{-1}$ and by resemblance to the spectrum of 2-phenyl-2-butene.[8]


III


IIIa

Acknowledgment. We wish to thank Dr. J. D. Stroupe and his staff for spectroscopic data and physical-chemical interpretation and Mr. C. W. Nash and his staff for analytical data reported.

EXPERIMENTAL[9]

4-Amino-2-phenyl-2-butanol (II). (*Method A*). *From 6-methyl-6-phenyltetrahydro-1,3-oxazine* (I). A mixture of 50 g. (0.28 mole) of 6-methyl-6-phenyltetrahydro-1,3-oxazine (I), 100 g. (3.13 moles) of methanol, and 28 g. (0.28 mole) of concentrated hydrochloric acid was heated at 72° for 6 hours and then to 95° during another hour while the methanol distilled off. The mixture was cooled, poured into

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[1] Hartough, Dickert, and Meisel, U. S. Patent 2,647,117 (July 28, 1953); *Chem. Abstr.*, **48**, 8265 (1954).

[2] Schmidle and Mansfield, *J. Am. Chem. Soc.*, **78**, 1702 (1956).

[3] Subsequent to submission of this communication Hartough, Dickert, and Meisel reported the reaction of 6-phenyltetrahydro-1,3-oxazine with methanol and acid to give 3-amino-1-phenyl-1-propanol and methylal. Abstracts of Papers, First Regional Meeting Delaware Valley, American Chemical Society, Philadelphia, Pa., February 16, 1956.

[4] Hirst, Jones, Minahan, Ochynski, Thomas, and Urbanski, *J. Chem. Soc.*, 924 (1947).

[5] Gurne and Urbanski, *Bull. acad. polon. sci., Classe III*, **3**, 175 (1955); *Chem. Abstr.*, **49**, 13998 (1955).

[6] Schmidle and Mansfield, *J. Am. Chem. Soc.*, **78**, 425 (1956).

[7] Tsukervanik and Grebenyuk, *Doklady Akad. Nauk S.S.S.R.*, **76, 223** (1951); *Chem. Abstr.*, **45**, 6304 (1951).

[8] Cram, *J. Am. Chem. Soc.*, **74, 2137** (1952).

[9] All melting points are uncorrected.