[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYMENE STUDIES. IX. THE NITRATION OF 2-AMINO-p-CYMENE[1]

BY ALVIN S. WHEELER AND F. P. BROOKS

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The nitration of 2-amino-*p*-cymene or carvacrylamine has not hitherto been undertaken. A pure acetyl derivative was difficult to obtain if the aminocymene was boiled with glacial acetic acid. A quicker and better method recently noted in this Laboratory is to treat an acetone solution of aminocymene with acetyl chloride. The acetyl derivative was nitrated at 0° in sulfuric acid solution with nitric acid. Hydrolysis of the nitro compound gave an aminonitrocymene which is a liquid. Its hydrochloride turns purple readily in the light. The benzoyl derivative of aminocymene was prepared with the hope of more readily obtaining a pure compound for nitration. A nitro derivative was obtained from the benzoate but its hydrolysis was impossible in open vessels. Its reduction gave benzamido-aminocymene. The acetyl derivative and the hydrochloride of the latter were prepared.

Two dyes were obtained by coupling diazotized aminonitrocymene with 2-naphthol and with Neville-Winther's salt.

Experimental Part

2-Aceto-amido-5-nitro-*p*-cymene, $C_6H_2CH_3C_3H_7NHCOCH_3NO_2$.—Nineteen parts of acetyl cymidine, m. p. 71°, was dissolved in 84 parts of sulfuric acid (1.84), cooled to 0° and treated dropwise with 10 parts of 70% nitric acid. The nitration mixture was poured into ice water. The solid product was filtered and washed with much water. It was then broken up into small pieces, washed with sodium hydroxide and recrystallized from hot alcohol. It is usually difficult to get the product into crystalline form; pale yellow prisms, m. p. 148°, very soluble in chloroform, fairly soluble in alcohol, benzene and acetic acid and insoluble in petroleum ether.

Anal. Subs., 0.1816: N_2, 19.4 cc. (20°, 745 mm.). Calcd. for $C_{12}H_{16}O_3N_2$: N, 11.87. Found: 12.23.

2-Amino-5-nitro-*p*-cymene, $C_6H_2CH_3C_3H_7NH_2NO_2$.—The aceto-amido compound was hydrolyzed with boiling concd. hydrochloric acid. The free base was thrown out with alkali and extracted with ether. The orange-colored oil left after evaporation of the ether was steam distilled. The distillate was saturated with salt and extracted with ether. The yellow liquid left after evaporation of the ether was distilled at atmospheric pressure, a considerable portion decomposing. The pure nitro-amine distilled above 250° and possessed a sweet taste.

Anal. Subs., 0.2009: N_2, 25.8 cc. (23°, 752 mm.). Calcd. for $C_{10}H_{14}O_2N_2$: N, 14.43. Found: 14.24.

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[1] This paper is an abstract of a thesis submitted to the faculty of the University of North Carolina in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1926.

Hydrochloride.—The hydrochloride crystallizes in clusters of white needles which turn purple in the light. It is quickly hydrolyzed by alcohol or the moisture of the air, turning yellow. It was recrystallized from alcohol containing hydrochloric acid. It was rapidly dried and analyzed by titration, using phenolphthalein as indicator.

Anal. Subs., 0.1000, 0.1000: 21.44, 21.44 cc. *N*/50 NaOH. Calcd. for $C_{10}H_{14}O_2N_2.HCl$: HCl, 15.81. Found: 15.71, 15.71.

2-Benzamido-5-nitro-*p*-cymene, $C_6H_2CH_3C_3H_7NHCOC_6H_5NO_2$.—Aminocymene was benzoylated in the usual way. The melting point of the product remained at 90.5° after repeated recrystallizations from hot alcohol although Andrews[2] gives 96.5°. The product was nitrated by dissolving 10 g. in 50 cc. of concd. sulfuric acid, cooling to 0° and slowly adding 10 g. of concd. nitric acid, holding the temperature at 0°. The mixture was poured into 600 cc. of water containing ice. The yellow precipitate was filtered, well washed with water and dried on a porous plate; weight, 36 g. A preparation with 30 g. gave a yield of 95 g. These are very high yields but recrystallizing from alcohol brings the yields down at once to expected figures. About 16 g. dissolve in 100 cc. of boiling alcohol and 2 g. remain in solution at room temperature. The crystals are very pale yellow, six-sided prisms which melt at 215–218°.

Anal. Subs., 0.2516: N_2, 21.2 cc. (23°, 754 mm.). Calcd. for $C_{17}H_{18}O_3N_2$: N, 9.39. Found: 9.39.

2-Benzamido-5-amino-*p*-cymene, $C_6H_2CH_3C_3H_7NHCOC_6H_5NH_2$.—Ten g. of benzamidonitrocymene was reduced in alcoholic solution with tin and hydrochloric acid. The alcohol was evaporated off, the residue taken up with water and the solution made strongly alkaline. The solution was extracted with ether, the latter evaporated off and the yellow residue dissolved in hydrochloric acid and the solution filtered and treated with ammonia. The free base was purified by reprecipitating several times. It is a pale yellow solid, melting at 115°. It is soluble in alcohol and acetic acid, less soluble in ether and insoluble in water. The yellow alkaline solution rapidly becomes bluish. The ether solution is yellow with a bluish fluorescence.

Anal. Subs., 0.2333: N_2, 23 cc. (29°, 757 mm.). Calcd. for $C_{17}H_{18}ON_2$: N, 10.53. Found: 10.66.

Hydrochloride.—Hydrogen chloride was passed into an ether solution of the amine, giving pale yellow crystals which deepen in color on drying. It melts with decomposition above 200°.

Anal. Subs., 0.1000: 33 cc. of *N*/10 NaOH. Calcd. for $C_{17}H_{20}ON_2HCl$: HCl, 11.97. Found: 12.03.

2-Benzamido-5-aceto-amido-*p*-cymene was prepared by boiling the 5-amino compound with glacial acetic acid for ten hours. The solution was concentrated and the acid neutralized. The precipitate was dissolved in ether, from which it separated as a yellow powder, melting at 120°. Analysis for nitrogen gave 8.11% against a theoretical value of 9.04%, showing the compound to be impure, but scarcity of material prevented further purification.

New Azo Dyes

1-(5-Nitrocarvacrylazo)-2-naphthol, $C_6H_2CH_3C_3H_7NO_2N_2C_{10}H_6OH$.—Diazotized nitro-aminocymene was coupled with 2-naphthol in the usual way. The dye was recrystallized from glacial acetic acid. It formed well-shaped deep red prisms melting at 245°.

Anal. Subs., 0.2145: N_2, 23.4 cc. (20°, 752 mm.). Calcd. for $C_{20}H_{19}O_3N_3$: N, 12.04. Found: 12.30.

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[2] Andrews, *J. Ind. Eng. Chem.*, **10**, 453 (1918).

2-(5-Nitrocarvacrylazo)-1-naphthol-4-sulfonic Acid, $C_6H_2CH_3C_3H_7NO_2N_2C_{10}H_5OHSO_2ONa$.—Nitro-aminocymene was diazotized and coupled with Neville-Winther's salt. The product was salted out of solution. It is a red dye, soluble in water and alcohol and was recrystallized from alcohol.

Anal. Subs., 0.1511: N_2, 13 cc. (24°, 753 mm.). Calcd. for $C_{20}H_{19}O_6N_3SNa$: N, 9.33. Found: 9.51.

The Constitution of Aminonitrocymene

It is possible for the nitro group to enter any of the vacant positions, 3, 5 and 6. Position 6 is eliminated because the nitro compound does not correspond to the 2-amino-6-nitro-*p*-cymene described by one of us and Harris.[3] Its acetyl derivative melts at 115° and not 148°. Similarly the benzoyl derivatives are wide apart in melting points. The expectation is that the nitro group will enter para to the amino group, that is, Position 5. That this is the case is indicated by our conversion of the acetyl derivative into 2,5-diaceto-amido-*p*-cymene, described by Kehrmann and Messinger,[4] who obtained it from thymoquinonedioxime. We reduced aceto-amidonitrocymene with tin and hydrochloric acid and purified the hydrochloride of 2-aceto-amido-5-amino-*p*-cymene.

Anal. Subs., 0.1000: 44.9 cc. $N/10$ NaOH. Calcd. for $C_{12}H_{18}ON_2HCl$: HCl, 16.09. Found: 16.35.

It is white but readily turns pink. The free base quickly turns to a blue compound. The diacetyl derivative was obtained by boiling with acetic anhydride and sodium acetate. The product, recrystallized from alcohol, melted at 260°, which is the melting point given by Kehrmann and Messinger for 2,5-diacetylamido-*p*-cymene.

Summary

1. 2-Amino-5-nitro-*p*-cymene was obtained by the nitration of 2-aceto-amido-*p*-cymene.
2. Its constitution was determined by its conversion into 2,5-diaceto-amido-*p*-cymene, previously made from thymoquinonedioxime.
3. The following new compounds were made: 2-aceto-amido-5-nitro-*p*-cymene and its hydrochloride; 2-benzamido-5-nitro-*p*-cymene; 2-benzamido-5-amino-*p*-cymene, its hydrochloride and acetate; the hydrochloride of 2-aceto-amido-5-amino-*p*-cymene.
4. Two azo dyes were made by coupling the aminonitrocymene with 2-naphthol and with 1-naphthol-4-sulfonic acid.

CHAPEL HILL, NORTH CAROLINA

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[3] Wheeler and Harris, THIS JOURNAL, **49**, 496 (1927).

[4] Kehrmann and Messinger, *Ber.*, **23**, 3557 (1890).