

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

PARA-CYMENE STUDIES. IV. THE CHLORINATION OF 2-AMINO-PARA-CYMENE

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The previous papers in this series dealt with (1) the reaction between *p*-cymene and benzene in the presence of aluminum chloride,² (2) *p*-cymene as a solvent³ and (3) the bromination of 2-amino-*p*-cymene.⁴ This study is concerned with the chlorination of 2-amino-*p*-cymene which, when carried out at room temperature, yields a monochloro substitution product. The *p*-cymene was prepared from spruce turpentine and the fraction boiling at 175–178° was nitrated according to the method of the Eastman Kodak Company as described in detail by Wheeler and Smithey. The nitrocymene was reduced with tin and hydrochloric acid and isolated by shaking out with benzene. In the acetylation of the aminocymene a change was made by using 1 mole of acetic anhydride and 1 mole of glacial acetic acid. The acetyl derivative was chlorinated in carbon tetrachloride solution at room temperature. The chlorinated product consists of colorless needles melting at 109–111°. It can be hydrolyzed with dil. sodium hydroxide solution or hydrochloric acid. The free chloro-amine is a liquid of aniline-like odor, boiling above 240°. Its hydrochloride crystallizes in pearly white plates. A pure sulfate could not be obtained owing to the difficulty of separating a neutral and an acid sulfate and to its hygroscopic character. The chloroplatinate was also difficult to obtain in the pure state. The benzoate crystallizes in needles, m. p. 137.5°. The diazo reaction was fruitful in results. Reactions in which the nitrogen was lost were first carried out, but we did not go far in this direction. A new chlorocarvacrol was prepared and a new acid of the C₁₁ series, a methyl *isopropyl*-chlorobenzoic acid. In reactions where the nitrogen was retained the amine was condensed with itself, giving an analog of diazo-aminobenzene.

New Dyes

The coupling of the amine with other amines was not successful, but its condensation with hydroxy (phenol) compounds proceeded very smoothly. A series of azo dyes was prepared by coupling the chloro-aminocymene with phenol, 1-naphthol, 2-naphthol, resorcinol, salicylic acid, 1-naphthol-2-sulfonic acid, 1-naphthol-4-sulfonic acid and 2-naphthol-

¹ A portion of a thesis submitted in June, 1922, to the Faculty of the University of North Carolina by I. V. Giles in candidacy for the degree of Doctor of Philosophy.

² Wheeler, *J. Ind. Eng. Chem.*, **10**, 359 (1918).

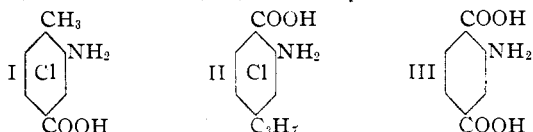
³ Wheeler, *THIS JOURNAL*, **42**, 1842 (1920).

⁴ Wheeler and Smithey, *ibid.*, **43**, 2611 (1921).

7-sulfonic acid. Those containing the sulfo group act as direct dyes when employed in weak acetic acid solution. The others are developed dyes. The colors produced on wool and silk are yellow, orange, scarlet, red and brown. They are fast to light and washing. The brilliancy of some is quite striking, undoubtedly due to the presence of the chlorine atom. To test this point 2-amino-*p*-cymene was diazotized and coupled with 2-naphthol-7-sulfonic acid. This dyed wool a dull reddish-brown, whereas the corresponding chloro compound described below far excelled it in luster and brilliancy.

Orientation

The constitution of the chloro-aminocymene was definitely established. The chlorine atom enters Position 5 which is *para* to the amino group. It cannot be present in any of the side chains, for the compound is a true aromatic substance, possessing no aliphatic characteristics, such as the easy replaceability of the chlorine atom with the hydroxyl group. There are 3 positions open in the ring, 3,5 and 6. Oxidation of one or both of the side chains suggested a method of attack. It seemed possible to form a toluic acid, I, a cuminic acid, II, or a terephthalic acid, III.



The chloro-acetyl compound was, therefore, oxidized with neutral permanganate solution. A monobasic acid was obtained, the acetyl derivative melting at 207–209° and the amino acid at 159°. This threw the terephthalic acid, III, out of consideration as our product was monobasic, and it also seemed to eliminate the toluic acid, I, as the substance with the chlorine at Position 5 is known, its melting point being 220°.⁵ A cuminic acid was apparently formed, for titration of its hydrochloride gave results agreeing with this theory; likewise, a chlorine determination of the free amino acid indicated the same product. While the position of the chlorine atom in our compound is not yet proved, as this is a new cuminic acid, its location at Position 5 is strongly suggested by results obtained by Remsen⁶ who concludes from a study of many cases, "In all cases now on record in which hydrocarbon residues are shown to be protected from oxidation by the presence of negative groups, the latter are in the *ortho* position with reference to the former, whereas oxidizable residues situated in the *meta* or *para* position with reference to the negative groups are, under the circumstances, transformed just as if the negative groups were not present." This statement was based on a study of many

⁵ Claus and Davidson. *Ann.*, **265**, 346 (1891).

⁶ Remsen, *Am. Chem. J.*, **1**, 32, 114, 426 (1879); **2**, 50, 130, 405, 413 (1880); **3**, 204, 426 (1881); **5**, 106, 149 (1883).

toluene, xylene and cymene derivatives. Furthermore, Gerichten⁷ has shown that when chlorocymene obtained from carvacrol is oxidized, it yields a toluic acid. Thus the methyl group *ortho* to the chlorine is protected. Furthermore, when the chlorocymene made from thymol is oxidized, a cuminic acid is obtained, the methyl group now being oxidized. Thus there is a very strong indication that in the cuminic acid which we obtained the chlorine atom is *ortho* to the *isopropyl* group. To establish fully the position of the chlorine atom, the chloro-aminocymene was converted into a known dichloro-terephthalic acid. By employing the Sandmeyer diazo reaction, the amino group was replaced by chlorine. The dichlorocymene thus obtained was a liquid. It was proved to be 2,5-dichloro-*p*-cymene by oxidation with nitric acid in a sealed tube at 180°, the product so obtained being 2,5-dichloro-terephthalic acid, melting at 305°. Bocchi⁸ obtained this acid from 2,5-dichloro-*p*-cymene which he obtained from thymol. Our analysis indicated identity of our product with this acid; furthermore, it was converted into its dimethyl ester which melts at 136° as given by Levy.⁹ This leaves no doubt, then, that in the chlorination of 2-amino-*p*-cymene at room temperature the chlorine atom enters Position 5, *para* to the amino group. This study of orientation produced the new compound, a chloro-aminocuminic acid and its acetyl derivative.

Experimental Part

2-Aceto-amido-5-chloro-*p*-cymene, $C_6H_2CH_3NHCOC_2H_5Cl$.—Chlorine was passed into a solution of 10 g. of aceto-amido-*p*-cymene dissolved in 50 cc. of carbon tetrachloride. The solution was maintained at room temperature by shaking the flask in a vessel of cold water. Hydrogen chloride was evolved and after a short time a precipitate began to form. Finally, on completion of the reaction the whole mass was seemingly solid. The product was immediately filtered off with suction, dried on a porous plate and recrystallized from alcohol, forming fine colorless glistening needles, melting at 109–111°; yield 80%.

Analysis. Subs., 0.1920: AgCl, 0.1211. Calc. for $C_{12}H_{16}ONCl$ (m. w., 225): Cl, 15.72. Found: 15.60.

It is also possible to chlorinate in a solution in glacial acetic acid, preferably in the presence of a little iron powder, but the yield is distinctly lower, about 50% only.

2-Amino-5-chloro-*p*-cymene Hydrochloride, $C_{10}H_{14}NCl.HCl$.—The chloro derivative was hydrolyzed by boiling with dil. sodium hydroxide solution and the product isolated by distilling with steam. The free amine was light red in color, heavier than water and only slightly soluble therein. It had an aniline-like odor. The main portion of the dried oil distilled between 240° and 250° at atmospheric pressure. Work which will lead to a more accurate characterization of the amine is under way. Hydrolysis was regularly carried out with hydrochloric acid because the hydrochloride was so much used in the subsequent reactions. Boiling dil. hydrochloric acid carried the acetyl

⁷ Gerichten, *Ber.*, 11, 364 (1878).

⁸ Bocchi, *Gazz. chim. ital.*, 26, (II), 406 (1896).

⁹ Levy and Andreocci, *Ber.*, 21, 1960 (1888). Levy and Curchod, *Ber.*, 22, 2111 (1889).

compound into solution in 30 minutes. On cooling the solution, pearly-white plates crystallized. The hydrochloride is slightly hydrolyzed by water. When heated, it begins to darken at about 206° and decomposes at 228°. The chlorine of the hydrochloric acid was determined.

Analysis. Subs., 0.2294: AgCl, 0.1515. Calc. for $C_{10}H_{14}NCl.HCl$ (m. w., 220): Cl, 16.12. Found: 16.34.

THE SULFATE.—Chloro-aminocymene was dissolved in an excess of warm dil. sulfuric acid. As the solution cooled, the sulfate crystallized out in needles. On recrystallizing from dil. sulfuric acid, the salt came out in plates which melted at 139°. After standing in the air for a few days the substance became light brown in color. When kept in a desiccator the odor of the amine was noticed. Determination of sulfate gave a result more than 1% too high. Analyses of sulfates given in the literature very often differ by 1% or more from the calculated value.

Analysis. Subs., 0.4525: BaSO₄, 0.2410. Calc. for $(C_{10}H_{14}NCl)_2.H_2SO_4$ (m. w., 465): SO₄, 20.65. Found: 21.92.

When recrystallized from a stronger sulfuric acid, the salt appeared again in needles and the melting point increased to 179°; the amount of sulfate fell to 17.48%, which seems to indicate the presence of water of crystallization.

2-Benzamido-5-chloro-*p*-cymene, $C_6H_2CH_2NHCOC_6H_5C_3H_7Cl$.—Eight g. of the amino-chlorocymene was dissolved in 20 cc. of benzene, an excess of benzoyl chloride was added and the solution heated for 4 hours, when no more fumes of hydrochloric acid were given off. As the liquid cooled a thick mush of crystals formed. The solvent was removed by suction and the product recrystallized from alcohol. Clear, prismatic needles were obtained, melting at 137.5°; yield 8 g.

Analysis. Subs., 0.2334, 0.4048: AgCl, 0.1153, 0.2022. Calc. for $C_{17}H_{15}ONCl$ (m. w., 287.5): Cl, 12.35. Found: 12.22, 12.36.

2-Hydroxy-5-chloro-*p*-cymene (5-Chlorocarvacrol), $C_8H_2CH_2OHC_3H_7Cl$.—Ten g. of chloro-aminocymene was dissolved in dil. sulfuric acid and the volume made up to 200 cc. with water. It was cooled with ice, and the equivalent amount of sodium nitrite solution was added. Diazotization redissolved some of the sulfate which had crystallized. The mixture was then heated on the water-bath until no more nitrogen was evolved. On distillation with steam a heavy oily liquid was obtained. It was fully extracted with ether and the ether solution dried with anhydrous sodium sulfate. On fractional distillation in a vacuum 2 cc. of a viscous liquid with a slight odor distilled at 158° at 52 mm.

Analysis. Subs., 0.1744: AgCl, 0.1343. Calc. for $C_{10}H_{13}OCl$ (m. w., 184.5): Cl, 19.24. Found: 19.05.

2-Methyl-4-chloro-5-isopropylbenzoic acid, $C_9H_2CH_3C_3H_7ClCOOH$.—The hydrochloride of chloro-aminocymene was diazotized and the diazo solution was added with shaking to a solution of cuprous cyanide in an excess of potassium cyanide. After heating on a water-bath until gases ceased to be evolved, steam was passed in to remove the nitrile. The oil was shaken with sodium hydroxide to remove phenolic compounds. As the oil was cooled with ice and salt it solidified, crystallizing in colorless plates which, after washing with ligroin, melted at 103°. A chlorine determination gave low results for the nitrile. In another preparation the oily distillate was extracted with ether and the ether solution dried with solid potassium hydroxide. After driving off the ether, the oil was distilled at 100 mm. pressure but it showed a constantly increasing boiling point, ranging from 150° to 200°. Four fractions were collected but none of these solidified until cooled with solid carbon dioxide. Again, analyses for chlorine gave results which were too low. Therefore, the fractions were combined and hydrolyzed

by boiling with 50% sulfuric acid until crystals appeared in the tube of the reflux condenser. As the liquid cooled a brownish precipitate was obtained. This was filtered, redissolved in sodium hydroxide and boiled with kelp char until the solution became colorless. Acidification produced a white, flocculent precipitate. Recrystallization from alcohol gave silky, white needles which melted sharply at 125°. Again, low results for chlorine were obtained. However, on heating the bomb oven to 300° and above, and continuing the heating for a longer period the compound was completely decomposed.

Analysis. Subs., 0.2031: AgCl, 0.1396. Calc. for $C_{11}H_{13}O_2Cl$ (m. w., 212.5): Cl, 16.71. Found: 17.00.

2,2'-Diazo-amino-5,5'-dichloro-*p*-cymene, $(CH_3C_3H_7ClC_6H_2)_2N_3H$.—Two g. of amino-chlorocymene hydrochloride was added to 20 cc. of water. The solution was cooled to 0° and exactly 1/2 of the equivalent amount of sodium nitrite was added. After stirring for 20 minutes, an equal volume of saturated sodium acetate solution was mixed in, causing a dense precipitate. When dry this was recrystallized from hot ligroin. The crystals are long yellow needles, melting at 135–137°, and are only slightly soluble in cold alcohol; yield, 80%.

Analysis. Subs., 0.1559: AgCl, 0.1201. Calc. for $C_{20}H_{25}N_3Cl_2$ (m. w., 378): Cl, 18.78. Found: 19.06.

New Dyes¹⁰

4-(5-Chlorocarvacrylazo)-phenol, $(C_6H_2CH_3C_3H_7ClN_2)_2C_6H_3OH$.—Amino-chlorocymene hydrochloride was diazotized and the solution mixed with an alkaline solution (1 mole) of phenol. When the mixture was acidified with hydrochloric acid a brown substance was precipitated. On recrystallizing from glacial acetic acid it was obtained in fine yellowish-bronze needles which melted at 196° but not sharply. The fused substance as well as the acetic acid solution was dark red; a sulfuric acid solution was rose-red. It belongs to the class of developed dyes. Wool is dyed a capucine yellow and silk a cadmium yellow. The fabrics are quite fast to light and washing. It is a disazo compound, as is shown by the analysis. Several attempts were made to prepare the mono-azo compound but in every case the disazo dye was produced.

Analyses. Subs., 0.1597, 0.1642, 0.2295: AgCl, 0.0970, 0.0970, 0.1370. Calc. for $C_{26}H_{23}ON_4Cl_2$ (m. w., 483): Cl, 14.76. Found: 15.03, 14.61, 14.77.

4-(5-Chlorocarvacrylazo)-resorcinol, $C_6H_2CH_3C_3H_7ClN_2C_6H_3(OH)_2$.—Amino-chlorocymene hydrochloride was diazotized and the solution mixed with an alkaline solution of resorcinol. Acidification produced a red flocculent precipitate which gradually changed to a crystalline mass. The product was difficult to purify on account of its slight solubility in most solvents. From ligroin it crystallized in bronze-colored needles. When heated, the substance begins to darken at 170°, and at 188° melts with decomposition. From alcohol it precipitates almost completely on the addition of a slight amount of water. Its solution in conc. sulfuric acid is carmine-colored. Wool is dyed a Brazil red and silk a Morocco red. It is a developed dye.

Analysis. Subs., 0.1515: AgCl, 0.0702. Calc. for $C_{16}H_{15}O_2N_2Cl$ (m. w., 305.5): Cl, 11.64. Found: 11.46.

4-(5-Chlorocarvacrylazo)-salicylic Acid, $C_6H_2CH_3C_3H_7ClN_2C_6H_3OHCOOH$.—The diazotized amino-chlorocymene hydrochloride was mixed with the equivalent amount of salicylic acid in alkaline solution. The sodium salt separated out as a dark orange-

¹⁰ The colors given for the dyes were determined by comparison with the color charts in Ridgway's Color Standards and Color Nomenclature, Pub. by Robert Ridgway, Washington, D. C., 1912.

colored precipitate. It was difficultly soluble in hot water. The free acid was best obtained by acidifying a concentrated solution of the sodium salt. It is difficultly soluble in ligroin and on slow evaporation of such a solution a crystalline product was obtained, which under a high powered microscope was seen to consist of clusters of very fine brown needles. The acid melts at 165°. Its solution in conc. sulfuric acid is scarlet. Wool is dyed a Mars orange color.

Analysis. Subs., 0.1428: AgCl, 0.0619. Calc. for $C_{17}H_{17}O_3N_2Cl$ (m. w., 332.5): Cl, 10.68. Found: 10.72.

4-(5-Chlorocarvacrylazo)-1-naphthol, $C_6H_2CH_3C_3H_7ClN_2C_{10}H_5OH$.—The diazotized amino-chlorocymene hydrochloride was mixed with an equivalent amount of 1-naphthol dissolved in an excess of sodium hydroxide solution. A brown precipitate was formed but it changed to reddish-brown on acidification. It was recrystallized from alcohol or ligroin, forming microscopic clusters of brown needles which melt at 128° with decomposition. The dye is slightly soluble in glacial acetic acid, and the solution is red. The color of the conc. sulfuric acid solution is dark nigrosine violet. Wool is dyed evenly a claret brown.

Analysis. Subs., 0.1463: AgCl, 0.0605. Calc. for $C_{20}H_{19}ON_2Cl$ (m. w., 338.5): Cl, 10.45. Found: 10.23.

1-(5-Chlorocarvacrylazo)-2-naphthol, $C_6H_2CH_3C_3H_7ClN_2C_{10}H_6OH$.—The amine and 2-naphthol were coupled as described above. A deep red precipitate formed when the solutions were mixed. On recrystallizing from alcohol, the product was obtained in beautiful, red hexagonal plates which melted at 163°. It is soluble in water, cold dil. alkali, cold dil. sulfuric acid, and is sparingly soluble in alcohol. It imparts an intense violet color to conc. sulfuric acid. Wool and silk are dyed scarlet.

Analysis. Subs., 0.1941: AgCl, 0.0824. Calc. for $C_{20}H_{19}ON_2Cl$ (m. w., 338.5): Cl, 10.49. Found: 10.50.

4-(5-Chlorocarvacrylazo)-1-naphthol-2-sulfonic Acid, $C_6H_2CH_3C_3H_7ClN_2C_{10}H_5OH\cdot SO_3H$.—The Sodium Salt. The sodium salt of 1-naphthol-2-sulfonic acid was treated with an equivalent amount of diazotized amino-chlorocymene. On acidification a reddish-brown oil separated. This was so difficult to purify that it was converted into its sodium salt, which was nearly insoluble in sodium chloride solution. On recrystallization, it was obtained in the form of prismatic plates of a burnt-sienna color. Its conc. sulfuric acid solution was prune-purple in color. It acts as a direct dye in the presence of a little acetic acid. Wool is dyed a burnt-sienna color and silk an English red. The free acid was obtained only in the form of a non-crystalline brittle cake.

Analysis. Subs., 0.1363: AgCl, 0.0471. Calc. for $C_{20}H_{17}O_4N_2ClSNa_2$ (m. w., 462.5): Cl, 7.67. Found: 7.58.

2-(5-Chlorocarvacrylazo)-1-naphthol-4-sulfonic Acid, $C_6H_2CH_3C_3H_7ClN_2C_{10}H_5OH\cdot SO_3H$.—The diazotized amino-chlorocymene was mixed with an alkaline solution of 1-naphthol-4-sulfonic acid. From the bright red solution a red flocculent was precipitated on acidification. It could not be filtered readily until it had been boiled for some time. The product was purified by recrystallizing the sodium salt. The pure acid was obtained by acidifying and washing out all of the mineral acid. It is scarlet-red and melts at 246° with decomposition. Its conc. sulfuric acid solution is carmine. Wool and silk are dyed a brilliant scarlet.

Analysis. Subs., 0.1902: AgCl, 0.0649. Calc. for $C_{20}H_{19}O_4N_2ClS$ (m. w., 418.5): Cl, 8.48. Found: 8.44.

1-(5-Chlorocarvacrylazo)-2-naphthol-7-sulfonic Acid, $C_6H_2CH_3C_3H_7ClN_2C_{10}H_5OH\cdot SO_3H$.—The mixed diazotized amino-chlorocymene and alkaline solution of 2-naphthol-7-sulfonic acid gave a red solution and a red precipitate on acidifying. The dye was re-

crystallized from alcohol, coming out in Nopal red crystals of no definite shape. It melts at 228° with decomposition. The conc. sulfuric acid solution is pomegranate-purple in color. Wool is dyed a brilliant scarlet red and silk a scarlet.

Analysis. Subs., 0.2446: AgCl, 0.0884. Calc. for $C_{20}H_{19}O_4N_2ClS$ (m. w., 418.5): Cl, 8.48. Found: 8.94.

Orientation

As stated in the introduction, the first experimental step was the oxidation of the amino-chlorocymene after introduction of the acetyl group for protection.

2-Acetamido-4-isopropyl-5-chlorobenzoic Acid, $C_8H_2COOHNHCOCH_3C_3H_7Cl$.—This may also be called a cuminic acid. Two g. of aceto-amido-chlorocymene in 240 cc. of water containing 4 g. of magnesium sulfate was heated to 80° and 6 g. of potassium permanganate was added. The heating was continued for 2 hours. Excess of permanganate was removed by alcohol. The colorless filtrate was acidified and the fine hair-like needles thus obtained were recrystallized from dil. alcohol. They soften at 206.5° and melt at 207–209°.

Analysis. Subs., 0.1000. Calc. for $C_{12}H_{14}O_3NCl$ (m. w., 255.5): KOH, 0.0220. Found: 0.0247.

2-Amino-4-isopropyl-5-chlorobenzoic Acid, $C_8H_2COOHNH_2C_3H_7Cl$.—The acetyl derivative was boiled with dil. hydrochloric acid until fully hydrolyzed. The solution was neutralized with sodium hydroxide and then acidified with acetic acid. The precipitated amino acid was recrystallized from alcohol. It consists of light grayish-yellow needles which melt at 159°.

Analysis. Subs., 0.0722: AgCl, 0.0463. Calc. for $C_{10}H_{12}O_2NCl$ (m. w., 203.5): Cl, 16.04. Found: 15.87.

The Hydrochloride, $C_{10}H_{12}O_2NCl.HCl$.—The hydrochloride, obtained in the hydrolysis of the acetyl derivative, was recrystallized from dil. hydrochloric acid and formed white plates melting at 178°.

Analyses. Subs., 0.0600: 0.0574. Calc. for 2 KOH (HCl salt, m. w., 250), 0.0269, 0.0257. Found: 0.0277, 0.0264.

2,5-Dichloro-terephthalic Acid, $C_6H_2Cl_2(COOH)_2$.—Amino-chlorocymene was diazotized in hydrochloric acid solution and subjected to Sandmeyer's reaction with cuprous chloride. The oily product was distilled with steam. It was light red and heavier than water. It was oxidized to the acid by heating with 20 parts of nitric acid of sp. gr. 1.15 at 180° in a sealed tube for 10 hours. The tube then contained a white crystalline mass which was purified by recrystallization from water and then sublimation. Its melting point, 305°, and analysis proved it to be 2,5-dichloro-terephthalic acid, obtained by Bocchi who oxidized 2,5-dichlorocymene.

Analysis. Subs., 0.1106: AgCl, 0.1358. Calc. for $C_8H_4O_4Cl_2$ (m. w., 235): Cl, 30.21. Found: 30.37.

Subs., 0.1015. Calc.: KOH, 0.0484. Found: 0.0489.

The acid was further characterized by conversion into its dimethyl ester which was found to melt at 136°, identical with Levy's revised figure.

Summary

1. Chlorination of 2-amino-*p*-cymene at ordinary temperature gives 2-amino-5-chloro-*p*-cymene. Its hydrochloride, sulfate, acetate and benzoate were prepared.

¹¹ Levy and Curchod, *Ber.*, **22**, 2111 (1889).

2. By the diazo reaction a new chlorocarvacrol was prepared; also a new acid, 2-methyl-4-chloro-5-*isopropyl*benzoic acid.

3. Amino-chlorocymene was condensed with itself, forming 2,2'-diazo-amino-5,5'-dichloro-*p*-cymene.

4. A new series of azo dyes, some of striking brilliance, was prepared by coupling with the following phenols: phenol, resorcinol, salicylic acid, 1-naphthol, 2-naphthol, 1-naphthol-2-sulfonic, 1-naphthol-4-sulfonic acid and 2-naphthol-7-sulfonic acid.

5. The location of the chlorine atom was determined (1) by conversion of the compound into 2-amino-4-*isopropyl*-5-chlorobenzoic acid which is new, and (2) by conversion into 2,5-dichloro-terephthalic acid and its dimethyl ester. The acetate of the new benzoic acid and its hydrochloride were prepared.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

SOME CONDENSATION REACTIONS WITH PARA-PARA-BIS (DIMETHYLAMINO)-BENZOHYDROL (MICHLER'S HYDROL)

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Introductory

Fosse¹ has shown that *p*-substituted secondary aromatic alcohols, including Michler's hydrol, condense with one of the methylene hydrogens in compounds containing the $-\text{CO}-\text{CH}_2-\text{CO}-$ grouping, with elimination of a molecule of water and the insertion of the alcohol residue in place of the hydrogen removed.

Inasmuch as the hydrogen of the imino group in imides of dibasic acids often behaves in a way recalling that of the hydrogen in reactive methylenes similar to the above (for example, compare the Gabriel imide reactions with those of malonic ester), it was thought of interest to test this experimentally, particularly in view of the fact that Möhlau and Heinze² found it impossible to effect such condensation with any amides except urea, and that Reitzenstein and Breuning³ have reported that the hydrol reacts with isatin (an isomer of phthalimide) by removal of nuclear and not of imide hydrogen. The experiments of Möhlau and his co-workers⁴ have indicated, further, that the hydrol condenses with primary or secondary aromatic amines in alcoholic solution with formation of the corre-

¹ Fosse, *Chem. Zentr.*, **1907**, I, 1696; *C. A.*, **2**, 823, 2387, 2689 (1908); *Ann. chim. phys.*, [8] **18**, 400, 503, 531 (1909); *Bull. soc. chim.*, [4] **7**, 229 (1910); *Compt. rend.*, **150**, 179 (1910); *Ann. chim. phys.*, [9] **13**, 118, 154 (1920); *C. A.*, **15**, 1711 (1921).

² Möhlau and Heinze, *Ber.*, **35**, 359 (1902).

³ Reitzenstein and Breuning, *Ann.*, **272**, 257 (1910).

⁴ Möhlau and others, *Ber.*, **33**, 799 (1900); **34**, 882, 3384 (1901); **35**, 359 (1902).