[Contribution from the Chemical Laboratory of the University of North Carolina]

THE CHLORINATION OF 2-AMINO-PARA-XYLENE AND CERTAIN NEW AZO DYES[1]

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The purpose of this work was to prepare a monochloro-2-amino-*p*-xylene and a group of its derivatives, especially those with dyeing properties. A similar work was done by Wheeler and Constable in the bromination of 2-amino-*p*-xylene.[2] In 1874, Jannasch[3] obtained a monochloro-2-amino-*p*-xylene as a by-product in the reduction of mononitro-*p*-xylene with tin and hydrochloric acid. This product crystallized in silky, leaf-like crystals melting at 92.5°. He made no attempt to orient the chlorine atom. The hydrochloride, sulfate and oxalate were prepared, the hydrochloride containing two molecules of water of crystallization. We purified this salt by sublimation, thus obtaining it in the anhydrous state. In 1885, Kluge[4] reduced nitro-*p*-xylene with tin and hydrochloric acid and stated that the product was almost exclusively the chloro-*p*-xylidine of Jannasch. Its acetylation was readily effected by Kluge by boiling it with glacial acetic acid, although Jannasch failed in spite of a number of efforts. The acetyl derivative crystallized in needles, melting at 171° whereas our product melts at 176°. Kluge converted the chloro-xylidine into dichloro-*p*-xylene by the diazo reaction and gave 71° as its melting point which is in agreement with our determination. Kluge made no analyses of any of his products and guessed at the positions of the chlorine atoms, placing them at 2 and 5 since these positions were entered by bromine in the bromination of *p*-xylene.

In our first attempt to chlorinate amino-*p*-xylene we used a glacial acetic acid solution, but this method did not prove satisfactory. We then prepared the acetyl derivative and found that this worked well under certain conditions. Dry chlorine was passed into its acetic acid solution at room temperature until the solution became yellow, but the best results were obtained when the temperature of the solution was held closely to 16°. The monochloro compound may also be obtained by the method of Bender[5] as modified by Slosson[6] and Chattaway and Orton[7] using bleach-

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[1] This paper is a portion of a thesis submitted by Mildred Morse in partial fulfilment of the requirements for the degree of Master of Arts at the University of North Carolina.

[2] Wheeler and Constable, This Journal, **45**, 1999 (1923).

[3] Jannasch, *Ann.*, **176**, 55 (1874).

[4] Kluge, *Ber.*, **18**, 2098 (1885).

[5] Bender, *Ber.*, **19**, 2272 (1886).

[6] Slosson, *Ber.*, **28**, 3268 (1895).

[7] Chattaway and Orton, *J. Chem. Soc.*, **75**, 1050 (1889).

ing powder solution in the presence of carbonic acid. This method yields a nitrogen chloride which may be isolated if one determines the right conditions. We obtained this product in one experiment only, with a yield over 90% of that calculated. Armstrong[8] calls attention to the difficulty of isolating these nitrogen chlorides owing to their ready rearrangement to anilides, the chlorine atom wandering from the nitrogen to the nucleus. The bleaching powder method offers an excellent method for getting larger yields of the monochloro derivative, as high as 78% being obtained with a solution containing 5.8% of available chlorine. We are indebted to Mr. W. B. Sellars who carried out the experiments with bleaching powder.

The chlorine atom was shown to be in Position 5 by converting the chloroxylidine into the dichloro-xylene of Kluge (m. p., 71°) through the diazo reaction, oxidation of which yielded 2,5-dichloro-terephthalic acid (m. p., 305°).

A series of new azo dyes was prepared by coupling the diazotized monochloro-amino-xylene with the following phenols: phenol, resorcinol, 1-naphthol, 2-naphthol, thymol, 2-naphthol-6-sulfonic acid, 1-naphthol-5-sulfonic acid, 1,8-dihydroxy-3,6-disulfonic acid, R-acid and Neville-Winther's acid. Attempts to couple the chloro-xylidine with *o*- and *p*-chlorophenol, *o*- and *p*-nitrophenol, 2,4-dinitrophenol, *p*-cresol, hydroquinol, pyrogallol and carvacrol were not successful. The thymol dye is unique in being a *bis* compound. The colors on silk and wool are particularly beautiful, while on mercerized cotton they are only moderately good. The dyes containing the sulfo group were applied directly by the acid method whereas the others were applied by the development method since they were insoluble in water.

Experimental Part

Chlorination of 2-Amino-*p*-xylene

5-Chloro-2-aceto-amido-*p*-xylene, $(CH_3)_2C_6H_2NHCOCH_3Cl$.—Five g. of 2-aceto-amido-*p*-xylene was dissolved in 25–30 cc. of glacial acetic acid. The solution was frozen and the temperature then allowed to rise until a soft mush was obtained. The mixture was kept at this temperature during the chlorination by means of an ice water jacket. Dry chlorine was passed into the solution very slowly until it began to turn yellow and no more precipitation took place. The mass of crystals was filtered off and recrystallized several times from 50% boiling alcohol. The substance crystallizes in white plates; m. p., 176°. Kluge prepared this compound and gave 171° as the melting point, but did not analyze it.

Anal. Subs., 0.2137: AgCl, 0.1546. Calc. for $C_{10}H_{12}ONCl$ (mol. wt., 197.5): Cl, 17.79. Found: 17.89.

5-Chloro-2-amino-*p*-xylene Hydrochloride, $(CH_3)_2C_6H_2ClNH_2HCl$.—The aceto-amido compound was refluxed with concd. hydrochloric acid until no precipitation took

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[8] Armstrong, *J. Chem. Soc.*, **77**, 1047 (1900).

place, when a small quantity was poured into ice water. On cooling, the salt crystallized in long, white, silky needles. It sublimes when heated and was purified by this method. Jannasch analyzed the salt obtained from water solution and found two molecules of water of crystallization. Our product was of course anhydrous.

Anal. Subs., 0.2196: AgCl, 0.1632. Calc. for $C_8H_{11}ONCl$ (mol. wt., 192); Cl, 18.43. Found: 18.38.

5-Chloro-2-amino-*p*-xylene, $(CH_3)_2C_6H_2ClNH_2$.—The hydrochloride of chloro-amino-xylene was neutralized by a solution of sodium hydroxide. The precipitated base was recrystallized from boiling water, forming colorless plates, melting at 93° as given by Kluge, by whom it was analyzed.

(?)-Dichloro-2-aceto-amido-*p*-xylene, $(CH_3)_2C_6HCl_2NHCOCH_3$.—The dichloro derivative was best obtained by chlorinating a glacial acetic acid solution of aceto-amido-xylene at 18–20° until the solution became slightly yellow. On pouring the solution into ice water a white precipitate was formed. Any unchanged substance was extracted by boiling water. The undissolved product was recrystallized several times from boiling, 50% alcohol. The crystals consisted of white flakes, melting at 167°.

Anal. Subs., 0.1965: AgCl, 0.2402. Calc. for $C_{10}H_{11}ONCl_2$ (mol. wt., 232): Cl, 30.60. Found: 30.24.

Determination of the position occupied by the second chlorine atom is under way. We anticipate that it will be found in Position 3.

Orientation

2,5-Dichloro-*p*-xylene, $(CH_3)_2C_6H_2Cl_2$.—Chloro-2-amino-*p*-xylene hydrochloride was diazotized in the presence of an excess of cuprous chloride. On steam-distilling the reaction mixture a yellowish-red oil passed over which solidified in the condenser tube. The product was recrystallized from hot alcohol, water being added until crystals began to form. The glistening white plates, melting at 71°, appeared to be identical with the dichloro-*p*-xylene described by Kluge.

2,5-Dichloro-terephthalic Acid, $(COOH)_2C_6H_2Cl_2$.—The dichloro-xylene was oxidized by heating it with 20 parts of nitric acid of d. 1.13 in a sealed tube at 180° for eight hours. The product, obtained on cooling the solution, was recrystallized from hot water. It proved to be 2,5-dichloro-terephthalic acid, since it crystallized in fine, white needles melting at 305°. This definitely located the chlorine atom in chloro-amino-*p*-xylene in Position 5.

New Azo Dyes

The chloro-xylidine was coupled with a series of phenols. One molecular equivalent of the xylidine was diazotized at 0° and to this solution was added one molecular equivalent of the phenol dissolved in sodium hydroxide. In the case of thymol one-half molecular equivalent of thymol was used. After ten minutes the solution was acidified with acetic acid. The precipitated dye was recrystallized from a suitable solvent. The dyes crystallized uniformly in needles. The color names used are those proposed by Ridgway.[9] The formulas adopted were derived by analogy and not based on any special experimental work.

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[9] "Color Standards and Color Nomenclature," published by Robert Ridgway, Washington, D. C., 1912.

TABLE I

NEW AZO DYES DERIVED FROM 2-AMINO-5-CHLORO-PARA-XYLENE

						Analysis				Dyeing colors		
	Coupler	Recryst. from	Color of crystals	M. p. °C.	Formula	Subs. G.	Weight AgCl G.	Cl Calcd. %	Cl Found %	Wool	Silk	Mer. cotton
1	Phenol	Hot acetic acid	Brown-yellow	223	$C_{14}H_{13}ON_2Cl$	0.1100	0.0606	13.62	13.62	Orange-buff	Maize-yellow	Light-buff
2	Resorcinol	Hot benzene	Orange-red	200–220	$C_{14}H_{13}O_2N_2Cl$	.1355	.0703	12.83	12.83	Sudan-brown	Gold	Capucine-buff
3	Thymol	Hot benzene	Dull brown	290	$C_{26}H_{28}ON_4Cl_2$	.1669	.0981	14.69	14.54	Orange-buff	Maize-yellow	Pale peach
4	1-Naphthol	Hot alcohol	Dark red	163–164	$C_{18}H_{16}ON_2Cl$	.1224	.0562	11.43	11.35	Sudan-brown	Apricot-buff	Cinnamon
5	2-Naphthol	Hot alcohol	Scarlet-red	165	$C_{18}H_{15}ON_2Cl$	.1756	.0794	11.43	11.18	Mars-orange	Cinnamon	Pale cinnamon
6	2-Naphthol-6-sulfonic acid	Hot alcohol	Red	above 360	$C_{18}H_{15}O_4N_2ClS$	.0500	.0190	9.09	9.40	Grenadine red	Flame-scarlet	Strawberry
7	1-Naphthol-5-sulfonic acid	Hot alcohol	Brown-red	above 360	....	...	...	...	...	Nopal-red	Carmine	Deep rose
8	1,8-Dihydroxy-3,6-disulfonic acid	Dilute alcohol	Purplish-red	above 360	....	...	...	...	...	Purple-red	Deep-heliotrope	Mallow-pink

1. 4(5-Chloro-2-*p*-xylylazo)-phenol.
2. 4(5-Chloro-2-*p*-xylylazo)-resorcinol.
3. 2,6(5-Chloro-2-*p*-xylyl*bis*azo)-thymol.
4. 4(5-Chloro-2-*p*-xylylazo)-1-naphthol.
5. 1(5-Chloro-2-*p*-xylylazo)-2-naphthol.
6. 1(5-Chloro-2-*p*-xylylazo)-2-naphthol-6-sulfonic acid.
7. 2(5-Chloro-2-*p*-xylylazo)-1-naphthol-5-sulfonic acid.
8. 2(5-Chloro-2-*p*-xylylazo)-1,8-dihydroxy-3,6-disulfonic acid.

Summary

1. The chlorination of 2-amino-*p*-xylene (acetyl derivative) at the freezing point of glacial acetic acid yields a monochloro derivative. The location of the chlorine atom at Position 5 was proved by converting the compound into 2,5-dichloro-terephthalic acid. The hydrochloride is described.

2. A dichloro derivative is obtained if the chlorination is carried out at a slightly higher temperature, 18–20°.

3. A series of new azo dyes was obtained by coupling the monochloro-xylidine with: phenol, resorcinol, thymol, 1-naphthol, 2-naphthol, 2-naphthol-6-sulfonic acid, 1-naphthol-5-sulfonic acid and 1,8-dihydroxy-3,6-disulfonic acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

2-CHLOROMETHYL-FURAN FROM 2-FURANCARBINOL

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The number of known halogen derivatives of the simpler furan compounds is extremely small. In a large measure, this is due to the long-known sensitiveness of the furan nucleus to halogen acids. Because of the recent availability of furfural in large quantities and at a price that makes it the least expensive aldehyde, 2-furancarbinol ($C_4H_3OCH_2OH$) is now a readily accessible alcohol.[2]

By analogy with benzyl chloride, 2-chloromethyl-furan ($C_4H_3OCH_2Cl$) should be prepared from 2-furancarbinol. A series of studies has shown the correctness of this view despite the rather marked instability of the chloride. Apart from the actual synthesis of the compound, the problem may not be without some interest in an interpretation of the resinification of some furan derivatives and the scission of the furan ring by mineral acids.

Many workers have reported on the instability of 2-furancarbinol towards halogen acids, without considering the possibility of the intermediate formation of the halide. Limpricht,[3] working with an alcohol that was not entirely pure, found that it was decomposed readily by dil. hydrochloric acid and explosively by concd. hydrochloric acid. Baeyer[4] observed that the pure 2-furancarbinol gave a green color with alcoholic

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[1] This paper is an abstract of a thesis presented by Clarence C. Vernon in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

[2] Large quantities can be prepared in a single run from furfural by the Cannizzaro reaction in yields of over 80%.

[3] Limpricht, *Ann.*, **165**, 300 (1873).

[4] Baeyer, *Ber.*, **10**, 356 (1877).