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

THE BROMINATION OF 2-AMINO-PARA-XYLENE AND CERTAIN NEW AZO DYES

BY ALVIN S. WHEELER AND E. W. CONSTABLE[1]

Received June 16, 1923

E. Fischer and Windhaus[2] prepared a bromine derivative of 2-amino-*p*-xylene by brominating its formyl derivative. The product contained 1 bromine atom and as for the constitution of the compound they merely say, "The location of the bromine, for which three possibilities exist, is still not known, but we hold it as probable that the halogen is in the position *para* to the amino (2) group." We have established the location of the bromine definitely at Position 5 by a short series of reactions. Instead of using the formyl derivative of Fischer and Windhaus, we prepared the acetyl derivative and treated this with bromine in glacial acetic acid solution. The monobromo compound thus obtained was hydrolyzed with strong hydrobromic acid, giving the hydrobromide of 2-aminobromo-*p*-xylene, melting at 255°. The free amino acid was identical with the one prepared by Fischer and Windhaus. Its diazotization by the Sandmeyer method gave 2,5-dibromo-*p*-xylene, m. p. 75.5°, a compound of known constitution. While this was sufficient to locate the bromine at Position 5, we extended the proof by oxidizing this compound with fuming nitric acid to 2,5-dibromoterephthalic acid, m. p. 316°, and finally converting this into its diethyl ester which melts at 125°.

Having established the constitution of the compound as 2-amino-5-bromo-*p*-xylene, we prepared a few azo dyes. It was found that the bis compound was produced when the bromo derivative was coupled with phenol, resorcinol and α-naphthol, but not in the case of β-naphthol. The β-naphthol derivative is very brilliant in color, a scarlet-red and the crystals are splendid, long needles. The other dyes are quite ordinary in appearance. Owing to difficulty in making sodium salts, the tinctorial properties on silk and wool were tried by employing the development method of application.

Experimental Part

2-Aceto-amido-5-bromo-*p*-xylene, $(CH_3)_2C_6H_2NHCOCHBr_3$.—Five g. of 2-aceto-amido-*p*-xylene (m. p., 137°) was dissolved in 20 cc. of glacial acetic acid by gentle heating and then cooled. The solution was kept cold while 1 molecular equivalent (4.9 g.) of bromine was slowly added. Five volumes of water were added to the thick mush of crystals that formed and the mixture was well stirred. The yield was equal to the weight

---

[1] This paper constitutes a portion of a thesis submitted by E. W. Constable in candidacy for the degree of Master of Science in June, 1923, at the University of North Carolina.

[2] Fischer and Windhaus, *Ber.*, **33,** 1974 (1900).

of the raw material taken. The crude product melted at 185°, recrystallization from alcohol raising the melting point to 187°. It crystallizes in colorless needles grouped in fluffy masses of rosets, and is very difficultly soluble in water, but soluble in alcohol and in ether. One g. dissolves in 8 cc. of hot alcohol.

Analysis. Subs., 0.2180: AgBr, 0.1639. Calc. for $C_{10}H_{12}ONBr$ (242): Br, 33.05. Found: 33.08.

This compound was prepared by C. K. Brooks in this Laboratory.

2-Amino-5-bromo-*p*-xylene Hydrobromide, $(CH_3)_2C_6H_2BrNH_2.HBr$.—Five g. of the aceto-amido compound was heated with 75 cc. of hydrobromic acid, d., 1.3. Hydrolysis was completed in a short time, the hydrobromide crystallizing out as the solution cooled. The product weighed 20% more than the raw material. It was recrystallized from absolute alcohol or, better, hydrobromic acid. It consists of flat needles; m. p., 255°, (decomp.).

Analyses. Subs., 0.2059, 0.4346. Calc. for $C_8H_{10}NBr.HBr$: NaOH, 0.0293, 0.0618. Found: 0.0294, 0.0615.

2,5-Dibromo-*p*-xylene, $(CH_3)_2C_6H_2Br_2$.—The hydrobromide described above was dissolved in water containing some hydrobromic acid and diazotized at a low temperature. After the addition of copper powder and potassium bromide, the mixture was distilled with steam. The crystals that appeared in the distillate were recrystallized from dil. alcohol, water being added to the alcoholic solution until crystallization began. The product consisted of plates; m. p., 75.5°. It was, therefore, identical with the 2,5-dibromo-*p*-xylene described by Jannasch.[3]

2,5-Dibromoterephthalic Acid, $(COOH)_2C_6H_2Br_2$.—The dibromoxylene was heated above 300° with 20 parts of nitric acid, d., 1.15, in a sealed tube for 8 hours. The product consisted of leaf-like crystals that melted at 313° (uncorr.). Fileti and Crosa[4] give 316–317° as the melting point of 2,5-dibromoterephthalic acid.

2,5-Dibromo-diethylterephthalate, $(COOC_2H_5)_2C_6H_2Br_2$.—The acid was readily esterified by boiling it with absolute alcohol containing a little dry hydrogen chloride. The glistening leaf-like crystals that appeared as the solution cooled melted at 125°. Fileti and Crosa[5] state that this ester melts at 125°.

Azo Dyes

2,4-(Bis-5-bromo-2-*p*-xylylazo)phenol, $[(CH_3)_2C_6H_2BrN_2]_2C_6H_3OH$.—One molecular equivalent of aminobromoxylene hydrobromide was diazotized and then treated with $^1/_2$ molecular equivalent of phenol dissolved in a minimum quantity of dil. alkali. After 10 minutes the solution was acidified with acetic acid. The dull brown precipitate that formed was recrystallized from glacial acetic acid. The pure compound consists of small, dark brown scales with a metallic luster when viewed in the mass, while under the microscope they are pale green; m. p., 233–234°. By employing the development method of application this dye may be made to color silk an écru and wool an orange-brown.

Analysis. Subs., 0.1029: AgBr, 0.0759. Calc. for $C_{22}H_{20}ON_4Br_2$ (516): Br, 30.98. Found: 31.39.

2,4-(Bis-5-bromo-2-*p*-xylylazo)resorcinol, $[(CH_3)_2C_6H_2BrN_2]_2C_6H_2(OH)_2$.—One molecular equivalent of the hydrobromide was diazotized and then treated with $^1/_2$ molecular equivalent of an alkaline solution of resorcinol. After 10 minutes acetic acid was added in excess, producing a dark brown precipitate. This was boiled with ben-

---

[3] Jannasch, *Ber.*, **10**, 1357 (1877).

[4] Fileti and Crosa, *Gazz. chim. ital.*, **18**, 309 (1888).

[5] Ref. 4, p. 310.

zene and the solution filtered hot. From the filtrate the product crystallized in fine, microscopic crystals of claret-brown color in the mass. It was further purified by recrystallizing from a 1:1 mixture of benzene and acetone. The pure substance melts at 263°. By employing the development method of application the dye may be made to color silk an écru and wool a Brazil-red.

Analysis. Subs., 0.0205: AgBr, 0.0146. Calc. for $C_{22}H_{20}O_2N_4Br_2$ (532): Br, 30.08. Found: 30.01.

2,4-(Bis-**5-bromo-2-*p*-**xylylazo)*α*-naphthol, $[(CH_3)_2C_6H_2BrN_2]_2C_{10}H_5OH$.—This dye was prepared in the same way as were those described above. The product was purified by boiling it in a large quantity of alcohol, filtering the solution while hot and allowing the filtrate to cool. The crystals separating from the cold solution are of indefinite shape, very dark brown to black when viewed in the mass and melt at 222–223°. When applied by the development method, this dye colors silk a Mars-orange and wool a claret-brown.

Analysis. Subs., 0.0325: AgBr, 0.0216. Calc. for $C_{26}H_{22}ON_4Br_2$ (566): Br, 28.23. Found: 28.28.

1-(5-Bromo-2-*p*-xylylazo)*β*-naphthol, $(CH_3)_2C_6H_2BrN_2C_{10}H_6OH$.—One molecular equivalent of the hydrobromide was diazotized, made alkaline and treated with 1 molecular equivalent of *β*-naphthol in alkaline solution. Acidification produced a brilliant red precipitate, weighing 40% more than the hydrobromide taken. On recrystallizing from acetone it was obtained in very beautiful, long scarlet-red needles in felted masses. Applied as the other dyes above, this dye colors silk a light red and wool a Nopal-red.

Analysis. Subs., 0.0673: AgBr, 0.0360. Calc. for $C_{18}H_{15}ON_2Br$ (355): Br, 22.51. Found: 22.76.

Summary

1. Bromination of 2-aceto-amido-*p*-xylene yields a monobromo derivative in which the bromine is located at Position 5 as proved by the following series of reactions: 2-aceto-amido-bromo-*p*-xylene (new) ⟶ 2-amino-bromo-*p*-xylene ⟶ 2,5-dibromo-*p*-xylene ⟶ 2,5-dibromoterephthalic acid ⟶ 2,5-dibromo-diethylterephthalate.

2. The following new azo dyes were prepared: 2,4-(bis-5-bromo-2-*p*-xylylazo)phenol; 2,4-(bis-5-bromo-2-*p*-xylylazo)resorcinol; 2,4-(bis-5-bromo-2-*p*-xylylazo)*α*-naphthol; 1-(5-bromo-2-*p*-xylylazo)*β*-naphthol.

CHAPEL HILL, NORTH CAROLINA

NEW BOOKS

Beiträge zur Geschichte der Naturwissenschaften und der Technik. (**Contributions to the History of Science and Technology.**) By Prof. Dr. EDMUND O. VON LIPPMANN, Dr. Ing. E. H. at the Technischen Hochschule at Dresden, Director of the "Zuckerraffinerie Halle" at Halle A.S. 314 pp. 2 figs. Verlag von Julius Springer, 1923, Berlin. 16.5 cm. × 24.5 cm. $1.60 paper, $1.90 bound.

This last work by Professor Lippmann comprises a selection of miscellaneous papers upon the history of alchemy, chemistry and chemical technology which have been published during the past 10 years in the *Chemiker Zeitung*, *Zeitschrift für Angewandte Chemie* and other periodicals.