

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

PARA-CYMENE STUDIES. VIII. A. PARA-CYMYLENE-2,5-DIAMINE. B. NEW DYES DERIVED FROM 2-AMINO- AND 2-AMINO-5-BROMO-*p*-CYMENE

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In order to obtain cymylene-2,5-diamine we first acetylated 2-aminocymene (an Eastman Kodak product) but in view of the difficulty encountered in purifying the acetate we examined the statement of Wallach and Schrader² that a di-acetyl derivative, melting at 66°, may be prepared. We carried out six experiments, as follows: (1) boiled one mole of aminocymene (A) with one mole of acetic anhydride (B); (2) boiled A with a large excess of B; (3) one mole of A with one mole of acetyl chloride (C) in ether; (4) one mole of A with two moles of C in ether; (5) two moles of A with one mole of C in ether; (6) A with large excess of C in ether. In all cases the mono-acetyl compound, melting at 71°, was obtained. Our own method was to treat an acetone solution of aminocymene with a large excess of acetyl chloride, pouring the mixture into a large quantity of water. The acetate was nitrated as described by Andrews,³ modifying the process by pouring the nitration mixture into a sodium hydroxide solution containing ice. Even so the product was purified with difficulty. Its acetone solution was boiled many times with kelp char before the product could be recrystallized from alcohol. The nearly white needles melted at 168°. The location of the nitro group was proved by converting it into di-acetylcymylene-2,5-diamine prepared by Kehrmann and Messinger⁴ and by Wallach,⁵ these authors giving 260° as the melting point. The usual reducing agents failed to give a product which could be purified, but success was obtained with titanium trichloride and hydrochloric acid in an atmosphere of carbon dioxide, with the assistance of H. A. Ljung in this Laboratory. The desired compound, melting at 260°, was obtained on acetylating the reduction product with acetic anhydride and sodium acetate. Kehrmann and Messinger obtained it from thymoquinonedioxime. We then obtained this diacetate by a very different method. Aminocymene was coupled with diazotized sulfanilic acid. The dye produced was reduced with stannous chloride and the diamine ob-

¹ This paper is an abstract of a thesis submitted by Lillie F. P. Cutlar in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of North Carolina, in June, 1927.

² Wallach and Schrader, *Ann.*, **279**, 375 (1893).

³ Andrews, *J. Ind. Eng. Chem.*, **10**, 453 (1918).

⁴ Kehrmann and Messinger, *Ber.*, **23**, 3562 (1890).

⁵ Wallach, *Ann.*, **336**, 23 (1904).

tained was acetylated. This method also indicates that the second amino group is in position 5 and also the nitro group because the coupling must take place in a position para to the amino group.

Three new salts of aminocymene were prepared: the nitrate, the hydrobromide and the trichloro-acetate. Two new dyes were prepared by coupling aminocymene with sulfanilic acid and with *p*-nitrosodimethylaniline, the latter dye being of the Eurhodine type. The sulfanilic acid dye furnishes a splendid raw material for the preparation of cymylene-2,5-diamine.

The bromination of aminocymene was first carried out by the method used by one of us and Smithey⁶ in which a carbon tetrachloride solution of aceto-amidocymene is treated with bromine, the product then being hydrolyzed. But since the hydrobromide of aminobromocymene was needed for most of the work, the acetylation step was omitted and the aminocymene directly brominated. Apparently the only product of the reaction was the hydrobromide of 2-amino-5-bromo-*p*-cymene. It will be recalled that Kekulé⁷ brominated aniline directly and obtained a bad mixture of aniline hydrobromide, monobromo-, dibromo- and tribromo-aniline. As two more hydrogen are substituted in aminocymene than in aniline we have a very different situation. Azo dyes were obtained by coupling aminobromocymene with *o*-cresol, catechol, phloroglucinol, carvacrol and *p*-toluidine. In addition sulfanilic acid and anthranilic acid were diazotized and coupled with aminobromocymene.

Their color reactions with sulfuric acid were noted. The names given to the colors are based on Ridgway's Standards.⁸

Experimental Part

Salts of 2-Amino-*p*-cymene

The three salts described below were made by mixing the constituents in the cold. They were recrystallized from a mixture of ether and petroleum ether. All are soluble in water, alcohol, acetone and ether and melt with decomposition. Analysis was made by titration with potassium hydroxide, using methyl red as indicator.

Compound	Crystals	M. p., °C.	Subs., g.	0.1095 <i>N</i> KOH, cc.	Analysis, acid	
					calcd., %	found, %
Nitrate	Plates	140	0.5248	22.71	31.47	31.66
Hydrobromide	Needles	169	.2066	8.32	35.14	35.49
Trichloroacetate	Plates	162	.3282	11.55	52.27	52.52

Dyes Derived from 2-Amino-*p*-cymene

5-(4-Sulfobenzene-azo)-carvacrylamine Hydrochloride, C₁₆H₂₀O₂N₂ClS.—Ten g. of sulfanilic acid was diazotized and added to a solution of 7.5 g. of aminocymene suspended in 50 cc. of water containing 10 cc. of concd. hydrochloric acid. The red precipi-

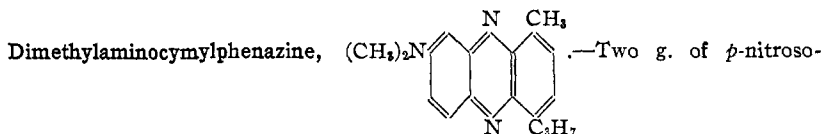
⁶ Wheeler and Smithey, *THIS JOURNAL*, **43**, 2611 (1921).

⁷ Kekulé, *Zeit. für Chem.*, **9**, 687 (1866).

⁸ Ridgway, "Color Standards and Color Nomenclature," Washington, D. C., 1912.

tate was recrystallized from methyl alcohol, giving Nopal red needles melting at 282°. It gives a cherry red color with dil. sulfuric acid, red brown with the concd. acid, becoming ruby red when heated.

Anal. Subs., 0.2513: AgCl, 0.0938. Calcd. for $C_{16}H_{20}O_3N_3ClS$: Cl, 9.58. Found: 9.24.



dimethylaniline was dissolved in hot methyl alcohol and to the solution was added 2.0 g. of aminocymene. The solution was boiled and the alcohol evaporated off, the residue being taken up with water. On standing, crystals separated which on recrystallizing from boiling water formed deep slate-blue needles, melting with decomposition at 48°. The dye is soluble in acetone and alcohol. Alkaline hydrosulfite reduces it to a colorless compound which is oxidized back to its original color with sodium perbromate. It belongs to the Eurhodine group of dyes. In dilute sulfuric acid it gives a red-green fluorescence, a dark brown color with the concd. acid and no change when heated.

Anal. Subs., 0.2722: 19.45 cc. of 0.1515 *N* HCl required for NH_3 . Calcd. for $C_{18}H_{21}N_3$: N, 15.04. Found: 14.84.

Derivatives of 2-Amino-5-bromo-*p*-cymene

Sulfate, $CH_3C_6H_7BrC_6H_3H_2SO_4$.—Aceto-amidobromocymene was refluxed with an excess of 50% sulfuric acid until solution took place. The crystals which separated on cooling were recrystallized from dilute alcohol. If recrystallized from sulfuric acid they remained wet; shining white needles, melting with decomposition at 123°.

Anal. Subs., 0.1964: 10.93 cc. of 0.1095 *N* KOH. Calcd. for $C_{10}H_{10}O_4NBrS$: H_2SO_4 , 30.08. Found: 29.62.

New Azo Dyes

These dyes were prepared by diazotizing the aminobromocymene at 0°, adding the phenol dissolved in alkali, precipitating the dye with acid and recrystallizing the dye from a suitable solvent.

TABLE I
PREPARATION

No.	Name ^a	Formula	Coupler	Solvent
1	5-(5-Bromocarvacrylazo)-2-cresol	$C_{17}H_{19}ON_2Br$	<i>o</i> -Cresol	Alcohol
2	5-(5-Bromocarvacrylazo)-catechol	$C_{16}H_{12}O_2N_2Br$	Catechol	Toluene
3	2-(5-Bromocarvacrylazo)-1,3,5-trihydroxybenzene	$C_{16}H_{17}O_3N_2Br$	Phloroglucinol	Alcohol
4	5-(5-Bromocarvacrylazo)-carvacrol	$C_{20}H_{22}ON_2Br$	Carvacrol	Alcohol
5	3-(5-Bromocarvacrylazo)-4-aminotoluene hydrochloride	$C_{17}H_{21}N_2BrCl$	Toluidine	Methyl alc.
6	3-(4-Sulfobenzene-azo)-5-bromocarvacrylamine hydrochloride	$C_{16}H_{19}O_3N_3BrCl$	Sulfanilic acid ^b	Chloroform
7	3-(2-Carboxybenzene-azo)-5-bromo-carvacrylamine hydrochloride	$C_{16}H_{18}N_3BrCl$	Anthranilic acid ^b	Methyl alc.

^a Based on analogy.

^b These acids were diazotized and coupled with aminobromocymene.

TABLE II
PROPERTIES

No.	Color	M. p., °C.	Behavior with concd. H ₂ SO ₄			Analyses			
			Cold	Hot	Dilute	Weight		Percentage halogen	
						Subs.	Ag hal.	Calcd.	Found
1	Chestnut-brown	112	Red-brown	Dark brown	Pale straw	0.1856	0.0972	22.96	22.38
2	Buffy-brown	235	Red-brown	Deep brown	Pale straw	.3916	.2238	24.21	24.32
3	Morocco-red	280	Red-purple	Deep purple	Pale pink	.1696	.0882	21.88	21.52
4	Liver-brown	192	Garnet	Dark red	Insol.	.2130	.1263	20.01	20.48
5	Mikado-brown	188	Ruby-red	Deep red	Straw	.2208	.1679 ^a	31.46	31.09
6	Deep chrome	+300 ^b	Dull brown	Dark brown	Light orange	.2374	.1460 ^a	25.71	25.62
7	Diamine brown	189	Deep purple	Deep red	Red-purple	.3162	.2512 ^a	32.62	32.48

^a AgCl + AgBr.^b Decomp.

Summary

1. The nitrate, hydrobromide and trichloro-acetate of 2-amino-*p*-cymene were prepared.

2. Aminocymene gave dyes with sulfanilic acid and with *p*-nitrosodimethylaniline, the latter being a Eurhodine.

3. The sulfanilic acid dye is an excellent raw material for making *o*-mylene-2,5-diamine.

4. The sulfate of 2-amino-5-bromo-*p*-cymene was prepared.

5. New azo dyes were prepared by coupling 2-amino-5-bromo-5-cymene with *o*-cresol, catechol, phloroglucinol, carvacrol and *p*-toluidine. Sulfanilic and anthranilic acids were diazotized and coupled with aminobromocymene.

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A NOTE CONCERNING A NEW METHOD FOR THE PRODUCTION OF CELLOBIOSE FROM CELLOBIOSE OCTA-ACETATE

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Cellobiose (or cellose as it was formerly called) is a disaccharide sugar obtained by partial hydrolysis or acetolysis of either cotton or wood cellulose. It is also the product of the action of certain microorganisms on cellulose.

Cellobiose is at present attracting considerable interest in the field of bacteriology. It has been found that cellobiose may be used as a test for the separation of two types of bacteria commonly found in water. Previously the identification of these two types of organisms has been the result of data compiled from correlated tests. Cellobiose, however, is utilized by *A. aerogenes* with acid and gas formation, whereas no changes