and calcium sulfate (plaster of Paris), a method applied by Palmer in the removal of pigments from blood serum, and that this pigment is carotin.

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

PARA-CYMENE STUDIES.

X. PARA-CYMYLENE-2,5-DIAMINE AND CERTAIN NEW DYES

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Of the four possible *p*-cymylenediamines two are known, the 2,6-diamine described by Alfthan[2] and the 2,5-diamine, the latter only in the form of its hydrochloride as described by Liebermann and Ilinski.[3] The free base was apparently isolated by Kehrmann and Messinger[4] for they state that it was so easily oxidized in the air that it could only be kept as the hydrochloride. Wallach and Schrader[5] prepared the diacetate, melting at 260°. Wheeler and Brooks[6] obtained the same diacetate on reducing 2-acetoamido-5-nitrocymene, followed by acetylation. A method superior to all others was found in the reduction of an azo derivative of 2-aminocymene, a method first used by Martius and Griess.[7] The aminocymene was coupled with diazotized sulfanilic acid, the resulting dye being reduced with stannous chloride. A poor yield is obtained if aniline is substituted for sulfanilic acid.

We locate the second amino group in position 5 for several reasons. This position is para to the amino group already present and is the point where coupling should take place according to analogous reactions. Secondly, the melting point of the diacetate is 260°, which is the same as that of the diacetate obtained from the reduction product of thymoquinonedioxime. Further proof was obtained by converting the diamine into thymoquinone, melting at 45° and described by Carstanjen,[8] and its monoxime, melting at 154–6°, and finally into hydrothymoquinone, melting at 139.5°.

p-Cymylene-2,5-diamine is so unstable in the air that no description of it has appeared in the literature. We isolated it in an atmosphere of nitrogen and at reduced pressure in a specially constructed apparatus.

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[1] An abstract of a thesis submitted in June, 1928, to the Faculty of the University of North Carolina by R. W. Bost in candidacy for the degree of Doctor of Philosophy.

[2] Alfthan, *Ber.*, **53**, 86 (1920).

[3] Liebermann and Ilinski, *Ber.*, **18**, 3200 (1885).

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

[5] Wallach and Schrader, *Ann.*, **279**, 375 (1894).

[6] Wheeler and Brooks, THIS JOURNAL, **49**, 2834 (1927).

[7] Martius and Griess, *Chem. Zentr.*, **1866**, 136.

[8] Carstanjen, *J. prakt. Chem.*, [2] **3**, 53 (1871).

It is a light yellow solid which on exposure to the air changes color within a few minutes, passing through deep red and green to blue. Oxidizing agents readily convert it into the quinone, ferric chloride in the cold giving a quantitative yield in less than fifteen minutes. Neither *p*-phenylenediamine nor *p*-toluylenediamine is oxidized to a quinone under like conditions. The diamine forms salts with great readiness, the picrate and benzoate forming almost instantaneously, whereas an ether solution of aniline, *o*-toluidine or aminocymene gives no apparent reaction with benzoic acid in twenty-four hours.

The diamine was characterized by its conversion into the following new compounds: 2,5-*bis*-(thioureido)-1-methyl-4-*iso*propylbenzene, 2,5-diureido-1-methyl-4-*iso*propylbenzene and *p*-aminocymyloxamido acid.

Two series of dyes were prepared: first, a group of diazo dyes by coupling with certain naphthols and amino acids; second, a group of azine dyes of the Eurhodine class. The first group gave blue, yellow and red colors while the second gave brown and purple shades. The dye obtained with 2-naphthol colors wool a blackish violet, whereas the thionaphthol dyes wool a light buff; thus the sulfur shows a strong hypsochromic effect. The dye obtained with the naphthol disulfonic acid possesses a very high tinctorial power and the dye-bath exhausts completely.

The *iso*propyl group in the diamine is very sensitive, for in bromination and nitration reactions it is largely destroyed.

Experimental Part

Reduction of 5-(4-Sulfobenzeneazo)-carvacrylamine Hydrochloride.—This compound was prepared as described by Wheeler and Cutlar,[9] who coupled 2-aminocymene with diazotized sulfanilic acid. Its reduction was carried out as follows: 47 g. of the hydrochloride was slowly added to a boiling solution of 75 g. of stannous chloride, 65 cc. of concd. hydrochloric acid and 500 cc. of water. When the last trace of color had disappeared, the solution was cooled and treated with an excess of sodium hydroxide. The diamine was extracted with ether and converted into the hydrochloride by passing hydrogen chloride gas into the solution; yield, 26 g. or 77.9% of the theoretical.

***p*-Cymylene-2,5-diamine,** $C_6H_2CH_3C_3H_7(NH_2)_2$.—The free base was isolated by distillation in an atmosphere of nitrogen and at reduced pressure in an apparatus shown in the accompanying diagram. The air in the system ABIDJR was displaced by nitrogen from a cylinder connected with A. Stopcock B was then turned so that the nitrogen displaced the air in the system ABGC. An aqueous solution of the diamine and 200 cc. of ether was admitted through buret E into funnel G and the solution saturated with nitrogen. In the meantime the system IDJR was evacuated by a pump connected to R. A 15% solution of sodium hydroxide was added to the diamine salt solution in G through buret E until the phenolphthalein present showed excess thereof. The stream of nitrogen passing through the solution served to stir the diamine so that it readily dissolved in the ether layer. The water layer was drawn off through F. The path of the nitrogen stream was changed so as to pass from A through C into G. Stopcock B was opened into the evacuated system IDJR, whereupon the ether solution was drawn from G into flask I. A gentle stream of nitrogen was then passed through the

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[9] Wheeler and Cutlar, This Journal, **49**, 2819 (1927).

system ABIDJR and the ether distilled off spontaneously from flask I at a pressure around 120 mm. A light yellow solid remained in the flask into which 200 cc. of methyl alcohol, previously saturated with nitrogen, was admitted in a manner similar to that in which the ether was admitted. The alcohol took up the few droplets of moisture present and also dissolved the diamine. The alcohol was distilled at 120–130 mm. and a temperature around 30°. The diamine remained as a yellow, solid mass, apparently consisting of needles though not well defined.

The diamine in I was dissolved in ether saturated with nitrogen and admitted through the same channel as the alcohol. A partial vacuum was produced in G by evacuating the system ACGBIDJR. C was closed and a rapid stream of nitrogen was passed through ABIDJR until the pressure was one atmosphere. D was closed and B opened into the partial vacuum G whereupon the ether solution of the diamine in I was drawn over into G. Nitrogen was then bubbled through ABGC and the diamine precipitated by the addition of petroleum ether to G through buret E. Then F was connected with L by rubber tubing and the finely divided precipitate of the diamine filtered by suction into the nitrogen filled desiccator P.

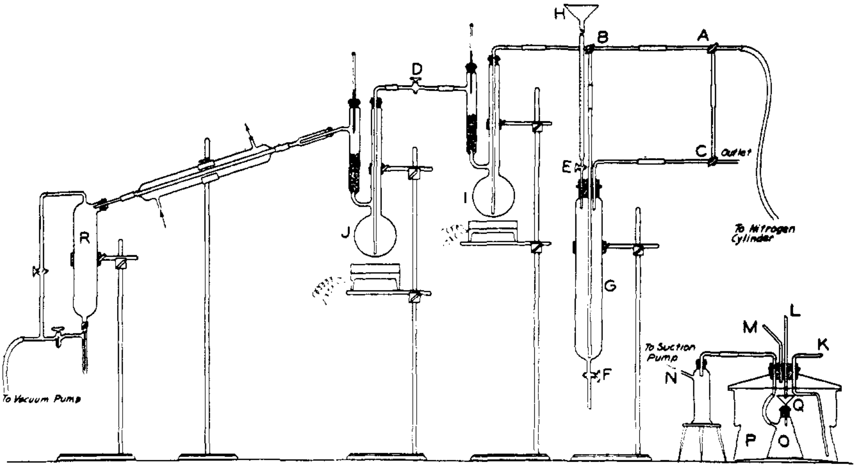

Fig. 1.—Apparatus.

Dibenzoate, $C_6H_2CH_3C_3H_7(NHCOC_6H_5)_2$.—The benzoate was prepared in the usual way in alkaline solution with benzoyl chloride. The product was recrystallized from hot alcohol giving fine, white needles, soluble in acetone and alcohol; m. p. 280°; yield, quantitative.

Anal. Subs., 0.2082: 7.27 cc. of 0.1524 *N* HCl required for NH_3. Calcd. for $C_{24}H_{24}N_2O_2$: N_2, 7.52. Found: 7.45.

Quinones

The 2,5-cymo-*p*-quinone, its oxime and the corresponding hydroquinone were prepared for orientation purposes. They have been described by Carstanjen.[8]

2,5-Cymo-*p*-quinone.—Four g. of the diamine salt was dissolved in 200 cc. of 2% acetic acid. To this solution was added 5 g. of chromic acid in 200 cc. of water. After stirring for thirty minutes, the brownish black precipitate was filtered off, dried and purified by sublimation to give long, slender, glistening yellow needles; m. p. 45.5°.

Its monoxime was prepared by heating the quinone with hydroxylamine hydrochloride for five hours on the water-bath. The product was recrystallized by dissolving in ether and adding petroleum ether, yielding fine, brownish-yellow needles, m. p. 154–156°.

2,5-Cymo-*p*-hydroquinone.—The quinone was dissolved in the least possible amount of acetone and a 2% solution of titanium chloride added until reduction was complete. The product was extracted with ether; fine, white needles; m. p. 139°.

Salts

The salts indicated in the table were made by mixing the constituents in the cold. To obtain the hydrochloride dry hydrogen chloride was passed into an ether solution of the diamine. For the hydrobromide and nitrate the corresponding acids were used with gentle heating. These three salts were recrystallized from absolute alcohol. The other salts were prepared by mixing ether solutions of the constituents and washing the salt with ether. All are soluble in water, alcohol and acetone but difficultly soluble in ether. Analyses were made by titrating with sodium hydroxide, using phenolphthalein as indicator.

TABLE I

DATA ON THE SALTS

Salt	Crystal form	M. p., ° C.	Analysis, acid Calcd., %	Found, %
Hydrochloride (di)	Fine granules	323 (decomp.)	30.75	30.77
Hydrobromide (di)	Microscopic needles	330 (decomp.)	49.63	49.13
Nitrate (di)	Microscopic needles	196 (decomp.)	43.42	43.13
Chloro-acetate (mono)	Microscopic needles	144	36.53	36.65
Dichloro-acetate (di)	Microscopic needles	165	61.10	60.70
Trichloro-acetate (di)	Granular	171	66.56	67.08
Bromo-acetate (mono)	Needles	148 (decomp.)	45.85	44.32
Benzene sulfonate (di)	Granular	Decomp.	69.28	69.22
Benzoate (mono)	Microscopic needles	145	42.65	42.53
o-Chlorobenzoate (mono)	Microscopic needles	161	48.81	49.10
3,5-Dinitrobenzoate (mono)	Granular	199 (decomp.)	56.37	56.67
2,4,6-Trinitrobenzoate (mono)	Needles	130 (decomp.)	61.05	60.85
Picrate (di)	Needles	207 (decomp.)	18.10	17.93

Condensation Products

2,5-Bis-(thio-ureido)-1-methyl-4-*iso*propylbenzene, $C_{10}H_{12}(NHCSNH_2)_2$.—A solution of 2.0 g. of the diamine salt was poured into a solution of 1.64 g. of potassium sulfocyanate. The solution was evaporated to dryness and the residue kept on the steam-bath for two hours. The material was then washed several times with boiling water, filtered and recrystallized from hot methyl alcohol; white, granular substance; m. p. 235–237°. It is soluble in alcohol but insoluble in water, ether and benzene; yield, 1.2 g.

Anal. Subs., 0.2024: 18.69 cc. of 0.1524 N HCl required for NH_3. Calcd. for $C_{12}H_{18}N_4S_2$: N_2, 19.85. Found: 19.70.

2,5-Diureido-1-methyl-4-*iso*propylbenzene, $C_{10}H_{12}(NHCONH_2)_2$.—To a solution of 0.5 g. of the diamine salt dissolved in 10 cc. of water was added dropwise a solution of 1 g. of potassium cyanate in 5 cc. of water. The mixture was heated on the steam-bath for one hour, the product filtered off, washed with hot water, then with alcohol and finally with ether. It consisted of a white powder insoluble in water and rather difficultly soluble in alcohol and ether. It did not melt under 350°; yield, 0.6 g.

Anal. Subs., 0.1076: 11.37 cc. of 0.1524 *N* HCl required for NH_3. Calcd. for $C_{12}H_{18}O_2N_4$: N_2, 22.39. Found: 22.54.

***p*-Aminocymyloxamido Acid,** $C_{12}H_{16}O_3N_2$.—1.44 g. of the diamine salt was dissolved in 50 cc. of water and the base set free by the addition of sodium hydroxide. The diamine was shaken out with ether and the ether solution carefully dried. To this solution was added an ether solution of 0.55 g. of anhydrous oxalic acid. A precipitate formed immediately but the mixture was refluxed for two hours, the ether distilled off and replaced with 75 cc. of absolute alcohol and then refluxed for fifteen hours. The crystals melt at 210–211°. The product is rather soluble in water but difficultly soluble in alcohol and ether; yield, 0.21 g. The success of the reaction depends upon having the ether solution of the diamine dry before adding the oxalic acid.

Anal. Subs., 0.2040: 11.10 cc. of 0.1524 *N* HCl required for NH_3. Calcd. for $C_{12}H_{16}O_3N_2$: N_2, 11.86. Found: 11.60.

Diazo Dyes

These dyes were prepared by diazotizing *p*-cymylene-2,5-diamine at 0°, adding the phenol dissolved in alkali, precipitating the dye with acetic acid and recrystallizing the product from a suitable solvent.

Table II

Disazo Dye Data

No.	Coupler	Solvent	Formula	Calcd., %	Found, %	M. P., °C.
1	Resorcinol	Dilute alcohol	$C_{22}H_{22}O_4N_4$	N, 13.72	13.43	168–170
2	2-Naphthol	Benzene	$C_{30}H_{26}O_2N_4$	N, 11.81	11.34	295–298 (dec.)
3	Sulfanilic acid	Alcohol	$C_{22}H_{26}O_6N_6S_2Cl_2$	S, 10.59	10.19	100 (dec.)
4	2-Naphthol-3,6-disulfonic acid	Methyl alcohol	$C_{30}H_{20}O_{14}N_4S_4Na_6$	S, 13.84	12.42	Above 340
5	Naphthionic acid	Alcohol	$C_{30}H_{28}O_6N_6S_2$	S, 10.13	10.33	270–272 (dec.)
6	2-Thionaphthol	Carbon tetrachloride	$C_{30}H_{26}N_4S_2$	S, 12.66	13.07	138–140

Table III

Dyeing Colors

The amount of dye used was 4% of the weight of the fiber

No.	Wool	Silk	Cotton	Behavior with sulfuric acid		
				Cold	Hot	Dilute
1	Chestnut brown	Deep chestnut brown	Pale salmon	Brown	Deep brown	Pale brown
2	Dull violet black	Blackish-purple	Dusky violet blue	Light blue	Dark brown	Brown
3	Pale orange yellow	Pale orange yellow	Pale orange yellow	Pale brown	Dark brown	Brown
4	Diamine azo blue	Diamine azo blue	Light Windsor blue	Dark violet	Reddish-brown	Pale brown
5	Dragon's blood red	Dragon's blood red	Salmon	Cherry red	Reddish-brown	Brown
6	Light buff	Warm buff	White	Pale straw	Greenish yellow	Greenish brown

Azine (Eurhodine) Dyes

Three Eurhodine dyes were prepared by dissolving the nitroso compound in 100 cc. of hot methyl alcohol and adding to this solution the diamine salt dissolved in 50 cc. of methyl alcohol. The mixture was refluxed for thirty minutes when the alcohol was distilled off and replaced with water. The dye was set free on the addition of weak ammonia. The product was recrystallized from dilute alcohol.

TABLE IV

AZINE (EURHODINE) DYES

	1	2
Intermediate	*p*-Nitrosodimethylaniline	*p*-Nitrosophenol
Solvent	Dilute alcohol	Dilute alcohol
Crystal color	Blue black	Dark brown
Formula	$C_{18}H_{22}N_4$	$C_{16}H_{17}ON_3$
M. p., ° C.	300 (dec.)	200–206 (dec.)
N, calcd., %	19.04	15.73
N, found, %	18.96	15.91
Color on wool	Purplish black	Dusky brown
Color on silk	Purplish black	Dusky brown
Color on cotton	Plumbeous	Pale purple drab

Summary

1. *p*-Cymylenediamine prepared by reducing the dye obtained by coupling 2-amino-*p*-cymene with diazotized sulfanilic acid is shown to be the 2,5-diamine.

2. A series of thirteen salts with inorganic and organic acids was prepared.

3. Condensation products were obtained with potassium sulfocyanate, potassium cyanate and oxalic acid.

4. A series of disazo dyes was prepared by coupling the diamine with certain naphthols and amino acids.

5. Two azine dyes of the Eurhodine class were prepared.

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