[COMMUNICATION NO. 1190 FROM THE KODAK RESEARCH LABORATORIES]

CERTAIN DERIVATIVES OF *sym.*-DIMETHYL-*p*-PHENYLENEDIAMINE

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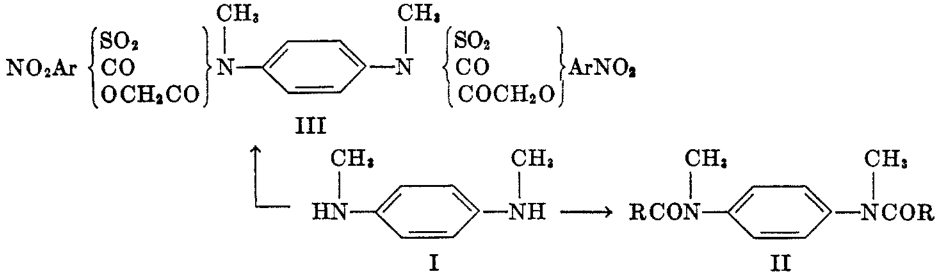
Received April 12, 1948

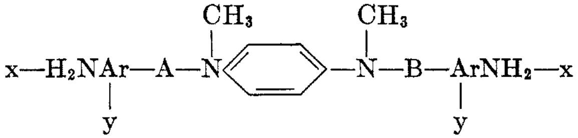
sym.-Dimethyl-*p*-phenylenediamine (I) can be converted by relatively simple reactions into amines which can be tetrazotized and transformed into azo dyes, and into surface-active substances such as *bis*-quaternary salts, and *bis*-acyl derivatives.

For instance, it is easily acylated, the nature of the product depending upon the acyl halide selected. Dipalmitoyl and distearoyl derivatives (II; R = $C_{15}H_{31}$, $C_{17}H_{35}$) result when palmitoyl and stearoyl chlorides are used. Of more interest are the chlorides of nitrated aromatic carboxylic or sulfonic acids, which give rise to nitro derivatives (III), the reduction of which leads to diazotizable amines, and, hence, to azo dyes. The use of the acid chlorides of halogenated aliphatic acids (*e.g.*, chloroacetyl chloride) furnishes a means of preparing *bis*-quaternary salts with bases, some of which have surface-active properties. A variation in the acid chloride is 2,4-dinitrochlorobenzene; selective reduction of the product of the reaction leads to a diamine, which can be used for preparing azo dyes.



The following nitrated aromatic acid chlorides have been used: *p*-nitrobenzoyl-; *m*- and *p*-nitrobenzenesulfonyl-; 2-sulfo-4-nitrobenzoyl-; 4-nitrophenoxyacetyl-; and 1-nitro-2-naphthoxyacetyl-.

The corresponding amines (IV) were prepared by catalytic reduction of the nitro compounds, using Raney nickel. In the general formula, A and B represent the linkages between the aromatic ring, Ar, and the nitrogen of the phenyl-



IV

enediamine, and x is the position of the amino group (y is any other substituent; unless otherwise indicated, it represents hydrogen).

A list of the amines is as follows:

V. 1,4-*bis*-(4′ -Aminobenzoyl-N-methylamino)benzene; A, B = CO; x = 4; Ar = C_6H_4

VI. 1,4-*bis*-(3′-Aminobenzenesulfonyl-N-methylamino)benzene; A, B = SO_2; x = 3; Ar = C_6H_4

VII. 1,4-*bis*-(4′-Aminobenzenesulfonyl-N-methylamino)benzene; A, B = SO_2; x = 4; Ar = C_6H_4

VIII. 1,4-*bis*-(4′-Amino-2′-sulfobenzoyl-N-methylamino)benzene; A, B = CO; x = 4; y = 2 (SO_3H); Ar = C_6H_3

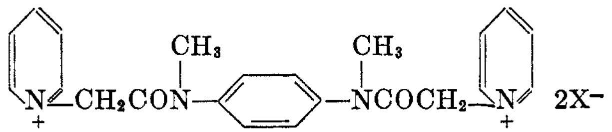
IX. 1,4-*bis*-(4′-Aminophenoxyacetyl-N-methylamino)benzene; A = OCH_2-CO; B = $COCH_2O$; x = 4; Ar = C_6H_4

X. 1,4-*bis*-(1′-Amino-2′-naphthoxyacetyl-N-methylamino)benzene; A = OCH_2CO; B = $COCH_2O$; x = 1′; Ar = $C_{10}H_6$

XI. 1,4-*bis*-[4′(or 2′)-Amino-2′(or 4′)-nitrophenyl-N-methylamino]benzene; no A; x = 4′ (or 2′); y = 2′ (or 4′)

Azo dyes were subsequently prepared from the *bis*-diamines and the usual benzene and naphthalene dye intermediates. Those obtained from sulfonic acids dyed wool directly; those from J acid dyed both wool and cotton; while those without sulfonic acid groups colored cellulose acetate. The dyes formed are summarized in Table I, which shows the amine used, the coupling component, and the color of the dyed fabric. Mixed disazo, trisazo, and tetrakisazo dyes were also prepared. The most brillant colors resulted when the aminophenoxyacetyl derivative (IX) was used.

The *bis*-quaternary salt shown in Formula XII (X = Cl) was obtained by treating the *sym.*-dimethyl-*p*-phenylenediamine with two equivalents of chloroacetyl chloride, followed by addition of the *bis*-halide (II; R = $ClCH_2$) thus formed to pyridine.



XII

EXPERIMENTAL

Acylation. N,N′-Dimethyl-*p*-phenylenediamine was isolated as the solid oxalate; this salt was used in most operations, the free base being liberated by alkali. In some instances when the absence of water was essential, the free base was extracted with ether.

N,N′-Distearoyl-N,N′-dimethyl-p-phenylenediamine (II; R = $C_{17}H_{35}$). To a suspension of 3.2 g. of the oxalate of N,N′-dimethyl-*p*-phenylenediamine in sodium hydroxide solution (4 g. of the solid dissolved in 50 ml. of water) 6.7 g. of stearoyl chloride was added over a period of one-half hour. The reaction mixture became very viscous. The purplish solid was then triturated with alcohol and separated by filtration. It was twice recrystallized from acetone; the yield was 52%; it melted at 77–79°.

N,N′-Dipalmitoyl-N,N′-dimethyl-p-phenylenediamine (II; R = $C_{15}H_{21}$) was similarly prepared in a yield of 73.5%, and recrystallized from pyridine. It melted at 88–90°.

Anal. Calc'd for $C_{40}H_{72}N_2O_2$: C, 78.4; H, 11.8.
Found: C, 78.5; H, 11.9.

TABLE I

SYMMETRICAL DISAZO DYES

AMINE USED	COUPLING COMPONENT	COLOR OF DYE FORMED	
		ON WOOL	OTHER FIBER[a]
V	1-Hydroxynaphthalene-5-SO_3H	Red-orange	
V	2-Hydroxynaphthalene-7-SO_3H	Orange	
V	1-Hydroxynaphthalene-3,6-diSO_3H	Red-orange	
V	1-Hydroxynaphthalene-3,8-diSO_3H	Red-orange	
V	2-Hydroxynaphthalene-3,6-diSO_3H	Scarlet	
V	2-Hydroxynaphthalene-6,8-diSO_3H	Orange	
V	1,8-Dihydroxynaphthalene-3,6-diSO_3H	Dull magenta	
V	1-Amino-8-hydroxynaphthalene-2,4-diSO_3H	Magenta	
V	1-Amino-8-hydroxynaphthalene-3,6-diSO_3H	Dull magenta	
V	1-Acetamino-8-hydroxynaphthalene-3,6-diSO_3H	Rose	
V	2-Amino-5-hydroxynaphthalene-7-SO_3H	Orange	Old rose, C
V	2-Benzamido-5-hydroxynaphthalene-7-SO_3H	Red-orange	Red-orange, C
V	2-Amino-8-hydroxynaphthalene-6-SO_3H	Maroon	
V	2-Amino-8-hydroxynaphthalene-3,6-diSO_3H	Maroon	
V	N-Ethyl-N-β-hydroxyethylaniline		Yellow, CA
V	N,N-Di-[β-hydroxyethyl] aniline		Yellow, CA
V	7-Methyl-1-glyceryl-1,2,3,4-tetrahydroquinoline[b]		Red, CA
VI	1-Hydroxynaphthalene-4-SO_3H	Orange	
VI	1-Amino-8-hydroxynaphthalene-2,4-diSO_3H	Maroon	
VI	5-Hydroxy-1-glycerylaminonaphthalene[b]		Violet, CA
VII	4-Acetamino-2-glycerylaminoanisole[b]		Salmon, CA
IX	1-Hydroxynaphthalene-4-SO_3H	Carmine	
IX	1-Amino-8-hydroxynaphthalene-2,4-diSO_3H	Violet	
X	1-Amino-8-hydroxynaphthalene-2,4-diSO_3H	Brown-violet	
XI	5-Hydroxy-1-glycerylaminonaphthalene[b]		Red-violet, CA

[a] C = cotton; CA = cellulose acetate. [b] Glyceryl = 2,3-dihydroxypropyl.

TABLE II

ANALYSES FOR NITROGEN

AMINE	EMPIRICAL FORMULA	CALC'D, %	FOUND, %
V	$C_{22}H_{22}N_4O_2$	14.9	14.5
VI	$C_{20}H_{22}N_4O_4S_2$	12.6	12.6
IX	$C_{24}H_{26}N_4O_4$	12.9	12.8

These two derivatives are softening agents for textiles. Analogous products are mentioned in a patent (1) as being water-repellent, but no examples are given.

N,N'-Dichloroacetyl-N,N'-dimethyl-p-phenylenediamine (II; R = $ClCH_2$). To a suspension of 31.6 g. of the diamine oxalate in 42.4 g. of sodium carbonate and 300 ml. of water was added gradually 40 g. of chloroacetyl chloride. The mixture was stirred for an additional two hours, and the product separated by filtration. The yield was 30 g. It was recrystallized from acetic acid; the pink crystals melted at 190°, with decomposition.

N,N'-Di-3'-chloroacetylaminobenzenesulfonyl-N,N'-dimethyl-p-phenylenediamine (IV; A = SO_2, Ar = C_6H_4, x = 3) was prepared from a solution of 4 g. of the diamine, VI, in 100 ml. of dioxane, to which was added 1 g. of solid sodium carbonate, followed by 5 g. of chloroacetyl chloride, dropwise. The solid product was removed after three hours and recrystallized from acetic acid. It melted at 184°.

Anal. Calc'd for $C_{24}H_{24}Cl_2N_4O_6S_2$: N, 9.4. Found: N, 9.2.

N,N'-Di-ω-carbomethoxyvaleryl-N,N'-dimethyl-p-phenylenediamine [II; R = $CH_3OCO-(CH_2)_4$] was prepared from the oxalate as above. It melted at 73–74°.

Anal. Calc'd for $C_{22}H_{32}N_2O_6$: C, 62.9; H, 7.6; N, 6.7.
Found: C, 63.1; H, 7.6; N, 6.6.

N,N'-Di-p-nitrobenzoyl-N,N'-dimethyl-p-phenylenediamine.[1] To a suspension of 15 g. of N,N'-dimethyl-*p*-phenylenediamine oxalate and 15.7 g. of sodium carbonate in 200 ml. of water, 29.5 g. of *p*-nitrobenzoyl chloride was added, with stirring, at room temperature during one-half hour, after which the whole was warmed at 50–60° for three hours. The cooled solution was filtered from the brownish solid, and the latter extracted with 350 ml. of boiling alcohol to remove *p*-nitrobenzoic acid. The crude residue (14.2 g.) was recrystallized from 200 ml. of glacial acetic acid; the acylated diamine separated as pale yellow needles; m.p. 256°.

In a similar manner there was prepared *N,N'-di-m-nitrobenzenesulfonyl-N,N'-dimethyl-p-phenylenediamine*; m.p. 215–217°, from dioxane or acetic acid, in 68% yield. It was also obtainable by using the free base instead of the oxalate, in which case the solution was allowed to stand at room temperature for two days instead of being heated. The *para*-nitro isomer melted above 300°. The di-*p*-nitrophenoxyacetyl (m.p. 233°) and 1-amino-2-naphthoxyacetyl derivatives (m.p. above 275°) were likewise prepared from the oxalate.

The 2-sulfo-4-nitrobenzoyl derivative was obtained as follows: The acid chloride of 2-sulfo-4-nitrobenzoic acid was first prepared from 43 g. of the potassium salt of the acid by means of 21 g. of thionyl chloride in 300 ml. of pyridine. To this solution was added 15 g. of the free base (prepared from the oxalate by making its aqueous suspension alkaline, shaking, extracting with ether, and removing the solvent) and the mixture stirred on the steam-bath for three hours. Upon cooling, 18 g. of the nitro compound separated.

The *1,4-bis-(2',4'-dinitrophenyl-N-methylamino)benzene* was obtained by refluxing a mixture of 50 g. of the oxalate, 98.5 g. of 2,4-dinitrochlorobenzene, 76 g. of anhydrous sodium acetate, and 400 ml. of alcohol, with stirring, for five hours; the product that separated on cooling was removed and recrystallized from acetic acid, from which it separated in minute red-brown crystals, m.p. 238°.

All the nitroacyl compounds were reduced to the corresponding amines catalytically in alcohol in the presence of Raney nickel. The 2,4-dinitrophenyl derivative was reduced selectively, using sodium sulfide, but the location of the amino group was not determined. The melting points of the amines were as follows: *p*-aminobenzoyl, 255°; *m*-aminobenzenesulfonyl, 218°; *p*-aminobenzenesulfonyl, 212–226°; *p*-aminophenoxyacetyl, 207°; 2(or 4)-amino-4(or 2)-nitrophenyl, 221°. Analytical figures for representative amines are collected in Table II.

Quaternary salts. The "double-ender" salt (XII; X = Cl) was formed very easily by merely warming a mixture of pyridine and N,N'-dichloroacetyl-N,N'-dimethyl-*p*-phenylenediamine until the solid was entirely dissolved. In a few minutes the salt began to separate, and soon the mixture was completely solid. It was triturated with acetone and the salt collected. The salt dissolved readily in methanol and water, but was insoluble in ether and acetone. It has no true melting point; if a specimen in a capillary tube is inserted in a bath, preheated to about 190°, it decomposes at about 195°.

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[1] Dr. Walter A. Gregory assisted in the preparation of large quantities of certain of these intermediates.

Anal. Calc'd for $C_{22}H_{24}Cl_2N_4O_2$: Cl, 15.9. Found: Cl, 15.2.

The perchlorate (XII; X = ClO_4) separated on mixing aqueous solutions of the above chloride and sodium perchlorate. It required several crystallizations from water, using Norit, to get a colorless product. It decomposed above 220°.

bis-Azo dyes from the various diamines (Table I). These were all made in the same general way: (a) *Sulfonic acid group present.* The diamine (2.5 g.) was dissolved in hot hydrochloric acid (5 ml. of concentrated acid in 25 ml. of water), chilled to precipitate the salt in a finely-divided condition, and tetrazotized at 5° by sodium nitrite. After fifteen minutes, the solution was added, with stirring, to 3 g. of 1-naphthol-4-sulfonic acid in 35 ml. of water containing 2.8 g. of sodium hydroxide. The orange dye was salted out after one hour and purified by two re-saltings.

(b) *No sulfonic acid group.* The tetrazotization was performed in the same manner, and the solution added to a solution of an equivalent amount of the amine, dissolved in 5% hydrochloric acid. Coupling was brought about by adding a strong solution of sodium acetate; when coupling was complete, the dye was precipitated by the addition of aqueous sodium hydroxide.

(c) *Mixed disazo dye.* A representative dye was prepared by coupling the 4′-aminobenzoyldiamine (V) first with 2,4-diaminotoluene in acid solution, and then, after making strongly alkaline, with R salt. It dyes wool orange.

(d) *Trisazo dye.* The 4′-aminophenoxyacetylamine (IX) was tetrazotized and coupled first with *m*-aminooxanilic acid in weakly acid solution, and then with R salt in alkaline solution. A reddish dye separated; it was collected and dried. It was next diazotized and again coupled with R salt in alkaline solution; the dye slowly separated, was filtered off, and purified by dissolving and salting out with a saturated solution of sodium chloride. It dyes wool a maroon red.

(e) *Tetrakisazo dye.* The diamine (V) was tetrazotized as usual, and coupled in acid solution, *p*H 4.2, with 2-ethoxy-1-naphthylamine-6-sulfonic acid. The *p*H was raised first to 5.3 and then to 6.0, whereupon the dye precipitated. The dried dye was dispersed in very weak alkali, acidified and tetrazotized in the usual manner, and coupled with chromotropic acid in strongly alkaline solution. The brown dye was salted out with saturated salt solution. It dyes wool a dull reddish-brown, which becomes yellow-brown on top-chroming.

SUMMARY

sym.-Dimethyl-*p*-phenylenediamine has been acylated by a variety of acyl halides. The latter included long-chain aliphatic acyl, haloacyl, ω-carboalkoxyacyl, nitroarylcarboxy, nitroarylsulfonyl, and nitroaryloxyacyl chlorides, and 2,4-dinitrochlorobenzene.

The acyl derivatives were converted, by suitable manipulation, into azo dyes, and quaternary ammonium salts.

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REFERENCE

(1) AELONY, U. S. Patent 2,342,624 (1944); [*Chem. Abstr.*, **38**, 4812 (1944)].