TABLE I

DIBENZOFURYL-TRIPHENYL-LEADS AND THE HYDROGEN CHLORIDE CLEAVAGE PRODUCTS

$R(C_6H_5)_3Pb$ compounds						Cleavage products[a]	
				Pb, %			
R	Yield, %	Solvent for crystn.	M. p., °C.	Calcd.	Found	Phenyl-lead compounds, %	Dibenzofuran, %
2-Dibenzofuryl	71.4	Pet. ether	158.5–159.5	34.24	33.96, 33.74	56	53
3-Dibenzofuryl	53	Pet. ether	125–126	34.24	33.90	42.8	34[b]
4-Dibenzofuryl	[c]	[c]	99–100	34.24	34.19	47.2	24[d]

[a] The percentages of phenyl-lead compounds are those calculated from the sum of triphenyl-lead chloride and diphenyl-lead dichloride isolated. These values are lower than the quantities actually formed, for the yield of diphenyl-lead dichloride was based on the yield of pure tetraphenyl-lead formed after heating the non-melting diphenyl-lead dichloride with phenylmagnesium bromide. For example, from the cleavage of 2-dibenzofuryl-triphenyl-lead there was isolated from 2.42 g. (0.004 mole) of unsymmetrical lead compound, 0.8 g. of crude dibenzofuran which gave 0.36 g. or 53.8% of pure dibenzofuran. The yield of triphenyl-lead chloride was 0.4 g. or 21.1%, and that of diphenyl-lead dichloride was 0.6 g. or 34.7%. The yield of dibenzofuran based on the phenyl leads isolated was 96.5%. [b] 0.87 g. or 0.0014 mole of 3-dibenzofuryl-triphenyl-lead was used in the cleavage experiment. The yield of dibenzofuran based on the phenyl-leads isolated was 79.4%. [c] The 4-dibenzofuryl-triphenyl-lead was crystallized with difficulty, the product (after removing excess dibenzofuran by steam distillation) forming a colorless oil that partially solidified to a plastic mass on standing. An alcoholic solution that was allowed to stand for several days deposited the white crystals. 2.85 g. (0.0047 mole) of 4-dibenzofuryl-triphenyl-lead was used in the cleavage experiment. [d] The yield of dibenzofuran based on the phenyl-leads isolated was 50.8%.

RMgBr compounds (determined by the usual titration procedure), was 73.5% for the 2-compound and almost quantitative for 3-dibenzofurylmagnesium bromide.

The cleavage reactions with hydrogen chloride were effected in chloroform. The scission products were identified in the customary manner: triphenyl-lead chloride and dibenzofuran by the method of mixed melting points and diphenyl-lead dichloride by conversion to tetraphenyl-lead by means of phenylmagnesium bromide.

Summary

1. Indirect resolution of the supposed isomeric nitrodibenzofuran melting at about 110° has shown that some 2-nitrodibenzofuran is obtained incidental to the nitration of dibenzofuran.
2. Pyrolysis of resorcinol over heated tungstic oxide gives 3- and not 1-hydroxydibenzofuran.
3. The relative ease of nuclear substitution reactions of dibenzofuran can be correlated with the hydrogen chloride scission of the 2-, 3- and 4-dibenzofuryl-triphenyl-leads. The predominant RH product isolated from cleavage of the unsymmetrical lead compounds is dibenzofuran.

AMES, IOWA RECEIVED NOVEMBER 19, 1934

[CONTRIBUTION NO. 247 FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Magenta Series. I. The Preparation and Spectrophotometric Study of the Lower Basic Members

BY JOHN T. SCANLAN

Basic Magenta (Fuchsine) is a most important biological stain. Unfortunately, commercial samples of this dye vary widely in quality. These variations are quite troublesome in the exacting technique of biological staining. The object of this investigation is to determine the causes of the difficulties and to produce a standard product of uniform quality. Most commercial Magentas are mixtures of two or more of the lower homologs (see Table I) of the series. In their manufacture subsidiary dyes are also produced, such as the yellow diaminodiphenylacridine, known as Chrysaniline or Phosphine, and its homologs, and dyes of the Induline and Nigrosine groups. Furthermore, the products may be contaminated by the intermediates used.

The first step in this investigation was the preparation of the four lower homologs of the series for the determination of their relative merits in biological applications. In the course of this work certain anomalies were observed, and considerable further study was necessary to explain them. The spectrophotometric data necessary for the identification and evaluation of commercial samples were obtained.

Nomenclature.—Considerable confusion has resulted from the various names acquired by the members of this group, many of them relics from the days when their constitution was not known. The only accepted system of nomenclature which can be applied to all the compounds to be discussed is rather cumbersome. Therefore, to distinguish between the homologs in the simplest way, the name Magenta is used with a number which indicates the number of methyl groups substituted in the nuclei. In this paper we are concerned only with those homologs in which the methyl groups are ortho to the amino groups and in which there is not more than one in each nucleus. The relationship between the various names is made clear in Table I.

TABLE I

Name used in this paper	Scientific name	Common name
Magenta O[a]	4,4′-Diaminofuchsonimonium chloride	Pararosaniline chloride
Magenta I	3-Methyl-4,4′-diaminofuchsonimonium chloride	Rosaniline chloride Homorosaniline chloride Fuchsine[b] Magenta[b]
Magenta II	3,3′-Dimethyl-4,4′-diaminofuchsonimonium chloride	None
Magenta III	3,3′,3″-Trimethyl-4,4′-diaminofuchsonimonium chloride	New Fuchsine New Magenta

[a] The name in the first column means the chloride. The corresponding acetate, carbinol base and sulfonated derivative would be referred to as Magenta O Acetate, Magenta O Base and Acid Magenta O, respectively.

[b] These two names are usually applied to various mixtures of the three lowest homologs.

Method of Preparation.—Magenta[1] was first prepared by the oxidation of crude aniline with stannic chloride. Many other oxidizing agents have been used. The most common one is nitrobenzene, used in conjunction with ferrous chloride or iron filings. In the nitrobenzene process as generally used commercially, the other ingredients are *p*-toluidine, *o*-toluidine and aniline, and the product is a mixture of three homologs, Magenta O,[2] Magenta I[3] and Magenta II.[4]

A newer process, known as the New Magenta or Formaldehyde Process, also employs nitrobenzene with ferrous chloride or iron filings. The other intermediates usually are 3,3′-dimethyl-4,4′-diaminodiphenylmethane and *o*-toluidine, in which case the product is Magenta III.[5] When 4,4′-diaminodiphenylmethane and aniline are used instead, the product is Magenta O. This latter process was at first chosen for the preparation of the pure homologs because of statements in various text-books to the effect that it gives homogeneous products instead of the mixtures obtained by the older method, but it proved unsatisfactory for the purpose.

The reaction involved is always given so as to imply that the product is obtained simply by the addition of a third benzene nucleus to the diphenylmethane compound. That the reaction does not follow this course becomes evident from an examination of the data recorded in Table II and the corresponding curves in Fig. 1.

It will be observed that when all three nuclei have similar substituents, the resulting dyes are those which would be obtained if the reaction took place as indicated, but when one of the three nuclei differs from the other two, anomalous results are obtained. For example, an examination of the spectrophotometric data and curves for the products obtained in Experiments 2F and 3F shows that the maximum absorption of the dye, which presumably contains one benzene nucleus with a substituted methyl group, lies at a point closer to the red end of the spectrum than does that of the dye which presumably contains two such methyl substituted benzene nuclei. This fact is also illustrated by the value of the ratio of the extinction coefficient, E, at 520 mμ to that of E at 560 mμ. The value of this ratio in Experiment 2F is lower than in Experiment 3F, indicating that the maximum absorption of the former product lies at a higher wave length than that of the latter product. This is, of course, the reverse of what it should be.

The possibility that this anomaly in the absorptive properties might be due to development of the quinoid structure in a methyl substituted nucleus in one case and in an unsubstituted nucleus in the other, was eliminated by converting the products to the bases and regenerating the dye

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(1) The most complete bibliography of the Magentas is given in Schultz, "Farbstofftabellen," Akademische Verlagsgesellschaft m. b. H., Leipzig, 7th ed., 1931, p. 323–326, but references to the individual homologs can be found more readily in Beilstein. For this reason, a reference to Beilstein is given for each homolog, together with the most important references to the original literature.

(2) Beilstein, 4th ed., Vol. XIII, p. 750, 1st Suppl., XIII, p. 297; Rosenstiehl, *Ann. chim. phys.*, [5] **8**, 192 (1876); E. and O. Fischer, *Ber.*, **13**, 2205 (1880); *Ann.*, **194**, 267 (1878); Schmid and Baldensperger, *Dinglers polytech. J.*, **233**, 339 (1879).

(3) Beilstein, 4th ed., Vol. XIII, p. 763, 1st Suppl., XIII, p. 300; Rosenstiehl and Gerber, *Ann. chim. phys.*, [6] **2**, 340 (1884); Coupier and Schützenberger, *Jahresber. Fortschr. Chem.*, 1162 (1869).

(4) Beilstein, 4th ed., Vol. XIII, p. 770; Kalle and Co., German Patent 93,540, *Friedländer*, **4**, 180; Rosenstiehl and Gerber, *Ann. chim. phys.*, [6] **2**, 348 (1884); Coupier, *Bull. Soc. Ind. Mulhouse*, **36**, 259 (1866); O. Fischer, *Ber.*, **15**, 679 (1882); Höchster Farbwerke, German Patents 70,905 and 72,032; *Friedländer*, **3**, 110.

(5) Beilstein, 4th ed., Vol. XIII, p. 771, 1st Suppl., XIII, p. 302; Schmidlin, *Ann. chim. phys.*, [8] **7**, 232 (1906); Rosenstiehl and Gerber, *ibid.*, [6] **2**, 352 (1884); Gomberg and Anderson, THIS JOURNAL, **47**, 2022 (1925).

TABLE II

COMPARISON OF PRODUCTS OBTAINED BY THE TWO METHODS OF PREPARATION

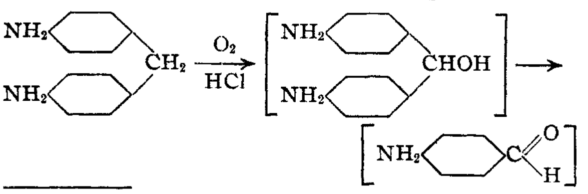
(See Absorption Curves in Fig. 1)

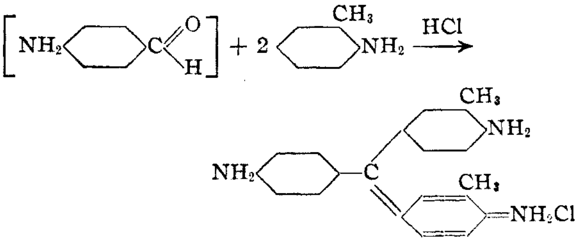
Expt.[a]	Intermediates used	Magenta expected	Analyses of carbinol base N, % Calcd.	Found	Ratio[b] $\frac{E \text{ at } 520\ m\mu}{E \text{ at } 560\ m\mu}$ Orig. dye	Dye from base	Magenta obtained
1N	*p*-Toluidine, aniline, nitrobenzene	0	13.77	13.88	1.00	1.02	0
1F	4,4′-Diaminodiphenylmethane, aniline, nitrobenzene	0	13.77	13.75	1.02	1.02	0
2N	as-*m*-Xylidine, aniline, nitrobenzene	I	13.17	13.44	0.93	0.95	I
2F	4,4′-Diaminodiphenylmethane, *o*-toluidine, *o*-nitrotoluene	I	13.17	12.60	.74	.72	Principally II
3F	4,4′-Diamino-3,3′-dimethyldiphenylmethane, aniline, nitrobenzene	II	12.61	12.89	.86	.84	Principally I
3N	*p*-Toluidine, *o*-toluidine, *o*-nitrotoluene	II	12.61	12.46	.70	.70	II
4F	4,4′-Diamino-3,3′-dimethyldiphenylmethane, *o*-toluidine, *o*-nitrotoluene	III	12.10	12.23	.68	.67	III
4N	as-*m*-Xylidine, *o*-toluidine, *o*-nitrotoluene	III	12.10	12.28	.68	.68	III

[a] Letter indicates method employed: N, nitrobenzene process; F, formaldehyde or new magenta process. [b] Solvent 50% alcohol.

with acid. The change in absorption which would have occurred in such a case was not observed. It is evident, therefore, that when 4,4′-diaminodiphenylmethane reacts with *o*-toluidine the product is not Magenta I, as would be expected, but principally Magenta II. Similarly, when 3,3′-dimethyl-4,4′-diaminodiphenylmethane reacts with aniline the principal product is Magenta I instead of Magenta II. This is corroborated by the nitrogen content.

Since the product obtained by the new magenta or formaldehyde process contains only one methyl group when a dimethyldiaminodiphenylmethane reacts with aniline and two methyl groups when diaminodiphenylmethane reacts with *o*-toluidine, it follows that scission of the diphenylmethane molecule must occur, and that it supplies only one of the benzene nuclei and the central carbon atom of the triphenylmethane. The other two nuclei, therefore, are supplied by the other amino compound, aniline or *o*-toluidine, as the case may be. Weil[6] states that when 4,4′-tetramethyldiaminobenzhydrol is heated with dilute acid it splits into dimethylaniline and *p*-dimethylaminobenzaldehyde. Assuming that the 4,4′-diaminodiphenylmethane is converted in this reaction first to the corresponding hydrol, and that this primary amine behaves like the tertiary amine, the following mechanism is possible





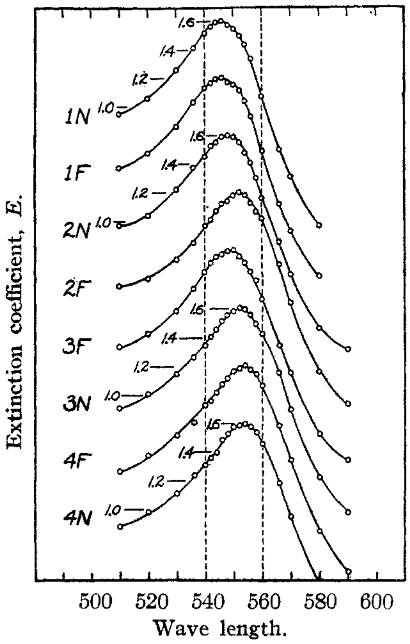


Fig. 1.—Absorption curves of the products obtained in the experiments indicated by the numbers. The value of *E* at the maximum is the same for each curve. Curves 1N, 2N, 3N and 4N are typical absorption curves for magenta O, I, II, III, respectively. The solvent used was 50% alcohol. Further data are given in Table II.

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(6) Weil, *Ber.*, **27**, 3316 (1894).

For the preparation of the pure homologs the nitrobenzene process was, therefore, selected, and although the commercial dyes prepared by this method are usually mixtures, it was demonstrated that by judicious selection of intermediates any of the desired homologs could be prepared. Examination of Curves 1N, 2N, 3N and 4N (Fig. 1) and the corresponding data in Table II reveals that the anomalies observed in the other method are absent. The positions of the absorption maxima are in proper relationship to one another, and the identity of the various homologs is confirmed by the nitrogen content.

Experimental

Method of Identification.—Spectrophotometric examination, supplemented by analysis for nitrogen, was the means employed for verifying the identity of the various homologs obtained. By means of the absorption curves it is possible to distinguish between two compounds which differ by only one methyl group substituted in a phenyl nucleus. Comparison of the "absorption ratios,"[7] as given in Table III, gives the same information, while it reduces to a minimum the number of readings necessary. For the nitrogen analyses the regular Kjeldahl method, modified to adapt it to the micro-apparatus of Parnas and Wagner,[8] was used.

TABLE III

ABSORPTION RATIOS FOR IDENTIFICATION

Actual Averages of Several Different Batches of Each Dye. Solvent, 50% Alcohol

Dye		Absorption ratios				
		$\frac{E \text{ at } 520 \text{ m}\mu}{E \text{ at } 560 \text{ m}\mu}$	$\frac{E \text{ at } 530 \text{ m}\mu}{E \text{ at } 560 \text{ m}\mu}$	$\frac{E \text{ at } 540 \text{ m}\mu}{E \text{ at } 560 \text{ m}\mu}$	$\frac{E \text{ at } 540 \text{ m}\mu}{E \text{ at } 570 \text{ m}\mu}$	$\frac{E \text{ at } 550 \text{ m}\mu}{E \text{ at } 570 \text{ m}\mu}$
Magenta O	Range observed	0.98–1.02	1.14–1.19	1.37–1.46	....	....
	Average	1.00	1.16	1.39	....	....
Magenta I	Range observed	0.92–0.95	1.07–1.11	1.29–1.34	....	....
	Average	0.94	1.09	1.32	....	....
Magenta II	Range observed	0.70–0.71	0.80–0.82	0.95–0.97	1.55–1.62	1.79–1.86
	Average	0.70	0.81	0.96	1.58	1.82
Magenta III	Range observed	0.67–0.69	0.77–0.78	0.92–0.94	1.46–1.53	1.73–1.77
	Average	0.68	0.77	0.93	1.49	1.75

Since the structure of the magentas has long been established, the information obtained was adequate to determine the suitability of the products for the purpose of determining fundamental spectrophotometric data for future reference. These data are recorded as curves in Fig. 1, and the corresponding absorption ratios are given in Table III. Only one ratio is needed to distinguish between two adjacent homologs, but no single ratio is suitable for the entire series, so several are given.

For the nitrogen analyses the dyes were converted to the carbinol bases which, because of their insolubility, are much more readily purified than the dyes themselves and are also much better suited for analysis, especially by combustion methods. These bases were converted to dyes again and examined with the spectrophotometer. The results agreed in every case with those obtained with the original dyes.

Preparation of Intermediates

4,4'-Diaminodiphenylmethane.—The method used is a modification of that of Stebbins.[9] To a solution of 188 cc. (2 moles) of concentrated hydrochloric acid (sp. gr. 1.18) in 400 cc. of water, 186 g. (2 moles) of aniline was added and the solution was cooled to 15°. To the cool solution 76 g. (1 mole) of 40% formaldehyde solution was added and the mixture was heated at 55–60° for four hours. During the heating the yellow precipitate, which formed when the formaldehyde was added, gradually dissolved. The reaction mixture was made alkaline with sodium carbonate and steam-distilled until the distillate gave no test for aniline. The precipitate was then redissolved by the addition of a slight excess of hydrochloric acid, and the solution was chilled in an ice-bath and fractionally precipitated with dilute ammonium hydroxide.[10] Three fractions were thus obtained, each of which was redissolved by the addition of excess hydrochloric acid. To each of these three solutions ammonium hydroxide was added slowly. At first resinous material was

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[7] Holmes, *Ind. Eng. Chem.*, **17**, 918 (1925); Holmes and Peterson, *Stain Tech.*, **5**, 65 (1930).

[8] Parnas and Wagner, *Biochem. Z.*, **125**, 253 (1921); Clark and Collip, *J. Biol. Chem.*, **67**, 621 (1926).

[9] Stebbins, *Ind. Eng. Chem.*, **10**, 445 (1918).

[10] Eberhardt and Welter, *Ber.*, **27**, 1804 (1894).

precipitated but as the addition of ammonium hydroxide was continued, white crystalline material began to separate. At this point the addition of ammonium hydroxide was stopped, and the resinous material was filtered off. An excess of ammonium hydroxide was then added to each of the three filtrates and the three precipitates thus obtained were combined. The product was white but turned brown upon standing: total yield 112 g., 57% of theoretical; m. p. 85–88°. This product was found to be satisfactory for use but it can be purified further by recrystallization from alcohol or water. Neither is very satisfactory, as it is too soluble in cold alcohol and insufficiently soluble in hot water. Recrystallized from alcohol it melted at 90–91°, from water at 91.5–92°. Melting points reported in the literature range from 80 to 94°.

3,3′ - Dimethyl - 4,4′ - diaminodiphenylmethane.—To a solution of 188 cc. (2 moles) of concentrated hydrochloric acid (sp. gr. 1.18) in 800 cc. of water, 214 g. (2 moles) of *o*-toluidine was added. The solution was cooled to room temperature, 76 g. (1 mole) of 40% formaldehyde solution added with stirring, and the mixture was heated for four hours at 70–76°. The purification was carried out as described for 4,4′-diaminodiphenylmethane except that the combined precipitates were recrystallized from alcohol. The product crystallizes satisfactorily from this solvent in large prisms with a faint amber color: yield 143 g., 63% of theoretical; m. p. 155.5–157°.

After two more recrystallizations from alcohol a melting point of 158–159° was observed. Further recrystallization had no effect upon the melting point. A further yield of 26 g. of less pure material was obtained by concentrating the original filtrate. The melting point of this compound is given in the literature as 149°. When the fractional precipitation with ammonium hydroxide to eliminate resinous impurities was omitted, the product, after recrystallization from alcohol, melted over the range 149–155°.

Preparation of the Dyes by the New Magenta or Formaldehyde Process.[11]—The intermediates used in each experiment are listed in Table IV, together with the other details. To avoid the possibility of mixtures, the nitro compound was so chosen that if it was reduced to the corresponding amine, the amine so formed would be one already present. These intermediates were intimately mixed in a flask equipped with a mechanical stirrer and a reflux air condenser designed to allow water vapor to escape but to return most of the volatile amino and nitro compounds. The flask was heated in an oil-bath at the desired temperature for four hours and then poured

TABLE IV

PREPARATION OF THE DYES BY THE NEW MAGENTA OR FORMALDEHYDE PROCESS

	Experiment			
	1F	2F[a]	3F[a]	4F[a]
4,4′-Diaminodiphenylmethane, g.	40	40	...	...
3,3′-Dimethyl-4,4′-diaminodiphenylmethane, g.	...	...	20	45
Aniline, g.	100	...	50	...
Aniline hydrochloride, g.	20	...	10	...
o-Toluidine, g.	...	107	...	107
o-Toluidine hydrochloride, g.	...	21.5	...	21.5
Nitrobenzene, g.	20	...	10	...
o-Nitrotoluene, g.	...	22	...	22
$FeCl_2 \cdot 4H_2O$, g.	10	10	5	10
Temp., °C.	165	180	180	180
Time, hours	4	4	4	4
Best yield g.	6.5	8	4	15
%	10	11	12	20
Dye used to prepare carbinol base, g.	3	3	3	3.5
Yield of base, g.	1.5	1.5	0.5	2
Formula, carbinol base	$C_{19}H_{19}N_3O$	$C_{20}H_{21}N_3O$	$C_{21}H_{23}N_3O$	$C_{22}H_{25}N_3O$
Nitrogen, calcd., %	13.77	13.17	12.61	12.10
Nitrogen, found, %	13.75	12.60	12.89	12.23
Product was	Magenta O	Principally Magenta II	Principally Magenta I	Magenta III

[a] In Nos. 2F, 3F and 4F, the dye was recrystallized from alcohol.

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(11) Cain, "The Manufacture of Dyes," The Macmillan Co., New York, 1922, p. 96; Möhlau and Bucherer, "Farbenchemisches Praktikum," Walter de Gruyter & Co., Berlin, 1908, p. 181; *Friedländer*, **3**, 110–114.

TABLE V

PREPARATION OF DYES BY THE NITROBENZENE PROCESS

	Experiment			
	1N	2N	3N[a]	4N[a]
Aniline, g.	49	49	...	...
Aniline hydrochloride, g.	68	68	...	...
o-Toluidine, g.	...	...	56	56
o-Toluidine hydrochloride, g.	...	...	75	75
p-Toluidine, g.	32	...	32	...
as-*m*-Xylidine, g.	...	36	...	36
Nitrobenzene, g.	74	74	...	...
o-Nitrotoluene, g.	...	...	82	82
$FeCl_2 \cdot 4H_2O$, g.	12	12	12	12
Temp., °C.	185	185	185	185
Time, hours	5	5	5	5
Best yield g.	7.5	15	30	63
Best yield %	8	15	29	57
Dye used to prepare carbinol base, g.	3.5	3	3.5	3.5
Yield of base, g.	2	1.2	2.4	2.6
Formula of carbinol base	$C_{19}H_{19}N_3O$	$C_{20}H_{21}N_3O$	$C_{21}H_{23}N_3O$	$C_{22}H_{25}N_3O$
Nitrogen, calcd., %	13.77	13.17	12.61	12.10
Nitrogen, found, %	13.88	13.44	12.46	12.28
Product	Magenta O	Magenta I	Magenta II	Magenta III

[a] In Nos. 3N and 4N the dye was recrystallized from alcohol.

while hot into 1,000 cc. of water and steam-distilled to remove the amino and nitro compounds. The contents of the distilling flask were then acidified with 10 cc. of concentrated hydrochloric acid, boiled a few minutes and filtered hot. After the filtrate had cooled the dye was precipitated by the addition of 500 cc. of saturated sodium chloride solution. The carbinol base of each was prepared by the method of Jennings[12] and dried over phosphorus pentoxide in a vacuum desiccator.

Preparation of the Dyes by the Nitrobenzene Process.—Practically every book on dye chemistry gives a different version of this process. The one used is a compromise based principally upon Coupier's method as described by Fierz-David.[13] The amino compounds were so selected that only one homolog would be obtained in each case, and the nitro compounds were chosen so that no unwanted amines could be produced by reduction. The procedure was identical with that followed in the other process, except that the temperature used was higher, the time of heating longer and only 8 cc. of concentrated hydrochloric acid was used for acidification after the steam distillation. The details are given in Table V.

Summary

1. The details of an improved method for the preparation and purification of 4,4′-diaminodiphenylmethane and 4,4′-diamino-3,3′-dimethyldiphenylmethane, which were used as intermediates, are given.

2. It is demonstrated by means of spectrophotometric data and analysis that when the new magenta or formaldehyde process is used in the preparation of the unsymmetrical magenta homologs, the products obtained are not those which should result if the accepted mechanism for the reaction were correct. A new mechanism is suggested.

3. It is also demonstrated that when the nitrobenzene process is employed these anomalous results are not obtained.

4. The four lowest members of the magenta series were prepared by the latter method and purified. Absorption curves and absorption ratios, suitable for the identification of each of these four homologs by means of the spectrophotometer, are given.

5. The carbinol base of each dye was prepared and analyzed for nitrogen. These bases are more suitable for this purpose than the dyes themselves. By means of this analysis, reconversion of the bases to the dyes, and spectrophotometric examination, the identity of each homolog was confirmed.

WASHINGTON, D. C. RECEIVED NOVEMBER 23, 1934

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(12) Jennings, *Ber.*, **36**, 4025 (1903).

(13) Fierz-David, "Künstliche organische Farbstoffe," Julius Springer, Berlin, 1926, p. 247.