centage of the nitrate groups is reduced to nitrite.

The production of carbon dioxide and of reducing substances appears to be related to time, concentration of alkali, ratio of alkali to cellulose nitrate and the temperature.

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The Magenta Series. II. Some Higher Basic Members

BY JOHN T. SCANLAN

In a previous publication[1] the results of an investigation of the "nitrobenzene process" and the "formaldehyde process" for the preparation of Magenta (Fuchsine) were given. In the latter process 4,4′-diaminodiphenylmethane, or one of its homologs, reacts with aniline or its homologs, and it was shown that the reaction involves a scission of the diphenylmethane. This report covers an extension of the same investigation to three of the higher members of the series in which the methyl groups are ortho to the amino groups and not more than two occur in any benzene nucleus. The simplified system of nomenclature explained in the previous publication is used (see Table I).

TABLE I

NOMENCLATURE

Name used in this paper	Scientific name
Magenta IV	3,3′,3″,5-Tetramethyl-4,4′-diaminofuchsonimonium chloride
Magenta V	3,3′,3″5,5′-Pentamethyl-4,4′-diaminofuchsonimonium chloride
Magenta VI	3,3′,3″,5,5′,5″-Hexamethyl-4,4′-diaminofuchsonimonium chloride

The results are even more clean-cut than those obtained with the lower homologs and confirm the conclusions previously stated. As shown by the data in Table II and the corresponding absorption curves in Fig. 1, when 4,4′-diamino-3,3′-dimethyldiphenylmethane reacts with *v*-*m*-xylidine (Experiments 5Fa and 5Fb) the product is not Magenta IV but Magenta V and when 4,4′-diamino-3,3′,5,5′-tetramethyldiphenylmethane reacts with *o*-toluidine (Experiment 6F) the product is not Magenta V, but Magenta IV. This conclusion is readily arrived at by comparing the products of the above two reactions with that of the reaction between *as*-*m*-xylidine and *v*-*m*-xylidine (Experiment 6N, "nitrobenzene process") which must obviously be Magenta V. No attempt was made to prepare Magenta IV and Magenta VI by the "nitrobenzene process" because a necessary intermediate, mesidine, was not readily available and it was thought that further evidence was not required.

(1) Scanlan, THIS JOURNAL, 57, 887 (1935).

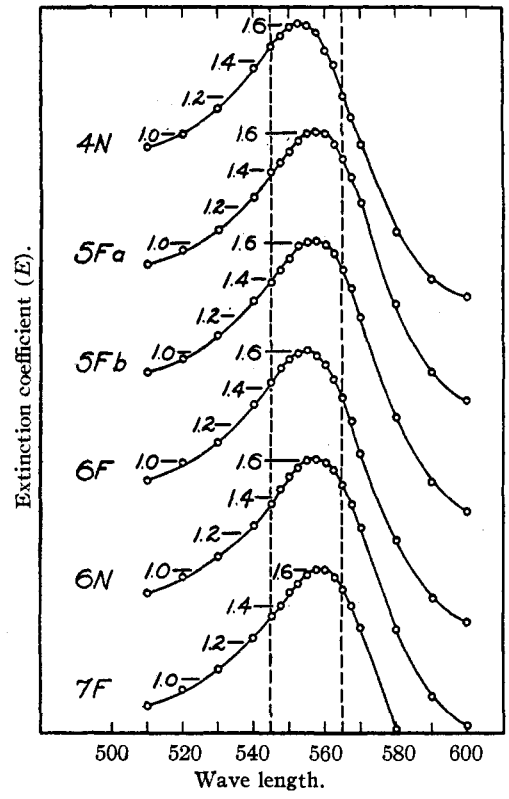

Fig. 1.—Absorption curves of the products obtained in the experiments indicated by the numbers. Solvent, 50% alcohol. The dyes corresponding to the curves are as follows: 4N, magenta III (repeated from previous paper for comparison); 6F, magenta IV; 5Fa, 5Fb and 6N, magenta V; 7F, magenta VI. Further data are given in Table II.

As in the case of the lower homologs, the solubility of these dyes (hydrochlorides) in alcohol decreases with increasing molecular weight. How-

TABLE II

COMPARISON OF PRODUCTS OBTAINED BY DIFFERENT METHODS OF PREPARATION

(See absorption curves in Fig. 1)

Experiment[a]	Intermediates used	Magenta obtained	Analysis of carbinol base %, N Calcd.	Found	Ratio E at 545 mμ[b] / E at 565 mμ Original dye	Dye from base
5Fa	4,4′-Diamino-3,3′-dimethyldiphenylmethane, *v-m*-xylidine, nitro-*m*-xylene	V	11.20	11.04	0.93	0.92
5Fb	4,4′-Diamino-3,3′-dimethyldiphenylmethane, *v-m*-xylidine, *o*-nitrotoluene	V	11.20	11.19	.92	.92
6F	4,4′-Diamino-3,3′,5,5′-tetramethyldiphenylmethane, *o*-toluidine, *o*-nitrotoluene	IV	11.63	11.68	1.06	1.05
6N	*as-m*-Xylidine, *v-m*-xylidine, nitro-*m*-xylene	V	11.20	11.08	0.92	0.91
7F	4,4′-Diamino-3,3′,5,5′-tetramethyldiphenylmethane, *v-m*-xylidine, *o*-nitrotoluene	VI	10.80	10.89	.87	.88

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

ever, while Magenta IV and Magenta V are quite soluble in water, Magenta VI is much less so. All three are easily salted out. The carbinol bases show decreasing solubility in hot, aqueous alkaline solutions with increasing molecular weight. The absorption bands, of course, show progressive shifting toward the red end of the spectrum.

Experimental

Method of Identification.—These higher homologs were identified by the method described in the previous paper; namely, spectrophotometric examination and analysis of their carbinol bases. The absorption ratios[2] are given in Table III.

TABLE III

ABSORPTION RATIOS FOR IDENTIFICATION

Solvent, 50% Alcohol

The ratios for Magenta III are repeated from the previous paper for comparison. The others represent only one batch in each case.

	Absorption ratios					
E, mμ... / Dye E, mμ...	520/560	530/560	540/560	545/565	540/570	550/570
Magenta III	0.68	0.77	0.93	1.19	1.49	1.75
Magenta IV	.63	.70	.84	1.07	1.23	1.48
Magenta V	.58	.66	.78	0.92	1.02	1.23
Magenta VI	...	...	.75	.87	0.92	1.12

Preparation of Intermediates

4,4′ - Diamino - 3,3′ - dimethyldiphenylmethane.—The method of preparing this compound was described in the previous publication.

Nitro-*m*-xylene.—Prepared by nitration of *m*-xylene[3] and purified by fractional distillation. The fraction boiling at 243–252° was used.

***v-m*-Xylidine.**—Technical xylidine[4] from which *as-m*-xylidine had been removed was freed from *p*-xylidine[5] and treated according to the method of Winkelhausen[6] to obtain *v-m*-xylidine sulfate. Part of this was converted to the chloride by treatment with barium chloride and the balance to the base by treatment with sodium hydroxide. Two kilograms of the technical xylidine yielded 130 g. of *v-m*-xylidine base and 189 g. of *v-m*-xylidine hydrochloride.

4,4′ - Diamino - 3,3′,5,5′ - tetramethyldiphenylmethane.—Fifty-seven grams of *v-m*-xylidine hydrochloride, 2 cc. of concentrated hydrochloric acid and 14 g. of 40% formaldehyde solution were dissolved in 150 cc. of water and heated at 70–75° for four hours. Near the end of the reaction time sufficient warm water was added to dissolve the precipitated hydrochloride. The mixture was then made alkaline with potassium hydroxide and steam distilled. The residual material was redissolved by the addition of hydrochloric acid and fractionally precipitated with ammonium hydroxide as described in the previous paper.[1] The first of the two fractions thus obtained was rejected and the second recrystallized from alcohol; yield 32 g.; m. p. 122.5–123.5°.

Friedländer and Brand[7] give the melting point as 126°.

Preparation of the Dyes

Experiment 5Fa (Magenta V, Formaldehyde Process).—The intermediates used were 40 g. of 4,4′-diamino-3,3′-dimethyldiphenylmethane, 25 g. of *v-m*-xylidine hydrochloride, 60 g. of *v-m*-xylidine (base), 25 g. of nitro-*m*-xylene and 16 g. of $FeCl_2 \cdot 4H_2O$. The procedure was the same as described for this process in the previous publication. The product was salted out and recrystallized from alcohol. It separates from this solvent in feathery clusters of very fine needles which form a felt-like mass on the filter. When thoroughly dried and ground it has a dull, gray-green color; yield 46 g.; 65% of the theoretical.

The carbinol base was prepared by mixing a hot solution of 4 g. of the dye in 1000 cc. of water with a hot solution of 5 g. of sodium hydroxide in 800 cc. of water. The base precipitated immediately and after boiling the mixture for about an hour, it was allowed to cool, the base was filtered off, washed with dilute ammonium hydroxide and dried over phosphorus pentoxide; yield 2.5 g.; small, ir-

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

(3) Noelting and Forel, *Ber.*, **18**, 2674 (1885).

(4) Obtained through the courtesy of Dr. E. K. Bolton of E. I. du Pont de Nemours & Co.

(5) Hodgkinson and Limpach, *J. Chem. Soc.*, **77**, 65 (1900); German Patent 39,947; *Friedländer*, **1**, 19 (1888).

(6) Winkelhausen, German Patent 251,334; *Friedländer*, **11**, 153 (1915).

(7) Friedländer and Brand, *Monatsh.*, **19**, 640 (1898).

regular prisms, buff-colored and showing only a very slight tendency to become red on standing.

Anal. Calcd. for $C_{24}H_{29}N_3O$: N, 11.20. Found: N, 11.04.

Experiment 5Fb (Magenta V, Formaldehyde Process).— The intermediates used were 26 g. of 4,4′-diamino-3,3′-dimethyldiphenylmethane, 14.5 g. of *v-m*-xylidine hydrochloride, 68 g. of *v-m*-xylidine (base), 12.6 g. of *o*-nitrotoluene and 9.1 g. of $FeCl_2 \cdot 4H_2O$; procedure as above. The product separated from alcohol in feathery clusters of very fine needles. When thoroughly dried and ground it was dull, gray-green in color; yield 13.5 g.; 30% of theoretical.

The carbinol base was prepared as above using 3.5 g. of the dye; yield 1.5 g.; small, irregular prisms, buff-colored and showing only a very slight tendency to become red on standing.

Anal. Calcd. for $C_{24}H_{29}N_3O$: N, 11.20. Found: N, 11.19.

Experiment 6F (Magenta IV, Formaldehyde Process).— The intermediates used were 25 g. of 4,4′-diamino-3,3′,-5,5′-tetramethyldiphenylmethane, 12 g. of *o*-toluidine hydrochloride, 57 g. of *o*-toluidine (base), 12 g. of *o*-nitrotoluene and 8 g. of $FeCl_2 \cdot 4H_2O$; procedure as above. The product separated from alcohol as very bright green, rather coarse needles; yield 13.5 g., 36% of theoretical.

Using 3 g. of dye the carbinol base was prepared as above except that in this case it was sufficiently soluble in hot aqueous alkali to permit filtration before it separated; yield 1.3 g.; small, irregular prisms, faintly pink when first precipitated, but acquiring an intense purple coloration on standing.

Anal. Calcd. for $C_{23}H_{27}N_3O$: N, 11.63. Found: N, 11.68.

Experiment 6N (Magenta V, Nitrobenzene Process).— The intermediates used were 36 g. of *as-m*-xylidine, 83 g. of *v-m*-xylidine hydrochloride, 64 g. of *v-m*-xylidine (base), 91 g. of nitro-*m*-xylene and 12 g. of $FeCl_2 \cdot 4H_2O$. The procedure was the same as described for the nitrobenzene process in the previous publication. The product was salted out and recrystallized from alcohol. It separated as feathery clusters of very fine needles. When dried and ground it was dull, gray-green in color; yield 32 g., 27% of theoretical.

The carbinol base was prepared from 4 g. of the dye as described under Experiment 5Fa; yield 3.2 g.; small irregular prisms with only a very slight tendency to become red on standing.

Anal. Calcd. for $C_{24}H_{29}N_3O$: N, 11.20. Found: N, 11.08.

Experiment 7F (Magenta VI, Formaldehyde Process).— The intermediates used were 25 g. of 4,4′-diamino-3,3′-5,5′-tetramethyldiphenylmethane, 13 g. of *v-m*-xylidine hydrochloride, 65 g. of *v-m*-xylidine (base), 12 g. of *o*-nitrotoluene and 8 g. of $FeCl_2 \cdot 4H_2O$.

The procedure was the same as that previously described for the formaldehyde process except that, because of the low solubility of this homolog, it could be separated by filtration from the hot solution immediately after the steam distillation. Some large, fused lumps of tarry material were removed manually and the balance was recrystallized from alcohol. A voluminous precipitate of feathery clusters of very fine needles was obtained which, when dried and ground, had a dark gray-blue color; yield 25 g., 60% of theoretical.

The carbinol base was prepared from 4 g. of the dye as described under Experiment 5Fa; yield 3.6 g.; small, irregular prisms, golden-yellow with practically no color change on standing.

Anal. Calcd. for $C_{25}H_{31}N_3O$: N, 10.80. Found: N, 10.89.

Summary

1. Three new homologs of Magenta were prepared, and their identity was established by spectrophotometric examination of the dyes and analysis of their carbinol bases. Absorption curves and absorption ratios suitable for their future identification are given.

2. Examination of these data confirms the conclusion, previously published, that in the "formaldehyde process" for the preparation of Magenta, scission of the diaminodiphenylmethane nucleus occurs.

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