1,1-dibenzylhydrazine. To this solution kept at 0° was added very carefully, dropwise, 8.08 g. (0.0708 mole) of 95% *t*-butyl hypochlorite over a 15-minute period. A more rapid addition appears to be unsafe as each drop of *t*-butyl hypochlorite gave a loud report on striking the reaction solution. A white slurry appeared almost immediately and the reaction mixture developed orange tones toward the end of the addition of the hypochlorite. An excess of potassium hydroxide pellets was added, followed by 40 ml. of absolute ethanol to help solubilize the base. The reaction was allowed to come to room temperature and stirred overnight, protected from outside moisture. An inorganic precipitate in the reaction mixture was removed and the filtrate evaporated at room temperature to yield an oil and a large amount of precipitate which was separated by filtration. The precipitate was washed with ether to separate insoluble inorganic salts and after filtration the ether was dried and removed to yield 2.3 g. (15.5%) of a white precipitate, m.p. 96–99°. Recrystallization from ether gave a melting point of 99–100°; a mixed melting point with tetrabenzyltetrazene,[1] m.p. 99–100°, melted at 99–100°.

The oil remaining after the separation of the precipitate described above was fractionally distilled through a small center tube column at reduced pressure. A fraction 3, 1.05 g., b.p. 85.5° (0.65 mm.), n^{27}_{D} 1.5581, was a water white oil and solidified on standing to yield a white solid, m.p. 50–55°; recrystallization from ether gave 0.85 g., m.p. 52–53°. A mixed melting point with a known sample of bibenzyl was not depressed, and the infrared spectra of both were identical. An additional 0.7 g. of bibenzyl was obtained from a fraction 4, see below, or a total of 1.55 g. (12.04%).

Fraction 4 was dissolved in ether, any solid removed by filtration, and the filtrate washed with 20% hydrochloric acid solution to yield 0.6 g., m.p. 250–256° of white precipitate the hydrochloride of 1,1-dibenzylamine (see later section). The water–acid layer was extracted with ether which was combined with the original ether layer, to give after drying and removal of the ether, 0.7 g. of white precipitate, bibenzyl, m.p. 49–52°. From the water layer, after having been made basic, there was obtained 0.35 g. of a dark oil which only gave small amounts of an impure solid, melting near tribenzylhydrazine (see below).

In another experiment an initial separation of tetrabenzyltetrazene followed by acid, base extraction procedures, to separate neutral and basic components, there was found in the neutral fraction on distillation a white precipitate which after recrystallization from ether gave a m.p. 86–87° (4.5%), probably tribenzylhydrazine (from benzyl chloride and hydrazine, reported as hydrochloride).[19]

Anal[20]: Calcd. for $C_{21}H_{22}N_2$: C, 83.44; H, 7.29; N, 9.27. Found: C, 83.59; H, 7.16; N, 9.10.

The picrate was prepared in ethereal solution; m.p. 140–141° dec. after recrystallization from ethanol.

Anal. Calcd. for $C_{27}H_{25}N_5O_7$: C, 61.02; H, 4.71; N, 13.17. Found: C, 61.43; H, 4.68; N, 13.33.

Fraction 5 was dissolved in ether, any solid material removed by filtration, and to the ether solution was added 20 ml. of 25% hydrochloric acid solution to give 1.2 g. of precipitate, m.p. 254–256°. A mixed m.p. with the salt obtained in fraction 4 melted at 252–256°, and both gave no depression in melting point when mixed with an authentic sample of the hydrochloride of dibenzylamine (m.p. 246° uncor.).[21]

An additional 0.30 g. of dibenzylamine was obtained from the water layer, determined as the hydrochloride salt, total yield, 2.1 g. of salt or 12.71%. The dried ether layer gave 0.4 g. of a white precipitate, m.p. 82.5–105°. After two recrystallizations from ethanol, it melted at 117–120°. A mixed melting point with *trans*-stilbene, m.p. 122°, gave no depression.

Fraction 6, a light yellow green oil was dissolved in ether and dilute hydrochloric acid added, to yield a white precipitate in the ether phase. In another experiment, the yellow oil was refractionated and the fraction boiling at 192° (6 mm.) –208° (8 mm.) collected. Its infrared spectrum indicated the C=N frequency at 6.08 μ, but complete purification failed. The white precipitate from above was removed, m.p. 248° dec., the hydrochloride of benzylamine melts at 248° dec.[17]

The ether extract was removed to give 1.85 g. of a sweet smelling reddish purple oil. Some of the oil was treated with 2,4-dinitrophenylhydrazine to yield a derivative which melted at 235–238° dec. Recrystallization from ethanol gave a product melting at 237–238° and it gave no depression in the melting point when mixed with the 2,4-dinitrophenylhydrazine derivative of benzaldehyde. However, only a small part of the original oil actually reacted. Distillation of the oil gave a solid which could not be purified.

Infrared Spectra.—A Perkin–Elmer model 21 double beam recording infrared spectrophotometer was employed with a NaCl prism to study the 2–15 μ range.

Acknowledgment.—We wish to gratefully acknowledge the support of this work by the Office of Ordnance Research, Contract DA30-069-ORD-1158.

BROOKLYN, N. Y.

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[19] J. Kenner and J. Wilson, *J. Chem. Soc.*, 1108 (1907). A number of other references report the preparation of the free base but no physical constants are reported; see O. Diels and J. Reese, *Ann.*, **519**, 147 (1935) ,and previous references.

[20] Analyses by Dr. K. Ritter, Basel, Switzerland, and Dr. F. Schwarzkopf, New York, N. Y.

[21] T. Curtius and G. Lederer, *Ber.*, **19**, 2463 (1886).

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

New Pigments from 3,3'-Dichloro- and 3,3'-Dimethoxy-4,4'-diaminostilbene

BY D. W. HEIN AND ELLIOT S. PIERCE

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Two new pigment intermediates, 3,3'-dichloro-(I) and 3,3'-dimethoxy-4,4'-diaminostilbene (II), and from them, by tetrazotizing and coupling with variously substituted aceotacetanilides, 1-phenyl-3-methyl-5-pyrazolone and 3-hydroxy-2-naphthoic acid arylides, a number of new pigments have been prepared. The new pigments show bathochromic color shifts as expected when compared with the corresponding pigments from 3,3'-dichlorobenzidine. The differences in the visual light absorption curves are explained.

Pigments prepared by tetrazotizing 3,3'-dichlorobenzidine or 3,3'-dimethoxybenzidine, and coupling with two molecules of a coupling component, such as acetoacetanilides, 1-phenyl-3-methyl-5-pyrazolone or 3-hydroxy-2-naphthoic acid arylides, are well known and a few have achieved commercial prominence; *e.g.*, 3,3'-dichlorobenzidine coupled with two moles of acetoacetanilide, *o*-acetoacetotoluidide or 1-phenyl-3-methyl-5-pyrazolone, and 3,3'-dimethoxybenzidine coupled with 2 moles of 3-hydroxy-2-naphtho-*o*-toluide or 1-phenyl-3-methyl-5-pyrazolone. It was considered of interest to prepare the corresponding vinylogous series of pigments from 3,3'-dichloro-4,4'-diaminostilbene (I) and 3,3'-dimethoxy-4,4'-diaminostilbene (II) for comparison with the benzidine analogs with respect to color value, light absorption and pigment properties. Some of the corresponding pigments also

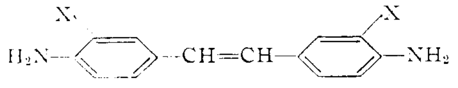
TABLE I

STILBENE PIGMENTS

Coupling component	Yield, %	Microanalyses			Mass tone	Tint tone
		Formula	Nitrogen, %			
			Calcd.	Found		
3,3'-Dichloro-4,4'-diaminostilbene pigments						
1-Phenyl-3-methyl-5-pyrazolone	98	$C_{34}H_{26}O_2N_8Cl_2$	17.2	17.2, 17.4	Bright red	Yellow-red
Acetoacetanilide	72	$C_{34}H_{28}O_4N_6Cl_2$	12.8	12.3, 12.4	Red-brown	Orange-yell.
o-Acetoacetotoluidide	94	$C_{36}H_{32}O_4N_6Cl_2$	12.3	11.9, 12.1	Red-brown	Orange-yell.
Acetoacet-α-naphthylamide	84	$C_{42}H_{32}O_4N_6Cl_2$	11.1	11.1	Red-brown	Orange-yell.
o-Acetoacetanisidide	76	$C_{36}H_{32}O_6N_6Cl_2$	11.7	11.2, 11.2	Red-brown	Orange-yell.
Acetoacetcresidide	122[a]	$C_{38}H_{36}O_6N_6Cl_2$	11.3	11.3	Orange-br.	Orange
Acetoacetcumidide (pseudo)	89	$C_{40}H_{40}O_4N_6Cl_2$	11.4	11.4	Yell.-brown	Orange-yell.
2,4-Acetoacetoxylide	93	$C_{38}H_{36}O_4N_6Cl_2$	11.8	11.5	Red-brown	Orange-yell.
Benzoylacetanilide	85	$C_{44}H_{32}O_4N_6Cl_2$	10.8	11.0, 11.1	Orange-br.	Orange-yell.
p-Nitro-acetoacetanilide	89	$C_{34}H_{26}O_8N_8Cl_2$	15.0	14.8	Dull red	Light dull red
o-Chloro-acetoacetanilide	105[a]	$C_{34}H_{26}O_4N_6Cl_4$	11.6	11.4	Red-brown	Orange-yell.
p-Acetoacetanisidide	97	$C_{36}H_{32}O_6N_6Cl_2$	11.7	11.5	Red-brown	Yell.-orange
3-Hydroxy-2-naphthanilide	127[a]	$C_{48}H_{32}O_4N_6Cl_2$	10.1	10.2	Blue-black	Blue gray
3-Hydroxy-2-naphtho-*o*-phenetidide	92	$C_{52}H_{40}O_6N_6Cl_2$	9.18	8.76	Red-black	Lavender
3,3'-Dimethoxy-4,4'-diaminostilbene pigments						
1-Phenyl-3-methyl-5-pyrazolone	94	$C_{36}H_{32}O_4N_8$	17.5	17.1	Red-black	Dull red-br.
3-Hydroxy-2-naphtho-*o*-phenetidide	116[a]	$C_{54}H_{46}O_8N_6$	9.27	9.19, 9.24	Blue-black	Red blue
2,2'-Dichloro-4,4'-diaminostilbene pigments						
1-Phenyl-3-methyl-5-pyrazolone	93	$C_{34}H_{26}O_2N_8Cl_2$	17.2	17.1	Bright red	Orange
Acetoacetanilide	88	$C_{34}H_{28}O_4N_6Cl_2$	12.8	12.7	Orange-br.	Orange-yell.
o-Acetoacetotoluidide	94	$C_{36}H_{32}O_4N_6Cl_2$	12.3	12.3	Orange-br.	Orange-yell.
o-Acetoacetanisidide	86	$C_{36}H_{32}O_6N_6Cl_2$	11.7	11.6	Red-brown	Orange-yell.
3-Hydroxy-2-naphtho-*o*-phenetidide	113[a]	$C_{52}H_{40}O_6N_6Cl_2$	9.18	9.30, 9.66	Red-black	Violet
4,4'-Diaminostilbene pigments						
1-Phenyl-3-methyl-5-pyrazolone	97	$C_{34}H_{28}O_2N_8$	19.3	18.7, 18.9	Bright-red	Yellow red
o-Acetoacetotoluidide	91	$C_{36}H_{34}O_4N_6$	13.7	13.2	Yell.-brown	Yell.-orange

[a] Yields in excess of 100% were due to the presence of excess coupling component, precipitated by the acid coupling condition and not washed out by the hot water washing. The excess coupling component was removed by extraction with hot alcohol. The color values, mass tones, and tint tones listed were those of the crude, pigmentary product, since hot alcohol caused crystallization and loss of pigmentary color values in some cases. The N values were those of the purified products; the yields were essentially quantitative after hot alcohol extraction.

were made from 2,2'-dichloro-4,4'-diaminostilbene, and from 4,4'-diaminostilbene, to demonstrate the effect of the Cl-group and of its position. The pigments made, together with their colors, are presented in Table I.



I, X = Cl-
II, X = CH_3O-

Compounds I and II were prepared by the action of oxygen upon solutions of 3-chloro- and 3-methoxy-4-nitrotoluene, respectively, in 33% methanolic potassium hydroxide at 10°, followed by reduction of the nitro groups. The method was similar to that used by Treves[1] for the preparation of 2,2'-dimethoxy-4,4'-dinitrostilbene from 2-methoxy-4-nitrotoluene. While the point was not proved conclusively by the preparation of the pure *cis* and *trans* isomers and by interconversion, the ultraviolet absorption curves show that the *trans* isomer was obtained in each case. The only 3,3'-disubstituted-4,4'-diaminostilbene which has been described previously is 3,3'-dicarboxy-4,4'-diaminostilbene[2] which was prepared by the alkaline hypochlorite condensation of 4-nitrotoluene-3-carboxylic acid. *trans*-2,2'-Dichloro-4,4'-diaminostilbene was made in the same way as I and II.

Extremely variable results were obtained when 30% hydrogen peroxide was used in place of oxygen in the preparation of compound I. The yields of product varied from 0 to 56%, and some of the dibenzyl derivative always was present as contaminant. The Treves[1] method gave 85% yields of the desired stilbene.

Solubility difficulties prevented obtaining quantitative absorption data; accordingly we can only compare the absorption maxima wave lengths; these are presented in Table II. The group of nine compounds, formed by all combinations of the three coupling agents with three tetrazonium salts, shows a good consistency in absorption maxima throughout. First, there is observed a 20–23 mμ shift to longer wave lengths upon insertion of a central vinyl group into each 3,3'-dichlorobenzidine

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[1] G. R. Treves, THIS JOURNAL, **70**, 875 (1948).

[2] F. Straub and W. Hanhart, U. S. Patent 1,936,277.

coupling product. This is the expected result of a simple extension of the conjugated system.[3]

TABLE II

ABSORPTION MAXIMA WAVE LENGTHS (mμ)

Coupling component	Tetrazo component				
		Substituted 4,4′-diaminostilbene			
	3,3′-Dichlorobenzidine	3,3′-Dichloro-	2,2′-Dichloro-	No subst.	3,3′-Dimethoxy-
Acetoacetoanilide	429	450	435		
Acetoacet-*o*-toluidide	428	448	436	452	
1-Phenyl-3-methyl-5-pyrazolone	454	477	448	484	502

Next, the change in positions of the two chlorine atoms from 3,3′ to 2,2′ effects a hypsochromic shift of 12 to 29 mμ. Steric interference with stilbene planarity by the two *o*-chlorines (even though in only one of the two possible planar configurations of each phenyl[4]) may be responsible. If analogy can be drawn between 4-aminostilbene and the 4,4′-bis-(azo)-stilbene portion of the pigment, planarity is more important to the first excited state than to the ground state[5,6] so that interference with planarity raises the energy of the excited state more than that of the ground state and produces the hypsochromic shift.

Very little difference is found between corresponding pairs in the acetoacetanilide and *o*-acetoacetotoluidide series. This demonstrates that the terminal phenyl groups enter into conjugation with the bis-(azo)-stilbene system practically not at all, because the steric interference with phenyl-NHCO planarity by the *o*-methyl group, as demonstrated in models, is sufficient to decrease such conjugation and produce more than the observed 1 or 2 mμ hypsochromic shift. Indeed, in the 2,2′-dichlorostilbene pair a 1 mμ opposite shift is seen.

The bathochromic shift shown by the series from 1-phenyl-3-methyl-5-pyrazolone, in comparison with the series from acetoacetanilide or *o*-acetoacetotoluidide, indicates that in the first there is a degree of continuity of π-electrons between the stilbene and pyrazolone portions of the molecules, through the azo groups. It is conceivable that this conjugation extends through to the terminal phenyl, but that can be ascertained only by comparison with absorption of the unphenylated compound or that compound having a cyclohexyl group in place of the phenyl.

In view of the solubility difficulties mentioned above and the fact that most of these compounds showed changes in absorption spectra after a few minutes in solution, perhaps due to *trans–cis* isomerization,[4] it is apparent that valid comparisons cannot be made further among these compounds in the absence of more accurate data.

Experimental

3-Chloro-4-nitrotoluene.—The method outlined by Kornblum[7] for the deamination of 3-nitro-4-aminotoluene was used on 2-amino-4-nitro-5-chlorotoluene.[8] Chloroform extraction and vacuum distillation gave a 65% yield of a clear yellow oil, b.p. 108° (3 mm.), m.p. 22.5°, $n^{26}\text{D}$ 1.5617, $n^{68.5}\text{D}$ 1.5426. Deamination in alcohol by the method of Wibaut[9] gave a 43% yield.

3,3′-Dichloro-4,4′-dinitrostilbene (Oxygen Method).—The method was similar to that used by Treves[1] for 2-methoxy-4-nitrotoluene. A solution of 5 cc. of acetone in 200 cc. of 33% methanolic potassium hydroxide was cooled to 10°, a slow stream of oxygen was turned on, high speed stirring was commenced, and 5 g. (0.029 mole) of 3-chloro-4-nitrotoluene was added. The solution was stirred rapidly with oxygen for two hours with ice-bath cooling, and for three hours without external cooling. The mixture was poured into 2 l. of water, and the solid was removed by filtration. It was washed with water until base-free, three times with alcohol, and was dried. There was obtained 4.2 g. (85%) of a yellow solid; recrystallization from 250 cc. of glacial acetic acid gave uniform yellow needles, m.p. 284–285° (*ca.* 55% recovery in all runs made).

Anal. Calcd. for $C_{14}H_8O_4N_2Cl_2$: C, 49.6; H, 2.38; N, 8.26; Cl, 20.9. Found: C, 49.7; H, 2.60; N, 8.37, Cl, 21.0.

Many other runs made in the same way gave similar results. When the condensation was conducted in the same way at room temperature only a red solid was produced. When the preparation was conducted on a 10-g. scale red colored by-products always resulted, probably because our equipment was not capable of dispersing the oxygen rapidly and efficiently enough on a larger scale. One run drowned after one hour stirring at 3° contained considerable 1,2-bis-(3-chloro-4-nitrophenyl)-ethane (*vide infra*).

3,3′-Dichloro-4,4′-dinitrostilbene (Hydrogen Peroxide Method).—3-Chloro-4-nitrotoluene, 5.0 g. (0.029 mole), was stirred with 100 cc. of 33% methanolic potassium hydroxide at 0°. No color formation took place. The solution was allowed to warm slowly. The red color which formed was discharged each time with 30% hydrogen peroxide solution. The solution was warmed on a steam-bath and hydrogen peroxide was added portionwise until no further color formation took place. The mixture was diluted with five volumes of water and was filtered. The solid was washed with water and alcohol, and was dried. There was obtained 1.0 g. (20%) of product; recrystallization from 100 cc. of glacial acetic acid gave long yellow needles, m.p. 285–286°.

Anal. Calcd. for $C_{14}H_8O_4N_2Cl_2$: C, 49.6; H, 2.38; N, 8.26; Cl, 20.9. Found: C, 49.8; H, 2.48; N, 8.46; Cl, 20.5.

This procedure was not reproducible. In subsequent runs using 3, 10 or 30% hydrogen peroxide, under the same apparent conditions, the yields varied from 0 to 56% and the product always contained some of the dibenzyl derivative.

1,2-Bis-(3-chloro-4-nitrophenyl)-ethane.—Several of the low melting batches of 3,3′-dichloro-4,4′-dinitrostilbene, prepared by the hydrogen peroxide method, were composited and boiled with ethyl acetate, filtered, and the ethyl acetate solution allowed to cool. The crystals, mainly rhombs, were removed by filtration and dried, m.p. 173–185°. One more recrystallization from ethyl acetate gave material melting at 178–180°. There was only a minute contamination with needles when viewed under the microscope. Further recrystallizations were not made due to the small amount of material.

Anal. Calcd. for $C_{14}H_{10}O_4N_2Cl_2$: C, 49.3; H, 2.95. Found: C, 49.5; H, 3.10.

3,3′-Dichloro-4,4′-diaminostilbene.—A mixture of 31.5 g. (0.09 mole) of 3,3′-dichloro-4,4′-dinitrostilbene, 126 g. (1.5 moles) of 70–72% real sodium hydrosulfide, and 1600 cc. of 95% alcohol was heated under reflux with stirring for four hours and was drowned in 6 l. of water. The solid was removed by filtration, washed sulfide-free with water, and dried *in vacuo*. There was obtained 16.8 g. (65%) of a light tan solid. Recrystallization from 1300 cc. of absolute alcohol, including a treatment with 2 g. of Norite, gave 7.5 g. of very light tan leaflets, m.p. 200–201°.

Anal. Calcd. for $C_{14}H_{12}N_2Cl_2$: C, 60.2; H, 4.33; N, 10.0; Cl, 25.4. Found: C, 60.5; H, 4.52; N, 10.0; Cl, 25.1.

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[3] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice–Hall Inc., New York, N. Y., 1945, p. 164.

[4] D. W. Hein and Elliot S. Pierce, THIS JOURNAL, **76**, 2725 (1954).

[5] R. N. Beale and E. M. F. Roe, *ibid.*, **74**, 2302 (1952).

[6] C. A. Coulson and J. Jacobs, *J. Chem. Soc.*, 1983 (1949).

[7] N. Kornblum, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 294.

[8] Ad. Claus and E. Stapelberg, *Ann.*, **274**, 294, 299 (1893).

[9] J. P. Wibaut, *Rec. trav. chim.*, **32**, 295 (1913).

Saturation of an alcohol solution of the above product with hydrogen chloride gas gave the dihydrochloride as needles, decomposition point 276–277°. Another sample, prepared similarly from a less pure diamine, decomposition point 271°, gave the following analysis.

Anal. Calcd. for $C_{14}H_{14}N_2Cl_4$: C, 47.8; H, 4.01; N, 7.96; Cl, 40.3. Found: C, 47.4; H, 4.68; N, 7.77; Cl, 39.8.

3,3′-Dichlorostilbene-4,4′-tetrazonium Chloride.—A mixture of 5.28 g. (0.015 mole) of 3,3′-dichloro-4,4′-diaminostilbene dihydrochloride, 12 cc. of 5 *N* hydrochloric acid, and 45 cc. of water was cooled to 5° and was tetrazotized with 30 cc. of 1 *N* sodium nitrite solution at 0–5°. The solution was stirred an additional 20 minutes, the excess nitrite was destroyed with sulfamic acid, Super-cel was added, and the solution was filtered cold.

The Coupling of 3,3′-Dichlorostilbene-4,4′-tetrazonium Chloride with Acetoacetanilide.—Acetoacetanilide, 3.9 g. (0.022 mole), was dissolved in 6 cc. of 5 *N* sodium hydroxide and 40 cc. of water. It was precipitated by the dropwise addition of glacial acetic acid until the slurry was slightly acid to litmus. The tetrazonium chloride solution, buffered with 13.5 cc. of 2 *N* sodium acetate solution, was added dropwise to the acetoacetanilide slurry at 5–10°. Coupling was rapid. The mixture was stirred for two hours without further cooling, and for one hour at 85–90°. It was filtered hot, the solid was washed with water until acid-free, and dried at 60°. There was obtained 4.7 g. (72%) of an orange-yellow pigment. The other couplings were made in the same general manner.

3,3′-Dimethoxy-4,4′-dinitrostilbene.—A solution of 2 g. (0.012 mole) of 3-methoxy-4-nitrotoluene[10] in 3 cc. of acetone was added to 100 cc. of 33% methanolic potassium hydroxide at 10°. The deep bluish-red color of the intermediate which developed was discharged by bubbling in oxygen for two hours while stirring rapidly. The color changed from red to tan to brown. The mixture was diluted with 500 cc. of water and filtered. The solid was washed with water and with a small amount of methanol. After several recrystallizations from glacial acetic acid, it melted at 195–196.5°.

Anal. Calcd. for $C_{16}H_{14}O_6N_2$: C, 58.2; H, 4.27; N, 8.48. Found: C, 58.1; H, 4.23; N, 8.76.

In another run, the mixture was stirred for six hours. From 8 g. (0.05 mole) of 3-methoxy-4-nitrotoluene there was obtained 5.7 g. (72%) of product, m.p. 194–196°. In a series of experiments it was found necessary to bubble in oxygen for about six hours and to stir the mixture for a short time before the oxygen was introduced. If the oxygen was introduced at the same time as the acetone solution of 3-methoxy-4-nitrotoluene, then a product was obtained which melted at 190–240°. The higher melting fraction was not characterized.

3,3′-Dimethoxy-4,4′-diaminostilbene.—A solution of 5 g. (0.01 mole) of 3,3′-dimethoxy-4,4′-dinitrostilbene and 15 g. (0.06 mole) of sodium sulfide monohydrate in 200 cc. of alcohol was heated under reflux for four hours, cooled, and poured onto ice (total volume 500 cc.). The light colored solid was removed by filtration, washed with water and dried. There was obtained 4 g. (98%) of light yellow-tan flakes, m.p. 148–150°.

Anal. Calcd. for $C_{16}H_{18}O_2N_2$: N, 10.4; CH_3O-, 23.0. Found: N, 10.2; CH_3O-, 23.8, 23.5.

3,3′-Dimethoxystilbene-4,4′-tetrazonium Chloride.—3,3′-Dimethoxy-4,4′-diaminostilbene, 1.35 g. (0.005 mole), was dissolved in 100 cc. of water and 10 cc. of 1 *N* hydrochloric acid by heating and stirring. The solution was cooled to 10° and the dihydrochloride was precipitated by the dropwise addition of 5 cc. of 5 *N* hydrochloric acid. 1 *N* Sodium nitrite solution, 11 cc., was added and the solution was stirred for one hour. The excess nitrous acid was destroyed by the addition of a small amount of sulfamic acid.

***trans*-2,2′-Dichloro-4,4′-dinitrostilbene.**—Two hundred cc. of 33% methanolic potassium hydroxide was placed in a flask, a fairly rapid stream of oxygen was passed into it, and high speed stirring was commenced. 2-Chloro-4-nitrotoluene,[11] 5 g. (0.015 mole), dissolved in 30 cc. of warm absolute alcohol, was added, and stirring and oxygen addition were continued for 20 minutes. The purple color was discharged and the mixture became yellow within two minutes. It was drowned in three liters of water, filtered, the solid was washed base-free with water, and then three times with 95% alcohol. There was obtained 4.5 g. (91%) of a yellow crystalline solid, m.p. 260–290°. Recrystallization from 25 cc. of nitrobenzene gave 2.2 g. of uniform long yellow needles, m.p. 294–296°.

Anal. Calcd. for $C_{14}H_8O_4N_2Cl_2$: C, 49.6; H, 2.38; N, 8.26; Cl, 20.9. Found: C, 50.0; H, 2.52; N, 8.34; Cl, 21.0.

Green[12] reported a melting point of 302° after repeated recrystallizations from nitrobenzene and phenol. The above method was found to give much better yields than Green's method. This preparation was conducted on a 10-g. scale as readily as on the 5-g. scale.

***trans*-2,2′-Dichloro-4,4′-diaminostilbene.**—A mixture of 57 g. (0.17 mole) of 2,2′-dichloro-4,4′-dinitrostilbene and 220 g. (2.75 moles) of 70–72% real sodium hydrosulfide in 2,850 cc. of 95% alcohol was heated under reflux for three hours with stirring, drowned in ten liters of water, filtered, and the solid was washed sulfide-free with water. There was obtained 37.0 g. (79%) of uniform yellow needles, m.p. 180–185°. No solvent or solvent combination was found from which this material could be recrystallized satisfactorily.

Anal. Calcd. for $C_{14}H_{12}N_2Cl_2$: C, 60.2; H, 4.33; N, 10.0; Cl, 25.4. Found: C, 59.4; H, 4.50, 4.68; N, 9.93; Cl, 25.2.

The dihydrochloride was formed by passing hydrogen chloride gas into an alcohol solution of the compound, decomposition point 286°.

2,2′-Dichlorostilbene-4,4′-tetrazonium Chloride.—2,2′-Dichloro-4,4′-diaminostilbene dihydrochloride, 1.76 g. (0.005 mole), was slurried with 100 cc. of water and 4 cc. of 5 *N* hydrochloric acid, cooled to 0°, and treated with 10 cc. of 1 *N* sodium nitrite solution. The mixture was stirred for 15 minutes, the excess nitrite was destroyed with sulfamic acid, Super-cel was added. and the mixture was filtered cold.

Stilbene-4,4′-tetrazonium Chloride.—4,4′-Diaminostilbene, 1.05 g. (0.005 mole), was dissolved in a hot solution of 6 cc. of 5 *N* hydrochloric acid in 50 cc. of water. The solution was cooled to 5° and was tetrazotized with 10 cc. of 1 *N* sodium nitrite solution. It was stirred for 15 minutes, the excess nitrite was destroyed with sulfamic acid, Super-cel was added, and the mixture was filtered.

Mass Tone and Tint Tone Inks.—Color comparisons were made by Hoover Muller rub-out using 0.5 g. of pigment and 1.0-g. UV-1C vehicle, mulled 4 × 100 revolutions with 150 lb. pressure. Tints were prepared using 100 parts zinc oxide paste to 1 part colored pigment paste.

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BOUND BROOK, N. J.

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