bined with the organic layer and dried over anhydrous potassium carbonate. Removal of the solvent under reduced pressure and nitrogen gave a mass of pasty, brown crystals which were recrystallized twice from "Skelly A" to give 16 g. (72.5%) of a yellow crystalline material, m.p. 46–49°. An analytical sample was prepared by successive recrystallization followed by chromatographing on alumina followed by recrystallization, m.p. 51.5–52.0° (52°, no yield reported from diacetosuccinic ethyl ester and hydrazine followed by saponification and decarboxylation[27]) (52°, from acetonylacetone and the formyl derivative of hydrazine followed by saponification, no yield reported[28]).

Anal. Calcd. for $C_6H_{10}N_2$: C, 65.41; H, 9.15; N, 25.43. Found: C, 65.34; H, 9.21; N, 25.12.

Benzoylation of 1-Amino-2,5-dimethylpyrrole.—A benzoyl derivative was prepared by treating 2.25 g. (0.02 mole) of 1-amino-2,5-dimethylpyrrole with benzoyl chloride in pyridine[29] to obtain 2.1 g. (49%) of crystals, m.p. 178–183°. Recrystallization from 85% ethanol gave crystals, m.p. 184–185.5°. A mixed melting point with a sample prepared according to the procedure described in reference 11 was not depressed, m.p. 180–182° (177–179°, no yield, from N-aminopyrrole[27]) (184–185°, 60–66%, from reaction of acetonylacetone with benzoyl derivative of hydrazine[11]).

Reduction of 1-Amino-2,5-dimethylpyrrole to 1-Amino-2,5-dimethylpyrrolidine.—Hydrogenation of 11 g. (0.1 mole) of 1-amino-2,5-dimethylpyrrole in 65 ml. of glacial acetic acid with 2 g. of 5% rhodium on alumina catalyst was carried out at 3 atmospheres. Hydrogen absorption amounted to 112%, based on two double bonds, at room temperature in 2 hours. The catalyst was removed, the solution made basic with potassium hydroxide, and then extracted with methylene chloride. The extract was dried over anhydrous potassium carbonate and the solvent removed under reduced pressure to give 10 g. of a brown liquid. Distillation resulted in 4.5 g. (39%) of 1-amino-2,5-dimethylpyrrolidine, b.p. 36–37° (13 mm.), n^{24}D 1.4488.

A picrate was prepared from a solution of picric acid in ether. m.p. 154–156° dec. A mixed melting point with the picrate prepared by the hydrogenation of the N-nitroso compound melted at 154–156° dec.

The tetrazene was prepared by oxidation with potassium permanganate as described previously, m.p. 43–44°. A mixed melting point with the sample prepared by oxidation of the N-amino product from reduction of the nitroso intermediate melted at 41–43°.

Infrared Spectra.—A Perkin-Elmer model 21 double beam recording 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 No. DA 30-069-ORD-1158.

BROOKLYN, N. Y.

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[27] C. Bulow, *Ber.*, **35**, 4311 (1902).

[28] E. E. Blaise, *Compt. rend.*, **172**, 221 (1921).

[29] Reference 21, p. 177.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo Compounds. Oxidation Studies of 1,1-Disubstituted Hydrazines[1]

BY C. G. OVERBERGER AND BURTON S. MARKS[2]

RECEIVED MARCH 4, 1955

The oxidation of 1,1-dibenzylhydrazine with bromine in ethanol and with *t*-butyl hypochlorite followed by reaction with base has been studied. Two reaction paths are proposed, one to form bibenzyl by an unusual nitrogen elimination and two, the formation of a tetrazene and its decomposition products, benzylamine, dibenzylamine and benzaldehyde. From the bromine oxidation, ethyl benzoate was also isolated. From the oxidation with the hypochlorite in addition to normal products some tribenzylhydrazine was found. The oxidation of 1-amino-2,6-dicyano-2,6-dimethylpiperidine with permanganate was examined and the products compared with the previously reported bromine oxidation of the same compound. It is concluded that resonance stabilization of the intermediate after loss of nitrogen favors the abnormal reaction, that is, nitrogen elimination without tetrazene formation.

A large number of oxidations of 1,1-disubstituted hydrazines are recorded, many of which were reported by Wieland.[3] These oxidations were carried out with commonly employed oxidizing agents, including benzoquinone, potassium permanganate, bromine, sodium hypochlorite, ferric chloride, mercuric oxide, etc. A tetrazene was the usual primary product.

As a result of a review of this previous work, two anomalous results from these oxidations were noted. The first example was reported by Busch and Weiss[4] who treated 1,1-dibenzylhydrazine with mercuric oxide and obtained bibenzyl as the only product along with the theoretical evolution of nitrogen. Curtius and Franzen[5] performed the same oxidation with mercuric oxide, using as a solvent, instead of ethanol, chloroform. They obtained, in good yield, tetrabenzyltetrazene, and do not report any bibenzyl. Wieland[6] repeated this oxidation and obtained small amounts of tetrazene and largely bibenzyl.

Michaelis[7,8] treated 1-allyl-1-phenylhydrazine with mercuric oxide and obtained instead of the expected tetrazene the rearranged benzeneazopropene-2, indicative of a type of allylic rearrangement. If, however, ferric chloride was used instead of mercuric oxide, then the expected tetrazene was obtained.[7] Similarly, 1-allyl-1-*p*-tolylhydrazine reacted with mercuric oxide to give *p*-tolylazopropene-2[8] but yielded the tetrazene with ferric chloride.

Bromine oxidation of a compound reported to

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[1] This is the 14th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger, L. C. Palmer, B. S. Marks and N. R. Byrd, THIS JOURNAL, **77**, 4100 (1955).

[2] This paper comprises a portion of a thesis presented by B. S. Marks in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] H. Wieland, "Die Hydrazine," Verlag von Ferdinand Enke, Stuttgart, 1913, pp. 38, 39.

[4] M. Busch and B. Weiss, *Ber.*, **33**, 2701 (1900).

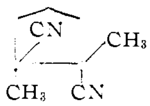
[5] T. Curtius and H. Franzen, *ibid.*, **34**, 552 (1901).

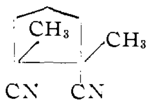
[6] H. Wieland and H. Fressel, *Ann.*, **392**, 133 (1912).

[7] A. Michaelis and C. Claessen, *Ber.*, **22**, 2233 (1889).

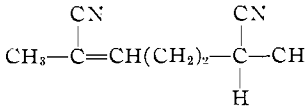
[8] A. Michaelis and K. Luxembourg, *ibid.*, **26**, 2174 (1893).

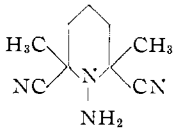
be 2,7-dicyano-2,7-dimethylhomopiperidazine,[9,10] yielded three products, *cis*- and *trans*-1,2-dicyano-1,2-dimethylcyclopentane (I and II) and 2,6-dicyanoheptene-2, (III).[10]


I


II

Careful scrutiny of the products[10] failed to show any tetrazene formation from the bromine–ethanol oxidation. Reinvestigation[11] of the structure of 2,7-dicyano-2,7-dimethylhomopiperidazine has demonstrated that it was not a seven-membered ring but instead a 1,1-disubstituted hydrazine, namely, 1-amino-2,6-dicyano-2,6-dimethylpiperidine (IV).

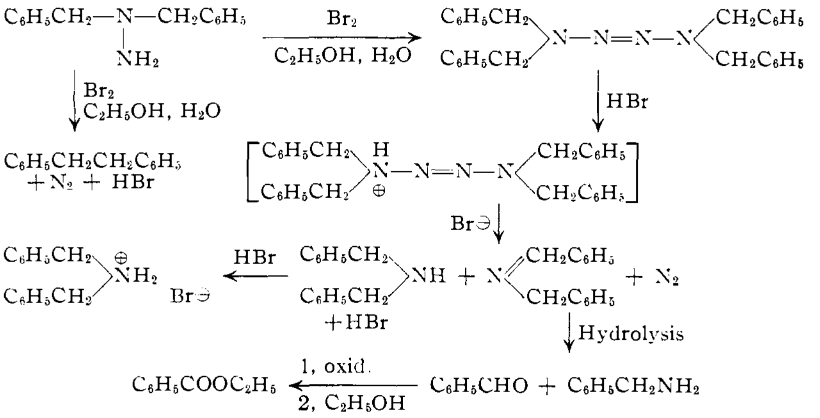

$CH_3-C(CN)=CH(CH_2)_2-CH(CN)-CH_3$
III


IV

Oxidation of IV with potassium permanganate in acetone solution yielded 26.3% of the tetrazene and 32.4% of the mixed *cis* and *trans* isomers, I and II.

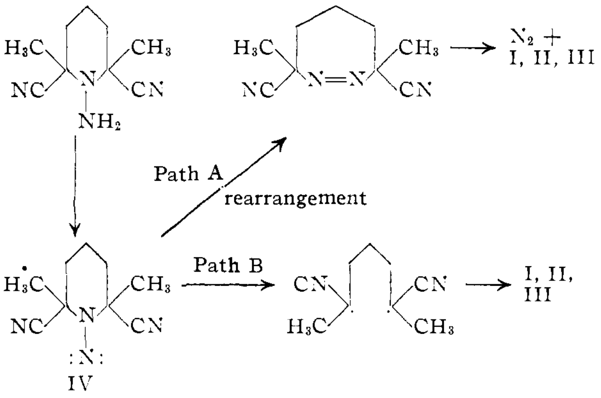
Infrared spectra of one of the cyclic isomers and a mixture of the cyclic isomers obtained from both oxidation methods were identical. III was not obtained from the permanganate oxidation.

Oxidation of 1,1-dibenzylhydrazine with bromine in a 2:1 ethanol water mixture produced as expected the acid decomposition products of the tetrazene,[6] namely, benzylamine, dibenzylamine (hydrogen bromide salt), benzaldehyde, ethyl benzoate (probably derived from the benzaldehyde) and a trace of the tetrazene. Bibenzyl which was probably not derived from the tetrazene was also found and a 68% yield of the theoretical nitrogen was evolved. A general reaction scheme is outlined below.



Oxidation studies with bromine and chlorine on 1-amino-2,6-dimethylpiperidine were attempted. Yields of nitrogen evolved ranged from 60–95% of the theoretical. Product identification was unsuccessful except for 2,6-dimethylpiperidine, which was obtained in yields up to 18%. The products could not be identified because of the high degree of bromination and certain apparent carbon skeletal changes. The oxidation with halogen seemed to be quite complex, and further study with other oxidizing agents is contemplated.

Reaction of 1,1-dibenzylhydrazine with an equimolar quantity of *t*-butyl hypochlorite followed by alcoholic potassium hydroxide gave 15.5% of the expected tetrazene, 12.71% of dibenzylamine and 12.04% of bibenzyl. There were also obtained in small amounts the products of the hydrolysis of benzylidenebenzylamine as well as *trans*-stilbene and tribenzylhydrazine. Presumably the N-chloro compound was first formed followed by reaction with base to give a possible intermediate (IV) shown later, or regeneration of N-amine with the resultant formation of potassium hypochlorite. An attractive suggestion is that one oxidation path yields the tetrazene and its decomposition products, whereas another path leads to bibenzyl. Tribenzylhydrazine also was found in the isolation of products from the reaction of *t*-butyl hypochlorite with 1,1-dibenzylhydrazine in which no base was added, together with the hydrochloride salt of the 1,1-dibenzylhydrazine.



The formation of tetrazene and the mechanism of its acid decomposition has been suggested by Wieland.[6] The mechanism of the formation of bibenzyl in the oxidations of 1,1-dibenzylhydrazine and I and II, in the oxidation of IV was of interest, because of the possibility of biradical intermediates.

Possible mechanisms[10] for the appearance of I, II, and III from an azo intermediate obtained from a 1,2-disubstituted hydrazine are suggested below.

"Path A" and "path B" should both be possible with 1-amino-2,6-dicyano-2,6-dimethylpiperidine.

"Path B" is attractive since it readily explains the formation of bibenzyl from 1,1-dibenzylhydrazine. In this case, if "Path A" was correct and rearrangement occurred, then the rearranged prod-

[9] C. G. Overberger, T. B. Gibbs, Jr., S. Chibnik, P. Huang and J. J. Monagle, THIS JOURNAL, **74**, 3290 (1952).

[10] C. G. Overberger, P. Huang and T. B. Gibbs, Jr., *ibid.*, **75**, 2082 (1953).

[11] C. G. Overberger and B. S. Marks, *ibid.*, **77**, 4097 (1955).

uct, azodibenzyl, $C_6H_5CH_2N{=}NCH_2C_6H_5$, should have been isolated in the hypohalite oxidation. In the halogen oxidation, the acid media would have probably rearranged the azodibenzyl to the hydrazone which would have hydrolyzed to benzaldehyde and benzylhydrazine. No benzylhydrazine was isolated, however, although it is clear that these negative results do not eliminate the possibility of "Path A."

It is noted that in both the cases studied the intermediate fragment after loss of nitrogen (path B) whether it involves ions or radicals can be stabilized by resonance through either a nitrile group or a phenyl group and this fact may provide some driving force for the loss of nitrogen by "path B" rather than tetrazene formation. We are at present attempting to elucidate the details of this novel nitrogen elimination reaction.

Experimental[12]

Bromine Oxidation of 1,1-Dibenzylhydrazine.—This procedure represents the optimum separation procedure after numerous trials.

To a solution of 42.4 g. (0.2 mole) of 1,1-dibenzylhydrazine, 1200 ml. of ethanol and 600 ml. of water was added dropwise 70.4 g. (0.44 mole) of bromine. Nitrogen evolution was measured and 3.047 l. (cor.) (68%) was obtained over a 3-hour period. The reaction was stirred for an additional 18 hours, which transformed the orange color of the solution to yellow. At reduced pressure, the volume of the reaction mixture was reduced to 800 ml. A chart of the separation procedure is included for clarity. A copious white precipitate (A) appeared and yielded after filtration 14 g. (0.05 mole), m.p. 258–259°. The addition of hydrogen bromide to a pure sample of dibenzylamine gave a white salt which melted at 259–261° (266°)[13] and a mixed m.p. with the white precipitate melted at 259–261°. By recrystallization from an ethanol–ether solution, the m.p. of both salts were raised to 265–266°.

To the acidic filtrate was added 1.4 l. of water and the filtrate was extracted ten times with ether. The combined ether extracts (B) were washed with water until the washings were neutral and then dried over anhydrous magnesium sulfate. The residue, after removal of the solvent, was fractionally distilled at 0.4 mm. pressure until (C) began to distil at 85°, which solidified on the condenser as a white solid. The white precipitate was dissolved in ether and washed with 5% potassium hydroxide solution, water, sodium bisulfite solution and water, respectively. After drying and removal of the solvent, a white precipitate (C) was obtained, m.p. 49–52°, 3.3 g. (9%); recrystallized from an ethanol–water solution, m.p. 52–53°. A mixed melting point with bibenzyl, m.p. 52–53°, gave no depression. The infrared spectra of both were identical.

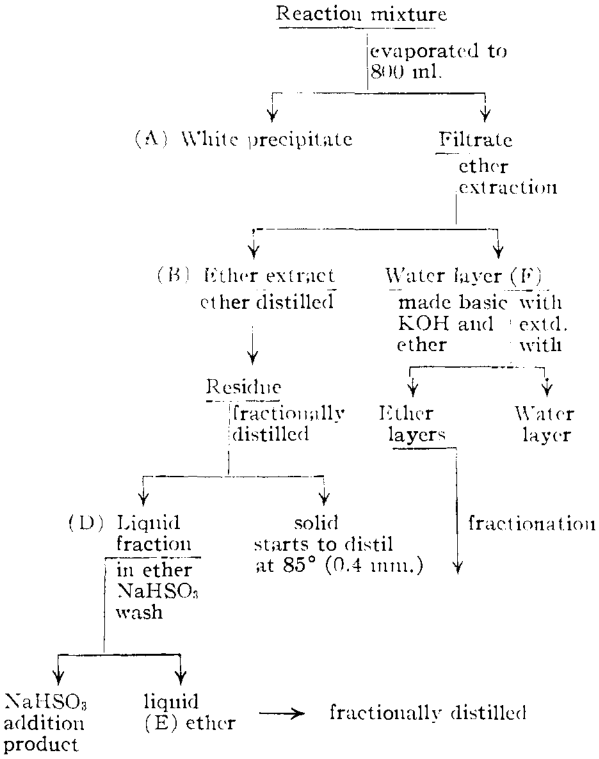
The fractionated liquid (D) was treated with 40% sodium bisulfite solution and extracted three times with ether. The ether extracts were further washed with 40% sodium bisulfite two times to yield a total of 10.4 g. (0.05 mole) of a bisulfite addition product. The 2,4-dinitrophenylhydrazone derivative of the aldehyde melted at 234–236°. The 2,4-dinitrophenylhydrazone of benzaldehyde melts at 236°, and a mixed melting point with the isolated derivative was not depressed.

The ether solution (E) was dried and the residue fractionally distilled several times with separate portions[14] being redistilled to give a yield of 2.44 g. of slightly impure ethyl benzoate, equivalent to 1.73 g. (0.0163 mole) of benzaldehyde, b.p. 64.5–67° (3.25 mm.), n^{26}_D 1.5090 (n^{15}_D 1.5079).[15] An infrared comparison with a known sample indicated that the fraction was largely ethyl benzoate.

The acidic water residue (F) that remained after extraction was cooled and made strongly basic with solid potassium hydroxide. The solution was extracted with ether five times, and these combined extracts dried over anhydrous magnesium sulfate. The residue was fractionally distilled to give 5.1 g., b.p. 36–38° (1.3 mm.), 42° (1.75 mm.) of benzylamine. $n^{25.5}_D$ 1.5385 (n^{20}_D 1.5402).[16] Picrates were prepared from individual fractions of the above 5.1 g., m.p. 196–198° dec. A mixed m.p. of each of these picrates, m.p. 196–198° dec. with the picrate of benzylamine, m.p. 196–198° dec. (195–199°)[17] was not depressed.

A second major fraction, 3.4 g., b.p. 102° (0.6 mm.), $n^{25.5}_D$ 1.5720 proved to be dibenzylamine ($n^{21.6}_D$ 1.5743).[18] Picrates were prepared from several fractions, m.p. 91–93°. A mixed melting point with the picrate of dibenzylamine, m.p. 93–94°, melted at 91–93°.

SEPARATION CHART



Potassium Permanganate Oxidation of 1-Amino-2,6-dicyano-2,6-dimethylpiperidine.—This oxidation was carried out in a similar way to that reported previously.[11] Instead of evaporating most of the ether and subsequently cooling the residue to obtain the tetrazene, the ether solution was chromatographed through a column of alumina with dry ether used as the eluent. Five fractions were collected. Fractions 1 and 2 which were not part of a yellow band gave a residue which was washed with ether. The ether washings were removed and the residue crystallized from ethanol to give a white precipitate, m.p. 162–163°. A mixed melting point with *cis*-1,2-dicyano-1,2-dimethylcyclopentane, m.p. 161.8–162.8°, from the bromine oxidation[10] melted at 162–163°. The infrared spectra of the compounds from both sources were identical. The total yield of mixed isomers was 1.35 g. (32.4%, based on 5 g. of starting material). The infrared spectrum of the impure white precipitate before washing was identical with the spectrum of a mixture of *cis*- and *trans*-1,2-dicyano-1,2-dimethylcyclopentane.[10]

The last three fractions gave a yellow precipitate, 1.3 g. (26.3%) and this compound showed no depression in melting point when mixed with the tetrazene of 1-amino-2,6-dicyano-2,6-dimethylpiperidine.[11]

Reaction of 1,1-Dibenzylhydrazine with *t*-Butyl Hypochlorite and Potassium Hydroxide.—This procedure represents the optimum separation procedure after many trials. In 150 ml. of dry ether was dissolved 15 g. (0.0708 mole) of

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(12) All melting points are corrected.

(13) H. Lempricht, *Ann.*, **144**, 314 (1867).

(14) Experimental details for this separation are available on request of the senior author.

(15) J. S. Lumsden, *J. Chem. Soc.*, **87**, 94 (1905).

(16) M. Konowalow, *Ber.*, **28**, 1861 (1895).

(17) G. Jerusalem, *J. Chem. Soc.*, **95**, 1283 (1909).

(18) J. W. Brühl, *Z. physik. Chem.*, **16**, 218 (1895).

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.

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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).

BROOKLYN, N. Y.

[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

RECEIVED NOVEMBER 6, 1954

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