bonates isolated, while previous investigators found that the corresponding normal carbonates were formed when phosgene was allowed to stand in contact with ethylene glycol[3] or with hydroquinone or resorcinol.[4]

Some chlorocarbonates not previously described were prepared in the course of this study and their properties are summarized in Table I. The identity of several of these was more definitely established by conversion into solid derivatives already known or by analysis of the new products.

Summary

A study has been made of the yields of chlorocarbonates derived from aromatic alcohols by two patented procedures. Chlorocarbonates not previously described have been prepared.

Cincinnati, Ohio

[Contribution from the Chemical Laboratory of the University of Illinois]

A SEARCH IN THE DIPHENYLMETHANE SERIES FOR THE ISOMERISM CHARACTERISTIC OF CERTAIN DIPHENYL DERIVATIVES

By C. L. Butler, Jr.[1] with Roger Adams

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The peculiar type of isomerism that exists in many diphenyl derivatives is most satisfactorily explained by assuming that no free rotation can occur between the two benzene rings[2] and that the two rings are superimposed over each other. In no other compounds in organic chemistry has such a type of isomerism been found. Since the assumption of the free rotation of atoms when attached by a single bond is the very basis of structural organic chemistry, it is somewhat disconcerting to consider the possibilities if free rotation does not take place. Even though the diphenyl isomerism seems to be specific for the single series, the reason for this specificity is not obvious. This paper describes experiments to obtain analogous isomers in the diphenylmethane series.

The peculiar isomerism of diphenyl was discovered and the Kaufler formula[3] for benzidine (I) was suggested following a consideration of two important reactions of benzidine; tetrazotized benzidine reacts in such

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[3] Nemirowsky, *J. prakt. Chem.*, [2] **28**, 439 (1882). Vorländer, *Ann.*, **280**, 185 (1894).

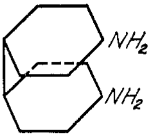
[4] Einhorn, *Ann.*, **300**, 152 (1898).

[1] This paper is an abstract of a thesis submitted by C. L. Butler, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy in chemistry at the University of Illinois.

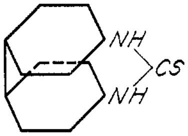
[2] (a) Cain, *J. Chem. Soc.*, **101**, 2298 (1912); **103**, 586, 2074 (1913); **105**, 1437 (1914). (b) Brady, *ibid.*, **123**, 2047 (1923). (c) Compare Turner, *Nature*, **112**, 439 (1923).

[3] (a) Kaufler, *Ber.*, **40**, 3250 (1907); *Ann.*, **351**, 151 (1907). Ref. 2 a. (b) Adams, Bullock and Wilson, This Journal, **45**, 521 (1923).

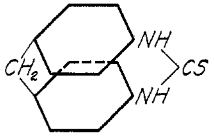
a way that one diazo group may couple or may be replaced quantitatively without affecting the other diazo group;[4] benzidine reacts with carbon disulfide (II), oxalic acid and other reagents to form ring structures through the two amino groups.[5,3] The discovery of isomeric 3,3′-dinitro and other substituted benzidines followed,[2a] and finally came the resolution of various substituted diphenic acids.[6]



I



II



III

The expectation that this type of isomerism might occur in the diphenylmethane series came from a consideration of the fact that 4,4′-diaminodiphenylmethane forms a cyclic compound with carbon disulfide[3] (III) similar to that formed from benzidine. Moreover, it is reported in the literature that two 2,2′-dinitro-4,4′-diaminodiphenylmethanes have been isolated.[7]

This investigation resolved itself into four parts: (1) further study of the formation of ring structures from 4,4′-diaminodiphenylmethane; (2) the mechanism of the coupling of tetrazotized 4,4′-diaminodiphenylmethane with one and two molecules of various components; (3) the study of the reported isomeric 2,2′-dinitro-4,4′-diaminodiphenylmethanes and of analogous isomers; (4) the formation and resolution of dicarboxy- and substituted dicarboxydiphenylmethanes.

The preparation of various ring structures from 4,4′-diaminodiphenylmethane was first attempted. Both oxalic acid and phosgene reacted readily but yielded products that were so insoluble that they could not be purified and the determination of whether the compounds were monomolecular or not was impossible. Phthalic anhydride also condensed readily but always to give a diphthalyl derivative; no compound of one molecule of each of the reacting substances was obtained.

The mode of reaction of tetrazotized 4,4′-diaminodiphenylmethane

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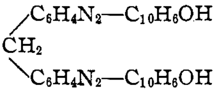
[4] (a) Schultz, *Ber.*, **17**, 461 (1884). (b) Lange, *Ber.*, **19**, 1697 (1886). (c) Ger. pat. 39,096; Friedländer, **1**, 474 (1887). (d) Patent Ann. C3327; Friedländer, **2**, 385 (1891). (e) Cain and Thorpe, "The Synthetic Dyestuffs and Intermediate Products," Charles Griffin and Co., Limited, London, **1923**, p. 70. (f) Fierz, "Grundlegende Operationen der Farbenchemie," Schulthess and Co., Zurich, **1920**, p. 151.

[5] (a) Borodine, *Jahresber.*, **1860**, 356. (b) Michler and Zimmerman, *Ber.*, **14**, 2177 (1881). (c) Strakosch, *Ber.*, **5**, 236 (1872). (d) Koller, *Ber.*, **37**, 2880 (1909).

[6] (a) Kenner and Stubbings, *J. Chem. Soc.*, **119**, 593 (1921). (b) Christie and Kenner, *ibid.*, **121**, 614 (1922); (c) **123**, 779 (1923). (d) Christie, James and Kenner, *ibid.*, **123**, 1948 (1923).

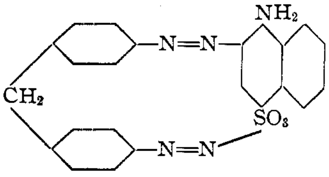
[7] Montagne and van Charante, *Rec. trav. chim.*, **31**, 343 (1912).

has not been previously investigated, due unquestionably to the fact that the dyes from this base are not substantive to cotton and are of no commercial value. A careful study of the mechanism of the conversion of 4,4′-diaminodiphenylmethane[8] into dyes has been made. The tetrazotized base couples with two molecular proportions of β-naphthol (IV) and two of naphthionic acid to give the expected dyes but it was impossible, by using one proportion of β-naphthol, to cause the formation of a substance containing one diazonium group and one β-naphthol group; the reaction product consisted always of a mixture of a dye containing two β-naphthol residues and unchanged tetrazotized base. With one molecular proportion of naphthionic acid and one of tetrazotized base an intermediate was isolated (V) which could not be purified, but which upon boiling with dil. alkali formed a readily purified dye (VI).

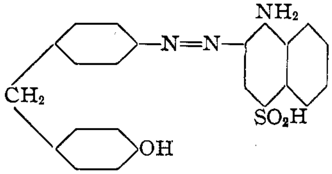


$$CH_2\begin{cases}C_6H_4N_2—C_{10}H_6OH\\C_6H_4N_2—C_{10}H_6OH\end{cases}$$

IV



V



VI

Further proof of the structure of this intermediate was obtained by causing it to react with a molecular proportion of β-naphthol to give a dye containing one proportion of β-naphthol and one of naphthionic acid. It appears, therefore, that when certain acid groupings, such as the sulfonic acid group, are present in the coupling component, tetrazotized 4,4′-diaminodiphenylmethane gives readily an intermediate product in which only one diazo group has coupled, a reaction which is also characteristic of tetrazotized benzidine.[4e,4f] With a coupling component not containing such an acid group it is impossible to obtain from tetrazotized 4,4′-diaminodiphenyl methane any product except one in which two molecules of the coupling component have entered the reaction and it is, therefore, obvious that in this respect tetrazotized 4,4′-diaminodiphenylmethane differs from tetrazotized benzidine.

Montagne and van Charante nitrated 4,4′-diaminodiphenylmethane in concd. sulfuric acid.[7] Upon dilution of the reaction mixture, a com-

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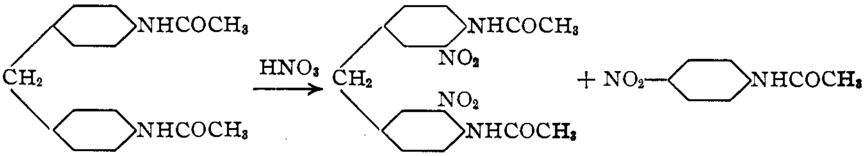
[8] It is reported [Ger. pat. 140,690, Friedländer, 7, 458 (1903)] that tetrazotized 3,3′-diamino-4,4′-dimethoxydiphenylmethane reacts with two molecular proportions of β-naphthol without the formation of an intermediate.

pound separated which the authors crystallized from alcohol; m. p., 229°. When this compound was dissolved in dil. sulfuric acid and made alkaline with ammonia a precipitate formed which on purification melted at 210°. The authors reported these substances as isomeric 2,2′-dinitro-4,4′-diaminodiphenylmethanes, but the higher-melting product was not analyzed. The experiments were repeated in this Laboratory with slightly different results. Upon pouring the reaction mixture into water no precipitate formed at once, but one gradually formed upon standing. This product after crystallization from dil. sulfuric acid melted at 229° and upon analysis proved to be the salt made up of one molecular proportion of sulfuric acid and one of 2,2′-dinitro-4,4′-diaminodiphenylmethane. If, on the other hand, this salt was crystallized from alcohol a different compound separated, which melted at 235° and proved to be a salt consisting of one molecular equivalent of sulfuric acid and two of the 2,2′-dinitro-4,4′-diaminodiphenylmethane. Either of these salts upon treatment with aqueous ammonia yielded the base that melted at 211° as compared with 210° given in the literature. The previous investigators undoubtedly had in hand the normal salt (m. p. 235°, their m. p. 228°) since their method of formation would yield this and the physical properties as reported by them agree with those of the substance produced in this research.

Upon nitrating diacetyl benzidine with nitric acid followed by hydrolysis, a 3,3′-dinitrobenzidine[2a] is produced.. A like treatment of diphthalylbenzidine yields an isomeric 3,3′-dinitrobenzidine. A like nitration was carried out with the diacetyl and the diphthalyl derivatives of 4,4′-diaminodiphenylmethane. The diacetyl derivative yielded two products, the chief one being 3,3′-dinitro-4,4′-diaceto-amidodiphenylmethane (VII) and the other *p*-nitro-acetanilide. Two products were also obtained from the diphthalyl derivative, the one in smaller amounts being 3,3′-dinitro-4,4′-diphthalimidodiphenylmethane and the larger quantity being *p*-nitrophthalimidobenzene. Upon hydrolysis the same 3,3′-dinitro-4,4′-diaminodiphenylmethane was obtained from the dinitrodiacetyl and dinitrodiphthalyl derivatives of 4,4′-diaminodiphenylmethane. Nitration of 4,4′-diaminodiphenylmethane[9,7] in sulfuric acid gave exclusively the 2,2′-dinitro derivative. In none of these reactions, however, were isomeric dinitrodiamino compounds obtained.



VII

The final part of the investigation was an attempt to resolve three

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[9] Schnitzspalm, *J. prakt. Chem.*, [2] **65**, 315 (1902).

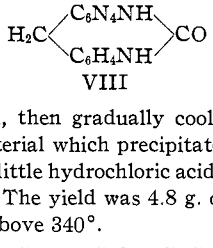
dicarboxydiphenylmethanes. The substances studied were 2,2′-dicarboxydiphenylmethane, 2,2′-dicarboxy-4,4′-dinitrodiphenylmethane and 4,4′-dicarboxy-2,2′-dinitrodiphenylmethane. In every case the dibrucine salts were obtained in crystalline form. These were fractionated from an aqueous or alcoholic solution but in each instance the same rotation was obtained from the main portion of crystals and that portion which was obtained from the mother liquors, thus showing only a single substance in solution.

The results indicate that only in the formation of rings through the two amino groups does 4,4′-diaminodiphenylmethane resemble benzidine. Whether the diphenylmethane derivatives exist sometimes in a closed form with the aryl groups superimposed over each other and at other times in an open form cannot be decided definitely from the experimental details at hand. There is a possibility of mobility within the molecule similar to that assumed for benzidine[3b] with the open form, in general, representing the more usual configuration.

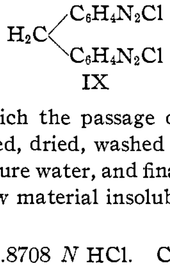
Experimental Part

Thiocarbonyl-4,4′-diaminodiphenylmethane, II.—This was prepared according to the method of Kaufler;[3a] m. p., 211°.

Carbonyl-4,4′-diaminodiphenylmethane, VIII.—Phosgene gas was passed through a solution of 10 g. of 4,4′-diaminodiphenylmethane in 125 cc. of chloroform. The mixture became warm, then gradually cooled, after which the passage of phosgene was stopped. The material which precipitated was filtered, dried, washed thoroughly with water containing a little hydrochloric acid, then with pure water, and finally was digested with hot alcohol. The yield was 4.8 g. of pale yellow material insoluble in all organic solvents, melting above 340°.


$$H_2C\langle\begin{matrix}C_6N_4NH\\C_6H_4NH\end{matrix}\rangle CO$$

VIII


$$H_2C\langle\begin{matrix}C_6H_4N_2Cl\\C_6H_4N_2Cl\end{matrix}$$

IX

Anal. Subs., 0.5000, 0.5000: 5.15, 4.85 cc. of 0.8708 *N* HCl. Calcd. for $C_{14}H_{12}ON_2$: N, 12.50. Found: 12.55, 11.83.

Action of Oxalic Acid on 4,4′-Diaminodiphenylmethane.—A mixture of 10 g. of the base and 4.5 g. of anhydrous oxalic acid was ground to a powder and heated to 205–210° for 45 minutes. The cooled product was pulverized and digested with hot alcohol. A yield of 8 g. of grayish material insoluble in all organic solvents and melting above 340° was obtained. It is probably oxalyl-4,4′-diaminodiphenylmethane, even though the analysis does not agree perfectly with the requirements for this substance.

Anal. Subs., 0.5000, 0.5000: 5.2, 5.6 cc. of 0.8237 *N* HCl. Calcd. for $C_{15}H_{12}O_2N_2$: N, 11.11. Found: 11.99, 12.91.

Condensation of 4,4′-Diaminodiphenylmethane and Phthalic Anhydride.—A thorough mixture of 14.8 g. of phthalic anhydride and 19.8 g. of the base was heated to 200–210° for an hour. The cooled product was ground, extracted with a little hot alcohol and crystallized from glacial acetic acid. The yield was 17 g. of 4,4′-diphthalimidodiphenylmethane;[3a] m. p., 327°.

The diphthalyl derivative was the only reaction product, when one molecular equivalent of phthalic anhydride, or one molecular equivalent of phthalic acid, and one of the base were refluxed together with water.

Diphenylmethane-4,4′-tetrazonium Chloride, IX.—Solutions to be used in the coupling experiments described below were prepared by dissolving 4 g. (0.02 mole) of base in 12 cc. of concd. hydrochloric acid, diluting to 300 cc., cooling the solution, and adding slowly during stirring 2.76 g. of sodium nitrite in 20% aqueous solution.

Coupling with β-Naphthol, IV.—Upon mixing a solution of 4 g. (0.02 mole) of tetrazotized base and a solution of 5.76 g. of β-naphthol (0.04 mole) in 200 cc. of 0.5% sodium hydroxide solution at 0°, there was an immediate red precipitate of dye which, after being stirred for one and a half hours, was filtered off, washed with water, dried at 50° and crystallized from 1500 cc. of hot glacial acetic acid; yield, 7.5 g. of red crystals; m. p., 259–260°.

Anal. Subs., 0.5000: 4.8 cc. of 0.8200 *N* HCl. Calcd. for $C_{33}H_{24}O_2N_4$: N, 11.02. Found: 11.02.

On adding a solution of 4 g. of tetrazotized base to 2.88 g. (0.02 mole) of an alkaline solution of β-naphthol at 0°, the same product was precipitated. This was filtered off and purified as described above; yield, 4.1 g. of red crystals; m. p., 259–260°.

Anal. Subs., 0.5000: 4.8 cc. of 0.8200 *N* HCl. Calcd. for $C_{33}H_{24}O_2N_4$: N, 11.02. Found: 11.02.

To the filtrate was added a solution of 2.88 g. of β-naphthol (0.02 mole). More dye was precipitated and purified as described above; yield, 3.7 g. of red crystals; m. p., 259–260°.

Coupling with Two Molecular Equivalents of Naphthionic Acid.—A solution of 8.92 g. of naphthionic acid (0.04 mole) was made by dissolving this amount of substance in a dilute solution containing 1.8 g. of sodium hydroxide, adding 15 g. of sodium acetate crystals and diluting to 250 cc.

Upon mixing 4 g. (0.02 mole) of a tetrazotized base solution with the cold solution of 0.04 mole of naphthionic acid at 0°, stirring for three hours, then making alkaline with sodium carbonate, the dinaphthionic acid dye[10] was formed. This was salted out by means of sodium chloride and purified by dissolving in a little water, heating, adding alcohol until a precipitate started to form, and then cooling; yield, 9.0 g. of red dye which did not melt below 340°. It is very soluble in water, and insoluble in organic reagents. Addition of acids to the aqueous solution gives a blue precipitate, soluble in dil. alkali to give a red solution.

Anal. Subs., 0.2000, 0.2000: $BaSO_4$, 0.1308, 0.1390. Calcd. for $C_{33}H_{24}O_6S_2Na_2$: S, 9.01. Found: 8.98, 9.54.

Coupling with One Molecular Equivalent of Naphthionic Acid, V.—A solution of 4.46 g. (0.02 mole) of naphthionic acid was made by dissolving this amount of substance in a dilute solution containing 1.0 g. of sodium hydroxide, adding 15 g. of sodium acetate crystals and diluting to 250 cc.

Upon mixing 4 g. (0.02 mole) of a tetrazotized base solution with the cold solution of 0.02 mole of naphthionic acid at 0°, 8 g. of a black precipitate separated. This was filtered off and washed with water, but could not be purified. Upon addition of dil. sodium hydroxide solution and warming, a red solution formed from which was salted out by means of sodium chloride 5.5 g. of a red dye, 4-azo-sodium-naphthionate-4′-hydroxydiphenylmethane, VI. This was purified in the same way as the dinaphthionic acid dye, but is less soluble in water. The dye did not melt below 340°.

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[10] Wennerberg, "Beiträge zur Kenntniss der substantiven Baumwollfarbstoffe," Ph.D., *Dissertation*, Friedrich Alexander University, Erlangen, **1918**.

Anal. Subs., 0.1655: $BaSO_4$, 0.0768. Calcd. for $C_{23}H_{18}O_4N_3SNa$: S, 7.03. Found: 6.37.

A solution of 4.46 g. (0.02 mole) of naphthionic acid, made by dissolving this amount of substance in a dilute solution of 1 g. of sodium hydroxide, adding 15 g. of sodium acetate and diluting to 200 cc., was added to a cold suspension of 8 g. (about 0.08 mole) of the black precipitate.

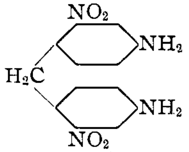
A solution of 1 g. of sodium hydroxide in 50 cc. of water was then added over a period of three hours. Stirring was continued for three hours longer at 0–5°. The reaction mixture was allowed to stand overnight and the product then salted out and purified. The product was 4-azo-sodium-naphthionate-4′-hydroxydiphenylmethane and not the expected dye.

Anal. Subs., 0.1330, 0.5000: $BaSO_4$, 0.0644; Na_2SO_4, 0.0792. Calcd for $C_{23}H_{18}O_4N_3SNa$: S, 7.03; Na, 5.05. Found: S, 6.65, Na, 5.13.

Using the procedure described in the preceding paragraph the black precipitate was coupled with β-naphthol giving the expected dye containing one β-naphthol group and one sodium naphthionate group. The product was purified by recrystallization from water. The yield was 10.5 g. of red dye quite soluble in hot water, but insoluble in organic reagents. It did not melt below 340°.

Anal. Subs., 0.2000, 0.2000: $BaSO_4$, 0.0734, 0.0753. Subs., 0.5000: Na_2SO_4, 0.0992. Calcd. for $C_{33}H_{23}O_4N_5SNa_2$: S, 5.07; Na, 7.29. Found: S, 5.04, 5.16; Na, 6.42.

2,2′-Dinitro-4,4′-diaminodiphenylmethane, X.—The directions for nitration of 4,4′-diaminodiphenylmethane used were those of Montagne and van Charante.[7] After pouring the product from a 50g. run onto 2 kg. of ice and allowing to stand in acid solution for 12 days, 50 g. of material which proved to be 2,2′-dinitro-4,4′-diaminodiphenylmethane acid sulfate separated. After crystallization from dil. sulfuric acid, it melted at 228–229° with decomposition.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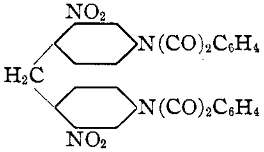

XI

Anal. Subs., 1.000, 1.000: 5.9, 6.0 cc. of 0.8237 *N* NaOH. Calcd. for $C_{12}H_{12}O_4N_2.H_2SO_4$: H_2SO_4, 25.38. Found: 24.22, 23.82.

Upon crystallization from hot alcohol, yellow-brown crystals formed. These proved to be *n*-2,2′-dinitro-4,4′-diaminodiphenylmethane sulfate; m. p., 235–236°.

Anal. Subs., 1.0000, 1.0000: 3.6, 3.6 cc. of 0.8237 *N* NaOH. Calcd. for $(C_{13}H_{12}O_4N_2)_2.H_2SO_4$: H_2SO_4, 14.54. Found: 14.53, 14.53.

One g. of each of the salts described above was added to 250 cc. of warm water. The salts hydrolyzed immediately, giving precipitates of the known 2,2′-dinitro-4,4′-diaminodiphenylmethane which, after crystallization from ethyl alcohol, melted at 211–212°.

2,2′-Dinitro-4,4′-diphthalimidodiphenylmethane, XI.—A mixture of 5.0 g. of 2,2′-dinitro-4,4′-diaminodiphenylmethane and 5.1 g. of phthalic anhydride was heated to 200° for 45 minutes and the cooled product recrystallized twice from chlorobenzene; yield, 7.3 g. of buff-colored crystals, m. p., 250°.

Anal. Subs., 0.5000, 0.5000: 4.10, 4.05 cc. of 0.8708 *N* HCl. Calcd. for $C_{29}H_{16}O_8N_4$: N, 10.21. Found: 9.99, 9.87.

4,4′-Diaceto-amidodiphenylmethane, $CH_2(C_6H_4NHCOCH_3)_2$.—A mixture of 250 cc. of glacial acetic acid, 150 cc. of acetic anhydride and 50 g. of base was warmed for 30 minutes on a hot water-bath. The product was precipitated by pouring the mixture into cold water and crystallized from 75% acetic acid; yield, 54 g.; m. p., 236–237° (Staedel and Haase,[11] 228°).

3,3′-Dinitro-4,4′-diaceto-amidodiphenylmethane, VII.—This was prepared according to the directions of Meyer and Rohmer.[12] The crude product from the nitration of 2 g. of 4,4′-diaceto-amidodiphenylmethane on recrystallization from glacial acetic acid yielded 1.4 g. of 3,3′-dinitro-4,4′-diaceto-amidodiphenylmethane; m. p., 265–266° (the literature gives 259–260°). The filtrate from this crystallization after evaporation deposited 1.0 g. of dull yellow crystals of *p*-nitro-acetanilide which, after recrystallization from acetic acid, melted at 208–209°. A little of the latter compound was hydrolyzed with dil. aqueous potassium hydroxide solution giving *p*-nitro-aniline; m. p., 146–147°. A mixed melting point with a known sample of *p*-nitro-aniline showed no depression from 146–147°.

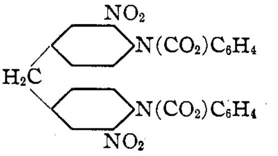
The hydrolysis of 2 g. of 3,3′-dinitro-4,4′-diaceto-amidodiphenylmethane was carried out according to the directions of Meyer and Rohmer.[12] The yield of 3,3′-dinitro-4,4′-diaminodiphenylmethane after crystallization from alcohol was 1.2 g. of red crystals; m. p., 232–233° (the literature gives 228°).

The catalytic reduction of 3,3′-dinitro-4,4′-diaminodiphenylmethane was carried out by dissolving 3.0 g. of the nitro base in 150 cc. of concd. hydrochloric acid, and reducing with hydrogen by means of 0.25 g. of platinum-oxide catalyst prepared as directed by Adams and Shriner.[13] Reduction did not start until a little reduced platinum was added, after which it ran smoothly. When the calculated amount of hydrogen was absorbed the reaction mixture containing the partially crystallized tetramine salt was warmed, filtered and evaporated nearly to dryness. Water was then added, the tetramine precipitated by adding *N* sodium hydroxide solution and the product crystallized from hot water after boiling the solution with a little Norite; yield, 1.8 g. of 3,3′,4,4′-tetra-aminodiphenylmethane; m. p., 138–139°.

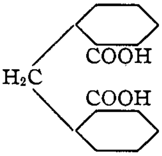
The tetramine was converted to the tetraphenyldiquinoxaline according to the directions of Meyer and Rohmer; m. p., 247° (the literature gives 244°).

4,4′-Diphthalimidodiphenylmethane.—This was prepared according to the method of Kaufler;[3a] m. p., 327°.

3,3′-Dinitro-4,4′-diphthalimidodiphenylmethane, XII.—A mixture of 300 cc. of c. p. fuming nitric acid (d., 1.50) and 300 cc. of concd. nitric acid (d., 1.4) was cooled to —5° to 0° and 60 g. of 4,4′-diphthalimidodiphenylmethane was added during stirring. When all was in solution the product was precipitated by pouring onto chipped ice, filtered, washed with water, dried and crystallized from hot ethylene chlorohydrin. *p*-Nitrophthalimidobenzene, m. p. 271–272°, resulted; yield, about 30 g.



XII



XIII

Anal. Subs., 0.3000, 0.3000: 2.46, 2.46 cc. of 0.8667 *N* HCl. Calcd. for $C_{14}H_8O_4N_2$: N, 10.44. Found: 9.95, 9.95.

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[11] Staedel and Haase, *Ber.*, **23**, 2577 (1890).

[12] Meyer and Rohmer, *Ber.*, **33**, 257 (1900). Gram, *Ber.*, **25**, 302 (1892).

[13] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

The filtrates from these crystallizations were combined with the main bulk of filtrate, and on partial evaporation 10 g. of 3,3′-dinitro-4,4′-diphthalimidodiphenylmethane crystallized as yellow needles. On recrystallization from ethylene chlorohydrin, 9.5 g. of pure substance, m. p. 311°, was obtained.

Anal. Subs., 0.5000, 0.5000: 4.10, 4.15 cc. of 0.8944 *N* HCl. Calcd. for $C_{29}H_{16}O_8N_4$: N, 10.21. Found: 10.27, 10.39.

On hydrolyzing 5.0 g. of 3,3′-dinitro-4,4′-diphthalimidodiphenylmethane by boiling with 50 cc. of 5% potassium hydroxide solution for one hour, 3,3′-dinitro-4,4′-diaminodiphenylmethane was formed; yield, after crystallizing from alcohol, 2.1 g. of red crystals; m. p., 232–233°. A mixed melting point with the nitro base obtained by hydrolysis of 3,3′-dinitro-4,4′-diaceto-amidodiphenylmethane showed no depression.

When 10 g. of 4,4′-diphthalimidodiphenylmethane was nitrated in sulfuric acid solution, the only product formed was 8.5 g. of *p*-nitrophthalimidobenzene.

Nitration of Phthalimidobenzene.—Phthalimidobenzene[14] was prepared by refluxing 9.1 g. of aniline and 14.8 g. of phthalic anhydride in 1000 cc. of water for eight hours. The product separated as a white solid which was filtered off, dried and crystallized from glacial acetic acid; yield, 17 g. of white crystals; m. p., 211°.

p-Nitrophthalimidobenzene[15] was prepared by adding 10 g. of phthalimidobenzene to a mixture of 50 cc. of fuming nitric acid (d., 1.5) and 50 cc. of concd. nitric acid (d., 1.4). When all was in solution the mixture was poured onto chipped ice, the product filtered off, washed with water, dried and thrice crystallized from chlorobenzene; yield 8.0 g. of white crystals; m. p., 271–272° (the literature gives 262°). A mixed melting point with the compound obtained by the nitration of diphthalimidodiphenylmethane showed no depression from 271–272°.

2,2′-Dicarboxydiphenylmethane, XIII.—Benzohydrolcarboxylic acid lactone was prepared according to the method of Graebe and Juillard[16] and was reduced according to the method of Clarke.[17] A mixture of 400 cc. of glacial acetic acid, 12 g. of red phosphorus and 6 g. of iodine was put into a 1-liter round-bottom flask and allowed to stand for 15 to 20 minutes to allow the phosphorus and iodine to react. After addition of 30 g. of benzohydrolcarboxylic acid lactone and 4.0 cc. of water, the mixture was refluxed for 24 hours. The hot mixture was then filtered into a solution of 15 g. of sodium bisulfite in 1.5 liters of cold water, during stirring. The product that precipitated was filtered off, washed with water, dried and crystallized from alcohol; yield, 25 g. of white crystals; m. p., 261° (the literature gives 254°).

Dibrucine-diphenylmethane-2,2′-dicarboxylate.—A suspension of 7.0 g. of 2,2′-dicarboxydiphenylmethane in 3 liters of hot water was treated with 25 g. of brucine, the salt thus formed dissolving completely. On evaporation and recrystallization of the residue from water two fractions of salt were obtained, making a total of 17 g., with rotation constant within 0.3°. The average rotation was $[\alpha]_D = -27.30°$ in chloroform solution. The salt melted and decomposed at 180–182°. The acid from this salt, after crystallization from alcohol, melted at 260° and did not rotate the plane of polarized light.

Anal. Subs., 0.5000, 0.5000: 2.05, 1.95 cc. of 0.9160 *N* HCl. Calcd. for $C_{61}H_{64}O_{12}N_4$: N, 5.36. Found: 5.25, 5.00.

2,2′-Dicarboxy-4,4′-dinitrodiphenylmethane, XIV.—This was prepared according

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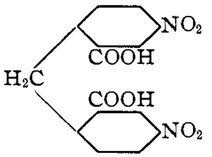
[14] Michael and Palmer, *Am. Chem. J.*, **9**, 202 (1887).

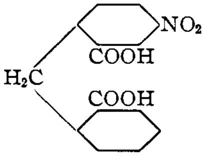
[15] Pawlewski, *Ber.*, **28**, 1118 (1895).

[16] Graebe and Juillard, *Ann.*, **242**, 214 (1887).

[17] Clarke, "Organic Syntheses," John Wiley and Son, Inc., New York, **1923**, Vol. 3, p. 45.



XIV



XV

to Duval's directions for the nitration of the 4,4'-acid.[18] It formed pale yellow crystals from 50% acetic acid; m. p., 237–238°.

Anal. Subs., 1.0000, 1.0000: 4.8, 4.9 cc. of 1.3008 *N* HCl. Subs., 1.0000 g.: 4.3 cc. of 1.3008 *N* NaOH. Calcd. for $C_{15}H_{10}O_8N_2$: N, 8.09; neutr. equiv., 173. Found: N, 8.74, 8.92; neutr. equiv., 178.7.

Dibrucine-4,4'-dinitrodiphenylmethane-2,2'-dicarboxylate.—This was prepared from 7 g. of 2,2'-dicarboxy-4,4'-dinitrodiphenylmethane and 18 g. of brucine in a manner similar to that for the brucine salt of the unsubstituted acid. A yield of 19.3 g. of salt was thus obtained. This material was recrystallized from alcohol, giving four fractions, having a constant rotation within 0.5°. A further crystallization gave a salt with the rotation $[\alpha]_D$ —6.5° in chloroform solution. The salt softened and decomposed at 210°. The acid from this salt melted at 235–237° and had no rotation.

Anal. Subs., 0.5000, 0.5000: 3.25, 3.15 cc. of 0.8181 *N* HCl. Calcd. for $C_{61}H_{62}O_{16}N_6$: N, 7.40. Found: 7.44, 7.21.

Mononitro-2,2'-dicarboxydiphenylmethane, XV.—This was the only product that resulted from an attempt to introduce four nitro groups into 2,2'-dicarboxydiphenylmethane. A solution of 2 g. of 2,2'-dicarboxydiphenylmethane in 20 cc. of concd. sulfuric acid was cooled to 10° and 1.0 cc. of fuming nitric acid (d., 1.50) was added, with stirring. The solution was then warmed to 80° and 0.8 cc. more of fuming nitric acid was added, after which it was kept at 80–85° for 18 hours and then poured into ice water. The crude product was recrystallized from 50% acetic acid; yield, 1.0 g. of pale yellow crystals; m. p., 284–285°.

Anal. Subs., 0.2500, 0.2500: 1.05, 1.07 cc. of 0.8082 *N* HCl. Calcd. for $C_{15}H_{11}ON$: N, 4.65. Found: 4.75, 4.84.

2,2'-Dinitro-4,4'-dicarboxydiphenylmethane.—This was prepared according to the directions of Duval.[18] It formed pale yellow crystals; m. p., 286°.

Dibrucine-2,2'-dinitrodiphenylmethane-4,4'-dicarboxylate.—A hot solution of 6.89 g. of brucine in 100 cc. of absolute alcohol was added to a hot solution of 2.55 g. of the nitro acid in 400 cc. of absolute alcohol. On evaporation and recrystallization, 6.5 g. of salt was obtained, which had the rotation $[\alpha]_D$ —2.47° in chloroform solution, and which softened and decomposed at 136–141°.

Anal. Subs., 0.5000, 0.5000: 3.05, 3.15 cc. of 0.8181 *N* HCl. Calcd. for $C_{61}H_{62}O_{16}N_6$: N, 7.40. Found: 7.21, 6.98.

Summary

1. 4,4'-Diaminodiphenylmethane forms ring structures through the two amino groups similar to the rings formed from benzidine.

2. Tetrazotized 4,4'-diaminodiphenylmethane differs from benzidine in that it is impossible to cause one diazo group to couple quantitatively before the other diazo group reacts.

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[18] Duval, *Compt. rend.*, **141**, 198 (1905).

3. No isomeric 3,3′- or 2,2′-dinitro-4,4′-diaminodiphenylmethanes could be obtained.
4. Various dicarboxylic acids of diphenylmethane could not be resolved.

URBANA, ILLINOIS

NOTE

The Chemistry of Jaffe's Reaction for Creatinine. III. 2,6-Dinitrophenol.—The writer has previously shown[1] that Jaffe's reaction for creatinine cannot be obtained if any one of a number of substances, including 2,4-dinitrophenol, is substituted for the picric acid. At that time, 2,6-dinitrophenol was not available to him. Recently he has obtained some from Kahlbaum. This also fails to give a red color with creatinine and sodium hydroxide. The writer's hypothesis[1] that all three nitro groups of the picric acid undergo a change in the formation of the red tautomer of creatinine picrate is, therefore, made the more probable.

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NEW BOOKS

Ukrainskii Khemichnii Zhurnal. (Ukrainian Chemical Journal.) Editor, Professor K. A. KRASUSKII. Volume 1, No. 1. Published by the All-Ukrainian Council of the Society of Friends of Chemical Defense and Industry of the Ukrainian Soc. Sov., Kharkov, 1925. 182 pp. 15 × 23 cm. Price, 5 rubles a year.

An editorial announcement states that this new Journal is published in the interests of Ukrainian culture and has been rendered possible by the munificence of the Ukrainian Soc. Sov.

It is to contain two sections, one devoted to matters of purely scientific interest, the other to applied chemistry. Of the nineteen articles one is in Ukrainian, another in German, and the remainder are in Russian. The table of contents is in French and there is an occasional summary in German. The equations and tables are printed chiefly in Latin characters. It is, of course, gratifying to see this evidence of renewed scientific activity. The articles, judging solely by the French index, appear to be interesting.

An outsider cannot, however, but regret the multiplicity of tongues and in this instance the added difficulty of a strange alphabet.

ARTHUR B. LAMB

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[1] Greenwald and Gross, *J. Biol. Chem.*, **59**, 601 (1924). Greenwald, THIS JOURNAL, **47**, 1443 (1925).