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A NEW CYCLIC AZOXY COMPOUND

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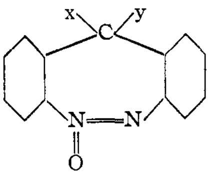
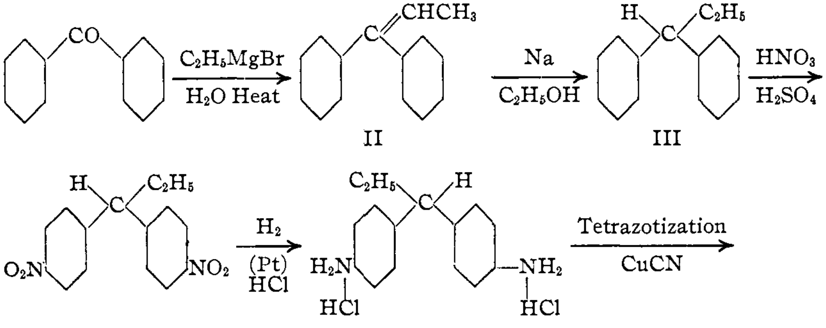
The work of Angeli[1] has left very little question concerning the unsymmetrical structure of the azoxy grouping. However, if a molecule of the type indicated in Formula I could be prepared and resolved it would furnish a new kind of evidence to confirm the views of Angeli. The present communication describes some experiments in which such a molecule has been prepared.



I

Very few compounds have been described in which the azoxy group is part of a ring system. Täuber[2] and later Ullmann and Dieterle[3] have prepared *o,o'*-azoxydiphenyl by the reduction of *o,o'*-dinitrodiphenyl. Duval[4] and later King[5] have prepared 2,2'-azoxy-4,4'-diaminodiphenylmethane by reduction of the corresponding dinitro compound. Duval[6] has also prepared 2,2'-azoxydiphenylmethane-4,4'-dicarboxylic acid and its diethyl ester by the same general method.

In some preliminary work attempts were made to nitrate benzilic acid to the *o,o'*-dinitro derivative. However, these were unsuccessful. An attempt to obtain 2,2'-dinitro-4,4'-diaminodiphenylcarbinol by the oxidation of the methane derivative was also unsuccessful. The following synthesis starting with benzophenone was finally accomplished.



II III

IV V

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[1] A summary of Angeli's work is given in *Ahren's Sammlung Chem. und Chem. tech. Vorträge*, **19**, 447 (1913), and also in *Gazz. chim. ital.*, **46**, II, 67 (1916).

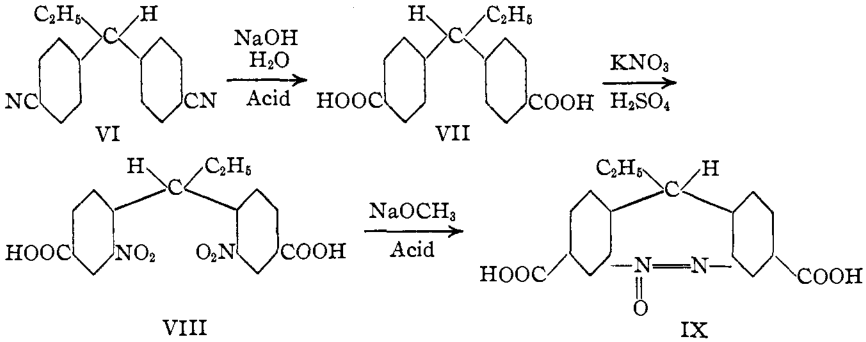
[2] Täuber, *Ber.*, **24**, 3083 (1891).

[3] Ullmann and Dieterle, *ibid.*, **37**, 24 (1904).

[4] Duval, *Compt. rend.*, **141**, 198 (1905); *Bull. soc. chim.*, [4] **7**, 527 (1910).

[5] King, *J. Chem. Soc.*, **117**, 988 (1920).

[6] Duval, *Bull. soc. chim.*, [4] **7**, 681 (1910).



In this series of reactions the first two steps have been previously described. The structure of ethyl-*bis*-(4-nitrophenyl)-methane (IV) was established by the fact that upon oxidation only *p*-nitrobenzoic acid could be isolated. The free diamino compound (V) was not isolated but was used in the form of its salt. The dicyano compound (VI) was never isolated in a pure state. The crude product was hydrolyzed directly to the dibasic acid (VII). The final product (IX) was quite insoluble and very high melting. This might be considered as an indication that the molecule was not a simple one but made up of a number of units connected through the nitrogen atoms. However, this did not seem likely as the solubility and melting point of the new compound resembled those of the azoxy compounds from *m*- and *p*-nitrobenzoic acids.[7]

An attempt was made to shorten the synthesis of the desired type of compound by nitrating the diamino compound (V) in sulfuric acid to give ethyl-*bis*-(2-nitro-4-aminophenyl)-methane and then to reduce this product to an azoxy compound. The nitro compound was obtained but the azoxy compound was not isolated in a pure form.

The cyclic azoxy compound (IX) became deeply colored in alkali and it was not possible to titrate it with alkali using indicators. It formed a dibrucine salt which was crystalline but deeply colored. This salt did not seem to separate into isomers on crystallization from alcohol. The attempted resolution was not conclusive as only one salt and only two solvents were used. The solutions were deeply colored and small rotations might have been overlooked. Further work is in progress on the resolution of this type of molecule.

Experimental Part

1,1-Diphenylpropene-1 was prepared according to the method of Sabatier and Murat[8] with the exception that ethylmagnesium bromide was substituted for the iodide. The yield on a three mole run was 68–70% of the theoretical amount. This hydrocarbon has previously been reduced by hydrogen in the presence of nickel[8] and of plati-

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[7] Elliott, *J. Chem. Soc.*, **73**, 145 (1898).

[8] Sabatier and Murat, *Ann. chim.*, **4**, 287 (1915).

num[9] but neither method was satisfactory for use on the amounts needed in this work. Klages[10] has mentioned its reduction by means of sodium and alcohol but has not given the details of the method.

Ethyl-*bis*-(phenyl)-methane (Formula III).—In a five-liter, two-necked flask fitted with an efficient reflux condenser and a mechanical stirrer was placed a solution of 300 g. of 1,1-diphenylpropene-1 in 1500 cc. of absolute alcohol. The stirrer was started and 150 g. of sodium, cut into small pieces, was introduced as rapidly as possible without loss of material through the condenser. This addition usually required about forty minutes. The flask was then heated until the sodium had entirely reacted. When necessary more alcohol was added. After the sodium was entirely in solution one liter of water was added and the alcohol was removed by steam distillation. The oily layer of hydrocarbon was separated from the water solution and the water extracted twice with a little ether. The ether extracts were added to the main body of the hydrocarbon, which was then dried over anhydrous sodium sulfate. The product was then distilled and the portion boiling at 129–131° (7 mm.) was collected and washed seven to ten times with cold concd. sulfuric acid to remove any diphenylpropene. When the sulfuric acid was no longer colored after shaking with the hydrocarbon, the latter was washed with water and again distilled. The yield of pure product boiling at 129–131° (7 mm.) was 260–275 g. (85–90% of the theoretical amount).

Ethyl-*bis*-(4-nitrophenyl)-methane (Formula IV).—In a three-liter, three-necked flask fitted with a mechanical stirrer were placed 314 g. of ethyldiphenylmethane and 340 cc. of concd. sulfuric acid (sp. gr. 1.84). The stirrer was started and the flask was surrounded by an ice-bath. When the temperature of the mixture reached about 10° a mixture of 230 cc. of concd. nitric acid (sp. gr. 1.42) and 570 cc. of concd. sulfuric acid was added with stirring over a period of one and one-half hours. The temperature was never allowed to go above 20°. Toward the end of the nitration a white gummy material began to precipitate out of solution.

Stirring was continued for about fifteen minutes after the addition of the last of the acid and then the reaction mixture was poured into four volumes of ice water. A gummy precipitate slowly settled on the bottom of the vessel. After this had separated, the aqueous acid layer was decanted and the residue was washed with water and then with ether. The ether dissolved some tarry material and left a white powder. This was recrystallized twice from acetic acid. In this way glistening white needles which melted at 143–144.5° were obtained. The yield was 180–190 g. (40–42% of the theoretical amount).

Anal. Subs., 0.2131: CO_2, 0.4190; H_2O, 0.0936. Calcd. for $C_{15}H_{14}O_4N_2$: C, 63.9; H, 4.9. Found: C, 63.2; H, 4.9.

A sample of the nitro compound was oxidized with chromic oxide in glacial acetic acid. The only oxidation product which could be isolated was *p*-nitrobenzoic acid, m. p. 238°.

Ethyl-*bis*-(4-aminophenyl)-methane Hydrochloride (Formula V).—A suspension of 15 g. of the nitro compound in 150 cc. of boiling alcohol was reduced with hydrogen in the presence of the platinum catalyst of Adams and Shriner.[11] The theoretical amount of hydrogen was absorbed in eleven minutes in the shortest run and in one hour in the longest. When the reduction was complete the catalyst was removed by filtration. An excess of concd. hydrochloric acid was added to the solution and it was then evaporated to dryness. The hydrochloride thus obtained weighed 15 g. (practically 100% of the theoretical amount). The salt was ground to a fine white powder. It melted at 232–235°.

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[9] Kern, Shriner and Adams, THIS JOURNAL, **47**, 1147 (1925).

[10] Klages, *Ber.*, **35**, 2648 (1902).

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

Anal. Subs., 0.2165: 14.48 cc. of 0.1001 *N* $AgNO_3$. Calcd. for $C_{15}H_{20}N_2Cl_2$: Cl, 23.70. Found: Cl, 23.72.

The free amine was prepared by treating an aqueous solution of the hydrochloride with sodium hydroxide solution. The white crystalline product which separated darkened very rapidly in the air.

Ethyl-*bis*-(2-nitro-4-aminophenyl)-methane.—In a flask fitted with a mechanical stirrer and a separatory funnel was placed 400 cc. of concd. sulfuric acid. The stirrer was started and 30 g. of the diamine dihydrochloride was added in portions. Stirring was continued until the hydrogen chloride was expelled. The remaining solution was dark red in color. This solution was cooled to about 0° and a solution of 13 g. of concd. nitric acid in 22 cc. of concd. sulfuric acid was added from the separatory funnel at such a rate that the temperature did not go above 5°.

After the nitrating mixture was added the solution was stirred for one-half hour while the temperature was maintained at 5°. The mixture, which had become opaque and more viscous, was then poured on a kilo of cracked ice. On standing some dark flocculent material separated This was removed by filtration. To the filtrate were added small portions of sodium carbonate. The first precipitate was tarry. This was removed by filtering and further addition of sodium carbonate precipitated the dinitro diamino compound as a yellow product. This material when collected on a filter and partially dried became resinous. The moist product was ground up with one and one-half times the theoretical amount of concd. hydrochloric acid and enough boiling water was added to dissolve the salt. This boiling solution was twice treated with decolorizing carbon (Norit) and filtered hot. The filtrate was then concentrated on a steam cone until crystals began to appear. On cooling the hydrochloride separated as grayish white crystals. These were collected on a filter and the filtrate was concentrated to give a second and third crop of crystals. After that tarry material began to separate and the mother liquors were discarded.

The hydrochloride obtained in the three crops of crystals was ground up with a slight excess of aqueous ammonia. The free dinitro diamine separated as an orange colored precipitate. It was collected on a filter, dried and recrystallized from boiling absolute alcohol. The product thus obtained melted at 146.5–148° after drying at 110°.

Anal. Subs., 0.2323: CO_2, 0.4793; H_2O, 0.1014. Calcd. for $C_{15}H_{16}O_4N_4$: C, 56.96; H, 5.12. Found: C, 56.52; H, 4.90.

An attempt was made to reduce this compound in the same manner that King[5] had reduced 2,2′-dinitro-4,4′-diaminodiphenylmethane. Only tarry material was obtained. No other conditions for the reduction were investigated.

Ethyl-*bis*-(4-cyanophenyl)-methane (Formula VI).—The replacement of the amino groups by cyano groups in ethyl-*bis*-(4-aminophenyl)-methane was accomplished by the procedure described by Clarke and Read[12] for *p*-toluonitrile. The sodium cuprous cyanide solution was prepared by reducing a solution of 32 g. of copper sulfate and 8 g. of sodium chloride with 4.4 g. of sodium hydroxide and 6.6 g. of sodium bisulfite and dissolving the cuprous chloride thus obtained in a solution of 16 g. of sodium cyanide in about 200 cc. of water.

To a suspension of 15 g. of ethyl-*bis*-(4-aminophenyl)-methane hydrochloride in 50 cc. of water enough hydrochloric acid was added to give a solution distinctly acid to litmus paper. This mixture was cooled to 0° and 7 g. of sodium nitrite was added with stirring over a period of about ten minutes. The mixture was maintained at 0 to 5° for about another fifteen minutes or until a clear dark red solution resulted. The excess

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[12] Clarke and Read, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1925**, Vol. IV, p. 69.

hydrochloric acid was neutralized by adding sodium carbonate. This neutral solution was added to the cold solution of sodium cuprous cyanide described above over a period of thirty minutes. Vigorous stirring was maintained during the addition and small portions of ether were added from time to time to break up the foaming. The reaction mixture was maintained at 0 to 5° for two hours after the two solutions were mixed and the temperature was then allowed to rise to 25° over a period of about two hours. Vigorous stirring was maintained during all of this time. The mixture was then slowly warmed to 50–60° with occasional stirring and filtered. The precipitate when dry was a light brown powder. It could not be recrystallized from any common solvents and it decomposed when an attempt was made to distil it under reduced pressure. This crude product was used directly in the preparation of the following acid.

Ethyl-*bis*-(phenyl-4-carboxylic acid)-methane (Formula VII).—The crude dicyano compound from two preparations of the size just described was added to 320 cc. of 20% aqueous sodium hydroxide solution and the mixture was boiled vigorously under a reflux condenser for about forty hours until no more ammonia was evolved. During the heating the powder gradually dissolved in the alkaline solution.

When the hydrolysis was completed the solution was cooled and acidified with excess hydrochloric acid. The crude dibasic acid separated as a brownish mass and was collected on a suction filter and washed with water. It was then dissolved in aqueous ammonia solution, and the solution was filtered and evaporated to dryness on a steam cone. The brownish salt was finely ground and extracted with two 200-cc. portions of warm (50°) water. From this solution the acid was thrown down as a voluminous white precipitate by the addition of excess hydrochloric acid. This precipitate retained considerable water. It was dried at 120° from four to six hours and then recrystallized from boiling glacial acetic acid using a little decolorizing carbon. After three recrystallizations from glacial acetic acid a white crystalline product was obtained. This was then dried for an hour at 120°. The yield was 6.2–6.6 g. (20–22% of the theoretical amount based on the diamine dihydrochloride) of a product which melted at 258–260°.

Neutral equivalent. Subs., 0.3000: 21.45 cc. of 0.0976 *N* NaOH. Calcd. for $C_{15}H_{14}(CO_2H)_2$: N. E., 142.1. Found: N. E., 143.1.

Anal. Subs., 0.2046: CO_2, 0.5394; H_2O, 0.1049. Calcd. for $C_{17}H_{16}O_4$: C, 71.9; H, 5.68. Found: C, 71.8; H, 5.46.

Ethyl-*bis*-(2-nitrophenyl-4-carboxylic acid)-methane (Formula VIII).—To a solution of 15.6 g. of the pure dibasic acid in 100 cc. of concd. sulfuric acid was added in portions 12 g. of powdered potassium nitrate. The temperature was held at 24–28° and vigorous stirring was maintained. After the reaction mixture showed no further tendency to evolve heat, it was allowed to stand for about twenty hours. Usually a white precipitate appeared on the top of the reaction mixture during this time. The material was poured into cold water and the dinitro dibasic acid separated as a yellowish gummy mass. It was filtered and recrystallized two or three times from boiling glacial acetic acid. The yield was 12.3 to 13 g. (60–65% of the theoretical amount) of a product which melted at 273–275°.

Anal. Subs., 0.2052: CO_2, 0.4140; H_2O, 0.0698. Calcd. for $C_{17}H_{14}O_8N_2$: C, 54.54; H, 3.77. Found: C, 55.00; H, 3.80.

The compound became deeply colored in alkaline solution and a satisfactory titration was not obtained.

Ethyl-2,2′-azoxydiphenylmethane-4,4′-dicarboxylic Acid (Formula IX).—To a solution of 1.3 g. of metallic sodium in 15 cc. of absolute methyl alcohol was added 2 g. of the above dinitro dibasic acid. The mixture was boiled under a reflux condenser for about five hours. After heating for a short time the sodium salt separated as a hard mass which was then broken up with a stirring rod. A deep red color soon developed. After this heating period most of the alcohol was evaporated. The residue was dissolved in water and the solution cooled nearly to 0°. On the addition of excess hydrochloric acid the azoxy compound separated as a reddish-yellow solid. This was collected on a filter and washed thoroughly with dilute hydrochloric acid and then with dilute alcohol (80 cc. of 95% alcohol and 20 cc. of water). This treatment removed considerable color from the product. After drying the residue at 120°, it weighed 0.65 g. (36% of the theoretical amount). The product did not melt sharply. It slowly darkened above 270° and appeared to char completely at 320–330°. The product was an orange-colored powder. No success was met in any attempts at recrystallization. The compound was quite insoluble in all common solvents except pyridine and it showed little difference in solubility with change in temperature in this solvent. However, several preparations were tried and each gave the same product. Moreover, the following analyses on products made at different times indicated that the product thus obtained was quite pure.

Anal. Subs., 0.1993, 0.2267, 0.2130: CO_2, 0.4601, 0.5234, 0.4917; H_2O, 0.0768, 0.0881, 0.0837. Calcd. for $C_{17}H_{14}O_5N_2$: C, 62.55; H, 4.33. Found: C, 62.97, 62.96, 62.9; H, 4.30, 4.35, 4.39.

The Brucine Salt of 2,2′-Ethyl-azoxydiphenylmethane-4,4′-dicarboxylic Acid.—Ten grams of *l*-brucine was dissolved in 200 cc. of absolute alcohol and 4 g. of the azoxy acid was added. The solution was boiled under reflux condenser for about four hours and then filtered to remove a light red, insoluble precipitate. On standing 9.4 g. of a yellow crystalline compound separated from the filtrate. It was filtered and dried. It melted at 230–243° with considerable decomposition.

Anal. Sub., 0.1885: CO_2, 0.4717; H_2O, 0.1030. Calcd. for $C_{63}H_{66}O_{13}N_6$: C, 67.85; H, 5.96. Found: C, 68.2; H, 6.1.

A solution containing 0.0339 g. of salt per cc. of pyridine in a 1-dm. tube gave a rotation of $-1.6°$, $[\alpha]^{20}_{D}$ $-47.3°$.

The filtrate from this fraction was concentrated to about 100 cc. and another 2 g. of salt separated. This product had properties very similar to the insoluble material which first separated. A solution containing 0.0356 g. of salt per cc. of pyridine in a 1-dm. tube gave a rotation of $-1.56°$, $[\alpha]^{20}_{D}$ $-43.8°$.

The two fractions were treated with hydrochloric acid and the two samples of the free azoxy acid were dissolved in pyridine to give solutions containing about 0.02 g. of acid per cc. No rotation was observed in a 1-dm. tube.

Considerable difficulty was met in attempting to read the rotations on the salt and the acid as the solutions were deeply colored. A Schmidt and Haensch saccharimeter with a conversion factor of 0.3468 was used for taking the readings. The source of light was a 1000-watt projection lamp. The light was passed through a 3-cm. length of 3% potassium dichromate solution to screen out the blue and violet rays.

The brucine salt could be crystallized from water and came out in a better crystalline form containing water of hydration. A sample weighing 0.3448 g. was dried at 145–155° for four and one-half hours. The loss in weight was 0.0167 g. Calcd. for $C_{63}H_{65}O_{13}N_6 \cdot 3H_2O$: H_2O, 4.62. Found: H_2O, 4.84.

The insoluble fraction from water was less than from alcohol but again the free acid obtained from the salt showed no rotation.

Summary

1. A new cyclic azoxy compound has been prepared from a substituted diphenylmethane derivative.
2. An attempt to resolve this compound was not successful.

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