

Phthalylsemicarbazide dissolves readily in cold alkalis, momentarily turning yellow. When this solution is acidified, a white crystalline precipitate is obtained, which is readily purified by crystallization from water, in which it is readily soluble and from which it separates in slender, white prisms. This product is soluble in alcohol and glacial acetic acid, but insoluble in ether, chloroform and benzene.

This substance, like phthalylsemicarbazide, melts at about 262° , with gas evolution, the melt being yellow. That this phthalic acid monsemicarbazide has the same melting-point as the phthalylsemicarbazide, is due to the fact that the former is converted into the latter before fusion takes place.

On analysis, the following results were obtained:

	Calculated for $C_9H_9O_4N_3$.	Found.	
		I.	II.
Carbon.....	48.43	48.72	...
Hydrogen.....	4.04	4.28	...
Nitrogen.....	18.83	...	18.84

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
July 1, 1905.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA
WESLEYAN UNIVERSITY.]

THE BENZALDEHYDE-AZO-BENZOIC ACIDS.

BY FREDERICK J. ALWAY AND WALTER D. BONNER.

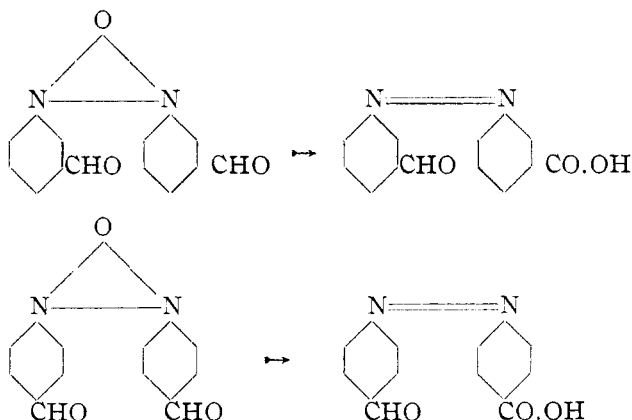
Received July 5, 1905.

THE ISOMERIC *m*- and *p*-azoxybenzaldehydes and many of their derivatives were described by one of us¹ three years ago, it being stated² at the time that when *p*-azoxybenzaldehyde is heated with concentrated sulphuric acid to 110° to 120° it is changed into a brown substance, which shows the characteristic properties of the oxyazo compounds. Since then Human and Weil³ in several publications have contended that, instead of the change indicated above taking place, the two azoxybenzaldehydes when heated with concentrated sulphuric acid, pass into the isomeric benzaldehydeazobenzoic acids, as represented by the following equations:

¹ *Am. Chem. J.*, **28**, 34, 475.

² *Ibid.*, **28**, 476.

³ *Ber.*, **36**, 3469, 3801; Human: Inaugural Dissertation, Univ. of Basel, 1904.



As is well known, the change of the poorly characterized azoxy compounds into the highly colored oxyazo compounds, whose salts act as powerful dyes, has long been used as a means of deciding whether newly discovered compounds contain the azoxy group. "The most interesting reaction of the azoxy compounds is the change into oxyazo compounds, which many of them undergo when gently warmed with concentrated sulphuric acid."¹ The reaction, indicated above, appeared remarkable not only in that it was new to the azoxy compounds, but also in that it was the first instance in which an oxygen atom attached to a nitrogen atom had been found to pass to a carbon atom in the meta position. Moreover, in this case, both the para and the ortho positions were free for the oxygen atom to enter. Human and Weil recognized the unusual character of the reaction but believed that the presence of one carboxyl group and of only one aldehyde group in the molecule was fully established by the following:

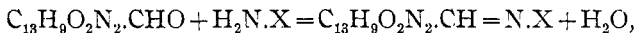
(1) The meta compound forms a sodium salt, $C_{14}H_9O_3N_2Na$. They observed, however, that this salt, when brought into contact with pure water, dissociated, setting free the compound $C_{14}H_{10}O_3N_2$.

(2) By treating the meta compound $C_{14}H_{10}O_3N_2$, melting at 163° , with alcohol and hydrochloric acid, according to the method of Victor Meyer, they obtained a substance melting at 156° and not entirely dissolved by sodium carbonate solution. The single analysis of the compound made, a nitrogen determination, sup-

¹ Meyer u. Jacobson: *Lehrb. organ. Chem.*, 2, Part I, 257.

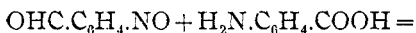
ported the idea that this substance was the ethyl ester of *m*-benzaldehydeazobenzoic acid.

(3) They obtained condensation products of the meta compound with one molecule each of aniline, hydroxylamine, hydrazine and phenylhydrazinesulphonic acid, according to the equation:

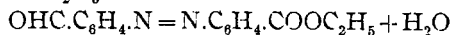
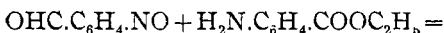


where X represents the groups $-C_6H_5$, $-OH$, $-NH_2$, and $-NH \cdot C_6H_4 \cdot SO_3H$. Their conclusions in regard to the para compound seem to have been based upon analogy rather than upon experimental data, as while they describe *p*-benzaldehydeazobenzoic acid as a reddish brown powder, melting above the boiling-point of sulphuric acid, and its ethyl ester as melting at 60° , they report no analyses of the para compound or of its derivatives.

As the result of our investigations we conclude that *m*-azoxybenzaldehyde, when heated with concentrated sulphuric acid, changes to the isomeric oxyazobenzaldehyde, the position of the oxy group in the latter not having been determined, and that *p*-azoxybenzaldehyde by similar treatment is changed into several oxyazo compounds of unknown constitution. That the compound obtained by Human and Weil is not *m*-benzaldehydeazobenzoic acid is evident from the fact that we obtained *m*-benzaldehydeazobenzoic acid synthetically, condensing *m*-nitrosobenzaldehyde with *m*-amidobenzoic acid, and by saponifying its ethyl ester, which itself was prepared by the condensation of *m*-nitrosobenzaldehyde with the ethyl ester of *m*-amidobenzoic acid. The acid melts at 230° and the ethyl ester at 90° . The acid condenses with a single molecule of phenylhydrazine to form a hydrazone. Its salts are stable in contact with water and do not stain the skin or dye silk or wool. The synthesis of the acid and its ester according to the equations

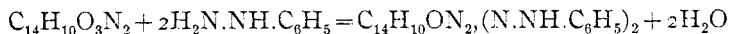
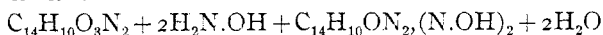
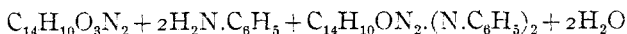


and



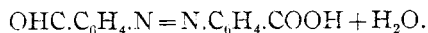
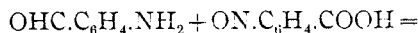
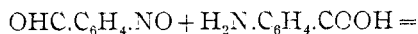
leaves no doubt as to their being the compounds to which the formulas of *m*-benzaldehydeazobenzoic acid and its ester should be assigned. The compound of acid nature obtained by Human and Weil melts at 163° and its supposed ester at 156° . Its salts

are unstable in contact with water, stain the skin and dye silk and wool orange. These properties are characteristic of oxyazo compounds and not of carboxyl derivatives of azobenzene, the latter not acting as dyes. "Carboxyl derivatives of azobenzene possess scarcely any dyeing properties."¹ Repeated attempts to esterify the compound failed, the unchanged original substance remaining. The assumption of Human and Weil that, after the attempted esterification, the portion that does not dissolve in sodium carbonate solution is an ester, is not justified, because the compound melting at 163° is, itself, only sparingly soluble in cold sodium carbonate. The presence of two aldehyde groups in the molecule is apparent from the formation of condensation products with two molecules each of aniline, hydroxylamine and phenylhydrazine when these three compounds were used in excess under favorable conditions.

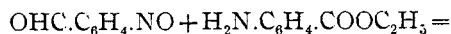


The dianilide, $C_{14}H_{10}ON_2.(N.C_6H_5)_2$, when treated with aqueous alcohol, splits off one molecule of aniline and forms the mono-anilide described by Human and Weil.

p-Benzaldehydeazobenzoic acid was obtained by the condensation of both *p*-nitrosobenzaldehyde with *p*-amidobenzoic acid and *p*-amidobenzaldehyde with *p*-nitrosobenzoic acid:



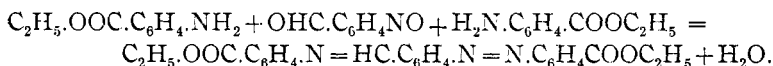
The ethyl ester of *p*-benzaldehydeazobenzoic acid was prepared by the condensation of *p*-nitrosobenzaldehyde with the ethyl ester of *p*-amidobenzoic acid, and by the analogous condensation of *p*-amidobenzaldehyde with the ethyl ester of *p*-nitrosobenzoic acid:



¹ *Lehrb. organ. Chem.*, 2, Part 1, p. 270.

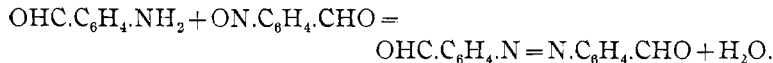
The acid is infusible below the boiling-point of sulphuric acid, while the ester melts at 159°. The salts of the acid are stable and do not act as dyes. The substance obtained by heating *p*-azoxybenzaldehyde with concentrated sulphuric acid forms unstable salts which act as powerful dyes. We were unable to esterify it, although Human and Weil claim to have obtained the ester, melting at 60°. The transposition product of *p*-azoxybenzaldehyde is clearly not *p*-benzaldehydeazobenzoic acid. It is evidently a mixture of several oxyazo compounds, none of which we were able to isolate.

p-Nitrosobenzaldehyde condenses also with two molecules of the ethyl ester of *p*-amidobenzoic acid, according to the equation



This compound when treated with dilute acids readily splits off one molecule of the ethyl ester of *p*-amidobenzoic acid, forming the ethyl ester of *p*-benzaldehydeazobenzoic acid.

p-Azobenzaldehyde was obtained by the condensation of *p*-amidobenzaldehyde with *p*-nitrosobenzaldehyde:

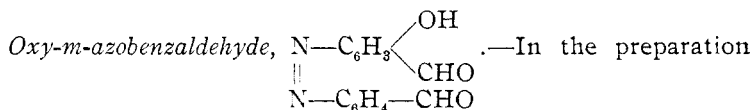


It had previously been prepared by Freundler¹ by the action of dilute sulphuric acid upon the acetal $(\text{CH}_3\text{O})_2\text{CH.C}_6\text{H}_4\text{.N} = \text{N.C}_6\text{H}_4\text{.CH}(\text{O.CH}_3)_2$, which was obtained by the alkaline reduction of the dimethylacetal of *p*-nitrobenzaldehyde.

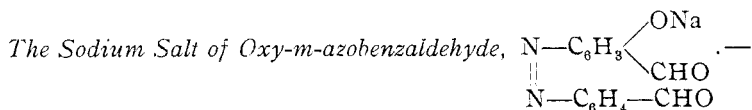
EXPERIMENTAL PART.

Preparation of m-Azoxybenzaldehyde.—Fifteen grams of *m*-nitrobenzaldehyde were dissolved in 2 liters of boiling water and treated with 60 grams of ferrous sulphate; this mixture was heated a short time and then poured gradually, with constant stirring, into 150 cc. of 15 per cent. solution of sodium hydroxide. After the mixture had been allowed to stand, with frequent stirring, half an hour, we added, instead of the bisulphite used by Human and Weil, 120 cc. of concentrated hydrochloric acid, then warmed and stirred until the iron compounds, that had been precipitated, were dissolved. The *m*-azoxybenzaldehyde was filtered out, thoroughly washed with water and dried. The yield was 12 grams, Human and Weil having obtained only 8 grams by the bisulphite method.

¹ C. R., 134, 1359.

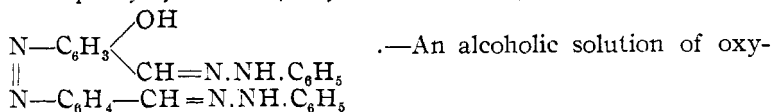


of this compound we followed the method described by Human and Weil for the preparation of what they considered *m*-benzaldehydeazobenzoic acid. Five grams of *m*-azoxybenzaldehyde were placed in a flask with 25 grams of concentrated sulphuric acid, a yellow solution being formed, which was heated in an oil-bath for two hours, the temperature being kept at 110° by means of a thermoregulator. At the end of this time the solution, which had changed in color to a dark red, was poured into ice water, a yellow solid being precipitated. This substance, melting at 160° (uncorr.), (Human and Weil give 161°), is only slightly soluble in a cold solution of sodium carbonate. A specimen, melting at 165° (cor.), that had been purified by dissolving the crude substance in hot sodium carbonate solution and precipitating by means of a dilute acid, was ground in a mortar with a cold saturated solution of sodium carbonate. Very little gas was evolved and after grinding twenty minutes very little of the substance had gone into solution. The contents of the mortar were then transferred to a test-tube and heated, the solid being gradually dissolved with a vigorous evolution of gas, while the color changed first to brown and finally to deep red. This oxyazobenzaldehyde dissolves to a slight extent in cold solutions of alkaline carbonates and in dilute solutions of ammonia and the alkaline hydroxides, with a yellow to orange color. In concentrated solutions of the alkaline hydroxides or of ammonia and in hot solutions of the alkaline carbonates it is readily soluble, forming brown to deep red solutions. These solutions stain the skin and dye silk and wool an orange-yellow.



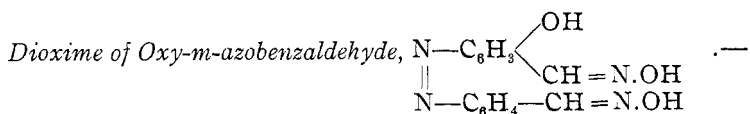
This salt was obtained by cooling the saturated solution of *oxy-m-azobenzaldehyde*, prepared by boiling the latter with a saturated solution of sodium carbonate. It forms very small, brick-red crystals that do not melt below the boiling-point of sulphuric acid.

Bis-phenylhydrazone of Oxy-m-azobenzaldehyde,



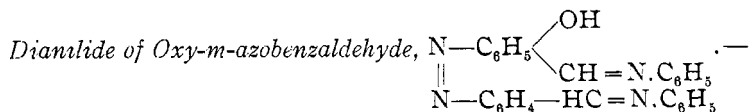
m-azobenzaldehyde was heated one hour on the water-bath with an excess of phenylhydrazine. On cooling the solution light brown crystals, melting at 234° (corr.), separated out.

	Calculated for C ₂₀ H ₂₂ O ₂ N ₆ .	Found.
Nitrogen.....	19.4	19.3



A solution of 0.8 gram of sodium hydroxide in water was treated with 0.5 gram of hydroxylamine hydrochloride and 0.6 gram of the sodium salt of the oxy-*m*-azobenzaldehyde and the whole heated an hour and a half on the water-bath. The red solution, so obtained, when filtered and acidified with dilute acetic acid gave a yellow gelatinous precipitate, which was filtered out, dried on a porous plate and recrystallized from dilute alcohol. The dioxime forms brownish yellow crystals, melting at 207° to 211° (cor.).

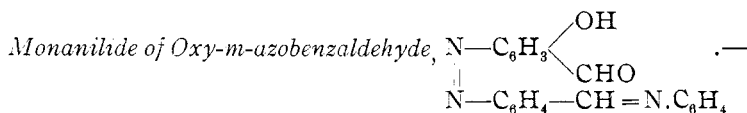
	Calculated for C ₁₄ H ₁₂ O ₂ N ₄ .	Found.
Nitrogen.....	19.7	19.8



Two grams of oxy-*m*-azobenzaldehyde were treated with 5 cc. of freshly distilled aniline. The mixture rose rapidly in temperature and assumed a red color. After it had been heated half an hour at 110°, the clear solution solidified, when cooled and stirred. The dark colored solid was dried on a porous plate, dissolved in boiling benzene and precipitated by the gradual addition of absolute alcohol.

The compound forms bright yellow crystals, melting at 141° (corr.).

	Calculated for C ₂₀ H ₂₀ ON ₄ .	Found.
Nitrogen.....	13.8	13.8



This compound was prepared in the same way as the dianilide, with the exception that the benzene solution was treated with 95 per cent. alcohol instead of absolute alcohol. It forms small yellow crystals, melting at 126° to 130°.

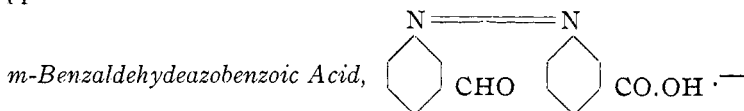
	Calculated for $\text{C}_{20}\text{H}_{15}\text{O}_2\text{N}_3$.	Found.
Nitrogen.....	12.8	12.9

This anilide was prepared also by the method of Human and Weil, who give the melting-point as 128°. The sodium salt of oxy-*m*-azobenzaldehyde was heated with an aqueous solution of sodium hydroxide and aniline. The crude anilide, recrystallized from 95 per cent. alcohol, was similar in properties to that described above.

Two specimens of monanilide, one from each method of preparation, were boiled with dilute hydrochloric acid. The yellow residues were well washed with water and dried. Both melted at 165°, the melting-point of the oxy-*m*-azobenzaldehyde.

The Action of Oxy-m-azobenzaldehyde with Alcohol and Hydrochloric Acid.—We made repeated attempts to obtain the ester, following the method described by Human and Weil. The phenomena were the same in each case and similar to those observed by these investigators. Two grams of oxy-*m*-azobenzaldehyde and 20 cc. of 95 per cent. alcohol were placed in a strong bottle. Dry hydrochloric acid gas was led into the mixture, which was kept cool by means of salt and ice, until an increase in weight of 6 grams had taken place. As the hydrochloric acid was introduced the color of the mixture changed to red and finally blood-red. The bottle was then stoppered tightly and allowed to stand twenty-four hours. It was then connected with a return-condenser and heated one hour on the water-bath. The reaction mixture was filtered and the filtrate evaporated to half its volume, a considerable amount of red solid separating out during the latter operation. Water was added to complete precipitation and the yellowish brown precipitate filtered out and treated with cold sodium carbonate solution. Part of it dissolved and the residue, which, when washed with water and dried, melted at 150° to 160°, was almost entirely soluble in hot sodium carbonate solution or in a

large quantity of cold sodium carbonate solution. The very small amount of substance that did not dissolve in sodium carbonate solution did not melt below 200° . The quantity of it was too minute for further investigation. When the mixture of oxyazobenzaldehyde, alcohol and hydrochloric acid was allowed to stand forty-eight hours the results were the same. In one case after adding the 6 grams of hydrochloric acid some of the red solution was poured into water. A yellow precipitate, melting at 155° to 159° and forming an anilide melting at 126° , was obtained. After the bottle had stood twenty-four hours the contents were filtered out. Blood-red crystals were obtained. On standing exposed to the air these lost hydrochloric acid and formed a brownish yellow solid, melting at 160° and yielding an anilide melting at 126° . Oxy-*m*-azobenzaldehyde, when exposed to a current of hydrochloric acid gas, became red. Evidently the oxyazoaldehyde forms an addition-product with hydrochloric acid. Human and Weil give 156° as the melting-point of their supposed ester.



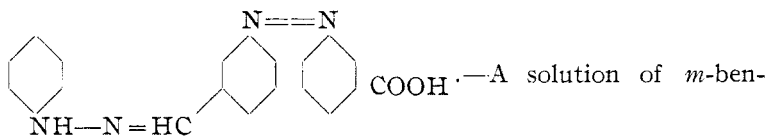
A solution of 1 gram of *m*-amidobenzoic acid in hot glacial acetic acid was added to a boiling solution of 1 gram of *m*-nitrosobenzaldehyde in glacial acetic acid. The color changed gradually from the deep green of the nitroso compound, to a dark green, then to a dark brown and finally to a black. The mixture was boiled a few minutes and then allowed to cool slowly. A light brown amorphous solid separated out. This was insoluble in ordinary organic solvents and decomposed, without melting, at 275° . It was dissolved in sodium carbonate solution, from which, on standing, a yellow solid, not melting below the boiling-point of sulphuric acid, separated out. This yellow substance, evidently the sodium salt, was dissolved in water and treated with hydrochloric acid. The crude substance, so obtained, melted at 222° . By recrystallization from acetic acid it was obtained in the form of small yellow to brownish yellow needles, melting at 230° (corr.).

	Calculated for $C_{14}H_{10}O_3N_2$.	Found.
Carbon.....	66.1	66.2
Hydrogen.....	3.9	3.7
Nitrogen.....	11.0	10.9

The acid was also easily obtained in pure form by warming its ethyl ester, described below, with concentrated hydrochloric acid, filtering and washing the residue with water, and finally recrystallizing from acetic acid.

The insoluble compound, first obtained from the interaction of *m*-nitrosobenzaldehyde and *m*-amidobenzoic acid is probably the condensation product, $\text{HO}_2\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{HC}\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, analogous to the para compound, melting at 152° , which is described below.

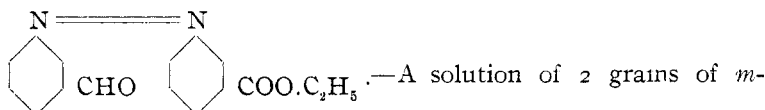
Phenylhydrazone of m-Benzaldehydeazobenzoic Acid,



zaldehydeazobenzoic acid in hot glacial acetic acid was treated with an excess of phenylhydrazine. The solution, on cooling, deposited orange-yellow crystals, melting at 195° (corr.).

	Calculated for $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_4$.	Found.
Nitrogen.....	16.3	16.6

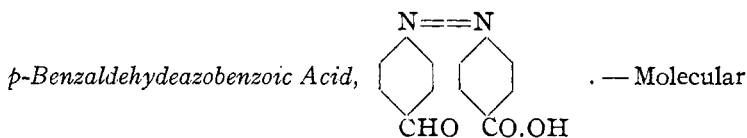
Ethyl Ester of m-Benzaldehydeazobenzoic Acid,



nitrosobenzaldehyde in boiling glacial acetic acid was added to a similar solution of 2.5 grams of the ethyl ester of *m*-amidobenzoic acid. The mixture was boiled a few minutes, allowed to cool and then again heated to boiling. Water was added until a distinct turbidity was produced. On cooling, this solution deposited crystals, which were recrystallized from 80 per cent. alcohol. The latter is a satisfactory solvent for the purification of the compound, although it is usually necessary to agitate or to seed the cool solution, in order to start crystallization.

The ester forms reddish yellow needles, melting at 90° (corr.), and very soluble in alcohol, benzene and glacial acetic acid.

	Calculated for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2$.	Found.
Nitrogen.....	9.9	10.2



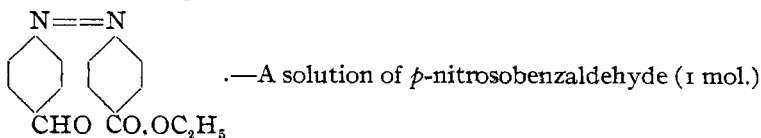
proportions of *p*-amidobenzoic acid and of *p*-nitrosobenzaldehyde were dissolved in separate portions of boiling glacial acetic acid. The solution of the former was poured into that of the latter. The color of the solution changed from green to dark brown and then, suddenly, a heavy yellow precipitate separated out, the solution changing to a solid mass. This was boiled, first with alcohol and then with glacial acetic acid to remove any unchanged amido acid or nitrosoaldehyde. The residue, when dried, formed an amorphous reddish yellow solid, insoluble in ordinary organic solvents and not melting below 300°.

	Calculated for C ₁₄ H ₁₀ O ₃ N ₂ .	Found.
Nitrogen.....	11.0	10.9

The same compound was obtained by the similar condensation of *p*-amidobenzaldehyde with *p*-nitrosobenzoic acid. As both of these compounds readily pass into insoluble modifications, a freshly prepared alcoholic solution of *p*-nitrosobenzoic acid was poured into an alcohol solution of freshly prepared *p*-amidobenzaldehyde. The mixture was heated to boiling, treated with three times its volume of glacial acetic acid and again heated to boiling. From this point on the method of procedure was the same as that just described.

Alkaline solutions of the acid are light yellow in color and neither dye silk and wool nor stain the skin. The solution of the acid in ammonia is quite stable and on evaporation deposits the ammonium salt, soluble in water.

Ethyl Ester of p-Benzaldehydeazobenzoic Acid,



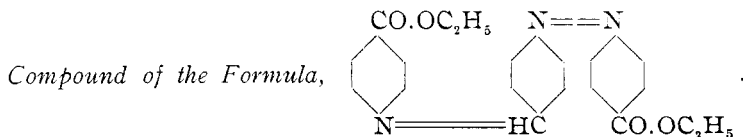
in boiling glacial acetic acid was slowly added to a similar solution of the ethyl ester of *p*-amidobenzoic acid (1 mol.) and the mixture kept gently boiling two or three minutes, after which it was allowed

to cool slowly. At the end of twenty minutes the dark red solution began to deposit crystals and after half an hour had changed to a solid mass of red crystals. These were filtered out and recrystallized several times from glacial acetic acid.

The ester forms light red, boat-shaped crystals, melting at 159° (corr.), slightly soluble in cold alcohol, readily soluble in hot alcohol, fairly soluble in cold glacial acetic acid and very readily soluble in the same solvent when hot.

	Calculated for $C_{10}H_{14}O_3N_2$.	Found.
Carbon.....	68.1	68.0
Hydrogen.....	5.0	4.9
Nitrogen.....	9.9	10.2

The compound was also obtained by the condensation of the ethyl ester of *p*-nitrosobenzoic acid with the freshly prepared soluble modification of *p*-amidobenzaldehyde. The two compounds, in molecular proportions, were dissolved in separate portions of hot absolute alcohol. When these solutions were mixed the green color of the nitroso compound persisted. Glacial acetic acid was added in excess and the whole heated to boiling, the color gradually changing to red. After standing thirty-six hours with separation of very little solid, the solution was again heated to boiling and treated with hot water until a distinct turbidity was produced. On cooling, the solution deposited a red precipitate, which, when twice recrystallized from glacial acetic acid, melted at 159° and showed the characteristic crystal form of the ester prepared by the first method.



—A solution of *p*-nitrosobenzaldehyde (1 mol.) in hot glacial acetic acid was poured slowly, with constant stirring, into a boiling solution of the ethyl ester of *p*-amidobenzoic acid (2 mols.). The red solution resulting from the mixture, was kept boiling a few minutes and then allowed to cool slowly. The reddish yellow crystals which separated out, were washed on the filter with alcohol, dried and recrystallized four times from benzene.

The compound forms rectangular plates, melting at 152° (corr.). The appearance of the crystals is very characteristic. Under the

microscope in transmitted light, they appear lemon-yellow. To the naked eye they appear bright red or golden yellow, according to the position of the crystals.

	Calculated for $C_{25}H_{23}O_4N_3$.	Found.
Carbon.....	69.8	70.1
Hydrogen.....	5.3	5.7
Nitrogen.....	9.8	9.8

The crude condensation-product, when examined under the microscope, was found to contain crystals of the ester, which melts at 159° , as well as of the compound melting at 152° . This would indicate that the condensation takes place in the two proportions, *viz.*, one molecule of nitrosoaldehyde with one molecule of the amido compound as well as one molecule of the nitrosoaldehyde with two molecules of the amido compound, even when the amido compound is present in excess.

For fuller evidence of the relation of the two condensation products, melting at 159° and 152° respectively, some of the latter was boiled with concentrated hydrochloric acid. The compound, melting at 159° , was obtained. Some of the latter compound (1 mol.), prepared by the first method, was dissolved in hot glacial acetic acid and treated with a similar solution of the ethyl ester of *p*-amidobenzoic acid (1 mol.). By cooling the mixture and recrystallizing the product from benzene, crystals were obtained which melted at 152° and possessed the characteristic appearance mentioned above.

p-Azobenzaldehyde, $OHC.C_6H_4.N:N.C_6H_4.CHO$.—Solutions in absolute alcohol of *p*-nitrosobenzaldehyde and of *p*-amidobenzaldehyde in molecular proportions, were mixed and then treated with glacial acetic acid. After the mixture had been boiled a few minutes and allowed to stand several hours it was subjected to distillation with steam until the distillate was colorless, in order to remove all unchanged nitrosobenzaldehyde. The dark-colored solid, remaining in the distilling-flask, when recrystallized from nitrobenzene formed long red needles, melting at 239° (corr.). When glacial acetic acid was used as the solvent the substance was obtained in the form of very lustrous orange-red crystals, melting at the same temperature. Freundler used nitrobenzene as solvent and found the melting-point 237° to 238° .

Action of Concentrated Sulphuric Acid upon p-Azoxybenzaldehyde.—Five grams of *p*-azoxybenzaldehyde were placed in a

flask with 25 grams of concentrated sulphuric acid and heated on an oil-bath to 110° for two hours. A slight evolution of gas was observed and the odor of sulphur dioxide was distinctly noticeable at the mouth of the flask. The dark red solution when poured into ice water gave a brown amorphous solid. This was sparingly soluble in cold sodium carbonate solution and readily soluble in hot sodium carbonate solution and in concentrated ammonia solution. It was reprecipitated from both by the addition of mineral acids. The ammonia solution when evaporated on the water-bath or allowed to evaporate at the temperature of the room deposited a red solid which was insoluble in water, but soluble in ammonia and alkalis. When heated with caustic alkalis it did not evolve ammonia. Its alkaline solutions stained the skin and dyed silk and wool orange-yellow. We did not succeed in isolating any compound in a pure condition from the crude transposition product, judging from the analytical data. As the product is insoluble in ordinary solvents and does not melt below 300° its purification is very difficult.

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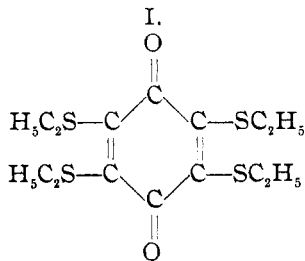
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE ACTION OF MERCAPTIDES ON QUINONES.

BY JOHN LANGLEY SAMMIS.

Received July 14, 1905.

IN A previous paper by Professor H. S. Grindley and the writer upon this subject¹, it was concluded that the reaction of sodium mercaptide on dichlorodiphenoxyquinone in dry ether consisted of *substitutions* and of *addition* and, at that time, three substances resulting from this reaction were given the following formulas:



Tetrathioethylquinone.

¹ *Am. Chem. J.*, 19, 293 (1897).