The extreme molecular conductivity of the free base, Λ_∞, is the sum of 28.4 and 195.8 (the extreme mobility of hydroxyl ions), or 224.2.

Ethyl phenylisourea was prepared, purified, and tested for purity exactly as the methyl derivative.

0.4806 gram substance required 29.30 cc. tenth-normal HCl. Calculated, 29.27 cc.

The measurements and the calculation of the affinity constant, K, follow:

TABLE VIII.

	Λv.		100α.		10^5 K.	
v.[1]	I.	II.	I.	II.	I.	II.
26.03	0.822	0.822	0.367	0.367	0.052	0.052
52.07	1.118	1.108	0.499	0.498	0.048	0.048
104.13	1.580	1.571	0.705	0.701	0.048	0.048
208.26	2.314	2.285	1.032	1.019	0.052	0.050
416.53	3.469	3.383	1.548	1.510	0.058	0.056
833.06	5.406	5.253	2.412	2.344	....	....
				Mean:	0.051;	0.051

Here again the substitution of the ethyl for the methyl group doubles the strength of the base.

For his interest, constant aid and advice, I wish here to express my great sense of obligation and gratitude to Professor Stieglitz.

KENT CHEMICAL LABORATORY,
UNIVERSITY OF CHICAGO.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 92.]

METAMINOBENZONITRILE AND SOME OF ITS DERIVATIVES.[2]

BY MARSTON TAYLOR BOGERT AND HAL TRUEMAN BEANS.[3]

Received February 6, 1904.

A NUMBER of derivatives of orthoaminobenzonitrile and some of the para compound have been prepared but of those of metaminobenzonitrile only the chloride, chlorplatinate, nitrate, sulphate, and picrate are described in the literature.

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[1] An error was made in calculating the amount of the base necessary for a N/32 solution. The volumes, v, given are those actually used.

[2] Read before the New York Section of the American Chemical Society, at its meeting November 6, 1903.

[3] From the dissertation submitted by Mr. H. T. Beans in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

The method of obtaining the orthoaminobenzonitrile published by Bogert and Hand[1] having given such satisfactory results in every respect, it seemed probable the meta compound could be as readily prepared by the same method. It was thought the amino group would prove to be as reactive as that in metanitraniline and by entering into the usual aniline reactions would yield a series of nitriles which apparently have not as yet been prepared, though their corresponding acids and amides have been studied by Chancel, Hofmann, Menschutkin, Griess, Schiff, Traube and others.

For the preparation of *m*-nitrobenzonitrile, two methods were used. The first was that described by Bogert and Hand[2] for the preparation of the corresponding ortho compound. Starting with metanitraniline, the amino group was replaced by cyanogen by the Sandmeyer reaction. This method was found to give fairly satisfactory results with the meta compound but the yields were always lower than those obtained with the ortho body, owing to the marked tendency of the metanitrodiazonium chloride to double into a 3-3'-dinitrodiphenyl by loss of nitrogen, similar to the reaction discovered by Niementowski[3] in the preparation of the chloranilines. The metanitraniline seems to be much more favorable to the production of diphenyl derivatives than the ortho compound and no conditions were found under which their formation in considerable quantities could be avoided.

This unavoidable decrease in the yield due to the formation of diphenyl compounds led to experiments on the direct nitration of benzonitrile and a method was finally found, practically that of Schöpff,[4] which gave entirely satisfactory results. For the reduction of the nitronitrile, the method used was that described by Bogert and Hand[5] for the preparation of the orthoaminonitrile. The reducing agent is a solution of stannous chloride in concentrated hydrochloric acid, the hydrochloride of the amino body being thrown out of solution by a large excess of the concentrated acid as recommended by Friedländer.[6] The free base is readily

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[1] This Journal, **24**, 1033.

[2] *Loc. cit.*

[3] *Ber. d. chem. Ges.*, **34**, 3325.

[4] *Ibid.*, **18**, 1063.

[5] *Loc. cit.*

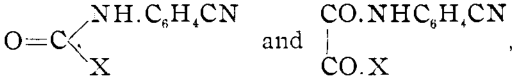
[6] *Monatsh. Chem.*, **19**, 627.

obtained from the hydrochloride by dissolving in water, adding dilute alkali in excess and extracting the solution with ether. By this procedure, the *m*-aminobenzonitrile is readily prepared in considerable quantity and the purification of the crude product is very easily accomplished. There is little or no loss by saponification in either the nitration or reduction reactions and both operations are entirely free from the production of tar or troublesome by-products.

m-Aminobenzonitrile reacts with acids, their anhydrides and chlorides and in some cases with their esters to form *m*-cyananilides which are analogous to the nitranilides produced by similar reactions with *m*-nitraniline.

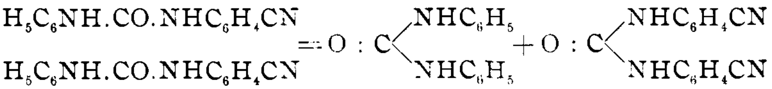
These substances are the hitherto unknown nitriles of previously described acids and in nearly all cases, are easily hydrolyzed by alkaline hydrogen peroxide to the intermediate amides, many of which have not as yet been described.

In general, the derivatives having the structures



$$\mathrm{O{=}C}\left\langle\begin{matrix}\mathrm{NH.C_6H_4CN}\\ \mathrm{X}\end{matrix}\right. \quad \text{and} \quad \begin{matrix}\mathrm{CO.NHC_6H_4CN}\\ |\\ \mathrm{CO.X}\end{matrix},$$

where X may be the group NH_2, NHC_6H_5 or OC_2H_5, undergo a rather interesting decomposition on heating. In cases where the decomposition occurs, two molecules of the unsymmetrical compound react to produce a molecule each of two symmetrical compounds, as for example,



$$\begin{matrix}\mathrm{H_5C_6NH.CO.NHC_6H_4CN}\\ \mathrm{H_5C_6NH.CO.NHC_6H_4CN}\end{matrix} = \mathrm{O:C}\left\langle\begin{matrix}\mathrm{NHC_6H_5}\\ \mathrm{NHC_6H_5}\end{matrix}\right. + \mathrm{O:C}\left\langle\begin{matrix}\mathrm{NHC_6H_4CN}\\ \mathrm{NHC_6H_4CN}\end{matrix}\right.$$

m-Aminobenzonitrile also reacts with chloral and bromal to produce addition and condensation products similar to those produced from chloral and the nitranilines.

EXPERIMENTAL.

PREPARATION OF METANITROBENZONITRILE.

(*1*) *From Metanitraniline.*—The method used was that described by Bogert and Hand[1] for the preparation of the *o*-nitrobenzonitrile. By making use of a mechanical stirring apparatus, it was found possible to work with half molecular quantities, the details of the operation being as follows:

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[1] *Loc. cit.*

To 100 cc. of concentrated hydrochloric acid, are added 69 grams of finely pulverized *m*-nitraniline and a little water and the mixture warmed gently. The warming and addition of the water in small portions are continued until solution is just effected, when the volume is made up to about 1500 cc. and the solution is stirred rapidly until cold. Usually no nitraniline separates but if it does, under these conditions it will be in a finely divided form and will diazotize very readily. When cooled to 20°, a solution of 35 grams of sodium nitrite in 200 cc. of water is allowed to run into the mixture, drop by drop, with constant stirring. About two hours are necessary for the addition of the sodium nitrite solution and the mixture should then be stirred for an hour longer to insure a complete reaction. The diazo compound is added in very small portions and with constant stirring to a cuprous-potassium cyanide solution prepared by dissolving 125 grams of crystallized copper sulphate in 750 cc. of water, adding 140 grams of potassium cyanide in sufficient water, to the hot solution. This cuprous-potassium cyanide solution is kept at a temperature between 90° and 100° during the addition of the diazo mixture. To secure the best results, it is essential to keep the temperature between the limits given and to add the diazo compound in very small portions and with constant agitation of the reaction-mixture. When all has been added, the solution is at once filtered through a hot-water funnel. On cooling, the *m*-nitrobenzonitrile separates from the solution in long, light yellow, feathery needles. The reddish-brown tar, chiefly 3-3'-dinitrodiphenyl, is repeatedly extracted with boiling water until it yields no more of the nitronitrile. The *m*-nitronitrile seems to show little tendency to retain mineral cyanides as is the case with the ortho compound and hence its purification is much simpler, a single recrystallization from dilute acetic acid usually being sufficient to yield a pure product.

The average of the results obtained from several experiments, using the charges given above, was about 40 grams of pure *m*-nitronitrile and about 30 grams of tarry by-products. Since these results are far from being as satisfactory as those obtained with the ortho compound, various modifications as to temperature, proportions and other conditions were tried but the best method seemed to be that given above.

(2) *By Nitration of Benzonitrile.*—Hofmann[1] nitrated benzonitrile by the action of a mixture of concentrated sulphuric acid and fuming nitric acid and obtained *m*-nitrobenzonitrile. He states that it is necessary to work with small quantities of material and to keep the temperature down to avoid the production of large amounts of nitrobenzoic acid.

Schöpff[2] has applied the method of nitrating benzaldehyde to benzonitrile, using a mixture of concentrated sulphuric acid and the calculated amount of potassium nitrate and it was by practically this same method that we were most successful in obtaining large quantities of *m*-nitrobenzonitrile. The method in detail is given as follows:

To 110 grams of pulverized potassium nitrate, are added 300 cc. of concentrated sulphuric acid and the mass well mixed and cooled to 10°. To this mixture are added, drop by drop, and with constant stirring, 100 grams of benzonitrile. During the addition of the nitrile, the temperature must be watched carefully as it is essential that it should not rise above 20°. In order to maintain this condition, the mixture is surrounded with ice-water when necessary. After a time the acid potassium sulphate begins to separate, forming a thick, pasty mass which is difficult to stir and at this point there is a constant tendency for the temperature to rise above 20°, so that ice or even ice and salt are necessary to prevent loss of the product by overheating. The addition of the benzonitrile requires about three hours and the mixture is then allowed to stand in the cold for an hour to insure a complete reaction. The thick, pasty mass is then added gradually and with stirring, to about two liters of water containing cracked ice. On coming into contact with the water, the product solidifies into a yellow mass, which is broken up and stirred well with the cold water. It is filtered with suction and washed several times with cold water. It is then removed from the funnel and the mass broken up with dilute ammonia, filtered and washed. This treatment is continued until the ammoniacal filtrate is only very slightly yellow in color.

About 118 grams of this product are usually obtained. This is recrystallized once or twice from dilute alcohol or dilute acetic acid, when a nearly pure product, melting at 115° to 116°, is ob-

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[1] *Loc. cit.*

[2] *Loc. cit.*

tained. By using this method as given, one kilo of benzonitrile yielded 889 grams of pure *m*-nitrobenzonitrile, or about 89 per cent. of the weight of the benzonitrile used.

When perfectly pure, *m*-nitrobenzonitrile forms long, slender, silky needles of a slightly yellowish color, melting at 117°-117.5° (corr.). When heated above its melting-point it readily sublimes in long, fluffy needles which are nearly colorless. It is easily volatile with steam. Cold glacial acetic acid, chloroform, ethyl acetate, acetone and ether dissolve the compound very readily. It is soluble in hot water, slightly in cold, and easily soluble in hot absolute alcohol, methyl alcohol, carbon tetrachloride, benzene and carbon disulphide, and insoluble in petroleum ether.

PREPARATION OF METAMINOBENZONITRILE.

The preparation of the *m*-aminobenzonitrile from the nitro compound is very readily accomplished by the method given by Bogert and Hand[1] for the reduction of the orthonitrobenzonitrile.

The method giving the best results is to dissolve 500 grams of stannous chloride in about 1500 cc. of concentrated hydrochloric acid. To this solution 100 grams of *m*-nitrobenzonitrile are very gradually added in small portions and with stirring. With each addition of the nitro compound, the temperature rises markedly and the rate of addition should be so regulated that the temperature does not exceed 40°. After a time silky white crystals of the double chloride of tin and the aminonitrile begin to separate. sometimes in such quantities as to render stirring the mass impossible. When this occurs, a little water is added and the reaction-mixture is gently heated in a water-bath until solution is effected and after cooling. the addition of the nitronitrile continued. After all has been added, the mixture is carefully heated until all the crystals are dissolved and then allowed to cool to room temperature, being finally cooled for several hours in a freezing mixture of ice and salt. If much water has been added during the reduction, an equal volume of concentrated hydrochloric acid should be added to the cold solution in order to insure a satisfactory precipitation of the chloride, but this will usually be unnecessary. The fine granular crystals of the chloride are filtered off on a porcelain plate and washed with a small quantity of concentrated hydrochloric acid, previously cooled to —10°.

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[1] *Loc. cit.*

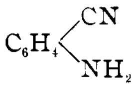
The crystals will still retain a considerable quantity of tin salts, but it is best to wash with only a very small amount of the acid and separate the rest of the tin by other means. Very little of the aminonitrile remains in the mother-liquors and it has not been found practicable to recover this. During the process of reduction there seems to be little or no tendency toward hydrolysis of the nitrile group at temperatures below 40°.

For obtaining the free base from the chloride, either of the following methods may be used.

(1) If the substance is sufficiently free from tin salts, it is convenient to add it in small portions to an excess of dilute ammonia water kept cold by ice. The free base will then separate almost completely in pure white needle crystals.

(2) Since it is very difficult and sometimes impossible to wash out all the tin salts without considerable loss of the amine chloride, it was found best to dissolve it in about 200 cc. of water contained in a liter separatory funnel. A quantity of cracked ice is then added, followed by ether and finally small portions of sodium hydroxide solution until the mixture becomes alkaline. The tin hydroxides at first precipitated will be redissolved and the free aminonitrile is at once taken up by the ether. The alkaline solution is extracted several times with ether, the ethereal solution dried with calcium chloride and the ether then nearly all removed by distillation. The concentrated ethereal solution is then allowed to crystallize, yielding, finally, a solid mass of fine needle crystals. The product thus obtained will usually be very nearly pure. If necessary, however, it may be recrystallized from carbon tetrachloride or gasoline. One crystallization will give a perfectly pure compound. The yield of the aminonitrile as obtained from the ethereal solution averaged from 65 per cent. to 70 per cent. of that theoretically obtainable from the nitronitrile.

m-Aminobenzonitrile,

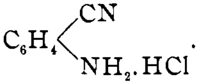


$$C_6H_4\begin{cases}CN\\NH_2\end{cases}$$

crystallizes from its ethereal solution in large hexagonal prisms, usually slightly colored. From carbon tetrachloride it is obtained perfectly pure, in long white, silky needles, melting at 53°-53.5° (corr.). It is very soluble in cold chloroform, ethyl acetate, acetone, methyl and ethyl alcohols. It is easily soluble in hot carbon disulphide, carbon tetrachloride, and somewhat soluble in hot water, gasoline and petroleum ether. It distils without decomposition.

Dr. Ferrero, working in this laboratory, attempted the preparation of *m*-aminobenzonitrile by the Griess method,[1] but found it to be quite unsatisfactory. From 20 grams of *m*-uraminobenzoic acid he succeeded in obtaining only 5 grams of very crude aminonitrile, which was difficult to purify. By recrystallization from carbon tetrachloride a fairly pure sample was finally obtained, melting only slightly lower than the product obtained by the other methods, but the process was troublesome and the method was abandoned.

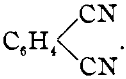
Chloride of m-Aminobenzonitrile,



$$C_6H_4\left\langle\begin{array}{l}CN\\NH_2.HCl\end{array}\right..$$

—To prepare this salt, *m*-aminobenzonitrile was dissolved in dry ether and to this solution a cold saturated solution of dry hydrochloric acid gas in dry ether was added in excess. The chloride is precipitated in fine, white crystals, from which the excess of acid is removed by careful washing with dry ether. The salt thus prepared forms a mass of silky, white crystals, which, on heating, decompose without melting. It is insoluble in ether, ethyl acetate, benzene, carbon tetrachloride, carbon disulphide and chloroform. Slightly soluble in absolute alcohol and very soluble in water. The salt may be recrystallized from alcohol, forming light, pearly flakes. It is apparently only slightly dissociated by water and is stable in the air, differing markedly in this respect from the ortho compound.

Isophthalonitrile,



$$C_6H_4\left\langle\begin{array}{l}CN\\CN\end{array}\right..$$

—This compound has been prepared almost entirely from the various sulpho salts by dry distillation methods, but usually in a more or less crude condition, as shown by the melting-points given in the literature.

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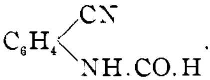
[1] *Ber. d. chem. Ges.*, 8, 860.

Luckenbach[1] prepared the compound by the removal of hydrogen sulphide from isophthalothiamide, giving the melting-point of the pure substance as 159°-160°. Reinglass[2] obtained the nitrile by dehydrating *m*-cyanbenzaldoxime and gives the melting-point as 157°.

For the preparation of the compound, *m*-aminobenzonitrile was diazotized and the diazo group replaced by the cyanogen group by the Sandmeyer reaction, as described for the preparation of the aminonitrile above. The brownish-yellow reaction-product was dried and extracted with benzene. The crystals obtained from the benzene solution are best purified by dissolving in ethyl acetate and adding gasoline to the hot solution. Thus purified, the isophthalonitrile is obtained as fine, white needles, melting at 161.5°-162° (corr.). It is very soluble in cold chloroform and in hot absolute alcohol, methyl alcohol, benzene, ethyl acetate and ether, and fairly soluble in hot carbon tetrachloride and water. It is insoluble in gasoline, petroleum ether and carbon disulphide.

DERIVATIVES OF METAMINOBENZONITRILE WITH THE FATTY ACIDS.

Formyl-m-aminobenzonitrile,



$$C_6H_4\left\langle\begin{matrix}CN\\NH.CO.H\end{matrix}\right. .$$

—Five grams of *m*-aminobenzonitrile were added to about 5 cc. of glacial formic acid. The aminonitrile dissolved with the evolution of considerable heat and the reaction was completed by gently warming for a half hour. On cooling, the reaction-product solidified to a brownish cake, which was broken up with cold water, filtered and washed to remove excess of the acid, and then recrystallized from hot water. The compound crystallizes in white, microscopic needles, which melt at 150.5°-151° (corr.). On adding ammoniacal silver nitrate to its aqueous solution, a white, crystalline precipitate of a silver derivative corresponding to that obtained with formanilide, is at once formed. If this compound is gently heated with water, it dissolves and then deposits metallic silver.

The formyl derivative is soluble in water, chloroform, absolute alcohol, methyl alcohol, and very soluble in ethyl acetate and

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[1] *Ber. d.chem. Ges.*, **17**, 1430.

[2] *Ibid*, **24**, 2416.

acetone. It is slightly soluble in hot benzene and ether, and insoluble in carbon tetrachloride, carbon disulphide and petroleum ether.

On analysis, the compound gave 19.25 per cent. N. Calculated, 19.18 per cent.

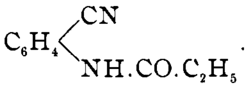
Acetyl-m-aminobenzonitrile,

$$C_6H_4\begin{cases}CN\\NH.CO.CH_3\end{cases}.$$

—*m*-Aminobenzonitrile dissolves in acetic anhydride with a lowering of the temperature and then after standing a few minutes, the reaction begins with the liberation of considerable heat. The excess of acetic anhydride and acetic acid is very gently boiled off and, on cooling, the brownish oil remaining solidifies. This is dissolved in hot water and allowed to crystallize. Sufficient water must be added to prevent separation as an oil. The acetyl derivative crystallizes in fine, white needles, melting at 130.5°-131° (corr.). It is very easily soluble in cold ethyl acetate, acetone, absolute alcohol, methyl alcohol, chloroform, glacial acetic acid, and in hot water and benzene. It is slightly soluble in hot ether, and insoluble in carbon tetrachloride, carbon disulphide and petroleum ether.

The analysis gave: C, 67.63; H, 4.96; N, 17.50. Calculated: C, 67.50; H, 5.00; N, 17.73.

Propionyl-m-aminobenzonitrile,



$$C_6H_4\begin{cases}CN\\NH.CO.C_2H_5\end{cases}.$$

—For the preparation of this derivative the aminonitrile is dissolved in propionic anhydride. The reaction takes place in much the same way as with the acetyl compound, except that there is apparently no evolution of heat. After warming gently for some time and then carefully distilling off the excess of anhydride and acid, the remaining oil is cooled and dissolved in dilute alcohol, treated with bone-black and allowed to crystallize. The crystals thus obtained are nearly colorless, minute needles. Recrystallized from benzene and a small amount of petroleum ether, the substance is obtained as perfectly white, brilliant needles, melting at 83.5°-84° (corr.).

The propionyl derivative is very easily soluble in cold ethyl acetate, absolute alcohol, methyl alcohol, chloroform, acetone and ether. It is soluble in hot benzene, carbon tetrachloride and carbon disulphide, and slightly soluble in hot water and petroleum ether.

The analysis of the substance gave 16.07 per cent. N. Calculated, 16.09 per cent.

Normalbutyryl-m-aminobenzonitrile,

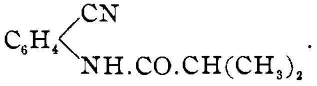
$$C_6H_4{<}\begin{matrix}CN\\NH.CO.C_3H_7\end{matrix}.$$

—This derivative was prepared by heating the aminonitrile with an excess of normal butyric anhydride at its boiling-point for an hour. The principal part of the anhydride and acid remaining was removed by careful evaporation and the resulting oil cooled and treated with hot water. On cooling in a freezing-mixture, the oil solidified and was removed from the water and recrystallized from dilute alcohol after treatment with bone-black to remove a slight reddish coloring matter. It was found best to crystallize the material by dissolving in a small amount of alcohol and then adding water till the solution became milky. The solution is then placed in a freezing-mixture and if, on cooling, an oil separates, just sufficient alcohol is added to effect complete solution. From such a solution the butyryl compound separates out almost completely in the form of white, shining flakes. By dissolving in benzene and adding a little petroleum ether, it is obtained in the same form, but the crystals are somewhat larger. The melting-point of the pure substance is 72.5°-73.5° (corr.).

The compound is very soluble in cold ethyl acetate, absolute alcohol, methyl alcohol, chloroform, benzene, ether and acetone. It is soluble in hot carbon tetrachloride, carbon disulphide, and very slightly in hot water. It is insoluble in petroleum ether.

The analysis gave 14.85 per cent. N. Calculated, 14.89 per cent.

Isobutyryl-m-aminobenzonitrile,



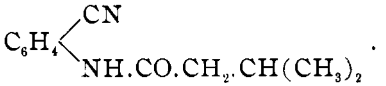
$$C_6H_4{<}\begin{matrix}CN\\NH.CO.CH(CH_3)_2\end{matrix}.$$

—The isobutyryl derivative was prepared and crystallized in the same general way as for the normal butyryl compound just described. From dilute alcohol or a mixture of benzene and petroleum ether it is obtained in brilliant, white, pearly flakes, melting at 101° (corr.).

It is very easily soluble in cold ethyl acetate, absolute alcohol, methyl alcohol, chloroform, acetone and ether, and in hot benzene, carbon tetrachloride and carbon disulphide. It is very slightly soluble in hot water and insoluble in petroleum ether.

An analysis of the substance gave 15.23 per cent. N. Calculated, 14.89 per cent.

Isovaleryl-m-aminobenzonitrile,



$$C_6H_4\begin{cases}CN\\NH.CO.CH_2.CH(CH_3)_2\end{cases}.$$

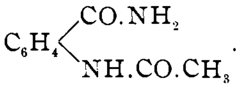
—This compound was prepared and crystallized in the same way as described for the butyryl derivatives. Considerable difficulty was experienced in obtaining a sharp-melting product, the melting-point rising slightly at each crystallization from dilute alcohol, from 74° up to 77°. Recrystallization of this product from a mixture of benzene and petroleum ether yielded crystals which melted at 77°-78° (corr.), and this melting-point could not be further raised by recrystallization. As obtained in this way, the substance forms nearly white, pearly flakes, which are very easily soluble in cold absolute alcohol, methyl alcohol, ethyl acetate, chloroform and ether. It is easily soluble in hot benzene, carbon tetrachloride and carbon disulphide, and is insoluble in petroleum ether.

A determination of nitrogen gave 13.95 per cent. N. Calculated, 13.86 per cent.

The acyl derivatives of *m*-aminobenzonitrile described are all well defined, crystalline bodies, and are easily obtained in pure condition. It is interesting to note that, with increasing number of carbon atoms in the aliphatic chain, there is a decrease in the melting-point, approaching that of the unsubstituted aminonitrile, and that compounds having the iso structure melt higher than those with normal chains. These facts were also observed with the corresponding compounds of the ortho series and with the quinazolines derived from them. The compounds of the meta series also show an increase in general solubility with increase of molecular weight. The formyl derivative is soluble in dilute caustic alkali and yields a silver derivative by direct precipitation with ammoniacal silver nitrate, but the other members of the series do not seem to be more soluble in alkali than in water, and do not yield silver salts by direct precipitation. None of the acyl derivatives of this series were found to be volatile with steam, differing in this respect from the ortho compounds.

HYDROLYSIS OF THE NITRILE GROUP.

m-Acetaminobenzamide,



$$C_6H_4\begin{cases} CO.NH_2 \\ NH.CO.CH_3 \end{cases}.$$

—A very convenient and satisfactory method for the hydrolysis of the nitrile group to the corresponding amide was found to be by use of alkaline hydrogen peroxide, as described by Radziszewski.[1] The method was carried out as follows:

Six grams of *m*-acetaminobenzonitrile were heated on the water-bath with about 50 cc. of a 3 per cent. solution of hydrogen peroxide and just sufficient potassium hydroxide to give an alkaline reaction. In about an hour all the crystals had dissolved to a clear, yellowish solution, which was digested for an hour longer, treated with bone-black and allowed to crystallize. The amide crystallizes in fine, white needles, which are purified by recrystallization from hot water. The melting-point of the pure substance was found to be 216°-216.5° (corr.). It is easily soluble in hot water, slightly in cold. It is soluble in hot absolute alcohol and methyl alcohol, very slightly in hot ethyl acetate, carbon tetrachloride, carbon disulphide, chloroform, acetone and benzene, and insoluble in ether and petroleum ether.

DERIVATIVES OF METAMINOBENZONITRILE WITH AROMATIC ACIDS.

For the preparation of the aromatic acid derivatives of *m*-aminobenzonitrile the Schotten-Baumann[2] reaction was used. It was later found that a much more convenient and satisfactory method was to dissolve the aminonitrile in pyridine and add to this solution the calculated amount of the acid chloride or a solution of the latter in pyridine. Under these conditions a complete reaction is secured without the use of alkali. The mixture becomes

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[1] *Ber. d. chem. Ges.*, **18**, 355.

[2] *Ibid.*, **19**, 3218.

warm and after the reaction is complete, water is added to take up the excess of pyridine and its hydrochloride. The product is then obtained as an oil, which changes to a crystalline solid on stirring.

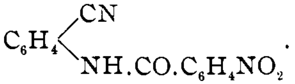
Benzoyl-m-aminobenzonitrile,

$$C_6H_4\left\langle\begin{matrix}CN\\ NH.CO.C_6H_5\end{matrix}\right. .$$

—This compound was prepared by dissolving 3 grams of the aminonitrile in dilute alcohol and adding 5 grams of benzoyl chloride. When the mixture had cooled, a little sodium carbonate solution was added and the mixture warmed on a water-bath. The addition of the carbonate was continued until the solution showed a slight alkaline reaction. On cooling and stirring, the oil solidified to a white, crystalline mass, which was recrystallized from dilute alcohol. The benzoyl derivative separates as pearly flakes which, when pure, melt sharply at 141.5°-142° (corr.). By crystallizing from carbon tetrachloride containing a little ethyl acetate it is obtained in long, glistening needles. It is very easily soluble in cold ethyl acetate, acetone and chloroform, and in hot absolute alcohol, methyl alcohol, benzene and carbon tetrachloride. The compound is slightly soluble in hot water, ether and petroleum ether, and insoluble in carbon disulphide.

An analysis of the substance gave: C, 75.48; H, 4.57; N, 12.85. Calculated: C, 75.67; H, 4.50; N, 12.61.

m-Nitrobenzoyl-m-aminobenzonitrile,



$$C_6H_4\left\langle\begin{matrix}CN\\ NH.CO.C_6H_4NO_2\end{matrix}\right. .$$

—This compound was prepared by dissolving the aminonitrile in dilute alcohol, adding the calculated amount of finely pulverized *m*-nitrobenzoyl chloride and then sodium carbonate, as in the preparation of the benzoyl derivative. It is much more conveniently prepared by dissolving the nitrile and chloride in separate portions of pyridine, mixing the solutions and precipitating the reaction-product by the addition of water.

By recrystallization from alcohol it is obtained in fine, white needles, which melt at 196.5°-197° (corr.). It is very soluble in cold acetone and ethyl acetate, and in hot absolute alcohol and methyl alcohol. It is slightly soluble in hot benzene and ether, and insoluble in water, chloroform, carbon tetrachloride, carbon disulphide and petroleum ether.

An analysis of the substance gave 15.63 per cent. N. Calculated, 15.73.

p-Nitrobenzoyl-m-aminobenzonitrile,

$$C_6H_4\left\langle\begin{array}{l}CN\\NH.CO.C_6H_4NO_2\end{array}\right. .$$

—The preparation of this substance was carried out exactly as described for the meta compound. As in the case of the latter, it was found much more convenient to bring about the reaction in pyridine solution.

The para compound is obtained from its solution in boiling alcohol as light yellow needles, which melt at 250°-251° (corr.). It is soluble in hot acetone, absolute alcohol, methyl alcohol, glacial acetic acid, ethyl acetate and isobutyl alcohol. It is insoluble in water, benzene, carbon tetrachloride, carbon disulphide and chloroform.

Benzenesulphone-m-aminobenzonitrile, $C_6H_5SO_2.NHC_6H_4CN$. —For the preparation of this compound 3 grams of the aminonitrile were dissolved in dilute alcohol and 4.5 grams of benzenesulphone chloride added and the mixture warmed with sodium carbonate solution. On cooling, a white, crystalline solid separates, which is best recrystallized from water or dilute alcohol. From the latter solvent it is obtained as long, silky, white needles, melting sharply at 126.5°-127° (corr.). It is soluble in cold ethyl acetate, acetone, ether, absolute alcohol, methyl alcohol and chloroform. It is soluble in hot benzene and water, and insoluble in carbon tetrachloride, carbon disulphide and petroleum ether.

The sulpho compound is easily soluble in cold dilute potassium hydroxide solution or carbonate solution, and is precipitated unchanged by neutralizing with dilute hydrochloric acid. It is also soluble in ammonia water and if silver nitrate solution is added to the ammoniacal solution, a white crystalline precipitate of a silver salt is produced.

A determination of sulphur in the compound gave 12.29 per cent. S. Calculated, 12.40 per cent.

DERIVATIVES OF CARBONIC AND THIOCARBONIC ACIDS.

m-Cyanphenylurethane,

$$C_6H_4\left\langle\begin{matrix}CN\\NH.CO.OC_2H_5\end{matrix}\right.$$

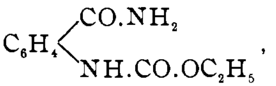
—The acid corresponding to this nitrile has been prepared by Griess[1] and the amide by Wachendorff.[2] The latter was obtained by heating the ethyl ester with aqueous ammonia and is described as crystallizing from benzene in fine needles, melting at 157°-158°.

For the preparation of the nitrile 5 grams of *m*-aminobenzonitrile are dissolved in dilute alcohol and a small amount of sodium carbonate added. To this cold solution are added 5 grams of ethyl chlorcarbonate. The mixture becomes hot and, as the reaction progresses, carbon dioxide is evolved. After a few minutes, more water is added and the mixture warmed on the water-bath. The urethane derivative separates as a dark-colored oil. The reaction mixture is cooled in ice-water and the oil gradually solidifies to a crystalline mass. This is recrystallized from dilute alcohol, best in a refrigerator, since the substance tends to separate as an oil, especially at room temperature. The yield of the pure substance is about 7 grams.

The urethane derivative forms short, prismatic crystals, melting at 61°-62° (corr.), and is very soluble in cold ethyl acetate, ether, benzene, absolute alcohol, methyl alcohol, acetone and chloroform. It is easily soluble in hot carbon disulphide and carbon tetrachloride, and slightly in hot water and petroleum ether.

An analysis of the compound gave 14.83 per cent. N. Calculated, 14.74 per cent.

On digesting the urethane derivative with hydrogen peroxide and a little sodium hydroxide the compound melts to an oil and gradually goes into solution, from which *m-urethanebenzamide,*



$$C_6H_4\left\langle\begin{matrix}CO.NH_2\\NH.CO.OC_2H_5\end{matrix}\right.,$$

crystallizes in fluffy, white flakes, melting at 159°-160°, and corresponding in every way to the compound obtained by Wachendorff.

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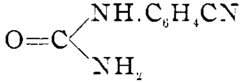
[1] *Ber. d. chem. Ges.*, 9, 796.

[2] *Ibid.*, 11, 701.

m-Cyanphenylurea,



$$O{=}C\begin{cases} NH.C_6H_4CN \\ NH_2 \end{cases}$$

—The acid and the amide corresponding to this nitrile and many derivatives of each have been prepared by Menschutkin[1] and Griess.

For the preparation of the nitrile 3.5 grams of *m*-aminobenzonitrile are dissolved in dry ether and to this solution is added a cold saturated solution of dry hydrochloric acid gas in dry ether. The chloride is at once precipitated as a fine, white, crystalline mass, which is filtered off and washed with ether until free of hydrochloric acid and the ether evaporated in a vacuum desiccator. The chloride is then dissolved in a small amount of water and to this solution is added an aqueous solution of 2.6 grams of potassium cyanate. A white precipitate forms, which redissolves on heating gently on the water-bath. After digesting for an hour, the solution is allowed to cool, causing the separation of a white, flocculent precipitate. When cold, this precipitate changes over into a mass of fine needle crystals, at the same time producing a peculiar crackling sound, sufficiently loud to be heard at a considerable distance. As nearly as could be learned without special study, this sound is produced by a change in crystalline condition. When the compound is crystallized from water solution its melting-point also shows some peculiarities. The compound usually softens very slightly at about 100°, then immediately hardens and melts at about 160°. By recrystallization from a mixture of ethyl acetate and petroleum ether it is obtained in nearly white, microscopic needles, which melt at 160°-162° (corr.).

m-Cyanphenylurea is easily soluble in cold absolute alcohol, methyl alcohol, acetone and ethyl acetate. It is slightly soluble in hot chloroform, and insoluble in petroleum ether, ether, carbon tetrachloride, carbon disulphide and benzene.

A determination of nitrogen gave 25.82 per cent. N. Calculated, 26.08 per cent.

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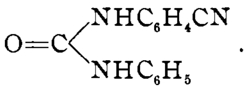
[1] *Ann. Chem.* (Liebig), **153**, 83.

[2] *Ztschr. Chem.*, 1868, 389.

m-Cyancarbanilide,



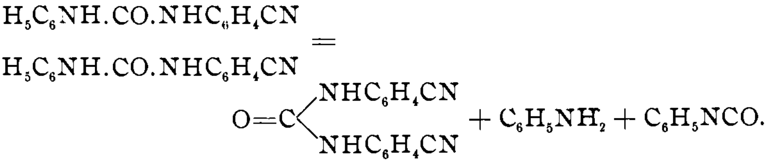
$$O{=}C\left\langle\begin{matrix}NHC_6H_4CN\\NHC_6H_5\end{matrix}\right. .$$

—Kühn[1] and Paal[2] have prepared the acid, phenyl-*m*-uramidobenzoic acid, corresponding to this nitrile, but neither the amide nor the nitrile are described in the literature.

For the preparation of the nitrile 5 grams of *m*-aminobenzonitrile are dissolved in dry benzene and to the cold solution 5 grams of phenyl isocyanate are added. The mixture becomes warm and, on cooling, a mass of fine white needles is deposited. This product is recrystallized from alcohol, forming beautiful white needles, which melt at 170.5°-171° (corr.), undergoing decomposition at the same time. The substance is easily soluble in cold absolute alcohol, methyl alcohol, ethyl acetate and acetone. It is slightly soluble in hot water and insoluble in petroleum ether, chloroform, carbon tetrachloride, ether, benzene and carbon disulphide.

A determination of nitrogen in the substance gave 17.61 per cent. N. Calculated, 17.72.

The decomposition of *m*-cyancarbanilide, on heating to its melting-point, seemed to present some interest, and a special study of this reaction was made. When a quantity of material is heated to about 175° in an oil-bath it first melts and then boils with the liberation of phenyl isocyanate, and if the temperature is raised somewhat higher aniline may also be distilled off. Sometimes these vapors reunite in the colder parts of the tube, giving a deposit of carbanilide. There is left behind, after the reaction is completed, a yellowish, glassy mass which, on recrystallization from alcohol, yields white needles, melting at 199°. These were found to be identical in every respect with the di-*m*-cyancarbanilide produced by another method. The decomposition may, therefore, be represented by the following equation:



$$\begin{matrix}H_5C_6NH.CO.NHC_6H_4CN\\H_5C_6NH.CO.NHC_6H_4CN\end{matrix} = O{=}C\left\langle\begin{matrix}NHC_6H_4CN\\NHC_6H_4CN\end{matrix}\right. + C_6H_5NH_2 + C_6H_5NCO.$$

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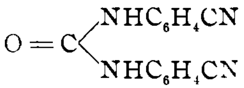
[1] *Ber. d. chem. Ges.*, **17**, 2882.

[2] *Ibid.*, **27**, 979.

Di-m-cyancarbanilide,



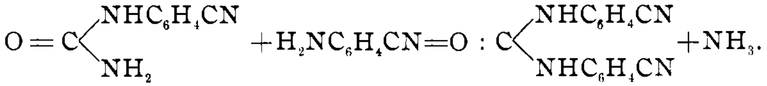
$$\mathrm{O=C}\left\langle\begin{matrix}\mathrm{NHC_6H_4CN}\\ \mathrm{NHC_6H_4CN}\end{matrix}\right.$$

—The acid and amide corresponding to this nitrile have been investigated by Griess,[1] Traube,[2] Schiff[3] and others.

In our work it was found possible to obtain the nitrile by a number of reactions.

(1) By heating *m*-cyancarbanilide above its melting-point, as described above.

(2) By heating 1 gram of *m*-aminobenzonitrile and 1.3 grams of *m*-cyanphenylurea to 150°-200° for three hours. Ammonia is liberated during the reaction and there is left a yellowish oil, which solidifies on cooling. This is dissolved in alcohol, treated with bone-black and allowed to crystallize. The crystals thus obtained correspond in every way to those obtained by the other methods, and melt sharply at 199°. The reaction is represented by the equation,



$$\mathrm{O=C}\left\langle\begin{matrix}\mathrm{NHC_6H_4CN}\\ \mathrm{NH_2}\end{matrix}\right. + \mathrm{H_2NC_6H_4CN = O : C}\left\langle\begin{matrix}\mathrm{NHC_6H_4CN}\\ \mathrm{NHC_6H_4CN}\end{matrix}\right. + \mathrm{NH_3}.$$

(3) The most direct and convenient method for the preparation of the di-*m*-cyancarbanilide was found to be from phosgen.

To 5 grams of *m*-aminobenzonitrile, dissolved in about 20 cc. of pyridine, were added 10 cc. of a 20 per cent. solution of phosgen in toluene. Considerable heat is liberated in the reaction and after heating for a few minutes, the mixture is cooled and a large volume of water added. As a result, there is obtained a white, crystalline mass which, on recrystallization from dilute alcohol, yields fine, white needles, showing a great tendency to mat down into a compact mass. The product thus obtained melts at 198°-199° (corr.). The substance is easily soluble in cold ethyl acetate, absolute alcohol, methyl alcohol and acetone. It is slightly soluble in hot water and is insoluble in petroleum ether, chloroform, ether, carbon tetrachloride and carbon disulphide.

An analysis of the substance gave 21.42 per cent. N. Calculated, 21.37 per cent.

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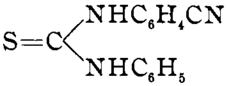
[1] *Ztschr. Chem.*, 1868, 650.

[2] *Ber. d. chem. Ges.*, **15**, 2128.

[3] *Ann. Chem.* (Liebig), **232**, 140.

m-Cyanthiocarbanilide,



$$S=C\begin{cases}NHC_6H_4CN\\NHC_6H_5\end{cases}$$

—The acid corresponding to this nitrile has been prepared and studied by Rathke and Schaefer[1] and Aschan,[2] though there are some wide discrepancies in the results obtained by the two investigators.

Considerable difficulty was experienced in obtaining the nitrile in pure condition, largely due to its great tendency to separate from most solvents either as a thick yellow oil or soft warty masses of crystals. The condensation was brought about in a number of ways: By heating equi-molecular quantities of phenyl mustard oil and *m*-aminobenzonitrile together without a solvent, heating the same in benzene solution, in alcoholic solution and, finally, in an isoamyl alcoholic solution. This last method gave by far the best results and was the one finally adopted.

To a solution of 5 grams of *m*-aminobenzonitrile in 50 cc. of isoamyl alcohol were added 5 grams of phenyl mustard oil and the mixture heated to boiling for about fifteen minutes. The reaction-mixture was allowed to stand in a cold place for some time, when 8 grams of a light yellow, crystalline mass separated out. This was washed free of the amyl alcohol with gasoline, dried on a porous plate, and finally recrystallized by dissolving in hot chloroform and adding petroleum ether until the solution became milky.

The *m*-cyanthiocarbanilide separates from its chloroform solution in light yellow, microscopic, rhombic crystals, melting at 143°-144° (corr.). It is very easily soluble in cold acetone and hot ethyl acetate, absolute alcohol, methyl alcohol and chloroform. It is slightly soluble in hot carbon tetrachloride, ether and carbon disulphide, and insoluble in petroleum ether.

A determination of the sulphur in the compound gave 12.70 per cent. S. Calculated, 12.64 per cent.

Several attempts were made to hydrolyze the nitrile to the corresponding amide, which is not described in the literature, but the compound suffers decomposition on heating with hydrogen peroxide, even in a neutral solution, phenyl mustard oil being liberated.

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[1] *Ann. Chem.* (Liebig), **169**, 106.

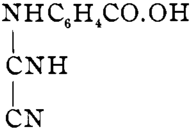
[2] *Ber. d. chem. Ges.*, **17**, 428.

It was also found impossible to obtain the di-*m*-cyanthiocarbanilide. The usual reaction with carbon disulphide and alkali was tried with negative results. It was then tried to bring about a reaction between *m*-aminobenzonitrile and sodium xanthogenate, but without result. Finally, thiourea and the aminonitrile were heated together, but no product corresponding to the carbanilide could be obtained.

On heating the *m*-cyanthiocarbanilide above its melting-point it undergoes decomposition and pure crystals of thiocarbanilide were obtained, hence the decomposition is probably analogous to that of the *m*-cyancarbanilide described above. It was not found possible, however, to isolate anything from the reaction-product corresponding to the compound sought.

DERIVATIVES OF OXALIC ACID.

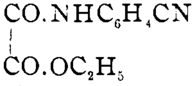
Various acids and amides produced by the condensation of *m*-aminobenzoic acid and its amide with oxalic ethyl ester have been prepared and described by Schiff[1] and Griess.[2] Schiff prepares his derivatives by condensation with oxalic ester, while Griess obtained some of the same compound through the hydrolysis of the compound, cyancarbimidaminobenzoic acid,



$$\begin{array}{l} NHC_6H_4CO.OH \\ | \\ CNH \\ | \\ CN \end{array}$$

, which results on passing cyanogen into *m*-aminobenzoic acid. The nitriles, however, are not described in the literature.

Oxal-m-cyananilic Acid Ethyl Ester,



$$\begin{array}{l} CO.NHC_6H_4CN \\ | \\ CO.OC_2H_5 \end{array}$$

—For the preparation of this ester 6 grams of *m*-aminobenzonitrile and 8 grams of ethyl oxalate were heated together for eight hours in a flask surrounded by boiling water. The reaction takes place with the liberation of alcohol and proceeds much more rapidly if the alcohol vapor is removed from the flask, from time to time, by a current of dry air. After from two to three hours' heating the reaction-product begins to separate as a fine crystal-

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[1] *Ann. Chem.* (Liebig), **232**, 129.

[2] *Ber. d. chem. Ges.*, **18**, 2410.

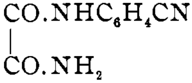
line powder, which continues to form until the whole mass becomes solid. At this point the flask is removed and the product washed with cold alcohol to remove the slight excess of oxalic ester and a small amount of a brown coloring-matter formed during the reaction. The fine, white, crystalline mass is then recrystallized from boiling alcohol, yielding usually about 10 grams of the pure product.

Oxal-*m*-cyananilic acid ethyl ester forms short needle crystals of a pure white color, melting sharply at 148°-148.5° (corr.). It is easily soluble in cold acetone, ethyl acetate and chloroform, and in hot absolute alcohol, methyl alcohol and benzene. It is slightly soluble in hot water, carbon tetrachloride, carbon disulphide and ether, and insoluble in petroleum ether.

When heated above its melting-point it undergoes decomposition with the liberation of oxalic ester and formation of oxaldi-*m*-cyananilide, a reaction analogous to the one discovered by Schiff[1] for the corresponding acid. Before this was known, much difficulty was experienced in the preparation of the ester because it was attempted to bring about the condensation by heating the aminonitrile and the oxalic ester at the boiling-point of the latter. Two products were always obtained, the compound sought and the dicyananilide, but the main portion consisted of products which could not be separated. By bringing about the reaction at 100°, as above described, the oxal-*m*-cyananilic ester is the sole product formed.

The analysis of the compound gave: C, 60.69; H, 4.55. Calculated: C, 60.55; H, 4.59.

m-Cyanphenyloxamide,



$$\begin{array}{l}CO.NHC_6H_4CN\\ |\\ CO.NH_2\end{array}$$

—The acid and amide corresponding to this nitrile have been prepared by Schiff[1] and Griess.[1]

For the preparation of the compound 2 grams of the oxal-*m*-cyananilic ester are heated in a beaker on the water-bath with about 20 cc. of concentrated ammonia solution. The reaction begins in the cold and is completed after a few minutes' heating

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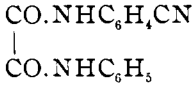
[1] *Loc. cit.*

on the water-bath. The heating is continued until the excess of ammonia is removed and the white, silky mass of the amide is then recrystallized from hot alcohol from which it separates in white, pearly flakes. The pure compound melts sharply at 245°-246° (corr.). It is easily soluble in boiling acetone, ethyl acetate, glacial acetic acid, absolute alcohol and methyl alcohol. It is very difficultly soluble in hot water and is insoluble in hot benzene, ether, petroleum ether, chloroform, carbon tetrachloride and carbon disulphide.

When heated above its melting-point it undergoes decomposition analogous to that of the oxal-*m*-cyananilic ester, oxamide subliming into the cool parts of the tube and oxaldi-*m*-cyananilide remaining behind.

An analysis of the *m*-cyanphenyloxamide gave: C, 57.32; H, 3.95. Calculated: C, 57.14; H, 3.70.

Oxal-m-cyananilide,



$$\begin{array}{l}\mathrm{CO.NHC_6H_4CN}\\ | \\ \mathrm{CO.NHC_6H_5}\end{array}$$

—The corresponding acid and amide have been prepared by Schiff[1] by heating the ester with aniline.

On boiling an aniline solution of oxal-*m*-cyananilic ester for a half hour and cooling, a crystalline mass was obtained which consisted mostly of the unchanged ester with a small amount of the *m*-cyananilide sought. Since the reaction takes place so slowly, various condensing agents were tried and of these anhydrous zinc chloride was found to give entirely satisfactory results.

To the aniline solution, as given above, a little anhydrous zinc chloride was added and the mixture boiled for ten minutes, cooled and then alcohol was added. A white, crystalline precipitate separated, which was recrystallized from alcohol.

Prepared in this way, the oxal-*m*-cyananilide forms fine, white, silky needles, which melt at 205°-206° (corr.). It is easily soluble in cold acetone and in hot ethyl acetate, absolute alcohol, methyl alcohol, chloroform and benzene. It is insoluble in petroleum ether, carbon tetrachloride, carbon disulphide, ether and water.

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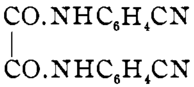
[1] *Loc. cit.*

Oxaldi-m-cyananilide,

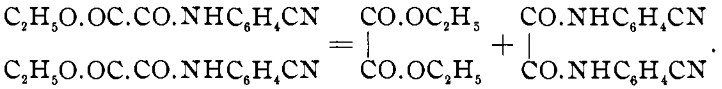


$$\begin{array}{l}\mathrm{CO.NHC_6H_4CN}\\ |\\ \mathrm{CO.NHC_6H_4CN}\end{array}$$

—Schiff and Griess have also prepared the acid and amide corresponding to this nitrile.

In this work it was found that a number of reactions would give the dicyananilide, though not all could be used as methods of preparation.

(1) As previously mentioned, when oxal-*m*-cyananilic ester is heated above its melting-point it suffers decomposition. Ethyl oxalate distils off and oxaldi-*m*-cyananilide remains behind as a fine, white, granular mass, hence the reaction probably takes place according to the equation:



$$\begin{array}{l}\mathrm{C_2H_5O.OC.CO.NHC_6H_4CN}\\ \mathrm{C_2H_5O.OC.CO.NHC_6H_4CN}\end{array} = \begin{array}{l}\mathrm{CO.OC_2H_5}\\ |\\ \mathrm{CO.OC_2H_5}\end{array} + \begin{array}{l}\mathrm{CO.NHC_6H_4CN}\\ |\\ \mathrm{CO.NHC_6H_4CN}\end{array}.$$

If, however, the heating is not very carefully performed, more deep-seated reactions take place and pure products are not obtained.

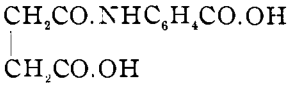
(2) On heating *m*-cyanphenyloxamide it decomposes in the same way as the ester above, oxamide subliming into the cold part of the tube and the cyananilide remaining behind as a crystalline powder.

(3) Though the compound sought is formed in each of the above reactions, neither is satisfactory as a method of preparation. It is easily prepared by gently melting equimolecular quantities of oxal-*m*-cyananilic ester and *m*-aminobenzonitrile in the presence of anhydrous zinc chloride. The reaction takes place smoothly and the resulting crystalline mass is recrystallized from hot aniline or amyl alcohol. It is thus obtained as a fine, crystalline powder, which does not melt at 300°, but turns very slightly brown in color. It is soluble in hot glacial acetic acid, aniline and amyl alcohol. It is slightly soluble in hot absolute alcohol, methyl alcohol and acetone, and insoluble in benzene, chloroform, carbon tetrachloride, carbon disulphide, ether, ethyl acetate and petroleum ether.

DERIVATIVES OF SUCCINIC ACID.

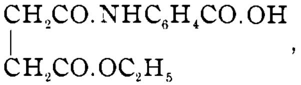
Muretow[1] prepared the compound,

which he called succinaminobenzoic acid, by heating *m*-aminobenzoic acid and succinic acid at 200°. By digesting this compound with barium hydroxide solution, he found the imide ring was easily opened with the production of the dicarboxylic acid,



$$\begin{array}{l} CH_2CO.NHC_6H_4CO.OH \\ | \\ CH_2CO.OH \end{array}$$

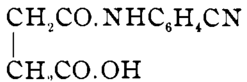
Pellizzari[2] obtained the monoethyl ester,



$$\begin{array}{l} CH_2CO.NHC_6H_4CO.OH \\ | \\ CH_2CO.OC_2H_5 \end{array},$$

of the above acid, by condensing succinic ethyl ester with *m*-aminobenzoic acid. From this ester he obtained the amide and finally the acid which corresponded in every way with the one previously obtained by Muretow. On heating this acid above its melting-point it lost a molecule of water, giving the succin-*m*-aminobenzoic acid of Muretow. As the nitrile and amide derivatives corresponding to these compounds are not described in the literature, it seemed of interest to prepare some of them and study their properties.

Succin-m-cyananilic Acid,



$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ | \\ CH_2CO.OH \end{array}$$

—After numerous attempts it was found impossible to produce the ester of this acid by condensing succinic ethyl ester with *m*-aminobenzonitrile, as Pellizzari had done with *m*-aminobenzoic acid. Even anhydrous zinc chloride failed to bring about the reaction and the method was abandoned.

It was found, however, that quantitative yields of the acid could be readily obtained by the following method, based upon that used by Auwers[3] in the preparation of the succinnitranilic acids.

A boiling, saturated solution of 4 grams (1 mol.) of succinic

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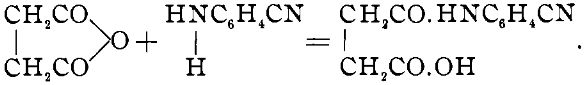
[1] *J. Russ. Chem. Soc.*, **4**, 295.

[2] *Gazz. chim. ital.*, **15**, 547.

[3] *Ann. Chem.* (Liebig), **292**, 188.

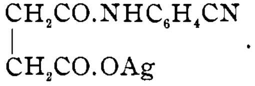
anhydride in chloroform is prepared, requiring about 200 cc. of chloroform. Benzene may be used in place of the chloroform, but the anhydride is somewhat more soluble in the latter. To this solution is added 4.7 grams (1 mol.) of *m*-aminobenzonitrile in about 50 cc. of chloroform or benzene, and the mixture maintained at the boiling-point of the solvent. Usually after boiling a few minutes the solution will become slightly turbid and then the whole of the reaction-product suddenly crystallizes out of the solution. Sometimes, however, the solution will remain clear, in which case the boiling must be continued until the crystallization occurs. When the reaction is complete the mixture is cooled and filtered, giving a yield of about 7.5 grams of nearly pure succin-*m*-cyananilic acid in the form of fine, glistening needles. An additional small amount of the substance may be obtained from the mother liquor, if desired. The acid is recrystallized from hot water or from a mixture of ethyl acetate and petroleum ether. The following equation represents the formation of the compound:



$$\begin{array}{l}CH_2CO\\|\\CH_2CO\end{array}\!>O+\begin{array}{l}HNC_6H_4CN\\|\\H\end{array}=\begin{array}{l}CH_2CO.HNC_6H_4CN\\|\\CH_2CO.OH\end{array}.$$

Succin-*m*-cyananilic acid crystallizes in silky flakes, which melt at 132°-133° (corr.). It is easily soluble in cold ethyl acetate, acetone, absolute alcohol and methyl alcohol. It is slightly soluble in hot chloroform, and is insoluble in ether, carbon disulphide, carbon tetrachloride, petroleum ether and benzene.

Silver Salt of Succin-m-cyananilic Acid,

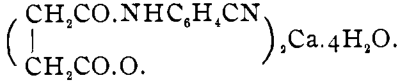


$$\begin{array}{l}CH_2CO.NHC_6H_4CN\\|\\CH_2CO.OAg\end{array}.$$

—The silver salt was prepared in the usual way by exactly neutralizing the acid with ammonia and to the hot solution adding silver nitrate solution in slight excess. The salt forms fine, colorless needles, nearly insoluble in cold water, but fairly soluble in hot water. The dry salt is fairly stable in the light.

A determination of the silver content by ignition gave 33.07 per cent. Ag. Calculated, 33.23 per cent.

Calcium Salt of Succin-m-cyananilic Acid,

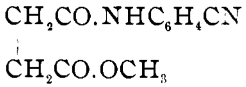


$$\left(\begin{array}{l}CH_2CO.NHC_6H_4CN\\|\\CH_2CO.O.\end{array}\right)_2Ca.4H_2O.$$

—The calcium salt was formed by adding an excess of pure calcium carbonate to the hot aqueous solution of the acid, filtering and allowing to crystallize. It crystallizes from water in fine, white needles, containing 4 molecules of water of crystallization.

By ignition of the salt to the oxide the following was obtained: 7.31 per cent. Ca. Calculated, 7.35 per cent.

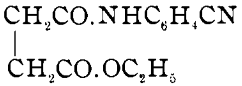
Succin-m-cyananilic Acid Methyl Ester,



$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ \vert \\ CH_2CO.OCH_3 \end{array}$$

—This ester was prepared by dissolving the acid in absolute methyl alcohol and passing dry gaseous hydrochloric acid into the cold solution until saturated. After cooling, water was cautiously added, care being taken to avoid a rise in temperature before the hydrochloric acid had become diluted. On the addition of the water the ester separates in very fine crystals, which are best recrystallized from dilute methyl alcohol. The pure ester forms long, slender needles, melting at 88°-89° (corr.). It is easily soluble in cold absolute alcohol, methyl alcohol, acetone, ethyl acetate and chloroform. It is easily soluble in hot benzene and carbon tetrachloride, and somewhat soluble in hot ether. The ester is insoluble in petroleum ether and carbon disulphide.

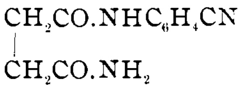
Succin-m-cyananilic Acid Ethyl Ester,



$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ \vert \\ CH_2CO.OC_2H_5 \end{array}$$

—The ethyl ester was prepared in the same way as the methyl ester, and on the addition of water to its alcoholic solution was obtained in fine, white needles. These may be recrystallized from dilute alcohol or best by dissolving in a very small amount of hot benzene and then adding just sufficient petroleum ether to cause a slight milky appearance. After standing some time, this solution will deposit long, delicate, colorless needles of the pure ethyl ester, melting sharply at 84°-84.5° (corr.). The ester is very easily soluble in cold absolute alcohol, methyl alcohol and chloroform, and in hot benzene, carbon tetrachloride and water. It is insoluble in petroleum ether.

Succin-m-cyananilic Amide,

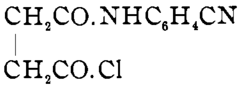


$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ \vert \\ CH_2CO.NH_2 \end{array}$$

—The amide may be prepared by treating either the methyl or the ethyl ester with concentrated ammonia water, and boiling gently until all the oily drops have dissolved. The excess of ammonia is then gently evaporated, the solution filtered and allowed to cool. The amide crystallizes from this solution in glistening plates, which are purified by recrystallization from hot water. The pure substance is obtained in fine, white, glistening plates which, if heated quickly, melt rather sharply at 184° (corr.). Immediately upon melting, the mass begins to boil with the evolution of ammonia and the formation of succin-*m*-cyananil. If the melting-point is taken by heating the substance very slowly, according to the usual method, it begins to decompose at a lower temperature and the melting-point is lowered to about 179°-180° (corr.).

The amide is very soluble in hot water and only slightly in cold. It is soluble in hot absolute alcohol, methyl alcohol, acetone and ethyl acetate, and insoluble in petroleum ether, ether, carbon disulphide, carbon tetrachloride, chloroform and benzene.

Succin-m-cyananilic Acid Chloride,



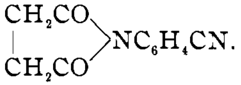
$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ | \\ CH_2CO.Cl \end{array}$$

—This chloride is difficult to prepare because of its marked tendency to lose hydrochloric acid and pass into the *m*-cyananil, but after numerous attempts it was finally obtained. To prepare it phosphorus pentachloride and the acid are ground up together and allowed to stand for several hours in the cold, or with only very gentle warming. The mass gradually softens to a pasty consistency and is then extracted with hot chloroform which dissolves the acid chloride. On cooling, the chloroform solution deposits nearly white, shining needles of the chloride, melting sharply at 80° (corr.). At a slightly higher temperature the substance boils with the evolution of hydrochloric acid gas and passes into the *m*-cyananil.

Owing to the difficulties in the preparation of the chloride an analysis was not made, but it was thought that the properties and reactions of the compound were sufficient to identify it as the one sought.

An attempt was made to convert the acid chloride into the methyl ester by dissolving in absolute methyl alcohol. On cooling, fine, white crystals separated, but these were identified as those of the *m*-cyananil, melting at 137°-137.5° (corr). This reaction illustrates the extreme ease with which hydrochloric acid is liberated from the molecule of the chloride and satisfactorily explains the difficulty of its preparation from the acid.

Succin-m-cyananil,



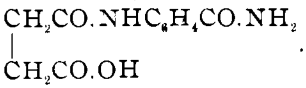
$$\left.\begin{array}{l}\mathrm{CH_2CO} \\ | \\ \mathrm{CH_2CO}\end{array}\right\rangle \mathrm{NC_6H_4CN}.$$

—This compound, the nitrile of the acid prepared by Pellizzari[1] and called by him succinamidobenzoic acid, is obtained, as already described, by the removal of hydrochloric acid from the molecule of the chloride of succin-*m*-cyananilic acid, of ammonia from that of succin-*m*-cyananilic amide and of water from that of succin-*m*-cyananilic acid.

The compound is very easily prepared in pure condition by the latter reaction, especially if a dehydrating agent is used. The best method of procedure is to dissolve the succin-*m*-cyananilic acid in acetic anhydride and distil off the excess of anhydride and acid. A somewhat brownish glass is left, which, on the addition of water, changes to a white crystalline mass. This is dissolved in hot water and allowed to crystallize. The pure anil is thus obtained in brilliant colorless needles, melting sharply at 137°-137.5° (corr.). It is easily soluble in cold chloroform, ethyl acetate and acetone, and in hot benzene, absolute alcohol, methyl alcohol and water. It is slightly soluble in hot ether, carbon tetrachloride and carbon disulphide, and is insoluble in petroleum ether.

The analysis of the compound gave: C, 66.05; H, 4.17; N, 14.08. Calculated: C, 66.00; H, 4.00; N, 14.00.

Succin-m-carbaminanilic Acid,



$$\begin{array}{l}\mathrm{CH_2CO.NHC_6H_4CO.NH_2} \\ | \\ \mathrm{CH_2CO.OH}\end{array}$$

—One gram of succin-*m*-cyananil was digested at 80°-90° for about one-half hour with 20 cc. of a 3 per cent. solution of hydrogen peroxide and sufficient sodium hydroxide to render the solution slightly alkaline. It was intended to hydrolyze the nitrile group to the amide according to the general reaction. The compound, however, dissolved in the hot solution and, on cooling, no

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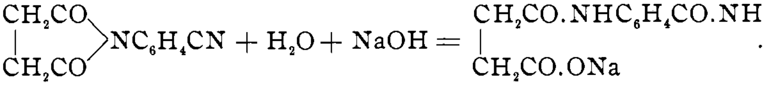
[1] *Loc. cit.*

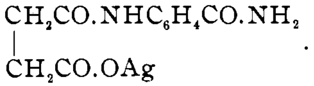
crystals were deposited. As it was expected that the amide sought would be quite insoluble in cold water, the solution was examined carefully and found to contain the sodium salt of the succin-*m*-carbaminanilic acid. On acidifying with acetic acid the free acid was obtained in the form of colorless microscopic needles, which melt at 203°-205° (corr.). After a number of trials it was found that hydrogen peroxide alone will not hydrolyze the nitrile group in the *m*-cyananil and the introduction of even a very small amount of alkali causes not only the hydrolysis of the nitrile to the amide, but also the opening up of the imide ring with the formation of an anilic acid derivative, according to the equation:



$$\left.\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}\right>NC_6H_4CN + H_2O + NaOH = \begin{array}{l}CH_2CO.NHC_6H_4CO.NH\\ |\\ CH_2CO.ONa\end{array}.$$

The acid thus produced is soluble in hot water and slightly soluble in hot absolute alcohol, methyl alcohol, ethyl acetate, chloroform, acetone and benzene. It is insoluble in carbon tetrachloride, carbon disulphide, petroleum ether and ether.

Silver Salt of Succin-m-carbaminanilic Acid,

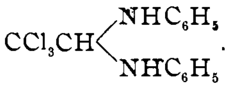


$$\begin{array}{l}CH_2CO.NHC_6H_4CO.NH_2\\ |\\ CH_2CO.OAg\end{array}.$$

—The silver salt was made in the usual way as described for the silver salt of succin-*m*-cyananilic acid. It precipitates from the hot solution in fine, white, silky crystals, which are not readily changed by the light. The silver content was determined by ignition, which gave 31.45 per cent. Ag. Calculated, 31.45 per cent.

CHLORAL AND BROMAL DERIVATIVES.

Chloral readily forms condensation products with aromatic amines and these products have been the subject of investigation by various workers. Wallach[1] describes the condensation of chloral and aniline with the production of trichlorethylidene-diphenamine, $CCl_3CH\left<\begin{array}{l}NHC_6H_5\\ NHC_6H_5\end{array}\right.$. In 1898 Eibner[2] carefully studied the reaction between aliphatic aldehydes and aromatic



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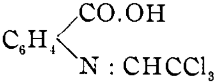
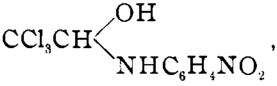
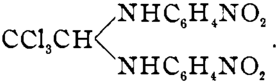
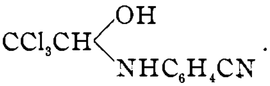
[1] *Ber. d. chem. Ges.*, **5**, 251, and *Ann. Chem.* (Liebig), **173**, 278.

[2] *Ann. Chem.* (Liebig), **302**, 335.

amines and their substitution products and, as a result of his work, was able to state that the true tertiary Schiff bases are not produced with aliphatic aldehydes and aromatic amines, if either are substituted by negative groups. In general, this seems to be true, although Niementowski and Orzechowski[1] describe the derivative of anthranilic acid,  $C_6H_4\left<\begin{array}{l}CO.OH\\ N:CHCCl_3\end{array}\right.$, which is a true Schiff base.

The action of chloral on the nitranilines has been investigated by Eibner,[2] and by Wheeler and Weller.[3] The former obtained, with *p*-nitraniline, two classes of substances, an addition product,  $CCl_3CH\left<\begin{array}{l}OH\\ NHC_6H_4NO_2\end{array}\right.$, and a condensation product,  $CCl_3CH\left<\begin{array}{l}NHC_6H_4NO_2\\ NHC_6H_4NO_2\end{array}\right.$. Wheeler and Weller describe only derivatives of the latter class.

Trichloroxyethylidene-m-cyanphenamine,



$$CCl_3CH\left<\begin{array}{l}OH\\ NHC_6H_4CN\end{array}\right..$$

—Anhydrous chloral was prepared by distilling a mixture of chloral hydrate and concentrated sulphuric acid. For the preparation of the addition product 5 grams (1 mol.) of *m*-aminobenzonitrile were dissolved in a mixture of dry gasoline and a small amount of ether. To this solution, cooled in ice-water, were added 6.5 grams (1 mol.) of chloral, diluted with 15 cc. of dry gasoline. The chloral must be added slowly and care taken to avoid a rise in the temperature of the solution. After standing about five minutes, salmon-colored, granular crystals begin to form. The crystallization is complete in a few minutes, and there are usually obtained about 10.5 grams of the reaction-product. This is recrystallized by dissolving in ether and then adding about three volumes of gasoline and evaporating in a current of air dried by sulphuric acid. The addition product, obtained in this way, forms short, prismatic crystals, which melt at 102°-103°

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[1] *Ber. d. chem. Ges.*, **28**, 2812.

[2] *Ann. Chem.* (Liebig), **302**, 335.

[3] This Journal, **24**, 1063.

(corr.), decomposing as described below. At 106° the mass becomes solid and remelts at about 165°.

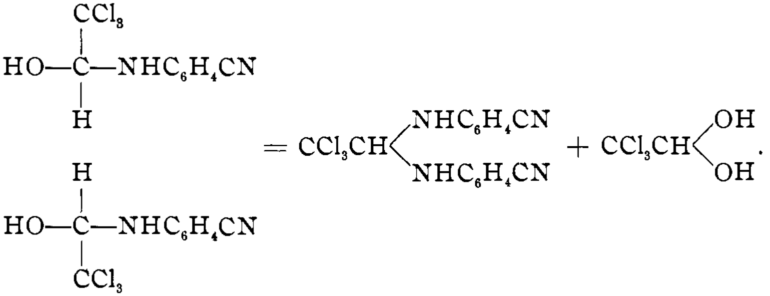
The substance dissolves with decomposition in hot water. It is very soluble in cold absolute alcohol, methyl alcohol, acetone and ether. Less easily in cold benzene, carbon tetrachloride and chloroform, and only slightly soluble in cold petroleum ether.

A determination of chlorine gave 39.69 per cent. Calculated, 40.04 per cent.

It was thought that on heating, the addition product might lose water with the formation of the Schiff base,

$$CCl_3CH : NC_6H_4CN,$$

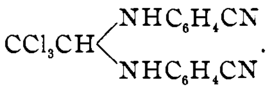
but on trying the reaction, chloral and water were liberated and the resulting product was found to be the diphenamine derivative to be described below. Hence the decomposition on heating takes place according to the following equation, and is analogous to that of the p-nitraniline derivative, as given by Eibner.[1]



$$\begin{array}{l} HO{-}\overset{\displaystyle CCl_3}{\underset{\displaystyle H}{C}}{-}NHC_6H_4CN \\ HO{-}\overset{\displaystyle H}{\underset{\displaystyle CCl_3}{C}}{-}NHC_6H_4CN \end{array} = CCl_3CH\left\langle\begin{matrix} NHC_6H_4CN \\ NHC_6H_4CN \end{matrix}\right. + CCl_3CH\left\langle\begin{matrix} OH \\ OH \end{matrix}\right. .$$

This same decomposition was found to take place on attempting to recrystallize the substance from hot solvents, as for example, boiling carbon tetrachloride. Hence it is essential to proceed according to the method described for the purification of the compound.

Trichlorethylidenedi-m-cyanphenamine,



$$CCl_3CH\left\langle\begin{matrix} NHC_6H_4CN \\ NHC_6H_4CN \end{matrix}\right. .$$

—This compound results on heating the addition product above its melting-point, as just described, but is best prepared by dissolving 5 grams (2 mol.) of m-aminobenzonitrile in about 150 cc. of toluene and adding 3.1 grams (1 mol.) of anhydrous chloral

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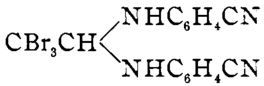
[1] *Loc. cit.*

in about 50 cc. of toluene. The mixture becomes warm and the flask is at once connected with a return condenser, the contents boiled for a few minutes and then distilled down to small volume. A reddish, granular mass of crystals separates, usually weighing about 6 grams. The reaction product is purified by dissolving in boiling alcohol, treating with bone-black and, after diluting the alcohol with about one-third its volume of water, allowing the solution to crystallize. The pure product thus obtained forms white, needle crystals or sometimes feathery plates, which gradually darken on heating, and melt to a tar at 162°-163° (corr.). If rapidly heated, the gradual charring can be partially prevented and the melting-point is then raised to 165°-167° (corr.). The compound is soluble in cold ethyl acetate and acetone, and in hot chloroform, absolute alcohol, methyl alcohol and benzene. It is insoluble in petroleum ether, water, ether, carbon tetrachloride and carbon disulphide.

It was found possible also to prepare the substance by melting the aminonitrile and chloral hydrate together in the proportion of two molecules of the former to one of the latter. The melt is maintained at a temperature just above 100° for about thirty minutes. On cooling, the reaction product separates, but is usually considerably colored and more difficult to purify than that obtained by the use of anhydrous chloral.

A determination of chlorine gave 29.17 per cent. Cl. Calculated, 29.08 per cent.

Tribromethylidenedi-m-cyanphenamine,



$$CBr_3CH\begin{cases}NHC_6H_4CN\\NHC_6H_4CN\end{cases}$$

Although the action of chloral on aromatic amines has been the subject of numerous investigations, the action of bromal on the same compounds does not appear to have been tried.

Anhydrous bromal is much more difficult to prepare than the chloral, but after a number of trials it was found that the condensation between the aminonitrile and bromal hydrate could be readily effected if sufficient care as to conditions was observed. This method renders the preparation of the anhydrous bromal unnecessary and greatly simplifies the process.

For the preparation 3 grams (2 mol.) of *m*-aminobenzonitrile and 3.8 grams (1 mol.) of bromal hydrate are heated together in a flask on a water-bath, which is kept just below the boiling-point. Soon after the substances have melted drops of water begin to separate throughout the mass. From time to time the flask is removed from the heat and the water, which has separated, is removed by drawing a current of dry air through the flask, after which the heating is continued until more water has formed. The reaction is complete when the contents of the flask have changed to a nearly white, granular, crystalline mass. The yield of the product thus obtained is nearly quantitative and if proper precautions have been observed, it is obtained practically pure by digesting a few minutes with petroleum ether to remove the slight excess of aminonitrile. The product is best recrystallized from absolute alcohol, but shows a marked tendency to liberate bromine when heated in any solvent, hence much care is necessary in its purification. If the reaction-product from the condensation is nearly colorless, it is usually better not to attempt to purify it further than with petroleum ether, as given above.

The substance thus prepared does not melt on heating, but suddenly chars to a black tar at about 130°. It is easily soluble in cold acetone, and slightly soluble in hot ethyl acetate, absolute alcohol, methyl alcohol, benzene, chloroform, carbon disulphide and carbon tetrachloride. It is insoluble in petroleum ether and ether.

Wheeler and Gleen[1] have shown that trichlorethylidenedi-*p*-nitrophenamine, on treatment with alcoholic potash, has one chlorine atom replaced by hydroxyl. Since the bromine derivative loses bromine so readily, it was thought that this replacement would occur much more easily than with the chlorine compound. On trying the reaction it was found that a practically quantitative separation of potassium bromide was obtained, but on evaporating the alcoholic solution in a vacuum desiccator only a small amount of a crystalline product was obtained and a brownish oil, having a distinct isonitrile odor, remained. After numerous attempts under various conditions, it was concluded that in the case of this compound the reaction takes a different course, giving a number of by-products, the nature of which has not been discovered.

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[1] *J. Elisha Mitchell Sci. Soc.*, **19**, 63.

ACTION OF BROMINE ON *m*-AMINOBENZONITRILE.

Griess[1] treated the aqueous solution of *m*-aminobenzonitrile with bromine water and obtained a precipitate of a bromine substitution product which crystallized from alcohol in white needles. Griess does not describe the compound further.

On adding bromine water to a dilute alcoholic solution of the aminonitrile, a bromine substitution product, identical with the one given by Griess, was obtained, but on repeated crystallization from various solvents it was found impossible to get a product of constant melting-point. The results usually obtained varied from 174° to 178°.

A determination of the bromine in the compound gave 66.86 per cent. Br. Calculated for $C_7H_8N_2Br_3$, 67.60 per cent. Hence the substance is probably a mixture of bromine substitution products, consisting mostly of the tribrom derivative.

On trying the same reaction in glacial acetic acid solution, using a solution of bromine in the same solvent, a product was obtained which showed a higher melting-point, but like the other, was not constant when crystallized from different solvents. However, after repeated crystallizations from alcohol, long, brilliant, colorless needles were obtained, which melted at 177°-178° (uncorr.). This substance, on analysis, was found to be a tribrom substitution product, as shown by the following results: Bromine found, 67.59 per cent. Calculated, 67.60 per cent.

The tribrom-*m*-aminobenzonitrile is easily soluble in cold ethyl acetate and acetone, and in hot absolute alcohol, methyl alcohol, chloroform, carbon tetrachloride and benzene. It is slightly soluble in carbon disulphide and ether, and insoluble in water and petroleum ether.

The bromaminonitrile was saponified by heating 2 grams with 30 cc. of concentrated hydrochloric acid in a sealed tube at 200° for ten hours. On opening the tube a clear solution was obtained which was evaporated to dryness on the water-bath, leaving a white residue almost completely soluble in dilute ammonia. From this solution dilute sulphuric acid precipitatès the acid as a fine, white crystalline substance which, on recrystallization from water, gives a product melting rather poorly at 154°-156° (uncorr.). The melting-point of the only tribrom-*m*-aminobenzoic

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[2] *Ber. d. chem. Ges.*, 1, 192.

acid, described in the literature, the 2-4-6-tribrom acid[1], is given as 170.5°

As it was found so difficult to obtain sharply melting products by this process of bromination, the work was suspended. It may be possible to obtain bromsubstitution products free of isomers by the method of bromination, so successfully used by Bogert and Hand[2] in their work on the ortho compound, and the matter will be further investigated.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, December, 1903.

ON THE VELOCITIES OF THE IONS IN LIQUID AMMONIA SOLUTIONS.

BY EDWARD C. FRANKLIN AND HAMILTON P. CADY.

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OBJECT OF THE RESEARCH.

INVESTIGATIONS on the electrical conductivity of liquid ammonia solutions, interpreted in accordance with the theory of electrolytic dissociation, have led to the conclusion that while salts at ordinary dilutions are dissociated to a much greater extent in water than in ammonia, the ions, nevertheless, in the latter solvent, travel with much the greater speed. It was to measure directly the speeds of the ions in liquid ammonia and compare the results thus obtained with the ionic velocities calculated by the method of Kohlrausch from conductivity measurements that this research was undertaken.

HISTORICAL.

Investigations on Liquid Ammonia.—In 1897, Cady[3] made the important discovery that liquid ammonia solutions of certain salts are excellent conductors of electricity, and in explanation of this fact he assumed that ammonia must approximate, or probably even surpass, water in its power to effect electrolytic dissociation.

The same opinion was expressed by Goodwin and Thompson[4] in a paper on the dielectric constant and electrical conductivity of

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[1] *Ber. d. chem. Ges.*, **10**, 1708.

[2] This Journal, **25**, 935.

Jour. Phys. Chem., **1**, 707 (1897).

[4] *Phys. Rev.*, **8**, 48 (1899).