[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 1.]

THE ACTION OF ORGANIC ACIDS UPON NITRILS.[1]

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THE action of organic acids upon nitrils has been the subject of a number of investigations which have been reported from this laboratory at intervals during the past seven years. The nitrils and acids employed in the various experiments have been made to react under the influence of elevated temperature and pressure in sealed tubes. In nearly every instance a few drops of acetic anhydride have been added to the mixtures of acids and nitrils to insure anhydrous conditions within the tubes. This precaution is believed to increase the yield of the principal products of the reaction. The reaction between acetic acid and acetonitril, whereby Gautier found diacetamid to be produced,[2] suggested to Colby the idea of trying parallel reactions between other acids and nitrils. Colby and Dodge[3] experimented with a large number of monobasic acids and mononitrils of both the fatty and the aromatic series. Their results show that under conditions of heat and pressure :

I. Fatty nitrils and fatty acids yield secondary amids.

II. Fatty nitrils and aromatic acids yield fatty acids and aromatic nitrils.

III. Aromatic nitrils and fatty acids give mixed secondary amids.

IV. Aromatic nitrils and aromatic acids give secondary amids. One exception was noted under the fourth head by these authors.

Not so much work has been done upon dibasic acids. Miller[4] and Seldner[5] worked with fatty dibasic acids, the former with succinic and the latter with glutaric acid. They proved that the imids of these acids result under three different conditions. From

I. Dibasic acid and acetonitril.

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[1] Read at the meeting of the New York Section, May 6, 1898.

[2] *Ztschr. anal. Chem.*, *1869*, p. 127, or *Compt. rend.*, 60, 1255.

[3] *Am. Chem. J.*, 13, 1.

[4] This Journal, 16, 443.

[5] *Am. Chem. J.*, 17, 532.

II. Dinitril and acetic acid, and

III. Equal molecules of the dibasic acid and its nitril.

Two years ago the author published his first experiments upon aromatic dibasic acids. Phthalic acid was first tried and its imid resulted by heating it with propionitril. In the following pages are given results obtained recently along the same line of experimentation. This work may be grouped under two heads. First, experiments with monobasic acids, simple and substituted ; second, experiments with aromatic, polybasic acids.

PART I.

UPON THE ACTION OF FATTY NITRILS ON MONOBASIC AROMATIC ACIDS, WITH A PRELIMINARY NOTE ON MALONIMID.

Before describing the experiments upon aromatic acids which compose the main part of this investigation, a few words upon some attempts to prepare the unknown imid of malonic acid may not be out of place, since in these attempts the methods employed were the same as those used in making the imids of the bibasic aromatic acids.

Malonic Acid and Ethylene Cyanide.—Two tubes containing equal molecules of malonic acid and ethylene cyanide were made by Miller in 1893. The first tube, when heated, exploded at 196° C. The second one was heated at 150° C. for five and one-half hours. This tube was set aside and when examined by me recently it was found that the contents were liquid and brown. Very strong outward pressure was noticed upon unsealing. Succinimid was found but no malonimid seems to have been produced. Malonic acid loses part of its carbon dioxide readily by heating, and for this reason it was thought better to use malonitril and treat it with glacial acetic acid. This method was unsatisfactory, too, for almost complete decomposition took place by heating. As throwing some light upon the question of the rearrangement of cyan acids to give imids, the next experiments were made upon cyanacetic acid. This acid was heated to 190° in benzol medium. There was strong pressure upon opening and the contents of the tube were evaporated upon the water-bath to drive off the benzol. The residue was extracted with absolute alcohol. This solution was treated with boneblack and by evaporation nearly to dryness and long standing a small amount of crystalline material separated. This was pressed and dried and recrystallized. It was soluble in acetone, ether, alcohol, and water, and almost insoluble in benzol. Its melting-point was 115° C. It gave a nitrogen test and was neutral in its reaction with litmus paper. By boiling with potassium hydroxide solution, acidifying and evaporating to dryness, and extracting with absolute alcohol, an acid was obtained melting at 130°, very soluble in water and alcohol. This seems to be malonic acid. It seems probable, therefore, that malonimid was produced by the rearrangement of the cyanacetic acid. Not enough of this supposed imid has as yet been obtained to make a thorough investigation, but the same material was obtained from two tubes made up and heated at different times and its further study will be interesting.

Benzoic Acid and Ethylene Cyanide.—Two sealed tubes containing ethylene cyanide and benzoic acids and a drop or two of acetic anhydride were prepared. The first contained equal molecules and the second contained two parts of acid to one part of nitril. Both were heated seven hours at 145° C. and then five and a half hours at 195° C. The contents were then black and semi-solid and crystalline. In the first tube benzonitril was found. The contents of the tube were treated with weak sodium carbonate solution and then evaporated to dryness and extracted several times with ether. The operations thus far described were carried out by Dr. E. H. Miller, in 1893. The ether extract gave a white crystalline solid upon evaporation. This residue was very soluble in acetone. After recrystallization from water and twice from acetone, succinimid, melting at 124° C., was obtained in characteristic crystals. These were tested for nitrogen and it was found.

The second tube contained originally three grams of ethylene cyanide and 9.15 grams of benzoic acid; *i. e.*, two molecules of acid to one of nitril. No pressure was observed upon opening. A strong odor of benzonitril was at once apparent. The tube contents were liquid at the temperature of a hot water-bath and were poured into dilute sodium carbonate solution. From results obtained by Colby and Dodge and by Miller, it was thought that this tube might contain benzoic acid, ethylene cyanide, benzonitril, succinic acid, succinimid, and dibenzamid. Dibenzamid and succinic acid were not found. Colby and Dodge showed that by heating together benzoic acid and acetonitril at 250°–260° C. there was formed principally benzonitril and acetic acid. At about the same temperature benzonitril and benzoic acid combine to give dibenzamid. In our tube probably the temperature had not been carried high enough to produce this condensation. The primary reaction which seems to have taken place in both tubes is :

$$C_6H_5COOH + C_2H_4(CN)_2 = C_6H_5CN + C_2H_4(CO)_2NH.$$

The second tube was examined as follows : Upon pouring the contents into sodium carbonate solution three and one-half cc. of black liquid material separated at the bottom. This was drawn off by means of a separatory funnel and showed to be benzonitril. It was distilled with steam, separated from the water, partly dried by evaporation upon a water-bath, and then with small fragments of calcium chloride. The once purified product boiled at 188° (uncorr.). The boiling-point of benzonitril is given as 191° C.

The sodium carbonate solution was evaporated to dryness and extracted with ether and then with water. The ether extract gave a residue upon evaporation which was succinimid. Recrystallized from acetone it gave oblong, colorless crystals (melting-point 125° C.).

The water extract above mentioned by acidifying with hydrochloric acid gave a bulky precipitate. This, filtered off, washed, and dried, melted at 117.5°. It was unchanged benzoic acid. Recrystallized from hot water, large plates were deposited (melting-point 120° C.). These crystals are sublimable at the temperature of boiling water. 2.75 grams of benzoic acid were recovered, which is also about the amount of benzonitril produced. After the ether and water extractions of the original tube contents, a large, charred, carbonaceous residue and a little tarry matter, believed to be partly ethylene cyanide, remained.

In Miller's dissertation upon succinimid are reported a number of attempts to prepare β-cyanpropionic acid in sufficient quantities to try whether it could be made to rearrange into its isomer, succinimid. It seems to me that these two experiments point to the formation of β-cyanpropionic acid as an intermediate product. Either it must be considered that the carboxyls of the benzoic acid change places with both nitril groups of one-half of the ethylene cyanide or with one of the nitril groups forming β-cyanpropionic acid, which rearranges into succinimid. Of course, if the first assumption is the correct one, the succinic acid formed would react with the unchanged ethylene cyanide and two molecules of succinimid would result as shown by Miller. It seems probable that had succinic acid been formed in either of these experiments some of it would have been found, for these reactions are not often complete. On the other hand, if β-cyanpropionic acid were the intermediate product we should not expect, because of its well-known instability, to find it withstanding a temperature of 195° unchanged. Only about one gram of succinimid was produced and this fact, together with the large amounts of decomposition-product, seems to strengthen the second assumption in regard to the course of the reaction.

Phenylacetic Acid and Ethylene Cyanide.—Two tubes, the first containing equal molecules of phenylacetic acid and the second two molecules of acid to one of nitril, were prepared by Miller in 1893. Both tubes were heated for six hours at 150° C. The contents were then black and semi-fluid. Not much outward pressure was noticed upon opening. These tubes were set aside and not examined until 1898. The reaction in tube I seems to be:

$$C_6H_5.CH_2.COOH + C_2H_4(CN)_2 = C_6H_5CH_2.CN + C_2H_4(CO)_2NH.$$

Phenylacetamid was also found in this tube and its presence cannot be explained except by the presence of some water in the tube which reacted upon the phenylacetonitril. The reaction of tube II was primarily the same as in I. The excess of phenylacetic acid then reacted with the phenylacetonitril and produced diphenyldiacetamid:

$$C_6H_5.CH_2.COOH + C_6H_5.CH_2.CN = (C_6H_5.CH_2.CO)_2NH.$$

No phenylacetamid was found in this experiment, but some phenylacetic acid was recovered.

Tube I was examined as follows: The contents were extracted with warm water. A black, oily residue was left. This proved to be impure phenylacetonitril. The water extraction was of a light yellow color and, by cooling, it gave crystals. These were flat plates melting at 155° C. They were found to contain nitrogen and, by boiling with hydrochloric acid and cooling, crystals of phenylacetic acid were deposited (melting-point 76° C.). A second crop of the crystals melting at 155° was obtained by concentrating the mother-liquor. These crystals were phenylacetamid. By evaporating the second mother-liquor nearly to dryness succinimid was found. This, recrystallized from acetone, melted at 124° C.

Tube II was examined in about the same way. The water extract by cooling gave no phenylacetamid. Upon concentration some phenylacetic acid separated and later succinimid was found. The black oily residue from the water extraction was soluble in hot alcohol. It was treated with boneblack and then upon cooling, needle crystals melting at 190° C. were obtained. These were recrystallized and deposited as slender filament-like needles, melting at 192°. They were insoluble in water and seemed to be diphenyldiacetamid, described by Colby and Dodge. The alcohol solution, after filtering off the diphenyldiacetamid, was distilled. The high-boiling fraction was caught separately and dried. The boiling-point of the benzyl cyanide thus obtained was 230° C.

It will be noticed that these results are parallel to those obtained with experiments with benzoic acid. The two series of experiments form a connecting link between the work of Colby and Dodge upon monobasic acids and their nitrils, and the work of Miller upon succinimid, and serve to confirm in several points the reported results of these chemists.

Salicylic Acid and Acetonitril.—Equal molecules of salicylic acid and acetonitril were heated five hours at 195°–200° C. No reaction seems to have taken place, unchanged salicylic acid being the only solid product. This experiment repeated at 215°-230° always gave a reddish liquid. Great pressure was noted in these last experiments and carbon dioxide was the principal gas evolved. Phenol was shown to be present in every case. No other products were identified. The tube contents were partly soluble in water and the insoluble portion consisted of a sticky, thick liquid substance. The water solution by cooling gave a few clusters of crystals, melting at 137°–138°, after recrystallization. These gave no nitrogen reaction. The first reaction seems, then, to result in the formation of phenol, and unidentified products mentioned above do not result by any action of a nitril upon an acid. The investigation was, therefore, discontinued for the present and will be resumed later.

Anthranilic Acid and Acetonitril.—Anthranilic acid and acetonitril were heated together in equal molecules for five hours at 220°–230° C. Very strong pressure was observed upon opening the tubes and the gases evolved consisted mainly of carbon dioxide. The tube contents were evaporated to dryness upon a water-bath. The black residue was almost entirely soluble in hot water. This solution upon cooling gave fine needle-like crystals (melting-point 230° C.). These, treated with boneblack and recrystallized, melt at 232° C. and may be sublimed. By boiling them with strong hydrochloric acid and cooling, long needles result, which do not melt at 280° C. but sublime. This material was not identified nor were the few drops of liquid (boiling-point 240°), which were isolated in one of the experiments. This liquid did not give a test for anilin with bleach solution but gave a deep brown color when so treated. On account of the partial decomposition taking place within the tubes, no further investigations upon anthranilic acid and acetonitril were made, but the reaction will be made the subject of future study.

PART II.

UPON THE ACTION OF FATTY NITRILS UPON AROMATIC POLYBASIC ACIDS.

Phthalic Acid and Propionitril.—In a number of reactions which I have tried phthalimid resulted. The first of these experiments was made in 1896.[1] This series of experiments is explained by the following reaction :

$$C_6H_4(COOH)_2 + C_2H_5CN = C_6H_4(CO)_2NH + C_2H_5COOH.$$

The tubes were made up containing both one and two molecules of nitril to one molecule of phthalic acid. The best

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[1] This Journal, 18, 679.

results, so far as the production of phthalimid was concerned, were obtained by heating equal molecules of the reagents at 180°–200° for a period of five and a half hours. The yield was ninety-two per cent. of the theoretical. The reaction seems to be practically completed in three and a half hours, for one tube heated thus yielded eighty-eight per cent. The crystalline product in these tubes was washed with a little dilute sodium carbonate solution to remove phthalic and propionic acids and any nitril remaining. The crystals remaining melted at 228° C. Portions recrystallized from alcohol, acetic acid, and alcohol with the addition of boneblack, melted a little higher, 229.5°–230° C. These crystals gave off ammonia by boiling with potassium hydroxide. By standing with concentrated ammonium hydroxide they were converted into phthalamid, microscopic needles melting at 217.5° (uncorrected). The amid is decomposed by boiling, giving off ammonia gas, and phthalimid crystallizes out again upon cooling.

Phthalic Acid and Ethylene Cyanide.—Equal molecules of phthalic acid and ethylene cyanide were heated together. Two tubes received four hours' heating at 220°–223°. Upon opening, strong outward pressure was noticed, and the contents of the tubes were black and charred. Thinking that succinimid might be present, the tube contents were extracted with water. This solution upon evaporation gave a small amount of material, very soluble in methyl or ethyl alcohol and acetone, difficultly soluble in benzol. It crystallized in needles (melting-point 165°–167°), and gave nitrogen test by boiling with alkali. By boiling with hydrochloric acid, crystals were obtained which melted above 200° with decomposition. The residue, after cooling, melted at 127° and sublimed in fine needles. This seems to be phthalic acid. The hydrochloric acid solution, after filtering off the above crystals, was shaken up with ether. The ether solution, by evaporation, gave a small residue (melting-point 183°–185)°, which corresponds with succinic acid and when boiled with sulphuric acid and alcohol gave an odor of succinic ester. The solution, after extracting with ether, was evaporated to dryness, dissolved in a little water and a platinic chloride test made for ammonia. The precipitate which was obtained was tested to make sure that no fixed alkalies were present. Unfortunately, the amount of this substance produced was too small for further investigation or analysis. The above tests, however, would indicate that the compound might be a double imid of phthalic and succinic acids. The second tube contained also a little of this material, having the same properties as before, but its melting-point was found to be a little higher, 170° C.

In a third tube, run as nearly as possible like these two, for the purpose of obtaining enough of this peculiar compound to analyze, none of it was found. In tube I no succinimid was found, but there was a great deal of phthalimid. In tubes II and III succinimid and phthalimid were found, the former in very small quantities. In all the tubes was found considerable black, charred, insoluble residue.

Tube IV was heated to 200° for five hours. Upon examination succinimid, phthalimid, and unchanged phthalic acid were found. In tube II the contents were moist and an attempt was made to filter off the solid portion by using a hot water funnel. The funnel was covered with a watch-glass and the vapors which arose from the funnel deposited upon the cover glass, white crystals, which upon drying and recrystallizing, proved to be succinimid. The reaction which works then to some extent in these experiments is :

$$C_6H_4(COOH)_2+C_2H_4(CN)_2 = C_6H_4(CO)_2NH+C_2H_4(CO)_2NH.$$

III. *Phthalic Anhydride and Acetonitril.*—When acetic anhydride and acetonitril are heated at 200° there is found triacetamid, $(CH_3CO)_3N$. To see if a similar reaction would take place between phthalic anhydride and acetonitril giving acetylphthalimid, these reagents were heated together in equal molecules, and also with excess of nitril, but in neither case was acetylphthalimid formed. According to Aschan[1] acetylphthalimid is produced when phthalimid is boiled for several hours with acetic anhydride in a flask with return condenser, thus :

$$C_6H_4(CO)_2NH + (CH_3CO)_2O = C_6H_4(CO)_2N.OC.CH_3 + CH_3.COOH.$$

Acetylphthalimid is easily decomposed by hot water or alcohol and by cold alkali. Aschan notes that the imid hydrogen does not readily submit to replacement by acid radicals.

[1] *Ber. d. chem. Ges.*, 19, 1400.

In my experiments tube I, containing equal molecules, was heated four hours at 145° C., and then four and a half hours at 195°–200° C. Upon examining the tube contents phthalic anhydride and phthalimid were found. The latter should not have resulted had the reagents used not contained moisture. Tube II received the same treatment as I and four hours additional at 225°–235° C. It showed no apparent change over tube I and was unsealed, more nitril added, and after resealing it was heated again at 200°–210° for five hours. Phthalimid was again found, together with acetic acid and unchanged phthalic anhydride. Tube III was made up as the other two except that the nitril used was twice distilled over phosphorus pentoxide. In this tube no reaction took place, except that a little imid was again found. The reaction expected seems therefore not to have worked under the conditions presented.

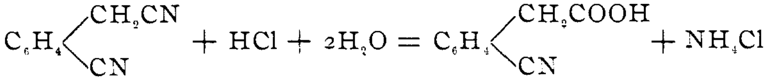
Terephthalic Acid and Propionitril.—Under the same conditions which gave phthalimid from *o*-phthalic acid and propionitril, no reaction takes place with *p*-phthalic acid, neither is any reaction obtained at a much higher temperature, 260° C. The tube contents, after heating, are completely soluble in dilute carbonate solution, except that at the higher temperatures a little tarry substance may remain. The solid contents do not give a nitrogen test and *p*-phthalic acid is recovered quantitatively by acidifying the sodium carbonate solution with hydrochloric acid.

Homophthalic Acid and Acetonitril.—The experiments with homophthalic acid and acetonitril, looking to the production of homophthalimid, were not entirely successful because of the small quantity of homophthalic acid obtainable. In but one instance was any product found resembling homophthalimid. This is rather surprising, inasmuch as the ammonium salt of this acid gives an imid by heating, and every other acid whose imid results in this way and that has been tried by our nitril reaction has given an imid. After five hours' heating of equal molecules of homophthalic acid and acetonitril at 190° C. and extracting the tube contents with carbonate solution, a small residue remained. Upon dissolving this in hot acetic acid and cooling, crystals were obtained which do not entirely melt, but darken, and give off a brown liquid at 230° C., leaving a charred residue. The crystals contain no nitrogen. The mother-liquor from them by concentration gave a few crystals which contain nitrogen and melt, after drying between filter-papers, at 215°. A third crop of crystals filtered off, washed, and dried, were light brown, contained nitrogen, and melt at 230°–232°, darkening before melting. These answer to the description of homophthalimid. The amount of this product was very small and nothing like it was isolated in two subsequent similarly conducted experiments. In all of them, however, the material not containing nitrogen and decomposing above 230° into a brown liquid and charred residue was found.

A peculiar compound very insoluble in cold alcohol and acetic acid and soluble in ammonia, was found. Its melting-point was indefinite, but by heating it left a residue infusible at 285° C. It crystallizes in fine filament-like crystals, which are snow-white and pack down to a spongy, felt-like mass of a texture which makes it scarcely visible upon the filter-paper. It contains no nitrogen and not enough of it was obtained to analyze.

Cyan-*o*-toluic acid did not rearrange by heating under pressure in benzol at 190° C. to yield its isomer, homophthalimid. In this regard it differs from *o*-cyanbenzoic acid, which so readily changes into phthalimid. An ether solution of the tube contents in one of these experiments gave a few long needle-shaped crystals, melting at 182° C. They contained nitrogen but were not identified.

Gabriel[1] states that cyan-*o*-toluic acid does not rearrange to give an imid but does not mention under what conditions the experiment was tried to produce this change. He concludes that when the cyanogen group is on the ring, rearrangements may be expected as was just mentioned of *o*-cyanbenzoic acid. In proof of this he shows that by acting upon orthocyanbenzyl cyanide with fuming hydrochloric acid at 100° for one hour homophthalimid is produced. He explains this by considering that the cyan group of the side chain is more reactive than the cyan group on the ring, hence *o*-cyanphenylacetic acid is first formed and this rearranges to give homophthalimid. That is:



$$C_6H_4\begin{cases} CH_2CN \\ CN \end{cases} + HCl + 2H_2O = C_6H_4\begin{cases} CH_2COOH \\ CN \end{cases} + NH_4Cl$$

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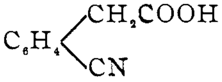
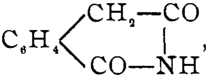
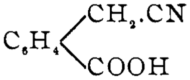
[1] *Ber. d. chem. Ges.*, 20, 2502.

and  $C_6H_4\left\langle\begin{matrix}CH_2COOH\\CN\end{matrix}\right.$ becomes  $C_6H_4\left\langle\begin{matrix}CH_2-CO\\ |\\CO-NH\end{matrix}\right.$,

but  $C_6H_4\left\langle\begin{matrix}CH_2.CN\\COOH\end{matrix}\right.$ does not rearrange.

Diphenic Acid and Acetonitril.—Diphenic acid and acetonitril in equal molecular proportions were heated together in a sealed tube for six hours, the temperatures increasing gradually from 225° to 240° C. A strong odor of acetic acid was noticed when the tube was opened. The contents were treated with cold dilute sodium carbonate solution and the solid crystalline residue was thrown upon a filter and washed with water. This product was dissolved in warm chloroform and from this solution long needles melting at 217° C. (uncorrected) were obtained. These crystals may be sublimed and were proved to be diphenimid by tests to be mentioned later. Recrystallized and treated with boneblack, long, colorless crystals, melting at 217.5° C., were obtained from alcoholic solution. There has been a difference of opinion among chemists as to the melting-point of diphenimid and diphenamid, respectively. Wegerhoff states that the imid and amid both melt at 215°. Graebe and Aubin give the melting-point of the imid as 219°–220° and of the amid as 208°–209°.[1] Later Wegerhoff[2] gives figures differing from his own statement in the *Berichte*, 21, 2356; *viz.*, 212°–213° and 217° for the amid and imid respectively. There is an obvious reason for different results upon the amid because it decomposes readily, losing ammonia, and gives the imid. My own experience confirms Wegerhoff's figures last mentioned. In determining the melting-point of diphenamid different results were obtained depending upon the rapidity with which it is heated to the point of fusion. By slow heating decomposition is gradual; the melting-point tube becomes clouded and complete fusion may not take place before 217°, while by rapid heating no apparent decomposition takes place and the crystals melt at 212°–213° C.

To confirm my results, I tested the diphenimid as follows: By standing with cold, concentrated ammonia, hexagonal crys-

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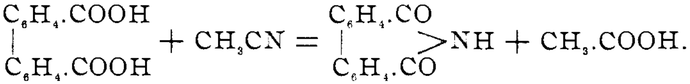
[1] *Ann. Chem.* (Liebig), 247, 270.

Ibid, 252, 16.

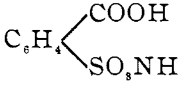
tals separate out. These melt at 212°–213°, give off ammonia by heating, and are apparently diphenamid. The separation of the crystals takes place almost immediately if the ammonia solution is warmed. By boiling diphenimid with concentrated potassium hydroxide solution, ammonia is evolved. The first product of the action of potassium hydroxide, however, is this :

$$\begin{array}{l} C_6H_4.CO \\ | \\ C_6H_4.CO \end{array}\!\!>NH + KOH = \begin{array}{l} C_6H_4.CONH_2 \\ | \\ C_6H_4.COOK \end{array}$$

By acidifying with hydrochloric acid and cooling after the brief action of potassium hydroxide solution, colorless plate-like crystals of diphenamic acid were deposited, melting at 190°–191° C. Diphenimid is almost entirely insoluble in boiling water. The yield of diphenimid by the reaction tried was about ninety per cent. of the theoretical, estimated upon the product once crystallized from chloroform. The reaction which accounts for this production of diphenimid is :



$$\begin{array}{l} C_6H_4.COOH \\ | \\ C_6H_4.COOH \end{array} + CH_3CN = \begin{array}{l} C_6H_4.CO \\ | \\ C_6H_4.CO \end{array}\!\!>NH + CH_3.COOH.$$

o-Sulphobenzoic Acid and Acetonitril.—The *o*-sulphobenzoic acid used in this series of experiments was made by Remsen's method from saccharin.[1] Briefly, the method is to decompose saccharin by boiling with strong hydrochloric acid. This solution is evaporated to dryness and cold water added. This dissolves the acid ammonium salt of *o*-sulphobenzoic acid,  $C_6H_4\begin{cases} COOH \\ SO_3NH_4 \end{cases}$, which is the first product of the decomposition of saccharin with hydrochloric acid. Any *p*-sulphaminebenzoic acid which the saccharin may have contained remains undissolved. The water solution, by evaporation and cooling, gives large diamond-shaped crystals of the ammonium salt. These are treated with phosphorus pentachloride. The mixture becomes semi-fluid, owing to the production of oxychloride of phosphorus and sulphobenzodichloride.

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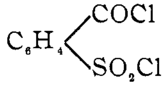
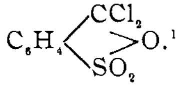
[1] *Am. Chem. J.*, 11, 332.



$C_6H_4\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right.$

and



$C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O$.[1]

The reaction-product is poured in ice-water and a yellow oily layer of the acid chlorides separates and is thoroughly washed and then decomposed by boiling with water, producing *o*-sulphobenzoic acid. This crystallizes from a concentrated aqueous solution with four molecules of water of crystallization. To obtain the anhydrous acid, it was heated at 130°–135° several times, alternately cooling it in a vacuum desiccator over sulphuric acid. The last traces of water are hard to remove and at a temperature a little above that necessary to keep the sulphobenzoic acid liquid, it begins to darken.

An error seems to have crept into the literature of this compound regarding its melting-point. It is stated in nearly all the chemistries that have been consulted that *o*-sulphobenzoic acid melts at 250°. The melting-point is 68° for the hydrated acid and about 130° for the anhydrous. The acid ammonium salt mentioned above melts between 250°–260°, and this compound, when first made and described, was thought to be the free acid.[2]

The sulphobenzoic acid thus prepared was heated with acetonitril in equal molecules at 165°–170° for five hours. The first set of tubes examined exhibited no pressure upon unsealing and showed a light brown sirupy material in which were seen transparent crystals. The tube contents were treated with cold, absolute alcohol. The sirupy part dissolved readily and the crystals remained. They were soluble in hot absolute alcohol and were crystallized from this medium. They then appeared as large, diamond-shaped plates, melting at about 260°. They gave a nitrogen test and were acid in reaction and taste. They seemed to be the acid ammonium salt of sulphobenzoic acid, and their presence is explained by the fact that the first sulphobenzoic acid prepared was not completely anhydrous. A portion of it, further heated at 135° and then treated with the nitril as before, gave only the sirupy material. The second lot of sulphobenzoic acid prepared gave, when heated with the nitril, no residue insoluble in cold absolute alcohol. Some of the dia-

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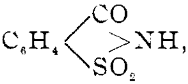
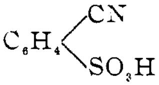
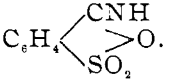
[1] Remsen: *Ibid*, 17, 309.

[2] Brackett, Hayes: *Ibid*, 9, 405.

mond-shaped crystals were boiled with potassium hydroxide and evaporated to dryness. The residue, by treatment with phosphorus pentachloride, gave a yellow oily substance resembling *o*-benzosulphodichloride. This disappeared by adding ammonia, probably with the formation of an amid.

The sirupy portion in alcohol solution, treated with boneblack and evaporated to dryness, became crystalline by cooling. When redissolved in alcohol and set aside to crystallize, minute, indistinct, white crystals separated. They give a faint acid reaction to litmus and phenolphthalein, no reaction with methyl orange. They contain nitrogen and sulphur, are very soluble in water and alcohol, insoluble in ether. They do not form an ammonium salt by evaporating to dryness with ammonia water and seem to be unchanged by this treatment. They possess no sweet taste. The first product of this kind examined melted at 220°–221°. This is the same melting-point as that given for saccharin. The product from the second set of experiments melts at 225°. I have reason to believe that this was a purer product than the first material examined. It softens before melting and the melting-point tube becomes clouded. It is not sweet after melting and begins to darken a little above its melting-point.

From the parallel with phthalic acid it was expected that these experiments might give saccharin,  $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NH$, or possibly its isomer *o*-sulphobenzonitril,  $C_6H_4<\begin{matrix}CN\\SO_3H\end{matrix}$ The product is not the latter compound because its solution does not decompose carbonates and an ammonium salt corresponding to that described by Remsen[1] could not be formed. Its different solubilities and lack of sweet taste show that it is not saccharin, but a quantitative determination of nitrogen shows it to be isomeric with it, and it may therefore be the unsymmetrical sulphobenzimid,  $C_6H_4<\begin{matrix}CNH\\SO_2\end{matrix}>O$. Still another isomer is possible, pseudo-saccharine, whose derivatives of this type are known,

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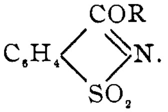
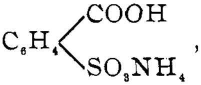
[1] *Am. Chem. J.*, 18, 819.



$C_6H_4\left\langle\begin{matrix}COR\\SO_2\end{matrix}\right\rangle N$. More thorough investigation will be made of our compound to establish its constitution. The determination of nitrogen resulted as follows :

	1.	2.
Weight of sample	0.3187	0.3333
Weight of nitrogen	0.0232	0.0252
Per cent. nitrogen	7.28	7.56
“ “ calculated for $C_7H_5O_3SN$	7.65	

The presence of the acid ammonium salt of sulphobenzoic acid in our first tubes is really a confirmation of the fact that the main reaction has given an imid, for by the action of water we should get,



$C_6H_4\left\langle\begin{matrix}COOH\\SO_3NH_4\end{matrix}\right.$, just as is the case when saccharin is acted upon by strong hydrochloric acid, whereas if *o*-sulphobenzonitril had been formed, it would have given *o*-sulphobenzamid by the action of water under pressure.

Mellitic Acid and Acetonitril.—A tube containing mellitic acid (one molecule) and acetonitril (three molecules) with a few drops of acetic anhydride, was heated four hours at 265°–275° C. The contents of the tube were very dark-colored and were extracted with water and washed on the filter until the washings were no longer acid. The insoluble residue being still dark was extracted with alcohol and with dilute sodium carbonate solution. Very little material dissolved by this treatment, but this residue was lighter colored. Nitrogen was tested for in this residue and its presence detected.

The sodium carbonate washings, by acidifying, gave a very dark and mostly flocculent precipitate. This gave the euchronic acid test. The final residue, after the extraction mentioned above, was insoluble in hydrochloric acid, but dissolved in sulphuric. When the acid solution was poured into water and let stand a very fine precipitate appeared. This was paramid and still retained its brown tint.

This experiment was repeated at a lower temperature, heating for three hours at 180°–200°, and three hours at 225°–235° C. The tube contents were only slightly discolored. About ninety per cent. of the paramid was found after extractions with hot water and with very dilute ammonia had been made. The insoluble residue dissolves in strong ammonia and gives a precipitate which seems to be euchronamic acid upon the addition of hydrochloric acid. This precipitate, as was stated by Wöhler, yields the same color reactions as euchronic acid.

The color imparted to a solution by euchron is very unstable. It disappears instantly by shaking with access of air and in a test-tube containing a solution of a very small amount of euchronic acid a color may appear at the bottom when the zinc is added while the top of the solution remains colorless. The purple-red color obtained in an alkaline solution behaves in the same way, but is a more delicate test for the presence of euchronic acid. The red color is produced whether the zinc is added first to the water solution and then ammonia added, or the zinc may be added to an ammoniacal solution of euchronic or euchronamic acid. If paramid and zinc dust be shaken together in water, no color reaction takes place, but by adding ammonia a red color appears, showing the production of euchronamic acid.

Schwartz[1] found very few reducing agents available for producing euchron. In the course of this investigation it was discovered that aluminum amalgam gives the red color. The reaction progresses slowly, the aluminum foil being first colored red, before any color is imparted to the solution.

In the examination of the contents of tube II it was found that the original water extraction, upon cooling, gave a crystalline precipitate. This was filtered off and found to be readily soluble in hot water, from which it could be precipitated by adding nitric acid. The crystals thus obtained were square prisms of euchronic acid. In working with mixtures containing euchronic acid one notices that nearly every solution obtained during the examination will give euchron by adding zinc dust, provided the solution tested is not strongly acid with inorganic acid. The color reaction in alkaline solution is so delicate that one part of euchronic acid in more than 100,000 parts of solvent may be detected. Under such conditions the

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[1] *Ann. Chem.* (Liebig), 66, 46.

color develops slowly and the solution should be kept corked during the test.

It was thought by heating together equal molecules of mellitic acid and acetonitril that mellitmonimid would result. A tube containing these reagents and a few drops of acetic anhydride were heated during four and one-half hours at 215°–220°. The tube contents were white and all soluble in water. No monimid was found, only euchronic acid and unchanged mellitic acid being produced. A repetition of this experiment verified these results, a large amount of euchronic acid having been found. Euchronic acid crystallizes from water in the form of six-sided plates and in long prisms from an acid solution.

Another attempt to prepare mellitmonimid was made by employing the two-thirds neutralized mellitic acid. A standard solution of sodium hydroxide was used and four of the six carboxyls were saturated. The solution was evaporated to dryness and dehydrated. The acid salt remaining was heated with acetonitril for several hours at 230°, and even at 290° no nitrogen was found to have entered the mellitic compound. This argues rather that the sodium atoms have not entered consecutively than that there is any reason why a monimid should not exist.

The conversion of paramid into euchronamic acid would indicate that Wöhler's euchronic acid is an ortho compound. In confirmation of this the following experiment should be recorded. A quantity of euchronic acid was dried at 200°. The crystals do not lose their form at this temperature but become opaque and dull. The dried euchronic acid was heated with an excess of acetonitril for three and a half hours at 223° C. Paramid was not produced and the euchronic acid was recovered and tested. As the paramid of my previous experiments had been made at a higher temperature than 223°, the experiment was repeated at 240°–260° C. After three hours' heating the contents were examined and paramid found. The reaction was not complete, for some euchronic acid was recovered. This seems to show that the carboxyls of this euchronic acid are in the ortho position. The paramid produced in these experiments was always dark-colored and no means of purification has been found. The euchronic acid, however, was always white or a very pale yellow tint. The reactions which have been found to take place in this series of experiments are :

1. $C_6(COOH)_6 + 3CH_3CN = C_6(C_2O_2NH)_3 + 3CH_3.COOH.$

2. $C_6(COOH)_6 + 2CH_3.CN =$
$C_6(C_2O_2NH)_2(COOH)_2 + 2CH_3COOH.$

3. $C_6(C_2O_2NH)_2(COOH)_2 + CH_3.CN =$
$C_6(C_2O_2NH)_3 + CH_3COOH.$

Another series of experiments was tried upon the partly neutralized mellitic acid, two objects being in view ; *i. e.*, the determination of the order in which the carboxyls combine with sodium, and second, to prepare the other two possible imids. Only partial success was obtained along both these lines. If large quantities of mellitic acid could be used, so that the partially neutralized salts could be isolated and crystallized, there is no doubt that both of these objects would be attained. Two tubes containing the tetra acid disodium salt $[C_6(COO)_6H_4Na_2]$ were heated with acetonitril, two molecules of the latter to each molecule of the acid salt. They received five hours' heating at 225°–240°. Very slight pressure was noted upon opening. The contents were washed with ether several times and with ninety-five per cent. alcohol. The ether extract contained acetic acid. The solid contents were soluble in water and by acidifying thin needle-like crystals came down. Recrystallized from water they came down as thin plates. These crystals give the euchron test but are very different from the euchronic acid previously prepared. They consist of large thin plates, imperfectly formed and twinning somewhat. They give an acid reaction and do not melt below 295° C., but lose water of crystallization. They undergo no other change at this temperature and after heating give the euchron test as before. To further prove that they were not *o*-euchronic acid they were heated for five hours at 240°–260° with propionitril. No paramid was produced. The *p*-euchronic acid recovered was recrystallized from water and gave very thin six-sided plates. The first two sodium atoms seem to have entered at 1 and 4. From two tubes, in which what was thought to be the triacid trisodium salt had been used and heated with nitril as before, no monimid was isolated. It may be that the saturation with sodium hydroxide gives a mixture of compounds, for euchronic acid was obtained from this experiment. Its analysis resulted as follows :

	H_2O. Per cent.	N. Per cent.
$C_{12}O_8H_4N_2(+ 2H_2O)$	10.6	9.31
Found	10.0	9.13

The figures for nitrogen are based upon the anhydrous euchronic acid. The previous experiments upon the tetrasodium salt of mellitic acid show that the sodium atoms enter at 1, 2, 4, and 5.

CONCLUSIONS.

In the foregoing experiments it has been shown that

I. Cyanacetic acid under certain conditions appears to rearrange to yield its isomer malonimid.

II. Benzoic acid and ethylene cyanide give benzonitril and succinimid.

III. Phenylacetic acid and ethylene cyanide give phenylacetonitril and succinimid. As a secondary product phenylacetic acid and phenylacetonitril give diphenyldiacetamid.

IV. In II and III it seems probable that β-cyanpropionic acid is an intermediate product and rearranges to give succinimid, and that in general, when an imid is produced by this reaction, it may be considered as resulting from an intermediate cyanacid.

V. The substituted monobasic acids, salicylic and anthranilic, give no similar results on account of the decompositions they undergo by heating.

VI. Phthalimid results from phthalic acid and propionitril, and phthalimid and succinimid result from phthalic acid and ethylene cyanide.

VII. Phthalic anhydride and acetonitril do not react under the conditions presented.

VIII. Terephthalic acid and propionitril do not react under the conditions presented.

IX. Homophthalimid is not readily formed from homophthalic acid and a nitril. It does not result by a rearrangement of cyan-*o*-toluic acid.

X. Diphenimid results in nearly theoretical amounts from diphenic acid and acetonitril.

XI. *o*-Sulphobenzoic acid and acetonitril yield a compound isomeric with saccharin which may be the unsymmetrical *o*-sulphobenzimid.

XII. By varying the conditions three of the four possible imids of mellitic acid were produced by heating this acid with acetonitril. The *p*-euchronic acid is a new compound; *o*-euchronic acid and paramid were known but have resulted also by our nitril reaction. It has been shown that aluminum amalgam can be used to give the euchron test.

To sum up then briefly, I believe I have made three new imids; *viz.*, malonimid, *p*-euchronic acid, and an imid of sulphobenzoic acid. The known imids of succinic, phthalic, homophthalic, diphenic, and mellitic acids have been made by a new method. The conclusions of Colby and Dodge, stated in the introduction, have been confirmed and the first method used by Miller and Seldner for producing fatty imids has been found applicable for producing aromatic imids. The widest general conclusion to be drawn from the work of these earlier investigators of the action of nitrils upon acids and from my own work is that when acids and nitrils are heated together they tend to form disubstituted ammonia compounds, secondary amids from monobasic acids and nitrils, imids from dibasic acids and nitrils.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 2.]

THE ACTION OF METALLIC THIOCYANATES UPON ALIPHATIC CHLORHYDRINS.[1]

BY WILBER DWIGHT ENGLE.

Received July 7, 1898.

THE alcohols form the most important class of organic compounds which have no representatives containing the thiocyan group. It would seem that such compounds would be produced by the double decomposition between alcohols having one or more atoms of hydrogen displaced by halogen and a metallic thiocyanate, and it was with this expectation that the following experiments were undertaken. In all cases tried, a reaction occurred as was shown by the separation of the halogen

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[1] Read at the meeting of the New York Section, May 6, 1898.