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Mellitonitrile and Polyphthalocyanines

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MELLITONITRILE AND POLYPHTHALOCYANINES

BY

JOSEPH A. ANTONELLI

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

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MASTER OF SCIENCE THESIS

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ABSTRACT

Several methods were investigated in an attempt to synthesize mellitonitrile which was to be used to prepare a cross-linked polymer with copper. The trimerization of butyne dinitrile with a one-to-one mixture of glacial acetic acid and pyridine gave a white crystalline product containing nitrogen. It was not characterized but may have been mellitonitrile. This product was isolated by chromatography.

Oxidation of some of the eluates obtained from the chromatographic separation of the trimerization mixtures gave a compound with a melting point close to that of mellitic acid. This may have been impure mellitic acid. No solid derivatives were prepared, and the compound was not characterized.

A modification in the Diels' preparation of hexamethylmellitate by the trimerization of dimethyl acetylenedicarboxylate gave an increased yield. A diluted catalyst was used.

A compound exhibiting phthalocyanine-like properties was prepared by the reaction of pyromellitic dianhydride with urea, boric acid and cupric chloride.

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I. INTRODUCTION

The preparation of hexacyanobenzene, or mellitonitrile, and its subsequent polymerization to a phthalocyanine type polymer was the primary object of this research. The metal phthalocyanines represent some of the most stable organic compounds and possess interesting properties. They are planar, highly conjugated molecules, which can be recrystallized from concentrated sulfuric acid. They sublime at very high temperatures. The phthalocyanines are used mainly as pigments - the most common of these being phthalocyanine blue (9).

Copper phthalocyanine, a typical phthalocyanine, is prepared by the reaction of four molecules of phthalonitrile and one atom of copper.



An exhaustive study of the structure and dimensions of the phthalocyanines by x-ray diffraction has shown that their central portions are porphyrin-like structures (16). (Figure 2.)

It is possible that mellitonitrile can be polymerized to a similar substance, and the resulting polymer, copper polyphthalocyanine, would be linear and highly cross-linked. Nelson made a stereochemical study of the so-called polyphthalocyanines, and he concluded that all bond angles and bond strains in such a compound were stereochemically possible. He further stated, however, that phthalonitrile would have to be used as a cross-linking agent if cross-linking were to

take place between every second unit of the polymer.

(Figure 2.) This long chain, cross-linked polymer would be sheet-like in form and quite stable. Its high degree of conjugation might possibly make the polymer electrical conducting (15).

Figure 1. Structure of Copper Phthalocyanine.

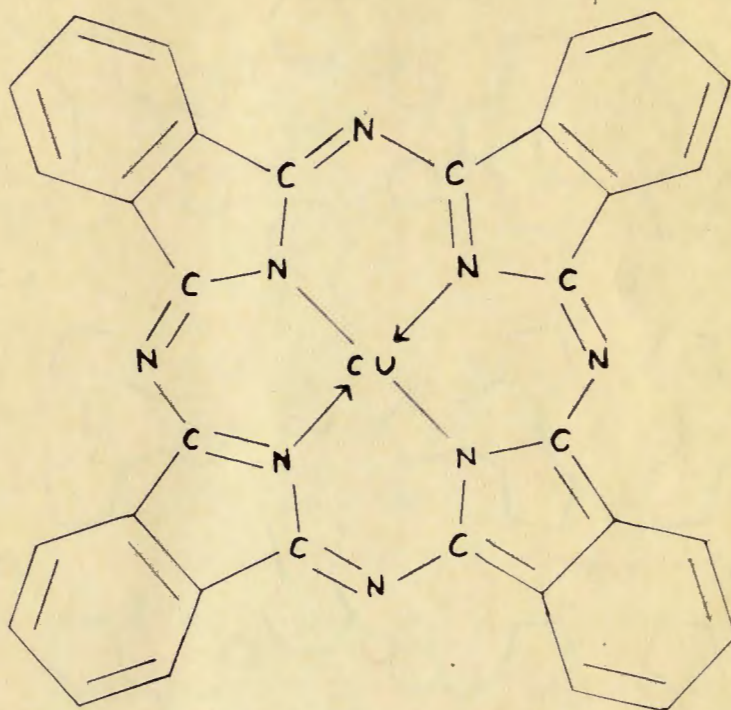


Figure 1. Structure of Copper Phthalocyanine.

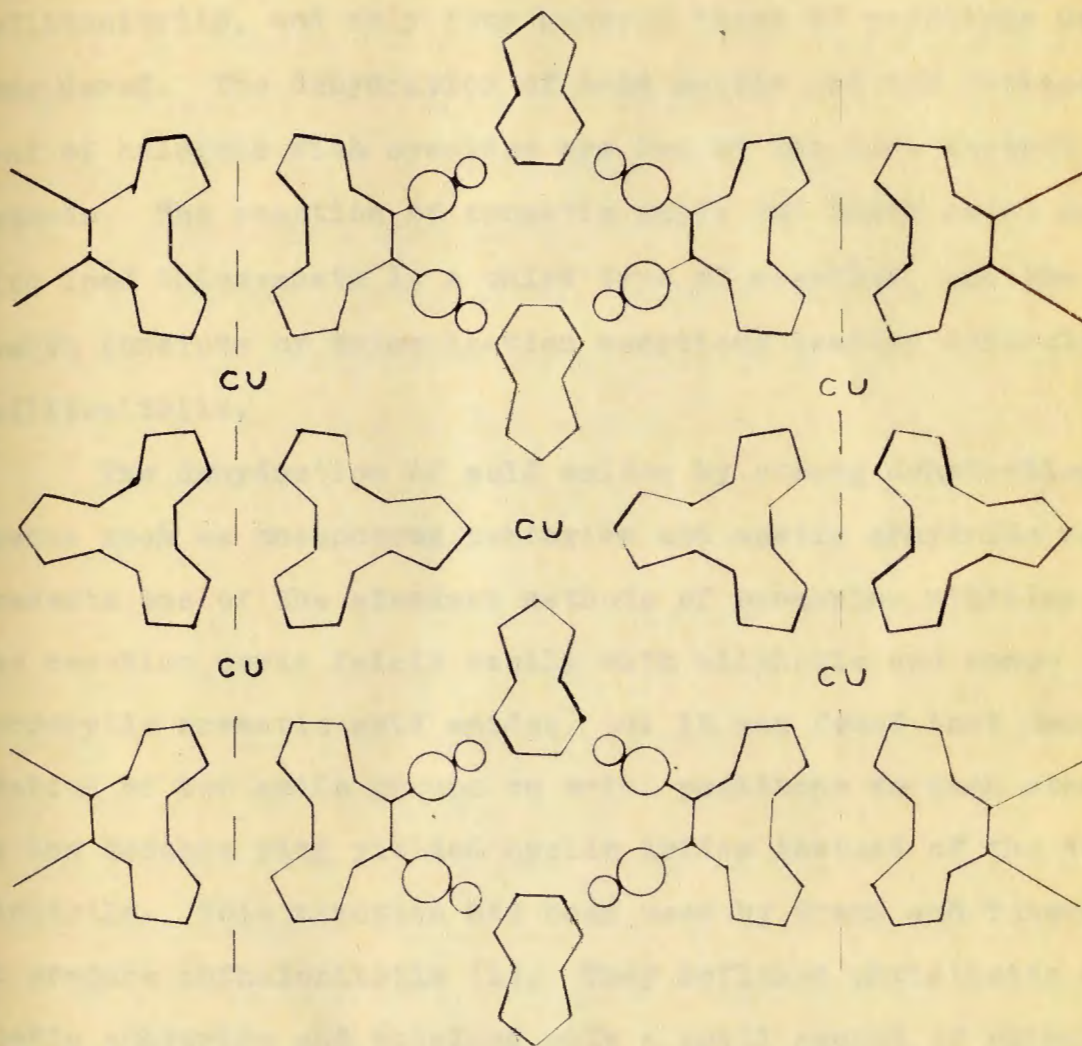


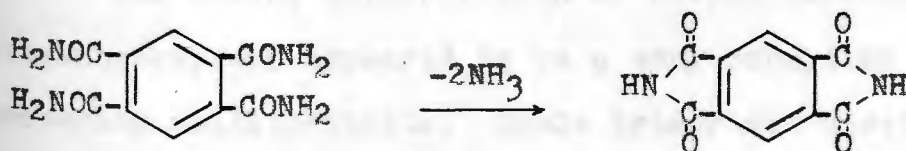
Figure 2. Portion of a Polyphthalocyanine as proposed by Nelson.

II. INVESTIGATION

A. DISCUSSION OF THE ATTEMPTED PREPARATION OF MELLITONITRILE

The attempted preparation of mellitonitrile represented the major portion of this research. Many methods of preparing nitriles are not feasible for the preparation of mellitonitrile, and only four general types of reactions were considered. The dehydration of acid amides and the replacement of halogens with cyanides are two of the more general methods. The reaction of aromatic acids and their metal salts with lead thiocyanate is a third type of reaction, and the fourth consists of trimerization reactions leading directly to mellitonitrile.

The dehydration of acid amides by strong dehydrating agents such as phosphorus pentoxide and acetic anhydride represents one of the standard methods of preparing nitriles. The reaction works fairly easily with aliphatic and monocarboxylic aromatic acid amides, but it was found that dehydration of two amide groups on ortho positions to each other on the benzene ring yielded cyclic imides instead of the desired dinitrile. This reaction had been used by Braun and Tcherniac to prepare phthalonitrile (1). They refluxed phthalamide with acetic anhydride and obtained only a small amount of phthalonitrile. The reaction was attempted with pyromellittotetraamide but was not successful.



Only the diimide was formed. Dehydration of mellitohexamide was not attempted because it was expected to react in the same manner.

The replacement of a halide with cyanide is another general method of preparing nitriles. The reaction is simple, fast, and produces good yields with alkyl compounds. Aromatic halides do not work well, however. Nelson attempted to prepare mellitonitrile by a replacement reaction using hexaiodobenzene and hexabromobenzene with potassium cyanide (15). The reactions were unsuccessful.

Nelson also attempted the Rosenmund-von Braun nitrile synthesis with hexaiodobenzene and hexabromobenzene (15). The reaction consisted in the heating of the aromatic halide with cuprous cyanide in pyridine solution. This was also unsuccessful.

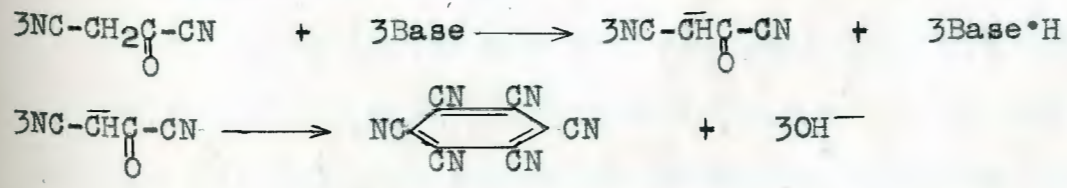
The reaction of aromatic acids and their zinc salts with lead thiocyanate or phospham was suggested by Migridichian as a method of preparing aromatic nitriles (13). Much work was done by Nelson using this method, but his attempts were unsuccessful (15). The reaction consisted in heating a mixture of the acid or its zinc salt with lead thiocyanate and sea sand in a high vacuum sublimation apparatus. Nelson did obtain some products containing nitrogen, but they were not characterized. The percentages of nitrogen in the compounds were not that of mellitonitrile.

The direct trimerization of butyne dinitrile or dicyanoacetylene appeared to be a very promising method of preparing mellitonitrile. Diels trimerized dimethyl acetylene-

dicarboxylate to hexamethylmellitite (5). A one-to-one mixture of glacial acetic acid and pyridine was added as catalyst to an equal volume of dimethyl acetylenedicarboxylate. The reaction was maintained at -10°C. and then allowed to stand at room temperature for a long time. Crystals formed and were picked out. They were characterized by hydrolysis to mellitic acid. This procedure was duplicated and it was found that the reaction was more easily controlled and gave better yields by diluting the catalyst in benzene and by dropwise addition of the reactant with stirring. The trimerization of butyne dinitrile was attempted using the same procedures with varying concentration of catalyst in benzene. The reaction was also attempted at different temperatures and pressures and with different catalysts. Chromatography was used as a means of separation in an attempt to obtain a sample of mellitonitrile.

The dehydration of glyoxal cyanohydrin followed by trimerization was another possible route to mellitonitrile. However, Nelson reported difficulties in preparing the cyanohydrin and the reaction was not attempted (15).

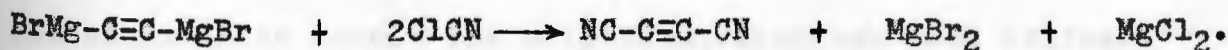
It is possible that oxaloacetic acid dinitrile would trimerize and with dehydration produce mellitonitrile. Oxaloacetic acid dinitrile could be made from diethyl oxaloacetate by methods analogous to those used to prepare butyne dinitrile. Masterson prepared diethyl oxaloacetate in ninety per cent yields by the method of Wislicenus (10).



B. DISCUSSION OF THE PREPARATION OF BUTYNE DINITRILE

The preparation of butyne dinitrile was of prime importance in this investigation, and the method used was long and gave poor yields. Dimethyl acetylenedicarboxylate was prepared from the monopotassium salt of acetylenedicarboxylic acid by esterification procedures (7). The ester was then allowed to react with aqueous ammonia to form the diamide of acetylenedicarboxylic acid. The dehydration of the diamide yielded butyne dinitrile. The process used for dehydration of the diamide was that of Moureu and Bongrand (14). Modifications in the procedures were used in an effort to increase yields of the intermediates but were successful only in the preparation of dimethyl acetylenedicarboxylate.

There was a possibility that butyne dinitrile might have been prepared by the use of a Grignard reagent. An acetylenic Grignard reagent added to a solution of cyanogen chloride in ether with subsequent hydrolysis would yield an acetylenic nitrile (13). Because acetylenedimagnesium bromide can be made, it is conceivable that it might react with two moles of cyanogen chloride to produce dicyanoacetylene. McNally attempted the reaction using cyanogen and was unsuccessful (11).



C. DISCUSSION OF REACTIONS TO PREPARE POLYPHTHALOCYANINES

Many methods of preparing phthalocyanines have been developed ranging from vapor phase procedures to simply heating the reactants in an open beaker. Although copper was the most commonly used metal and formed the most stable compound, beryllium, magnesium, calcium, barium, zinc, cadmium, nickel, manganese, cobalt, chromium, lead, tin, and iron have all been used in the preparation of the phthalocyanines (4).

Fundamentally the reactions consisted in the interaction of the aromatic dinitrile and the metal or metallic salt. Ortho-cyanobenzamides, ortho-sulfobenzonitriles, ortho-halogenobenzonitriles, ortho-dihalogenobenzenes, and phthalic anhydride plus ammonia have all been used as reactants with the metals to prepare the metal phthalocyanines (4).

Three general methods have been considered for the preparation of a polyphthalocyanine. The first was the reaction of mellitonitrile or pyromellitonitrile with metallic copper. The reaction of cupric chloride with mellitonitrile or pyromellitonitrile was the second method (4). Neither of the two methods was used because of the lack of mellitonitrile and pyromellitonitrile. It was believed, however, that the reactions would work easily because of the ease with which the phthalocyanines form. The polyphthalocyanines were believed to be possible sterically.

The third method involved the heating of pyromellitic dianhydride or mellitic acid with boric acid, urea, and cupric chloride (4). This reaction was attempted with both pyro-

mellitic dianhydride and with mellitic acid. With pyromellitic dianhydride a bright, blue-green, lustrous compound was formed. It resembled a phthalocyanine in that it was highly coloured and recrystallized from concentrated sulfuric acid. The compound was not characterized. The reaction with mellitic acid yielded a dark brown substance which did not resemble a phthalocyanine in color or in acid reprecipitation. This compound was not characterized either.

D. DISCUSSION OF THE PREPARATION OF MELLITIC ACID

Mellitic acid has been prepared by many methods but mostly in very small yields. The method of Feist (6) with modifications by Nelson (15) has proven to be the most successful. Tetrachlorophthalic anhydride heated with potassium cyanide, cuprous cyanide, and potassium hydroxide under pressure resulted in the replacement of the chlorides with cyanides which were then hydrolyzed to carboxyl groups. Nelson's method of separation and purification included the precipitation of the ammonium salt of the acid from the reaction mixture and recrystallization from concentrated nitric acid.

Chaigneau developed a procedure for the preparation of mellitic acid in which he started with phenol (2). Phenol was converted to hexamethyl benzene, then to hexabromomethyl benzene, then to the hexaacetate and finally hydrolyzed to hexamethylol benzene. Oxidation of hexamethylol benzene yielded mellitic acid. This procedure was used by Nelson but proved to be too time consuming and was discarded (15).

Trimerization of butynediol was reported by Smith as a means of preparing hexamethylol benzene which could be quantitatively oxidized to mellitic acid (17). Nelson reported unsuccessful results. Unsuccessful attempts were also made in this investigation.

Direct oxidation of hexamethyl benzene and charcoal were also reported as means of preparing mellitic acid, but the yields were very poor, and the procedure time consuming.

E. EXPERIMENTAL PROCEDURE

Trimerization Reactions

Preparation of dimethyl acetylenedicarboxylate: The mono-potassium salt of acetylene dicarboxylic acid (94.8 g.) was added to a mixture of 500 ml. absolute methanol and 98 ml. concentrated sulfuric acid in a three necked flask. The flask was fitted with a mechanical stirrer and two water condensers. Both condensers were furnished with calcium chloride drying tubes. The mixture was refluxed on a steam bath for three hours, cooled, and filtered. The precipitate was washed with ether, and the washings, along with an additional 150 ml. ether, were added to the filtrate. A saturated salt solution (325 ml.) was added, and the ether layer was removed. Five extractions with ether were made and combined. These were washed with water and then with saturated sodium carbonate. The ether solution was dried over anhydrous magnesium sulfate, and the ether solvent was distilled off on a steam bath. The residual liquid was vacuum distilled, and the fraction boiling at 91°C. to 97°C. was selected as the product. The yield was 41.2 g. (45 per cent). This yield was increased to approximately 80 per cent in a subsequent reaction by using 800 ml. methanol and refluxing for 24 hours. The ether extractions were increased to 10 in the modified procedure.

Trimerization of dimethyl acetylenedicarboxylate: Hexamethyl mellitate was prepared by the Diels trimerization of dimethyl acetylenedicarboxylate. A one-to-one mixture (by volume) of

glacial acetic acid and pyridine (3 g.) was added to an equal volume of the ester. A violent reaction took place almost immediately and the solution turned dark. The reaction was kept below 10°C . and then allowed to stand at room temperature for approximately one week. Some crystals were formed and removed with a spatula. They were recrystallized from acetic acid. Only about 25 mg. of product was obtained.

The reaction was repeated using a dilute solution of catalyst. One gram of the catalyst was diluted in 50 ml. benzene and cooled in an ice bath. Dimethyl acetylenedicarboxylate (3 g.) was added dropwise under mechanical agitation. The reaction was much slower but still formed a dark tarry substance. The benzene was allowed to evaporate and the tarry mass set. After standing for about two weeks crystals formed and were removed. The yield was about 0.2 g.

In another reaction the ester (3 g.) was added dropwise to a solution of 0.5 g. acetic acid-pyridine catalyst in 50 ml. benzene. This procedure yielded approximately the same amount of ester as the preceding: 0.2 g.

Two drops of the catalyst diluted in 50 ml. benzene was then used with 3 g. of the ester. A reaction took place, but after the reaction ceased, a portion of the mixture was tested with one more drop of catalyst. It was found that the reaction was not complete so more catalyst was added. The final yield was 0.2 g. Chromatography was then used to separate the trimerized product from the mixture, but the yields were not increased by any appreciable amount.

Preparation of Acetylenedicarboxamide: Acetylenedicarboxamide was prepared by the reaction of dimethyl acetylenedicarboxylate with aqueous ammonia. The ester was added dropwise to 800 ml. of concentrated ammonium hydroxide which was cooled in an ice bath to -10°C . The addition was continued until 20 ml. of the ester had been added. A mechanical stirrer was employed to keep the reaction agitated and was continued for one hour after all the ester had been added. The amide formed was filtered and boiled with ethanol and methanol. The reaction gave a yield of 12.3 grams.

Attempted trimerization of acetylenedicarboxamide: Acetylenedicarboxamide (5.6 g.), phosphorus pentoxide (60 g.), copper powder (3.2 g.), and cuprous chloride (3.2 g.) were mixed in a glass pressure bottle. The bottle was flushed out with nitrogen, stoppered and heated in a loosely covered large steel bomb for protective purposes. A vigorous reaction took place when heated to approximately 100°C . The mixture was extracted with acetone and methyl alcohol, but nothing could be recovered. An attempt was made to sublime the residue, but no sublimate formed. A polyphthalocyanine might possibly have been part of the residue, but it was not isolated or characterized.

Preparation of butyne dinitrile: The method of Moureu and Bongrand was used to prepare butyne dinitrile (14). Acetylenedicarboxamide (6 g.), P_2O_5 (50 g.), and sea sand (100 g.) were mixed to a homogeneous state and then poured into four test tubes. The tubes were connected to a glass arm leading to a receiving tube in an acetone-dry ice bath at -80°C . The

apparatus was then evacuated by means of a high vacuum pump, and nitrogen was introduced. The system was again evacuated to 5 mm. pressure, and the tubes were heated to 220°C. by quickly immersing in a hot oil bath. The distillation was continued for 30 minutes, and a solid product formed in the receiving tube. When the receiver was allowed to come to room temperature, the crystals melted, and the liquid was collected. The yield was 1.28 g. (31.14 per cent). The reaction was attempted using other apparatus, but no increase in yield was obtained and cleaning difficulties were encountered.

Attempted trimerization of butyne dinitrile: The methods used to trimerize dimethyl acetylenedicarboxylate were repeated using butyne dinitrile. One gram of butyne dinitrile was added dropwise to one gram of acetic acid-pyridine catalyst. A violent reaction took place and dark fumes evolved. A tarry substance formed which set into a resinous mass after standing for approximately two hours. It appeared that high polymer formation had taken place. Chromatographic technique yielded no crystalline products.

The catalyst mixture was then diluted to 0.5 g. in 50 g. of benzene, and one gram of butyne dinitrile was added dropwise. The reaction was maintained at 0°C. by an ice bath, and a mechanical stirrer was used for continuous agitation. The reaction was slowed considerably by the dilution of the catalyst, and the solvent took on a deep red color. The benzene solution was then passed through a chromatographic column which was prepared by methods described by Williams (18). Benzene was

poured into a burette to the 25 ml. mark. A plug of fibre glass, saturated with benzene to remove air bubbles, was then inserted into the tube and pushed to the bottom. Fisher adsorbent alumina, 80-200 mesh, was then sprinkled into the tube and allowed to settle. The adsorbent was added to fill the tube to the 10 ml. mark. Another glass wool plug was inserted above the top of the adsorbent, and the column was allowed to drain. More benzene was added to prevent the solvent level from dropping below the level of the adsorbent. In this manner the alumina settled, and the column was ready for operation. The benzene solution from the reaction was poured into the top of the burette, and a definite separation was affected on the alumina. A bright yellow band appeared lowest on the column and was followed immediately by a red band. Benzene was used as an eluent. Fractions of approximately 50 ml. were taken. The fractions obtained before the elution of the yellow and red bands left no residue upon evaporation at room temperature. Yellow and red residues were obtained upon evaporation of their respective eluates from the column. So little of each was obtained, however, that they could not be analyzed. They both melted at approximately 185-200°C. The large melting point range indicated that the fractions were probably impure. No other solids were isolated with the benzene eluent. Acetone and methyl alcohol were then used as eluents and only dark impure residues were obtained.

The same procedure was repeated with the glacial acetic acid and pyridine catalyst diluted 0.5 ml. in 100 ml. of benzene. The reaction behaved in the same manner and

chromatography was again attempted. The same bands were developed, but the fraction eluted before the yellow band yielded some long clear crystals which sublimed at 220-225°C. The compound was not made in a large enough quantity to provide for nitrogen analysis.

The attempted trimerization of butyne dinitrile with high temperature and pressure: The trimerization of butyne dinitrile was attempted under pressure. Dicyanoacetylene (1.28 g.) was mixed with 0.5 g. copper powder in a glass pressure bottle. The bottle was flushed with nitrogen and heated for 24 hours at 180°C. The heat and pressure were sufficient to convert the dinitrile to the gaseous state, and upon cooling the gas condensed. Cuprous chloride (0.5 g.) was then added to the glass bomb, and the heating was continued for 8 hours. No condensation took place upon cooling and nothing was obtained. Extraction of the substance remaining in the bottle was attempted with acetone, methyl alcohol, and sulfuric acid with negative results.

The attempted trimerization of butyne dinitrile with high temperature: Another attempt to trimerize butyne dinitrile was made at high temperature but at atmospheric pressure. In this attempt approximately 1 g. of butyne dinitrile was diluted in 25 ml. benzene and refluxed for 12 hours. At the end of the heating period a portion of the benzene solution was treated with one drop of the acetic acid-pyridine catalyst. A vigorous reaction took place indicating that the dicyanoacetylene had not reacted without catalyst. The remainder of the solution was treated with the catalyst and subjected to

chromatography. The same products were isolated from this mixture as from the attempt at low temperature and pressure.

Attempted trimerization of butyne dinitrile with nickel cyanide: One gram of butyne dinitrile was then refluxed with benzene (25 ml.) and nickel cyanide powder (0.5 g.) as a catalyst. After refluxing for 8 hours, evaporation of the benzene yielded a minute amount of residue. It was similar to the residues obtained from the chromatographic separations. The catalyst used in this attempt was prepared by the method described by Gopenhaver and Bigelow (3). A saturated solution of nickel chloride in ethyl alcohol was made, and HCN gas was passed through the solution. The gas was produced in a generator with KCN and H₂SO₄. Nickel cyanide was precipitated and collected. It was washed with water and heated to 175°C. to convert it to the anhydrous salt.

Attempted trimerization of butyne dinitrile in ether: Butyne dinitrile was then treated with an ether solution of the acetic acid-pyridine catalyst at 0°C. The same reaction took place as in the benzene solution, and chromatography yielded the same components.

Oxidation of the trimerization reactions' products: The red and yellow products isolated from the trimerization attempts were added to 15 ml. of 40 per cent HNO₃ and refluxed for one hour. The solution turned dark and gave off dark fumes characteristic of NO₂. The heating was stopped after the solution cleared. Evaporation to dryness yielded some

crystals that melted at approximately 280°C. to 281°C. An insufficient amount was obtained to prepare a solid derivative. A mixed melting point determination with mellitic acid did not markedly change the melting point, but the melting range was lengthened to 275°C. to 284°C.

Oxidation of all other eluates produced no solid products.

Reactions of pyromellitic acid and its derivatives

Reaction of pyromellitic acid with lead thiocyanate: Ten grams of lead thiocyanate, six grams of pyromellitic acid, and thirty grams of sea sand were mixed and heated in a high vacuum sublimation apparatus to 240°C. and 5 mm. pressure. A yellow sublimate formed containing sulfur but no nitrogen. The procedure was repeated twice with the same results.

Reaction of zinc pyromellitate with lead thiocyanate: Zinc pyromellitate was prepared by the method of Karmrodt (8). Five grams of the zinc salt of pyromellitic acid and ten grams of lead thiocyanate were mixed with an equal volume of sea sand. The mixture was heated to 300°C. under 5 mm. pressure in the sublimation apparatus. A sublimate formed containing no nitrogen.

Preparation of the tetraamide of pyromellitic acid: Pyromellitotetraamide was prepared by the method described by Meyer and Steiner (12). Pyromellitic acid (10 g.) was added to aqueous ammonia and a white precipitate of the ammonium salt was formed. Heating the ammonium salt overnight at 180°C. converted it to the diimide of pyromellitic acid. The diimide was then treated with aqueous ammonia with vigorous stirring. An exothermic reaction occurred and the mixture was cooled in an ice bath. The precipitated tetraamide was collected, washed with alcohol and dried.

Reaction of pyromellitotetraamide with phosphorus pentoxide: Two grams of the tetraamide was mixed with four grams of

phosphorus pentoxide and an equal volume of sand, and the mixture was heated to 250°C. in a sublimation apparatus at 5 mm. pressure. A white sublimate formed containing 12.0 per cent nitrogen by Kjeldahl analysis. This agreed closely with the diimide of pyromellitic acid which contains 12.9 per cent nitrogen.

Preparation of a phthalocyanine with pyromellitic dianhydride:

Twenty-six grams of urea and two grams of boric acid were melted together in an open beaker by means of an oil bath, and the temperature was raised to 150°C. While the mixture was being stirred, a mixture of twenty grams of pyromellitic dianhydride and four grams of anhydrous cupric chloride was dusted into the beaker. The reaction mixture became very thick and hardened, and the temperature was raised to 180°C. After cooling the hardened mass was ground and washed with dilute NaOH and dilute HCL. The white residue was then dissolved in concentrated sulfuric acid. Dilution with water induced precipitation. The white precipitate sublimed at 270°C. and was believed to be the diimide of pyromellitic acid. A sodium fusion gave a positive test for nitrogen.

The same procedure was repeated in a glass pressure bottle, and in this attempt a bright blue substance was formed. Urea (13 g.), boric acid (1 g.), pyromellitic dianhydride (10 g.), and cupric chloride (2 g.) were mixed in a glass bomb and heated overnight at 180°C. The blue substance that formed was washed with dilute alkali and then with dilute acid. Concentrated sulfuric acid was used to dissolve the substance and precipitation was effected by dilution with ice. A

Reactions involving mellitic acid

Preparation of mellitic acid from tetrachlorophthalic anhydride: Mellitic acid was prepared by the method of Feist (6) using the modifications proposed by Nelson (15).

Attempted preparation of mellitic acid by the trimerization of butynediol: One mole of butynediol, five grams of nickel acetate, and 250 ml. of alcohol were mixed in a large steel bomb and heated for 30 hours at 120°C. The alcohol was then evaporated off, the residue dissolved in water, and the nickel ions were removed with H₂S. The solution was again evaporated to dryness and the residue subjected to oxidation with 40 per cent nitric acid. No mellitic acid was obtained. The reaction was repeated in aqueous solution with negative results.

Attempted preparation of a phthalocyanine with mellitic acid: Mellitic acid (1 g.), urea (3.9 g.), boric acid (0.15 g.), and anhydrous cupric chloride (0.6 g.) were mixed in a glass bomb and heated overnight at 180°C. A dark brown substance was formed. It was washed with dilute NaOH and HCl. The reaction product was soluble in concentrated sulfuric acid but would not precipitate upon dilution. When heated with soda lime the substance gave off ammonia.

III. DISCUSSION OF RESULTS AND CONCLUSIONS

The preparation of mellitonitrile by the trimerization of butyne dinitrile showed definite signs of success. Some solid crystals containing nitrogen were isolated from the reaction mixture. Although they were never characterized because of their extremely small quantities, oxidation of the mixtures did yield a product which melted at approximately 280°C. to 281°C. The hydrolysis of mellitonitrile itself would yield mellitic acid which melts at 286°C. The product of the oxidations was believed to be mellitic acid. Recrystallization was not attempted since such small yields of the crystals were obtained.

The dark tarry substances formed in the trimerization reactions indicated a large number of side reactions. Probably polymerization of some type occurred.

As was evidenced by the various trimerization reactions of dimethyl acetylenedicarboxylate, the concentration of catalyst had a definite effect on the quantity of trimerized product produced. The reaction using equal quantities of catalyst and reactant was too vigorous, and it appeared that most of the reactant went into high polymer reactions. By dilution of the catalyst the reaction was slowed considerably and more trimerized product was obtained. High dilution of the catalyst produced an incomplete reaction.

Only one attempt was made to dehydrate and trimerize acetylenedicarboxamide. A resinous residue was formed which may have been a polyphthalocyanine but was not characterized. It appeared plausible to predict that the reaction would

work. Even though the reaction would be going from a stable diamide to an unstable dinitrile, which is unfavorable, the acetylenic dinitrile going to the stable hexacyanobenzene should be very favorable. The production of water in the dehydration should also be favorable. In addition to this, the formation of a polyphthalocyanine, which would most likely be even more stable because of its highly conjugated system, would increase the probability of the reaction.

The blue compound prepared by the reaction of pyromellitic dianhydride with urea, boric acid, and cupric chloride might possibly be a polyphthalocyanine. The reaction would not work under atmospheric pressure but was more successful under the pressure produced in a glass pressure bottle. This blue substance exhibited properties similar to copper phthalocyanine. It reprecipitated from sulfuric acid and was quite stable to heat.

In contrast to the product received from pyromellitic dianhydride, the same procedure with mellitic acid produced a dark brown substance which did not reprecipitate from sulfuric acid.

IV. SUMMARY

1. A study was made of the effect of various concentrations of catalyst in the Diels' trimerization of the dimethyl ester of acetylenedicarboxylic acid. A solution of 0.5 g. to 1.0 g. of acetic acid-pyridine catalyst in 50 ml. of benzene gave the best results.
2. The trimerization of butyne dinitrile in an attempt to prepare mellitonitrile yielded a solid crystalline compound containing nitrogen. The compound was not characterized.
3. Oxidation of the products of the trimerization reactions yielded a compound believed to be mellitic acid. It melted at 280°C to 281°C. (uncorr.). The melting point of mellitic acid as reported in the literature is 286°C.
4. The reaction of pyromellitic dianhydride with urea and cupric chloride yielded a phthalocyanine-like compound. It might possibly have been a linear polymer.
5. Mellitic acid, urea, and cupric chloride yielded a compound which was dark brown in color and did not reprecipitate from sulfuric acid.

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