Hultzsch[37] by heating the intermediate methylol compound (m.p. 64°).

Zigeuner and Ziegler[28] have likewise reported formation of the dibenzyl ether of the analogous 2,4-dimethylphenol without use of high temperatures, simply by treating the corresponding methylol compound with dilute HCl in boiling acetone–benzene mixture.

PITTSBURGH, PA.

(37) K. Hultzsch, *J. prakt. Chem.*, **159**, 169 (1942).

[CONTRIBUTION FROM BATTELLE MEMORIAL INSTITUTE]

Synthesis of Pyromellitonitrile and Related Compounds[1]

EMIL A. LAWTON[2] AND DONNA D. McRITCHIE

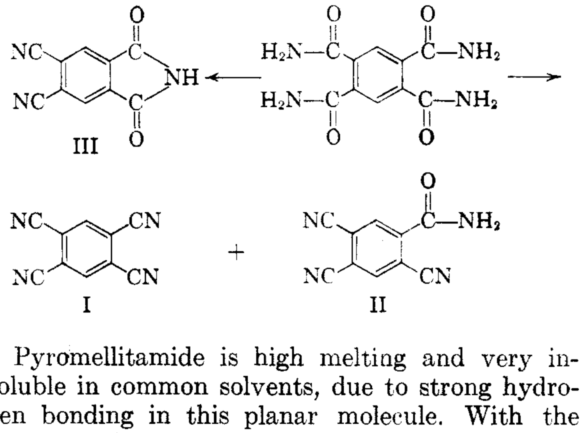
Received June 23, 1958

Pyromellitonitrile was prepared by the dehydration of pyromellitamide with thionyl chloride in dimethylformamide. The tetramide could not be dehydrated to the tetranitrile with acetic anhydride, phosphorus oxychloride, phosphorus pentachloride, or benzenesulfonyl chloride. By-products of the thionyl chloride dehydration were 4,5-dicyanophthalimide, and 2,4,5-tricyanobenzamide. 2,5-Dibromoterephthalic acid reacted quantitatively with cuprous cyanide to form pyromellitimide, but dimethyl 2,5-dibromoterephthalate reacted under the same conditions to form dimethyl 2,5-dicyanoterephthalate. Tetrakis(*N*-ethyl)pyromellitamide reacted with phosphorus pentachloride to form *N,N'*-diethylpyromellitimide.

During a study of the preparation of various phthalocyanines, it was necessary to prepare pyromellitonitrile (1,2,4,5-tetracyanobenzene, I) as an intermediate. The compound proved unexpectedly difficult to prepare and until a successful synthesis was achieved several new compounds were prepared, the syntheses of which we are reporting. The only reference to I in the literature was a patent[3] which stated that it was prepared "from pyromellitic acid tetramide by conventional methods"; no other description was given. Accordingly, pyromellitamide was prepared from pyromellitic acid by the method of Meyer and Steiner[4] in 88 per cent yield. However, the next step of dehydration of the tetramide to I proved unexpectedly difficult. Although good yields of *o*-phthalonitrile can be obtained by dehydration of *o*-phthalamide, using various methods, the analogous dehydrations of the tetramide to I were generally unsuccessful. For example, acetic anhydride in the presence of chlorobenzene was reported[5] to give a quantitative yield of *o*-phthalonitrile from *o*-phthalamide. An attempt to dehydrate the tetramide by a similar procedure gave only starting material. Similarly, dehydrations with phosphorus pentachloride, phosphorus oxychloride,[6] benzenesulfonyl chloride,[7] phosphorus pentoxide, and carbonyl chloride, yielded starting material, pyromellitimide, or chars.

This dehydration was finally accomplished with thionyl chloride in dimethylformamide at 60°. Stoichiometric proportions yielded a mixture of 2,4,5-tricyanobenzamide (II), pyromellitimide, and some I. Further reacting this mixture with additional thionyl chloride and recrystallizing from ethanol gave I.

When pyromellitamide reacted with an excess of thionyl chloride at a slightly higher tmeperature, the new compound 4,5-dicyanophthalimide (III) was the major product. All these *o*-dicyanobenzenes pass through a characteristic sequence of color changes from white at room temperature, slowly changing to green on heating above 200°, and abruptly turning deep blue between 255° and 260°. *o*-Phthalonitrile does likewise in a sealed capillary. This apparently is a characteristic of the *o*-dinitrile grouping.



III

I

II

Pyromellitamide is high melting and very insoluble in common solvents, due to strong hydrogen bonding in this planar molecule. With the objective of reducing the hydrogen bonding, leaving the molecule more susceptible to attack by dehydrating agents, both tetrakis(*N,N*-diethyl)pyromellitamide (IV) and tetrakis(*N*-ethyl)pyromel-

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(1) This project was supported by the Unites States Air Force under Contract No. AF33(616)-3477, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

(2) Present address: Rocketdyne, 6633 Canoga Avenue, Canoga Park, Calif.

(3) Farbenfabriken Bayer, Brit. Patent **698,049** (1953).

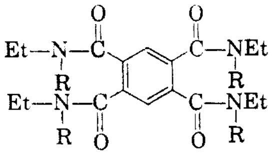
(4) H. Meyer and K. Steiner, *Monatsch.*, **35**, 39 (1914).

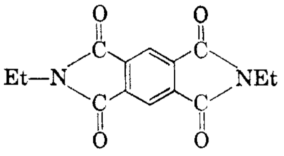
(5) E. Koike, M. Okawa, and K. Uchiyama, *J. Chem. Soc., Japan, Ind. Chem. Sect.* **57**, 925 (1954); *Chem. Abstr.*, **50**, 884*g* (1956).

(6) M. H. Fleysher, U. S. Patent **2,387,435** (1945).

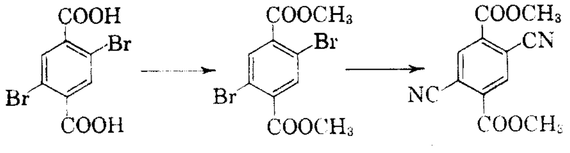
(7) C. R. Stephens, F. J. Bianco, and F. J. Pilgrim, *J. Am. Chem. Soc.*, **77**, 1701 (1955).

litamide (V) were prepared from pyromellitoyl chloride and diethylamine and ethylamine respectively. Compound V reacted smoothly with phosphorus pentachloride in carbon tetrachloride to give the new compound *N,N'*-diethylpyromellitimide (VI), m.p. 273–274°. Compound IV, however, did not react with phosphorus pentachloride under the same conditions, and tars were formed when the reaction was carried out in higher boiling solvents.


IV. R = Et
V. R = H


VI

Since four amide groups seemed so difficult to dehydrate simultaneously, it was thought that two para amide groups would dehydrate more readily. Accordingly, *p*-xylene was brominated to yield, 2,5-dibromo-*p*-xylene,[8] which in two steps was converted to 2,5-dibromoterephthalic acid (VII).[9] VII was esterified and the dimethyl 2,5-dibromoterephthalate (VIII) converted to dimethyl 2,5-dicyanoterephthalate (IX) using a variation of the Rosenmund-Von Braun substitution.[10] On recrystallization from ethanol, two fractions were obtained. One fraction melting at 219° was identified by elemental and spectral analysis as the expected dimethyl 2,5-dicyanoterephthalate. A second fraction melting at 195–198° was less pure and contained another compound, possibly 4-cyano-5-carbomethoxyphthalimide as evidenced by mixed melting point and infrared spectra. It was planned to convert IX to the dicyano diamide which might subsequently be dehydrated to I, but upon the successful dehydration of pyromellitamide this approach was abandoned.


VII VIII IX

In an attempt to prepare 2,5-dicyanoterephthalic acid directly from VII before esterification, a quantitative yield of pyromellitimide was obtained. Apparently the desired 2,5-dicyanoterephthalic acid underwent rearrangement to the diimide. Scholl and Neuberger[11] reported that the analogous rearrangement of *o*-cyanobenzoic acid to phthalimide occurs on heating to 180°, and at 60° in the presence of thionyl chloride. The tendency for this rearrangement to occur in the presence of a Lewis acid such as thionyl chloride may explain in part the conversion of pyromellitamide to pyromellitimide by phosphorus pentachloride and other dehydrating agents, and also the presence of 4,5-dicyanophthalimide as a product of the reaction of pyromellitamide with a large excess of thionyl chloride.

EXPERIMENTAL

All melting points were determined in capillary tubes and are corrected.

Pyromellitonitrile (I). A stirred suspension of pyromellitamide (10 g., 0.04 mole) in dimethylformamide (56 g.) was warmed to 60° before thionyl chloride (19.2 g., 0.16 mole) was added dropwise. After the mixture was heated for 7 hr. at 60°, dilute hydrochloric acid was added to decompose unreacted thionyl chloride, and the mixture was filtered. The residue was washed with water until it was neutral to litmus and then was slurried four times in hot, glacial acetic acid and filtered hot. The insoluble fraction was crude pyromellitimide, m.p. 450–454° dec. (lit. value[3] 440°). The products recovered from the acid extract, when added to a boiling solution of sodium isoamyloxide in isoamyl alcohol, gave an immediate blue color of phthalocyanine, indicating the presence of ortho nitrile groups.[12] The infrared spectrum showed a strong CN absorption at 4.5 μ and weaker NH and CO bands at 3.2 and 5.8μ, respectively. The flat platelets exhibited the unusual melting point characterisics attributed to *o*-dicyanobenzenes. Elemental analysis indicated the material to be essentially II.

Anal. Calcd. for $C_{10}H_4N_4O$: C, 61.2; H, 2.0; N, 28.6. Found: C, 63.5; H, 1.2; N, 28.9.

Five grams of the crude product were dissolved in dimethylformamide and 12 ml. (0.16 mole) of thionyl chloride were added. The solution was heated for 2 hr. with stirring. The reaction mixture was poured slowly onto crushed ice, and the white precipitate was extracted with glacial acetic acid as before. A light tan powder recovered from the acetic acid solution was crystallized in fine needles from boiling ethanol to yield 2.0 g. of I, m.p. 258° (sealed tube), turning blue. The infrared spectrum (KBr pellet) had bands at 4.5μ (CN), 3.2μ, 3.3μ (CH), and 10.8μ (1,2,4,5-substitution). It gave a positive sodium isoamyloxide test for ortho nitrile groups.

Anal. Calcd. for $C_{10}H_2N_4$: C, 67.3; H, 1.1; N, 31.4. Found: C, 67.0; H, 1.5; N, 31.2.

4,5-Dicyanophthalimide (III). Pyromellitamide and thionyl chloride in a ratio of 1:16 were dissolved in dimethylformamide and heated for 1 hr. on a steam bath at 98°. The cooled reaction mixture yielded a yellow precipitate when poured into a slurry of crushed ice and hydrochloric acid. The precipitate was filtered, washed with water until the washings were neutral, and extracted twice with hot glacial acetic acid. The residue was pyromellitimide; addition of water to the extract precipitated a brown powder m.p. 275–280° dec. which gave a negative sodium isoamyloxide test and was not characterized. Ether extraction of the aqueous acetic acid solution yielded a yellow powder, which turned blue at 260° and which was shown to contain ortho nitrile groups by the sodium isoamyloxide test. Infrared absorption bands at 4.5μ (CN), 3.2μ (NH), and 5.7–5.9μ (CO) indicated that the compound was 4,5-dicyanophthalimide.

Anal. Calcd. for $C_{10}H_3N_3O_2$: N, 21.3. Found: N, 21.0.

Tetrakis(N-Ethyl)Pyromellitamide (V). Compound V was prepared by dropping an ether solution of ethylamine into

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(8) R. Fittig, W. Ahrens, L. Mattheides, *Ann.*, **147**, 26 (1868).

(9) B. Schultz, *Ber.*, 18, 1762 (1885).

(10) Lester Friedman, private communication.

(11) R. Scholl and W. Neuberger, *Monatsh.*, **33**, 517 (1912).

(12) Ciba Brit. Patent **698,048**, April 28, 1954; *Chem. Abstr.*, **48**, 11803 (1954).

a stirred, ice-cooled, ether solution of pyromellitoyl chloride until the solution was basic. The precipitates were filtered from the ether and excess amine and were water washed until the washings were chloride free. The product was insoluble in cold but soluble in hot ethanol and methanol. It was insoluble in ether, ligroin, benzene, nitrobenzene, and chloroform. Recrystallization from ethanol yielded pure white needles of V, m.p. 280–281°.

Anal. Calcd. for $C_{18}H_{26}N_4O_4$: N, 15.4. Found: N, 15.1.

Tetrakis(N,N-diethyl)pyromellitamide (IV). Compound IV was prepared by dropping an ether solution of diethylamine into a stirred, ice-cooled, ether solution of pyromellitoyl chloride until the solution was basic. The precipitates were filtered from the ether and excess amine and were water washed until the washings were chloride free. The product was very soluble in ethanol, methanol, glacial acetic acid, and hot carbon tetrachloride. It was recrystallized from chloroform by adding ether with strong cooling to give pure white needles of IV, m.p. 190–192°.

Anal. Calcd. for $C_{26}H_{46}O_4N_4$: N, 11.7. Found: N, 11.3.

N,N'-Diethyl pyromellitimide (VI). In a three-necked flask equipped with a thermometer, stirrer, and reflux condenser were placed IV (5.0 g., 0.014 mole), phosphorus pentachloride (12.5 g., 0.06 mole), and chloroform (250 ml.). The mixture was heated slowly to reflux and maintained there for 6 hr. The cooled chloroform solution was poured into crushed ice, and the chloroform layer was separated, filtered, and washed alternately with aqueous sodium bicarbonate followed by water until the washings were no longer acid. Evaporation of the solvent left a yellow-brown powder, 3.2 g., m.p. 270–273°. The product was soluble cold in chloroform, benzene, dioxane, and glacial acetic acid and soluble hot in carbon tetrachloride, ethanol, and methanol. It was insoluble in ligroin and ether. Recrystallization from ethanol yielded 2.3 g. (61%) of VI, m.p. 273–274°.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.8; H, 4.4; N, 10.3. Found: C, 61.6; H, 4.2; N, 10.3.

The Friedman modification of the Rosenmund-Von Braun reaction. In a 50 ml. resin kettle were placed 2,5-dibromoterephthalic acid (2.0 g., 0.0062 mole), cuprous cyanide (1.4 g., 0.015 mole), and dimethylformamide (3 ml.). The mixture was heated slowly with stirring to reflux and after an hour was poured into a solution of ferric chloride (3.0 g.), concd. hydrochloric acid (1.0 ml.) and water (4.0 ml.). The mixture was heated to 60° for 10 min. to decompose the complex, cooled, and filtered. The product was insoluble in glacial acetic acid and was recrystallized from dimethylformamide to yield pyromellitimide (1.3 g., 98%) as shown by melting point and comparison of its infrared spectrum with that of an authentic sample.

Dimethyl-2,5-dibromoterephthalate (VIII). Anhydrous hydrogen chloride was passed into a flask containing 2,5-dibromoterephthalic acid (7.0 g., 0.216 mole) dissolved in absolute methanol (80.0 ml.) until the solution was nearly saturated. After refluxing for 8 hr., the solution was cooled to room temperature to precipitate white crystalline platelets of VIII, m.p. 148.6° (7.2 g., 97%).

Anal. Calcd. for $C_{10}H_8Br_2O_4$: C, 33.6; H, 2.3. Found: C, 34.2; H, 2.3.

Dimethyl-2,5-dicyanoterephthalate (IX). The Friedman modification[9] of the Rosenmund-Von Braun reaction was repeated on 2.0 g. of VIII. The pink filter cake obtained from the ferric chloride solution weighed 1.3 g. (m.p. 197–200°). Recrystallization from ethanol gave 0.4 g. of VIII, m.p. 219°. Infrared absorption showed the presence of CN (4.5μ), and CO plus CH_3OCO (5.8–5.9μ, 7.8–8.1μ, and 8.8μ). There were no bands characteristic of NH.

Anal. Calcd. for $C_{12}H_8N_2O_4$: N, 11.5. Found: N, 11.3.

Another fraction from the ethanol mother liquid melted at 195–198°. A mixed melting point with dimethyl-2,5-dicyanoterephthalate was 205–212°. The intermediate temperature but wider range makes it appear that this second fraction was another compound. Its infrared spectrum showed the presence of NH but was otherwise quite similar to that of the first fraction. It is possible that this material was a mixture of some dimethyl-2,5-dicyanoterephthalate with a substantial amount of 4-cyano-5-carbomethoxyphthalimide. Neither fraction contained halogen. The identity of the second fraction was not established.

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COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Substituted γ-Lactones. I. Preparation of α-Substituted γ-Butyrolactones by Condensation of γ-Butyrolactone with Aldehydes. Hydrogenation of the Condensation Products

HANS ZIMMER AND JOHANNES ROTHE[1]

Received June 30, 1958

The base-catalyzed condensation of γ-butyrolactone with various aldehydes is described. These condensation products can be hydrogenated to the corresponding saturated α-substituted γ-butyrolactones.

The γ-lactone ring occurs in a large variety of natural products, many of which exhibit considerable pharmacological interest.[2] As examples, the digitalis-glycosides, santonin, lignans like podophyllotoxin, and antibiotic substances like patulin may be cited. Among the more recent findings, only the antibiotic PA-147[3] and acetomycin[4] shall be mentioned.

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[1] Chattanooga Medicine Co. Postdoctorate Research Fellow 1956–1958. Recipient of a Fulbright Travel Grant. Present address: Department of Chemistry, Harvard University, Cambridge, Mass.

[2] *Cf.* L. J. Haynes, *Quart. Rev.*, **2**, 46 (1948).

[3] H. Els, B. A. Sobin, and W. D. Celmer, *J. Am. Chem. Soc.*, **80**, 878 (1958).

[4] L. Ettlinger, E. Gäumann, R. Hütter, W. Keller-Schierlein, F. Kradolfer, L. Neipp, V. Prelog, and H. Zahner, *Helv. Chim. Acta*, **41**, 216 (1958).