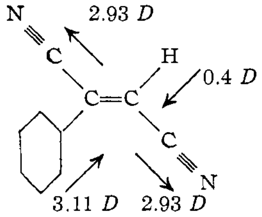

Fig. 1.

$\mu_{obs} = \mu_{C_6H_5} - \mu_{H-C}$
$\mu_{C_6H_5} = 3.11\ D$

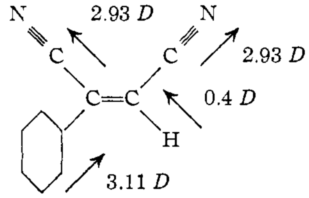

Fig. 2

with the experimental value. Figure 2 indicates the configuration of the moment vectors.

Assuming valence angles of 120°, $\mu_{calc.} = 8.3\ D$. This agreement is adequate since inductive effects should lower the calculated value in the actual molecule. Obviously, this calculation does not confirm the assumption about abnormal contributions from an ionic form, but it does demonstrate its consistency.

Acknowledgment.—The author wishes to express his indebtedness to Dr. D. W. Hein of the Bound Brook Laboratories of the American Cyanamid Company for proposing this problem and supplying the compounds.

STAMFORD, CONN.

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID COMPANY]

Phenylmaleonitrile and Phenylfumaronitrile. A New Reaction Observed on Activated Alumina

BY D. W. HEIN

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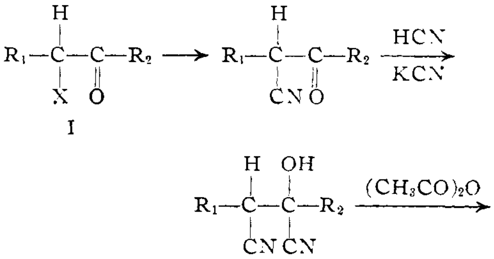
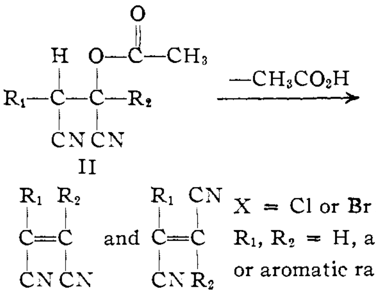
A mixture of phenylmaleonitrile and phenylfumaronitrile was obtained in 75–85% over-all yields from α-cyanophenylacetaldehyde by conversion to the cyanohydrin, acetylation of the cyanohydrin and then splitting acetic acid from the acety derivative on an activated alumina column. The isomers were readily separated by recrystallization, chromatography on alumina or vacuum distillation. Their configurations were established.

The preparation of pure phenylmaleonitrile and phenylfumaronitrile has not been reported previously. Mowry[1] has reported the preparation of "1,2-dicyano-1-phenylethylene" by the chlorination of phenylsuccinonitrile which was prepared by the method of Gitsels and Wibaut.[2] His purification techniques (vacuum distillation and dilute alcohol recrystallization) should have resulted in a separation of the isomers, but no further details are given in the patent. The preparation of phenylsuccinonitrile by the method of Gitsels and Wibaut[2] is extremely laborious. In our work we sought an easier route to substituted 1,2-dicyanoethylenes which are useful in the preparation of tetrazaporphin pigments and in the preparation of other derivatives. The splitting of acetic acid from the cyanohydrin acetates of α-cyanoaldehydes or ketones (II) as outlined below, appeared to be a particularly attractive route, as the latter





X = Cl or Br:
R₁, R₂ = H, alkyl,
or aromatic radicals

are readily prepared from α-haloketones or aldehydes (I). Since the completion of our work, France and Jones[3] have reported in patents that 3,4,5,6-tetrahydrophthalonitrile can be prepared by the dehydration of the cyanohydrin of α-cyanocyclohexanone, and that dimethylmaleonitrile can be made by the dehydration of the cyanohydrin of α-methylacetoacetonitrile, but no further details are given. However, Ficken and Linstead[4] did not use this method for the preparation of 3,4,5,6-tetrahydrophthalonitrile, when they elucidated the chemistry of hexadecahydrophthalocyanine.

We chose to test the above route by the preparation of phenylmaleonitrile, since the successful preparation of tetraphenyltetrazaporphin from it has not previously been reported. By the following sequence of reactions we were able to prepare a mixture of phenylmaleonitrile and phenylfumaronitrile

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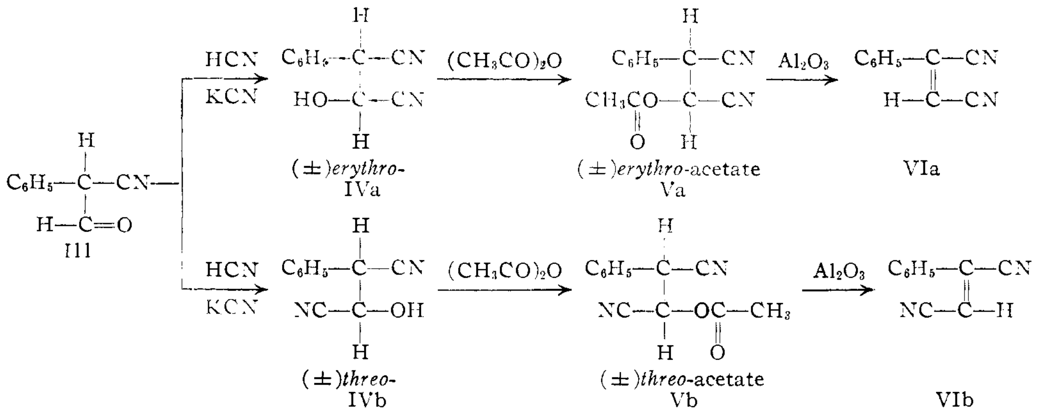
(1) D. T. Mowry, U. S. Patent 2,447,813 (1948).

(2) H. L. P. Gitsels and J. P. Wibaut, *Rec. trav. chim.*, **59**, 1093 (1940).

(3) H. France, Brit. Patent 686,395 (1953); H. France and W. O. Jones, Brit. Patents 688,768 (1953), 689,387 (1953), and 689,389 (1953).

(4) G. E. Ficken and R. P. Linstead, *J. Chem. Soc.*, 4846 (1952).



in 75–85% over-all yield from α-cyanophenylacetaldehyde (III). The latter was prepared by the Claisen condensation of phenylacetonitrile with ethyl formate in the presence of sodium methoxide according to Walther and Schickler.[5] The cyanohydrin (IVa and b) was prepared according to the method of Keller,[6] except that we stabilized the cyanohydrin in the usual manner by acidification with sulfuric acid. In our hands, the cyanohydrin was a viscous liquid. We were unable to obtain a solid, m.p. 89°, on recrystallization from benzene as reported by Keller. As a matter of fact when we followed Keller's directions carefully and drowned the reaction mixture in water without acidification, the cyanohydrin decomposed to a tarry mass, in contrast to the stable, clear viscous liquid obtained if it was acidified with sulfuric acid and the excess hydrogen cyanide evaporated *in vacuo*. Keller failed to mention the presence of the (±)*threo*- and (±)*erythro*-isomers although their presence would certainly be expected, and we proved this by the formation of geometrically isomeric acetates (Va and b) by acetylation. Since Keller's melting point (89°) was quite close to the 87–88° melting point we found for phenylmaleonitrile we thought it possible that recrystallization from benzene might have caused the elimination of water from the cyanohydrin, followed by deposition of the less soluble phenylmaleonitrile on cooling. However, longer boiling of the cyanohydrin in benzene failed to cause any dehydration in our experiment. An attempt to purify the cyanohydrin and separate the isomers by vacuum distillation, led to gross decomposition; water and hydrogen cyanide were eliminated and an evil-smelling liquid was produced.

Addition of acetic anhydride to the cyanohydrin (IVa and b) caused the spontaneous formation of the acetyl derivative (Va and b) as a result of catalysis by the excess sulfuric acid present. Passage of a benzene solution of 1-phenyl-2-acetoxysuccinonitrile (Va and b) through an Alcoa F20 Activated Alumina column gave an equimolecular mixture of phenylmaleonitrile (VIa) and phenylfumaronitrile (VIb) in 75–85% over-all yields from α-cyanophenylacetaldehyde and in a state of high purity. The by-products were strongly adsorbed on the column. Originally, the isomers were separated chromatographically on the Alumina column, but this required a rather long column, and recrystallization from 1-propanol was found to be more convenient. This method gave phenylmaleonitrile in a high state of purity, and vacuum distillation of the low melting residues from the recrystallizations gave pure phenylfumaronitrile. Other bases such as pyridine and Amberlite IRA-400 resin also split acetic acid readily from 1-phenyl-2-acetoxysuccinonitrile, but Activated Silica and the weakly basic Amberlite IR-4B resin failed to eliminate acetic acid. While the basic character of Alcoa F20 Activated Alumina no doubt aided in this reaction, it also took place on neutral Activated Alumina. Even so the neutral Activated Alumina no doubt behaved as a base in the Lewis sense and in all cases the mechanism probably consisted of the abstraction of the proton alpha to the phenyl group followed by elimination of the acetate group. In a similar experiment, water was not eliminated from 1-phenyl-2-hydroxysuccinonitrile by Alcoa F20 Activated Alumina.

The configurations of the phenylmaleonitrile and phenylfumaronitrile were established by Dr. W. C. Schneider[7] of our Stamford Laboratories by dipole moments. This assignment of configuration was supported by the more facile conversion of the isomer assigned the phenylmaleonitrile configuration to tetraphenyltetrazaporphin, and also to phenylmaleic anhydride.

Linstead, Owen and Webb[8] have reported a similar elimination reaction. They found that when β-acyloxy-esters were treated with alkali the ratio of elimination to hydrolysis increased with the strength of the acid eliminated, and was greater when the unsaturated acid produced by elimination was highly conjugated.

Recrystallization of crude 1-phenyl-2-acetoxysuccinonitrile from 1:1 benzene:*n*-heptane gave a white solid, m.p. 97–98°, which gave pure phenylfumaronitrile on passage through an Alumina column. This then would be the (±)*threo*-isomer, assuming *trans*-elimination. We failed to obtain the pure (±)*erythro*-isomer by recrystallization during the limited amount of work we did.

Hydrolysis with 1:1:1 by volume sulfuric acid: glacial acetic acid:water solution gave phenylmaleic anhydride in 75% yield from phenylmaleonitrile, in 46% yield from mixed phenylmaleo- and fumaro-

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(5) R. Walther and P. G. Schickler, *J. prakt. Chem.*, [2] **55**, 331 (1897).

(6) R. Keller, *Helv. Chim. Acta*, **20**, 447 (1937).

(7) W. C. Schneider, THIS JOURNAL, **77**, 2796 (1955).

(8) R. P. Linstead, L. N. Owen and R. F. Webb, *J. Chem. Soc.*, 1211, 1218, 1225 (1953).

nitriles, and in 29% yield from mixed (±)*threo*- and (±)*erythro*-1-phenyl-2-hydroxysuccinonitriles. Hydrolysis of phenylfumaronitrile in the same way gave no isolable product; further experiments were not tried.

Previously, the only satisfactory procedures reported for the preparation of phenylmaleic anhydride were those of Miller, Staley and Mann[9] which involved the dehydrogenation of phenylsuccinic anhydride with N-bromosuccinimide, and of Rondestvedt Jr. and Filbey[10] which involved the dehydration of α-phenylmalic acid prepared by the Reformatsky reaction, and of Taylor and Strojny[11] who prepared phenylmaleic and phenylfumaric acids in low yield by the Meerwein reaction. The first two methods suffer severe limitations in the preparation of substituted phenylmaleic anhydrides, especially where the substituent is a methoxy group. The use of the Meerwein reaction for the preparation of substituted phenylmaleic anhydrides has not been reported. Our procedure offers an additional convenient route to phenylmaleic anhydride and should be amenable to the preparation of substituted phenylmaleic anhydrides from the various substituted benzyl halides available.

Solution of phenylmaleonitrile in concentrated sulfuric acid, followed by drowning in water gave a diamide, the configuration of which was not established. Phenylfumaronitrile was recovered unchanged when treated in the same way.

Phenylmaleonitrile formed a crystalline Diels–Alder adduct with 2,3-dimethylbutadiene, whereas phenylfumaronitrile under the same conditions gave an oil not further investigated.

The substitution of α-acetylphenylacetonitrile for α-cyanophenylacetaldehyde in the above procedure resulted in the formation of a mixture of 1-phenyl-2-methylmaleo- and fumaronitriles. It would appear that this procedure should be quite general for the preparation of substituted maleo- and fumaronitriles.

Experimental

Mixed (±)*threo*- and (±)*erythro*-1-Phenyl-2-acetoxysuccinonitrile.—The procedure followed was essentially that of Keller.[6] α-Cyanophenylacetaldehyde[5] (199 g., 1.37 moles), 200 cc. of liquid hydrogen cyanide (American Cyanamid's Aero Liquid HCN distilled free from acid stabilizer), and 2 g. of finely powdered potassium cyanide were stirred together for two hours while cooled externally in an ice-bath. (Note: usually one hour's stirring was sufficient. The mixture should be stirred until all of the solid α-cyanophenylacetaldehyde has dissolved.) Two cc. of 100% sulfuric acid was added and the excess hydrogen cyanide was evaporated at water pump pressure from a warm water-bath. The residue was treated with 200 ml. of acetic anhydride, and the solution was swirled. The temperature of the mixture rose to 100°. It was allowed to stand overnight, after which it was stirred for one-half hour with three liters of water and the water was decanted. The semi-solid residue was dissolved in 1.5 liters of benzene and the benzene solution was washed with two 1-l. portions of 10% salt solution. The benzene was evaporated and the solid residue was finely ground and dried in a vacuum desiccator at 0.1 mm. pressure, whereupon there was obtained 276 g. (94%) of a white solid, m.p. 53–75°.

Anal. Calcd. for $C_{12}H_{10}O_2N_2$: C, 67.3; H, 4.67; N, 13.1. Found: C, 67.3; H, 4.42; N, 13.4.

Other runs gave yields of 95–100%. Washing the above benzene solution with sodium carbonate solution resulted in cleavage of acetic acid from about 10–20% of the 1-phenyl-2-acetoxysuccinonitrile. This makes no difference if the product is to be converted to phenylmaleo- and fumaronitrile.

Mixed Phenylmaleo- and Fumaronitriles. (A) Using Alcoa F-20 Activated Alumina.—If the mixed phenylmaleo- and fumaronitriles are desired, it is not necessary to isolate the 1-phenyl-2-acetoxysuccinonitrile from the above benzene solution. It can be passed directly through a 7.5 cm. × 50 cm. column of Alcoa F-20 Activated Alumina. The reaction zone warms to about 70°. The column is eluted with further benzene solvent; about three liters of eluate is collected for the above size run. Yields of pure white product, m.p. 45–70°, usually amounted to 75–85% over-all from α-cyanophenylacetaldehyde. The isomers can be separated chromatographically but this requires a rather long column.

Only starting material was recovered when 1-phenyl-2-acetoxysuccinonitrile was passed in the same way through Activated Silica (Davison's #923, 100–200 mesh) or Amberlite IR-4B[12] (Rohm & Haas).

(B) **Using Amberlite IRA-400.**—A solution of 10 g. (0.047 mole) of 1-phenyl-2-acetoxysuccinonitrile in 100 cc. of 1:1 by volume methanol–ethanol was passed through a 1 in. × 8 in. column of Amberlite IRA-400[12] (Rohm & Haas) which had been washed with 500 cc. of 5% sodium hydroxide solution, 2 l. of de-ionized water, and 1 l. of absolute alcohol. The column was eluted with methanol. Evaporation of the first 500 cc. of eluate gave 4.7 (65%) of clear crystals contaminated with a brown semi-liquid material. Recrystallization from 20 cc. of 1-propanol gave 1.56 g. (22%) of white prisms, m.p. 87–88°.

Anal. Calcd. for $C_{10}H_6N_2$: C, 78.0; H, 3.89; N, 18.2. Found: C, 78.2; H, 3.87; N, 18.2.

(C) **Using Neutral Activated Alumina.**—A solution of 25 g. (0.12 mole) of 1-phenyl-2-acetoxysuccinonitrile in 125 cc. of benzene was passed through a 4.5 cm. × 40 cm. column of neutral Activated Alumina prepared by washing Alcoa F20 Activated Alumina with water until the washings were neutral, then drying, and reactivating the Alumina by heating it at 240° for four hours. Elution of the column with benzene and evaporation of the eluate gave 12.6 g. (72%) of a white solid, m.p. 40–70°. The chromatogram behaved much in the same way as when unwashed Alcoa F20 Activated Alumina was used as the adsorbent.

Anal. Found: C, 77.0, 76.7; H, 4.04, 3.79; N, 18.3.

(D) **Using Woelm Non-alkaline Aluminum Oxide.**—1-Phenyl-2-acetoxysuccinonitrile (3 g., 0.014 mole) dissolved in 15 cc. of benzene was passed through a 13 mm. × 40 cm. column of Woelm non-alkaline Aluminum Oxide (Alupharm Chemicals), Activity Grade I, using benzene as the eluent. Evaporation of the eluate gave 1.83 g. (87%) of a white solid, m.p. 40–70°.

Anal. Found: C, 77.7; H, 3.50; N, 17.9.

(E) **Using Pyridine.**—1-Phenyl-2-acetoxysuccinonitrile (25 g., 0.13 mole) and 50 cc. of pyridine were heated under reflux for one-half hour, allowed to cool, and poured into 500 cc. of water. The solid was removed by filtration, thoroughly washed with water, and air-dried. There was obtained 16.0 g. (89%) of a very light brown solid, m.p. 40–70°. Recrystallization from 60 cc. of 1-propanol gave 7.9 g. (89%) of phenylmaleonitrile, m.p. 87–88°.

Phenylmaleonitrile.—Mixed phenylmaleo- and fumaronitriles (Alumina method), 367 g., were recrystallized from 1450 cc. of 1-propanol. The solution was allowed to stand overnight, and the crystals were removed by filtration and dried in a vacuum desiccator. There was obtained 118.1 g. of white prisms, m.p. 84–87°.

Anal. Calcd. for $C_{10}H_6N_2$: C, 78.0; H, 3.89; N, 18.2. Found: C, 78.1; H, 3.99; N, 18.1.

One additional recrystallization gave a product which melted at 87–88°. The mother liquor was cooled in a refrigerator to 5° and filtered again. Recrystallizing this 2nd crop from 300 ml. of 1-propanol gave, after drying *in*

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(9) L. E. Miller, H. B. Staley and D. J. Mann, THIS JOURNAL, **71**, 374 (1949).

(10) C. S. Rondestvedt, Jr., and A. H. Filbey, *J. Org. Chem.*, **19**, 119 (1954).

(11) E. C. Taylor and E. J. Strojny, THIS JOURNAL, **76**, 1872 (1954).

(12) C. J. Schmidle and R. C. Mansfield, *Ind. Eng. Chem.*, **44**, 1388 (1952).

vacuo, an additional 35.5 g. of white prisms, m.p. 84–86°. The product remaining in the mother liquors after cooling to 5° was mainly phenylfumaronitrile and could be isolated either by evaporation of the solvent or by cooling to −70°. The phenylfumaronitrile was best purified by vacuum distillation.

Phenylfumaronitrile.—The low melting residues from phenylmaleonitrile recrystallizations, 93.4 g., were distilled under reduced pressure through a 15-inch Helipak column. A trace of hydroquinone was added to the distilland. There was obtained 70.8 g. of a white solid, b.p. 95–96° (0.5 mm.) [83° (0.1 mm.)], m.p. 42.0–42.5°.

Anal. Calcd. for $C_{10}H_6N_2$: C, 78.0; H, 3.89; N, 18.2. Found: C, 78.1, 77.8; H, 3.92, 4.23; N, 18.1.

Further phenylmaleonitrile could be recovered from the still residue. We made no attempt to vacuum distil phenylmaleonitrile although this probably could be done.

(±)*threo*-1-Phenyl-2-acetoxysuccinonitrile.—Recrystallization of 13 g. of crude 1-phenyl-2-acetoxysuccinonitrile from 50 cc. of 1:1 by volume benzene:*n*-heptane gave 3.8 g. of a white solid, m.p. 97–98°.

Anal. Calcd. for $C_{12}H_{10}O_2N_2$: C, 67.3; H, 4.67; N, 13.1. Found: C, 67.4; H, 4.57; N, 13.3.

Chromatography of a benzene solution of this product through a 1 in. × 8 in. column of Alcoa F-20 Activated Alumina gave a 73% yield of a white solid, m.p. 43.0–43.5°. A mixed melting point with pure phenylfumaronitrile, prepared by chromatography of mixed phenylmaleo- and fumaronitriles, showed no depression.

Phenylmaleic Anhydride from the Hydrolysis of Phenylmaleonitrile.—Phenylmaleonitrile (2.0 g., 0.013 mole) was dissolved in 5 cc. of concentrated sulfuric acid, and 5 cc. of glacial acetic acid and 5 cc. of water were added in that order. The mixture was heated under reflux for one hour, cooled, diluted with water, filtered, and the filter cake was washed with water and dried at 50°. There was obtained 1.7 g. (75%) of a white solid, m.p. 115–118°. Recrystallization from 11 cc. of 1:1 acetone: *n*-heptane gave 0.6 g. of white prisms, m.p. 116–118°.

Anal. Calcd. for $C_{10}H_6O_3$: C, 69.0; H, 3.47. Found: C, 69.1; H, 3.56.

Miller, Staley and Mann[9] reported m.p. 119–120°. The preparation of the phenylmaleic anhydride–anthracene adduct according to the method of Miller and Mann[13] gave clear colorless rectangular prisms, m.p. 160–162°, after recrystallization from toluene:*n*-heptane. Miller and Mann[13] reported m.p. 166–168°.

Anal. Calcd. for $C_{24}H_{16}O_3$: C, 81.8; H, 4.58. Found: C, 81.7, 82.0; H, 4.69.

The hydrolysis of phenylfumaronitrile by this same technique failed to yield any solid upon cooling of the acid hydrolysis mixture or upon dilution with water. The hydrolysis of the mixture of phenylmaleo- and fumaronitriles in the same way gave a 46% yield of phenylmaleic anhydride, m.p. 116–117°.

Phenylmaleic Anhydride from the Hydrolysis of 1-Phenyl-2-hydroxysuccinonitrile.—*α*-Cyanophenylacetaldehyde (29 g., 0.2 mole), 50 cc. of liquid hydrogen cyanide (Cyanamid's Aero Liquid HCN distilled free from acid stabilizer) and 0.5 g. of finely powdered potassium cyanide were stirred together for one hour with external ice-bath cooling. It was acidified with 0.5 cc. of concentrated sulfuric acid, and the excess HCN was evaporated. A mixture of 60 ml. of concentrated sulfuric acid, 60 ml. of glacial acetic acid and 60 ml. of water was added to the residue, and the solution was heated under reflux for 90 minutes. It was allowed to stand overnight without further heating. The resulting slurry was filtered through a medium sintered glass funnel and the filter cake was washed thoroughly with water and dried at 50°. There was obtained 10.0 g. (29%) of a light tan crystalline solid, m.p. 116–118°. The mixed melting point with phenylmaleic anhydride prepared by the hydrolysis of phenylmaleonitrile showed no depression.

Phenylmaleamide or Phenylfumaramide.—Phenylmaleonitrile, 2.5 g., was dissolved in 10 cc. of concentrated sulfuric acid and the solution was allowed to stand for one-half hour. It was then poured onto ice and the resultant slurry was filtered. The filter cake was thoroughly washed with water and dried at 65°. There was obtained 1.8 g. of a white solid, m.p. 160–170°, with much preliminary softening. It was recrystallized from pyridine to give a microcrystalline white solid, m.p. 205° dec.

Anal. Calcd. for $C_{10}H_{10}O_2N_2$: C, 63.3; H, 5.32; N, 14.7. Found: C, 63.4; H, 5.26; N, 14.6.

It was insoluble in aqueous sodium carbonate solution and soluble in aqueous sodium hydroxide solution. The configuration of this diamide was not determined. When phenylfumaronitrile was treated in the same way, it was recovered unchanged. When phenylfumaronitrile was heated with concentrated sulfuric acid on a steam-bath before drowning, sulfonation apparently took place since no solid separated on dilution of the solution.

2,3-Dimethyl-4,5-dicyano-5-phenylcyclohexene.—The adduct was prepared by heating phenylmaleonitrile and 2,3-dimethylbutadiene in toluene for 70 hours under reflux according to the method used by Miller and Mann[13] for the phenylmaleic anhydride adduct. There was obtained 2.4 g. (78.5%) of light brown crystals. Recrystallization from 95% alcohol gave 1.2 g. (39%) of white crystals, m.p. 155–156°.

Anal. Calcd. for $C_{16}H_{16}N_2$: C, 81.3; H, 6.83; N, 11.9. Found: C, 80.9, 80.8; H, 6.87, 6.58; N, 11.7.

Phenylfumaronitrile under the same conditions gave an 8% yield of the phenylmaleonitrile adduct, probably as a result of the presence of phenylmaleonitrile in the starting material, plus an oil which we did not identify.

Mixed (±)*threo*- and (±)*erythro*-1-Phenyl-2-methyl-2-acetoxysuccinonitriles.—*α*-Acetylphenylacetonitrile (79.5 g., 0.5 mole; Benzol Products), 200 cc. of liquid hydrogen cyanide (Cyanamid Aero liquid HCN distilled free from acid stabilizer) and 1 g. of finely powdered potassium cyanide were stirred together for one hour with external ice-bath cooling. Sulfuric acid (1 cc. of 100% acid) was added and the excess hydrogen cyanide was distilled from a warm water-bath at water pump pressure. Acetic anhydride (75 cc.) and 1 cc. of 100% sulfuric acid were added to the residue, and the solution was heated under reflux for ten minutes and allowed to cool. The solution was stirred with 1 liter of water and the water was decanted from the semi-solid residue. The residue was dissolved in 1 liter of benzene and the solution was washed with three 1-l. portions of water, filtered and dried over anhydrous sodium sulfate. One tenth of the benzene solution was used in the experiment outlined below. Evaporation of the remaining nine-tenths gave 78 g. of clear crystals mixed with a sirupy liquid. Recrystallization of 27 g. of this product from 60 cc. of 1-propanol gave 6.0 g. of a white crystalline solid, m.p. 100–101°. Its configuration was not established.

Anal. Calcd. for $C_{13}H_{12}O_2N_2$: C, 68.4; H, 5.30; N, 12.3. Found: C, 68.3; H, 5.49; N, 12.2.

Mixed 1-Phenyl-2-methyl maleo- and fumaronitriles.—Passage of one-tenth of the benzene solution from above through a 4.5 × 50 cm. column of Alcoa F20 Activated Alumina gave 4.75 g. (56.5%) of a white solid, m.p. 45–65°.

Anal. Calcd. for $C_{11}H_8N_2$: C, 78.6; H, 4.79; N, 16.7. Found: C, 78.3; H, 4.81; N, 16.4.

Recrystallization from 15 cc. of 1-propanol gave 0.94 g. of white prisms, m.p. 70–71°. Its configuration was not established.

Passage of a benzene solution of 1-phenyl-2-methyl-2-acetoxysuccinonitrile, m.p. 100–101°, through an Alcoa F20 Activated Alumina column gave white prisms, m.p. 70–71°. The configuration of this product was not established.

Acknowledgment.—The author wishes to thank Mr. O. E. Sundberg and his associates for the microanalyses and Mrs. Nena Barabutes for certain of the preparations.

BOUND BROOK, N. J.

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[13] L. E. Miller and D. J. Mann, THIS JOURNAL, 72, 1484 (1950).