15 ml. (175 millimoles) of concentrated hydrochloric acid and 5 ml. of water gave a reaction mixture from which 0.67 g. (69%) of β-benzylmercaptopropionic acid (XII) of m.p. 80–81.5° was isolated. One recrystallization from hexane gave colorless acid of m.p. 81.2–82°, reported[15] m.p. of β-benzylmercaptopropionic acid 82–84°.

Oxidation of an aqueous solution of the sodium salt of XII with aqueous potassium permanganate gave a 57.4% yield of β-benzylsulfonylpropionic acid of m.p. 177–178°, reported[15] m.p. 177–178°.

**Acknowledgment.**—The author is indebted to T. L. Gresham for his interest and encouragement, to J. R. Kubik for microanalyses, and to A. K. Kuder for certain analyses, molecular weight determinations and viscosity measurements.

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[15] B. Holmberg, *Arkiv Kemi, Mineral. Geol.*, **14A**, No. 8 (1940); *C. A.*, **35**, 2114[6] (1941).

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[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

# Vinylidene Cyanide. X. Reaction of Polyvinylidene Cyanide with Active Hydrogen Compounds of the Type $XCH_2Y$

BY J. C. WESTFAHL

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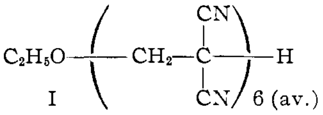
Base-catalyzed reaction of low molecular weight polyvinylidene cyanide with active hydrogen compounds of the type $XCH_2Y$ does not give the expected open chain compounds, $XYC(CH_2CH(CN)_2)_2$. Instead, 2,2,6-tricyano-4,4-disubstituted-cyclohexanonimines are formed. The preparation, physical properties and the evidence for the assigned structures of these unusual compounds are given.

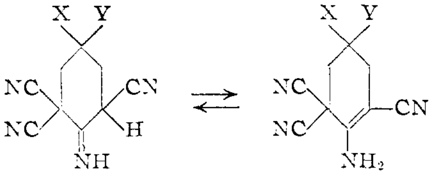
In a previous paper,[1] the base-catalyzed reaction of ethanol-initiated polyvinylidene cyanide (I)



$$C_2H_5O\left(CH_2-\overset{CN}{\underset{CN}{C}}\right)_{6\ (av.)}H \qquad I$$

with active hydrogen compounds containing a single active hydrogen atom (A–H) to give products of the type $A-CH_2CH(CN)_2$ was reported. The base-catalyzed reaction of I with active hydrogen compounds of the type $XCH_2Y$ is the subject of this paper.

The addition of pyridine to a stirred suspension of I in benzene containing the active hydrogen compound gave a reaction mixture from which II was isolated. The compounds of Table I were prepared in this manner.



II

The structures of the products of Table I were assigned on the basis of the acids formed on hydrolysis, the similarities in the infrared spectra of all of the bis compounds (II) with the spectrum of the known compound 2,2,4,4,6-pentacyanocyclohexanonimine[2] (III), and the fact that III is formed by the reaction of I with malononitrile.

The hydrolysis of III has been reported previously.[2] The manner in which several representative examples of II were expected to hydrolyze is given in Charts I, II and III. The mixture of acids produced in the hydrolysis of IV (Chart I) was converted to ammonium salts and separated by circular paper chromatography. The mixture was shown to consist of six individual acids and four of these were shown to be chromatographically identical with X, XI, XII and XIII. The hydrolysis products of VII (Chart II) were separated and identified by conventional methods. γ-Benzoylpimelic acid (XIV) does not appear to be reported in the literature. Attempts to prepare XIV by reaction of an appropriate active hydrogen compound with acrylonitrile followed by hydrolysis failed. Thus, reaction of ethyl benzoylacetate with two moles of acrylonitrile using Triton B[4] as the catalyst gave only the monocyanoethylation product. Similarly, reaction of benzoylacetone with two moles of acrylonitrile using potassium hydroxide as the catalyst gave the monocyanoethylation product.[5]

Hydrolysis of VIII (Chart III) gave a mixture of acids from which pure XIV was isolated. The XIV isolated from this hydrolysis was shown to be identical with the XIV isolated from the hydrolysis of VII. The criteria used to establish the identity were the m.p. of a mixture, comparison of their infrared spectra, and paper chromatography. The mixture of acids formed in the hydrolysis of VIII was shown to contain, in addition to XIV, acids which were chromatographically identical with X, XII and XV. The formation of X, XII, XV and an acid $C_{14}H_{16}O_5$ in the hydrolysis of VIII as well as the formation of XV and the acid $C_{14}H_{16}O_5$ from the hydrolysis of VII leaves little doubt that the structure of the $C_{14}H_{16}O_5$ acid is XIV. The small amounts of neutral, water-insoluble liquids with odors similar to acetophenone, which were observed in the hydrolyses of those products in which X or Y was acyl or aroyl, were not investigated.

The hydrolysis of IX proceeded abnormally and will be the subject of a separate paper.

The infrared spectra of II all have absorption

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[1] Paper IX of this series, THIS JOURNAL, **80**, 871 (1958).

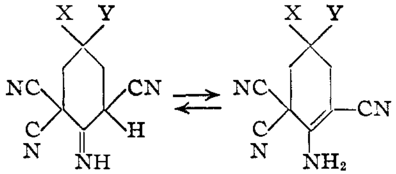
[2] J. C. Westfahl and T. L. Gresham, *J. Org. Chem.*, **21**, 319 (1956).

[3] J. C. Westfahl and T. L. Gresham, THIS JOURNAL, **78**, 2588 (1956).

[4] Rohm and Haas Co., Philadelphia, Penna.

[5] This is contrary to the observations of A. B. Boese, Jr., U. S. Patent 2,438,961 (1948).

TABLE I



II

| | | | | | Analyses, % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Calcd. | | | Found | | |
| | X[a] | Y | Yield, % (M.p., °C.) | M.p., °C.[b] pure | C | H | N | C | H | N |
| III | CN | CN | 59.2 (234–235 d.) | 234–235 d. | [c] | | | | | |
| IV | $CH_3CO$ | $CO_2C_2H_5$ | 41.2 (118.5–121.5 d.) | 115–120 d. | 58.75 | 4.93 | 19.57 | 58.80 | 5.25 | 19.58 |
| V | $CO_2C_2H_5$ | $CO_2C_2H_5$[d] | 52.5 (141.5–143) | 143.5–144.5 | 56.95 | 5.10 | 17.71 | 57.09 | 5.14 | 17.71 |
| VI | $CH_3CO$ | $CH_3CO$ | 41 (163-167 sl. d.) | 173–175 d. | 60.93 | 4.72 | 21.86 | 60.95 | 4.90 | 21.89 |
| VII | $C_6H_5CO$ | $C_6H_5CO$ | 58.3 (165.5–168.5 d.) | 175.5–177 d.[e] | 72.62 | 4.24 | 14.73 | 72.54 | 4.19 | 14.62 |
| VIII | $CH_3CO$ | $C_6H_5CO$ | 55.4 (160–161.5) | 160.5–162 sl. d. | 67.91 | 4.43 | 17.60 | 67.92 | 4.43 | 17.61 |
| IX | $CH_3$ | $NO_2$ | 16.3 (210–212 d.) | 216.5 d. | 51.94 | 3.93 | 30.29 | 51.86 | 4.06 | 30.13 |

[a] Catalyst was pyridine. [b] M.p. depends on heating rate. Some of the compounds darken on standing at room temperature. [c] Identical with 2,2,4,4,6-pentacyanocyclohexanonimine prepared from malononitrile and formaldehyde.[2] [d] The crude product is a mixture of $CH(CO_2C_2H_5)_2CH_2CH(CN)_2$[1] and V. [e] This compound was identical with the bis product formed in the reaction of vinylidene cyanide with dibenzoylmethane.[3]

CHART I

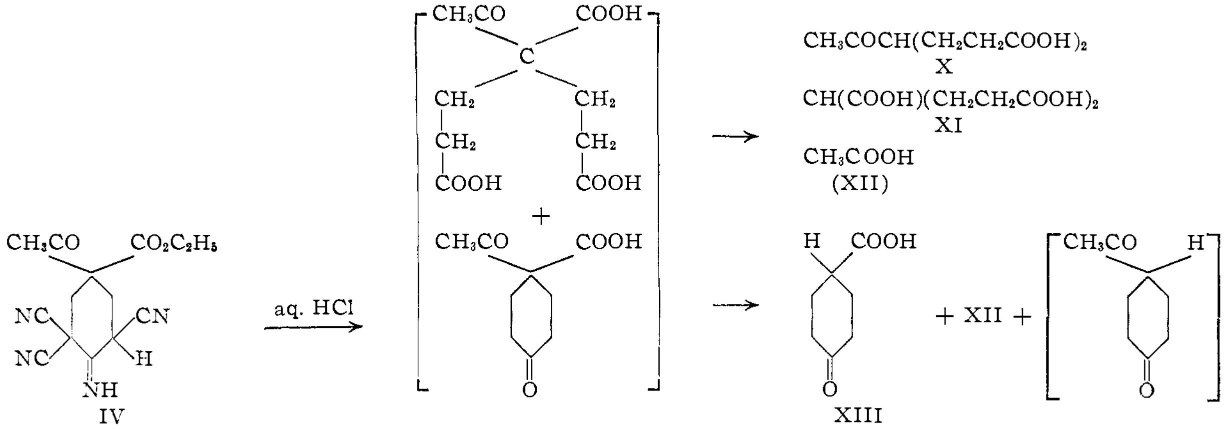


CHART II

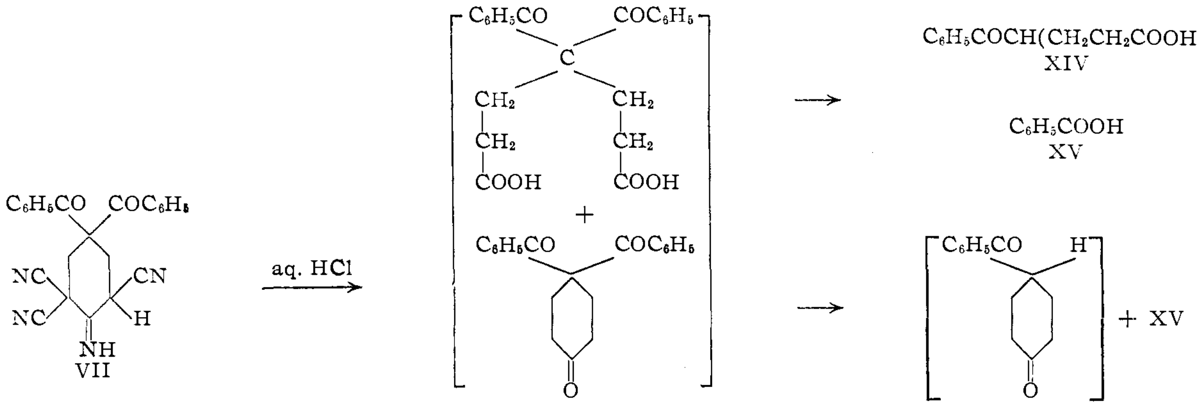
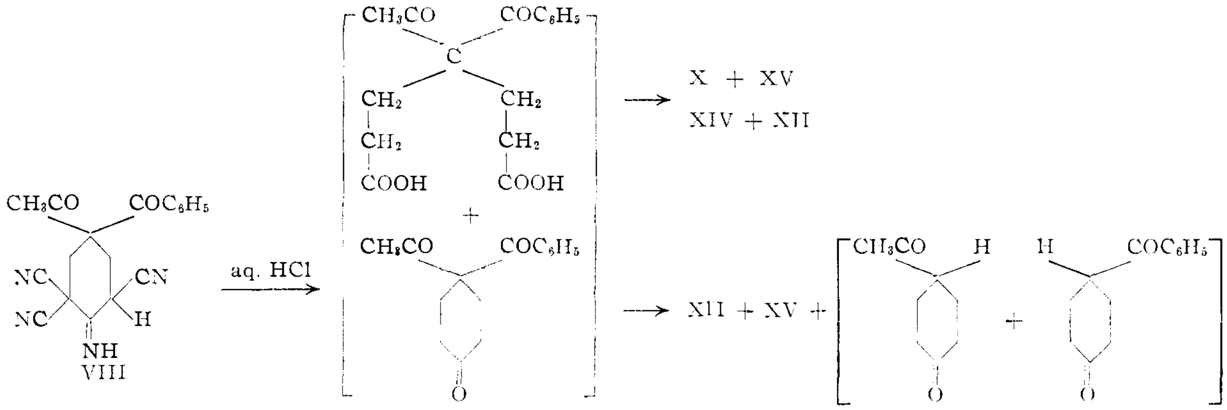


CHART III



bands between 2.89 and 3.09 μ due to N–H and some of the compounds have bands between 5.96 and 6.16 μ due to C=C or C=N. In the region from 7.5 to 10 μ several sharp bands are present in all of the spectra. These have been interpreted as ring vibrations. The positions of some of the absorption bands are collected in Table II.

TABLE II

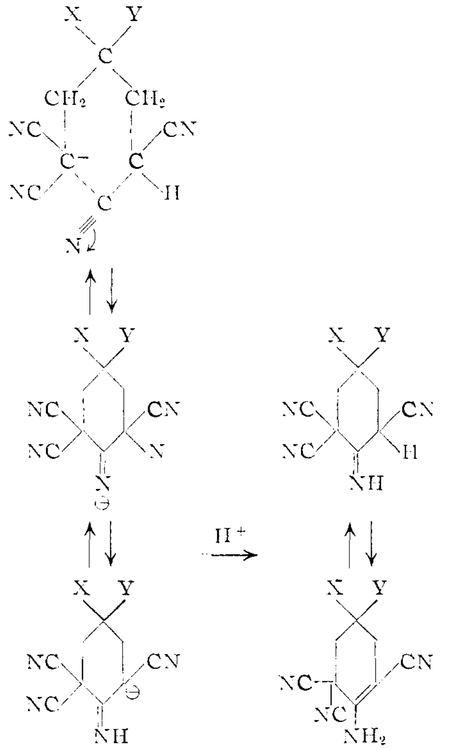
POSITION OF N—H AND C=C OR C=N ABSORPTION IN II[a]

| | X | Y | N—H, μ | C=C (C=N), μ |
|---|---|---|---|---|
| III | CN | CN | 2.92, 2.98, 3.09 | 6.06, 6.13 |
| V | $CO_2C_2H_5$ | $CO_2C_2H_5$ | 2.89, 2.98, 3.08 | 6.00, 6.12[b] |
| IX | $CH_3$ | $NO_2$ | 2.91, 2.98, 3.09 | 6.03, 6.12 |
| VII | $C_6H_5CO$ | $C_6H_5CO$ | 2.91 | 5.96[b] |
| VIII | $C_6H_5CO$ | $CH_3CO$ | 2.91 | 5.97[b] |
| VI | $CH_3CO$ | $CH_3CO$ | 2.93 | |
| IV | $CH_3CO$ | $CO_2C_2H_5$ | 2.95 | 6.16[b] |

[a] Spectra were determined as mulls in Nujol (25–7.5 μ) and Fluorlube (7.5–2 μ). [b] The contribution due to the presence of carbonyl is not known.

A plausible mechanism for the base-catalyzed reaction of active hydrogen compounds with I has been reported.[1] Chart IV gives the additional steps leading to the cyclic products.

CHART IV



## Experimental[6]

**Preparation of I.**—The ethanol-initiated polymerization of vinylidene cyanide has been described previously.[1]

**Preparation of V.**—A solution of 8.8 ml. of 90% vinylidene cyanide (0.1 mole) in benzene was polymerized with ethanol and Compound I was recovered as a dry powder.[1] Compound I was stirred with 50 ml. (53 g., 0.33 mole) of diethyl malonate while a solution of 8.1 ml. (7.9 g., 0.1 mole) of pyridine in 15 ml. (15.8 g., 0.099 mole) of diethyl malonate was added over a 4-minute interval. After heating the stirred solution for two hours at 50–60°, it was cooled in ice, and 100 ml. of water and 10 ml. of concentrated hydrochloric acid were added. The emulsion was filtered (Filter-aid) and the aqueous layer of the filtrate was extracted with ether. The ether extract and the ester layer of the filtrate were combined and dried with magnesium sulfate. After filtering, the ether was removed *in vacuo* to leave 67.3 g. of ester mixture. Removal of the unreacted diethyl malonate (51.77 g.) at 0.03 mm. and an oil-bath temperature of 120° left a partly crystalline residue weighing 14.83 g. The residue, which consisted of V and $CH(CO_2C_2H_5)_2CH_2CH(CN)_2$,[1] was recrystallized from ethanol to give 8.31 g. (52.5%) of yellow product of m.p. 141.5–143°. A further recrystallization gave 7.15 g. (45.1%) of colorless V of m.p. 143.5–144.5°.

**Preparation of VII.**—To a stirred suspension of 4.90 g. (0.057 equivalent) of I in a solution consisting of 25 ml. of benzene and 7.04 g. (0.031 mole) of dibenzoylmethane, was added 5.1 ml. (5.0 g., 0.063 mole) of pyridine in one portion. After 8 minutes solid began to separate from the red solution which was nearly free of suspended I. The mixture was heated at 50–60° for 15 minutes, cooled in ice, and treated with 65 ml. of cold water and 6.5 ml. of concentrated hydrochloric acid. The mixture was filtered and the tan solid was washed with benzene and water and then dried. When the tan solid (8.61 g.) was boiled with ethyl acetate, a small amount of degraded I remained insoluble. After filtering the hot mixture, the hot filtrate was diluted with hot hexane, cooled and the crystalline product was filtered, washed with hexane and dried to give 6.10 g. (56.2%) of VII of m.p. 165.5–168.5 dec. On standing, the filtrate deposited a further 0.95 g. of nearly colorless product of m.p. 164–165.5° dec.

**Hydrolysis of VII.**—A mixture consisting of 1.00 g. (2.6 millimoles) of VII, 10 ml. of concentrated hydrochloric acid and 5 ml. of water was refluxed for 24 hours. The cooled mixture was shaken with chloroform to give a yellow chloroform solution containing XV and an aqueous solution containing suspended XIV, which is only slightly soluble in cold water and chloroform. Pure XV was isolated from the chloroform solution by extraction with sodium bicarbonate solution, acidification, steam distillation and recrystallization. The pure XV had m.p. 122.5–123.5°. The melting

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(6) All melting points and boiling points are uncorrected.

point of a mixture of this acid with authentic XV of m.p. 122.2–123.2 was not depressed. The colorless XIV, filtered from the aqueous layer of the hydrolysis mixture, was dissolved in aqueous sodium bicarbonate solution and the solution was filtered, cooled and acidified. After filtering, washing, and drying, the colorless XIV weighed 0.32 g. (46%) and had m.p. 133.2–136.5°. Recrystallization from water and from hexane–ethanol gave pure XIV of m.p. 137.5–138°.

*Anal.* Calcd. for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10; neut. equiv., 132. Found: C, 63.68; H, 6.25; neut. equiv., 131.

**Preparation of IV.**—To a stirred suspension of 8.7 g. (0.10 equivalent) of I in a solution consisting of 40 ml. of benzene and 6.51 g. (6.4 ml., 0.05 mole) of ethyl acetoacetate was added 7.91 g. (8.1 ml., 0.10 mole) of pyridine in one portion. The reaction mixture was stirred at room temperature for 15 minutes and then heated for one hour with stirring in a bath at 50–60°. After cooling, 100 ml. of cold water, 10 ml. of concentrated hydrochloric acid and 50 ml. of ether were added with stirring and the mixture was filtered with suction. After separating the aqueous layer of the filtrate, it was extracted with ether and the combined ether solution was dried with magnesium sulfate. The magnesium sulfate was filtered and the ether removed *in vacuo* to leave 13.15 g. of yellow, greasy, crystalline product. Because of the unstable nature of this material it was dissolved in ethyl acetate at room temperature, filtered, and diluted with four volumes of hexane at room temperature. When cooled in ice, colorless crystals of IV separated which when filtered and dried weighed 4.32 g. (30.2%) and had m.p. 117–121° dec.

The crude product (12.00 g.) from a similar preparation was stirred with benzene at room temperature, filtered, washed with benzene and dried to give 5.91 g. (41.2%) of colorless IV of m.p. 118.5–121.5° dec. Attempts to purify these materials further gave crystals having lower and broader melting points.

**Hydrolysis of IV.**—A solution of 1.00 g. (3.5 millimoles) of IV in 15 ml. of concentrated hydrochloric acid (175 millimoles) and 5 ml. of water was refluxed for 17 hours, cooled, and freed of most of the water and hydrogen chloride *in vacuo*. The wet salt ($NH_4Cl$) residue was shaken with six 10-ml. portions of ether at the boiling point. After drying the combined ether extract with magnesium sulfate and filtering, the ether was removed to leave 0.83 g. of a liquid mixture of acids. The mixture was dissolved in 5 ml. of distilled water, made basic with aqueous ammonia and diluted to 10 ml.

When this solution was chromatographed on circular filter paper as previously described[2] using a developer prepared by mixing 85 ml. of commercial absolute ethanol, 15 ml. of distilled water and 1.0 ml. of 28% aqueous ammonia (developer 1), it separated into four spots. One of these had not moved from the point of application of the mixture. The remaining three were identified as X, XII and XIII; $R_f$ values for mixture: 0.36, 0.56, 0.61. The $R_f$ values of the authentic acids are X, 0.37; XII, 0.58; XIII, 0.60.[2] When the mixture was chromatographed using a more polar developer prepared from 75 ml. of commercial absolute ethanol, 25 ml. of distilled water and 1.0 ml. of 28% aqueous ammonia (developer 2), the spot remaining at the point of application with developer 1 was separated into three components. The middle spot of these three was identified as XI. $R_f$ values for the three inner spots were 0.31, 0.38 and 0.47. $R_f$ value of authentic XI (developer 2) is 0.41.[2] The identification of all acids was made by running the authentic acids on the same sheet of paper with the mixture as well as by $R_f$ values.

**Preparation of VIII.**—To a stirred suspension of 17.2 g. (0.2 equivalent) of I in 80 ml. of benzene containing 16.22 g. (0.1 mole) of benzoylacetone was added 15.8 g. (16.2 ml., 0.2 mole) of pyridine in one portion. The stirred mixture was heated for one hour with a bath at 50–60°, cooled, and 200 ml. of cold water, 18 ml. of concentrated hydrochloric acid and 200 ml. of hexane were added. The mixture was filtered and the brown granular solid was washed with water and hexane and dried. The solid (32.46 g.) was continuously extracted with ether in a Soxhlet extractor for 6 hours. Removal of the ether from the extract left 23.1 g. of pale yellow crystalline VIII. One recrystallization from benzene gave 17.67 g. (55.4%) of product having m.p. 160–161.5°.

**Hydrolysis of VIII.**—A mixture of 1.68 g. (5.28 millimoles) of VIII, 15 ml. of concentrated hydrochloric acid, and 5 ml. of water was refluxed for 16 hours. A partly crystalline mixture of acids (1.16 g.) was isolated and converted to ammonium salts as previously described. When chromatographed using developer 1, the mixture separated into six spots whose $R_f$ values were 0.34, 0.44, 0.61, 0.68, 0.78 and 0.86. The four inner spots were shown to be due to X, XIV, XII and XV. The $R_f$ values for the authentic acids are X, 0.37; XIV, 0.44; XII, 0.58; and XV, 0.70.

Refluxing 5.00 g. (15.7 millimoles) of VIII with 15 ml. of concentrated hydrochloric acid and 5 ml. of water for 18 hours gave a reaction mixture from which 1.74 g. (41.8%) of impure XIV of m.p. 129.5–134.5° was isolated. The XIV was isolated by diluting the reaction mixture with water, steam distilling to remove XV and crystallizing the XIV from the distilland by cooling. The pure XIV from this hydrolysis was shown to be identical with the XIV formed in the hydrolysis of VII by the melting point of a mixture, comparison of their infrared spectra and paper chromatography.

**Preparation of Authentic X.**—Reaction of acrylonitrile with ethyl acetoacetate by the method of Bruson and Riener[7] gave $\gamma$-acetyl-$\gamma$-carboxyethylpimelonitrile (48%) of m.p. 82–83°, reported[7] m.p. 82°. Refluxing 10.00 g. (0.042 mole) of this solid with 20 ml. (0.65 mole) of concentrated hydrochloric acid and 10 ml. of water for 16.5 hours gave a solution from which 8.53 g. (99.8%) of crude X was isolated by removing the water and hydrogen chloride *in vacuo* and extracting the acid from the ammonium chloride with ether. The crude acid was a clear, yellow, viscous liquid[8] which could not be distilled at 0.1 mm. without decomposition (*i.e.*, formation of a water-insoluble neutral liquid with an ester-like odor). When a solution of the ammonium salt of this crude acid was chromatographed using developer 1, an $R_f$ value of 0.37 was obtained. Small amounts of three acid impurities of greater $R_f$ value also were present. These may be incomplete hydrolysis products containing only one carboxyl group.

**Acknowledgments.**—The author is indebted to T. L. Gresham for his interest and encouragement, to J. R. Kubik and A. K. Kuder for analyses, and to J. P. Kiehl, J. J. Shipman and A. Hawthorne for the determination and interpretation of infrared absorption spectra.

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