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

Vinylidene Cyanide. IX.[1a,b] Reaction of Polyvinylidene Cyanide with Compounds Containing a Single Active Hydrogen Atom

BY J. C. WESTFAHL

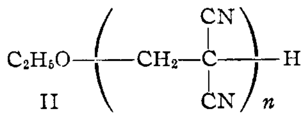
RECEIVED SEPTEMBER 20, 1957

Because of the structural similarity of vinylidene cyanide (I) and acrylonitrile, vinylidene cyanide was expected to react with active hydrogen compounds when catalyzed by bases. The great ease of anionic polymerization of vinylidene cyanide by such weak bases as water, however, precludes such reactions. This paper reports the base-catalyzed reaction of low molecular weight polyvinylidene cyanide with active hydrogen compounds containing a single active hydrogen atom (A–H) to give products having the structure A–$CH_2CH(CN)_2$.

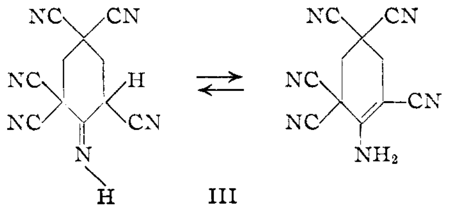
An uncatalyzed reaction of vinylidene cyanide (I) with enolized 1,3-dicarbonyl compounds was reported previously.[1a] The great ease of anionic polymerization of vinylidene cyanide[2,3] makes the base-catalyzed reactions of vinylidene cyanide with active hydrogen compounds virtually impossible. This paper reports the base-catalyzed reaction of low molecular weight polyvinylidene cyanide with certain active hydrogen compounds.

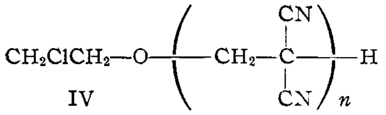
When an attempt was made to add vinylidene cyanide to a stirred solution of diethyl malonate containing pyridine, polyvinylidene cyanide formed immediately as an amorphous solid. On warming the mixture, heat was evolved, the polymer dissolved and a mixture of $CH(COOC_2H_5)_2$-$CH_2CH(CN)_2$ and a bis product derived from one molecule of diethyl malonate and two $-CH_2C(CN)_2-$ units was formed. The preparation and structure of the bis compounds derived from active hydrogen compounds of the type XCH_2Y is the subject of a subsequent paper. The products of Table I were prepared using preformed low molecular weight polyvinylidene cyanide prepared by polymerizing vinylidene cyanide with ethanol.

The structure of the ethanol initiated polymer was assumed to be II.[3] Since the end group and the monomer unit contain distinctive elements, two values of n were calculated from the composition of the polymer. The value of n based on the nitrogen content (n_N) was 7.8 and the value based on oxygen content (n_O) was 4.8. Polymer II thus has an average n of approximately six. Attempts to determine the molecular weight of polymer II ebullioscopically in acetonitrile or acetone failed because of the reactivity of polymer II as indicated by the development of a brown color in the refluxing solution and by molecular weight values near one hundred. The high reactivity of polymer II was further shown by the formation of III[4] when an acetone solution of II was allowed to stand for 30 minutes at room temperature.


II

$$C_2H_5O\left(CH_2-\overset{CN}{\underset{CN}{C}}\right)_n H$$

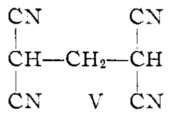

III


IV

$$CH_2ClCH_2-O\left(CH_2-\overset{CN}{\underset{CN}{C}}\right)_n H$$

A polymer prepared using 2-chloroethanol to initiate the polymerization of vinylidene cyanide was assumed to have structure IV. The three values of n calculated from the composition of the polymer were n_N 7.0, n_{Cl} 8.1 and n_O 5.2 or an average n of approximately seven. A solution of 0.4 g. of polymer IV per 100 ml. of dimethylformamide containing 2% of sulfur dioxide had an intrinsic viscosity of 0.052 as compared with an intrinsic viscosity of 3.52 for an identical solution of a high molecular weight polyvinylidene cyanide prepared by the method of Gilbert, *et al.*[3] These results lend support to the low molecular weight nature of polymers II and IV.

Polymers II and IV and the high molecular weight polyvinylidene cyanide all functioned as sources of $-CH_2-C(CN)_2-$ units in the base-catalyzed reaction with active hydrogen compounds, although the yield of product obtained with the high molecular weight polymer was considerably lower than with polymers II and IV. The considerable structural similarity between polymer II and 1,1,3,3-tetracyanopropane (V)[5] suggested that V might also act as a source of $-CH_2C(CN)_2-$ units in the base-catalyzed reaction with active hydrogen compounds. Reaction of 2-nitropropane with V using piperidine as a catalyst gave a 42.4% yield of α-cyano-γ-methyl-γ-nitrovaleronitrile (VI) and a small amount (11.7%) of III. The formation of III is not surprising since V can function both as a source of $-CH_2C(CN)_2-$ units and as an active hydrogen compound. The conversion of V to III by boiling water has been reported.[5]


V

$$\underset{CN}{\overset{CN}{CH}}-CH_2-\underset{CN}{\overset{CN}{CH}}$$

It is evident from Table I that the basicity of the catalyst should be suited to the active hydrogen

---

[1] (a) For the preceding paper in this series, THIS JOURNAL, **78**, 2588 (1956). (b) Presented in part at the 132nd Meeting of the American Chemical Society in New York, N. Y., September 9, 1957.

[2] A. E. Ardis, *et al.*, THIS JOURNAL, **72**, 1305 (1950).

[3] H. Gilbert, *et al.*, *ibid.*, **76**, 1074 (1954).

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

[5] O. Diels, H. Gartner and R. Kaack, *Ber.*, **55**, 3439 (1922).

TABLE I

$A{-}CH_2CH(CN)_2$

No.	A–H	Base	Yield, % (M.p., °C.)	M.p., °C. pure	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
VI	$CH(CH_3)_2NO_2$	Piperidine	55.6 (79–81.5)	82–83	50.29	5.43	25.14	50.20	5.46	25.26
VII	$CH(Et)(COOEt)_2$	$NaOC_2H_5$	66.8 (55.5–56.5)	55.5–56.5	58.63	6.81	10.52	58.90	6.89	10.56
VIII	$CH_2(COOEt)_2$	Pyridine	13.9 (distilled)	Liquid[a]						
IX	$CH_3(CH_2)_{11}SH$	Pyridine	74.2 (37–39)	40.5–41.5	68.53	10.06 11.43[b]	9.99	68.52	9.90 11.17[b]	10.04
XI	$C_6H_5CH_2SH$	Pyridine	56.0 (42–47)	47.5–48.5	65.52	4.98 15.85[b]	13.85	65.47	4.99 15.90[b]	13.8

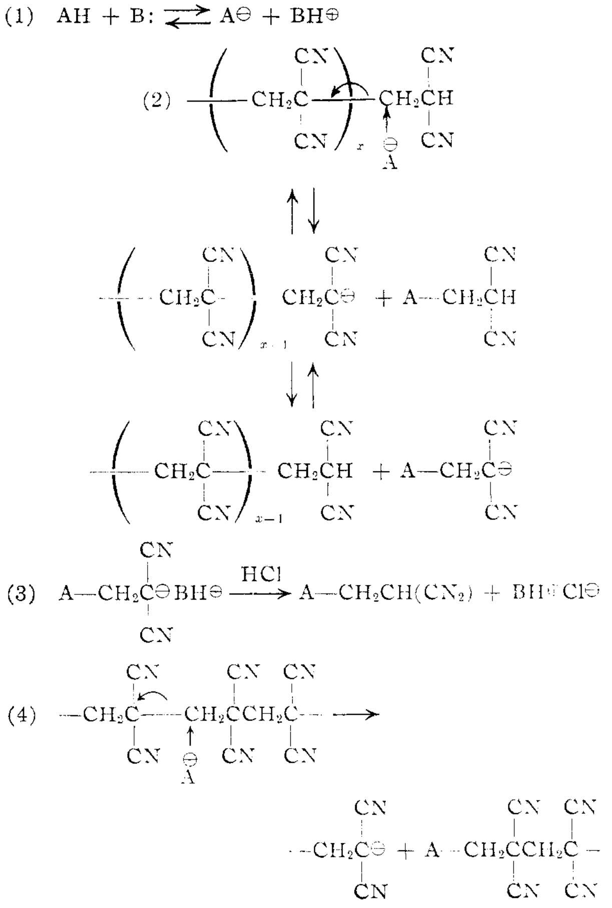
[a] Impure liquid distilled from a mixture of mono and bis product. [b] Sulfur, %.

component. Thus, diethyl malonate reacts readily using pyridine as the catalyst. For reaction of diethyl ethylmalonate, sodium ethoxide is the most desirable catalyst, and for 2-nitropropane reaction occurs readily when piperidine is used.

The structures assigned to the compounds of Table I were based on the acids formed on hydrolysis. The hydrolysis of the product derived from 2-nitropropane (VI) proceeded abnormally and will be the subject of a separate paper.

A plausible mechanism for this reaction is given in Chart I. It may be argued that the polymer anion of equation 2 could "unzip" to produce vinylidene cyanide and that the product may then be formed by reaction of vinylidene cyanide with A^-. Attempts to detect the monomer in a suspension of polymer II in refluxing toluene containing piperidine and anthracene failed. No decrease in anthracene concentration was detected spectrophotometrically. This experiment was based on the analytical procedure of Tyler, Beesing and Averill.[6] In order to demonstrate that the Diels–Alder adduct of anthracene with vinylidene cyanide[7] was stable under the experimental conditions, the experiment was repeated with added preformed adduct. Again no change in anthracene concentration was observed. In these experiments the suspended polymer darkened but did not dissolve. In unsuccessful reactions with active hydrogen compounds and base, polymer II darkened but usually did not dissolve. These observations suggest that the polymer is attacked by A^- and that vinylidene cyanide is not present. The importance of equation 4 (Chart I) is not known. The occurrence of polymer chain scission such as suggested in equation 4 has been reported in solutions of high molecular weight polyvinylidene cyanide containing base.[3] Recent work on the alkaline degradation of polyacrylonitrile also has been interpreted as being due to random attack by base along the polymer chain.[8]

CHART I



Experimental[9]

Preparation of II.—To 143 ml. of a stirred solution consisting of vinylidene cyanide (approximately 39 g., 0.5 mole), acetic acid and chlorobenzene obtained by flash distilling the pyrolysis product of di-(acetyl cyanide),[10] was added 50 ml. of ethanol over an interval of seven minutes. The temperature was kept below 30° and the mixture was stirred for 35 minutes. Hexane (200 ml.) was added, the mixture was stirred for a further ten minutes and then filtered with suction. The polymer was washed with hexane and dried *in vacuo* (0.01 mm. and 60°) to give 37.6 g. of polymer II as a nearly white powder. Assuming structure II (n = 6), the equivalent weight of the polymer is 85.76 g. and the yield is

---

(6) W. P. Tyler, D. W. Beesing and S. J. Averill, *Anal. Chem.*, **26**, 674 (1954).

(7) S. J. Averill and H. L. Trumbull, THIS JOURNAL, **76**, 1159 (1954). The m.p.'s reported for the anthracene adduct with vinylidene cyanide are in error. The m.p. of the adduct is 157.8–158.8°. The m.p. of the benzene solvate is 180–188.5° (previous softening and evolution of gas).

(8) J. R. McCartney, *Modern Plastics*, **30**, 118 (1951); *C. A.*, **48**, 5076 (1954).

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

(10) A. E. Ardis, U. S. Patent 2,663,726 (1953).

87.7%. The polymer was stored at room temperature in dry air.

Anal. Found for II: C, 59.72, 59.78; H, 3.07, 3.06; N, 33.37, 33.40.

Preparation of IV.—To a stirred solution of 10 ml. (9.05 g., 0.116 mole) of 91.35% vinylidene cyanide in 20 ml. of benzene was added 15 ml. of 2-chloroethanol. After stirring for 1.5 hours without cooling the hazy mixture was allowed to stand at room temperature overnight; 50 ml. of hexane was added and the lower polymer layer was stirred to resuspend the polymer. After filtering, washing with hexane and drying as previously described, the white powder (IV) weighed 10.16 g. Assuming the polymer to have structure IV ($n = 7$), the equivalent weight is 89.57 and the yield is 80.7%.

Anal. Found for IV: C, 57.37, 57.32; H, 3.11, 3.14; N, 31.22, 31.29; Cl, 4.95, 4.99; (η), 0.4 g./100 ml. = 0.052 (in dimethylformamide containing 2% SO_2).

α-Cyano-γ-methyl-γ-nitrovaleronitrile (VI).—To a stirred solution prepared from 8.8 ml. of 90% vinylidene cyanide (7.8, 0.1 mole) and 40 ml. of benzene was added a solution of 10 ml. of ethanol in 10 ml. of benzene over an 8-minute interval without cooling. After stirring for a further 30 minutes monomer could no longer be detected by odor. The benzene and ethanol were removed *in vacuo* (60° and 0.01 mm.) and the colorless polymer (II) was suspended in an excess (40.0 g., 0.45 mole) of 2-nitropropane (b.p. 118–118.5°, $d^{25}{}_4$ 0.991, $n^{25}{}_D$ 1.3925). To the stirred suspension at 23° was added 10.0 ml. (8.52 g., 0.1 mole) of piperidine from a pipet whose efflux time was 30 seconds. When the pipet was empty the temperature of the reaction mixture was 45°, its color was reddish-brown, and no suspended polymer was evident. The uncooled mixture reached a maximum temperature of 47° and after 15 minutes was at 28.5°. After cooling in ice, 100 ml. of cold water, 8 ml. of concentrated hydrochloric acid and 100 ml. of ether were added and the mixture was filtered with suction to remove a small amount of II. The aqueous layer of the filtrate was separated and extracted once with ether and the combined ether solution was dried with magnesium sulfate. After filtering, the ether and excess 2-nitropropane were removed (60° and 0.05 mm.) to leave 13.03 g. (77.9%) of brown crystalline VI. One recrystallization from ethanol gave 9.32 g. (55.6%) of pale yellow VI of m.p. 79–81.5°.

α-Cyano-γ,γ-dicarbethoxycapronitrile (VII).—A solution of 2.30 g. (0.1 g. atom) of sodium in 35 ml. of ethanol was treated with 56.46 g. (0.3 mole) of diethyl ethylmalonate[11] and the resulting solution was freed of ethanol *in vacuo*. A small amount of ester was distilled off (60° and 0.01 mm.) to ensure removal of ethanol. To the stirred solution of the sodium salt was added 7.81 g. (0.091 equivalent) of polymer II in one portion. After four minutes the suspension was dark yellow and slightly warm. The mixture was heated for 25 minutes in a water-bath at 50–60° during which time a white finely divided solid separated. After cooling the mixture in ice, 100 ml. of water, 10 ml. of concentrated hydrochloric acid and 50 ml. of ether were added. The mixture was filtered with suction (Filter-aid) to remove a small amount of polymer. The aqueous layer of the filtrate was extracted with ether and the combined ether solution was dried with magnesium sulfate. After filtering off the magnesium sulfate, the ether was removed *in vacuo* to leave 59.60 g. of ester mixture. The excess diethyl ethylmalonate, removed at 5.0 mm. and an oil-bath temperature of 150–160°, weighed 35.44 g. (94.1% of excess taken). The brown liquid residue (23.19 g.) was distilled at 0.01 mm. to give 21.97 g. (91%) of nearly colorless product. When seeded, the distillate crystallized to a greasy solid. One recrystallization from ethanol gave 15.92 g. (66.1%) of VII of m.p. 55.5–56.5°.

Hydrolysis of VII.—A mixture of 5.00 g. (18.8 millimoles) of VII and 5.00 g. (125 millimoles) of sodium hydroxide in 50 ml. of water was refluxed 17 hours and then boiled to reduce the volume to approximately 25 ml. The solution was cooled, adjusted to *p*H 6 with hydrochloric acid, and filtered to remove silica. After adding 25 ml. of concentrated hydrochloric acid, the solution was refluxed for four hours to decarboxylate the malonic acid groups. The water and hydrogen chloride were removed *in vacuo* and the residue was extracted with five 10-ml. portions of boiling ether. After drying the ether solution with magnesium sulfate and filtering, the ether was removed *in vacuo* to leave 2.55 g. (83.6%) of liquid α-ethylglutaric acid.

The acid was identified by conversion to the anhydride by refluxing with acetyl chloride and reaction of the anhydride with *p*-toluidine to give a 38.7% yield of the benzene-insoluble isomeric N-*p*-tolyl-α-ethylglutaramic acid. The purified glutaramic acid had m.p. 148–148.5°, reported[12] m.p. of the benzene-insoluble isomer 145.5°.

Refluxing the glutaramic acid gently at atmospheric pressure eliminated water to give N-*p*-tolyl-α-ethylglutarimide of m.p. 96–97°, reported[12] m.p. 94–95°.

Reaction of II with Diethyl Malonate.—To 0.1 equivalent of polymer II suspended in 160 g. (1.0 mole) of diethyl malonate was added 8.1 ml. (7.9 g., 0.1 mole) of pyridine in one portion. After stirring for ten minutes the reaction mixture was red in color and suspended polymer was absent. The stirred solution was heated for two hours at 50–60° and allowed to stand at room temperature unstirred overnight. The reaction mixture was treated with 100 ml. of water and 10 ml. of concentrated hydrochloric acid and worked up as described previously. The crude ester mixture weighed 161.6 g. Removal of excess diethyl malonate (144.7 g.) left 15.1 g. of a partly crystalline mixture of mono and bis product. One recrystallization from ethanol gave 5.75 g. of light yellow bis compound of m.p. 140.5–142°. Recrystallization gave colorless bis compound of m.p. 143.5–144.5°.

Anal. Calcd. for $C_{15}H_{16}N_4O_4$: C, 56.95; H, 5.10; N, 17.71. Found: C, 57.09; H, 5.14; N, 17.71.

The filtrate from the above mixture when freed of ethanol weighed 8.50 g. Distillation gave 3.31 g. of colorless α-cyano-γ,γ-dicarbethoxybutyronitrile (VIII) of b.p. 115–127° (0.02 mm.) and a residue of 4.79 g. The distilled VIII (3.31 g., 13.9 millimoles) was refluxed for 23 hours with a solution prepared from 4.0 g. (100 millimoles) of sodium hydroxide and 30 ml. of water. The solution was cooled, acidified to congo red, filtered, and extracted with 100 ml. of ether in ten portions. The combined ether extract was dried with magnesium sulfate and freed of ether to leave 0.87 g. (28.4%) of crude 1,1,3,3-tetracarboxypropane. When dissolved in ethyl acetate–ethanol and precipitated with hexane, the colorless acid had m.p. 173° (with evolution of gas). 1,1,3,3-Tetracarboxypropane is reported to melt at 168–170° (with evolution of carbon dioxide) and to yield glutaric acid on decarboxylation.[13] Decarboxylation by heating at 180–185° followed by one recrystallization from benzene gave glutaric acid of m.p. 94–97°. The m.p. of a mixture with authentic glutaric acid was not depressed.

α-Cyano-β-dodecylmercaptopropionitrile (IX).—To a stirred suspension of 4.40 g. (0.051 equivalent) of polymer II in a solution consisting of 40 ml. of benzene and 10.12 g. (0.05 mole) of dodecylmercaptan was added 4.1 ml. (4.0 g., 0.05 mole) of pyridine in one portion. After heating in a water-bath at 50–60° for 30 minutes, the mixture was cooled and 50 ml. of water and 5 ml. of concentrated hydrochloric acid was added. When the mixture was filtered and the benzene layer of the filtrate was separated, dried and freed of benzene, the yellow liquid (13.90 g.) crystallized. One recrystallization from hexane gave 10.50 g. (74.8%) of pale yellow IX of m.p. 37–39°.

Refluxing a mixture consisting of 2.00 g. (7.1 millimoles) of IX, 15 ml. (175 millimoles) of concentrated hydrochloric acid and 10 ml. of glacial acetic acid for 16 hours gave, after cooling and diluting with water, 1.47 g. (75%) of crude β-dodecylmercaptopropionic acid (X) of m.p. 54–58°. Recrystallization from hexane raised the m.p. to 59–61.5°. The reported[14] m.p. of β-dodecylmercaptopropionic acid is 61–62°.

Oxidation of X as its sodium salt in aqueous solution, with potassium permanganate gave β-dodecylsulfonylpropionic acid (41.8%) of m.p. 135–137°, reported[14] m.p. 134–135°.

α-Cyano-β-benzylmercaptopropionitrile (XI).—Reaction of 3.90 g. (45.4 millimoles) of II, 6.21 g. (50 millimoles) of benzyl mercaptan and 3.96 g. (50 millimoles) of pyridine in 40 ml. of benzene gave 5.14 g. (56%) of crude XI of m.p. 42–47°. The solid could be recrystallized from ethanol–water or benzene–hexane.

Refluxing 1.00 g. (4.9 millimoles) of XI for 16.5 hours with

---

[11] Benzol Products Co., Newark, N. J.

[12] K. Auwers and A. W. Titherley, *Ann.*, **292**, 213 (1896).

[13] C. Kleber, *Ann.*, **246**, 106 (1888).

[14] L. Rapoport, A. Smith and M. Newman, This Journal, **69**, 693 (1947).

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.

BRECKSVILLE, OHIO

---

[15] B. Holmberg, *Arkiv Kemi, Mineral. Geol.*, **14A**, No. 8 (1940); *C. A.*, **35**, 2114[5] (1941).

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

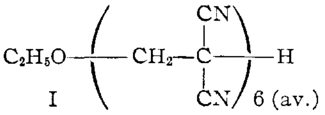
Vinylidene Cyanide. X. Reaction of Polyvinylidene Cyanide with Active Hydrogen Compounds of the Type XCH_2Y

BY J. C. WESTFAHL

RECEIVED OCTOBER 8, 1957

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)

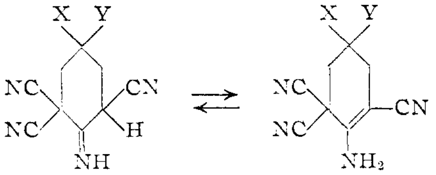


$$C_2H_5O\left(CH_2-\overset{CN}{\underset{CN}{\overset{|}{\underset{|}{C}}}}\right)_{6\ (av.)}H$$

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

---

[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).