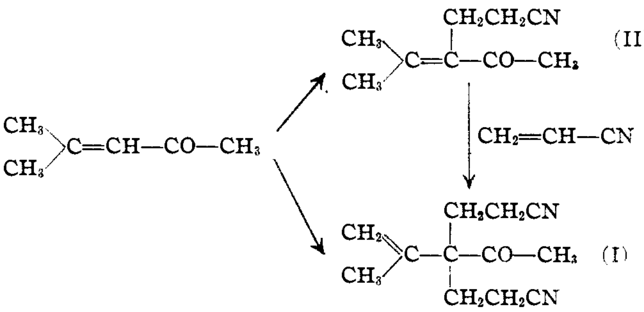
[Contribution from Röhm and Haas Co., Inc., and Resinous Products and Chemical Co.]

The Chemistry of Acrylonitrile. III. Cyanoethylation of Alpha,Beta-unsaturated Compounds

By Herman Alexander Bruson and Thomas W. Riener

The reaction of two moles of acrylonitrile with one mole of mesityl oxide in the presence of trimethylbenzylammonium hydroxide or potassium hydroxide as a catalyst by the general method of cyanoethylation described in the preceding paper[1] yielded two products, one of which was a crystalline dicyanoethylation product (75% yield) and the other a liquid mono-cyanoethylation product (10–15% yield).

The structure of the dicyanoethylation product is that of γ-acetyl-γ-isopropenylpimelonitrile (I) which is formed by a 1,3-shift of one of the isopropyl hydrogens of the mesityl oxide, induced by the action of the alkali and the very powerful acceptor characteristics of acrylonitrile. The liquid mono-cyanoethylation product (II) upon treatment with additional acrylonitrile in the presence of alkali is converted into γ-acetyl-γ-isopropenylpimelonitrile. The reaction, therefore, can be formulated as follows

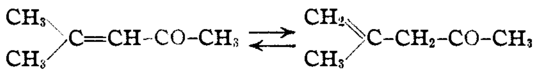


(II)

(I)

The fact that mesityl oxide appears to exist in two slightly different isomeric forms has already been noted by Harries.[2]

In view of the work of Kon,[3] Linstead[4] and others upon α,β-unsaturated ketones which possess a three-carbon desmotropic system, it appears probable that mesityl oxide exists in two desmotropic forms in equilibrium with each other



$$(CH_3)_2C{=}CH\text{-}CO\text{-}CH_3 \rightleftarrows CH_2{=}C(CH_3)\text{-}CH_2\text{-}CO\text{-}CH_3$$

The tendency of acrylonitrile to first di-cyanoethylate the —CH_2— group in ketones having the radical —CH_2—CO—CH_3 undoubtedly freezes this equilibrium toward the right, the —CH_2— group being activated both by the carbonyl and vinylidene group in the mesityl oxide desmotrope.

The structure of (I) was determined by the sequence of reactions shown in the flow diagram, Fig. 1.

Compound I was hydrolyzed by boiling with aqueous sodium hydroxide solution. Upon acidification the dicarboxylic acid (III) was obtained in 90% yield. This acid was subjected to the haloform reaction whereupon chloroform was evolved and the tricarboxylic acid (IV) was isolated in pure form. Compound IV was then hydrogenated in aqueous solution in the form of its sodium salt, by means of Raney nickel catalyst. The γ-carboxy-γ-isopropylpimelic acid (V) obtained from this hydrogenated sodium salt was found to be identical with that synthesized by dicyanoethylating methyl isobutyl ketone to form (VI), hydrolyzing (VI) to γ-acetyl-γ-isopropylpimelic acid (VII), and subjecting the latter to the haloform reaction whereby chloroform was evolved and (V) isolated in pure form. A mixed melting point of the two compounds gave no depression of the melting point of either.

Since mesityl oxide showed this behavior with acrylonitrile it was of interest to investigate also the action of acrylonitrile upon α-β unsaturated nitriles which are known to form three-carbon desmotropic systems that readily undergo a 1,3-hydrogen shift.[5]

The reaction of crotononitrile with two moles of acrylonitrile in the presence of trimethylbenzylammonium hydroxide as a catalyst yielded two products. One of these was a liquid mono-cyanoethylation product and the other a crystalline dicyanoethylation product. The same products were also obtained by treating acrylonitrile with allyl cyanide, which under the influence of alkali rearranges to crotononitrile.

The liquid mono-cyanoethylation product upon

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(1) Bruson and Riener, This Journal, **64**, 2850 (1942).

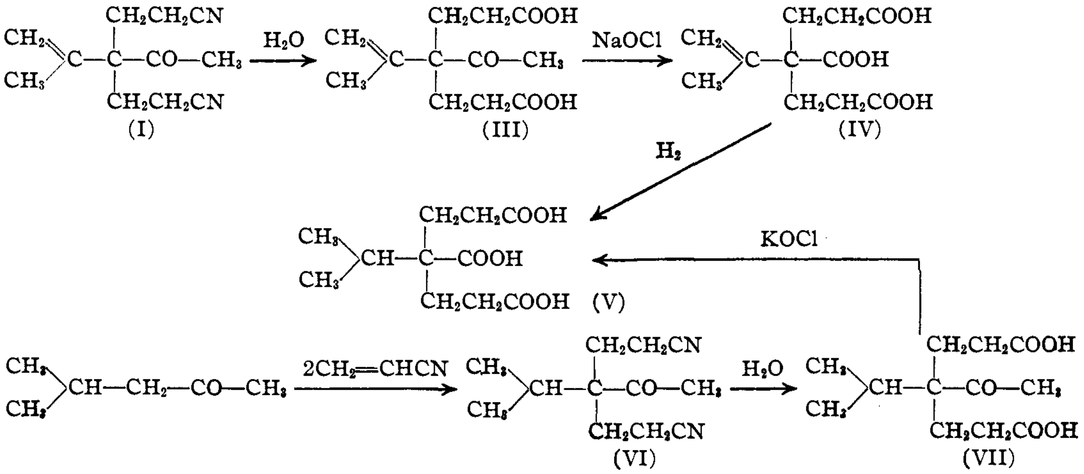
(2) Harries, *Ber.*, **32**, 1326 (1899); *Ann.*, **330**, 189 (1904).

(3) Birch, Kon and Norris, *J. Chem. Soc.*, 1364 (1923).

(4) Kon and Linstead *ibid.*, 1269 (1929); Eccott and Linstead, *ibid.*, 905 (1930).

(5) Birch and Kon, *ibid.*, 2440 (1923); Kandiah and Linstead, *ibid.*, 2139 (1929).

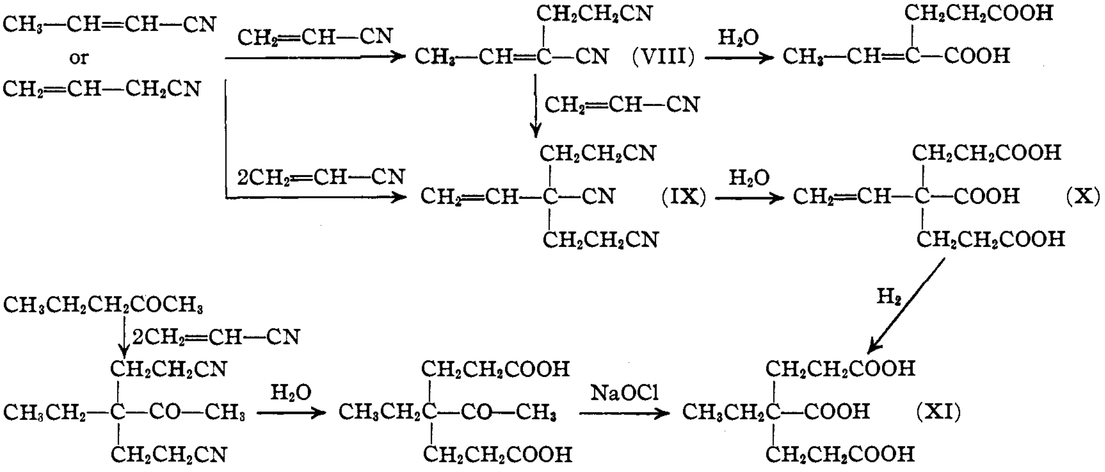
FIGURE 1



treatment with one mole of acrylonitrile in the presence of alkali was converted into the crystalline di-cyanoethylation product. The mono-cyanoethylation product was identified as α-ethylideneglutaronitrile (VIII) since upon saponification it yielded the known α-ethylideneglutaric acid.

The dicyanoethylation product was found to be γ-cyano-γ-vinylpimelonitrile (IX), by the sequence of reactions shown in the flow diagram, Fig. 2.

FIGURE 2



Upon saponification, the di-cyanoethylation product yielded the tricarboxylic acid (X). This upon hydrogenation in aqueous solution in the form of its sodium salt by means of Raney nickel catalyst, yielded γ-carboxy-γ-ethylpimelic acid (XI), which was found to be identical with that synthesized by dicyanoethylating methyl-*n*-propyl ketone to γ-acetyl-γ-ethylpimelonitrile, and subjecting the γ-acetyl-γ-ethylpimelic acid derived therefrom to the haloform reaction as described in the preceding paper.[6]

It is thus evident that the equilibrium between allyl cyanide and crotononitrile

$$CH_2{=}CH{-}CH_2CN \rightleftarrows CH_3{-}CH{=}CH{-}CN$$

which is almost 95% toward the right in the presence of alkali[7] appears to be in the reverse direction when acrylonitrile is present as an acceptor of the shifting hydrogen atom, the —CH_2 group in the allyl cyanide being activated both by the ethylene linkage and the cyano group.

In a similar manner, acrylonitrile was condensed with β-methylcrotononitrile or with methallyl cyanide, to give a liquid mono-cyanoethylation product and a crystalline di-cyanoethylation

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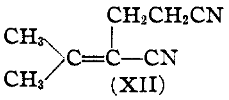
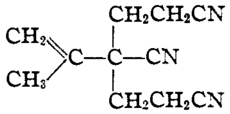
[6] Bruson and Riener, THIS JOURNAL, 64, 2850 (1942).

[7] Letch and Linstead, *J. Chem. Soc.*, 443 (1932).

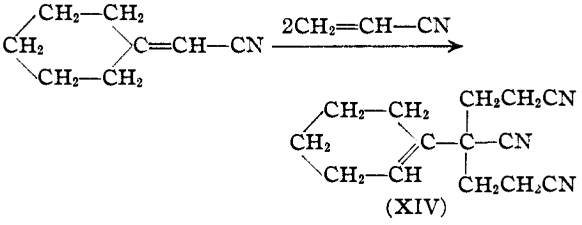
which by analogy should possess the structures (XII) and (XIII), respectively.


(XII)

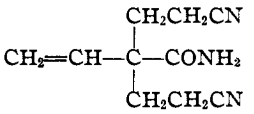

(XIII)

One attempt was made to prove the structure of (XIII) by saponifying it to the tricarboxylic acid, which upon hydrogenation should yield γ-carboxy-γ-isopropylpimelic acid (V) identical with that derived by the haloform reaction from the dicyanoethylation of mesityl oxide as shown in Fig. 1. The attempt failed, however, because under the experimental conditions used, namely, boiling under reflux with aqueous 10% sodium hydroxide solution for fourteen hours, only two cyano groups were hydrolyzed, leaving the third cyano group, presumably the tertiary one, intact. This resistance toward hydrolysis was surprising in view of the relative ease of hydrolysis of compound IX which differs from XIII by only a methyl group.

Acrylonitrile was also condensed with cyclohexylidene-acetonitrile in the presence of trimethylbenzylammonium hydroxide as a catalyst. In this case the main product was a crystalline dicyanoethylation product which, in view of the foregoing discussion, is undoubtedly represented by Formula (XIV)


(XIV)

The reaction of acrylonitrile with crotonamide in the presence of aqueous 40% trimethylbenzylammonium hydroxide as a catalyst, yielded a crystalline dicyanoethylation product, which, by analogy with the crotononitrile reaction, is α,α-di-(2-cyanoethyl)-vinylacetamide (XV).


$$CH_2{=}CH{-}C(CH_2CH_2CN)_2{-}CONH_2 \quad \text{(XV)}$$

No reaction occurred when cinnamonitrile was treated with acrylonitrile in the presence of trimethylbenzylammonium hydroxide. Nor did acrylonitrile condense under the above conditions with α-methylacrylonitrile, possibly because these compounds do not possess a mobile hydrogen atom capable of a 1,3-shift.

Experimental

I. **γ-Acetyl-γ-isopropenylpimelonitrile.**—To a solution of 98 g. of pure mesityl oxide (1 mole) and 100 g. of tertiary butyl alcohol, 5 g. of aqueous 40% trimethylbenzylammonium hydroxide ("Triton B") was added at 25° with rapid stirring. The stirred mixture was held in an ice-salt bath at 5-10° while 106 g. of acrylonitrile (2 moles) was added dropwise thereto during a period of two hours. The crystals were filtered off from the cold reaction mixture and air dried; yield 150 g. (73.5% of theory). Upon recrystallization from methanol the product formed colorless crystals melting at 116-117°. *Anal.* Calcd. for $C_{12}H_{16}N_2O$: C, 70.54; H, 7.90; N, 13.71. Found: C, 70.90; H, 7.98; N, 13.59.

The filtrate was made slightly acid with dilute hydrochloric acid and evaporated to dryness at 90° in vacuum. From the sticky residue more of the above crystalline product can be separated.

II. **1-(β-Cyanoethyl)-1-isopropylidene-acetone.**—By combining the slightly acidified filtrates from several of the above preparations and distilling the sticky residue in vacuum, a colorless oil boiling at 110-115° (2 mm.) was isolated in 10-15% yield. *Anal.* Calcd. for $C_9H_{13}NO$: N, 9.26. Found: N, 9.37.

Upon mixing one mole equivalent of (II) in an equal volume of tertiary butyl alcohol with 5% by weight of "Triton B" and one mol equivalent of acrylonitrile at 10-15° a crystalline product identical with compound I separated in about 50% yield.

III. **γ-Acetyl-γ-isopropenylpimelic Acid.**—A mixture consisting of 45 g. of potassium hydroxide, 500 cc. of water and 65 g. of (I) was boiled under reflux for four hours. The solution was treated with bleaching charcoal, filtered and the filtrate acidified with concentrated hydrochloric acid at 5-10°. The precipitated acid weighed 62 g. After recrystallization from water it formed colorless crystals; m. p. 136-137°. *Anal.* Calcd. for $C_{12}H_{18}O_5$: C, 59.47; H, 7.49. Found: C, 59.85; H, 7.51.

IV. **γ-Carboxy-γ-isopropenylpimelic Acid.**—A solution of 175 g. of potassium carbonate (anhydrous), 50 g. of potassium hydroxide and 500 cc. of water was added to a stirred suspension of 250 g. of calcium hypochlorite ("HTH" containing 70% available Cl) in 1000 g. of water at 50°. The precipitated calcium carbonate was filtered off and to the clear filtrate at 60-70° there was added dropwise a solution of 121 g. of compound III in 300 g. of aqueous 20% sodium hydroxide, with constant stirring. Chloroform was evolved. The mixture was stirred for several hours after reaction had apparently ceased; excess hypochlorite was destroyed by sodium bisulfite solution, and the product acidified with concentrated hydrochloric acid and evaporated to dryness in vacuum on a steam-bath. The dry residue was extracted with acetone. Upon evaporation of the acetone 115 g. of crystalline product was obtained. After recrystallization from water in which it is very soluble, or from nitromethane, it formed colorless crystals, m. p. 160°. *Anal.* Calcd. for $C_{11}H_{16}O_6$: C, 54.07; H, 6.60. Found: C, 53.84; H, 6.49.

V. γ-Carboxy-γ-isopropylpimelic Acid.—A solution comprising 24.4 g. of IV, 68 cc. of water and 12 g. of sodium hydroxide was made exactly neutral to phenolphthalein with a little 10% sodium hydroxide solution; 7 g. of Raney nickel catalyst was added and the whole hydrogenated at 135° for several hours at 115 atm. pressure. The solution, after filtration, was acidified with concentrated hydrochloric acid, cooled to 5° and the crystals filtered off. After several recrystallizations from nitromethane they melted at 158–159°, and after one more recrystallization from water, at 160°. A mixed melting point with IV (m. p. 160°) gave a 16° depression. *Anal.* Calcd. for $C_{11}H_{18}O_6$: C, 53.63; H, 7.37. Found: C, 53.80; H, 7.25.

VI. γ-Acetyl-γ-isopropylpimelonitrile.—To a stirred solution of 150 g. of methyl isobutyl ketone, 150 g. of tertiary butyl alcohol and 10 g. of aqueous 40% trimethylbenzylammonium hydroxide there was added dropwise 159 g. of acrylonitrile during the course of eighty minutes while maintaining the reaction mixture at 32–35°. The mixture was stirred for three hours longer, then faintly acidified with dilute hydrochloric acid, and shaken with an equal volume of ethylene dichloride. The ethylene dichloride solution was washed several times with water, then evaporated to dryness in vacuum on a steam-bath. The residual dark oil (163 g.) was distilled in vacuum, to give a poor yield of the dicyanoethylation product. The fractions boiling at 175–195° (2 mm.) (6 g. partially crystalline) and at 195–225° (2 mm.) (13 g. crystals) yielded the same product, m. p. 101° after recrystallization from methanol. Calcd. for $C_{12}H_{18}N_2O$: N, 13.58. Found: N, 13.50.

The residue was a high-boiling tar containing higher cyanoethylation products.

VII. γ-Acetyl-γ-isopropylpimelic Acid.—A mixture of 10 g. of VI melting at 100–101°, 80 g. of water and 8 g. of sodium hydroxide was boiled under reflux for nine hours. The solution was treated with "Norite," filtered, acidified with concentrated hydrochloric acid, cooled to 5° and the crystalline product filtered off; yield 10 g. The analytical sample after recrystallization from water to a constant melting point melted at 148°. *Anal.* Calcd. for $C_{12}H_{20}O_5$: C, 58.98; H, 8.26. Found: C, 59.10; H, 8.15.

Oxidation of VII to γ-Carboxy-γ-isopropylpimelic Acid.—A solution of 13 g. of potassium carbonate (anhydrous), 3.7 g. of potassium hydroxide and 37 cc. of water was added to a stirred suspension of 18.5 g. of calcium hypochlorite ("HTH" containing 70% available Cl) in 75 cc. of water at 50°. The precipitated calcium carbonate was filtered off, the precipitate washed with 50 cc. of water and the washings combined with the filtrate. To this clear stirred solution, a solution of 9 g. of VII in 22.2 g. of aqueous 20% sodium hydroxide was added dropwise at 55–65°. Chloroform was evolved. The mixture was stirred for one hour at 65° after the reaction had apparently ceased and excess hypochlorite destroyed by adding sodium bisulfite solution. The product was acidified with concentrated hydrochloric acid, cooled to 0°, and the crystals filtered off. They melted at 160–161° after recrystallization from either water or nitromethane, and gave no depression of melting point when mixed with V. *Anal.* Calcd. for $C_{11}H_{18}O_6$: C, 53.63; H, 7.37. Found: C, 53.50; H, 7.28.

Cyanoethylation of Allyl Cyanide.—A mixture of 134 g. of allyl cyanide (2 moles) and 106 g. of acrylonitrile (2 moles) was added dropwise during three hours to a stirred solution of 50 g. of tertiary butyl alcohol and 4 g. of "Triton B" while maintaining the reaction mixture at 10–15° by means of an ice-bath. The mixture was then stirred for one hour longer at 10° and finally at room temperature for one hour. Since the odor of acrylonitrile still seemed to be present, 3 g. more of "Triton B" was added and the mixture stirred for one hour longer. Dilute hydrochloric acid was then added dropwise until the mixture was acidic toward congo red. The product was taken up in an equal volume of ethylene dichloride, shaken with 25 cc. of water, and the ethylene dichloride layer separated and evaporated to dryness in vacuum (30 mm.) on a steam-bath. The residual oil (189 g.) was distilled in vacuum, to give: (A) 41.5 g., boiling up to 210° (1 mm.) (mostly 100–120° (1 mm.)), (B) 96 g., b. p. 210–245° (1 mm.) viscous yellow oil.

VIII. α-Ethylidene-glutaronitrile.—Fraction (A) above was redistilled at 10 mm. and the fraction boiling at 134–137° (10 mm.) as a colorless oil, was collected; yield 21 g. *Anal.* Calcd. for $C_7H_8N_2$: N, 23.32. Found: N, 22.86. It possessed the following constants: n^{25}_D 1.4636, d^{25}_4 0.9622.

Hydrolysis of (VIII) to α-Ethylidene-glutaric Acid.—A mixture of 20 g. of (VIII), 18 g. of sodium hydroxide and 150 cc. of water was boiled under reflux for eight hours, treated with "Norite," filtered, acidified with concentrated hydrochloric acid and evaporated to dryness. The sticky crystalline residue was dissolved in 100 cc. of water and allowed to crystallize at 5–10°. About 7 g. of crystalline material was isolated which upon recrystallization from water melted at 151–153°. Fichter and Eggert[8] recorded a melting point 152° for α-ethylidene-glutaric acid.

IX. γ-Cyano-γ-vinylpimelonitrile.—Fraction (B) obtained by the distillation of the allyl cyanide–acrylonitrile condensation described above, gradually solidified to a crystalline mass on standing or upon scratching and cooling. Upon recrystallization from hot water or from methanol it formed colorless, long needles melting at 60–61°. The yield of pure product was 80 g. *Anal.* Calcd. for $C_{10}H_{11}N_3$: C, 69.33; H, 6.41; N, 24.26. Found: C, 68.79; H, 6.44; N, 24.27.

Cyanoethylation of α-Ethylidene-glutaronitrile.—To a stirred solution of 18 g. of compound VIII, 30 g. of tertiary butyl alcohol, and 2 g. of "Triton B," there was added dropwise 8 g. of acrylonitrile while cooling to 20–30°. The mixture was stirred for twenty-four hours at room temperature, made faintly acidic with dilute hydrochloric acid, taken up in an equal volume of ethylene dichloride, and shaken with 50 cc. of water to remove salts. The ethylene dichloride layer was evaporated to dryness in vacuum on a steam-bath. The residue (26 g.) was distilled *in vacuo*. About 11 g. of unchanged VIII was recovered (b. p. up to 210° (1 mm.)). At 210–220° (1 mm.) a fraction weighing 8 g. distilled and solidified in the receiver. Upon recrystallization from water it melted at 60–61° and gave no melting point depression when admixed with γ-cyano-γ-vinylpimelonitrile (IX).

X. γ-Carboxy-γ-vinylpimelic Acid.—A mixture of 90 g. of γ-cyano-γ-vinylpimelonitrile (IX), 80 g. of sodium

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(8) Fichter and Eggert, *Ber.*, **31**, 1998 (1898).

hydroxide and 600 cc. of water was boiled under reflux for eight hours. The product was treated with "Norite," filtered, and acidified with concentrated hydrochloric acid. The solution obtained was evaporated to dryness in vacuum on a steam-bath, the residue extracted with hot acetone, and the acetone removed under reduced pressure to yield 117 g. of almost white solid. After recrystallization from a mixture of nitromethane–acetone (5:1) this yielded 60 g. of purified crystalline product, m. p. 153°, which remained constant after two more recrystallizations from nitromethane. Calcd. for $C_{10}H_{14}O_6$: C, 52.14; H, 6.13; iodine no., 110. Found: C, 52.37; H, 6.22; iodine no., 107 (Wijs).

XI. γ-Carboxy-γ-ethylpimelic Acid.—A neutral solution of 23 g. of X, 68 cc. of water and 12 g. of sodium hydroxide was prepared, mixed with 7 g. of Raney nickel catalyst and hydrogenated at 135° for one hour at 100–135 atmospheres. The catalyst was filtered off, the filtrate acidified with concentrated hydrochloric acid, and cooled to 5°. The white crystalline precipitate melted crude at 169–170°. After two recrystallizations from water it melted at 171–172°, which melting point remained constant after one more recrystallization from nitromethane. *Anal.* Calcd. for $C_{10}H_{16}O_6$: C, 51.69; H, 6.95. Found: C, 51.60; H, 6.77.

A sample of the above compound showed no depression of melting point when mixed with the γ-carboxy-γ-ethylpimelic acid prepared from the hypochlorite oxidation of γ-acetyl-γ-ethylpimelic acid derived from the dicyanoethylation of methyl *n*-propyl ketone as described in the preceding paper.[9]

Cyanoethylation of Crotononitrile.—The crotononitrile used was a mixture of *cis*- and *trans*-isomers prepared by rearrangement of allyl cyanide as follows. Allyl cyanide (134 g.) was added dropwise to a stirred mixture of 20 g. of tertiary butyl alcohol and 2 g. of "Triton B" during one and one-half hours while maintaining the exothermic reaction at 28–30° by an ice-bath. The mixture was allowed to stand for twenty-four hours at room temperature. It was then carefully neutralized with dilute hydrochloric acid, and washed twice with cold water, dried over sodium sulfate and distilled through an efficient packed column. The following fractions of crotononitrile were obtained at 760 mm.: 36 g. up to 105°; 12.5 g., 105–111° (mostly *cis*); 50.5 g., 111–117° (mixture of *cis* and *trans*); 33.5 g., 117–120 (mostly *trans*); and a residue of 19 g., b. p. 105° (1 mm.) (mostly dicrotononitrile). The second and third fractions were combined since it was possible that the fourth might contain some allyl cyanide (b. p. 119°).

To 83.5 g. of *cis*- and *trans*-crotononitrile (from two runs as above) dissolved in 100 g. of tertiary butyl alcohol containing 5 g. of "Triton B," 199 g. of acrylonitrile (excess) was added dropwise during three and one-half hours while stirring and maintaining the reaction mixture at 29–34° by external cooling. The mixture was then stirred for twenty-two hours at room temperature, neutralized with dilute hydrochloric acid, washed with water, dried and distilled in vacuum. The following fractions were collected: (A) 41 g. up to 210° (1 mm.) (mostly 110–120° (1 mm.); (B) 52 g. 210–255° (1 mm.) (mostly 210–220° (1 mm.)).

Upon redistillation fraction (A) yielded 21.5 g., b. p. 134–137° (10 mm.) identical with α-ethylidene-glutaronitrile (VIII).

Fraction (B) after recrystallization from water yielded 30 g. of colorless, crystalline product m. p. 60–61° identical with γ-cyano-γ-vinylpimelonitrile (IX).

β-Methylcrotononitrile.—This compound was prepared by the rearrangement of methallyl cyanide prepared from methallyl chloride and cuprous cyanide.[10]

To a stirred solution of 10 g. of "Triton B" in 40 g. of tertiary butyl alcohol there was added dropwise 204 g. of methallyl cyanide during the course of two hours while maintaining the reaction temperature between 30 and 45° by external cooling. After the exothermic reaction had ceased, 5 g. more of "Triton B" was added, whereupon the temperature rose to 55°. The mixture after standing eighteen hours at room temperature was neutralized with dilute hydrochloric acid, washed twice with water, dried and distilled through an efficient packed column. The fraction boiling at 140–142° (760 mm.) was collected[11]; yield 161 g. or 80%.

Cyanoethylation of β-Methylcrotononitrile.—To a stirred solution of 81 g. of β-methylcrotononitrile (1 mole), 25 g. of tertiary butyl alcohol and 5 g. of "Triton B," there was added dropwise 53 g. of acrylonitrile (1 mole) during the course of forty minutes while the reaction temperature was maintained at 30–40° by external cooling. After stirring for an additional two hours at room temperature, the mixture was neutralized with dilute hydrochloric acid, taken up in an equal volume of ethylene dichloride, and then washed with 50 cc. of water. The ethylene dichloride layer was separated, dried and distilled in vacuum. The following fractions were collected: (A) 26 g., b. p. 70–185° (1 mm.), liquid; (B) 21.5 g., b. p. 185–205° (1 mm.), crystalline solid.

Fraction (A) was redistilled and the cut boiling at 150° (10 mm.) as a colorless oil, was collected; yield 6 g It is presumably α-isopropylidene-glutaronitrile (XII). *Anal.* Calcd. for $C_8H_{10}N_2$: N, 20.88. Found: N, 21.01.

Fraction (B) after recrystallization from methanol, formed colorless needles, m. p. 67–68°. It is presumably γ-cyano-γ-isopropenylpimelonitrile (XIII). *Anal.* Calcd. for $C_{11}H_{13}N_3$: C, 70.55; H, 7.00; N, 22.45. Found: C, 70.40; H, 6.90; N, 22.17.

Hydrolysis of XIII.—A mixture of 18 g. of XIII, 16 g. of sodium hydroxide and 50 g. of water was boiled under reflux for fourteen hours. The solution was treated with "Norite," filtered, and acidified with concentrated hydrochloric acid. Upon cooling to 5°, colorless crystals (12 g.) separated, which after recrystallization from water melted at 167–168°. The melting point remained unchanged after recrystallization from nitromethane. The compound still possessed one cyano group intact. *Anal.* Calcd. for $C_{11}H_{15}NO_4$: C, 58.63; H, 6.72; N, 6.22. Found: C, 58.60; H, 6.45; N, 6.23.

XIV. α,α-Di-(2-cyanoethyl)-cyclohexenyl-acetonitrile.—The cyclohexylideneacetonitrile used was prepared by condensing cyclohexanone with cyanoacetic acid in pyridine, as follows. To a solution of 140 g. of cyclohexanone

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[9] Bruson and Riener, THIS JOURNAL, 64, 2850 (1942).

[10] Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, 33, 118 (1941).

[11] Lemaire, *Rec. trav. chim.*, 29, 64 (1910).

and 120 g. of cyanoacetic acid, pyridine (150 g.) was added dropwise while stirring and cooling to 10–20°. The mixture was stirred for one-half hour at room temperature and then at 100–105° for four hours. The product was washed thoroughly with water and distilled in vacuum. The fraction boiling at 105–110° (21 mm.) was collected as the product; yield 82 g., $n^{15}D$ 1.4824.

Acrylonitrile (53 g.) was added dropwise to a stirred solution of 60.5 g. of cyclohexylidene-acetonitrile, 60 g. of tertiary butyl alcohol and 5 g. of "Triton B" while cooling to 28–37°. The mixture was stirred for two hours after the addition, then neutralized with dilute hydrochloric acid, taken up in an equal volume of ethylene dichloride and washed with water. The ethylene dichloride layer was evaporated to dryness in vacuum on a steam-bath and the residual oil (105 g.) distilled in vacuum.

The fraction boiling at 210–235° (1 mm.) solidified in the receiver to a crystalline mass; yield 43 g. After recrystallization from methanol the product, presumably XIV, formed colorless crystals, m. p. 81–82°. *Anal.* Calcd. for $C_{14}H_{17}N_3$: C, 73.96; H, 7.55; N, 18.49. Found: C, 74.27; H, 7.08; N, 18.73.

XV. α,α-Di-(2-cyanoethyl)-vinylacetamide.—To a stirred solution of 25.5 g. of crotonamide (0.3 mole), 100 g. of acetonitrile (a solvent which is inert toward acrylonitrile), and 3 g. of "Triton B," there was added dropwise 31.8 g. of acrylonitrile during the course of forty minutes at 25–30°. The mixture was stirred for two hours and then neutralized with dilute hydrochloric acid. The product was filtered to remove unchanged crotonamide (10 g.). The filtrate was distilled in vacuum. About 5 g. of additional crotonamide distilled over up to 235° (2 mm.). The fraction boiling at 235–240° (2 mm.) solidified on cooling in the receiver; yield 10 g. Upon recrystallization from ice-cold methanol it formed colorless crystals, m. p. 77°.

Anal. Calcd. for $C_{10}H_{13}N_3O$: C, 62.80; H, 6.80; N, 21.97. Found: C, 63.25; H, 6.44; N, 22.18.

Acknowledgment.—The analyses of the above products were performed by the semi-micro method by Mr. C. E. Nash.

Summary

1. Acrylonitrile was condensed in the presence of aqueous trimethylbenzylammonium hydroxide as an alkaline catalyst, with unsaturated compounds having a three-carbon atom desmotropic system activated by a —CO—, —CN, or —CO—NH_2 group, whereby cyanoethylation products were obtained.

2. In this manner mesityl oxide yielded 1-(β-cyanoethyl)-1-isopropylidene-acetone and γ-acetyl-γ-isopropenylpimelonitrile.

3. Allyl cyanide or crotononitrile added acrylonitrile to yield α-ethylidene glutaronitrile and γ-cyano-γ-vinylpimelonitrile. Analogous results were obtained by treating acrylonitrile with crotonamide, β-methylcrotononitrile and cyclohexylidene-acetonitrile as typical examples of compounds displaying a 1,3-hydrogen shift.

4. A number of polycarboxylic acids obtained from the hydrolysis of some of the above nitriles are described.

PHILADELPHIA, PA. RECEIVED SEPTEMBER 8, 1942

[CONTRIBUTION FROM RÖHM AND HAAS CO., INC., AND THE RESINOUS PRODUCTS AND CHEMICAL CO.]

The Chemistry of Acrylonitrile. IV. Cyanoethylation of Active Hydrogen Groups

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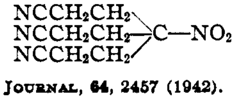
The action of acrylonitrile upon nitroalkanes follows the general observations already described with other reactive methylene compounds[1]: namely, the tendency to seek out every available reactive hydrogen atom and by direct Michael type addition introduce the —CH_2—CH_2—CN group in place thereof.

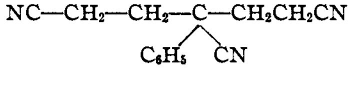
Nitromethane for example reacted vigorously with acrylonitrile in the presence of a strong alkali catalyst such as aqueous 40% trimethylbenzylammonium hydroxide ("Triton B") or potassium hydroxide to form a crystalline tri-cyanoethylation product (I)



$$(NCCH_2CH_2)_3C—NO_2 \qquad (I)$$

The high degree of activity of the methylene hydrogen atoms in compounds possessing the groupings aryl—CH_2—CN, ROOC—CH_2—CN, H_2NCO—CH_2—$CONH_2$, ROOC—CH_2—COOR, NC—CH_2—$CONH_2$, and aryl—CH_2—SO_2NH_2 is clearly evident when these compounds react with acrylonitrile in the presence of strong alkali catalysts. In each case di-cyanoethylation occurs readily.

Thus benzyl cyanide yielded γ-cyano-γ-phenylpimelonitrile (II) almost quantitatively with potassium hydroxide as a catalyst.



$$NC—CH_2—CH_2—C(C_6H_5)(CN)—CH_2CH_2CN \qquad (II)$$

In the same way *p*-nitrobenzyl cyanide yielded

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[1] Bruson, THIS JOURNAL, 64, 2457 (1942).