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., $n^{15}\text{D}$ 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—NH₂ 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

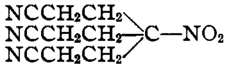
[CONTRIBUTION FROM RÖHM AND HAAS CO., INC., AND THE RESINOUS PRODUCTS AND CHEMICAL CO.]

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

BY HERMAN ALEXANDER BRUSON AND THOMAS W. RIENER

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 —CH₂—CH₂—CN group in place thereof.

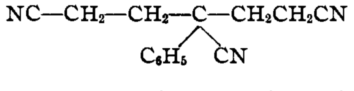
Nitromethane for example reacted vigorously with acrylonitrile in the presence of a strong alkali catalyst such as aqueous 40% trimethylbenzylammonium hydroxide ("Triton B") or potassium hydroxide to form a crystalline tri-cyanoethylation product (I)



$$\left.\begin{matrix}\mathrm{NCCH_2CH_2}\\ \mathrm{NCCH_2CH_2}\\ \mathrm{NCCH_2CH_2}\end{matrix}\right\rangle\mathrm{C{-}NO_2}\qquad\text{(I)}$$

The high degree of activity of the methylene hydrogen atoms in compounds possessing the groupings aryl—CH₂—CN, ROOC—CH₂—CN, H₂NCO—CH₂—CONH₂, ROOC—CH₂—COOR, NC—CH₂—CONH₂, and aryl—CH₂—SO₂NH₂ 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.



$$\mathrm{NC{-}CH_2{-}CH_2{-}}\underset{\mathrm{C_6H_5\quad CN}}{\mathrm{C}}\mathrm{{-}CH_2CH_2CN}\qquad\text{(II)}$$

In the same way *p*-nitrobenzyl cyanide yielded

---

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

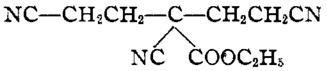
Table I

$NCCH_2CH_2—O—R—O—CH_2CH_2CN$

Value of R	B. p. °C.	B. p. Mm.	Formula	N Analyses, % Calcd.	N Analyses, % Found
$—CH_2—CH_2—$	158	2	$C_8H_{12}N_2O_2$	16.67	16.49
$—CH_2—CH(CH_3)—$	165	2	$C_9H_{14}N_2O_2$	15.38	14.99
$—CH_2CH_2CH_2—$	165	1	$C_9H_{14}N_2O_2$	15.38	15.19
$—CH(CH_3)(CH_3)CH—$	170 M. p. 53–54	2	$C_{10}H_{16}N_2O_2$	14.28	14.23
$—CH_2CH_2—O—CH_2CH_2—$	190	1	$C_{10}H_{16}N_2O_3$	13.20	13.14
$—CH_2CH_2—S—CH_2CH_2—$	225	2	$C_{10}H_{16}N_2O_2S$	12.28 S, 14.03	12.01 S, 14.27
$—CH_2CH_2—O—CH_2CH_2—O—CH_2CH_2—$	215	1	$C_{12}H_{20}N_2O_4$	10.93	10.78
$—CH_2—CH—CH_2—$ $O—CH_2CH_2CN$	260	1	$C_{12}H_{17}N_3O_3$	16.73	16.45
$—CH_2—(CH_2)_3—CH_2—$	185	1	$C_{11}H_{18}N_2O_2$	13.32	12.82
$—CH_2—(CH_2)_8—CH_2—$	225	1	$C_{16}H_{28}N_2O_2$	10.00	9.49

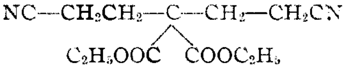
the corresponding γ-cyano-γ-(*p*-nitrophenyl)-pimelonitrile (III).

Ethyl cyanoacetate and acrylonitrile gave an almost quantitative yield of γ-carbethoxy-γ-cyanopimelonitrile (IV)



$$NC—CH_2CH_2—\underset{NC\ \ \ COOC_2H_5}{C}—CH_2CH_2CN \qquad (IV)$$

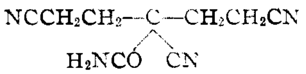
whereas ethyl malonate and acrylonitrile gave an 82% yield of γ,γ-di-(carbethoxy)-pimelonitrile (V).



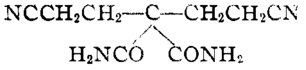
$$NC—CH_2CH_2—\underset{C_2H_5OOC\ \ \ COOC_2H_5}{C}—CH_2—CH_2CN \qquad (V)$$

Compounds IV and V have already been described by Clemo and Tenniswood[2] who prepared them by treating sodium ethyl cyanoacetate and sodium diethyl malonate, respectively, with β-cyanoethyl *p*-toluenesulfonate, repeating the operation twice for the introduction of the two β-cyanoethyl groups. The present method is obviously much simpler.

Cyanacetamide as well as malonamide also added to acrylonitrile to yield, respectively, γ-carbamyl-γ-cyanopimelonitrile (VI) and γ,γ-di-(carbamyl)-pimelonitrile (VII).

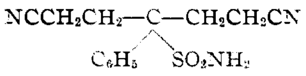


$$NCCH_2CH_2—\underset{H_2NCO\ \ \ CN}{C}—CH_2CH_2CN \qquad (VI)$$



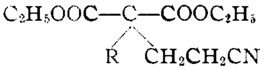
$$NCCH_2CH_2—\underset{H_2NCO\ \ \ CONH_2}{C}—CH_2CH_2CN \qquad (VII)$$

In the same way, ω-toluenesulfonamide added to acrylonitrile to form γ-phenyl-γ-(sulfonamido)-pimelonitrile (VIII).



$$NCCH_2CH_2—\underset{C_6H_5\ \ \ SO_2NH_2}{C}—CH_2CH_2CN \qquad (VIII)$$

Acrylonitrile also added readily to ethyl ethylmalonate, benzyl ethylmalonate and *n*-butyl ethylmalonate to give the corresponding monocyanoethylation products (IX).



$$C_2H_5OOC—\underset{R\ \ \ CH_2CH_2CN}{C}—COOC_2H_5$$

R = ethyl, benzyl, butyl

(IX)

The two hydrogen atoms of water are also replaceable by cyanoethyl radicals to yield bis-(β-cyanoethyl) ether (X). The reaction probably takes place through intermediate formation of hydracrylonitrile, since the latter reacts with acrylonitrile to form the ether in 90% yield.

$$CH_2{=}CH—CN + H_2O \longrightarrow HOCH_2CH_2CN$$
$$HOCH_2CH_2CN + CH_2{=}CH—CN \longrightarrow NCCH_2CH_2—O—CH_2CH_2CN \quad (X)$$

In a similar manner the two replaceable hydrogen atoms of ethylene glycol yield bis-(β-cyanoethoxy)-ethane-1,2 $NCC_2H_4—O—C_2H_4—O—C_2H_4CN$.

A number of analogous poly-cyanoethylation products were thus prepared from propylene glycol, trimethylene glycol, 2,3-butylene glycol, diethylene glycol, thiodiethylene glycol, triethylene glycol, glycerol, pentamethylene glycol and decamethylene glycol in 80–90% yields. Their physical properties and analytical data are given in Table I.

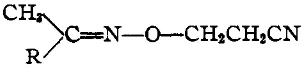
The reaction of acrylonitrile with monohydric unsaturated alcohols, cyclic alcohols and ether alcohols to form cyanoethyl ethers, in many cases almost quantitatively, has already been described in recently issued patents.[3]

Finally, oximes react with acrylonitrile in the presence of alkali to form oximino-O-cyanoethyl ethers. Thus ketoximes such as acetone oxime, methyl ethyl ketoxime and acetophenone oxime, gave compounds of Type XI.

---

[2] Clemo and Tenniswood, *J. Chem. Soc.*, 2549–2551 (1931).

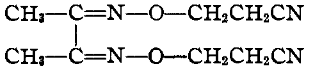
[3] Bruson, U. S. Pats. 2,280,790, 2,280,791, 2,280,792.



R = methyl, ethyl, phenyl

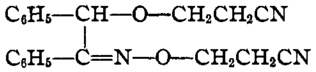
(XI)

Dimethylglyoxime gave the di-ether (XII), while benzoin oxime gave (XIII)



$$\begin{array}{l} CH_3-C=N-O-CH_2CH_2CN \\ \quad\;\; | \\ CH_3-C=N-O-CH_2CH_2CN \end{array}$$

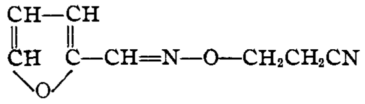
(XII)



$$\begin{array}{l} C_6H_5-CH-O-CH_2CH_2CN \\ \quad\quad\;\; | \\ C_6H_5-C=N-O-CH_2CH_2CN \end{array}$$

(XIII)

Aldoximes behaved in a similar manner. For example furfuraldoxime gave XIV.



(XIV)

Experimental

I. Tri-(β-cyanoethyl)-nitromethane.—Acrylonitrile (79.5 g.) was added dropwise to a stirred solution of 30.5 g. of nitromethane, 50 g. of dioxane, and 5 g. of aqueous 40% trimethylbenzylammonium hydroxide ("Triton B") during the course of twenty-five minutes while maintaining the exothermic reaction at 25–35° by external cooling. The mixture was allowed to stand eighteen hours at room temperature. It was then neutralized with dilute hydrochloric acid, taken up in an equal volume of ethylene dichloride, washed with 25 cc. of water and the ethylene dichloride evaporated in vacuum, on a steam-bath. The crystalline residue (49 g.) after recrystallization from ethanol formed colorless prisms, m. p. 114°. *Anal.* Calcd. for $C_{10}H_{12}N_4O_2$: C, 54.52; H, 5.50; N, 25.44. Found: C, 54.50; H, 5.06; N, 25.24.

II. γ-Cyano-γ-phenylpimelonitrile.—A solution of 10.6 g. of acrylonitrile (0.2 mole) in 10 g. of tertiary butyl alcohol was added dropwise to a stirred solution of 11.7 g. of benzyl cyanide (0.1 mole), 25 g. of tertiary butyl alcohol, and 1 g. of methanolic 30% potassium hydroxide solution, while maintaining the reaction temperature at 10–25° by cooling. The mixture was stirred for two hours longer at 10–25°, then neutralized with dilute hydrochloric acid and diluted with 25 cc. of ethanol to facilitate filtration of the crystalline magma; yield 21 g. or 94%. The compound after recrystallization from ethanol formed large colorless crystals m. p. 70°. *Anal.* Calcd. for $C_{14}H_{13}N_3$: C, 75.30; H, 5.87; N, 18.82. Found: C, 75.41; H, 5.76; N, 18.88.

III. γ-Cyano-γ-(*p*-nitro-phenyl)-pimelonitrile.—To a stirred solution of 32.4 g. of *p*-nitrobenzyl cyanide (0.2 mole), 75 g. of dioxane and 2 g. of "Triton B," there was added dropwise 21.2 g. of acrylonitrile (0.4 mole) at 35–37°. The mixture was stirred for two hours longer, then neutralized with dilute hydrochloric acid, and taken up in an equal volume of ethylene dichloride. This solution was washed with water and dried in vacuum on a steam-bath. The residual crystalline product (49 g.) separated in yellowish crystals m. p. 147–148° from methanol. *Anal.* Calcd. for $C_{14}H_{12}N_4O_2$: N, 20.88. Found: N, 20.71.

IV. γ-Carbethoxy-γ-cyanopimelonitrile.—Acrylonitrile (53 g.) was added dropwise to a stirred solution of 56.5 g. of ethyl cyanoacetate, 100 g. of dioxane, and 7 g. of "Triton B" during the course of seventy-five minutes while maintaining the reaction temperature at 30–35° by cooling. The mixture was stirred for one hour at room temperature, then neutralized with dilute hydrochloric acid, poured into 1 liter of water and the oil layer separated and dried in vacuum; yield 107 g. On standing it solidified to a crystalline mass which after recrystallization from ethanol formed colorless crystals melting at 37°. *Anal.* Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.25; H, 5.98; N, 19.17. Found: C, 60.60; H, 6.00; N, 19.29.

V. γ,γ-Di-(carbethoxy)-pimelonitrile.—To a stirred solution of 80 g. of ethyl malonate (0.5 mole), 100 g. of dioxane, and 10 g. of "Triton B," there was added dropwise 53 g. of acrylonitrile (1 mole) during the course of forty minutes while cooling the reaction mixture to 30–35°. The mixture was stirred thereafter for two hours at room temperature, then neutralized with dilute hydrochloric acid and poured into 1 liter of ice water. The product separated as an oil which rapidly solidified to a white crystalline solid; yield 110 g. Upon recrystallization from ethanol it melted at 62°. *Anal.* Calcd. for $C_{13}H_{18}N_2O_4$: N, 10.52. Found: N, 10.48.

VI. γ-Carbamyl-γ-cyanopimelonitrile.—To a stirred solution of 25.2 g. of cyanoacetamide in 50 cc. of water containing 3 g. of "Triton B," there was added dropwise 31.8 g. of acrylonitrile during the course of thirty-five minutes while maintaining the reaction temperature at 35–40° with cooling. The clear yellow solution set to a solid mass after about thirty minutes of stirring at room temperature. It was allowed to stand for one hour then dissolved in 200 g. of hot ethanol, neutralized with dilute hydrochloric acid, and allowed to crystallize; yield 42 g. of faintly greenish crystals. After one more recrystallization from ethanol the product separated in colorless crystals m. p. 118°. *Anal.* Calcd. for $C_9H_{10}N_4O$: N, 29.46. Found: N, 29.35.

VII. γ,γ-Di-(carbamyl)-pimelonitrile.—To a stirred solution of 25.5 g. of malonamide, 100 g. of water and 5 g. of "Triton B," there was added dropwise 26.5 g. of acrylonitrile during the course of twenty minutes while maintaining the reaction temperature at 35–38° by cooling. The mixture was then held at 35–38° for an additional hour and filtered warm; yield 7 g. of colorless crystals, m. p. 210° after recrystallization from water. *Anal.* Calcd. for $C_9H_{12}N_4O_2$: C, 51.90; H, 5.81; N, 26.91. Found: C, 52.10; H, 5.88; N, 26.94. Upon chilling the filtrate 16.5 g. of unchanged malonamide was recovered.

VIII. γ-Phenyl-γ-(sulfonamido)-pimelonitrile.—Acrylonitrile (10.6 g.) was added to a solution of 17.1 g. of ω-toluenesulfonamide, 50 g. of dioxane and 3 g. of "Triton B" at 35°. No heat was evolved. The mixture was stirred for twenty-four hours at room temperature, then mixed with an equal volume of ethylene dichloride, neutralized with dilute hydrochloric acid, washed with water and dried in vacuum on a steam-bath. The residue (27 g.) upon recrystallization from ethanol formed colorless crystals, m. p. 103–104°. ω-Toluenesulfonamide (m. p. 102°) gave a 31° depression in a mixed melting point determination with the above product. *Anal.* Calcd. for $C_{13}H_{15}N_3O_2S$: N, 15.15; S, 11.55. Found: N, 15.15; S, 11.93.

IX. α-Ethyl-α-(2-cyanoethyl)-diethyl Malonate.—To a stirred solution of 50 g. of ethyl ethylmalonate, 50 g. of dioxane and 3 g. of "Triton B," 28.2 g. of acrylonitrile was added dropwise at 30–40°. The mixture was stirred for five hours, then neutralized with dilute hydrochloric acid, mixed with 50 cc. of ethylene dichloride and washed with 25 cc. of water. The ethylene dichloride layer was evaporated to dryness in vacuum on a steam-bath. The residual oil (62 g.) crystallized on standing. After recrystallization from ice-cold ethanol it formed colorless crystals, m. p. 47°. *Anal.* Calcd. for $C_{12}H_{19}NO_4$: N, 5.81. Found: N, 5.83.

α-Butyl-α-(2-cyanoethyl)-diethyl Malonate.—To a stirred solution of 26.5 g. of *n*-butyl ethylmalonate, 50 g. of dioxane, and 3 g. of "Triton B," there was added dropwise 6.5 g. of acrylonitrile at 30–35°. The mixture was stirred six hours, neutralized with dilute hydrochloric acid, dissolved in 50 cc. of ethylene dichloride, and washed with 25 cc. of water. The ethylene dichloride layer was evaporated to dryness in vacuum on a steam-bath and the residual oil (31 g.) distilled in vacuum. The product came over as a colorless oil boiling at 145–150° (1 mm.); yield 20 g. *Anal.* Calcd. for $C_{14}H_{23}NO_4$: N, 5.20. Found: N, 5.18.

α-Benzyl-α-(2-cyanoethyl)-diethyl Malonate.—Acrylonitrile (5.9 g.) was added dropwise to a stirred solution of 26 g. of benzyl ethyl malonate, 50 g. of dioxane and 3 g. of "Triton B" at 30–35°. The mixture was stirred for three hours thereafter, then neutralized, washed, dried and distilled as described above. The product (25 g.) distilled at 175–180° (1 mm.) as a colorless oil which solidified to a crystalline solid, melting at 47° after recrystallization from ethanol. *Anal.* Calcd. for $C_{17}H_{21}NO_4$: N, 4.62. Found: N, 4.40.

X. Bis-(β-cyanoethyl) Ether.—A mixture of 53 g. of acrylonitrile, 50 cc. of dioxane, and 10 cc. of aqueous 10% sodium hydroxide solution was stirred for six hours at 45°. The alkali was then neutralized, the dioxane evaporated off in vacuum on a steam-bath, and the residual oil distilled in vacuum. The product boiled at 161–163° (5.5 mm.); yield 28 g. *Anal.* Calcd. for $C_6H_8N_2O$: C, 58.03; H, 6.49; N, 22.57. Found: C, 57.80; H, 6.51; N, 22.50.

The bis-(β-cyanoethyl) ether can be obtained in excellent yields as follows. To a stirred mixture consisting of 710 g. of ethylene cyanohydrin (10 moles) and 25 g. of 20% potassium hydroxide solution, there was added dropwise 530 g. of acrylonitrile (10 moles) during the course of two and three-quarters hours while maintaining the reaction temperature at 40°. The mixture was stirred for eighteen hours thereafter at room temperature. It was neutralized with dilute hydrochloric acid and evaporated to dryness in vacuum (30 mm.) on a steam-bath. The residual oil (1197 g.) was distilled in vacuum. The product distilled as a colorless liquid at 155–165° (3 mm.); yield 1126 g. or 90.8%.

Pure bis-(β-cyanoethyl) ether boils at 161–162° (5 mm.) and possesses n^{25}D 1.4407, d^{25}_{25} 1.0482. It is insoluble or only slightly soluble in petroleum ether, ethyl ether, or carbon tetrachloride, but is soluble in water, methanol, chloroform, dioxane, benzene and ethylene dichloride. Upon treatment with alkaline hydrogen peroxide it forms the corresponding bis-(β-carbamylethyl) ether, $H_2NCOCH_2CH_2\text{—}O\text{—}CH_2CH_2CONH_2$, melting at 146°. *Anal.* Calcd. for $C_6H_{12}N_2O_3$: N, 17.48. Found: N, 17.22.

Cyanoethylation of Polyhydric Alcohols.—The general method consisted in mixing 1 mole equivalent of the polyhydric alcohols with 5–7% by weight of aqueous 40% potassium hydroxide solution or 2% of powdered sodium methylate and gradually adding the calculated quantity of acrylonitrile required to react with each hydroxyl group, to the reaction mixture while stirring and maintaining the temperature at 25–35°. The mixture was then stirred eighteen hours, neutralized with dilute hydrochloric acid and distilled in vacuum. The yields were 80–95%.

The polycyanoethylation products prepared from the various polyhydric alcohols are described in Table I.

XI. O-(β-Cyanoethyl) Acetone Oxime.—A mixture of 24 g. of acetone oxime, 40 cc. of dioxane and 0.4 g. of powdered sodium methylate was stirred at 25–30° until a clear solution was obtained. Acrylonitrile (17.5 g.) was then added dropwise while the solution was stirred at 25–35°. Stirring was continued for fourteen hours. The product was then neutralized with dilute hydrochloric acid and the product distilled in vacuum. The desired product distilled at 85° (10 mm.) as a colorless liquid; yield 25 g.; n^{25}D 1.4388, d^{25}_{25} 0.9632. *Anal.* Calcd. for $C_6H_{10}N_2O$: N, 22.71. Found: N, 22.84.

O-(β-Cyanoethyl)-methyl Ethyl Ketoxime.—A mixture of 25 g. of methyl ethyl ketoxime, and 0.4 g. of sodium methylate was stirred at 50–60° until a clear solution was obtained. The solution was cooled to 20° and stirred while 15 g. of acrylonitrile was added dropwise. The mixture gradually became warm (40°). It was stirred for eighteen hours at room temperature, neutralized with dilute hydrochloric acid, and the oil layer separated, filtered, and distilled in vacuum. The product distilled at 109° (21 mm.) as a colorless oil; yield 28 g.; n^{25}D 1.4418; d^{25}_{25} 0.9484. *Anal.* Calcd. for $C_7H_{12}N_2O$: N, 20.00. Found: N, 19.59.

O-(β-Cyanoethyl)-acetophenone Oxime.—To a solution of 25 g. of acetophenone oxime, 100 cc. of benzene and 2 g. of aqueous 40% trimethylbenzylammonium hydroxide ("Triton B"), 9.8 g. of acrylonitrile was added dropwise while the solution was stirred rapidly. The mixture was stirred for two hours at room temperature and then for two hours at 40–50°. It was filtered and the clear filtrate evaporated to dryness in vacuum (30 mm.) on a steam-bath. The residual oil crystallized on cooling; yield 32 g. Upon recrystallization from methanol, the compound formed colorless needles, m. p. 44°. *Anal.* Calcd. for $C_{11}H_{12}N_2O$: N, 14.89. Found: N, 14.38.

XII. O,O-Di-(β-cyanoethyl) Dimethylglyoxime.—To a rapidly stirred mixture of 34.8 g. (0.3 mole) of dimethylglyoxime, 150 g. of water and 4 g. of 50% sodium hydroxide solution there was added dropwise during fifty minutes 31.8 g. (0.6 mole) of acrylonitrile. The temperature during this period gradually rose to 38° as the reaction proceeded. It was then cooled to 25° and stirred for twenty-four hours at this temperature. The thick crystalline magma was diluted with 250 cc. of water, filtered by suction, washed with water and dried. The air-dried crystalline material was extracted at room temperature with ethylene dichloride, filtered from traces of insoluble dimethylglyoxime and the extract concentrated and allowed to crystallize.

The product after recrystallization from ethylene dichloride separated as colorless plates, m. p. 123°; yield 40 g. *Anal.* Calcd. for $C_{10}H_{14}N_4O_2$: N, 25.21. Found: N, 25.29.

XIII. Di-(cyanoethyl) Ether of Benzoin Oxime.—To a stirred solution of 22.7 g. of α-benzoin oxime, 100 g. of dioxane, and 2 g. of "Triton B," there was gradually added 10.6 g. of acrylonitrile at 30–40°. The mixture was stirred for two hours and allowed to stand twenty-four hours at room temperature. It was then made slightly acidic with dilute hydrochloric acid; poured into 400 cc. of water, and the heavy oil taken up in benzene. After evaporation of the benzene, the residual oil (32 g.) was allowed to stand for several months during which time it crystallized. After recrystallization from ethanol to constant melting point the product formed colorless needles, m. p. 72–73°. *Anal.* Calcd. for $C_{20}H_{19}N_3O_2$: N, 12.61. Found: N, 12.42.

XIV. O-(β-Cyanoethyl)-furfuraldoxime.—A mixture of 18 g. of furfuraldoxime (*syn*-form m. p. 88°), 25 cc. of dioxane, and 0.3 g. of sodium methylate was stirred and heated at 50–60° until a clear solution was obtained. This was cooled to 20°, and 8.5 g. of acrylonitrile added gradually to the stirred solution, so that the reaction temperature was 30–40°. The mixture solidified after a short time to a crystalline magma. Dioxane (50 cc.) was added to assist stirring and the mixture filtered after stirring for two hours. The alkalinity was neutralized with dilute hydrochloric acid and the crystalline product filtered off; yield 12 g. After recrystallization from benzene, the pure compound formed water-soluble long colorless needles, m. p. 116°. *Anal.* Calcd. for $C_8H_8N_2O_2$: N, 17.07. Found: N, 16.80.

Summary

1. Acrylonitrile condensed in the presence of strong alkali catalysts with nitroalkanes, malonic esters, cyanoacetic ester, malonamide, benzyl cyanide, and ω-toluenesulfonamide types of compounds having activated methylene or methenyl groups, so as to replace each active hydrogen by a β-cyanoethyl radical.

2. Acrylonitrile also reacted with the hydrogen atoms of water to yield bis-(β-cyanoethyl) ether. This can be obtained in 90% yield by treating acrylonitrile with hydracrylonitrile.

3. Polycyanoethyl ethers were obtained from various glycols and from glycerol by the action of acrylonitrile in the presence of alkali.

4. Oximes reacted with acrylonitrile to yield cyanoethyl oximino ethers.

PHILADELPHIA, PA. RECEIVED SEPTEMBER 14, 1942

[CONTRIBUTION FROM DIVISION OF INSECTICIDE INVESTIGATIONS, AGRICULTURAL RESEARCH ADMINISTRATION, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Occurrence of Rotenone and Related Substances in the Seeds of the Berebera Tree. A Procedure for the Separation of Deguelin and Tephrosin*

BY E. P. CLARK

During 1932–1933, while making a survey of possible rotenone-bearing plants, we came in possession of some seeds of the African berebera tree (*Millettia ferruginea* Hochst.), which grows along the streets of Addis Ababa. When processed these seeds yielded about 1% of rotenone by direct crystallization, and the mother liquors, when treated with alkali, yielded some dehydrorotenone and about 0.2% of an unknown material. The latter, recrystallized from hot *n*-butanol, was obtained as long, narrow, light lemon-colored rods. While its appearance under the microscope was that of a uniform substance, it was unquestionably a mixture, as it began to sinter at 140° and did not melt clear until 198°.

Because of the low yield obtained, further investigation of this substance was not undertaken at the time, but the recent work by Harper,[1] Meyer and Koolhaas,[2] and Buckley[3] on new constituents of leguminous fish-poisoning plants stimulated further study of its nature.

Approximately 6 g. of material was available, and as preliminary experiments with various solvents indicated that it could not be resolved by recrystallization, it was subjected to chromatographic analysis. A few trials indicated a satisfactory procedure, which was followed. It resulted in the separation of the mixture into a main fraction of about 3 g. of tephrosin, 0.5 g. of a new substance melting at 189–190°, and 1 g. of a third material melting at 164–165°. There was also evidence of a lower melting substance, but not enough material was available to realize a complete purification.

Neither of the new compounds gave the Durham or ferric chloride test; they would not form dehydro compounds by iodine oxidation in alco-

---

(1) Harper, *J. Chem. Soc.*, 812, 1099 (1939); 309, 1178 (1940); 181 (1942).

(2) Meyer and Koolhaas, *Rec. trav. chim.*, **58**, 207 (1939).

(3) Buckley, *J. Soc. Chem. Ind.*, **55**, 285 (1936).