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Vinylidene Cyanide. I

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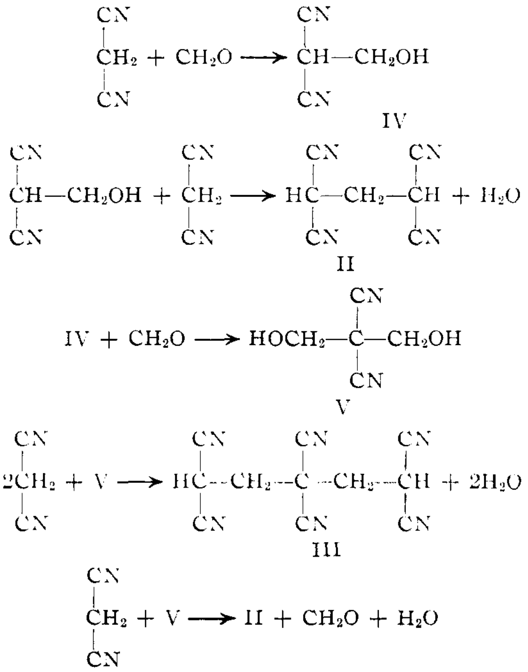
Vinylidene cyanide (I) was desired as a monomer for polymerization and copolymerization with the hope that its polymers would be useful for such purposes as synthetic fibers and films.

In this communication two methods of preparation of vinylidene cyanide are reported.

Part A. The Synthesis from 1,1,3,3-Tetracyanopropane

The synthesis of vinylidene cyanide from aqueous formaldehyde and malononitrile was attempted by G. J. Östling.[1] He obtained a product of m. p. 206–207°, the structure of which, as will be shown, was not that of I. The formaldehyde–malononitrile condensation was studied by O. Diels and his co-workers[2,3] who also were unsuccessful in the isolation of I. Diels, *et al.*, did prepare 1,1,3,3-tetracyanopropane (II) (m. p. 137°) and 1,1,3,3,5,5-hexacyanopentane (III) (m. p. 228°), and suggested that I was an intermediate in the reaction.

The preparation of II was accomplished by the method of Diels and Conn.[3] The synthesis of II and III from formaldehyde and malononitrile probably involves the formation of methylol compounds as intermediates.[4]



$$\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{CH_2}}} + \mathrm{CH_2O} \longrightarrow \underset{\mathrm{IV}}{\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{CH}}}\mathrm{{-}CH_2OH}}$$

$$\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{CH}}}\mathrm{{-}CH_2OH} + \underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{CH_2}}} \longrightarrow \underset{\mathrm{II}}{\mathrm{H}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{{-}CH_2{-}}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{H}} + \mathrm{H_2O}$$

$$\mathrm{IV} + \mathrm{CH_2O} \longrightarrow \underset{\mathrm{V}}{\mathrm{HOCH_2{-}}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{{-}CH_2OH}}$$

$$2\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{CH_2}}} + \mathrm{V} \longrightarrow \underset{\mathrm{III}}{\mathrm{H}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{{-}CH_2{-}}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{{-}CH_2{-}}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{H}} + 2\mathrm{H_2O}$$

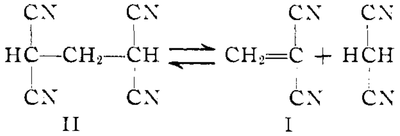
$$\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{CH_2}}} + \mathrm{V} \longrightarrow \mathrm{II} + \mathrm{CH_2O} + \mathrm{H_2O}$$

We have, in fact, isolated dimethylol malononitrile by the reaction of malononitrile and monomeric formaldehyde, using potassium acetate as the catalyst. The dimethylol compound was then treated with malononitrile to yield II. Attempts to repeat Östling's synthesis in this Laboratory produced high yields of III; therefore, the product melting at 206–207° obtained by Östling was probably impure III.

The stability of I is such that it exists in monomeric form only momentarily when in contact with water or alcohol, which indicates that neither the method of Östling nor that of Diels can be expected to yield the monomer I.

Preparation

When 1,1,3,3-tetracyanopropane is heated at 150 to 200° the following reversible reaction occurs



$$\underset{\mathrm{II}}{\mathrm{H}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{{-}CH_2{-}}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{H}} \rightleftharpoons \underset{\mathrm{I}}{\mathrm{CH_2{=}}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}} + \mathrm{H}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}\mathrm{H}$$

The recombination of I with malononitrile in the vapor or liquid phase occurs readily without base catalysis, and is effectively inhibited by traces of phosphorus pentoxide or sulfur dioxide. The pyrolysis products can be separated in a fractionating column if great care is taken to exclude from the apparatus all polymerization initiators for monomeric I, especially traces of water.

The Diels–Alder adduct of I with cyclopentadiene (see Experimental section) was prepared as added proof of structure of monomeric I.

Experimental

Dimethylol Malononitrile.—Gaseous formaldehyde was bubbled into 40 g. of glacial acetic acid containing 0.25 g. of potassium acetate until 1.6 g. (0.0534 mole) was absorbed. Malononitrile (3.6 g., 0.055 mole) was added to the solution which was then heated at 100° for fifteen minutes. After cooling the flask to room temperature, 20 ml. of benzene was added to bring down a flocculent white precipitate which was recrystallized from acetic acid–benzene (1:1) to give 0.8 g. (24%) of dimethylol malononitrile. It melts and resinifies at 93 to 98° with evolution of formaldehyde.

Anal. Calcd. for $C_5H_6O_2N_2$: N, 22.2. Found: N, 22.2, 21.9.

A solution of 0.6 g. of dimethylol malononitrile in 3 ml. of dioxane containing 0.32 g. of malononitrile was heated at 100° for two hours. The solution was cooled to room temperature and 5 ml. of ethanol was added, which precipitated a crop of white crystals; m. p. 137°, mixed m. p. with an authentic sample of 1,1,3,3-tetracyanopropane 137°.

1,1,3,3-Tetracyanopropane.—This compound was prepared by the method of Diels.[3] After recrystallization from acetonitrile–benzene (2:1) it melted sharply at 137°.

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[1] G. J. Östling, *Ofversigt of Finska Ventenskaps—Societetens Förhandl.*, **57**, Div. A, no. 11, 1-13 (1914-1915).

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

[3] O. Diels and B. Conn, *ibid.*, **56**, 2076 (1923).

[4] Compare with T. Enkvist, *J. prakt. Chem.*, **149**, 58-64 (1937).

Anal. Calcd. for $C_7H_4N_4$: C, 58.33; H, 2.78; N, 38.89. Found: C, 58.34; H, 2.79; N, 38.91.

Vinylidene Cyanide.—Forty-six grams of vacuum desiccated 1,1,3,3-tetracyanopropane was placed in a 125-ml. Claisen flask with side arm directly connected to a receiver containing phosphorus pentoxide and immersed in a Dry Ice-acetone-bath. A small amount of glass wool containing 2 g. of phosphorus pentoxide was placed on top of the tetracyanopropane crystals. The system was then evacuated to less than 2 mm. pressure and the flask heated with an oil-bath at 180° for thirty minutes. The vacuum was then broken by admitting dried air into the system. The receiver contained 19 g. of pyrolysis product which was fractionally distilled at 10 mm. to give 10 g. of vinylidene cyanide (yield 40%) and 8 g. of malononitrile (m. p. 32°).

Anal. Calcd. for $C_4H_2N_2$: C, 61.53; H, 2.58; N, 35.89; mol. wt., 78. Found[5]: C, 61.67; H, 2.63; N, 35.75; mol. wt. (cryoscopic in benzene), 80.

If, in place of phosphorus pentoxide, a stream of sulfur dioxide is employed, similar results are obtained. Ten grams of II yielded 8 g. of pyrolysis product, which on distillation gave 2.0 g. of I and 1.5 g. of malononitrile.

When the pyrolysis of II was carried out without phosphorus pentoxide or sulfur dioxide, crystalline II reappeared in the side arm, while a relatively small yield of I collected in the receiver.

Properties of Vinylidene Cyanide.—The boiling points at various pressures are: 40.0° (5 mm.), 42.5° (6 mm.), 46.8° (8 mm.), 50.5° (10 mm.), 154.0° (760 mm.). A fractionally crystallized sample had the following properties: m. p. 9.7°, d^{23}_4 0.992, n^{20}_D 1.4411, MR_D (obsd.) 20.7, MR_D (calcd.) 19.7, K_f 3.6,[6] L_v 13,900 cal./mole,[7] ΔH_f 3,400 cal./mole.[8] The monomer is completely miscible with benzene, nitromethane and trichloroethylene. It is substantially insoluble in aliphatic hydrocarbons. It polymerizes instantly in the cold upon contact with water, alcohols, amines, amides, ketones (except ketones without enol forms, such as benzophenone) and a large number of other organic and inorganic substances. Pure monomer may be kept almost indefinitely if stabilized by trace additions of phosphorus pentoxide.[9] Monomeric I is stable in thiophene-free benzene and in a few other dry, pure liquids. It is a very strong lachrymator. It exhibits delayed action on the mucous membranes, slowly developing a formaldehyde sting.

Polymerization of Vinylidene Cyanide. A. By Heat.—Two grams of monomeric I was heated for twenty-four hours at 80° in a sealed glass tube. This gave a transparent button of hard, glassy, polymeric I.

Anal. Calcd. for $C_4H_2N_2$: C, 61.53; H, 2.58; N, 35.89. Found: C, 61.30; H, 2.70; N, 35.69.

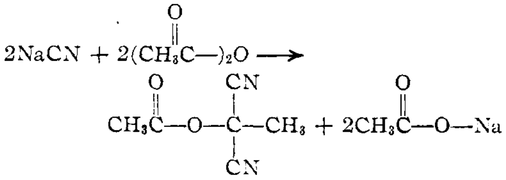
B. By Water.—One gram of I was added to 25 ml. of distilled water at 20°. An immediate exothermic reaction occurred with the formation of a white resinous precipitate. The precipitate was filtered, washed with benzene, and dried to yield 1 g. of polymer of considerably lower molecular weight than the polymer prepared in A. A similar infusible amorphous resin was obtained when I was added to ethanol.

5,5-Dicyano-bicyclo(2·2·1)-2-heptene.—This Diels-Alder adduct was prepared by dissolving 5 g. of vinylidene cyanide in 8.5 g. of cyclopentadiene. An almost immediate exothermic reaction ensued. After thirty minutes, 25 ml. of ethanol was added, the mixture filtered, and the filtrate cooled to −70° to crystallize out the adduct. The cold solution was then filtered and the white crystals washed with cold ether (in which the adduct is partly soluble); yield 1.4 g. of adduct, m. p. 94–96°.

Anal. Calcd. for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.44. Found: C, 74.80; H, 5.62; N, 19.29.

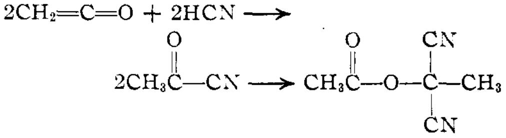
Part B. The Synthesis from Di-(acetyl cyanide)[10]

Di-(acetyl cyanide), in this paper referred to as D.A.C., can be made from relatively available starting materials and deacetoxylated to yield vinylidene cyanide. The D.A.C. can be prepared from sodium cyanide and acetic anhydride[11]

(1) 

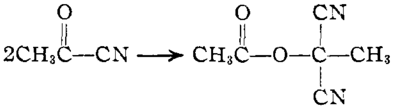
$$2\mathrm{NaCN} + 2(\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—})_2\mathrm{O} \longrightarrow \mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—}\underset{\underset{\mathrm{CN}}{|}}{\overset{\overset{\mathrm{CN}}{|}}{\mathrm{C}}}\text{—CH}_3 + 2\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—Na}$$

from ketene and hydrogen cyanide[12]

(2) 

$$2\mathrm{CH_2{=}C{=}O} + 2\mathrm{HCN} \longrightarrow 2\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—CN} \longrightarrow \mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—}\underset{\underset{\mathrm{CN}}{|}}{\overset{\overset{\mathrm{CN}}{|}}{\mathrm{C}}}\text{—CH}_3$$

and by the base-catalyzed dimerization of acetyl cyanide[13]

(3) 

$$2\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—CN} \longrightarrow \mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—}\underset{\underset{\mathrm{CN}}{|}}{\overset{\overset{\mathrm{CN}}{|}}{\mathrm{C}}}\text{—CH}_3$$

A comparison of reaction (3) has recently been made with the reaction of aldehydes and acyl chlorides.[14]

Pyrolysis of D.A.C.—The pyrolysis of esters to olefins has been a widely explored field.[15] Although many unsubstituted esters pyrolyze smoothly to the olefin of the alcohol residue, complications are met when the ester is substituted with other groups which split off at high temperatures. This is the case with esters of cyano alcohols where hydrogen cyanide may also be formed.[16]

Hagemeyer[17] has recently mentioned the formation of α-cyanovinyl acetate by pyrolyzing D.A.C. This course of the reaction is apparently favored by the presence of alkaline material, although details of the pyrolysis are not given. The pyrolysis of D.A.C., described in the present paper, yields mainly I.

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[5] Microcarbons and hydrogens by J. R. Kubik; semi-micro Kjeldahls by A. K. Kuder; molecular weight determinations by D. M. Kurtz.

[6] The cryoscopic constant was determined with benzophenone as solute.

[7] The latent heat of vaporization was calculated from the boiling point data using the Clausius-Clapeyron equation.

[8] The molar heat of fusion was calculated from: $\Delta H_f = RT^2K_f^{-1}n^{-1}$ where T is the freezing point and n is the number of moles in 1000 g. of the material.

[9] H. Gilbert, U. S. Patent 2,467,378 (April 19, 1949).

[10] A. E. Ardis, U. S. Patent 2,476,270 (July 19, 1949).

[11] S. Kleeman, *Ber.*, **18**, 256 (1885).

[12] F. Johnston and L. W. Newton, U. S. Patent 2,395,930 (1946).

[13] H. Hübner, *Ann.*, **120**, 335 (1861).

[14] C. S. Marvel, N. O. Brace, F. A. Miller and A. R. Johnson, THIS JOURNAL, **71**, 34 (1949).

[15] C. D. Hurd, "The Pyrolysis of Carbon Compounds," (Chemical Catalog Company) Reinhold Publishing Corp., New York, N. Y., 1929, p. 529.

[16] R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400 (1935).

[17] H. J. Hagemeyer, *Ind. Eng. Chem.*, **41**, 765 (1949).

To obtain monomeric I it has been found desirable to use high purity D.A.C., since I is polymerized by so many different materials, *e. g.*, water, alcohols and especially bases.

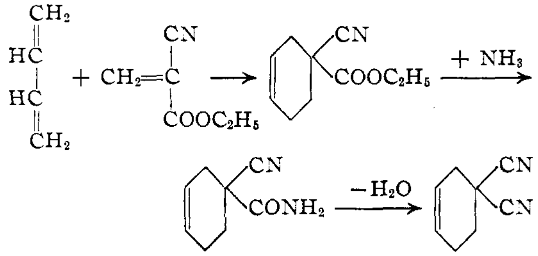
Purification of the Pyrolysis Product from D.A.C.—Monomeric I can be separated from the pyrolysis product of D.A.C. by distillation, crystallization or a combination of both. The monomer can also be polymerized and the polymer separated.

Distillation requires an efficient fractionating column operated under vacuum. A small amount of unidentified material has a boiling point close to that of I and efficient fractionation is required for a good separation. With proper precautions, such as the use of phosphorus pentoxide, it is possible to distil through an efficient column without sizable losses due to polymerization.

The pyrolysis product, which has been distilled in vacuum through a modified Vigreux column to obtain a cut of b. p. 54–57° (15 mm.) can be crystallized from chloroform to obtain pure monomer. When the monomer is in the neighborhood of 95% pure it is possible to crystallize fractionally, without added solvent, to obtain pure monomer.

Identification of Vinylidene Cyanide (I).—The vinylidene cyanide prepared from D.A.C. has been identified by comparison of physical properties with the monomer prepared via the method of Part A and also by its formation of the expected Diels–Alder adduct with butadiene, 4,4-dicyanocyclohexene. This compound has also been made by an independent synthesis

(4)



Experimental

D.A.C. was prepared by the method of Kleeman[11] with the exception that after filtering the reaction mixture the filtrate was vacuum distilled. The fraction boiling at 100–110° (10 mm.) amounted to a 60% yield. If the distillate has a melting point below 69°, the material should be recrystallized from carbon tetrachloride.

Vinylidene Cyanide from Pyrolysis of D.A.C.—The pyrolysis tube was of 85-15 brass, 3′ long, $^5/_8$″ i. d., wound with resistance wire and jacketed with $^3/_4$″ asbestos. It was equipped with an inside thermocouple-well and was packed with a tight roll of brass window screen. Both ends of the tube were wound with four turns of small copper tubing through which water was circulated so that rubber stopper connections would not soften. This tube has been used satisfactorily either in a vertical position or at a 15° incline from the horizontal. The tube was operated at 600–650°. A 125-ml. distilling flask was connected to the inlet of the tube and the outlet was connected to a 250-ml. suction flask which in turn led to a vacuum source. D.A.C. (80 g., m. p. 69–70°) was placed in the distilling flask and 2 g. of phosphorus pentoxide placed in the suction flask. The system was evacuated to 10 mm. A Dry Ice–acetone-bath was raised around the receiver and an oil-bath, preheated to 110°, raised around the distilling flask. A smooth distillation through the tube was completed in less than one hour. The collected pyrolysis product was allowed to melt while protected from moisture in the air. Seventy-two grams of light yellow liquid was collected. This contained 40% monomer as evidenced by polymerizing the monomer, filtering, washing with alcohol, drying and weighing the polymer.

Purification.—One hundred grams of pyrolysis product was distilled through a 6″ modified Vigreux column to obtain a 53-g. fraction of b. p. 54–57° (15 mm.) which contained 35.5 g. of I. This fraction was mixed with half its weight of dry chloroform and cooled slowly to −30° while stirring in a closed container. The filtrate was removed by suction with a filter stick, the crystals were washed with dry toluene (precooled to −30°, equal in weight to the chloroform used). The crystals were melted and flash distilled to yield 18 g. of pure monomer, m. p. 9°, *n* = 1.441 (Fisher refractometer).[18] In one such crystallization 50% of the monomer contained in the original distillate was obtained in pure form.

4,4-Dicyanocyclohexene from I.—Twelve grams of 1,3-butadiene and 4 g. of I were mixed in a pressure bomb which was capped and allowed to stand at room temperature for eighteen hours. The bomb was cooled, opened and the unreacted butadiene allowed to evaporate. The residue was distilled in vacuum. The fraction which distilled at 114° (10 mm.) weighed 6 g., m. p. 35–35.5° (uncor.). The melting point was not depressed by a sample prepared via the route of equation 4.

Anal. Calcd. for $C_8H_8N_2$: C, 72.69; H, 6.09; N, 21.20. Found: C, 72.28; H, 5.96; N, 21.15.

4,4-Dicyanocyclohexene from 4-Cyano-4-carbethoxycyclohexene.—Twenty-four grams of 4-cyano-4-carbethoxycyclohexene[19] was poured into 13.2 ml. of concentrate aqueous ammonia (sp. gr. 0.90). The solution was shaken until it was clear and then stored overnight at 0°. The crystals which formed were filtered, recrystallized from methanol, and dried. Ten grams of solid (m. p. 130–140°) was obtained. Without further purification the solid was mixed with 20 g. of phosphorus pentoxide and 20 g. of tricresyl phosphate and heated to 200° under 1 mm. vacuum. Five grams of distillate was collected (b. p. 114° (10 mm.)); the melting point was not depressed by a sample of the preceding preparation.

Summary

1. Monomeric vinylidene cyanide has been prepared by the pyrolysis of 1,1,3,3-tetracyanopropane. Its thermal polymerization yields a hard, glassy resin.

2. Vinylidene cyanide has also been prepared by pyrolyzing di-(acetyl cyanide).

3. Dimethylol malononitrile has been isolated from a formaldehyde–malononitrile condensation.

4. A method for the purification of vinylidene cyanide is given.

5. Vinylidene cyanide has been treated with butadiene and cyclopentadiene to give the expected Diels–Alder adducts.

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[18] Although more precise refractometers can be used, the monomer tends to polymerize on the frosted glass surface and cannot be easily removed.

[19] A. E. Ardis, U. S. Patents 2,467,926-7 (1949).