thioacetaldehyde (XVIIIb) with 2,4-Dinitrophenylhydrazine. 1.—2,4-Dinitrophenylhydrazine reagent (7.5 ml., 0.20 g. or 0.001 mole of 2,4-DNP) was added to a solution of XVIIIa[21] (0.14 g., 0.00049 mole) in 15 ml. of 95% ethanol, and the resulting solution was allowed to stand at room temperature. The formation of glyoxal 2,4-dinitrophenylosazone was noticed after 2.5 hours. The glyoxal 2,4-dinitrophenylosazone that had formed after five days weighed 0.06 g. (29%). The filtrate continued to deposit XVI.

When a mixture identical to that described above was heated at the reflux temperature for one hour and then allowed to stand for two days at room temperature, the yield of XVI was 73%.

2.—The same experiments described in 1 (above) were repeated using XVIIIb.[21] The yield of glyoxal 2,4-dinitrophenylosazone after five days at room temperature was 6%; after one hour at the reflux temperature followed by two days at room temperature the yield of XVI was 54%.

MINNEAPOLIS, MINNESOTA

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[21] W. E. Parham, THIS JOURNAL, **69**, 2449 (1947).

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

Vinylidene Cyanide. III[1]

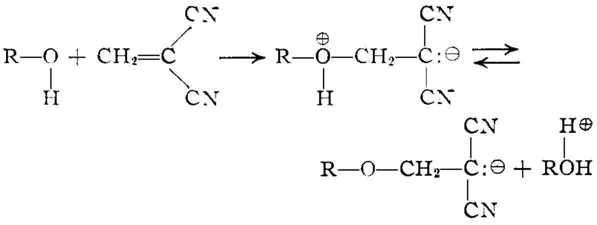
BY H. GILBERT, F. F. MILLER, S. J. AVERILL, R. F. SCHMIDT, F. D. STEWART AND H. L. TRUMBULL

RECEIVED SEPTEMBER 22, 1953

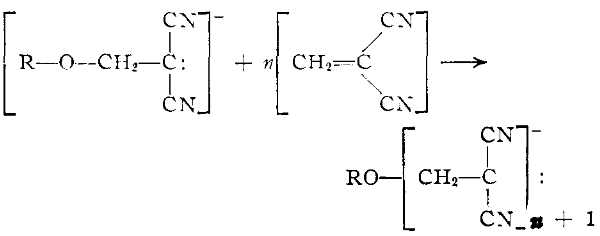
The homopolymerization of vinylidene cyanide proceeds vigorously by an ionic mechanism. Polymerization by free radical initiation is slow. The resulting polymer undergoes carbon chain scission in the presence of moisture.

Previous papers in this series[2] describe several syntheses of monomeric vinylidene cyanide, in this paper referred to as $V(CN)_2$. The present paper discusses the homopolymerization of this new monomer.[3]

Ionic Catalysis.—Monomeric $V(CN)_2$ polymerizes in the cold upon contact with water to form a hard, white, infusible resin. In this respect the monomer resembles nitroethylene.[4] The anionic initiation of $V(CN)_2$ proceeds rapidly upon contact with alcohols, amines and ketones and seems to be of the form



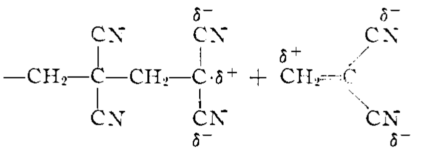
with polymerization occurring ionically



This rapid anionic polymerization of $V(CN)_2$ is attributable to the high electron withdrawal of the nitrile groups.

The water emulsion polymerization techniques commonly used with vinyl monomers have not been successful with authentic $V(CN)_2$ since we have always obtained contact polymerization before the emulsion can be formed.[5] Attempts to prepare copolymers of $V(CN)_2$ in water emulsion have also led to the homopolymeric vinylidene cyanide.

Free-Radical Catalysis.—When attempts are made to homopolymerize $V(CN)_2$ by the usual free-radical initiators, such as benzoyl peroxide or ultraviolet light, the propagation reaction is very slow and very little polymer is formed. The slow rate of addition of $V(CN)_2$ monomer to the radical chain end is probably due to high electrostatic repulsion



Resonance stabilization of the chain end also contributes to the slow rate of homopolymerization. Early in our work we found that rapid homopolymerization could be achieved with diazo catalysts, such as methoxyphenyldiazothionaphthalene. This, however, is believed to be an ionic polymerization caused by basic atoms in the diazo compound.

Polyvinylidene Cyanide.—The homopolymer is a hard, white, infusible, difficultly soluble resin (density 1.31) which darkens on standing in moist air. Depolymerization to monomer starts at about 160°, and continues at an increased rate as the temperature is raised.[6] No sharp melting point is observed, but X-ray diffraction patterns show some evidence of crystallinity. The polymer is soluble in dimethylformamide, tetramethylene cyclic sulfone, tetramethylurea,[7a] and triethyl phosphate.[7b] It is insoluble in all common solvents such as ketones, alcohols and hydrocarbons. The homo-

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[1] This paper was presented before the Division of Polymer Chemistry at the 124th Meeting of the American Chemical Society in Chicago, Ill., September 7, 1953.

[2] A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart and H. L. Trumbull, THIS JOURNAL, **72**, 1305 (1950); **72**, 3127 (1950).

[3] R. F. Schmidt, A. E. Ardis and H. Gilbert, U. S. Patent 2,589,294 (March 18, 1952); *C. A.*, **46**, 6430b (1952).

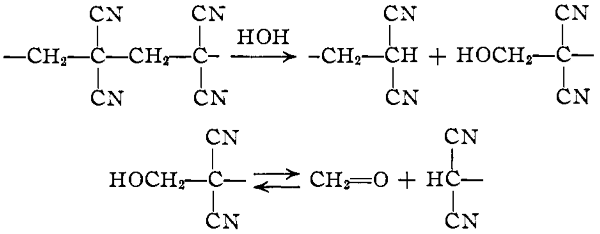
[4] H. Wieland and E. Sakellarios, *Ber.*, **52**, 898 (1919).

[5] Compare J. B. Dickey, U. S. Patent 2,466,395 (April 5, 1949); *C. A.*, **43**, 4897c (1949).

[6] A. E. Ardis and H. Gilbert, U. S. Patent 2,535,827 (December 26, 1950); *C. A.*, **45**, 3196b (1951).

[7] (a) A. E. Ardis, U. S. Patent 2,574,369 (November 6, 1951); *C. A.*, **46**, 1812g (1952); (b) R. F. Schmidt, U. S. Patent 2,594,353 (April 29, 1952); *C. A.*, **46**, 7367c (1952).

polymer is slowly decomposed by water and rapidly by bases. A preliminary study of the effect suggests that carbon–carbon bonds in the polymer chain are attacked. A suggested mechanism is



$$-\mathrm{CH_2}-\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}- \xrightarrow{\mathrm{HOH}} -\mathrm{CH_2}-\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{CH}}} + \mathrm{HOCH_2}-\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}-$$

$$\mathrm{HOCH_2}-\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}- \rightleftarrows \mathrm{CH_2{=}O} + \mathrm{H}\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}-$$

This mechanism accounts for the appearance of formaldehyde when the homopolymer remains in contact with water.

Experimental

Polymerization by Nitroanilines.—To pure $V(CN)_2$ was added 1% by weight of *o*-nitroaniline. Similar mixtures were made using the meta and para isomers. At the end of three days standing at room temperature the meta isomer had caused polymerization to a solid glass, the para isomer had produced a soft gel, and the ortho isomer a thin slurry. The rates of polymerization increase with increasing basicity of the nitroanilines.

Polymerization by Ketones.—To each of the following ketones was added 5% by weight of pure $V(CN)_2$, and the time to produce a gel at room temperature was recorded: acetylacetone (10 minutes), cyclopentanone (20 minutes), methyl ethyl ketone (40 minutes), *p*-methylacetophenone (120 minutes), chloroacetone (3,180 minutes), and benzophenone, no polymer. This indicates that the homopolymerization is roughly proportional to the enol content of the ketones.

Polymerization by Tertiary Butanol.—To anhydrous, liquid *t*-butyl alcohol was added a few drops of pure $V(CN)_2$. The monomer sank to the bottom of the flask and polymerized to a glassy disc. The alcohol had been purified by fractional distillation, and vacuum desiccating the solid alcohol over phosphorus pentoxide.

Polymerization by Water.—Pure $V(CN)_2$, when added to water ranging in *p*H from 0.94 to 11.8 polymerized rapidly in all cases, showing little effect of *p*H. Water saturated with picric acid at 20° polymerized the monomer within 3 minutes.

Polymerization by Dimethylformamide.—To a solution of 6.5 ml. of redistilled dimethylformamide in 10.0 ml. of dry benzene was added slowly a solution of 1.0 ml. of vinylidene cyanide in 1.0 ml. of benzene. The polymerization was complete in less than five minutes. The white polymeric vinylidene cyanide was filtered, washed with 100 ml. of benzene and dried. A 15% solution of this polymer in dimethylformamide could be spun into strong, white, lustrous fibers.

Into a 1-liter flask were charged 300 ml. of benzene and 120 ml. of dimethylformamide. A solution of 20 ml. of $V(CN)_2$ in 20 ml. of benzene was added dropwise, while stirring, over a 15-minute period. The contents of the flask was kept at 0–5° with an ice-bath. Polymer formed as each drop was added. After addition of monomer was complete, 300 ml. of benzene was added to thin the slurry. The polymer was filtered, washed with benzene and dried, to give 19 g. of polyvinylidene cyanide. The intrinsic viscosity, measured in dimethylformamide (stabilized with 1% SO_2) was 5.30.

It is interesting to compare the high molecular weight of this ionic homopolymer with that of polyisobutylene, where much lower temperatures are needed to give high molecular weight.

Polymerization at −70° by Dimethylformamide.—One gram of $V(CN)_2$ was added dropwise to 5 ml. of redistilled dimethylformamide. The solvent was maintained near −70° during the addition of the monomer by a Dry Ice–acetone-bath. Instantaneous polymerization occurred as each drop of monomer hit the cold solvent. As soon as the addition was complete, the polymer was isolated by adding 100 ml. of toluene, filtering, and washing with toluene. The yield was 0.95 g. of high molecular weight polyvinylidene cyanide. A 10% solution of the polymer in dimethylformamide containing 1% SO_2 was extremely viscous. Fibers spun from this solution had tenacities around 80,000 p.s.i. after being oriented by several successive hot stretches.

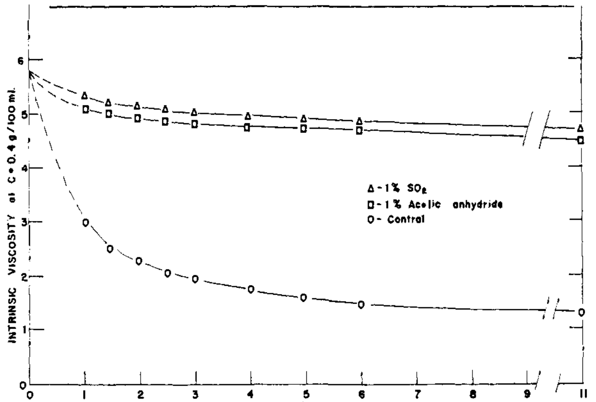


Fig. 1.—Degradation of polyvinylidene in dimethylformamide solution.

Polymerization by *o*-Chlorobenzoyl Peroxide.—To a 10% solution of pure $V(CN)_2$ in distilled monochlorobenzene was added 0.2% *o*-chlorobenzoyl peroxide. At the end of 24 hours, at 80°, only a trace of polymer had formed.

Polymerization by Ultraviolet Light.—A solution of 5.3 g. of benzene and 0.5 g. of $V(CN)_2$ was sealed into a quartz tube, the tube cooled by partial submersion, lying horizontally in ice-water. Irradiation by a mercury vapor source one foot above the tube produced about 2% conversion to polymer in six hours.

Polymerization by *p*-Methoxyphenyldiazothionaphthalene (MDN).—To a solution of 0.5 g. of $V(CN)_2$ in 9.5 g. of benzene was added dropwise during 45 minutes 1.0 ml. of a 1% solution of MDN in benzene. At the end of the addition the mixture was filtered, yielding 0.5 g. of polyvinylidene cyanide. Immediate formation of polymer could be observed with each addition of catalyst solution.

Polymerization by Tetramethylene Sulfone.—When a mixture of 85 g. of tetramethylene sulfone and 15 g. of pure $V(CN)_2$ was prepared, immediate polymerization followed. The polymeric vinylidene cyanide formed was swollen but not dissolved at room temperature by the sulfone. When a similar mixture was prepared, but with the addition of 0.025% sulfur dioxide to the sulfone before adding monomer, contact polymerization again occurred. Furthermore, with the sulfone containing 0.025% SO_2 and 0.50% water, the addition of pure monomer did not result in contact polymerization but mere solution. Polymerization subsequently occurred over a period of 18 hours. Finally, when the sulfone containing 0.50% water and no SO_2 was used, the addition of monomeric $V(CN)_2$ resulted in vigorous contact polymerization. Thus, anhydrous SO_2 alone has no effect on the rate of the ionic polymerization, but the hydrogen ions provided in the sulfone–water–SO_2 mixture probably acted as efficient chain terminators.

Degradation of Polyvinylidene Cyanide in Water.—One-tenth gram of finely powdered polyvinylidene cyanide, prepared by MDN catalysis, was dispersed in 100 ml. of distilled water at room temperature. At intervals 1-ml. aliquots were removed, filtered free of polymer, and the formaldehyde content determined colorimetrically (rosaniline test). At the end of 1.5 hours, formaldehyde appeared and steadily increased. After 102 hours, we found 20 p.p.m. formaldehyde in the aliquot. The formaldehyde was further identified by reaction with 2,4-dinitrophenylhydrazine. The non-recrystallized hydrazone melted at 161–163°, reported for this derivative 166–167°. Mixed melting point with authentic hydrazone, 164–165°.

Degradation of Polymer in Dimethylformamide.—A solution of 1.05 g. of polyvinylidene cyanide in 9.45 g. of dimethylformamide was placed in a Shoemaker viscosimeter[8]

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[8] David P. Shoemaker, E. Hoerger, R. M. Noyes and R. H. Blaker, *Anal. Chem.*, **19**, No. 2, 131 (1947).

and the times of flow measured at 33.8°. The readings in seconds were as follows: initial reading, 111.8 seconds; at 0.2 hours, 90.4 seconds; at 1.6 hours, 53.2 seconds; at 4.8 hours, 33.4 seconds; at 20.9 hours, 18.2 seconds; at 44.4 hours, 15.1 seconds; at 140.4 hours, 13.2 seconds.

Degradation of Polymer in Dimethylformamide in the Presence of Acids.—The homopolymer prepared as described previously, of intrinsic viscosity 5.30, was dissolved in dimethylformamide and the viscosity changes in the presence of acids observed. Figure I shows the effect of 1% sulfur dioxide and acetic anhydride in inhibiting the carbon chain scission of the homopolymer.

Degradation of Fibers in Water.—Fine filaments (diameter 2.7 × 10^{-4} inch) of polyvinylidene cyanide were spun from dimethylformamide solution, dried, and hot-stretched to a tenacity of 77,000 p.s.i., elongation of 22% at break.

FIBERS IMMERSED IN WATER AND TENACITIES OBTAINED

Time of immersion, hr.	*p*H of water	Final tenacity, p.s.i.
...	..	77,000
64.5	3.5	52,000
64.5	5.5	36,000
65.0	7.5	0
1.25	10.2	0
0.20	13.5	0
0.10	14.0	0

BRECKSVILLE, OHIO

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

Vinylidene Cyanide. V. The Aluminum Chloride Catalyzed Reaction of Vinylidene Cyanide and Aromatic Compounds

BY J. C. WESTFAHL AND T. L. GRESHAM

RECEIVED OCTOBER 7, 1953

Vinylidene cyanide reacts, in the presence of two equivalents of anhydrous aluminum chloride, with certain aromatic compounds to give monosubstituted malononitriles of the type $ArCH_2CH(CN)_2$. The reaction succeeds with aromatic hydrocarbons, phenols, phenol ethers and certain aromatic heterocycles. It fails with aromatic compounds which polymerize vinylidene cyanide or which are sufficiently deactivated by electron attracting groups. The introduction of two $-CH_2CH(CN)_2$ groups can occur with suitably active aromatic compounds.

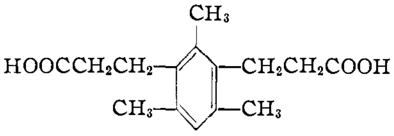
Recent communications[1,2] from this Laboratory described several syntheses of vinylidene cyanide (I). In the course of the study of this very reactive compound a new synthesis of monosubstituted malononitriles of the type Aryl $CH_2CH(CN)_2$ was developed. This paper describes the preparation of a number of monosubstituted malononitriles from I and aromatic compounds.

Reaction of I, a suitably reactive aromatic compound, and two equivalents of anhydrous aluminum chloride gave an aluminum chloride complex. The aluminum chloride complexes have been assumed to have the composition Aryl $CH_2CH(CN)_2\cdot 2AlCl_3$. Hydrolysis of the aluminum chloride complex gave Aryl $CH_2CH(CN)_2$ (equation 1).

$$\text{Aryl-H} + CH_2{=}C(CN)_2 + 2AlCl_3 \longrightarrow \text{Aryl } CH_2CH(CN)_2\cdot 2AlCl_3 \xrightarrow{H_2O} \text{Aryl } CH_2CH(CN)_2 \qquad (1)$$

All reactions were carried out with one mole of anhydrous aluminum chloride per mole of nitrile group unless otherwise noted. The results obtained with a number of aromatic compounds are presented in Table I. Structures of the products were established as shown in Table II.

The reaction of mesitylene with I in a molar ratio of one-to-two gave a viscous liquid which could not be crystallized. Acid hydrolysis produced a solid acid of m.p. 175–176° which gave analytical results in agreement with II.


II

Reaction of hydroquinone dimethyl ether with I in a one-to-two molar ratio gave 1,4-dimethoxy-2,5-bis-(2,2-dicyanoethyl)-benzene (III). In the preparation of 1,4-dimethoxy-2-(2,2-dicyanoethyl)-benzene (IV), III was formed as a by-product. The reaction of equimolar amounts of I and IV using four equivalents of aluminum chloride also gave III. The structure of III was established as shown in Chart I.

The 2,5-dimethoxyterephthalic acid (VII) was identified by its m.p.[3] and by conversion to its diethyl ester.[3]

No products were isolated from the action of I on *p*-nitroanisole or on 2-nitro-1,4-dimethoxybenzene. The lack of reaction with 2-nitro-1,4-dimethoxybenzene was unexpected since 2-nitroanisole has been acylated in the 4-position with acetyl chloride and aluminum chloride.[4]

Reaction of I with *p*-chloroanisole gave 2-methoxy-5-chlorobenzylmalononitrile (IX). The structure of IX was established as shown in Chart II. Since only two structures are possible for the product derived from one molecule of I and one molecule of *p*-chloroanisole, the isolation of a neutral solid XIII from the sequence of reactions in Chart II establishes the structure of the product as IX. The other possible structure would yield an acid by the sequence of reactions in Chart II.

The reaction of I with furan proceeded in an abnormal manner. Hydrolysis of the aluminum chloride complex gave practically no polymer of I thus indicating complete reaction. Distillation of the crude product gave only a small amount of volatile

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(1) A. E. Ardis, *et al.*, THIS JOURNAL, **72**, 1305 (1950).

(2) A. E. Ardis, *et al.*, *ibid.*, **72**, 3127 (1950).

(3) J. U. Nef, *Ann.*, **258**, 297, 299 (1890).

(4) F. Stockhausen and L. Gattermann, *Ber.*, **25**, 3523 (1892).