No depression of the melting point was observed on admixture with a sample obtained from method A. The infrared spectra were identical.

**Method C.**—A solution of 13.2 g. (0.2 mole) of malononitrile and 8 g. (0.2 mole) of sodium hydroxide in 50 ml. of water was added to 50 g. of cupric sulfate pentahydrate in 100 ml. of warm water. The mixture was heated to 90° and filtered to remove the insoluble inorganic salts. On cooling, the crude dimer separated (5.5 g., 42%) and was recrystallized from water, m.p. 170–171°. A mixture of this material and a sample from method A gave no depression of the melting point.

**Reactions of Malononitrile Dimer. A. With Bromine.**—To a suspension of 13.2 g. (0.1 mole) of malononitrile dimer in 150 ml. of water was added slowly 32 g. (10.3 ml., 0.2 mole) of bromine with shaking. The solid was collected by filtration, washed with water and dried. The yield was 26.9 g. (93%). Crystallization from 50% aqueous ethyl alcohol yielded an almost colorless crystalline solid, m.p. 155° dec.

*Anal.* Calcd. for $C_6H_2Br_2N_4$: N, 19.32; Br, 55.14. Found: N, 19.40; Br, 55.39.

B. **With *p*-Dimethylaminobenzaldehyde.**—A solution of 0.53 g. (0.004 mole) of the dimer and 1.2 g. (0.008 mole) of *p*-dimethylaminobenzaldehyde in 10 ml. of methanol containing a trace of piperidinium acetate was heated at reflux for 30 minutes. The color of the reaction mixture deepened to orange. On cooling, yellow-orange crystals of the benzylidene dye were obtained in 85% yield, m.p. 270–272° dec. The infrared spectrum of this compound showed bands at 2.9, 3.0 and 3.1 μ, indicating that the condensation occurred through the methylene rather than through the amino group. The ultraviolet spectrum in acetone gave a maximum at 434 mμ (ε 33,400).

*Anal.* Calcd. for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98; N, 26.60. Found: C, 68.63; H, 4.99; N, 26.56.

C. **With Diethyl Oxalate.**—A mixture of 13.2 g. (0.1 mole) of the dimer and 16 g. (0.11 mole) of diethyl oxalate was added quickly to 75 ml. of an ethyl alcohol solution containing 0.2 mole of sodium ethoxide. The mixture was stirred for two hours, diluted with two volumes of benzene and filtered. Crystallization of the solid from 90% aqueous *n*-propyl alcohol yielded bright yellow crystals of disodium-4-cyano-5-dicyanomethylene-2,3-dioxopyrrolidine.

*Anal.* Calcd. for $C_8N_4O_2Na_2$: Na, 19.99. Found: Na, 19.60.

The disodium derivative was dissolved in a minimum of water and treated with excess hydrochloric acid. However, one sodium atom was retained, demonstrating the strongly acidic nature of this substance. Crystallization from 90% aqueous *n*-propyl alcohol yielded yellow, hair-like crystals of the monosodium derivative.

*Anal.* Calcd. for $C_8HN_4O_2Na \cdot 2H_2O$: C, 39.35; H, 2.06; N, 22.94; Na, 9.42. Found: C, 39.69; H, 2.28; N, 22.81; Na, 8.82.

D. **With Hydrazines.** 1. **Hydrazine Hydrate.**—To a suspension of 6.6 g. (0.05 mole) of malononitrile dimer in 65 ml. of water was added 2.8 g. (0.056 mole) of hydrazine hydrate with stirring. When the exothermic reaction had subsided, the mixture was heated at 90° for 15 minutes. On cooling, 5.0 g. (68%) of the pyrazole derivative separated as rodlets. Recrystallization from water yielded a product melting at 197–198°.

*Anal.* Calcd. for $C_6H_5N_5$: C, 48.97; H, 3.43; N, 47.60; mol. wt., 147. Found: C, 49.23; H, 3.47; N, 47.69; mol. wt., 141.

2. **Phenylhydrazine.**—A mixture of the dimer (9.5 g., 0.072 mole) and 50 ml. of methanol was heated at reflux for one hour with 8.2 g. (0.075 mole) of phenylhydrazine. From the cooled mixture was obtained 7.7 g. (48%) of 1-phenyl-3-amino-4-cyano-5-pyrazoleacetonitrile, m.p. 166–167°.

*Anal.* Calcd. for $C_{12}H_9N_5$: C, 64.56; H, 4.06; N, 31.38. Found: C, 64.70; H, 4.21; N, 31.49.

E. **With Hydrogen Bromide.**[9]—Dry hydrogen bromide was passed through a solution of 3.96 g. (0.03 mole) of the dimer in 50 ml. of tetrahydrofuran while the mixture was cooled in an ice-bath. The solid (3.2 g.) which formed was collected by filtration, dissolved in a minimum amount of boiling water, and the solution made alkaline with dilute sodium hydroxide. The resulting solid was filtered, washed with water and dried. The infrared spectrum of this product indicated the presence of amino and conjugated nitrile groups. An identical product was obtained in 72% yield starting with malononitrile, m.p. 260–265° dec.

*Anal.* Calcd. for $C_6H_5BrN_4$: N, 26.30; Br, 37.51; mol. wt., 213. Found: N, 26.26; Br, 37.38; mol. wt., 214.

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[9] W. J. Middleton, U. S. Patent 2,790,806 (1957).

WILMINGTON, DELAWARE

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[CONTRIBUTION NO. 342B FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

# Cyanocarbon Chemistry. XII.[1] Some Physical Characteristics of Cyanocarbon Derivatives

BY CATHARINE E. LOONEY AND J. R. DOWNING

RECEIVED NOVEMBER 14, 1957

A study has been made of molecular spectra and thermal properties of some cyanocarbons and their salts. Infrared and Raman spectra showed that the —C≡N and —C=C— stretching frequencies of these compounds are highly dependent upon charge and resonance effects. The degree of conjugation also has a pronounced effect on ultraviolet spectra. Heats of combustion and sublimation of tetracyanoethylene were found to be 722 and 18.65 kcal. per mole. A spontaneous exothermic rearrangement of cyano groups was observed to occur in some of these compounds at elevated temperatures.

## Introduction

A new class of chemical compounds has been made available by the synthesis in this Laboratory of tetracyanoethylene (TCNE), highly cyano-substituted hydrocarbons (cyanocarbons) and cyanocarbon salts. Spectroscopic and thermal properties determined in the course of a physical study of these materials are presented in this paper.

**Infrared and Raman Spectra.**—Of primary interest in the infrared and Raman spectra of cyanocarbons are the positions of the C≡N and C=C stretching frequencies. The C≡N frequency in simple aliphatic nitriles is found at wave lengths between 4.40 and 4.45 μ. The effect of conjugation on the position of the nitrile absorption is to shift this band to slightly longer wave lengths (near 4.5 μ in acrylonitrile, 1,1-dimethyl-2,2-dicyanoethylene and benzonitrile). The $CN^-$ group in such inorganic cyanides as KCN and the ferri- and ferrocyanides is shifted to about 4.8 μ because of the ionic character of these compounds. The stretching frequency of an isolated C=C bond is

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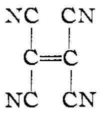
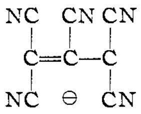
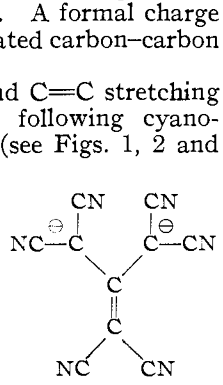
[1] Paper XI, R. A. Carboni, D. D. Coffman and E. G. Howard, THIS JOURNAL, **80**, 2838 (1958).

found at 6.0–6.1 $\mu$. Conjugation with another $C=C$ group usually results in a splitting into symmetric and asymmetric components with the longer wave length band located near 6.25 $\mu$. A formal charge shifts the absorption of a conjugated carbon–carbon system to longer wave lengths.

The positions of the $C\equiv N$ and $C=C$ stretching frequencies are given for the following cyanocarbons and cyanocarbanions: (see Figs. 1, 2 and 3)





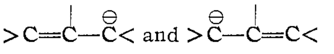


| | | |
|---|---|---|
| $C\equiv N$ 4.42, (4.49) $\mu$ (IR) | 4.53 $\mu$ (IR) | 4.56 (4.60)(4.70) $\mu$ (IR) |
| $C=C$ 6.55 $\mu$ (R) | 6.67 $\mu$ (IR) | 7.0 $\mu$ (IR + R) |

(R) indicates Raman and (IR) indicates infrared

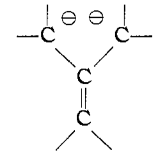
The wave length positions in parentheses indicate minor peaks.

Thus, conjugation and formal charge have a more pronounced effect on the $C=C$ frequencies than on the $C\equiv N$ frequencies. The position of the double bond in TCNE is indicative of considerable resonance between the $C=C$ and the nitrile groups. In the case of the 1,1,2,3,3-pentacyanopropenide ion, resonance between the two forms

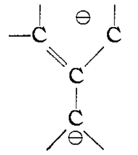


$>C=\overset{|}{C}-\overset{\ominus}{C}<$ and $>\overset{\ominus}{C}-\overset{|}{C}=C<$

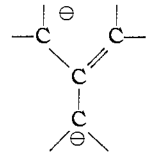
reduces still further the double bond character of the $C=C$ links. This shift becomes even more pronounced in 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide ion where resonance occurs among the three equivalent structures



(1)



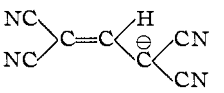
(2)



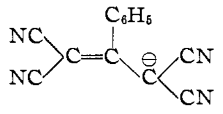
(3)

The compounds $(CH_3)_2C=C(CN)_2$ and $(CH_3)_3C\text{-}C(CN)=C(CN)_2$ both have nitrile bands near 4.47 $\mu$ which is the expected region for conjugated, neutral cyanocarbons. The extent of conjugation is less in these molecules than in TCNE, and this result is confirmed by the position of the $C=C$ frequencies at 6.20 and 6.35 $\mu$, respectively. The position of the nitrile frequency in $C_6H_5C(CN)=C(CN)_2$ is 4.48 $\mu$—again typical of a conjugated, neutral nitrile. The presence of a phenyl group interferes with assignment of the $C=C$ vibration.

The two singly charged anions



and



would be expected to have a $C=C$ stretching frequency similar to that of the 1,1,2,3,3-pentacyanopropenide ion (6.7 $\mu$). The first anion does, in fact, absorb at 6.7 $\mu$; in the second there is again interference from phenyl vibrations in this region. The $C\equiv N$ and $C=C$ stretching frequencies are thus in accord with that expected for cyanocarbanions in which resonance structures make a significant contribution to the ground state.

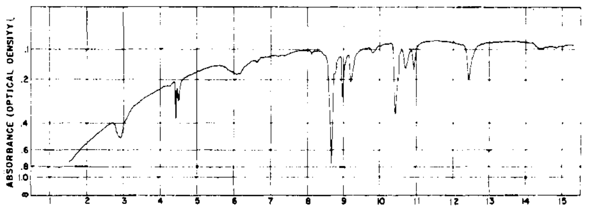


Fig. 1.—Infrared spectrum of tetracyanoethylene.

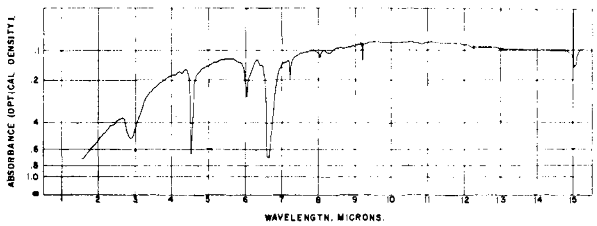


Fig. 2.—Infrared spectrum of 1,1,2,3,3-pentacyanopropenide anion.

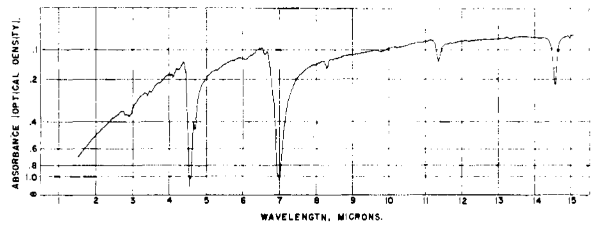
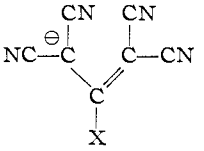
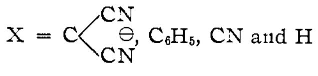


Fig. 3.—Infrared spectrum of 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide anion.

**Ultraviolet Spectra.**—In neutral cyano compounds there is a close parallel between the position of the $C=C$ stretching frequency in the infrared and the position of the first electronic transition in the ultraviolet (see Table I). The shifts to longer wave lengths are readily interpreted in light of the increased extent of the conjugation throughout this series of compounds.

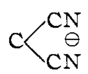
Since no simple correlation exists between the position of the $C=C$ stretching frequency and the position of the first ultraviolet absorption band of the anions, an alternate interpretation of the spectra in terms of resonance structures is presented. The anions to be discussed can be represented by the general formula





$X = C\langle^{CN}_{CN}\ominus$, $C_6H_5$, CN and H

The 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide ion can resonate freely among the three structures illustrated previously. Substitution of phenyl, nitrile or H for the group



$C\langle^{CN}_{CN}\ominus$

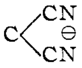
TABLE I

ULTRAVIOLET ABSORPTION AND C=C STRETCHING FREQUENCIES OF NEUTRAL CYANO COMPOUNDS

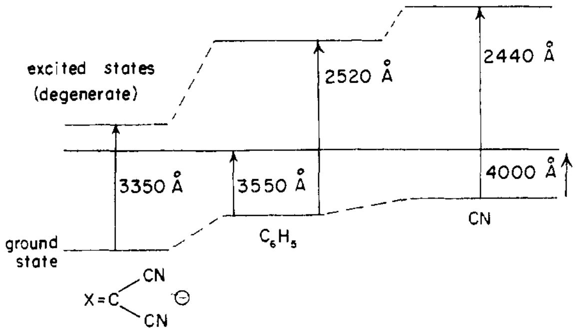
| Compound | First electronic transition in Å. | C=C stretching frequency in μ |
|---|---|---|
| $(CH_3)_2C{=}C(CN)_2$ | 2330 | 6.20 |
| $((CH_3)_3C)(CN)C{=}C(CN)_2$ | 2500 | 6.35 |
| $(CN)_2C{=}C(CN)_2$ | 2650 | 6.55 |
| $(C_6H_5)(CN)C{=}C(CN)_2$ | 3430 | ..[a] |

[a] Phenyl vibration interferences with assignment.

restricts the amount of resonance in the system, since resonance structure (1) no longer contributes as much to the stability of the ground state. By methods of the theory of the structure representation,[2-4] it can be shown that the first electronic band in the 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide ion would be expected to involve a transition between a totally symmetric and an orbitally degenerate state. Substitution of phenyl, nitrile or H for the group



splits the degenerate state into two components. One band shifts to longer, the other to shorter wave lengths. This splitting can be depicted diagrammatically as



The first transition in the 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide ion consists of two overlapping transitions of equal intensity. As the degeneracy is split by substitution, the theory of the structure representation predicts that the intensity of the longer wave length component increases and that of the shorter wave length band decreases. No absolute intensity measurements have been made, but a qualitative check from the ratios of the absorption coefficients of the two bands indicates that the intensities are in qualitative agreement with the theory.

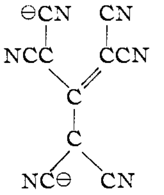
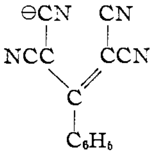
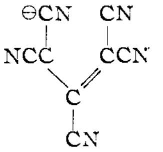
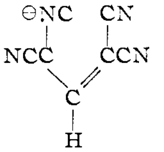
$$X = C_6H_5 \qquad\qquad X = CN$$

$$\frac{K3550\ \text{Å.}}{K2520\ \text{Å.}} \cong 2.8 \qquad \frac{K4000\ \text{Å.}}{K2440\ \text{Å.}} \cong 4.4$$

As the contribution of resonance structure (1) to the ground state decreases to 0 (corresponding to a very large perturbation of structure (1)), the wave length of the first transition increases to about 5000 Å. However, as found in the parallel case of crystal violet and Michler hydrol blue,[2-4] there is a corresponding increase in the interaction between structures (2) and (3). This effect can be interpreted as an increase in the central C–C–C bond angle from approximately 120° toward 180°. Complete linearity is of course prevented because of the presence of the hydrogen atom. Increased interaction between structures (2) and (3) is reflected in a reversal in the shift of the longer wave length component back to shorter wave length. This band is observed at 3440 Å. in the compound for which X = H. The ultraviolet spectra of these compounds are also in accord with the predicted effects of conjugation and resonance structure on wave length shifts. Table II summarizes the infrared and ultraviolet frequencies for these cyanocarbanions.

TABLE II

ULTRAVIOLET TRANSITIONS AND C=C STRETCHING FREQUENCIES OF SOME CYANOCARBANIONS

| Cyanocarbanion | First two electronic transitions in Å. | C=C stretching frequency in μ |
|---|---|---|
|  | 3350<br>3350 | 7.00 |
|  | 3550<br>2520 | ..[a] |
|  | 4000<br>2440 | 6.70 |
|  | 3440<br>2150 (?) | 6.70 |

[a] Phenyl vibration interferes with assignment.

**Heats of Combustion and Sublimation of Tetracyanoethylene (TCNE).**—The heat of combustion of TCNE was determined at our request by the United States Testing Co., Inc., of Hoboken, N. J., using an Emerson bomb calorimeter in accordance with standard laboratory procedures. The heat of combustion found for the following equation is 722 kcal. per mole.

$$(NC)_2C{=}C(CN)_2 + 6O_2 \longrightarrow 6CO_2 + 2N_2 + 722\ \text{kcal.}$$

The heat of sublimation of TCNE obtained from an Arrhenius treatment of the vapor pressure *vs.* temperature data shown in Fig. 4 is 18,650 calories per mole.

**Spontaneous Exothermic Rearrangement of Cyano Groups.**—Most of the cyano compounds investigated, with the exception of TCNE, rearranged spontaneously when heated to open the

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(2) W. T. Simpson, THIS JOURNAL, 75, 597 (1953).

(3) W. T. Simpson and C. W. Looney, *ibid.*, 76, 6285 (1954).

(4) W. T. Simpson and C. W. Looney, *ibid.*, 76, 6293 (1954).

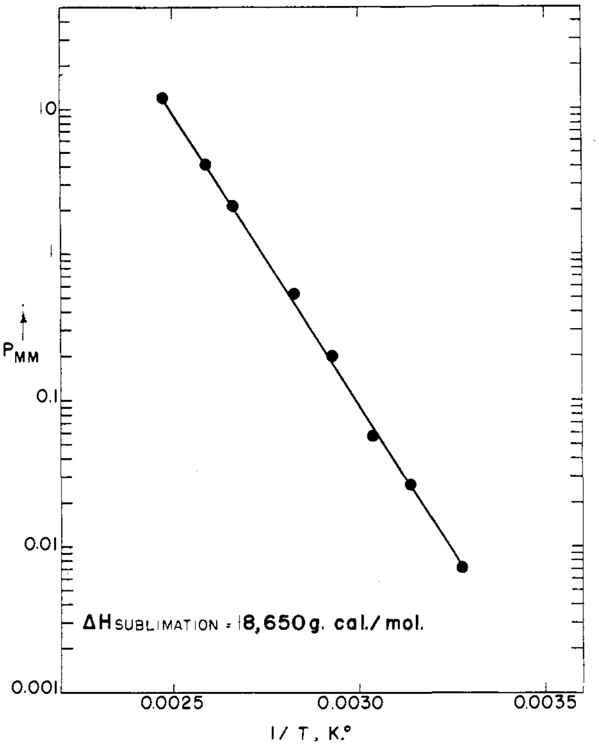

Fig. 4.—Vapor pressure of tetracyanoethylene.

cyano triple bond, *e.g.*, —C≡N → C=N—. This rearrangement occurred with evolution of heat and at temperatures which varied from one compound to another. The products of the rearrangement were black, refractory, powders containing about 40% nitrogen. The powders appeared amorphous by X-ray diffraction, and, although infrared spectra were poorly defined, no evidence was obtained for the presence of cyano groups.

Standard differential thermal analysis techniques (DTA)[5] were used to determine the temperatures at which exothermic rearrangement occurred in salts of cyanocarbon acids. A typical DTA pattern is shown in Fig. 5. Endothermic effects indicating loss of water of hydration or other structural changes were observed at lower temperatures. The energy release was usually sufficient to give a quick temperature rise ($\Delta T$) of from 25 to 275° at the rearrangement temperature ($T_R$). The values of $T_R$ and $\Delta T$ of Table III were taken from strip-chart recordings of the temperature registered on a thermocouple inserted directly into the samples during heating as shown in Fig. 6. The values of $\Delta T$ varied with sample packing and therefore have no quantitative thermochemical significance.

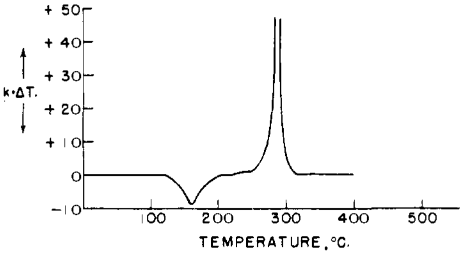

Fig. 5.—Differential thermal analysis of cupric 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide.

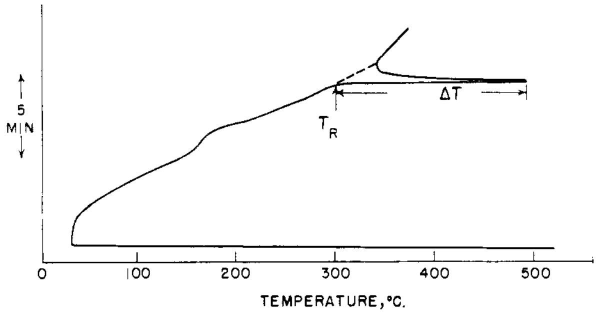

Fig. 6.—Heating curve for cupric 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide.

The data of Table III shows that the rearrangement temperature can be used as a characterization constant for cyanocarbon derivatives under controlled conditions of sample heating rate. Changing either the cation or the anion affects the temperature at which rearrangement occurs, but there does not appear to be a simple relationship between rearrangement temperature and chemical structure.

TABLE III

EXOTHERMIC DECOMPOSITION TEMPERATURES OF CYANO COMPOUNDS

| Compound[a] | $T_R$ | $\Delta T$ |
|---|---|---|
| $Ag[C(CN)_3]$ | 355 | 190 |
| $K[C(CN)_3]$ | 404 | 50 |
| $Ba[C(CN)_3]_2$ | 518 | 161 |
| $Ag_2[(NC)_2C{=}C(C(CN)_2)_2]$ | 225 | 35 |
| $K_2[(NC)_2C{=}C(C(CN)_2)_2]$ | 513 | 81 |
| $Ba[(NC)_2C{=}C(C(CN)_2)_2]$ | 533 | 25 |
| $Ba[(NC)_2C{=}C(C(CN)_2)_2]$[b] | 537 | 63 |
| $NH_4[(NC)_2C{=}CHC(CN)_2]$ | 242 | 103 |
| $K[(NC)_2C{=}CHC(CN)_2]$ | 313 | 150 |
| $Na[(NC)_2C{=}CHC(CN)_2]$ | 320 | 235 |
| $Ba[(NC)_2C{=}CHC(CN)_2]_2$ | 348 | 210 |
| $H[(NC)_2C{=}C(CN)C(CN)_2]$ | 212 | 158 |
| $Ag[(NC)_2C{=}C(CN)C(CN)_2]$ | 261 | 273 |
| $Cu[(CN)_2C{=}C(C_6H_5)C(CN)_2]_2$ | 197 | 41 |
| $Na[(CN)_2C{=}C(C_6H_5)C(CN)_2]_2$ | 425 | 100 |
| $Co[(NC)_2C{=}C(OEt)C(CN)_2]_2$ | 215 | 110 |
| $Ni[(NC)_2C{=}C(OEt)C(CN)_2]_2$ | 235 | 100 |
| $Na[(NC)_2C{=}C(OEt)C(CN)_2]$ | 295 | 130 |

[a] Formulas omit water of hydration. [b] Another preparation.

The energy of rearrangement per cyano group in these compounds was not determined quantitatively from the data, but it was evidently sufficiently high to be an important factor contributing to the high energies of combustion found for cyano compounds.

## Experimental

The samples used in this work were prepared and purified as described in the other papers of this series and were used as received unless otherwise indicated.

Infrared spectra were obtained using the KBr disk technique. The 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide ion was studied both as the potassium and barium salt, the 1,1,3,3-tetracyano-2-phenylpropenide ion as the sodium salt, the 1,1,2,3,3-pentacyanopropenide ion as the

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(5) R. E. Grim, *Ann. N. Y. Acad. Sci.*, 53, 1031 (1951).

corresponding acid, and the 1,1,3,3-tetracyanopropenide ion as the barium salt. Spectra were obtained on a Perkin-Elmer model 21 double beam infrared spectrometer equipped with NaCl optics (2–15 μ) and with a $CaF_2$ prism (2–8 μ). The Raman spectrometer used to determine the position of the C═C stretching frequency in tetracyanoethylene is similar to that described by Rank, *et al.*[6] Ultraviolet spectra were obtained in water or methanol solution using a Cary model 11 ultraviolet spectrometer.

Vapor pressure *vs.* temperature data for tetracyanoethylene (Fig. 4) were determined by a vapor saturation method. A metered stream of nitrogen were saturated by passing it slowly over crystals of tetracyanoethylene held at the several temperatures. Tetracyanoethylene vapor in the metered volume of nitrogen was trapped in N,N-dimethylaniline and the amount determined quantitatively by measuring absorbance of the red dye formed by the reaction of N,N-dimethylaniline with tetracyanoethylene.[7]

The differential thermal analysis apparatus and procedures were conventional, using Pt *vs.* Pt–10% Rh thermocouples. Powdered samples and the alumina reference were packed against the thermocouples in $^1/_8$ in. platinum tubes fitted over the ceramics holding the thermocouple wires. The data were recorded on a standard 5 millivolt double-X strip-chart recorder. By using a preamplifier in the differential temperature channel, the over-all sensitivity was set at 200 microvolts full scale deflection. The heating rate was 15° per minute. The modified apparatus consisted of a horizontal electric tube furnace lined with a Pyrex tube and activated by a Powerstat to control the heating rate to about 25° per minute. An iron–constantan thermocouple was surrounded by 0.1 g. of powdered sample in a small test-tube placed in the center of the furnace. As the sample was heated, the temperature was recorded on a conventional strip-chart recording potentiometer with a range of 0 to 800°. The low temperature edge of the sharp temperature rise, which marked the onset of the rearrangement reaction, could be read with an accuracy of ±5° in most cases.

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# Base-catalyzed Rearrangement of Epoxides

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The reaction of a series of phenyl-substituted ethylene oxides with the base lithium diethylamide has been investigated. *cis*-Stilbene oxide was isomerized to desoxybenzoin (70%), *trans*-stilbene oxide gave diphenylacetaldehyde (66%), triphenylethylene oxide formed benzhydryl phenyl ketone (80%) and 1,1-diphenyl-2-*p*-tolylethylene oxide yielded benzhydryl *p*-tolyl ketone (41%). Tetraphenylethylene oxide and 1,1-diphenylethylene oxide did not rearrange when treated with lithium diethylamide. A mechanism based on abstraction of a proton from the oxirane ring by the base followed by ring opening or rearrangement is proposed.

The fact that cycloöctatetraene oxide is isomerized to cycloöctatrienone by treatment with lithium diethylamide[1] has prompted further study of the reaction of epoxides with bases. The acid-catalyzed and thermal rearrangements of epoxides to carbonyl compounds are well known,[2,3] but there are few examples of the rearrangement of epoxides by bases, except for the isomerization of the oxides of α,β-unsaturated ketones to α-diketones.[4] The reaction of Grignard reagents with epoxides in many instances gives rise to products whose formation may be explained by rearrangement of the epoxide to a carbonyl compound, followed by addition of the organometallic agent. However, in several cases it has been shown that the rearrangements are caused by the magnesium halide present in the Grignard reagents and that these reactions therefore may be considered to be acid catalyzed.[2,3,5]

The epoxides derived from phenyl-substituted derivatives of ethylene were chosen for the study, namely, 1,1-diphenylethylene, *cis*- and *trans*-stilbene, triphenylethylene, 1,1-diphenyl-2-*p*-tolylethylene and tetraphenylethylene. They were prepared conveniently by oxidation of the olefins with commercial peracetic acid. This method failed only with 1,1-diphenylethylene, in which case the oxide was prepared from the corresponding bromohydrin.[6]

To bring about the isomerizations, the epoxides were treated with two equivalents of lithium diethylamide in ether at −20°. The stilbene oxides were found to have rearranged when the ether solutions were warmed to room temperature and refluxed for one hour. *cis*-Stilbene oxide gave desoxybenzoin, isolated in 70% yield, as the product of rearrangement. *trans*-Stilbene oxide yielded diphenylacetaldehyde which was isolated as its methone derivative in 66% yield.

Triphenylethylene oxide did not react completely under these conditions and required heating at 65° for several hours after replacement of the ether by benzene to bring about conversion to benzhydryl phenyl ketone in 80% yield.

1,1-Diphenyl-2-*p*-tolylethylene oxide was not converted cleanly to a ketone when subjected to conditions similar to those used with triphenylethylene oxide. By chromatographic separation of the mixture of products three pure compounds were isolated. These were the recovered oxide (23%), benzhydryl *p*-tolyl ketone (31%) and 2,2-diphenyl-1-*p*-tolylethanol (18%). The structures of the ketone and alcohol were established by comparison of melting points and infrared spectra with authentic samples. The isomeric ketone 2-phenyl-

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