

TABLE III

<div style="text-align: center;"> $\begin{array}{c} \text{CN} \quad \text{CN} \\ \quad \\ \text{X} - \text{C} - \text{C} - \text{SO}_2\text{OY} \\ \quad \\ \text{CN} \quad \text{CN} \end{array}$ SALTS OF 1,1,2,2-TETRACYANOSULFONIC ACID </div>													
X	Y	Empirical formula	M.p., °C.	Recrystn. solvent ^a	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %		
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
H	Na	C ₈ HN ₄ SO ₃ Na	180 d.	A	31.03	31.10	0.44	0.53	24.13	24.41	13.81	13.75	
H	N(CH ₃) ₄	C ₁₀ H ₁₂ N ₄ SO ₃ ^b	120–122 d.	B–C	42.39	42.50	4.62	4.72	24.74	24.45	11.31	11.50	
H	N(C ₂ H ₅) ₄	C ₁₄ H ₁₈ N ₄ SO ₃ ^c	98–100 d.	B–C	49.54	49.83	6.24	6.32	20.63	20.62	9.44	9.45	
H	C ₁₀ H ₁₀ N ^d	C ₁₂ H ₁₁ N ₄ SO ₃	85–86	C	54.38	54.57	3.14	3.16	19.82	19.66	9.07	9.19	
H	S(CH ₃) ₃	C ₉ H ₁₀ N ₄ S ₂ O ₃	84–85 d.	None	37.75	38.06	3.52	3.74	19.57	19.62	22.40	22.43	
C ₆ H ₅ CH ₂ N(CH ₃) ₃	C ₆ H ₅ CH ₂ N(CH ₃) ₃	C ₂₂ H ₂₂ N ₄ SO ₃	198–199	C	61.39	61.18	6.34	6.49	16.52	16.52	6.30	6.22	
C ₁₀ H ₁₀ N ^d	C ₁₀ H ₁₀ N ^d	C ₂₆ H ₂₆ N ₄ SO ₃	125–150 d.	C	62.89	62.72	4.06	4.00	16.93	17.04	6.46	6.75	
C ₁₁ H ₁₂ N ^e	C ₁₁ H ₁₂ N ^e	C ₂₈ H ₂₈ N ₄ SO ₃	172–173 d.	B	64.10	64.00	4.61	4.67			6.11	6.26	
Ag	N(CH ₃) ₄	C ₁₀ H ₁₂ N ₄ SO ₃ Ag	100 d.	None					17.95	17.77	27.65 ^f	27.81 ^f	

^a A = acetone-ether, B = methanol, C = water. ^b Calcd.: neut. equiv., 283.3. Found: neut. equiv., 285; *pK_a*, 2.70. ^c Calcd.: neut. equiv., 339.4. Found: neut. equiv., 338; *pK_a*, 2.62. ^d N-Methylquinolinium. ^e N-Methyllepidinium. ^f Silver analysis.

talline precipitate which formed was collected on a filter and washed thoroughly with acetone to give 15.2 g. of the silver salt of tetramethylammonium 1,1,2,2-tetracyanoethanesulfonate in the form of a white crystalline powder.

Hydrolysis of 1,1,2,2-Tetracyanoethanesulfonic Acid.—A solution of 1,1,2,2-tetracyanoethanesulfonic acid, prepared by treating a suspension of 6.4 g. (0.05 mole) of tetracyanoethylene with sulfur dioxide, was boiled for 30 minutes, and then cooled. White crystals (1.2 g.) of tetracyanoethane separated upon cooling.

Oxidation of Bis-(trimethylbenzylammonium) Salt of 1,1,2,2-Tetracyanoethanesulfonic Acid.—One gram of this salt was suspended in 10 ml. of water and 5 ml. of concd. nitric acid was added dropwise. An exothermic reaction occurred, and a precipitate of 0.21 g. of tetracyanoethylene formed.

Conversion of Bis-salt to Mono-salt.—One gram of the bis-(N-methylquinolinium) salt of 1,1,2,2-tetracyanoethanesulfonic acid was dissolved in 25 ml. of hot 2% hydrochloric acid solution. Upon cooling, long white needles (0.47 g.) of

N-methylquinolinium 1,1,2,2-tetracyanoethanesulfonate separated.

Reaction of α,α' -Azodiisobutyronitrile with Tetracyanoethylene.¹⁸—A mixture of 4.92 g. (0.03 mole) of α,α' -azodiisobutyronitrile, 1.28 g. (0.01 mole) of tetracyanoethylene and 150 ml. of benzene was heated at reflux for eight hours. Benzene was distilled off leaving 5.34 g. of solid residue. Sublimation of this solid at 80–100° (1 mm.) gave 1.83 g. (43% yield) of tetramethylsuccinonitrile. Further sublimation at 120° (0.8 mm.) gave 0.97 g. (37% yield) of crude 2,3,3,4,4,5-hexacyano-2,5-dimethylhexane. This product was obtained as white crystals, m.p. 150–151° after an additional sublimation at 120° (0.8 mm.).

Anal. Calcd. for C₁₄H₁₂N₆: C, 63.62; H, 4.58; N, 31.80. Found: C, 63.88; H, 4.71; N, 32.12.

(18) C. G. Krespan, U. S. Patent 2,717,261 (1955).

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 438 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. IV.¹ Dicyanoketene Acetals

BY W. J. MIDDLETON AND V. A. ENGELHARDT

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Dicyanoketene acetals were prepared by the urea-catalyzed reaction of tetracyanoethylene with alcohols. The dimethyl and diethyl acetals were prepared from tetracyanoethylene and methyl and ethyl alcohol, and several cyclic acetals were prepared from 1,2- and 1,3-glycols. The dicyanoketene acetals reacted with ammonia and primary and secondary amines to give 1-amino-1-alkoxy-2,2-dicyanoethylenes and 1,1-diamino-2,2-dicyanoethylenes. The dicyanoketene cyclic acetals behave as alkylating agents toward tertiary amines, alkyl sulfides, thioureas, thioamides and thiosemicarbazide, and adducts of the ethylene and trimethylene acetals with these bases were prepared and characterized as "inner-salt" compounds.

In a previous paper of this series,¹ addition reactions involving the ethylenic double bond of tetracyanoethylene were described. Inasmuch as certain active hydrogen compounds were demonstrated to add to tetracyanoethylene, it was of interest to study the reaction of alcohols with tetracyanoethylene.

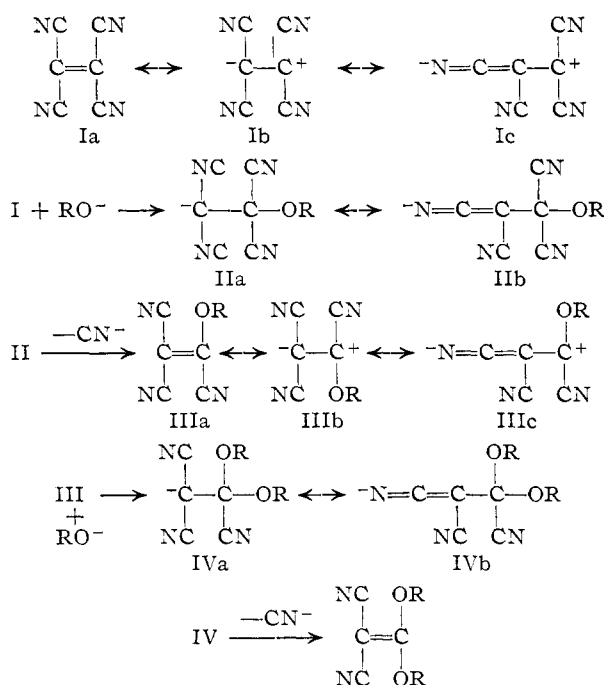
It was found that tetracyanoethylene could be recrystallized unchanged from methyl and ethyl alcohol, although prolonged heating in either solvent resulted in much degradation with the for-

mation of tarry products. However, if certain catalysts, such as urea or zinc acetate were added to the alcohol, a clean reaction occurred and a dicyanoketene acetal was formed. Similarly, when tetracyanoethylene was allowed to react with a 1,2- or 1,3-glycol, dicyanoketene cyclic acetals resulted. Attempts to replace only one of the cyano groups of tetracyanoethylene with an alkoxide group were not successful. When tetracyanoethylene was treated with only one equivalent of an alcohol, a mixture of the dicyanoketene acetal and unreacted tetracyanoethylene resulted.

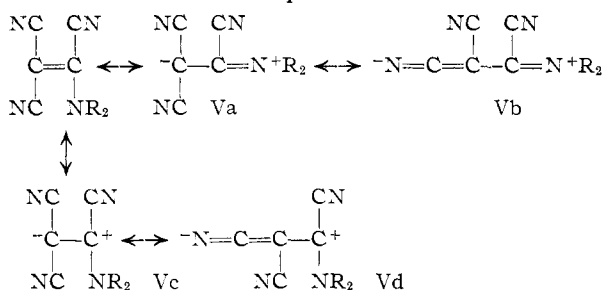
The reaction of tetracyanoethylene with an al-

(1) Paper III, W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *THIS JOURNAL*, **80**, 2783 (1958).

cohol can be visualized as



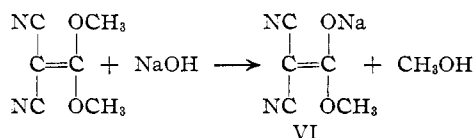
Presumably, the reaction with a second molecule of alcohol is favored by the contribution of resonance forms b and c of III, which should be greater than the contribution of resonance forms b and c of I due to the polarizing effect of the alkoxy group in III. In contrast to this reaction, the reaction of an amine with tetracyanoethylene usually results in replacement of only one cyano group with the formation of a tricyanovinylamine.² This can be explained by the greater electron-donating tendency of nitrogen as compared to oxygen, which would favor the resonance forms a and b instead of c and d of V and tend to prevent further reaction.



The exact role of the catalyst in the reaction of tetracyanoethylene with alcohols is not known. Urea was the best catalyst found, although other catalysts, such as pyridine and zinc salts, promoted the reaction. Pyridine and other strong bases are less desirable as catalysts since they can react with the acetals once they have formed. All of the catalysts probably function by increasing the concentration of alkoxide ion present in the reaction mixture. However, an additional effect was noted with urea; when urea was added to a solution of tetracyanoethylene in methyl or ethyl alcohol, a brilliant purple color developed. As hydrogen

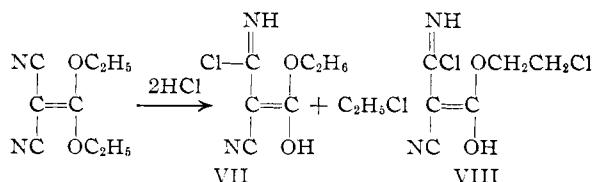
cyanide evolved, the color faded, and the reaction mixture became almost colorless when the reaction was completed. This would seem to indicate the formation of a complex between tetracyanoethylene and urea, which probably expedited the addition of the alkoxide ion.

Dicyanoketene acetals were prepared by reaction of tetracyanoethylene with methyl and ethyl alcohol, ethylene, propylene and trimethylene glycols and 3-cyclohexene-1,1-dimethanol. The structure of the dicyanoketene dimethyl acetal was confirmed by its conversion to the known sodium salt of methyl dicyanoacetate³ (VI) by reaction with aqueous sodium hydroxide.



All of the dicyanoketene acetals prepared in this study are white crystalline compounds with melting points ranging between 51 and 161°. The dimethyl and diethyl acetals are degraded by prolonged heating above their melting points, but the cyclic acetals are quite stable, even up to 200°. The dicyanoketene acetals are surprisingly inert toward water and alcohols, even in the presence of an acid catalyst. In this respect, they differ from other reported ketene acetals which are converted to esters and orthoesters by water or alcohols and acid catalysts.⁴

Also, in contrast to the other reported ketene acetals,⁴ the dicyanoketene acetals are inert to benzyl bromide. However, they react with anhydrous hydrogen chloride to give products in which one of the C-O bonds in the acetal linkage is broken, and one of the cyano groups is converted to -CCl=NH. Thus, reaction of dicyanoketene diethyl acetal with hydrogen chloride produced VII and ethyl chloride, and reaction of dicyanoketene ethylene acetal with hydrogen chloride resulted in VIII. These structures (VII and VIII) were tentatively assigned on the basis that the compounds gave a deep red color



with alcoholic ferric chloride (enolic OH test) and a precipitate of silver chloride with cold alcoholic silver nitrate (active halogen test). The infrared spectrum of the product from the diethyl acetal and hydrogen chloride had absorption bands at 3.05 and 3.20 μ that could be attributed to NH and OH, a band at 4.55 μ for CN, a band at 6.15 μ for conjugated C=C, and a band at 7.9 for C-O-C. This spectrum thus also supports the assignment of structure VII to this compound.

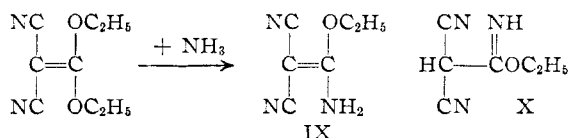
1-Alkoxy-1-amino-2,2-dicyanoethylenes.—The dicyanoketene acetals are very susceptible to

(3) F. Arndt, H. Scholz and E. Frobel, *Ann.*, **521**, 95 (1935).

(2) Paper VI, B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *THIS JOURNAL*, **80**, 2806 (1958).

(4) S. M. McElvain, *Chem. Revs.*, **45**, 470 (1949); S. M. McElvain and J. P. Schroeder, *THIS JOURNAL*, **71**, 47 (1949).

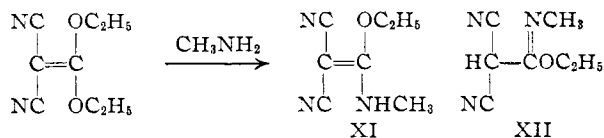
attack by basic reagents. The acetals react quite readily with ammonia or primary and secondary amines to produce 1-alkoxy-1-amino-2,2-dicyanoethylenes. Aqueous ammonia reacted rapidly with a molecular equivalent of dicyanoketene diethyl acetal to yield a crystalline compound identified as 1-amino-1-ethoxy-2,2-dicyanoethylene (2,2-dicyano-1-ethoxyvinylamine (IX)).



The infrared spectrum of this compound (IX) was identical with that of a compound prepared from ethyl alcohol and cyanoforn according to the directions of Hantzsch and Oswald⁵ and previously identified as the tautomeric ethyl ester of dicyanoacetimidic acid (X). However, the spectral data leave little doubt that this compound possesses the vinylamine structure IX. The ultraviolet absorption spectrum shows a strong maximum at 2540 Å. which indicates a high degree of conjugation. There is a doublet at 3.05 and 3.19 μ in the infrared absorption spectrum which could be due to a NH₂ group. There is also a very strong and sharp band at 6.05 μ, which probably is associated with the NH₂ group, and a band at 6.48 μ which is very similar to the absorption due to C=C in the dicyanoketene acetals. These spectral data are not what would be expected if structure X were correct.

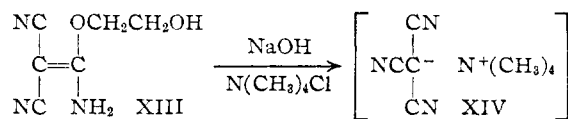
Similar vinylamines were prepared from ammonia and the dicyanoketene cyclic acetals. Thus, 1-amino-1-(2-hydroxyethoxy)-2,2-dicyanoethylene and 1-amino-1-(3-hydroxypropoxy)-2,2-dicyanoethylene were prepared from dicyanoketene ethylene acetal and dicyanoketene trimethylene acetal, respectively.

1-Ethoxy-1-methylamino-2,2-dicyanoethylene (XI) was prepared from dicyanoketene diethyl acetal and a molecular equivalent of aqueous methylamine. The infrared spectrum of XI possessed a band at 3.05 μ due to the NH group. The tautomeric form of this compound (XII) is thus excluded since this structure contains no NH group.



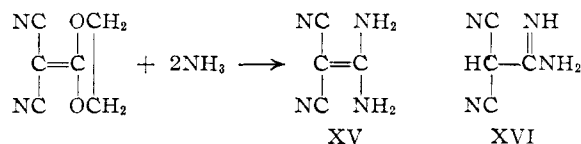
The 1-amino-1-alkoxy-2,2-dicyanoethylenes prepared from the dicyanoketene acetals possess properties that are markedly different from those that would normally be expected of vinylamines. These compounds are high-melting solids that are stable to heat and water. Instead of being basic, they behave as weak acids; they dissolve in dilute aqueous sodium hydroxide and can be recovered unchanged by acidification. However, boiling one of these vinylamines in dilute sodium hydroxide solution resulted in a rather unusual reaction. Cyanoforn, isolated as its tetramethylammonium salt (XIV), was produced when 1-amino-1-(2-

hydroxyethoxy)-2,2-dicyanoethylene (XIII) was



treated with boiling sodium hydroxide solution. Thus, the elements of ethylene glycol were removed and a new cyano group was generated under conditions which would normally hydrolyze a cyano group to an amide group. This reaction can be explained, at least in part, by the high degree of resonance stabilization in the cyanoform anion.

1,1-Diamino-2,2-dicyanoethylenes.—The replacement of the alkoxy groups of dicyanoketene acetals with amino groups appears to be a step-wise reaction. When the acetals were treated with an excess of ammonia or of primary or secondary amine, both of the alkoxy groups were replaced and 1,1-diamino-2,2-dicyanoethylenes (diamino-vinylidene cyanides) were formed. Thus, 1,1-diamino-2,2-dicyanoethylene (XV) resulted when dicyanoketene diethyl acetal or dicyanoketene ethylene acetal was boiled with ammonium hydroxide.



As in the case of 1-amino-1-ethoxy-2,2-dicyanoethylene, spectral data indicated that this compound exists as a tetrasubstituted ethylene (XV) and not as its tautomer, dicyanoacetimidine (XVI). A strong ultraviolet absorption maximum at 2510 Å. indicates a high degree of resonance. Bands due to NH₂ were observed at 6.04, 3.03 and 3.15 μ, and a band at 6.43 μ for C=C was present in the infrared spectrum of XV. Absence of absorption bands due to CH in the infrared spectrum also indicates that the tautomeric form XVI is not present. Over all, the spectra for XV are very similar to those observed for 1-amino-1-ethoxy-2,2-dicyanoethylene.

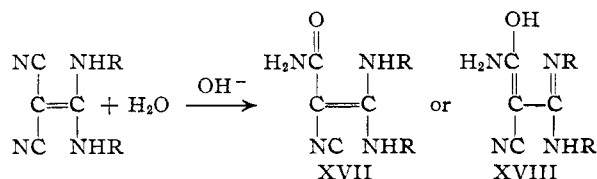
Substituted 1,1-diamino-2,2-dicyanoethylenes were prepared from dicyanoketene acetals and primary and secondary amines. 1,1-Bis-(methylamino)-2,2-dicyanoethylene and 1,1-bis-(dimethylamino)-2,2-dicyanoethylene were formed by treating dicyanoketene ethylene acetal with methylamine and dimethylamine, respectively. There is no doubt of the structure of the dimethylamine derivative, since no tautomer is possible in this case. Ethylenediamine also reacted with the dicyanoketene acetals to form the cyclic diamine, 2-dicyanomethyleneimidazolidine.

As mentioned earlier, the replacement of the alkoxy groups of the dicyanoketene acetals with amino groups appears to be a step-wise reaction. Thus, it was possible to prepare 1,1-diamino-2,2-dicyanoethylenes with different substituents on each amino group. The reaction of 1-ethoxy-1-methylamino-2,2-dicyanoethylene with ammonia resulted in the formation of 1-amino-2-methylamino-2,2-dicyanoethylene, and 1-amino-1-ethoxy-2,2-dicy-

(5) A. Hantzsch and G. Oswald, *Ber.*, **32**, 641 (1899).

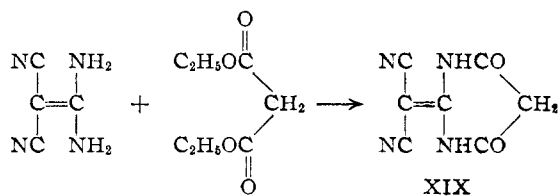
anoethylene and piperidine gave 1-amino-1-piperidino-2,2-dicyanoethylene.

Partially hydrolyzed derivatives of 1,1-diamino-2,2-dicyanoethylene and 2-dicyanomethyleneimidazolidine were formed by boiling these compounds in aqueous sodium hydroxide solution. Although these derivatives were not conclusively identified, examination of their infrared spectra indicates that they probably possess the tautomeric structures XVII or XVIII.



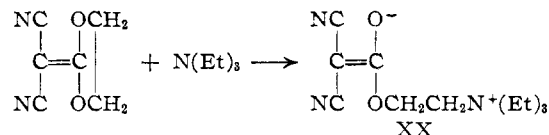
The 1,1-diamino-2,2-dicyanoethylenes in general are very stable high-melting, neutral white solids. The 1,1-diamino-2,2-dicyanoethylene differs sharply from the known 1,2-diamino-1,2-dicyanoethylene with which it is isomeric. For example, 1,1-diamino-2,2-dicyanoethylene is stable at its melting point (236–238°) and shows a *pH* of about 7 in aqueous solution, whereas the isomeric tetramer of hydrogen cyanide, variously described as 1,2-diamino-1,2-dicyanoethylene or 1,2-dicyano-1-amino-2-iminoethane (or an equilibrium mixture of the two) decomposes at its melting point (180°)⁶ and is monobasic and forms a stable monohydrochloride which can be isolated readily.⁷

The stability of the 1,1-diamino-2,2-dicyanoethylenes can be explained by assuming that the two cyano groups induce a positive charge on the carbon to which the amino groups are attached. Thus, the (CN)₂C=C< group would be somewhat analogous to the O=C< group in its electron-shifting effects, and 1,1-diamino-2,2-dicyanoethylene would be analogous to urea, in which two amino groups are also attached to a positive carbon. If this were true, 1,1-diamino-2,2-dicyanoethylene should undergo some of the same reactions that urea does. The diaminodicyanoethylene does indeed react with ethyl malonate to give 2-dicyanomethylene-4,6-dioxohexahydropyrimidine (XIX). This reaction is formally analogous to the reaction of urea with ethyl malonate to give barbituric acid.



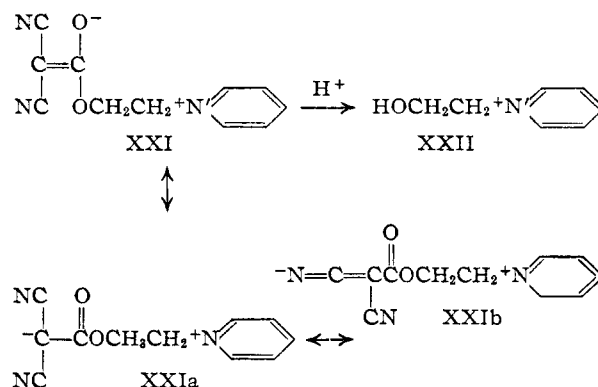
"Inner-salt" Compounds.—The dicyanoketene acetals can act as alkylating agents, similar in fashion to alkyl sulfates. The product from the reaction of dicyanoketene dialkyl acetals with tertiary amines are mostly oils (probably quaternary ammonium salts of alkyl dicyanoacetates) which could not be distilled or crystallized. However, reaction of the dicyanoketene cyclic acetals with tertiary

amines produced stable, crystalline inner-salt compounds. For example, the reaction of dicyanoketene ethylene acetal with triethylamine produced a nearly quantitative yield of 2,2-dicyano-1-[2-(triethylammonio)-ethoxy]-ethenolate (XX).⁸



Several other derivatives of this type have been prepared from both the ethylene and trimethylene acetal of dicyanoketene, and these products are listed in Table I. The adducts were formed by simply dissolving the amine and the cyclic acetal in a mutual solvent and allowing them to react spontaneously. In most cases, the adduct precipitated from the solution in a few minutes. The rate of the reaction appeared to increase with increasing base strength of the amine used. Triethylamine reacted almost instantaneously, whereas less basic amines, such as α -bromopyridine, reacted much more slowly.

The structure of these adducts was assigned on the basis of their hydrolytic degradation products and their infrared absorption spectra. The hydrolysis of the pyridine-dicyanoketene ethylene acetal adduct (XXI) with dilute hydrochloric acid produced the 1-(2-hydroxyethoxy)-pyridinium cation XXII, which was isolated as a reineckate salt. This indicates that a new carbon-nitrogen bond is formed in the reaction of the amine with the acetal. The infrared spectra of all of the cyclic acetal-amine adducts show a strong absorption



band between 6.00 and 6.05 μ , an indication that the C=C double bond is hybridized to some extent with a carbonyl group. Thus, these adducts are mesoionic compounds⁹ in that they are not well represented by an ordinary covalent structural formula but are more accurately portrayed as resonance hybrids of more than one ionic formula. While XXI is probably the predominant form, this compound is stabilized by resonance with other

(8) In naming the "inner-salt" compounds described in this paper, we have adopted the name "ammonio" for the R₃N⁺-subsequent group and the name "sulfonio" for the R₃S⁺-subsequent group, according to the suggestion of J. F. Bunnett, *et al.*, *THIS JOURNAL*, 75, 642 (1953). Analogously, the -SC(NH₂)₂⁺ substituent group is called "isothio-uronio" and the H₂N⁺ substituent group is called "imidio."

(9) W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, 307 (1949).

(6) D. W. Woodward, U. S. Patent 2,499,441 (1950).

(7) L. E. Hinkel, G. O. Richards and O. Thomas, *J. Chem. Soc.* 1436 (1937).

TABLE I: 2,2-DICYANO-1-ALKOXYETHENOLATE INNER SALTS

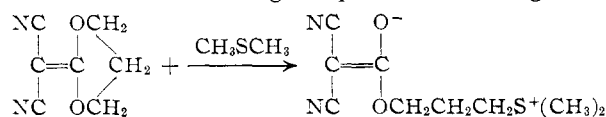
Reactants Acetal, n	Base, Q	Name	Formula	Reac- tion sol- vent ^a	Re- crystn. sol- vent ^a	Yield, %	Melting point, °C.	Adduct			
								Carbon, % Calcd.	Hydrogen, % Calcd.	Nitrogen, % Calcd.	Sulfur, % Calcd.
2	Trimethylamine	2,2-Dicyano-1-[2-(trimethylammonio)-ethoxy]-ethenolate	C ₉ H ₁₈ N ₃ O ₂	A	B	63	210-212	55.37	6.71	21.53	21.62
2	Triethylamine	2,2-Dicyano-1-[2-(triethylammonio)-ethoxy]-ethenolate	C ₁₂ H ₁₉ N ₃ O	A	B	97	184-186	60.74	8.07	17.71	17.58
2	Dimethyldodecylamine	2,2-Dicyano-1-[2-(dimethyldodecylammonio)-ethoxy]-ethenolate	C ₃₀ H ₅₃ N ₃ O ₂	A	C	72	70	68.73	10.09	12.02	12.12
2	N,N-Dimethylaniline	2,2-Dicyano-1-[2-(dimethylphenylammonio)-ethoxy]-ethenolate	C ₁₄ H ₁₆ N ₃ O ₂	A ^b	D	78	160-161	65.35	5.88	16.33	16.39
2	Pyridine	2,2-Dicyano-1-[2-(1-pyridinio)-ethoxy]-ethenolate	C ₁₁ H ₉ N ₃ O ₂	A	B	84	201-202	61.39	4.28	19.53	19.57
2	Quinoline	2,2-Dicyano-1-[2-(1-quinolinio)-ethoxy]-ethenolate	C ₁₅ H ₁₁ N ₃ O ₂	A	B	76	239-242	67.91	4.18	15.84	15.87
2	α-Picoline	2,2-Dicyano-1-[2-(1-α-picolinio)-ethoxy]-ethenolate	C ₁₂ H ₁₁ N ₃ O ₂	A	B	66	174	62.87	4.95	18.33	18.42
2	α-Bromopyridine	2,2-Dicyano-1-[2-(1-α-bromopyridinio)-ethoxy]-ethenolate	C ₁₁ H ₁₀ BrN ₃ O ₂	A	B	77	168-170	44.92	2.74	14.29	14.34
2	β-Dimethylaminoethyl methacrylate	2,2-Dicyano-1-[2-(β-methacryloxyethyl-dimethylammonio)-ethoxy]-ethenolate	C ₁₈ H ₁₉ N ₃ O ₄	E	B	80	137-138	57.33	6.53	14.33	14.35
3	Pyridine	2,2-Dicyano-1-[3-(1-pyridinio)-propoxy]-ethenolate	C ₁₂ H ₁₁ N ₃ O ₂	A	B	91	173-174	62.87	4.84	18.33	18.49
2	Methyl sulfide	2,2-Dicyano-1-[2-(dimethylsulfonio)-ethoxy]-ethenolate	C ₈ H ₁₀ N ₂ O ₂ S	E	B	84	180-182	48.47	48.93	5.08	5.22
3	Methyl sulfide	2,2-Dicyano-1-[3-(dimethylsulfonio)-propoxy]-ethenolate	C ₉ H ₁₂ N ₂ O ₂ S	E	B	83	170-171	50.92	5.13	5.70	5.66
2	Ethyl sulfide	2,2-Dicyano-1-[2-(diethylsulfonio)-ethoxy]-ethenolate	C ₁₀ H ₁₄ N ₂ O ₂ S	E	F	65	105-107	53.07	53.11	6.24	6.16
2	Thiourea	2,2-Dicyano-1-[2-(S-isothiuronio)-ethoxy]-ethenolate	C ₇ H ₈ N ₄ O ₂ S	D	A	88	235-237	39.61	39.60	3.79	3.84
2	Allylthiourea	2,2-Dicyano-1-[2-(S-N-allylthiothiuronio)-ethoxy]-ethenolate	C ₁₀ H ₁₂ N ₄ O ₂ S	E	A	98	204-205	47.60	47.58	4.80	4.82
2	N,N'-Diisopropylthiourea	2,2-Dicyano-1-[2-(S-(N,N'-diisopropylthiuronio)-ethoxy]-ethenolate	C ₁₃ H ₁₈ N ₄ O ₂ S	E	E	95	199-201	52.68	52.86	6.80	6.76
2	N,N'-Diphenylthiourea	2,2-Dicyano-1-[2-(S,N,N'-diphenylthiuronio)-ethoxy]-ethenolate	C ₁₉ H ₁₆ N ₄ O ₂ S	E	G	93	190-192	62.62	62.47	4.43	4.55
2	Thiosemicarbazide	2,2-Dicyano-1-[2-(S-isothiosemicarbazido)-ethoxy]-ethenolate	C ₇ H ₁₀ N ₅ O ₂ S	H	A	79	206-207	37.00	37.27	3.99	4.08
2	Thioacetamide	2,2-Dicyano-1-[2-(acetimidiothio)-ethoxy]-ethenolate	C ₃ H ₉ N ₃ O ₂ S	E	E ^c	61	177-180	45.49	45.67	4.29	4.42
2	Thiobenzamide	2,2-Dicyano-1-[2-(benzimidiothio)-ethoxy]-ethenolate	C ₁₃ H ₁₁ N ₃ O ₂ S	E	E ^c	50	213-214	57.13	57.19	4.06	4.12

^a A = tetrahydrofuran, B = water, C = alcohol-ether, D = methyl alcohol, E = acetone, F = alcohol, G = dimethylformamide-water, H = ethylene glycol. ^b Solution drowned in ether after reaction to precipitate product. ^c Washed with solvent, not recrystallized.

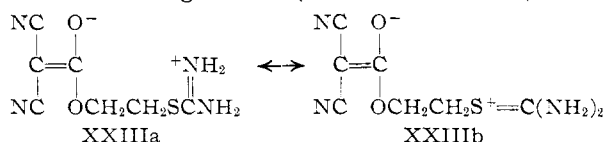
forms (XXIa, XXIb) which possess a carbonyl structure.

The 2,2-dicyano-1-(ammonioalkoxy)-ethenolates are stable, white crystalline solids characterized by relatively high melting points. Most of them are very soluble in hot water, but only slightly soluble in cold water and most organic solvents.

The dicyanoketene cyclic acetals are also sufficiently strong alkylating agents to react with simple alkyl sulfides. Stable inner-salt compounds were formed from the reaction of dicyanoketene ethylene acetal with methyl and ethyl sulfide and from dicyanoketene trimethylene acetal and methyl sulfide. Other sulfur-containing compounds, including thio-



urea, thioamides and thiosemicarbazide also reacted with the dicyanoketene cyclic acetals to give stable mesoionic compounds. These products possess even more ionic resonance forms than the products from the amines and sulfides. Thus a total of twelve resonance forms may be written for 2,2-dicyano-1-[2-(S-isothiuronio)-ethoxy]-ethenolate (XXIII), the product from the reaction of dicyanoketene ethylene acetal and thiourea, since in addition to the resonating negative charge, the positive charge can be written on either the sulfur or the nitrogen atom (as in XXIIIa and b).



The mesoionic compounds prepared from sulfides, thiourea and thioamides are all stable crystalline compounds the properties of which closely resemble those of the products prepared from the tertiary amines, although they are somewhat less stable. However, one interesting difference was noted. The sulfur-containing mesoionic compounds fluoresce when excited by X-rays.

Experimental

Dicyanoketene Dimethyl Acetal.—A solution of 6.4 g. (0.05 mole) of tetracyanoethylene and 1.0 g. of urea (catalyst) in 25 ml. of methyl alcohol was heated on a steam-bath until the deep purple color which formed at first had faded to light yellow. Two hundred ml. of dry ether was added, and the solution was cooled to -80° . The precipitate which formed was collected and recrystallized from ether. There was obtained 3.4 g. (50% yield) of dicyanoketene dimethyl acetal in the form of white needles, m.p. $50-51^\circ$.

Anal. Calcd. for $\text{C}_6\text{H}_6\text{N}_2\text{O}_2$: C, 52.17; H, 4.38; N, 20.28. Found: C, 51.99; H, 4.53; N, 20.17.

Dicyanoketene Diethyl Acetal.—A solution of 6.4 g. (0.05 mole) of tetracyanoethylene and 3.0 g. of urea in 50 ml. of ethyl alcohol was warmed over a steam-bath until the initial deep purple color of the solution had faded to yellow. The solution was cooled and poured into 500 ml. of cold water. The oil which separated solidified upon standing a few minutes. The solid was collected on a filter and recrystallized from alcohol-water. There was obtained 6.0 g. (72% yield) of dicyanoketene diethyl acetal as white needles, m.p. $58-59^\circ$.

Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.91; H, 6.20; N, 16.90.

Dicyanoketene Cyclic Acetals.—The dicyanoketene cyclic

acetals were prepared from the reaction of tetracyanoethylene with a 1,2- or 1,3-diol. In a typical example, a mixture of 6.4 g. (0.05 mole) of tetracyanoethylene, 1.0 g. of urea and 12 ml. of ethylene glycol was heated over a steam-bath until solution was complete. This mixture was cooled and poured into 500 ml. of cold water. The precipitate was collected on a filter (6.4 g., 94% yield) and recrystallized from alcohol-water. There was obtained 4.62 g. of dicyanoketene ethylene acetal in the form of white needles, m.p. $113-114^\circ$.

Anal. Calcd. for $\text{C}_6\text{H}_4\text{O}_2\text{N}_2$: C, 52.94; H, 2.96; N, 20.59; mol. wt. 136. Found: C, 52.94; H, 3.05; N, 20.65; mol. wt., 135, 137.

Dicyanoketene trimethylene acetal, white needles, m.p. $119-120^\circ$, was obtained in a similar manner from tetracyanoethylene and trimethylene glycol.

Anal. Calcd. for $\text{C}_7\text{H}_6\text{O}_2\text{N}_2$: C, 56.01; H, 4.03; N, 18.67; mol. wt., 150. Found: C, 56.13; H, 4.28; N, 18.76; mol. wt., 151.

Dicyanoketene propylene acetal (2-dicyanomethylene-4-methyl-1,3-dioxolane), white needles, m.p. $60-61^\circ$, was obtained from tetracyanoethylene and propylene glycol.

Anal. Calcd. for $\text{C}_7\text{H}_6\text{O}_2\text{N}_2$: C, 56.01; H, 4.03; N, 18.67. Found: C, 55.97; H, 4.08; N, 18.72.

2-Dicyanomethylene-1,3-dioxaspiro[5.5]undec-7-ene.—A mixture of 28.4 g. (0.2 mole) of 3-cyclohexene-1,1-dimethanol,¹⁰ 25.6 g. (0.2 mole) of tetracyanoethylene, 2.0 g. of urea and 100 ml. of tetrahydrofuran was heated on a steam-bath until all solids went into solution (about 10 minutes). The solution was cooled and diluted with 200 ml. of water. The precipitate that formed was collected on a filter, washed with water, and recrystallized from alcohol. There was obtained 27.5 g. of 2-dicyanomethylene-1,3-dioxaspiro[5.5]undec-7-ene in the form of white needles, m.p. $160-161^\circ$.

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$: C, 66.64; H, 5.60; N, 12.96. Found: C, 66.78; H, 5.59; N, 13.07.

Saponification of Dicyanoketene Dimethyl Acetal.—A mixture of 2.432 g. (0.0176 mole) of dicyanoketene dimethyl acetal and 17.30 ml. (0.0176 mole) of 1.018 N sodium hydroxide solution was warmed gently until solution was complete. The water was evaporated under reduced pressure, and the residue was recrystallized from a small amount of water. There was obtained 1.5 g. of white needles, m.p. $<300^\circ$. The X-ray diffraction pattern and infrared absorption spectrum of this material were identical with those of an authentic sample of the sodium salt of methyl dicyanoacetate prepared from the reaction of sodium malonitrile and methyl chloroformate.³

Reaction of Dicyanoketene Diethyl Acetal with Hydrogen Chloride.—A solution of 1.0 g. of dicyanoketene diethyl acetal in 20 ml. of anhydrous ether was saturated with dry hydrogen chloride gas. A white crystalline precipitate formed when the solution was allowed to stand at room temperature overnight. The ether was removed by evaporation, and the residue was recrystallized from ethyl alcohol. There was obtained 1.0 g. of 1-cyano-2-hydroxy-2-ethoxyacrylimidyl chloride (or tautomer) in the form of white prisms, m.p. $169-170^\circ$. This material gave a deep red color with alcoholic ferric chloride and an immediate precipitate of silver chloride with alcoholic silver nitrate.

Anal. Calcd. for $\text{C}_6\text{H}_7\text{N}_2\text{ClO}_2$: C, 41.27; H, 4.04; N, 16.05; Cl, 20.31. Found: C, 41.21; H, 4.10; N, 16.13; Cl, 20.25.

Reaction of Dicyanoketene Ethylene Acetal with Hydrogen Chloride.—A solution of 2.0 g. of dicyanoketene ethylene acetal in 20 ml. of acetone was saturated with dry hydrogen chloride gas and allowed to stand at room temperature for 2 days. The solution was evaporated to dryness and the dark residue was recrystallized from ethyl acetate-*n*-hexane (decolorizing charcoal). There was obtained 1.5 g. of 1-cyano-2-hydroxy-2-(2-chloroethoxy)-acrylimidyl chloride (or tautomer) as white plates, m.p. $133-134^\circ$.

Anal. Calcd. for $\text{C}_6\text{H}_6\text{N}_2\text{O}_2\text{Cl}_2$: N, 13.40; Cl, 33.92. Found: N, 13.51; Cl, 33.89.

1-Amino-1-alkoxy-2,2-dicyanoethylenes.—Four 1-amino-1-alkoxy-2,2-dicyanoethylenes were prepared by the reaction of a dicyanoketene acetal with a molecular equivalent

(10) Obtained from Carbide and Carbon Chemical Co.

of aqueous ammonia or methylamine. In a typical example, a mixture of 5.65 g. (0.034 mole) of dicyanoketene diethyl acetal, 30 ml. of water and 8.00 ml. (0.034 mole) of 4.25 *N* ammonium hydroxide was heated to boiling. The crystals which separated upon cooling were collected on a filter, washed with water, and recrystallized from ethyl alcohol. There was obtained 3.1 g. (67% yield) of 1-amino-1-ethoxy-2,2-dicyanoethylene in the form of white needles, m.p. 225–226°.

Anal. Calcd. for $C_6H_7N_3O$: C, 52.54; H, 5.15; N, 30.64. Found: C, 52.84; H, 5.20; N, 30.65.

1-Ethoxy-1-methylamino-2,2-dicyanoethylene, white plates, m.p. 98–99°, was prepared (96% yield) in a similar manner from dicyanoketene diethyl acetal and aqueous methylamine.

Anal. Calcd. for $C_7H_9N_3O$: C, 55.62; H, 6.00; N, 27.80. Found: C, 55.56; H, 6.11; N, 27.74.

1-Amino-1-(2-hydroxyethoxy)-2,2-dicyanoethylene, white needles, m.p. 164–165°, was prepared (60% yield) in a similar manner from dicyanoketene ethylene acetal and aqueous ammonia.

Anal. Calcd. for $C_6H_7N_3O_2$: C, 47.05; H, 4.61; N, 27.44. Found: C, 47.34; H, 4.69; N, 27.58.

1-Amino-1-(3-hydroxypropoxy)-2,2-dicyanoethylene, white plates, m.p. 166–167°, was prepared (66% yield) in a similar manner from dicyanoketene trimethylene acetal and aqueous ammonia.

Anal. Calcd. for $C_7H_9N_3O_2$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.30; H, 5.52; N, 25.10.

Reaction of 1-Amino-1-(2-hydroxyethoxy)-2,2-dicyanoethylene with Sodium Hydroxide.—A solution of 4.680 g. (0.0361 mole) of 1-amino-1-(2-hydroxyethoxy)-2,2-dicyanoethylene in 36.0 ml. (0.0361 mole) of 1.002 *N* sodium hydroxide was heated to reflux for 10 minutes and then allowed to stand at room temperature overnight. The solution was filtered and 5 g. of tetramethylammonium chloride in 10 ml. of water was added to the filtrate. The solution was cooled and the precipitate which formed was collected on a filter (*ca.* 1.0 g.) and recrystallized from ethyl alcohol. There was obtained 0.5 g. of the tetramethylammonium salt of cyanoform as white needles, m.p. 239–241°.

Anal. Calcd. for $C_3H_5N_3$: C, 58.51; H, 7.37; N, 34.12. Found: C, 58.35; H, 7.29; N, 33.93.

An authentic sample of the tetramethylammonium salt of cyanoform was prepared for comparative purposes from a concentrated aqueous solution of the potassium salt¹¹ and tetramethylammonium chloride. After two recrystallizations from water, the tetramethylammonium salt of cyanoform was obtained as long white needles, m.p. 240–241°. The infrared spectra of both samples of the tetramethylammonium salt were identical.

Anal. Found: C, 58.48; H, 7.38; N, 34.11.

1,1-Diamino-2,2-dicyanoethylene.—A mixture of 13.6 g. (0.1 mole) of dicyanoketene ethylene acetal and 50 ml. of concd. ammonium hydroxide was heated under reflux for 10 minutes, and then allowed to stand overnight. The white crystalline plates that formed were collected on a filter, washed with water, and recrystallized from water. There was obtained 10.0 g. (93%) of 1,1-diamino-2,2-dicyanoethylene as white needles, m.p. 236–238°. X-Ray diffraction patterns of the crude plates and the recrystallized needles were identical. 1,1-Diamino-2,2-dicyanoethylene was also prepared similarly from dicyanoketene dimethyl acetal and ammonia.

Anal. Calcd. for $C_4H_4N_4$: C, 44.44; H, 3.73; N, 51.82. Found: C, 44.34; H, 3.86; N, 51.67.

1,1-Diamino-2,2-dicyanoethylene was hydrolyzed by dissolving 1.0 g. in 10 ml. of hot 10% sodium hydroxide and boiling for 5 minutes. The white precipitate that formed on cooling was collected on a filter, washed with water, and recrystallized from water. There was obtained 0.7 g. (60% yield) of 1,1-diamino-2-cyano-2-carbamylethylene in the form of long white needles, m.p. 204–205°.

Anal. Calcd. for $C_4H_6N_4O$: C, 38.09; H, 4.80; N, 44.43. Found: C, 38.44; H, 4.70; N, 44.68.

1,1-Bis-(methylamino)-2,2-dicyanoethylene.—A mixture of 1.36 g. (0.01 mole) of dicyanoketene ethylene acetal and

2 ml. of 25% aqueous methylamine solution was heated to boiling until all of the solid had dissolved. The precipitate that formed upon cooling was collected on a filter, washed with water and recrystallized from a very small amount of water. There was obtained 0.4 g. (30% yield) of 1,1-bis-(methylamino)-2,2-dicyanoethylene in the form of white needles, m.p. 160–163°.

Anal. Calcd. for $C_6H_8N_4$: C, 52.93; H, 5.92; N, 41.15. Found: C, 53.08; H, 6.05; N, 41.29.

1,1-Bis-(dimethylamino)-2,2-dicyanoethylene.—A solution of 1.36 g. (0.01 mole) of dicyanoketene ethylene acetal in 20 ml. of dimethylamine was allowed to evaporate overnight at room temperature. The residue was dissolved in 10 ml. of hot water and heated on a steam-bath for 10 minutes. The white needles that formed upon cooling were collected on a filter, washed with water, and recrystallized from water. There was obtained 0.85 g. (52% yield) of 1,1-bis-(dimethylamino)-2,2-dicyanoethylene in the form of long white needles, m.p. 129–130°.

Anal. Calcd. for $C_8H_{12}N_4$: C, 58.51; H, 7.37; N, 34.12. Found: C, 58.55; H, 7.21; N, 34.06.

2-Dicyanomethyleneimidazolidine.—Ethylenediamine (1.20 g., 0.02 mole) was added dropwise to a solution of 2.72 g. (0.02 mole) of dicyanoketene ethylene acetal in 25 ml. of tetrahydrofuran. The mixture became warm, and a light yellow precipitate formed. The precipitate was collected on a filter, washed with tetrahydrofuran, and recrystallized from water. There was obtained 2.1 g. (79% yield) of 2-dicyanomethyleneimidazolidine in the form of white prisms, m.p. 279–280°.

Anal. Calcd. for $C_6H_8N_4$: C, 53.72; H, 4.51; N, 41.77. Found: C, 54.01; H, 4.51; N, 41.65.

2-Dicyanomethyleneimidazolidine was hydrolyzed in aqueous alkali as follows. A mixture of 2.0 g. of 2-dicyanomethyleneimidazolidine and 20 ml. of 10% sodium hydroxide was heated under reflux for 1 hour. All of the solid went into solution. The white precipitate that formed upon cooling was collected on a filter, washed with water, and recrystallized from 20 ml. of 10% sodium hydroxide solution. There was obtained 1.6 g. of 2-(carbamylcyanomethylene)-imidazolidine as long white needles, m.p. 241–243°.

Anal. Calcd. for $C_6H_8N_4O$: C, 47.36; H, 5.30; N, 36.83. Found: C, 47.39; H, 5.15; N, 36.84.

1-Amino-1-methylamino-2,2-dicyanoethylene.—A solution of 0.75 g. (0.005 mole) of 1-ethoxy-1-methylamino-2,2-dicyanoethylene in 10 ml. of concd. ammonium hydroxide was heated under reflux for 10 minutes. The solution was cooled, and the white solid that precipitated was collected on a filter, washed with water, and recrystallized from water. There was obtained 0.51 g. (84% yield) of 1-amino-1-methylamino-2,2-dicyanoethylene in the form of white prisms, m.p. 198–200°.

Anal. Calcd. for $C_6H_8N_4$: C, 49.17; H, 4.95; N, 45.88. Found: C, 49.18; H, 4.99; N, 45.60.

1-Amino-1-piperidino-2,2-dicyanoethylene.—A mixture of 0.68 g. (0.005 mole) of 1-amino-1-ethoxy-2,2-dicyanoethylene, 0.43 g. (0.005 mole) of piperidine and 5 ml. of water was heated under reflux for 30 minutes. The precipitate that formed upon cooling was collected on a filter, washed with water, and recrystallized from water. There was obtained 0.53 g. (60% yield) of 1-amino-1-piperidino-2,2-dicyanoethylene as white needles, m.p. 160–161°.

Anal. Calcd. for $C_8H_{12}N_4$: C, 61.34; H, 6.87; N, 31.80. Found: C, 61.58; H, 7.02; N, 31.54.

2-Dicyanomethylene-4,6-dioxohexahydropyrimidine Dihydrate.—A solution prepared by dissolving 2.3 g. (0.1 gram atom) of sodium and then 16.0 g. (0.1 mole) of diethyl malonate and 10.8 g. (0.1 mole) of 1,1-diamino-2,2-dicyanoethylene in 200 ml. of ethyl alcohol was heated to reflux for 2 hours. The solution was cooled and the white precipitate that formed was collected on a filter and washed with ether. There was obtained 12.2 g. of a white powder that contained sodium. This powder was dissolved in 100 ml. of water and 50 ml. of 5% hydrochloric acid solution was added. The white needles that separated upon acidification were collected on a filter and thoroughly washed with water. There was obtained 8.1 g. of 2-dicyanomethylene-4,6-dioxohexahydropyrimidine dihydrate in the form of off-white needles that did not melt below 300° but lost water when heated above 120°. This compound was not soluble in water,

(11) E. Cox and A. Fontaine, *Bull. soc. chim. France*, 948 (1954).

ethyl alcohol or acetone, but was very soluble in 5% sodium bicarbonate solution.

Anal. Calcd. for $C_7H_4N_4O_2 \cdot 2H_2O$: C, 39.63; H, 3.80; N, 26.40. Found: C, 39.72; H, 3.91; N, 26.50.

2,2-Dicyano-1-alkoxyethenolate Inner-salts.¹²—The inner-salts listed in Table I were all prepared by the same general procedure. The base (amine, sulfide, thiourea or thioamide) and the dicyanoketene cyclic acetal were dissolved in a mutual solvent and allowed to react spontaneously. In many cases, crystals of the inner-salt precipitated from the solution after standing only a few minutes. The more basic reagents, such as the trialkylamines, reacted almost instantaneously with the cyclic acetal, whereas less basic reagents such as the sulfides required a longer period of time (1 or 2 days).

In a typical example, a solution of 10.1 g. (0.1 mole) of triethylamine and 13.6 g. (0.1 mole) of dicyanoketene ethylene acetal in 50 ml. of tetrahydrofuran was allowed to stand at room temperature for 10 minutes. The white precipitate that formed was collected on a filter, washed with ether, and recrystallized from water. There was obtained 23.0 g. of 2,2-dicyano-1-[2-(triethylammonio)-ethoxy]-ethenolate in the form of white needles, m.p. 184–186° (see Table I).

1-(2-Hydroxyethyl)-pyridinium Reineckate.—A solution

(12) W. J. Middleton, U. S. Patent 2,721,206 (1955); and V. A. Engelhardt and W. J. Middleton, U. S. Patent 2,766,270 (1956).

of 3.54 g. (0.01 mole) of the reinecke salt in 50 ml. of water was mixed with a solution of 1.6 g. (0.01 mole) of 1-(2-hydroxyethyl)-pyridinium chloride¹³ in 10 ml. of water. The pink precipitate which formed was collected on a filter, washed with water, and recrystallized from acetone–water. There was obtained 5.0 g. of 1-(2-hydroxyethyl)-pyridinium reineckate in the form of lavender flakes, m.p. 186–192° dec.

Anal. Calcd. for $C_{11}H_{16}N_7S_2O_6$: C, 29.85; H, 3.66; N, 22.15. Found: C, 30.14; H, 3.82; N, 22.20.

Hydrolysis of 2,2-Dicyano-1-[2-(1-pyridinio)-ethoxy]-ethenolate.—2,2-Dicyano-1-[2-(1-pyridinio)-ethoxy]-ethenolate (2.15 g., 0.01 mole) was dissolved in 20 ml. of 5 N hydrochloric acid and the solution was heated under reflux for 30 minutes. The solution was cooled and mixed with a filtered solution of 3.54 g. (0.01 mole) of the reinecke salt in 50 ml. of water. The pink precipitate which formed was collected on a filter, washed with water, and recrystallized from acetone–water. There was obtained 4.0 g. of a reineckate salt in the form of lavender flakes, m.p. 186–189° dec. The X-ray diffraction pattern and infrared absorption spectrum of this product are identical with those of 1-(2-hydroxyethyl)-pyridinium reineckate.

(13) O. A. Barns and R. Adams, *THIS JOURNAL*, **49**, 1311 (1927).

WILMINGTON, DELAWARE

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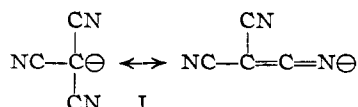
Cyanocarbon Chemistry. V.¹ Cyanocarbon Acids and their Salts

BY W. J. MIDDLETON, E. L. LITTLE, D. D. COFFMAN AND V. A. ENGELHARDT

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A number of new cyanocarbon acids and their salts have been prepared from tetracyanoethylene. 1,1,2,3,3-Pentacyanopropene was prepared by the basic hydrolysis of tetracyanoethylene, 1,1,2,4,5,5-hexacyano-3-azapentadiene was prepared from tetracyanoethylene and ammonia, and salts of the dibasic acid 1,1,2,5,6,6-hexacyano-3,4-diazahexadiene were prepared from tetracyanoethylene and hydrazine. 2-Dicyanomethylene-1,1,3,3-tetracyanopropane, another dibasic acid, was prepared by the reaction of dicyanoketene acetals with malononitrile. These four strongly acidic compounds ionize to give resonance-stabilized anions that are comprised entirely of carbon and nitrogen. Several strongly acidic tetracyanopropenes have been prepared from the dicyanoketene acetals derived from tetracyanoethylene. 2-Alkoxy-1,1,3,3-tetracyanopropenes were obtained from the reaction of these acetals with one equivalent of malononitrile. Reaction of the alkoxypropenes with ammonia, methylamine or dimethylamine resulted in the preparation of 2-amino-1,1,3,3-tetracyanopropenes. Diazotization of 2-amino-1,1,3,3-tetracyanopropene with nitrous acid in the presence of chloride or bromide ion produced 2-chloro- or 2-bromo-1,1,3,3-tetracyanopropene.

Cyanocarbon acids are a relatively unknown class of strong organic acids whose acidic strengths rival those of the mineral acids. Cyanocarbon acids can be defined as organic compounds that contain a plurality of cyano groups and are easily ionized to hydrogen ions and anions of high resonance stability. The structure of these anions can be represented by a number of resonance forms, all of which contain the negative charges on either carbon or nitrogen. Of the known cyanocarbon acids, tricyanomethane (cyanoform)² is of interest since its anion I contains only carbon and nitrogen.



Salts of five other cyanocarbon acids, 1,1,3,3-

tetracyanopropene,³ 2-methyl-1,1,3,3-tetracyanopropene,⁴ 1,1,5,5-tetracyanopentadiene, 1,1,7,7-tetracyanoheptatriene and 1,1,9,9-tetracyanononatriene,⁵ have been reported but have not been extensively studied. A number of new cyanocarbon acids and their salts have been synthesized from tetracyanoethylene, and this paper describes their preparation and some of their physical and chemical properties.

1,1,2,3,3-Pentacyanopropene.—Salts of 1,1,2,3,3-pentacyanopropene were formed by the reaction of tetracyanoethylene with water in the presence of a base. Thus, pyridinium pentacyanopropenide⁶ was formed in 81% yield when a solution of

(3) Y. Urushibara, *Bull. Chem. Japan*, **2**, 278 (1927); *C. A.*, **22**, 579 (1928).

(4) Y. Urushibara and M. Takebayashi, *Bull. Chem. Soc. Japan*, **11**, 557 (1936); *C. A.*, **31**, 1769 (1937).

(5) M. Strell, *et al.*, *Ann.*, **587**, 177 (1954).

(6) There appears to be no widely used general method for naming salts of non-carboxylic organic acids. This problem is usually overcome by merely specifying the "salt of" a given acid. However, this method can be ambiguous in cases where there is more than one type of hydrogen present in the acid molecule, e.g., $C(CN)_3=C(CH_2CH_2OH)-C(CN)_2H$. There is a need for a systematic method of nomenclature for the salts of non-carboxylic organic acids whose acidic hydrogens

(1) Paper IV, W. J. Middleton and V. A. Engelhardt, *THIS JOURNAL*, **80**, 2788 (1958).

(2) (a) A. Hantzsch and G. Oswald, *Ber.*, **32**, 641 (1899); H. Schmidtman, *ibid.*, **29**, 1171 (1896); L. Birkenbach and K. Huttner, *ibid.*, **64B**, 153 (1929); L. Birkenbach, K. Huttner and W. Stein, *ibid.*, **62B**, 2065 (1929); (b) E. Cox and A. Fontaine, *Bull. soc. chim. France*, 948 (1954).