[CONTRIBUTION NO. 437 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. III.[1] Addition Reactions of Tetracyanoethylene

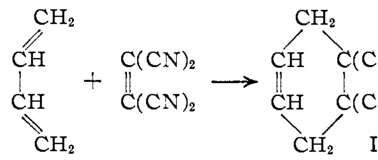
BY W. J. MIDDLETON, R. E. HECKERT, E. L. LITTLE AND C. G. KRESPAN

RECEIVED NOVEMBER 14, 1957

Reactions involving additions to the double bond of tetracyanoethylene have been studied. Tetracyanoethylene was found to be an extremely active dienophile in reactions with conjugated dienes. A number of unusual organic acids containing the $-C(CN)_2C(CN)_2H$ group were prepared from tetracyanoethylene. Acidic tetracyanoethane was formed by reduction of tetracyanoethylene with hydrogen, thiols and hydrogen iodide, and acidic $\beta,\beta,\gamma,\gamma$-tetracyanoketones were formed by the addition of ketones to tetracyanoethylene. Sulfurous acid and tetracyanoethylene formed 1,1,2,2-tetracyanosulfonic acid, a dibasic acid of which a number of salts have been prepared and characterized.

Tetracyanoethylene has been found to undergo four types of addition reactions: Diels–Alder addition of 1,3-dienes, reduction (addition of hydrogen), addition of certain active hydrogen compounds and addition of α-cyanoisopropyl radicals.

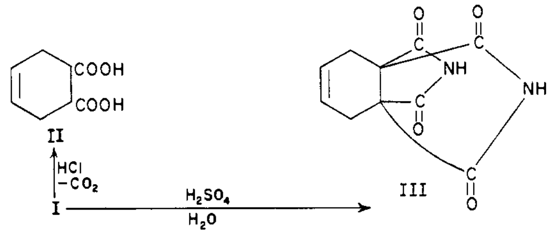
Diels–Alder Adducts of Tetracyanoethylene.—Tetracyanoethylene undergoes Diels–Alder additions with conjugated dienes with unusual ease at relatively low temperatures. The unexpected nature of the reactivity of tetracyanoethylene as a dienophile is attested by the fact that acrylonitrile requires several days to undergo Diels–Alder condensation with butadiene,[2] and that fumaronitrile requires still more forcing conditions of time and temperature to give only a fair yield of the condensation product with butadiene.[3] To obtain a Diels–Alder condensation of 1,1-dicyano-2-phenylethylene with 2,3-dimethylbutadiene, it is necessary to heat the reactants in an autoclave under pressure at 185–195° for an extended period.[4] In contrast, a vigorous and exothermic reaction ensues when tetracyanoethylene is mixed with most conjugated dienes in a solvent, even at temperatures well below 0°. Thus, when butadiene is bubbled into a cold solution of tetracyanoethylene in tetrahydrofuran, the adduct 4,4,5,5-tetracyano-1-cyclohexene (I) precipitates from the solution almost instantaneously in nearly quantitative yield. Even with more sluggish dienes such as β-vinylnaphthalene, the reaction occurs spontaneously and rapidly without added catalyst or application of external heat. Table I contains a list of the adducts prepared from tetracyanoethylene and several dienes.



I

In many cases, the progress of the reaction can be observed visually by the formation and then disappearance of a color. This transient color is undoubtedly due to the formation of a strong π-complex between the acidic tetracyanoethylene and the basic diene.[1] The formation of such a complex explains, at least in part, the extreme dienophilic activity of tetracyanoethylene.

The infrared and nuclear magnetic resonance spectra of the tetracyanoethylene–diene adducts are consistent with the proposed cyclohexene structures. The condensation product of tetracyanoethylene with butadiene was further demonstrated to be the conventional Diels–Alder adduct I by its conversion to 4-cyclohexene-1,2-dicarboxylic acid (II) by hydrolysis and decarboxylation. Less vigorous hydrolysis of the tetracyanoethylene–diene adducts resulted in diimides which possessed interesting polycyclic structures. When compound I was heated with aqueous sulfuric acid, 4-cyclohexene-1,1,2,2-tetracarboxylic diimide (III) was formed. A similar diimide was formed from the tetracyanoethylene–anthracene adduct by hydrolysis with hydrochloric acid at 150°. These diimides possess a high degree of hydrolytic and thermal stability, and are sufficiently acidic to dissolve in a 5% sodium bicarbonate solution. Reaction of the diimide prepared from the tetracyanoethylene–anthracene adduct with hydrazine expanded the 5-membered imide rings to 6-membered dihydrazide rings, in typical fashion.



Reduction of Tetracyanoethylene.—Catalytic hydrogenation of tetracyanoethylene with palladium black resulted in only moderate yields of tetracyanoethane[5] along with some by-products. However, chemical reduction with hydrogen iodide or thiols proceeded smoothly and rapidly with excellent yields of tetracyanoethane. The most convenient method for preparing tetracyanoethane in the laboratory was found to be the reduction of tetracyanoethylene with mercaptoacetic acid, since work-up of this reaction mixture was facilitated by the water solubility of both the acid and its disulfide.

---

(1) Paper II, R. E. Merrifield and W. D. Phillips, THIS JOURNAL, 80, 2778 (1958).

(2) W. D. Wolfe, U. S. Patent 2,217,632 (1940).

(3) K. Ziegler, G. Schenck, E. W. Krockow, A. Siebert, A. Wenz and H. Weber, *Ann.*, **551**, 1 (1942).

(4) K. Alder and H. F. Rickert, U. S. Patent 2,264,354 (1941).

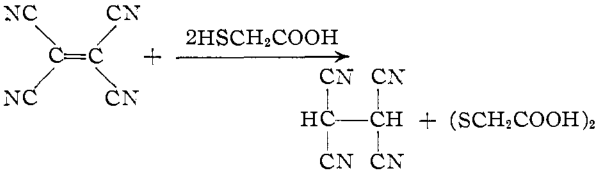
(5) R. Meier, *Ber.*, **86**, 1491 (1953), reported that a compound prepared by the reaction of sodiomalononitrile with nitrous oxide was tetracyanoethane. R. A. Carboni, D. D. Coffman and E. G. Howard, THIS JOURNAL, 80, 2838 (1958), have demonstrated that this report is in error, and the compound prepared by Meier actually was a dimer of malononitrile.

Table I

Adducts of Tetracyanoethylene with Dienes

Diene	Adduct	M.p., °C.	Recrystn. solvent	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Butadiene	$C_{10}H_6N_4$	201–202[a]	Methanol	94	65.92	65.87	3.32	3.42	30.76	30.65
2,3-Dimethylbutadiene	$C_{12}H_{10}N_4$	136–137	Benzene–petr. ether	88	68.55	68.52	4.79	4.92	26.65	26.58
Chloroprene	$C_{10}H_5N_4Cl$[b]	134–135	Ethanol	90	55.44	55.62	2.33	2.38	25.87	25.93
Myrcene	$C_{16}H_{16}N_4$	52.5	Petr. ether	90	72.70	72.61	6.10	6.12	21.20	21.26
Cyclopentadiene	$C_{11}H_6N_4$	223[a]	Cyclopentadiene	100	68.03	68.24	3.11	3.24	28.85	29.01
1,3-Cyclohexadiene	$C_{12}H_8N_4$	>300[a]	Chloroform	94	69.22	69.28	3.87	3.87	26.91	26.87
β-Vinylnaphthalene	$C_{18}H_{10}N_4$	166–168	Chloroform	95	76.56	76.66	3.57	3.51	19.85	19.81
Anthracene	$C_{20}H_{10}N_4$	268–270[a]	Acetone	100	78.42	78.59	3.29	3.41	18.29	18.35
α-Phellandrene	$C_{16}H_{16}N_4$	119–120	Ethanol	50	72.70	72.84	6.10	6.14	21.20	21.26

[a] Melting point was determined in a sealed capillary tube, since otherwise these compounds sublimed. [b] Calcd.: Cl, 16.37. Found: Cl, 16.34.

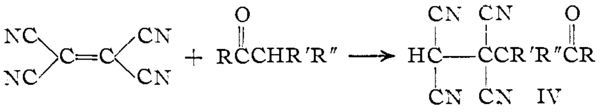


Tetracyanoethane is a white sublimable solid that is much less stable than the ethylene and slowly turns dark brown or black even in the absence of light. This ethane is a strong acid (pK_a 3.6). It dissolves in aqueous sodium bicarbonate and it can be reprecipitated by acidification with hydrochloric acid. Prolonged exposure to base, however, results in complete degradation. Tetracyanoethane is oxidized easily to tetracyanoethylene by a variety of oxidizing agents, including lead dioxide, cupric oxide and ferric chloride in boiling benzene, palladium-on-carbon in boiling xylene, and sulfur.

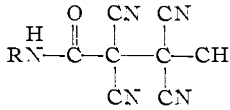
An adduct of tetracyanoethane with phenyl isocyanate has been prepared. Several other derivatives of tetracyanoethane will be described in another paper of this series.[6]

Addition of Active Hydrogen Compounds to Tetracyanoethylene.—Attempts to add active hydrogen compounds to the ethylenic bond of tetracyanoethylene were for the most part unsuccessful. Only ketones possessing an α-hydrogen and sulfurous acid gave adducts. Thiols, hydogen sulfide and hydrogen iodide reduced tetracyanoethylene to tetracyanoethane instead of forming adducts. Attempts to add alcohols,[7] water, ammonia[8] or amines[9] to tetracyanoethylene resulted in the replacement of one or two of the cyano groups, although it may be possible that the adducts were intermediate steps in these reactions.

Ketone Adducts.—A number of adducts of tetracyanoethylene with ketones possessing a methinyl, methylene or methyl group contiguous to the carbonyl group have been prepared (Table II). These adducts (IV) are white crystalline compounds that possess properties similar to those of tetracyanoethane. They are strong acids that will dissolve in sodium bicarbonate solution and can be reprecipitated with acid. In general, they are somewhat unstable. The adducts from relatively unsubstituted ketones such as acetone turn black upon standing a few days at room temperature. However, the adduct of tetracyanoethylene with diisopropyl ketone is much more stable in this respect and remains white indefinitely when stored. Also like tetracyanoethane, the ketone adducts react with organic isocyanates, and three such derivatives were prepared.



It is apparent from their acidic properties and other similarities to tetracyanoethane that the structure of these adducts is that of β,β,γ,γ-tetracyanoketones (IV). These adducts all show strong absorption in the carbonyl region of their infrared spectra, which supports this conclusion. The structures of the isocyanate derivatives of the tetracyanoethylene–ketone adducts are not known, but V appears to be the most probable.



$$RNH-C(=O)-C(CN)_2-C(CN)_2-CH_2C(=O)CH_3$$

V

The ketone adducts were formed by simple reaction of tetracyanoethylene with excess ketone without the use of a catalyst, but in most cases this method was unsatisfactory due to the formation of tarry by-products and the slowness of the reaction. It was also necessary to avoid basic catalysts and elevated temperatures due to the instability of the adducts. Volatile acid catalysts, such as hydrogen chloride or boron trifluoride, are operable, but by far the most satisfactory catalyst for this reaction was found to be Gomberg and Cone's "molecular" silver.[10] This silver catalyst effected reaction at room temperature between tetracyanoethylene and all ketones tried that possessed at least one α-hydrogen. Hexamethylacetone and benzophenone were, of course, unreactive.

Sulfurous Acid.—Alkali bisulfites in aqueous solution will add to the α,β-double bond of acrylonitrile to yield alkali metal salts of β-cyanoethanesulfonic acid.[11] Our work has indicated that the

---

[6] Paper VIII, W. J. Middleton, V. A. Engelhardt and B. S. Fisher, This Journal, 80, 2822 (1958).

[7] Paper IV, W. J. Middleton and V. A. Engelhardt, *ibid.*, 80, 2788 (1958).

[8] Paper V, W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *ibid.*, 80, 2795 (1958).

[9] Paper VI, B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, 80, 2806 (1958).

[10] M. Gomberg and M. Cone, *Ber.*, 39, 3286 (1906).

[11] E. L. Carpenter, U. S. Patent 2,312,878 (1943).

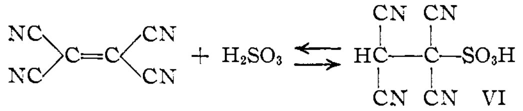
TABLE II

ADDUCTS OF TETRACYANOETHYLENE WITH KETONES

Ketone	Adduct	Empirical formula	M.p., °C.	Recrystn. solvent[a]	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Acetone	4,4,5,5-Tetracyano-2-pentanone	$C_9H_6N_4O$	120–122 d.	A	90	58.06	58.26	3.25	3.50	30.10	29.99
Methyl ethyl ketone	3-Methyl-4,4,5,5-tetracyano-2-pentanone	$C_{10}H_8N_4O$	135–137 d.	A	70	59.99	59.94	4.03	4.06	27.99	27.79
Diethyl ketone	4-Methyl-5,5,6,6-tetracyano-3-hexanone	$C_{11}H_{10}N_4O$	93–93.5 d.	B	80	61.67	61.64	4.71	4.72	26.16	26.19
Diisopropyl ketone	5,5,6,6-Tetracyano-2,4,4-trimethyl-3-hexanone	$C_{13}H_{14}N_4O$	119–121	C	50	64.45	64.26	5.82	5.80	23.13	23.07
Cyclopentanone	2-(1,1,2,2-Tetracyanoethyl)-cyclopentanone	$C_{11}H_8N_4O$	139–141 d.	D	85	62.26	62.55	3.80	3.94	26.40	26.37
Cyclohexanone	2-(1,1,2,2-Tetracyanoethyl)-cyclohexanone	$C_{12}H_{10}N_4O$	134	B	82	63.70	63.87	4.40	4.46	24.77	24.80
Acetophenone	3,3,4,4-Tetracyanobutyrophenone	$C_{14}H_8N_4O$	140–141 d.	B	80	67.74	67.75	3.25	3.26	22.56	22.49
p-Chloroacetophenone	*p*-Chloro-3,3,4,4-tetracyanobutyrophenone	$C_{14}H_7ClN_4O$[b]	150–152	B	60	59.48	59.80	2.50	2.49	19.82	19.77
1-Acetonaphthone	3,3,4,4-Tetracyano-1′-butyronaphthone	$C_{18}H_{10}N_4O$	132–133 d.	B	74	72.47	72.37	3.38	3.67	18.78	18.51
2-Acetonaphthone	3,3,4,4-Tetracyano-2′-butyronaphthone	$C_{18}H_{10}N_4O$	125–126 d.	B	94	72.47	72.30	3.38	3.49	18.78	18.80

[a] A = ethyl acetate, B = ethyl acetate–*n*-hexane mixture, C = benzene, D = ethanol. [b] Calcd.: Cl, 12.54. Found: Cl, 12.53.

reaction of bisulfite with tetracyanoethylene is even more facile than with acrylonitrile. Even sulfurous acid (sulfur dioxide in water) readily adds to tetracyanoethylene to produce an aqueous solution of 1,1,2,2-tetracyanoethanesulfonic acid (VI). The addition of sulfurous acid is easily reversed; evaporation of a solution of VI regenerates tetracyanoethylene quantitatively. 1,1,2,2-Tetracyanoethanesulfonic acid is a dibasic acid, as both hydrogens present in the molecule can be replaced by salt-forming cations. A number of crystalline salts of this acid, in which one or both of the hydrogens were replaced by metal or quaternary ammonium cations, have been prepared by simple metathetical reactions. Thus, tetramethylammonium 1,1,2,2-tetracyanoethanesulfonate was precipitated by adding a solution of tetramethylammonium chloride to an aqueous solution of the sulfonic acid. Other salts in which only one hydrogen was replaced were also prepared in a similar manner from other quaternary ammonium halides and from trimethylsulfonium iodide (Table III). These salts are still quite acidic due to the remaining hydrogen in the anion which readily can ionize. The tetramethylammonium salt possesses a pK_a of 2.62. This fact, along with the fact that tetracyanoethane and the ketone–tetracyanoethylene adducts are also strong organic acids, seems to indicate that the group $-C(CN)_2C(CN)_2H$ is strongly acidic. In common with tetracyanoethane and the ketone–tetracyanoethylene adducts, the sulfonic acid salts are somewhat unstable and will slowly darken upon standing a few days, a property which also may be attributed to the tetracyanoethyl group.



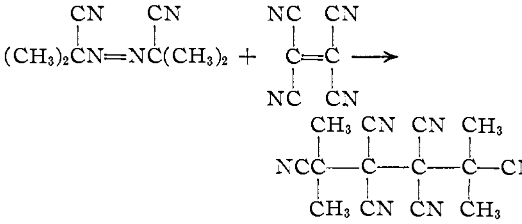
$$(NC)_2C{=}C(CN)_2 + H_2SO_3 \rightleftarrows HC(CN)_2{-}C(CN)_2{-}SO_3H$$

VI

Salts of 1,1,2,2-tetracyanoethane sulfonic acid also have been prepared by the addition of aqueous alkali bisulfites, sulfites or metasulfites to tetracyanoethylene. Sodium 1,1,2,2-tetracyanoethanesulfonate was obtained when sodium bisulfite was added to a suspension of tetracyanoethylene in water. When solutions of certain quaternary ammonium salts were added to an aqueous solution of the monosodium salt, bis-(quaternary ammonium) salts of 1,1,2,2-tetracyanoethanesulfonic acid precipitated. These salts were essentially neutral since both hydrogens of the acid had been replaced by salt-forming cations of strong bases. The same salts resulted when a solution of tetracyanoethylene in aqueous sodium sulfite and potassium metasulfite was treated with quaternary ammonium halides. The bis-(N-methylquinolinium) salt of 1,1,2,2-tetracyanoethanesulfonic acid was recrystallized unchanged from neutral water, but when it was recrystallized from dilute hydrochloric acid, the mono-N-methylquinolinium salt of 1,1,2,2-tetracyanoethanesulfonic acid was obtained. A mixed salt containing both silver and tetramethylammonium cations resulted when silver nitrate was added to a solution of tetramethylammonium 1,1,2,2-tetracyanoethanesulfonate. Thus, it appears that either the mono- or bis-salt can be precipitated from solution. The salt that is obtained depends both on the relative solubilities of the two salts and also upon the *p*H of the solution from which it is precipitated. Lower *p*H favors the precipitation of the mono-salt, and higher *p*H favors the precipitation of the bis-salt.

Although aqueous solutions of 1,1,2,2-tetracyanoethanesulfonic acid appeared to be relatively stable, prolonged boiling hydrolyzed the acid to tetracyanoethane. The salts of 1,1,2,2-tetracyanoethanesulfonic acid were oxidized easily. Addition of cold nitric acid to the bis-(benzyltrimethylammonium) salt of 1,1,2,2-tetracyanoethanesulfonic acid oxidized it to tetracyanoethylene.

Addition of Free Radicals to Tetracyanoethylene.—Free radicals, generated by the thermal decomposition of α,α'-azodiisobutyronitrile, reacted with tetracyanoethylene in benzene to form a white crystalline compound.



$$\overset{\text{CN}}{(\text{CH}_3)_2\text{C}}\text{N}{=}\text{N}\overset{\text{CN}}{\text{C}}(\text{CH}_3)_2 + \underset{\text{NC}\quad\text{CN}}{\overset{\text{NC}\quad\text{CN}}{\text{C}{=}\text{C}}} \longrightarrow \text{NC}\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\underset{\text{CN}}{\overset{\text{CN}}{\text{C}}}-\underset{\text{CN}}{\overset{\text{CN}}{\text{C}}}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CN} + \text{N}_2$$

VII

Elemental and spectroscopic analyses of the product indicate that it is the adduct 2,3,3,4,4,5-hexacyano-2,5-dimethylhexane (VII).

Experimental

Tetracyanoethylene–Diene Adducts (Table I).[12]—The Diels–Alder adducts of tetracyanoethylene with dienes were generally prepared by the interaction of tetracyanoethylene with the diene in tetrahydrofuran. Other solvents, such as acetone and benzene, also were used with equal success. Cooling was frequently necessary to keep the reaction under control. When the butadiene adduct was prepared, the reaction mixture was maintained below 0° to prevent the loss of butadiene. In most instances, the reaction was accompanied with the formation of a transient color. In general, the butadienes in Table I produced yellow colors, anthracene a bright green, and the other dienes produced transient purple or violet colors.

In a typical preparation, 1.82 g. (0.022 mole) of 2,3-dimethylbutadiene was added to a solution of 2.56 g. (0.02 mole) of tetracyanoethylene in 15 ml. of tetrahydrofuran. The reaction mixture was cooled to room temperature, and the solvent was evaporated at reduced pressure. The residue was recrystallized from benzene–petroleum ether to yield 3.7 g. (88%) of **1,2-dimethyl-4,4,5,5-tetracyanocyclohexene** in the form of white prisms.

Hydrolysis and Decarboxylation of 4,4,5,5-Tetracyanocyclohexene.—Fifteen grams of the tetracyanoethylene–butadiene adduct (4,4,5,5-tetracyanocyclohexene) was heated with 200 ml. of concd. hydrochloric acid in a sealed Hastelloy bomb with rocking at 150° for 15 hours. The solid residue was collected on a filter, washed several times with cold water, dried and then dissolved in ether and filtered. The ether filtrate was evaporated to dryness, and the residue was recrystallized from water to give a white crystalline solid, m.p. 170–171°. This solid proved to be identical with an authentic sample of 4-cyclohexene-1,2-dicarboxylic acid by comparison of their melting points, mixed melting points and infrared absorption spectra.

4-Cyclohexene-1,1,2,2-tetracarboxylic Diimide.[13]—A solution of 28 ml. of concd. sulfuric acid and 40 ml. of water was cooled to 0° and added to 4.3 g. of 4,4,5,5-tetracyano-1-cyclohexene. The mixture was heated under reflux. At the end of 3 hours, the solid was dissolved, and at the end of 5 hours, heating was discontinued. Cooling caused a white solid to precipitate. The solid was collected, washed with cold water, and then recrystallized from water. Glistening white plates of 4-cyclohexene-1,1,2,2-tetracarboxylic diimide were obtained which did not melt below 300°. This compound was sufficiently acidic to dissolve in a 5% sodium bicarbonate solution and was recovered unchanged from this solution by acidification. The infrared spectrum shows strong absorptions at 5.75 μ for carbonyl and at 3.15 μ for N–H.

Anal. Calcd. for $C_{10}H_8O_4N_2$: C, 54.57; H, 3.66; N, 12.73. Found: C, 54.67; H, 3.81; N, 12.97.

The same product also was obtained by hydrolysis of 4,4,5,5-tetracyano-1-cyclohexene with a boiling formic acid–hydrochloric acid mixture.

9,10-Dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarboxylic Diimide.[13]—Fifteen grams of tetracyanoethylene–anthracene adduct was heated with 200 ml. of concd. hydrochloric acid in a sealed Hastelloy bomb with rocking at 150° for 8 hours. Upon cooling, the solid residue was dissolved in 10% sodium hydroxide, treated with decolorizing charcoal and filtered. The filtrate was acidified with hydrochloric acid, and the white precipitate that formed was recrystallized from alcohol–water. There was obtained 4.6 g. of 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarboxylic diimide in the form of white needles, m.p. >300°. This compound was sufficiently acidic to dissolve in 5% sodium bicarbonate solution and was recovered unchanged from this solution by acidification. The infrared absorption spectrum shows a strong band at 5.75 μ for carbonyl and a band at 3.05 μ for N–H.

Anal. Calcd. for $C_{20}H_{12}O_4N_2$: C, 69.76; H, 3.51; N, 8.13. Found: C, 69.77; H, 3.73; N, 8.34.

This same product was also prepared by hydrolysis of the tetracyanoethylene–anthracene adduct with a boiling formic acid–hydrochloric acid mixture.

Attempted further hydrolysis of the diimide with sulfuric acid produced either a carbonaceous material or had no effect on the diimide, depending upon the concentration of the acid and the temperature.

9,10-Dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarboxylic Dihydrazide.—A suspension of 3.3 g. of the diimide prepared from the tetracyanoethylene–anthracene adduct and 10 ml. of hydrazine hydrate was heated under reflux for 4 hours. The solution was cooled, and the precipitate was collected and washed with alcohol. There was obtained 3.3 g. of 9,10-dihydro-9,10-ethanoanthracene-11,-11,12,12-tetracarboxylic dihydrazide in the form of a white powder that did not melt below 300°.

Anal. Calcd. for $C_{20}H_{14}O_4N_4$: C, 64.17; H, 3.77; N, 14.97. Found: C, 64.09; H, 3.89; N, 14.87.

Tetracyanoethane.[14] A. **Preparation by Catalytic Reduction.**—Tetracyanoethylene (5 g.) in tetrahydrofuran solution was catalytically reduced at room temperature with hydrogen at 3 atmospheres over 0.5 g. of palladium black. The reaction mixture was filtered and the solvent was removed from the filtrate by evaporation. Treatment of the solid residue with ether yielded a brown solid (3 g.) and a red solution. Sublimation of the brown solid at 130–150° (5 mm.) gave a 59% yield of tetracyanoethane in the form of white biaxial crystals which decomposed without melting when heated to 165–170°.

Anal. Calcd. for $C_6H_2N_4$: N, 43.07. Found: N, 43.24; pK_a, 3.6.

B. **Preparation by Reduction with Hydrogen Iodide.**—Tetracyanoethylene (12.8 g., 0.1 mole) was dissolved in 50 ml. of acetone, and the solution was cooled in ice. Then 50 ml. of concd. hydroiodic acid was added slowly with stirring. There was an immediate reaction, and white crystals precipitated. The reaction mixture was cooled for 30 minutes and then filtered. The tetracyanoethane was washed with cold distilled water to remove iodine and was then recrystallized from ethyl acetate–hexane to yield 12 g. (92% yield) of white crystals. Care is required in recrystallizing this material since prolonged boiling in solvents results in severe loss.

---

(12) R. E. Heckert and N. E. Searle, U. S. Patent 2,781,393 (1957).

(13) R. E. Heckert and W. J. Middleton, U. S. Patent 2,781,359 (1957).

(14) R. E. Heckert, U. S. Patent 2,788,356 (1957).

Anal. Calcd. for $C_6H_2N_4$: C, 55.38; H, 1.55; N, 43.07; mol. wt., 130. Found: C, 55.15; H, 1.62; N, 43.23; mol. wt., 128.

C. Preparation by Reduction with Mercaptoacetic Acid.—A solution of 19.2 g. (0.15 mole) of tetracyanoethylene in 75 ml. of acetone was cooled in an ice-bath, and 30 ml. of mercaptoacetic acid was added with stirring. The solution was cooled to 0°, and 150 ml. of cold water was added. The white needles which separated were collected on a filter and washed with water. After drying in a vacuum desiccator over phosphorus pentoxide, there was obtained 16.5 g. (83% yield) of tetracyanoethane in the form of long white needles. Additional recrystallization was not attempted since the small amount of mercaptoacetic acid left on the product appears to stabilize it against further decomposition upon standing.

Tetracyanoethane was further characterized by the preparation of a phenyl isocyanate adduct. A trace of sodium methoxide was added to a solution of 2.6 g. (0.02 mole) of tetracyanoethane and 2.4 g. (0.02 mole) of phenyl isocyanate in 50 ml. of tetrahydrofuran, and the mixture was allowed to stand overnight. Diethyl ether (100 ml.) was added and a white crystalline product slowly precipitated. This product was recrystallized from ethyl acetate–hexane to yield 4.0 g. (in two crops) of the **phenyl isocyanate adduct of tetracyanoethane** as white prisms which decomposed without melting at 220–240°.

Anal. Calcd. for $C_{13}H_7N_5O$: N, 28.10. Found: N, 28.10.

Dehydrogenation of Tetracyanoethane.[15]—In a large test-tube was placed a mixture of 0.5 g. of tetracyanoethane and 0.25 g. of sulfur. The tube slowly was heated in a sublimator at atmospheric pressure. The reaction began at 170° and proceeded vigorously at 180° with the evolution of hydrogen sulfide and the formation of colorless crystals in the cold region of the tube. The mixture was extracted with hot benzene and filtered. The benzene solution, which gave the typical tetracyanoethylene color test with anthracene,[16] was evaporated to dryness, leaving 0.2 g. of crystalline solid. Recrystallization from ether yielded a crystalline product, m.p. 198–200°, which showed no depression of melting point on admixture with authentic tetracyanoethylene. Other oxidizing agents that were found to be effective for the conversion of tetracyanoethane to tetracyanoethylene are lead dioxide, cupric oxide and ferric chloride in boiling benzene, and palladium-on-carbon in boiling xylene.

β,β,γ,γ-Tetracyanoketones (Table II).[17]—β,β,γ,γ-Tetracyanoketones were prepared by reaction of tetracyanoethylene with ketones over "molecular" silver catalyst. In reactions with liquid ketones, excess ketone was employed as the solvent, as illustrated by the preparation of the tetracyanoethylene–acetone adduct.

4,4,5,5-Tetracyano-2-pentanone.—"Molecular" silver, 2 g., was added to a solution of 6.4 g. (0.05 mole) of tetracyanoethylene in 50 ml. of acetone, and the solution was stirred for 8 hours and then allowed to stand overnight. The silver was removed by filtration, and the solution was evaporated to dryness under reduced pressure. The residual solid was recrystallized from ethyl acetate to give 4,4,5,5-tetracyano-2-pentanone as white waxy plates.

When less volatile ketones were used, *n*-hexane or a mixture of *n*-hexane and ether or benzene was used to precipitate the adduct from the excess ketone. The reaction of solid ketones required the use of an inert solvent, as illustrated by the preparation of the tetracyanoethylene–2-acetonaphthone adduct.

3,3,4,4-Tetracyano-2′-butyronaphthone.—"Molecular" silver, 1 g., was added to a solution of 6.4 g. (0.05 mole) of tetracyanoethylene and 17 g. (0.1 mole) of 2-acetonaphthone in 25 ml. of tetrahydrofuran, and the solution was allowed to stand for one week. The silver was removed by filtration, and the filtrate was drowned in a 1:1 mixture of ether and *n*-hexane. The white precipitate was collected on a filter and recrystallized from ethyl acetate–hexane to give 3,3,4,4-tetracyano-2′-butyronaphthone in the form of white plates.

4,4,5,5-Tetracyano-2-pentanone–*p*-Chlorophenyl Isocyanate Adduct.—A solution of 12.8 g. (0.1 mole) of tetracyanoethylene in 100 ml. of acetone was allowed to stand over 1 g. of "molecular" silver for 24 hours. The silver was removed by filtration, and 15.4 g. (0.1 mole) of *p*-chlorophenyl isocyanate was added to the filtrate. A trace of sodium methoxide was added, and an exothermic reaction ensued. Most of the acetone was removed by evaporation and the residue was collected on a filter, washed with ether until it was white, and then recrystallized from acetone–hexane to give 20 g. of the 4,4,5,5-tetracyano-2-pentanone–*p*-chlorophenyl isocyanate adduct as white plates, m.p. 192–193° dec.

Anal. Calcd. for $C_{16}H_{10}N_5ClO_2$: C, 56.56; H, 2.95; N, 20.62; Cl, 10.44. Found: C, 56.80; H, 3.04; N, 20.60; Cl, 10.58.

The 4,4,5,5-tetracyano-2-pentanone–phenyl isocyanate adduct was prepared in a similar manner, and was obtained as white plates, m.p. 200° dec.

Anal. Calcd. for $C_{16}H_{11}N_5O_2$: C, 62.94; H, 3.63; N, 22.94; mol. wt., 305. Found: C, 63.04; H, 3.67; N, 22.95; mol. wt., 322.

The 4,4,5,5-tetracyano-2-pentanone–α-naphthyl isocyanate adduct was also prepared in a similar manner, and was obtained as white prisms, m.p. 200–203° dec.

Anal. Calcd. for $C_{20}H_{13}N_5O_2$: C, 67.60; H, 3.69; N, 19.71. Found: C, 67.69; H, 3.92; N, 19.46.

Tetramethylammonium 1,1,2,2-Tetracyanoethanesulfonate.—A suspension of 25.6 g. (0.2 mole) of tetracyanoethylene in 100 ml. of water was saturated with sulfur dioxide until solution was complete. The solution was filtered and the filtrate was mixed with a solution of 20.6 g. (0.2 mole) of tetramethylammonium chloride in 75 ml. of water. The white precipitate which formed was collected on a filter, washed with water, and dried. There was obtained 52 g. (95% yield) of tetramethylammonium tetracyanoethanesulfonate. A sample was recrystallized from methanol–water to give long white needles.

Other salts (Table III) of this acid were prepared in a similar manner by substituting tetraethylammonium bromide, N-methylquinolinium iodide and trimethylsulfonium iodide for the tetramethylammonium chloride.

Sodium 1,1,2,2-Tetracyanoethanesulfonate.—Powdered tetracyanoethylene (12.8 g., 0.1 mole) was dissolved in a solution of 10.4 g. (0.1 mole) of sodium bisulfite in 50 ml. of water. A small amount of undissolved material was removed by filtration and the filtrate was evaporated to dryness under a stream of nitrogen at room temperature. The brown residue was triturated with alcohol, collected on a filter and washed with alcohol. The solid was dissolved in acetone, and the solution was treated with decolorizing charcoal, filtered and drowned in ether. White crystals of sodium 1,1,2,2-tetracyanoethanesulfonate separated upon standing. After an additional recrystallization from acetone–ether, there was obtained 2 g. of the purified sodium salt.

Bis-(benzyltrimethylammonium) Salt of 1,1,2,2-Tetracyanoethanesulfonic Acid.—Finely powdered tetracyanoethylene (6.4 g., 0.05 mole) was dissolved in a solution of 12.6 g. (0.1 mole) of sodium sulfite in 50 ml. of water. This solution was mixed with a solution of 27 g. (0.1 mole) of benzyltrimethylammonium iodide in 50 ml. of water. The precipitate that formed was collected on a filter, washed with water and recrystallized from water to give 22.5 (89% yield) of bis-(benzyltrimethylammonium) salt of 1,1,2,2-tetracyanoethanesulfonic acid in the form of long white needles.

Other bis-salts (Table III) of this acid were prepared in a similar manner by substituting N-methylquinolinium iodide and N-methyllepidinium iodide for the benzyltrimethylammonium iodide.

These same salts also were prepared by substitution of sodium bisulfite and potassium metasulfite for the sodium sulfite of the above procedure.

Silver Salt of Tetramethylammonium 1,1,2,2-Tetracyanoethanesulfonate.—A solution of 18.5 g. (0.067 mole) of tetramethylammonium 1,1,2,2-tetracyanoethanesulfonate in 150 ml. of acetone was mixed with a solution of 12.0 g. (0.07 mole) of silver nitrate in 50 ml. of acetonitrile. The crys-

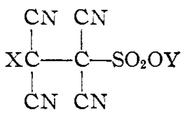
---

(15) We wish to thank Dr. R. A. Carboni, who conducted these dehydrogenation experiments.

(16) A dilute solution of anthracene in benzene will become green if a small portion of tetracyanoethylene is mixed with it. The green color soon fades, and a white precipitate of tetracyanoethylene–anthracene adduct forms. This is an extremely sensitive test for tetracyanoethylene.

(17) W. J. Middleton, U. S. Patent 2,762,833 (1956).

TABLE III

SALTS OF 1,1,2,2-TETRACYANOSULFONIC ACID 

$$XC(CN)_2—C(CN)_2—SO_2OY$$

X	Y	Empirical formula	M.p., °C.	Recrystn. solvent[a]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
H	Na	$C_6HN_4SO_3Na$	180 d.	A	31.03	31.10	0.44	0.53	24.13	24.41	13.81	13.75
H	$N(CH_3)_4$	$C_{10}H_{13}N_5SO_3$[b]	120–122 d.	B–C	42.39	42.50	4.62	4.72	24.74	24.45	11.31	11.50
H	$N(C_2H_5)_4$	$C_{14}H_{13}N_5SO_3$[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]	$C_{16}H_{11}N_5SO_3$	85–86	C	54.38	54.57	3.14	3.16	19.82	19.66	9.07	9.19
H	$S(CH_3)_3$	$C_9H_{10}N_4S_2O_3$	84–85 d.	None	37.75	38.06	3.52	3.74	19.57	19.62	22.40	22.43
$C_6H_5CH_2N(CH_3)_3$	$C_6H_5CH_2N(CH_3)_3$	$C_{26}H_{32}N_5SO_3$	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]	$C_{26}H_{20}N_6SO_3$	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]	$C_{28}H_{24}N_6SO_3$	172–173 d.	B	64.10	64.00	4.61	4.67			6.11	6.26
Ag	$N(CH_3)_4$	$C_{10}H_{12}N_5SO_3Ag$	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 $C_{14}H_{12}N_6$: 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

RECEIVED NOVEMBER 14, 1957

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 formation 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).