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Cyanocarbon Chemistry. I. Preparation and Reactions of Tetracyanoethylene

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Synthesis of the first percyanoolefin, tetracyanoethylene, is described. Tetracyanoethylene (TCNE) has been found to undergo a variety of reactions, including addition, replacement and cyclization reactions, to give dyes, strong acids and heterocyclic compounds.

The cyanocarbons are compounds containing only the $\text{—C}\equiv\text{N}$ group attached to carbon. They and their derivatives have not been recognized as a class of compounds and are, in fact, virtually unknown. Only two cyanocarbons, dicyanoacetylene¹ and dicyanobutadiyne,² have been reported. The only other known compounds in which more than half the hydrogen atoms of the parent hydrocarbon have been replaced by cyano groups are cyanoform³ and 1,1,3,3-tetracyanopropene.⁴ Steric considerations indicate that other compounds having many cyano groups should be capable of existence, and electronic considerations suggest that such compounds might have unusual reactivity. Investigation of this area of chemistry has led to the discovery of tetracyanoethylene, the first example of a percyanoolefin, and demonstration of its exceptional reactivity, especially as a source of other compounds having a large number of cyano groups.⁵ Many of these derivatives are characterized by intense color, high acidity or easy conversion into heterocyclic compounds.

Tetracyanoethylene (TCNE) has been synthesized from malononitrile by four different methods. The original preparation was accomplished by the reaction of sulfur monochloride with malononitrile in boiling chloroform-tetrachloroethylene. Subsequently, TCNE was synthesized by chlorination-dehydrochlorination of malononitrile in the vapor phase at 400–450°. It was also prepared by condensation of 1,3-bis-(acetoxylimino)-2-propanone with malononitrile, followed by pyrolysis of the product. However, for reasons of convenience and purity of product, the laboratory method that is now preferred is the debromination of dibromomalononitrile with copper powder in boiling benzene. By this method, pure TCNE can be prepared conveniently in 55–65% yield.

The formation of TCNE from dibromomalononitrile and copper powder may proceed through intermediate formation of dicyanocarbene which, in the absence of anything that reacts readily with carbenes, dimerizes to TCNE. Evidence for this view was obtained by repeating the experiment with cyclohexene, a carbene acceptor,⁶ as the reaction medium instead of benzene. The product was a

thick oil in which no TCNE could be detected. However, it was possible to isolate a 15% yield of cyclohexylidenemalononitrile, which probably resulted from thermal rearrangement of initially formed 7,7-dicyanobicyclo[4.1.0]heptane. Substituting ethyl dibromocycanoacetate for dibromomalononitrile in this reaction gave a 10% yield of the adduct of cyano-(ethoxycarbonyl)-carbene with cyclohexene, 7-cyano-7-ethoxycarbonylbicyclo[4.1.0]heptane.

Tetracyanoethylene is a colorless, crystalline solid that sublimes readily at temperatures above 120° at atmospheric pressure and melts at 198–200° in a sealed capillary. The infrared spectrum of this compound has a divided band in the nitrile region characteristic of conjugated, unsaturated nitriles.⁷ Elemental analyses and molecular weight determinations are in accord with theory for C_6N_4 . The high thermal stability of TCNE is shown by its ability to sublime unchanged at a pressure of 2.7 mm. through a tube packed with Carborundum chips heated at 600°. However, sublimation at atmospheric pressure through a tube heated at 1000° results in about 50% conversion of TCNE to cyanogen. Colored complexes⁸ are formed between TCNE and aromatic hydrocarbons. For example, TCNE gives an intense yellow color with benzene, orange with toluene and red with xylene. Anthracene and TCNE in benzene form a transient dark green solution from which white crystals of the Diels–Alder adduct separate.

Additions to the double bond of TCNE occur with several types of reagents, including dienes, ketones and hydrogen.⁹ Tetracyanoethylene is an unusually active dienophile, its reaction with butadiene, anthracene, 2-vinylnaphthalene and other 1,3-dienes to give tetracyanocyclohexenes (I) being rapid even at room temperature. Ketones possessing an α -hydrogen add to TCNE in the presence of catalysts, *e.g.*, boron trifluoride or "molecular" silver, to give $\beta,\beta,\gamma,\gamma$ -tetracyanopropyl ketones (II).

Tetracyanoethylene can be reduced to 1,1,2,2-tetracyanoethane (III) by catalytic hydrogenation, by mercaptans, or by hydrogen iodide. Tetracyanoethane is very prone to undergo addition reactions involving two cyano groups on adjacent carbon atoms. For example, base-catalyzed addi-

- (1) C. Moureu and J. Bongrand, *Compt. rend.*, **170**, 1025 (1928).
- (2) F. J. Brockman, *Can. J. Chem.*, **33**, 507 (1955).
- (3) E. Cox and A. Fontaine, *Bull. soc. chim. France*, 948 (1954).
- (4) Y. Urushibana, *Bull. Chem. Soc. Japan*, **2**, 278 (1927); *C. A.*, **22**, 579 (1928).
- (5) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, Edith G. McGeer, B. C. McKusick, and W. J. Middleton, *THIS JOURNAL*, **79**, 2340 (1957).
- (6) W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

(7) Paper XII, C. E. Looney and J. R. Downing, *ibid.*, **80**, 2840 (1958).

(8) Paper II, R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

(9) Paper III, W. J. Middleton, R. E. Heckert, E. L. Little, T. L. Cairns, D. D. Coffman and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

tion of hydrogen sulfide gives 2,5-diamino-3,4-dicyanothiophene (IV), which can be rearranged to a mercaptopyrrole (V). On the other hand, mercaptans add twice to give 1,4-diamino-1,4-bis-(alkylthio)-2,3-dicyano-1,3-butadienes (VI) which can be converted to pyrroles VII and VIII by loss of mercaptan or ammonia.¹⁰

Tetracyanoethylene is attacked by nucleophilic reagents with replacement of either one cyano group or two cyano groups attached to the same carbon atom by such groups as alkoxy, hydroxy or aminoaryl. Among the most versatile derivatives of TCNE are the dicyanoketene acetals (IX) obtained by reaction with alcohols in the presence of a catalyst such as urea.¹¹ If 1,2- or 1,3-glycols are used, the products are cyclic acetals (X), 2-dicyanomethylene-1,3-dioxolanes or 2-dicyanomethylene-1,3-dioxanes. The dicyanoketene acetals react with ammonia and primary and secondary amines to give 1-amino-1-alkoxy-2,2-dicyanoethylenes (XX) and 1,1-diamino-2,2-dicyanoethylenes (XXI). The cyclic acetals react with tertiary amines to give mesoionic quaternary ammonium salts (XI). Analogous inner sulfonium salts (XII) are formed when a sulfide is used instead of a tertiary amine. Replacement of one or both of the alkoxy groups of a dicyanoketene acetal with a dicyanomethyl group leads to an interesting series of acidic cyano compounds.¹² Reaction with two equivalents of sodiomalononitrile gives the disodium salt of 2-dicyanomethyl-1,1,3,3-tetracyanopropene (XIII). This salt was converted to an aqueous solution of the acid, which by comparative *pH* measurements was shown to be at least as strong an acid as sulfuric. The high acidity is ascribed to the high resonance stability of this dibasic anion, which is formally analogous to a carbonate anion. Reaction of dicyanoketene acetals with one equivalent of malononitrile gives a family of cyanocarbon acids, the 2-alkoxy-1,1,3,3-tetracyanopropenes (XIV), which are converted easily to 2-amino-3,5-dicyano-4-alkoxy-6-chloropyridines by action of hydrochloric acid (XV).¹³

A variety of heterocyclic compounds including pyrazoles and isoxazoles can be prepared from dicyanoketene acetals.¹⁴ In these reactions an alkoxy group of the dicyanoketene acetal is displaced by an amino reactant attached to a second group capable of adding across one of the cyano groups to effect cyclization. For example, dicyanoketene acetals react with hydrazine to give 3-alkoxy-4-cyano-5-aminopyrazoles (XVI) and with hydroxylamine to give 3-alkoxy-4-cyano-5-aminoisoxazoles (XVII).

Two new cyanocarbon acids, 1,1,2,3,3-pentacyanopropene (XVIII) and tricyanovinyl alcohol (XIX), are obtained from TCNE by hydrolysis under basic and acidic conditions, respectively.¹²

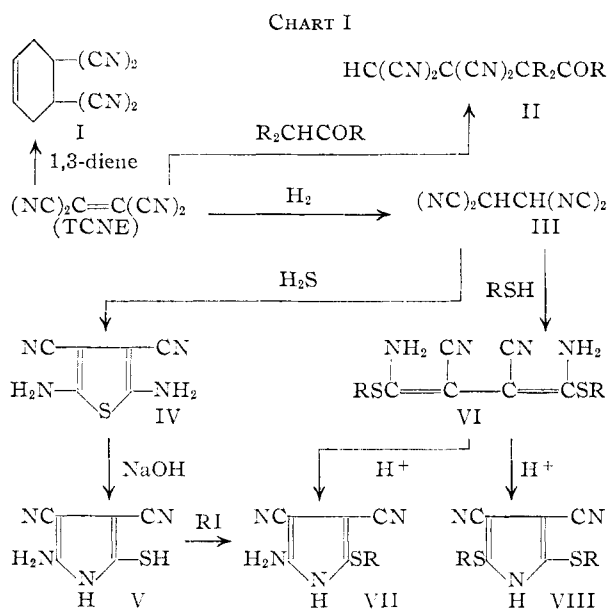
(10) Paper VIII, W. J. Middleton, V. A. Engelhardt and B. S. Fisher, *THIS JOURNAL*, **80**, 2822 (1958).

(11) Paper IV, W. J. Middleton, T. L. Cairns, D. D. Coffman and V. A. Engelhardt, *ibid.*, **80**, 2788 (1958).

(12) Paper V, W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *THIS JOURNAL*, **80**, 2795 (1958).

(13) Paper X, E. L. Little, W. J. Middleton, D. D. Coffman, V. A. Engelhardt and G. N. Sausen, *ibid.*, **80**, 2832 (1958).

(14) Paper IX, W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2829 (1958).



A large number of metal and ammonium salts of these cyanocarbon acids have been prepared.

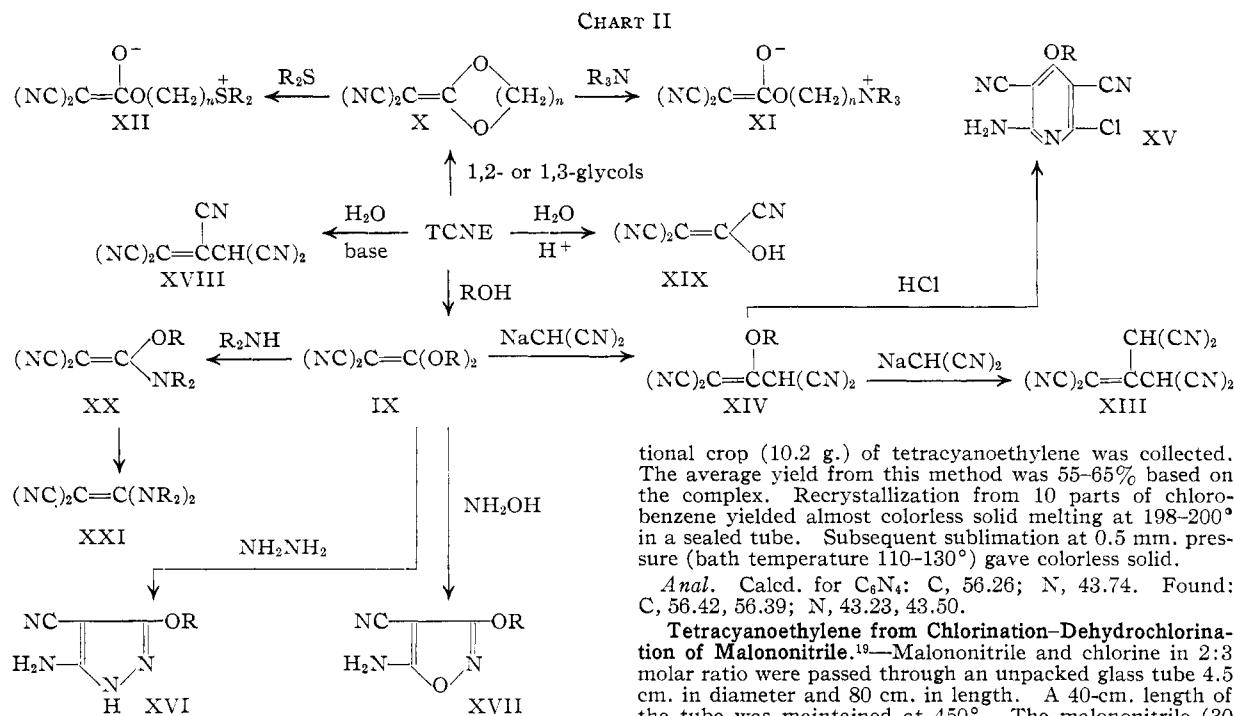
Orange and red quaternary ammonium salts of another new cyanocarbon acid, 1,1,2,4,5,5-hexacyano-3-aza-1,3-pentadiene (XXII), are prepared by passing a stream of ammonia into a cold solution of TCNE in acetone and then adding an aqueous solution of a quaternary ammonium halide.¹² The acid can be isolated as a red hydrate by use of ion-exchange techniques. Primary or secondary aliphatic amines and most primary and some secondary aromatic amines react with TCNE to give N-tricyanovinylamines (XXIII). However, reaction of TCNE with tertiary aromatic amines gives 4-tricyanovinylarylamines (XXIV), *e.g.*, N,N-dimethyl-4-tricyanovinylaniline, which comprise a new class of brilliant orange to blue dyes.¹⁵ Reaction of TCNE with phenols and pyrroles also gives C-tricyanovinyl derivatives, *e.g.*, 4-tricyanovinyl-2,6-dimethylphenol and α -tricyanovinylpyrrole.¹⁶

Experimental

Tetracyanoethylene from Malononitrile and Sulfur Monochloride.—In a 3-l. flask equipped with an addition funnel, efficient stirrer and a reflux condenser, 600 ml. of chloroform, 600 ml. of tetrachloroethylene and 410 g. (3 moles) of sulfur monochloride were heated under reflux. Malononitrile (198 g., 3 moles) was added dropwise over a period of approximately two hours. The hydrogen chloride liberated was trapped in a scrubbing tower while the solution was heated for a total of eight hours. The flask was heated on a steam-bath and the chloroform-tetrachloroethylene mixture was distilled under reduced pressure. The residue consisted of a tar which was dried by heating the reaction flask with a Glascol mantle for two hours at 100–150° and 20–40 mm. pressure. During this period, sulfur and most of the tetracyanoethylene sublimed to the cooler upper part of the flask. This material was separated mechanically and resublimed at 125–135° (1–2 mm.). In a typical run, the sublimate weighed 46 g. (24% yield, crude). Analysis indicated that the sublimate was more than 90% tetracyanoethylene. Pure tetracyanoethylene was obtained by two recrystallizations from dry chlorobenzene using a solvent–solid ratio

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

(16) Paper VII, G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *ibid.*, **80**, 2815 (1958).



tional crop (10.2 g.) of tetracyanoethylene was collected. The average yield from this method was 55-65% based on the complex. Recrystallization from 10 parts of chlorobenzene yielded almost colorless solid melting at 198-200° in a sealed tube. Subsequent sublimation at 0.5 mm. pressure (bath temperature 110-130°) gave colorless solid.

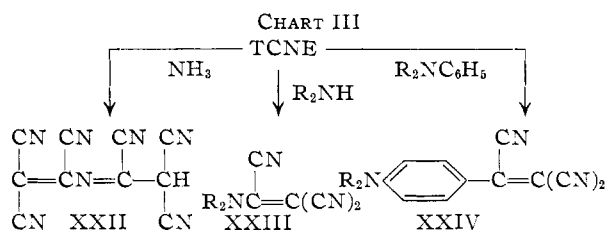
Anal. Calcd. for C_6N_4 : C, 56.26; N, 43.74. Found: C, 56.42, 56.39; N, 43.23, 43.50.

Tetracyanoethylene from Chlorination-Dehydrochlorination of Malononitrile.¹⁹—Malononitrile and chlorine in 2:3 molar ratio were passed through an unpacked glass tube 4.5 cm. in diameter and 80 cm. in length. A 40-cm. length of the tube was maintained at 450°. The malononitrile (30 g., 0.45 mole) was introduced at the rate of 0.25 mole/hr. Colorless crystals of tetracyanoethylene began to appear almost immediately. When the addition was completed, the product was recovered from the receiver and walls of the tube. The product was extracted with 10 times its weight of boiling chlorobenzene to obtain 9.2 g. (31%) of tetracyanoethylene. The product, after sublimation, melted at 197-199°, and the melting point was not depressed on admixture with an authentic sample of tetracyanoethylene.

1,3-Bis-(acetoxyimino)-2-propanone.—Whereas negligible yields of 1,3-bis-(acetoxyimino)-2-propanone were obtained by the procedure of Malachowski, *et al.*,²⁰ the following modification gave the compound conveniently and in good yield. 1,3-Dioximino-2-propanone²¹ (47 g., 0.40 mole) was stirred with acetic anhydride (125 ml.) and pyridine (1 ml.) while reaction was initiated by gentle warming on a steam-bath. The temperature of the mixture was kept between 25 and 35° by external cooling; below 25° reaction ceased, above 35° decomposition took place. When the solution became clear, it was stirred at room temperature for 15 minutes and then at 0° until it partially solidified. A mixture of ethyl ether and hexane (5:2 by vol.) was added with stirring and the light yellow solid was collected in a Büchner funnel. Additional solid was obtained by briefly cooling the dark filtrate in a Dry Ice-acetone-bath. The combined solids after trituration with three 50-ml. portions of ether-hexane (1:1 by vol.) and drying weighed 70.5 g. (88% yield) and melted at 77-78° (reported²⁰ m.p. 80-81°).

Anal. Calcd. for $C_7H_8N_2O_5$: C, 42.00; H, 4.03; N, 14.00. Found: C, 42.47; H, 3.96; N, 13.30, 13.30.

Bis-(acetoxyiminomethyl)-methylenemalononitrile.—1,3-Bis-(acetoxyimino)-2-propanone (13 g., 0.065 mole), malononitrile (10 g., 0.15 mole) and acetic anhydride (25 ml.) were heated together at reflux temperature for ten minutes. The cool solution was poured into 200 g. of ice-water and stirred for two hours in order to precipitate 15 g. (73% yield) of bis-(acetoxyiminomethyl)-methylenemalononitrile. After recrystallization from benzene, it weighed 10 g. and melted at 136-137°. Its infrared spectrum had bands in the regions ordinarily assigned to vinyl esters, conjugated carbonitrile groups and conjugated carbon-carbon double bonds and/or carbon-nitrogen double bonds. It is an un-



of 10 ml./g. The white crystals weighed 33.3 g. (17% yield). An infrared spectrum of the colorless product contained a divided band in the nitrile region characteristic of conjugately unsaturated nitriles.⁷ No carbon-hydrogen bond was detected in the spectrum nor were any alternative structures indicated.

Anal. Calcd. for C_6N_4 : C, 56.26; N, 43.74; mol. wt., 128. Found: C, 56.33, 56.63; N, 43.02, 43.48; mol. wt., 132.

Tetracyanoethylene from Dibromomalononitrile-Potassium Bromide Complex.¹⁷—Tetracyanoethylene was prepared conveniently by heating a stirred mixture of dry 4:1 dibromomalononitrile-potassium bromide complex and copper in an inert, anhydrous non-polar solvent such as benzene. The dibromomalononitrile-potassium bromide complex was prepared in 85% yield.¹⁸

Precipitated copper powder (50 g., 0.79 mole; Metals Disintegrating Co., Elizabeth, N. J.) was added in three portions to a well-stirred suspension of 100 g. (0.1 mole) of dried dibromomalononitrile-potassium bromide complex in 400 ml. of dry benzene at room temperature. The mixture was refluxed for eight hours with stirring. As the reaction progressed, the benzene solution became progressively deeper yellow due to the increasing concentration of tetracyanoethylene. The reaction mixture was filtered while hot to remove inorganic solids. The solids were washed with 50 ml. of hot benzene, stirred in 100 ml. of boiling benzene for a few minutes, and refiltered. The original benzene filtrate was kept at 5° overnight, then filtered to separate crystalline tetracyanoethylene, weight 6.9 g. after drying. The mother liquor was combined with the benzene from the extraction of the inorganic solids, concentrated to 50 ml. at slightly reduced pressure, and cooled at 5°. An addi-

(17) R. E. Heckert and E. L. Little, U. S. Patent 2,794,824 (1957).

(18) L. Ramberg and S. Wideqvist, *Arkiv. Kemi, Mineral Geol.*, **12A**, No. 22, 12 pp. (1937); *C. A.*, **32**, 2511 (1938).

(19) R. E. Heckert, U. S. Patent 2,794,823 (1957).

(20) R. Malachowski, L. Jurkiewicz and J. Wojtowicz, *Ber.*, **70B**, 1012 (1937).

(21) T. A. Geissman, M. J. Schlatter and I. D. Webb, *J. Org. Chem.*, **11**, 736 (1946).

stable substance, completely resinifying during a week's exposure to air. Although it was analyzed within a few hours of being prepared, enough decomposition may have occurred to account for low nitrogen values.

Anal. Calcd. for $C_{10}H_8N_4O_4$: C, 48.39; H, 3.25; N, 22.58. Found: C, 48.57; H, 3.09; N, 20.52, 20.62.

Tetracyanoethylene from Bis-(acetoxymethyl)-methylenemalononitrile.—Bis-(acetoxymethyl)-methylenemalononitrile sublimed unchanged at 150° (0.3 mm.). At 150–210° (250 mm.) it decomposed into tetracyanoethylene, which was collected on the cold finger condenser of a sublimation apparatus. It was identified by two characteristic color tests (anthracene in benzene⁹ and N,N-dimethylaniline in acetone¹⁵) and by comparison of its X-ray diffraction pattern with that of an authentic sample. Conversion was estimated to be about 50%.

Reaction of Dibromomalononitrile with Copper in the Presence of Cyclohexene.—A dry 500-ml. flask equipped with a stirrer, reflux condenser and addition funnel was charged with 250 ml. of cyclohexene and 63.5 g. (1 mole) of precipitated copper powder. With stirring, the mixture was heated to gentle reflux. The heat was removed and 44.8 g. (0.2 mole) of dibromomalononitrile¹⁸ dissolved in 50 ml. of cyclohexene was added dropwise over one hour. There was a mild exothermic reaction. The mixture was then stirred and refluxed for two hours, cooled and filtered, and the dark filtrate was subjected to rough distillation. There was obtained 29 g. of moderately viscous liquid boiling over the range 95–130° under full oil-pump vacuum. The distillate, as well as the original reaction mixture, gave no color test for TCNE with anthracene.⁹ Redistillation gave 15 g. of liquid boiling over the range 92–103° (0.07 mm.). The infrared spectrum of this material appeared consistent with the bicyclo[4.1.0]heptane structure and indicated the presence of only a trace of unsaturation. Repetition of the reaction gave a 60% yield of crude product boiling over the range 81–120° (0.35–1 mm.). When redistilled in an 18'' spinning-band column, approximately 25% was recovered boiling at 103–106° (1.1 mm.). This fraction proved to be cyclohexylidenemalononitrile as shown by analysis and agreement of its infrared spectrum with that of an authentic sample of cyclohexylidenemalononitrile.²²

Reaction of Ethyl Dibromocycanoacetate with Copper in the Presence of Cyclohexene. 7-Cyano-7-ethoxycarbonylcyclo[4.1.0]heptane.—In a dry flask equipped with a stirrer, thermometer, addition funnel and reflux condenser was placed 63.5 g. (1 mole) of precipitated copper powder and

(22) A. C. Cope and K. E. Hoyle, *THIS JOURNAL*, 63, 733 (1941).

250 ml. of cyclohexene. The mixture was heated to 80° and with stirring 54 g. (0.2 mole) of ethyl dibromocycanoacetate was added dropwise over a period of 30 minutes. There was a very mildly exothermic reaction. When the addition was complete, the mixture was stirred and refluxed for eight hours and filtered, and the filtrate was subjected to distillation. Four fractions that were collected over the boiling range 93–115° (0.7 mm.) partly crystallized. Filtration of these combined fractions gave 4 g. (10% yield) of 7-cyano-7-ethoxycarbonylcyclo[4.1.0]heptane as a white solid, m.p. 56–59°. On crystallization from hexane, it was obtained as stout needles, m.p. 60–62°. The infrared spectrum was consistent with the proposed structure and showed absorption at 3.3, 3.4 and 3.45 μ for saturated CH, 4.45 μ for CN, and 5.75 μ for ester carbonyl. The nuclear magnetic resonance spectrum also agreed with the proposed structure.

Anal. Calcd. for $C_{11}H_{15}O_2N$: C, 68.37; H, 7.82; N, 7.25; mol. wt., 193. Found: C, 68.34; H, 7.96; N, 7.11; mol. wt., 216, 207.

Thermal Stability of Tetracyanoethylene.—Tetracyanoethylene (10 g.) was sublimed through a vertical Vycor tube 1'' in diameter packed with Carborundum chips heated to 600° and at a pressure of 2.7 mm. The tube and packing were heated over a length of 15 cm. The vapors of tetracyanoethylene, entrained by a stream of nitrogen, were passed from top to bottom of the tube, and the stream was then led to a trap cooled in ice followed by one cooled in solid CO₂-acetone. The run required about three hours. Most of the tetracyanoethylene came through unchanged and condensed on the cold end of the tube. No material was found in either trap.

When tetracyanoethylene (12.8 g.) was sublimed in the manner just described through a tube heated to a temperature of 1000° at atmospheric pressure over a period of one hour, the ice-cooled trap was found to contain 4.1 g. of a light-brown solid. This solid consisted mainly of tetracyanoethylene as determined by elemental analysis and infrared spectra. The solid CO₂-cooled trap contained a brown solid which was allowed to vaporize at room temperature and was then recondensed at -50°. In this way there was obtained 3.9 g. of a white solid, m.p. -35 to -34°, identified as cyanogen by test with palladium dimethylglyoximate.²³

Reactions of Tetracyanoethylene.—Experimental details on reactions of tetracyanoethylene are given in papers II to XII on cyanocarbon chemistry.

(23) F. Feigl and H. E. Feigl, *Anal. Chim. Acta*, 3, 300 (1949).

WILMINGTON, DELAWARE

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Cyanocarbon Chemistry. II.¹ Spectroscopic Studies of the Molecular Complexes of Tetracyanoethylene

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Complex-formation equilibrium constants and spectroscopic data for twenty-three π -complexes involving tetracyanoethylene and various aromatic molecules are presented. It is found that the free energies of formation of these π -complexes and the base ionization potentials are connected by the linear relation $\Delta F^\circ = 0.0510I_p - 11,230$ cal. Comparison with such π -acids as maleic anhydride and chloranil reveals that tetracyanoethylene is the strongest π -acid yet examined. Discussions of solvent and geometrical effects in tetracyanoethylene π -complex formation are presented. Heats of formation of π -complexes between tetracyanoethylene and methylbenzenes are found to range from -2.3 kcal. for benzene to -7.0 kcal. for pentamethylbenzene.

Introduction

Since the initial work of Benesi and Hildebrand

(1) Paper I, T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, Edith G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, *THIS JOURNAL*, 80, 2775 (1958).

on the iodine/aromatic complexes,² there has been a great deal of theoretical and experimental interest in the nature of these and other non-ionic complexes.³ The systems studied include com-

(2) H. A. Benesi and J. H. Hildebrand, *ibid.*, 71, 2703 (1949).

(3) For a general review of the subject, see L. J. Andrews, *Chem. Revs.*, 54, 713 (1954).