THE CHEMISTRY OF TETRACYANOETHYLENE

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Received May 8, 1967

CONTENTS

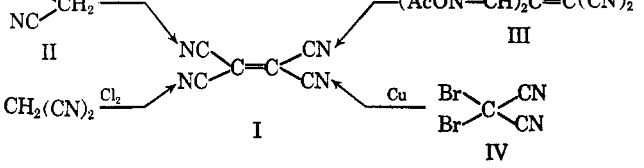
I. INTRODUCTION

Tetracyanoethylene (TCNE), the first percyanoolefin to be prepared, is a versatile compound of exceptional reactivity. The chemistry of this compound, though comparatively of recent date, was reviewed in the year 1962 (167, in German). During the preparation of this manuscript another review (96) devoted to the preparation and reactions of TCNE has appeared. The present review, however, is an attempt to survey the extensive literature on the subject with emphasis on more recent work and to summarize in one article an over-all view of the subject. For obvious reasons a short account of the preparation of TCNE has been incorporated in order to maintain the continuity of the subject. Emphasis has been laid on recent developments in the chemistry of TCNE, *viz.*, mechanism of alkylation with this reagent, retrograde Michael addition, photoaddition reaction, polymer–metal complexes, and preparation of tetracyanoethylene anion radical. In addition, the analytical and commercial applications of TCNE and its derivatives are reviewed. The chemistry of tetracyanoethylene oxide has, however, been excluded from this review.

For the present article relevant literature has been covered through the March 1967 issue of *Chemical Abstracts*.

II. METHODS OF PREPARATION

Tetracyanoethylene (I) has been prepared from malononitrile (II) by four different methods. The original preparation (24, 26, 28) consisted of the interaction of malononitrile with sulfur monochloride, in boiling chloroform–tetrachloroethylene. The second method (26, 56) involved the vapor-phase chlorination–dehydrochlorination of malononitrile at 450°. The preparation of TCNE was also accomplished by the condensation of malononitrile with 1,3-bis(acetoxyimino)-2-propanone, followed by pyrolysis of the product III (26). However, the preferred synthetic preparation of TCNE (62% yield) (26, 29, 57) involves the debromination of the KBr complex of dibromomalononitrile (IV) with copper powder in boiling benzene. The reaction may involve an intermediate dicyano-



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carbene, which dimerizes to tetracyanoethylene. A modification of this method, *i.e.*, the pyrolysis (325°) of the dibromomalononitrile, is reported to give quantitative conversion to tetracyanoethylene (89).

Tetracyanoethylene has been prepared, in poor yields, by heating dibromomalononitrile with zinc powder (57), by treating 1,2-dicyano-1,2-bis(*p*-tolylsulfonyl)ethylene with sodium cyanide in acetonitrile (88), by reacting dichlorofumaronitrile with HCN in the gas phase at 500° (90) or NaCN (39), and by pyrolysis of bromodicyanoacetamide (153). However, the reaction of tetracyano-1,4-dithiine with potassium cyanide and subsequent oxidation with chlorine or bromine provides a practical synthesis of TCNE (60%) from readily obtainable starting materials (156).

III. PURIFICATION

TCNE can be purified by recrystallization from chlorobenzene followed by vacuum sublimation (29). Alternatively, the impure product is converted to water-soluble potassium tetracyanoethylenide (160) by treatment with potassium iodide in acetonitrile. It is filtered and the filtrate oxidized to TCNE by either bromine, nitric acid, or silver trifluoroacetate.

IV. PHYSICAL PROPERTIES

A. GENERAL

TCNE is a colorless crystalline solid that sublimes around 120° at atmospheric pressure and melts at 198–200° in a sealed capillary. It has a high thermal stability (26). TCNE slowly evolves hydrogen cyanide when exposed to moist air at room temperature (25).

B. ELECTRONIC SPECTRA

The absorption band of TCNE lies at 265 mμ (82). Further, the character of the electronic spectrum in the 2600-A region offers a close analogy with N $\rightarrow$ V and N $\rightarrow$ R transitions of ethylene and alkylethylenes (125).

C. INFRARED AND RAMAN SPECTRA

In TCNE, the stretching frequency of C≡N lies at 4.42 μ, and a minor peak appears at 4.49 μ in the infrared region of spectrum, whereas the C=C stretching frequency lies at 6.55 μ (82) (6.37 μ (83)), in the Raman spectrum. Thus it is apparent that conjugation and formal charge in TCNE have a pronounced effect on the C=C frequency but not on the C≡N frequency. The position of the double-bond frequency is an indication of considerable resonance between the C=C and the nitrile group (82).

D. CRYSTALLOGRAPHIC DATA

Crystallization of TCNE from solution affords monoclinic crystals with $a = 7.51$, $b = 6.21$, $c = 7.00$ A, $\beta = 97° 10'$ (59). The molecule is strictly planar (7) and the bond lengths (angstrom units) corrected for vibrational motions, are d(C=C) = 1.317 ± 0.009; d(C—C), 1.454, 1.443 ± 0.007; d(C—N), 1.15, 1.15 ± 0.012.

E. THERMOCHEMICAL DATA

The heats of combustion and sublimation of TCNE are 7.22 and 18.65 kcal/mole, respectively (82).

F. MISCELLANEOUS DATA

TCNE has a high electron affinity, 150 kcal (118). It has a negative stabilization energy (−27 kcal/mole) indicating that electrostatic repulsion between highly polar cyano groups predominates over electronic delocalization stabilization (23).

G. CHARGE-TRANSFER COMPLEXES

The presence of four highly electronegative groups in TCNE decreases the electron density around the ethylenic group and thus makes it a strong electron acceptor (99). With suitable electron donors, for example, compounds with aromatic π-electron systems (35, 94, 99), it forms, usually in solution, colored molecular complexes by an intermolecular charge-transfer interaction (112). The reaction is reversible (49): donor, acceptor, and complex all exist in equilibrium. The charge-transfer complexes usually have a characteristic broad featureless band (30, 155) in the visible or ultraviolet region of the spectrum.

The π complexes of TCNE possess a sandwich structure (99), in which donor and acceptor molecules lie parallel to each other, so as to allow a maximum overlap between the π-molecular orbitals of the two components. Sometimes, steric effects may hinder a sufficiently close approach of the two partners, leading to instability of the resultant complex (149).

Some of the solid charge-transfer complexes, particularly of TCNE with polycyclic aromatic hydrocarbons and aromatic amines, are reported to exhibit semiconducting properties (1–3, 12, 15, 42, 43, 68–72, 74–76, 91, 119, 145, 154). In one case, *viz.*, benzene–TCNE, the phenomenon of fluorescence in ultraviolet light has been reported (169). Each year brings several additions to the list of donors whose π complexes with TCNE have been studied (31–34, 51, 60, 66, 73, 87, 98, 111, 136, 146, 150, 151, 155).

Table I lists the ultraviolet spectral data for a number of π complexes of TCNE.

V. CHEMICAL BEHAVIOR

Tetracyanoethylene is a reactive compound that undergoes a variety of reactions including addition, replacement, and cyclization reactions (26).

CHART I: ADDITION REACTIONS OF TCNE

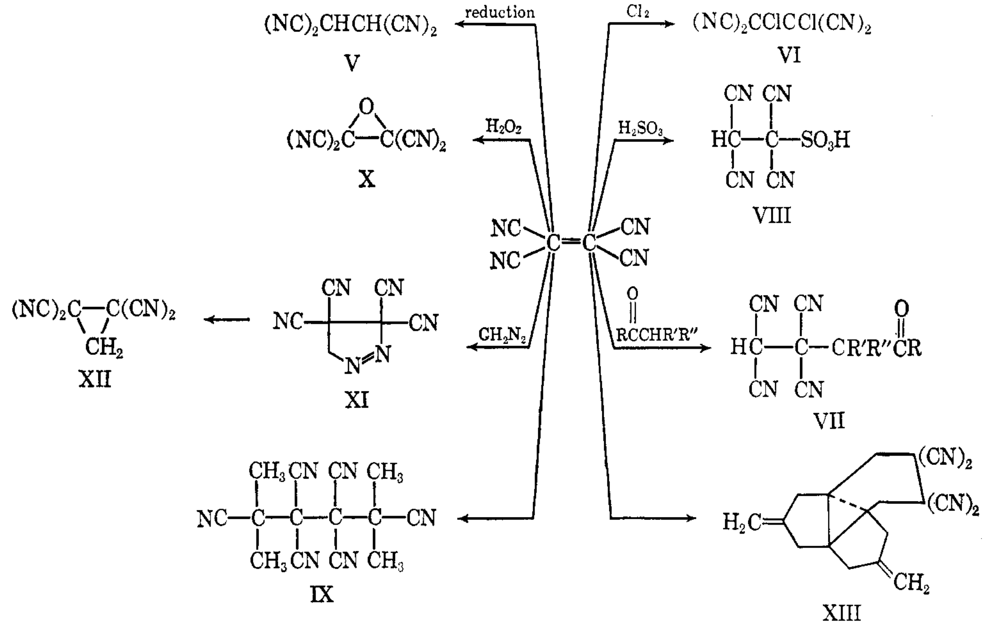


TABLE I[a]

π COMPLEXES OF TCNE AND AROMATIC BASES IN DICHLOROMETHANE SOLVENT

π base	λ_{max}(1), A	ε(1)	λ_{max}(2), A	ε(2)
Cyclohexane	4220	4,760	...	...
Benzene	3840	3,570	...	...
Toluene	4060	3,330	...	...
o-Xylene	4300	3,860	...	...
m-Xylene	4400	3,300	...	...
p-Xylene	4600	2,650	4150	2,770
Mesitylene	4610	3,120	...	...
Durene	4800	2,075	...	...
Pentamethylbenzene[b]	5200	3,270	...	...
Hexamethylbenzene[b]	5450	4,390	...	...
Hexaethylbenzene	5500	56	...	...
Biphenyl	5000	1,450	...	..
m-Terphenyl	5000	1,470	...	...
p-Terphenyl	5640	830	...	...
Tetraphenylethylene	6100	67	...	...
Naphthalene	5500	1,240	4290	1,120
Fluorene	5700	1,430	4160	1,060
Pyrene	7240	1,137	4950	856
Chlorobenzene	3790	3,840	...	...
Bromobenzene	3940	5,000	...	...
Iodobenzene	4500	2,500	...	...
Anisole	5070	2,080	3840	1,640
Pyridine	4215	10,500	4000	10,800

[a] Table reproduced from ref 99, p 2779. Copyright 1958 by the American Chemical Society. Reprinted by permission of the copyright owner. [b] The weak complexes have been shown to have about 10% electron transfer (150).

A. ADDITION REACTIONS

Addition to the double bond of tetracyanoethylene occurs with several reagents, *viz.*, hydrogen, hydrogen iodide, etc. (105), chlorine (37), some ketones (105), sulfurous acid (105), free radicals (105), hydrogen peroxide (79), diazomethane (5), allene tetramer (163), and conjugated dienes (105). A summary of the reactions is shown in Chart I.

1. *Reduction*

Tetracyanoethylene can be reduced to tetracyanoethane (V) by a variety of reagents: molecular hydrogen (palladium catalyst), hydrogen iodide, thiols, hydrogen sulfide, or mercaptoacetic acid. Reduction with the latter reagent, however, is preferred, since the work-up of this reaction mixture is facilitated by the water solubility of both the acid and its disulfide. Tetracyanoethane is a white sublimable solid. It is a strong dibasic acid ($pK_a = 3.6$). It dissolves in aqueous sodium bicarbonate from which it can be precipitated by acidification. Tetracyanoethane is easily oxidized to tetracyanoethylene by a variety of oxidizing agents: lead dioxide, cupric oxide, ferric chloride, etc. (105).

2. *Chlorination*

The chlorination of TCNE leads to the formation of 1,2-dichlorotetracyanoethylene (VI). This reaction is catalyzed by chloride ion and thus involves chloro carbanion as an intermediate (37).

3. *Reaction with Ketones*

TCNE adds at room temperature to ketones containing an α hydrogen, in the presence of catalysts such as boron trifluoride or molecular silver (50), to give tetracyanopropyl ketones (VII) (105). These ketone adducts are white crystalline compounds that possess properties similar to those of tetracyanoethane—they are strong acids (105).

4. *Reaction with Sulfurous Acid*

TCNE reacts readily with sulfurous acid to give 1,1,2,2-tetracyanosulfonic acid (VIII), a dibasic acid, of which a number of salts have been reported (105).

5. *Reaction with Free Radicals*

The α-cyanoisopropyl radical, generated by the thermal decomposition of α,α′-azodiisobutyronitrile, reacts with TCNE (in benzene) to form 2,3,3,4,4,5-hexacyano-2,5-dimethylhexane (IX) (105).

6. *The Epoxidation*

The epoxidation of TCNE takes place with 30% hydrogen peroxide, to tetracyanoethylene oxide (X), a crystalline solid, mp 177–178°. It is stable in air but decomposes in the presence of water (79).

7. *Reaction with Diazomethane*

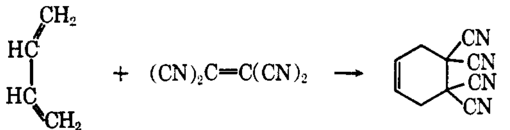
Diazomethane reacts with TCNE to give initially a pyrazoline (XI), an addition compound, which, however, can split off a molecule of nitrogen to give 1,1,2,2-tetracyanocyclopropane (XII) (5, 143).

8. *Reaction with Allene Tetramer*

1,3,5,7-Tetramethylenecyclooctane (allene tetramer) undergoes an unusual 1,7 addition of TCNE to give the tricyclic compound 3,3,4,4-tetracyano-8,11-dimethylenetricyclo[4.3.3.0]dodecane (XIII), formed by a transannular reaction (163).

9. *Reaction with Dienes*

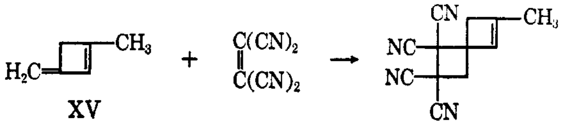
Tetracyanoethylene is a reactive dienophile (25, 105, 137) and undergoes a Diels–Alder type of addition reaction with conjugated dienes such as butadiene and anthracene, with unusual ease and at relatively low temperatures. Thus when butadiene is added to TCNE in tetrahydrofuran at 0°, the solution first takes on a bright yellow color of the π complex of the components within a few minutes, and the colorless adduct (tetracyanocyclohexene) (XIV) begins to separate almost instantaneously and nearly in quantitative yield (105).



XIV

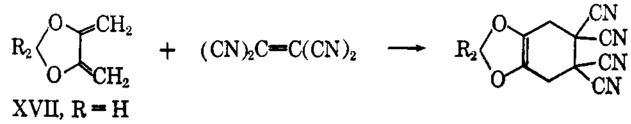
The Diels–Alder reaction of TCNE occurs even with sluggish dienes such as 2-vinylnaphthalene, spontaneously and rapidly, without added catalyst or application of external heat (105).

TCNE forms cyclobutane derivatives (16, 17, 92, 162) by 1,2-cycloaddition with a 1,3-diene system, to which Diels–Alder addition is difficult or impossible. The formation of 2-methyl-5,5,6,6-tetracyanospiro[3.3]hept-1-ene (XVI) by the interaction of TCNE with 1-methyl-3-methylenecyclobutene (XV) is illustrative (162). Besides, TCNE readily forms 1,1,2,2-tetracyanocyclobutanes with a variety of electron-rich alkenes such as methyl vinyl ether and *p*-methoxystyrene (164).



XV XVI

With some dienes, (110), *e.g.*, 4,5-dimethylenedioxolanes (XVII) and 4,5-dimethylene-2,2-diphenyldioxolane (XVIII), however, Diels–Alder reaction is favored over 1,2-cycloaddition, when both are possible (164).

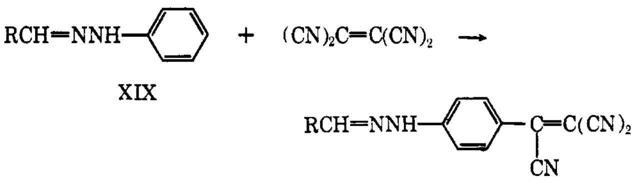


XVII, R = H
XVIII, R = C_6H_5

B. REPLACEMENT REACTIONS

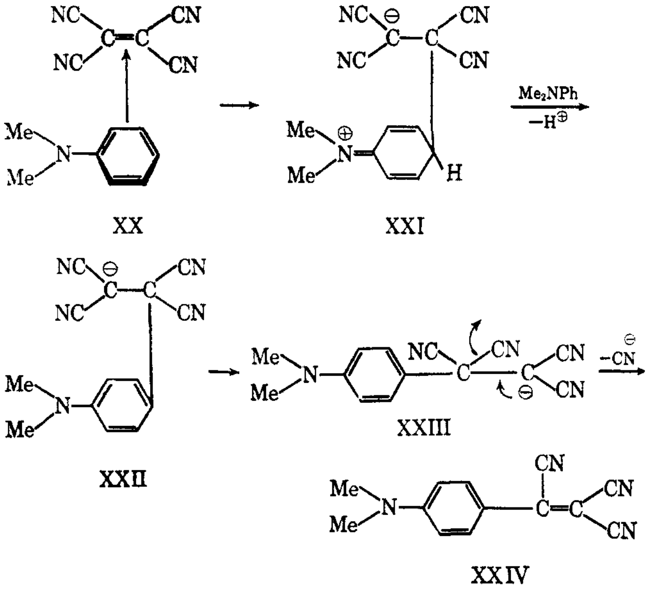
1. *Reaction with Benzenoid and Nonbenzenoid Aromatic Compounds, Heterocycles, and Aromatic Hydrazones*

TCNE is readily attacked by nucleophilic reagents (127) (selected aromatic and heterocyclic nuclei (138)) with the elimination of hydrogen cyanide and introduction of a tricyanovinyl group at one of the positions of high electron density (93, 114, 134). Thus alkylation with TCNE of phenanthrene (138), azulene (51), guaizulene (51, 52), and 2,6-dimethylphenol (55, 138) are illustrative. Other tricyanoethylenes, derived from heterocycles, are obtainable by interaction with TCNE in solvents like acetone, tetrahydrofuran, and N,N-dimethylformamide at room temperature. Examples are 5-(tricyanovinyl)-2-methylfuran (134), 2-(tricyanovinyl)pyrrole (53, 138), 2-(tricyanovinyl)-N-methylpyrrole (53, 138), 3-(tricyanovinyl)indole (114), and 2-(tricyanovinyl)pyrrocoline (134). Furan (134), unlike methylfuran, fails to react with TCNE. It is apparent that the methyl group possesses a sufficient electron-releasing capacity so as to cause a qualitative difference between these two compounds. With aromatic hydrazones (XIX) (134), the tricyanovinylation generally occurs at the *para* position of the molecule. Thus



2. *Reaction with Amines*

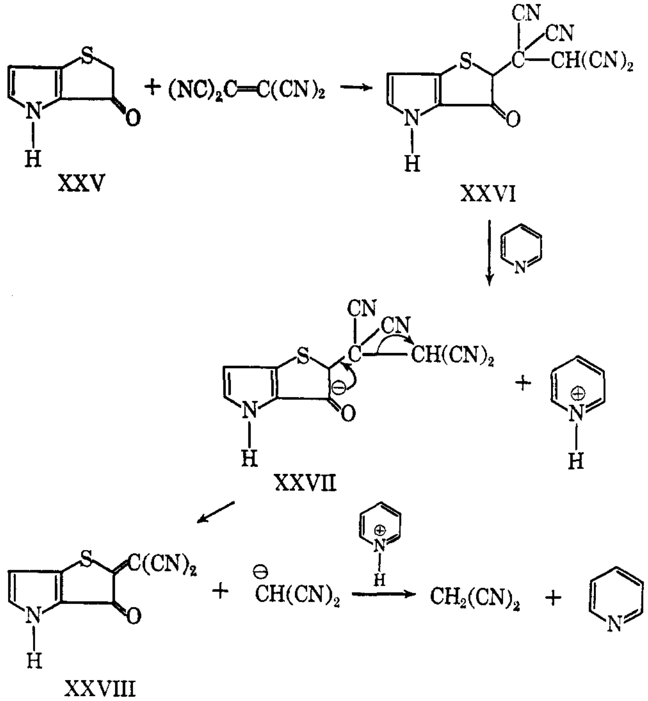
TCNE reacts readily with primary or secondary aliphatic amines and with most primary and secondary aromatic amines in boiling tetrahydrofuran, to give N-tricyanovinylamine (93). No more than a slight excess of amine is used to avoid the formation of 1,1-diamino-2,2-dicyanoethylenes (54). TCNE does not react with tertiary aliphatic amines, but it readily reacts with both tertiary and secondary aromatic amines, attacking the ring to give 4-tricyanovinylarylamine (93, 128). The mechanism of tricyanovinylation (127, 128) of N,N-dimethylaniline is a three-step reaction (127): (a) rapid formation of a 1:1 π complex, (b) formation of a σ complex, and (c) formation of N,N-dimethyl-4-tricyanovinylaniline and hydrogen cyanide. A kinetic isotope effect in the tricyanovinylation of dimethylaniline lends support to this mechanism (46). Thus in the formulation XX, the arrow serves only as a symbol for the interaction of the whole molecular orbital of the planar dimethylaniline (including the aromatic sextet and the lone pair of the nitrogen atom) with the molecular orbital of planar tetracyanoethylene. The abstraction of a proton from the σ complex XXI (catalyzed by amine) results in the formation of a new carbanion XXII. In this carbanion the electrostatic attraction between the two opposite charges in XXI is destroyed and the electrostatic repulsion develops between the aminonitrogen lone pair and the negative charge on the tetracyanoethylene moiety. This repulsion assists the rotation during the formation of XXIII, and the elimination of cyanide ion gives N,N-dimethyl-4-tricyanovinylaniline (XXIV). A similar mechanism has been advanced for the tricyanovinylation of N-methylaniline (129) and indole (47). Spectroscopic evidence as to the intermediacy of a σ complex in the reaction between N-methylaniline and TCNE has been reported (60).



On account of the bulkiness of tricyanovinyl group the steric factors play a dominant role in determining the course of reaction of TCNE with an arylamine (93). Thus *ortho* tricyanovinylation does not take place readily. Arylamines with one N substituent usually fail to undergo N-tricyanovinylation (129), unless the *para* position is already filled. Substituents situated *ortho* to amine group promote *para* tricyanovinylation in the ring at the expense of N-tricyanovinylation. These conclusions are based on the following observations. Aniline and N-methyl-*p*-toluidine undergo N-tricyanovinylation. With N-methylaniline, however, the tricyanovinylation occurs in the ring (129). With 2,6-dimethylaniline two products corresponding to *para* tricyanovinylation and N-tricyanovinylation are formed, the former predominating. However, with N,N-dimethyl-*p*-toluidine no tricyanovinylation was apparent.

3. Reaction with Active Methylene Compounds

An interesting example of retrograde Michael reaction, the addition of active methylene compounds to tetracyanoethylene, is illustrated by 2H,3H-thieno-[3,2-*b*]pyrrol-3-one (XXV). Instead of the expected tricyanovinyl derivative, 2-dicyanomethylene-2H,3H-thieno[3,2-*b*]pyrrol-3-one (XXVIII) was actually obtained. The following mechanism has been proposed for this reaction (40). After the addition across the double bond of tetracyanoethylene instead of abstraction of the terminal hydrogen by the base, the ring hydrogen is abstracted giving rise to the anion XXVII. The loss of malononitrile gives the product, XXVIII.



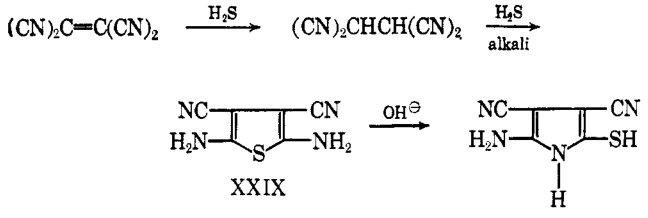
In a likewise manner, the formation of 2-dicyanomethylene-2H,3H-benzo[*b*]thiophen-3-one from 2H,3H-benzo[*b*]thiophen-3-one has been explained (40).

C. CYCLIZATION REACTIONS

Tetracyanoethylene has proved to be a useful starting material for the syntheses of five- or six-membered heterocycles, with one or two heteroatoms: thiophenes and pyrroles (108); isoxazoles, pyrazoles, pyridines, and pyrimidines (109).

1. *Reaction with Hydrogen Sulfide*

The base-catalyzed interaction of TCNE with hydrogen sulfide gives a cyclized product, 2,5-diamino-3,4-dicyanothiophene (XXIX), which can be rearranged to a mercaptopyrrole (XXX), under the influence of alkali (108).

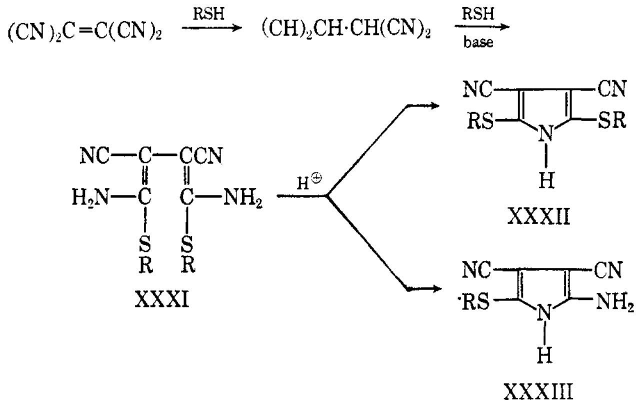


XXIX

XXX

2. *Reaction with Mercaptans*

Mercaptans add to TCNE to give 1,4-diamino-1,4-bis(alkylthio)-2,3-dicyano-1,3-butadiene (XXXI),



XXXI

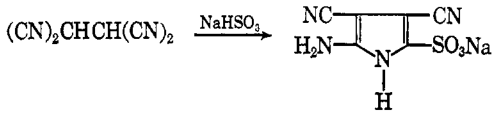
XXXII

XXXIII

which can be converted to pyrroles XXXII and XXXIII by the loss of mercaptan or ammonia (108).

3. *Reaction with Sodium Bisulfite*

Tetracyanoethylene reacts with sodium bisulfite to form 1,1,2,2-tetracyanoethanesulfonic acid (sodium salt) (105). However, tetracyanoethane on treatment with a boiling aqueous solution of sodium bisulfite affords 5-amino-3,4-dicyanopyrrole-2-sulfonic acid (sodium salt) (XXXIV) in moderate yields (108).



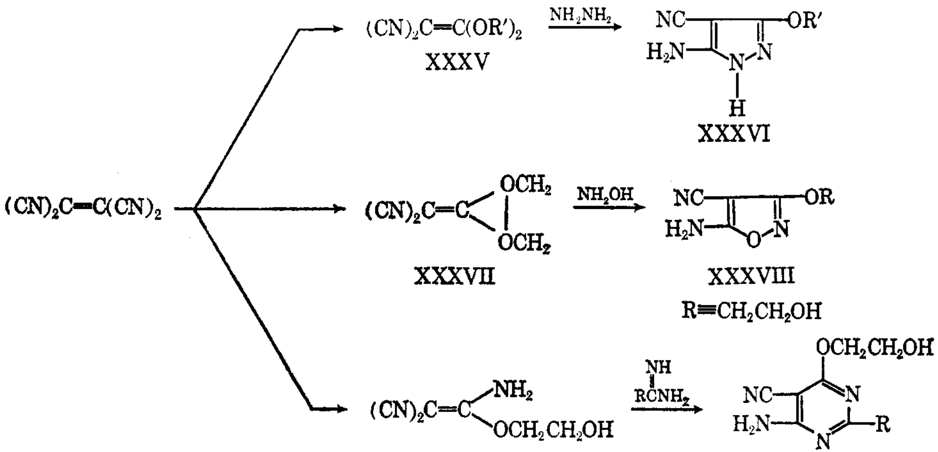
XXXIV

4. *Reaction with Hydrazine, Hydroxylamine, and Amidine*

Dicyanoketene acetals XXXV and XXXVII (106), secured by the urea-catalyzed reaction of tetracyanoethylene with an alcohol, and closely related compounds (XXXIX) react with nitrogen bases (109), hydrazine, hydroxylamine, and amidine, to give 5-amino-4-cyano-3-substituted pyrazole (XXXVI), 5-amino-4-cyano-3-substituted isoxazole (XXXVIII), and 4-amino-5-cyano-2,6-disubstituted pyrimidine (XL), respectively (109). 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 (109).

5. *Reaction with Sodium Malononitrile*

Dicyanoketene acetal on reaction with 1 equiv of sodium malononitrile yields the 2-alkoxy-1,1,3,3-tetracyanopropene salt (XLI) which on treatment with hydrogen chloride undergoes cyclization to 2-amino-3,5-dicyano-4-alkoxy-6-chloropyridine (XLII) (81). The reactive chlorine atom of these pyridines can be readily replaced by alkoxy, amino, arylsulfonyl, and dicyanomethyl groups.



XXXV

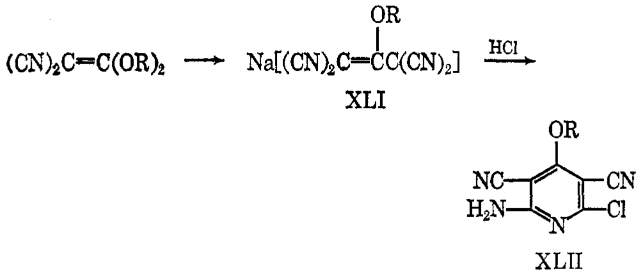
XXXVI

XXXVII

XXXVIII
R=CH₂CH₂OH

XXXIX

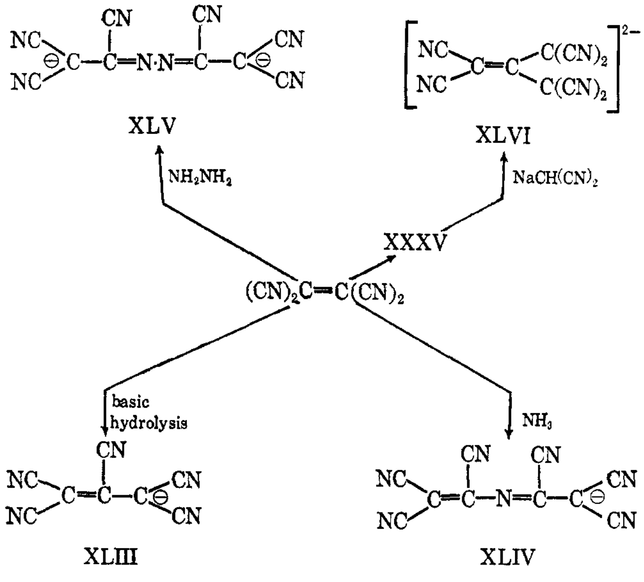
XL



D. MISCELLANEOUS REACTIONS

1. *Formation of Cyanocarbon Acids*

Cyanocarbon acids are preparable from TCNE and possess acidity comparable to that of mineral acids (107). The high acidity is ascribed to the high resonance stability of their corresponding anions (107). Thus 1,1,2,3,3-pentacyanopropene (XLIII) (102) results by the basic hydrolysis of TCNE. While 1,1,2,4,5,5-hexacyano-3-azapentadiene (XLIV) and 1,1,2,5,6,6-hexacyano-3,4-diazahexadiene (XLV) can be prepared by the interaction of TCNE with ammonia and hydrazine, respectively, the reaction of dicyanoketene acetal with 2 equiv of malononitrile gives rise to 2-dicyanomethylene-1,1,3,3-tetracyanopropenediide (XLVI). As many as 27 resonance structures can be written for the dianion (107).



2. *Photoaddition Reaction*

Upon irradiation with a G.E. sunlamp for a prolonged period, TCNE undergoes photoaddition reaction with tetrahydrofuran to give a 2:1 adduct (38).

VI. TETRACYANOETHYLENE ANION RADICAL

The high electron affinity of TCNE makes it susceptible to one-electron reduction to yield tetracyanoethylene anion radical, TCNE·⁻ (123). It is an unstable species and decays with a half-life of about 0.5 hr (115). It shows an absorption at 250–400 mμ (123, 130, 131). The fluorescence spectra of the anion has also been studied (126).

The various methods available for the preparation of TCNE·⁻ are outlined briefly. (a) TCNE is reduced to the anion radical by merely dissolving it in N,N-dimethylformamide (130). The resulting solution is pale yellow. The same anion can also be generated in about 10% yield when TCNE is dissolved in pyridine or in 2,4- or 2,6-lutidine *in vacuo* (10^{-2} mm) (120). (b) The anion radical is also formed by irradiation, either with mercury arc lamp of the solution of TCNE in tetrahydrofuran (157) or γ-ray irradiation at 77°K of the solution of TCNE in methyltetrahydrofuran (135), or by flash photolysis of degassed TCNE (soln) in acetonitrile (148). (c) TCNE·⁻ can also be generated by dissociation of the charge-transfer complex of TCNE with suitable donors, *viz.*, tetramethyl-*p*-phenylenediamine (80), by employing a solvent of high dielectric constant (41, 61, 64). (d) It is reported (124) to be formed when TCNE is adsorbed, under high vacuum, on certain metallic oxides, titanium dioxide, zinc oxide, or magnesium oxide, or by absorption of benzene solution by alumina (113). (e) TCNE readily undergoes a one-electron reduction with metals (sodium, potassium, copper, magnesium, aluminum), certain anions (cyanide and iodide ions), and tertiary amines to give the TCNE·⁻ derivative (123, 157–159). The reaction of TCNE with excess potassium iodide provides a convenient laboratory synthesis of TCNE·⁻ (158)

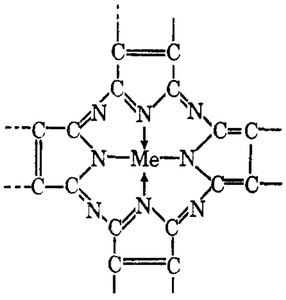
$$3KI + 2TCNE \longrightarrow 2K^+TCNE^- + KI_3$$

Polarographic reduction of TCNE in acetonitrile also gives rise to the anion radical (130).

VII. POLYTETRACYANOETHYLENE AND POLYMER–METAL COMPLEXES OF TCNE

The preparation of polytetracyanoethylene and a number of polymer–metal complexes have been reported (8–13, 18–20, 22, 77, 144). The polymerization of TCNE can be effected by various reagents (alcohols, phenols, amines, and amides) at 200° under appropriate conditions (11, 14). The polymeric chelate complexes of TCNE have, however, been prepared in the form of thin films (10^{-4} to 10^{-5} cm) on metallic surfaces by heating the metal with TCNE in evacuated ampoules at elevated temperatures for prolonged periods (12). The TCNE–metal complexes are formulated to have the phthalocyanine type of structure (XLVII) (8).

These complexes are thermostable up to 400–450°, partially crystalline, and semiconductive, and possess enhanced magnetic susceptibility (12). The polymer, as a thin film on metal, has an excellent durability and is unaffected by organic solvents, acids, or alkalis. The electric properties of these polymers have been reported (10, 11, 19–22).



XLVII

VIII. METHOD OF ESTIMATION OF TCNE

Based on the fact that N,N-dimethylaniline undergoes tricyanovinylation with TCNE to yield a colored derivative, a spectrophotometric method has been developed for the semiquantitative determination of TCNE (93).

IX. USES OF TCNE AND ITS DERIVATIVES

A. GENERAL APPLICATIONS

Tetracyanoethylene acts as a polymerization inhibitor for vinyl aromatic hydrocarbons, especially at room temperature (116). On the other hand, it effectively catalyzes, in solution, the addition polymerization of a monomer, N-vinylated carbazole (142), at or below room temperature. TCNE is used to increase the photosensitivity of some organic dyestuffs, *viz.*, phthalocyanines (97). It can also be effectively employed in the aromatization of certain nonconjugated cycloalkadienes, where it functions as an efficient hydrogen acceptor (85). TCNE has found some use as a component in fuel mixtures (86), which burn to give electron-rich gases (48) and also in propellant fuel compositions (45).

Some of the derivatives of TCNE are brilliant dyes. Thus *p*-tricyanovinylamine dyes possess fastness to light and washing and are therefore suited particularly for dyeing of fabrics (cellulose acetate, silk, and nylon) (93). Other fibers, like polyethylene terephthalate and polyacrylonitrile can also be dyed. The *p*-tricyanovinylhydrazone dyes, however, show improvement over the tricyanovinylarylamine dyes in resistance to degradation by alkali (36, 134). TCNE forms an ingredient of a dye composition (TCNE, pyrrole, and sulfur) suitable for black dyeing of polyamide and polyolefin textiles. The black dye obtained has good fastness to light and rubbing (132). Some colored complexes of TCNE are used as coloring agents for inks used in thermographic copying, as dyes for paints and plastics, and as dyes in impregnating solutions in impact printing (27). Some salts of 1,1,2,4,5,5-hexacyano-3-azapentadiene (XLIV) are useful for inks or dyes (101), and the red-brown copper salt of 2-substituted ethoxy-1,1,3,3-tetracyanopropene (XLIII) has been used as a pigment (104).

2,2-Dicyano-1-[2-(dimethylsulfonium)ethoxy]ethenolates, produced by the interaction of XXXVII and an organic sulfide, show promise in their use in scintillation counters for the detection of ionization radiations (44). The potassium, strontium, barium, and zinc salts of 2-dicyanomethylene-1,1,3,3-tetracyanopropene (XLVI) are luminescent in the ultraviolet region and cathode rays, and this property offers possibilities for their application as phosphors in television tubes (103). 2,2-Dicyano-1-[(trisubstituted ammonium)alkoxy]ethenenolate, derived from XXXVII and a tertiary amine, is useful as an antistatic compound (100). Some colored 1:1 complexes of TCNE with aromatic compounds (*viz.*, hexamethylbenzene) are useful in identifying paramagnetic materials (27).

Some other derivatives of TCNE, aryl-substituted polycyanocyclobutanes (168), hexacyanoethane (95), and TCNE polymers (28), are useful as ready sources of hydrogen cyanide for fumigation purposes. Hexacyanoethane may be useful as a high-temperature fuel for melting metals and as the reducing component in a thrust-producing fuel (95). Polymers with high cyano content are resistant to mildew, mold, or rot (58), and some of these find application as coating compositions and are useful for motor oil and transformer wire insulation (28).

Tetracyanoethylenide salts are useful as scavengers to remove oxygen from gases (161). Some cyanocarbons have proved useful as histochemical localization reagents (78). Some of the compounds of TCNE with metal salts (*viz.*, CuCl) find application as semiconductor components in thermoelectric devices, current amplification devices, thermistors, solar cells, photoelectric cells, panel lighting circuits, cathode-ray tube coatings, resistors, photocapacitors, etc. (65). The chelate polymers of TCNE have shown promise as catalysts (67, 133). Thus, the complex of copper with polytetracyanoethylene effectively catalyzes the oxidation of aryl aromatic hydrocarbons and cyclohexane to yield hydroperoxides (133).

B. ANALYTICAL APPLICATIONS

Tetracyanoethylene has a great analytical potential. Thus the π complexes of TCNE are useful for determining many pure organic molecules, aromatic hydrocarbons (140), phenols (147), and aryl ethers (141), analogous to the broad utility of metal–EDTA chelates in inorganic analysis. TCNE like EDTA is a fairly general complexing agent and reacts instantly under mild room-temperature conditions. It can be made somewhat selective by the use of certain reagents, *viz.*, acetic acid, perchloric acid in acetic acid, acetic anhydride in chloroform, etc. (141).

The property of TCNE to form intensely colored π complexes at room temperature with many aromatic compounds makes it useful as a color-forming reagent in the paper chromatography of these compounds (62, 63, 121, 152). It has also been used in the estimation of aliphatic, alicyclic, and aromatic 1,3-dienes (117). The diene is allowed to react with an excess of the reagent in dichloromethane and the excess titrated with cyclopentadiene, in ethanol. TCNE has been used as titrant in complexometric determination of aromatic hydrocarbons (140) and the end point is found photometrically. It is necessary, however, that the titrant be as concentrated as possible.

An indirect colorimetric method for the estimation of anthracene, involving TCNE, has been reported (139). It is based on the destruction of red color of the naphthalene–TCNE complex, after anthracene and TCNE have reacted *via* the Diels–Alder reaction.

$$\underset{\text{red complex}}{C_{10}H_8(\text{TCNE})} + C_{14}H_{10} \longrightarrow C_{10}H_8 + \underset{\text{colorless adduct}}{C_{14}H_{10}\text{–TCNE}}$$

TCNE has also been used for the rapid quantitative determination of total nitrogen in petroleum fractions (122). This method takes advantage of the fact that hydrocarbon–TCNE colors, which persist at room temperature, are unstable on heating. In contrast, however, many organic compounds, containing heteroatoms, especially nitrogen-containing compounds, leave a color on the filter paper on heating. Furthermore, the reaction between TCNE and phenols resulting in the formation of colored *p*-tricyanovinylphenols has been used for a qualitative test of phenols (147); exceptions are *p*-nitrophenols, polyhydric phenols, and their monoesters. The mode of reaction is reported to depend upon the structure of the phenol, thereby providing a means for investigating the latter (147).

Spectrophotometric measurements in the range 400–700 mμ for the determination of concentration of pheophytin in the extract of plant materials is invalidated in the presence of carotenoids. Addition of TCNE, however, annuls the interference by causing a shift of the carotenoid absorption toward shorter wavelengths (166). Some mono-, di-, tri- and tetrasubstituted ethylenes have been distinguished by the differences in the positions of the maxima of the ultraviolet charge-transfer band of their iodine and TCNE complexes. These maxima shift toward the visible (with increasing donor strength) as the double bond is increasingly substituted (6, 84).

Tetracyanoethylene has been shown to be a sensitive indicator of π-electron availability (4). In this way acyldurene has been demonstrated to be deficient in π electrons compared to durene, and this has been explained to be due entirely to the inductive effect of the carbonyl group (165).

ACKNOWLEDGMENTS.—The author wishes to thank Professor M. V. George for the helpful comments on the manuscript. He extends his thanks to Professor C. N. R. Rao for his kind encouragement during the preparation of this article.

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