Tetracyanoethylene Oxide. II. Addition to Olefins, Acetylenes, and Aromatics¹

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Tetracyanoethylene oxide adds to olefins by cleavage of the C-C bond of the epoxide ring to give tetracyanotetrahydrofurans. Tetracyanodihydrofurans are formed by an analogous reaction with acetylenes. Even more remarkable is the ability of the epoxide to disrupt an aromatic system and add to benzene and other aromatics.

Epoxides normally undergo facile ring-opening reactions promoted by acid catalysts. However, this type of reaction is not exhibited by tetracyanoethylene oxide (TCNEO) as a result of the diminution of electron density on the ring by the four electronegative cyano groups.² Conversely, attack by nucleophilic reagents is extremely rapid, but in these cases cleavage of the molecule usually occurs. Pronounced differences between the chemistry of this new oxirane and its hydrocarbon counterparts are readily shown by a study of the reactions of TCNEO with olefins, acetylenes, and aromatics.³

Reaction with Olefins

Ethylene and TCNEO condense readily at 130–150° to give a 1:1 adduct in better than 80% yield. The product exhibits a single proton resonance at τ 6.68,⁴ and the infrared spectrum shows an absorption at 4.43 μ attributed to unconjugated nitrile with no evidence of carbon-carbon unsaturation. Only one structural assignment, 2,2,5,5-tetracyanotetrahydrofuran (II), is compatible with this evidence. Chemical confirmation was obtained by acid hydrolysis with concomitant



decarboxylation to the known tetrahydrofuran-cis-2,5dicarboxylic acid.⁵ The conversion of II to the dicarboxylic acid is undoubtedly not a stereospecific

(1) This work was presented in part at the XIXth International Congress of Pure and Applied Chemistry, London, July 10-17, 1963, Abstracts A, p. 247.

(2) W. J. Linn, O. W. Webster, and R. E. Benson, J. Am. Chem. Soc., 87, 3651 (1965).

(3) A preliminary account of this work has been reported: W. J. Linn, O. W. Webster, and R. E. Benson, *ibid.*, **85**, 2032 (1963).

(4) Proton resonance spectra were obtained with a Varian A60 instrument. Unless otherwise noted, the spectra were obtained in deuterioacetone with tetramethylsilane as the internal reference.

(5) D. Lean, J. Chem. Soc., 77, 103 (1900); H. R. LeSueur and P. Haas, *ibid.*, 97, 173 (1910); W. N. Haworth, W. G. M. Jones, and L. F. Wiggins, *ibid.*, 1 (1945); A. C. Cope and W. N. Baxter, J. Am. Chem. Soc., 73, 395 (1955).

process, but the *cis* acid crystallizes more readily and no attempt was made to isolate and purify the *trans* acid that was probably present.

More than thirty substituted tetracyanotetrahydrofurans have been prepared by heating TCNEO with the appropriate olefin, and many of these are listed in Table I. Temperatures above 100° are desirable for reasonable rates and, therefore, a pressure vessel is advantageous for gaseous and low-boiling olefins. Electron-attracting substituents on the olefinic bond decrease the reaction rate, whereas electron-donating groups accelerate the reaction.⁶ In general, lower reaction temperatures and shorter reaction times should be used with the more electron-rich olefins in order to prevent the formation of undesirable by-products that interfere with the isolation of the desired adduct.

Halogenated solvents are useful for many TCNEO reactions, but aromatic hydrocarbons such as toluene are better solvents for reactive olefins. Although TCNEO will add to toluene (see below) the rate of addition to a simple olefin is sufficiently large to preclude any appreciable formation of the toluene adduct.

Substituents that are not basic or that do not contain an active proton source can be tolerated, as seen by an inspection of Table I.

The addition of TCNEO to allene is straightforward and leads to 3-methylene-2,2,5,5-tetracyanotetrahydrofuran (III). Evidence that the adduct is III is found in





the infrared and n.m.r. spectral data. Although the infrared spectrum of III shows absorption at 3.28 and 5.98 μ for ==CH and C==C, respectively, there is no absorption in the vicinity of 11.2-11.3 μ , a region normally associated with terminal methylene groups. The exocyclic methylene group also resists reduction by hydrogen in the presence of palladium on charcoal.

⁽⁶⁾ Following our initial reports of this reaction, P. Brown and R. C. Cookson, *Proc. Chem. Soc.*, 185 (1964), investigated some additional examples. They observed some instances in which derivatives of TCNE were formed. During our early studies of the TCNEO-olefan reaction we naturally attempted additions to electron-rich olefins and noted that TCNE or derivatives thereof are obtained. For example, TCNEO and 2,3-dimethyl-2-butene give TCNE and 2,3-dimethyl-2-butene epoxide. From 2,3-dihydropyran there is formed the same cyclobutane that one obtains with TCNE. We attributed these reactions to nucleophilic attack of the olefan on the electron-deficient epoxide oxygen.



 Table I.
 Adducts of TCNEO and Olefins

]	Method of				Recrys-						
			ara. Time		Vield	Mn and	7ation		- Caled	Analyses, 7		Found	
R ₁	\mathbf{R}_2	R₃	tionª	hr.	77	b.p. (mm.), °C.	solven	tC	H	N	C	H	N
н	н	CH₃	Α	10	55	78–79	b	58.05	3.25	30.09	58.05	3.32	30.19
н	Н	n-C₄H₃	В	10	65	104-111 (0.2)		63.13	5.30	24.54	63.67	5.44	25.55
н	н	$n-C_8H_{17}$	в	6.5	56.5	130 (0.35)		67.58	7.09	19.70	67.14	7.25	19.76
н	CH₃	CH₃	Α	10	11	130-131	с	59.99	4.03	27.99	59.47	4.07	27.96
CH₃	CH₃	Н	С	10	71	124-125	с	59.99	4.03	27.99	60.41	4.07	28.19
CH3	н	CH₃	С	10	82	108109	d	59.99	4.03	27.99	60.24	4.07	28.31
н	н	C_6H_5	D	6	50	147–148	с	67.73	3.25	22.57	67.79	3.55	22.36
C ₆ H ₅	C_6H_5	H	D	5.5	52	187-189	е	74.08	3.73	17.28	73.59	3.87	17.04
C₀H₅	H	C_6H_5	E	4.5	94	258-259	f	74.08	3.73	17.28	74.06	3.80	17.25
H	H	CH ₂ C ₆ H ₅	D	6.5	63	152-152.5	g	68.69	3.84	21.36	68.37	3.84	21.56
н	CH₃	C_6H_5	E	1	37	137-138	d	68.69	3.84	21.36	69.15	4.46	20.47
CH_3	H	C_6H_5	D	5	36	136.5-137	g	68.69	3.84	21.36	68.84	3.94	21.36
н	н	CH ₂ Br	В	17	71	141-142	c	40.75	1.90	21.14	40.28	2.17	21.37
н	н	CH ₂ OCOCH ₃	в	18	63	97.5-98	g	54.04	3.30	22.91	53.82	3.29	23.03
н	н	CH ₂ OC ₂ H ₅	В	23	64	109.5-110	c	57.38	4.38	24.34	57.31	4.50	24.30
н	Н	CI	Α	16	83	118-119	d	46.50	1.46	27.11^{i}	46.32	1.32	26.841
н	Н	F	Α	16	76	135-135.5	f	50.52	1.59	k	50.83	1.56	k
Cl	Н	Cl	Α	16	67	146.5-147	f	39.86	0.84	1	40.01	1.00	1
Cl	Cl	Н	G	16	89	152.5-153.5	č	39.86	0.84	m	40.06	1.11	m
н	н	OCOCH ₃	Α	16	66	88.5-89	С	52.17	2.63	24.34	52.66	2.90	24.42
C_6H_5	Н	$CO_2C_2H_5$	Е	3	85	117-118	h	63.76	3.78	17.50	63.86	3.97	17.70
H	CN	CH ₃	E	16	40	129-132	с	56.86	2.39	33.17	56.82	2.42	33.12
н	H	Si(CH ₃) ₃	В	41	72	105-105.5	g	54.07	4.95	22.94	54.41	4.92	22.89
H	H	CH ₂ CH ₂ CH=CH ₂	D	18	56	67-67.5	i	63.71	4.46	24.77	63.49	4.76	24.65

^a A, reactants heated to 130–150° in a sealed pressure vessel, 1,2-dichloroethane solvent; B, reflux in 1-bromo-2-chloroethane; C, reactants heated at 125° in a sealed pressure vessel, toluene solvent; D, reflux in toluene; E, reflux in 1,2-dibromoethane; F, reflux in xylene; G, heated in a sealed pressure vessel to 130° in excess *cis*-1,2-dichloroethylene. ^b Ether-benzene. ^c Benzene. ^d Benzene-hexane. ^e 1-Propanol. ^f 1,2-Dichloroethane. ^e 2-Propanol. ^b Carbon tetrachloride. ⁱ Ether. ^j Cl, calcd., 17.16; found, 17.16. ^k F calcd., 9.99; found, 10.17. ⁱ Cl calcd., 29.43; found, 29.66. ^m Cl calcd., 29.43; found, 29.66.

This result was not unexpected in view of the difficulties experienced with reduction of other tetracyanofuran derivatives discussed below.

The proton spectrum of III provides a good example of 1,3-coupling in an allylic system.⁷ The spectrum is a simple ABX₂ pattern amenable to first-order analysis. The two saturated protons are magnetically equivalent and appear as a four-line spectrum (central lines overlapping) at τ 6.15 in acetonitrile. The protons of the exocyclic methylene group, each of which is in a different, but fixed, environment, exhibit a 12-line spectrum centered at τ 3.87 and are coupled to each other (J = 3 c.p.s.) and to the ring proton (J = 2 c.p.s.).

Stereochemistry of the Reaction

TCNEO adds cleanly to 1,2-disubstituted olefins and examination of three separate *cis-trans* pairs shows the reaction to be stereospecific. The olefins examined were the *cis* and *trans* isomers of 2-butene, stilbene, and 1,2dichloroethylene.

From the reaction of TCNEO and *trans*-1,2-dichloroethylene, only one isomer is isolated. When the reaction was carried out in *cis*-1,2-dichloroethylene, however, the crude product isolated in 90% yield contained 7% of the *trans* adduct as indicated by the proton n.m.r. spectrum. The *trans* product probably arose from slight isomerization of the olefin, and is not considered significant since complete stereospecificity was noted with the other olefins studied.

Table II summarizes the chemical shifts determined for the ring protons of the adducts of TCNEO with *cis* and *trans* isomers compared to the corresponding

 Table II.
 Chemical Shifts (r-values) of
 Olefinic Protons in cis-trans Pairs and the

 Corresponding Protons in Adducts of TCNEO^a
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R	Contraction Contra	efin —— =CHR trans	R NC NC cis ^b	R CN CN trans ^b	
C ₆ H ₅	3.38°	2.85°	4.71	4.30	
Cl	3.47°	3.54°	3.65	3.88	
CH ₃	4.86ª	4.84 ^d	6.22 ^e	6.78 ^e	

^a Using tetramethylsilane unless otherwise noted. ^b Deuterioacetone solution. ^c Determined in this work in 1,2-dibromoethane. ^d Calculated from values given in J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 242. ^e Center of multiplet.

protons in the olefins. Shielding of the ring protons by the phenyl groups in *cis*-3,4-diphenyl-2,2,5,5-tetracyanotetrahydrofuran is greater than in the *trans*

⁽⁷⁾ See S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964), for leading references to 1,3-coupling in allylic systems.



 R1	\mathbb{R}_2	Method o prepa- ration ^a	of Time, hr.	Yield, %	M.p., °C.	Recrys- allization solvent		Calcd H	Analy	ysis, %— C	Found H	N
Н	CH₃	A	10.0	60	119.5-120.5	b	58.73	2.19	30.44	58,86	2.37	30.25
CH3	CH3	Α	10.0	43	134.0-135.0	b	60.58	3.05	28.27	60.73	3.12	27.86
н	C₅H₅	В	5.5	62	136.0-136.5	с	68.30	2.46	22.75	68.12	2.66	22.80
C_6H_5	C_6H_5	С	17.0	53	183.0-184.5	с	74.51	3.13	17.38	74.58	3.13	17.32
CO ₂ CH ₃	CO ₂ CH ₃	В	24.5	17	133.0-134.0	с	50.35	2.11	19.58	50.57	2.33	19.43
CH_3	C≡CCH ₃	D	17.0	68	96.0-97.0	d	64.84	2.72	25.21	64.62	2.98	25.31

^a A, heat in 1,2-dichloroethane in a sealed vessel at 130°; B, reflux in toluene; C, reflux in 1,2-dibromoethane; D, reflux in 1-bromo-2chloroethane. ^b Hexane-benzene mixture. ^c Benzene. ^d Cyclohexane.

isomer, an effect in opposition to that observed by Curtin, Gruen, and Shoulders⁸ for the isomers of 1,2-diphenylcyclopentane.

Reaction with Acetylenes

Acetylene and TCNEO also react at $130-150^{\circ}$ to give a 1:1 adduct in 70% yield. This product, identified as 2,2,5,5-tetracyanodihydrofuran (IV), has a single

$$HC \equiv CH + (NC)_2 C \xrightarrow{O} C(CN)_2 \rightarrow \frac{NC}{NC} \xrightarrow{O} CN_{CN}$$

proton resonance at τ 2.70. Proof of structure by catalytic reduction of IV to tetracyanotetrahydrofuran was not successful, the olefin being recovered unchanged from reactions conducted under mild conditions. Furthermore, the reduction of cyclohexene by hydrogen with palladium-on-charcoal catalyst was completely inhibited by IV. Chemical proof of structure was obtained by conversion of IV to the tetraester V with methanol and HCl. In contrast to the tetracyano compound, the ester was easily reduced under mild conditions to a saturated derivative VI, identical in all respects with the tetraester from methanol and HCl treatment of II.



Mono- and disubstituted acetylenes add TCNEO equally well to give substituted tetracyanodihydrofurans. Examples are listed in Table III.

Although the monoadduct VII is formed readily from 2,4-hexadiyne, efforts to form the bisadduct from the conjugated diyne were unsuccessful despite the use of

(8) D. Y. Curtin, H. Gruen, and B. A. Shoulders, Chem. Ind. (London), 1205 (1958).

an excess of the epoxide and forcing conditions. Insulation of the acetylenic bonds with methylene groups, as in 1,6-heptadiyne, made possible the synthesis of either the monoadduct VIII or the bisadduct IX.



Although the products listed in Table III were synthesized under the same conditions as the olefin adducts, a competitive experiment with equimolar amounts of ethylene and acetylene showed the olefin reacts faster by a factor of about 10.

Reaction with Aromatics

If benzene and TCNEO are heated in a sealed vessel at 130-150° for 17-18 hr. a 1:1 adduct is isolated in about 35% yield. In addition, there is formed a more insoluble product which has the composition of an adduct of 2 moles of TCNEO and 1 mole of benzene. The monoadduct in acetonitrile has an ultraviolet absorption maximum at 259 m μ with an extinction coefficient of 3800, in good agreement with the values reported for 1,3-cyclohexadiene.9 The destruction of the benzenoid system in the 1:1 adduct is also indicated by the infrared spectrum. Although there is absorption at 3.27 μ for hydrogen attached to unsaturated carbon, the spectrum is clear between 6 and 7 μ . The nitrile band is located at 4.45 μ and strong 9-10- μ region absorption is consistent with an ether linkage. At 5.73 μ there is a weak absorption that persists in repeatedly purified samples.

The proton resonance spectrum of the benzene adduct consists of a complex multiplet centered at -380 c.p.s. from the tetramethylsilane reference and a sharper resonance at -276 c.p.s. which is split into at least a triplet. The respective areas under these absorptions are in the ratio of 2:1.

(9) V. Henri and L. W. Pickett, J. Chem. Phys., 7, 439 (1939).

The analytical and spectral evidence cited above suggests that the addition of TCNEO to benzene is analogous to that of a simple olefin and that the product is 1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran (X). Although the spectral data are consistent with



the structure X, the chemical behavior casts some doubt on this assignment. In spite of numerous attempts under a variety of conditions, the double bonds of the adduct could not be reduced catalytically. This, however, was not unexpected since it had been shown earlier that the tetracyanofuran grouping is apparently a poison for noble metal catalysts. Somewhat more disturbing was the inability to aromatize the adduct or to bring about a Diels-Alder addition with maleic anhydride or tetracyanoethylene. Dehydrogenation was attempted with palladium on charcoal and also high potential quinones such as o-chloranil. In all cases the starting material was recovered.

Doubt concerning the structure of X was finally removed by a series of chemical transformations.

Methanol and hydrogen chloride convert the benzene adduct to a tetraester XI in low yield. Catalytic reduction of XI proceeds normally as does the Diels– Alder addition of tetracyanoethylene. Furthermore, the reduced tetraester XII is identical in all respects with the tetraester prepared from the adduct XIII of TCNEO and cyclohexene.



This structure proof assumes that TCNEO adds to cyclohexene in the same fashion as it does to ethylene, an assumption believed to be valid. Although the failure to reduce X can be explained by catalyst poisoning, the inability to add dienophiles must be due to a more subtle effect. Steric inhibition of the reaction seems unlikely since this factor should be at least as great in the corresponding tetraester. It seems more likely that the inactivity of the conjugated diene system of X is due to a field effect exerted by the four electronegative cyano groups.

Aromatization of 1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran (X) could also conceivably be accomplished by the elimination of HCN to form the



corresponding isobenzofuran. Preliminary attempts to effect this reaction with tertiary amines led only to decomposition. A more promising route would appear to be the formation of an anion at the allylic position with a reagent such as an alkali metal amide. Proton removal at this position should also be promoted by the electron-withdrawing character of the adjacent cyano groups. In fact, anion formation apparently occurs with sodamide in liquid ammonia. However, instead of elimination of cyanide ion, electron redistribution leads to elimination of carbonyl cyanide and formation of the phenylmalononitrile anion. The



carbonyl cyanide does not survive the reaction conditions, but, after acidification, phenylmalononitrile was isolated in 55% yield.

As mentioned above, the synthesis of the benzene adduct is always accompanied by a small amount of a product formed from 2 moles of TCNEO and 1 mole of benzene. This product can also be synthesized in good yield from the monoadduct X and TCNEO. The indefinite decomposition point (over 260°) and tendency of the bisadduct XIV to solvate make purification difficult. A solution of XIV in acetonitrile exhibits no ultraviolet absorption between 203 and 400 m μ .

The proton n.m.r. spectrum of the bisadduct in deuterioacetone is simple and consists of a single sharp peak at τ 3.35 and a typical AB quartet with gravity centers at τ 5.19 and 4.71 and $J_{AB} = 8$ c.p.s.

Two structures, XIVa and XIVb, are logical for the bisadduct and either is compatible with the spectral evidence.¹⁰ Molecular models show the adduct XIVa, in which the second mole of TCNEO has added in a 1,2-manner, to be somewhat more strained than XIVb. This latter isomer would result by a 1,4-addition to the conjugated diene system of X. The available evidence does not distinguish between XIVa and XIVb.



(10) Brown and Cookson⁶ describe the bisadduct and assign structure XIVa but offer no proof.

Only a single isomer is formed by the addition of TCNEO to p-xylene. The ultraviolet and infrared spectra are very similar to those of the benzene adduct and are again compatible with a 1,3-cyclohexadiene. Assignment of the structure as 4,7-dimethyl-1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran (XV) is confirmed by the proton resonance spectrum. Three



single sharp peaks are found at τ 7.92, 5.42, and 3.83 with area ratios of 3:1:1, respectively. In this case the spectrum is not complicated by allylic coupling as is that of the benzene adduct. Apparently TCNEO does not add readily to a substituted aromatic position. On this basis, in the absence of powerful directive influences, monosubstituted aromatics should give rise to two isomers. Isomers are evidently formed from toluene and TCNEO, although they have not been separated into the pure components.

Naphthalene undergoes a smooth reaction with TCNEO in 1,2-dibromoethane to give a single monoadduct XVI in better than 70% yield. The addition is believed to occur in the 1,2-position, although an unequivocal determination of structure has not been made. Support for the structure XVI is gained by a

comparison of the ultraviolet spectrum with that reported for 1,2-dihydronaphthalene.¹¹ Polyaddition products of naphthalene were not obtained even when an excess of TCNEO was used.

If addition occurs only in a 1,2-position and not on a carbon atom already substituted, it should be possible to obtain three separate adducts from a monosubstituted naphthalene derivative. Experience has shown that adduct mixtures are indeed obtained in such cases.

Similarly only a single product would be expected from a 1,4-disubstituted naphthalene, and this was ob-

(11) R. A. Morton and J. A. de Gouveia, J. Chem. Soc., 916 (1934).

served with 1,4-dibromonaphthalene. The adduct presumably has structure XVII, although it is more difficult to draw conclusions from the ultraviolet spectrum of this product.

Aromatic heterocycles also add TCNEO to give the expected products. The adduct of furan and TCNEO (XVIII) was obtained in 5% yield along with much decomposition. A considerable improvement could probably be effected by operating in a hydrocarbon solvent at a lower temperature.

Considerably better yields of products were obtained from thiophene and 2-chlorothiophene. Structure XX was assigned to the 2-chlorothiophene adduct on the

basis of the proton resonance spectrum. The two saturated protons form an AB quartet with the centers of gravity of the doublets at τ 4.13 and 4.57 with J_{AB} = 9 c.p.s. One of these doublets is further split into a quartet by coupling with the unsaturated proton which is observed as a doublet at τ 3.95. The coupling between these two protons is 2.5 c.p.s.

Experimental

Addition of TCNEO to Olefins and Acetylenes. The addition of TCNEO to olefins and acetylenes is conveniently carried out by mixing the two reactants, usually in molar proportions, in a solvent and heating for an appropriate length of time. If the solvent or reactant is low boiling, a pressure vessel may be required. Only a few representative reactions are detailed below. The conditions used for various unsaturated compounds may be found in Tables I and III.

2,2,5,5-Tetracyanotetrahydrofuran (II). A mixture of 75 g. (0.52 mole) of TCNEO and 450 ml. of 1,2dichloroethane in a 1-l. stainless-steel-lined pressure vessel was pressured to 1000 p.s.i. with ethylene and heated to 130° with repressuring as needed. After 4-5 hr. the pressure drop was complete. The reaction vessel was heated for an additional 2.5 hr. before cooling. The recovered pale tan solution was concentrated to leave a tan crystalline solid which was recrystallized from benzene to give 77.4 g. (87%) of nearly colorless needles of 2,2,5,5-tetracyanotetrahydrofuran, m.p. 107-108°.

Anal. Calcd. for $C_8H_4N_4O$: C, 55.84; H, 2.34; N, 32.56; mol. wt., 172. Found: C, 56.05; H, 2.50; N, 32.52; mol. wt., 183, 186 (ebullioscopic in ClCH₂CH₂Cl).

Acid Hydrolysis of 2,2,5,5-Tetracyanotetrahydrofuran. A suspension of 2.0 g. of II in 15 ml. of concentrated hydrochloric acid was gently shaken. An exothermic reaction occurred, and all of the solid went into solution, which was refluxed for 16 hr. The solution was concentrated, and the residue was suspended in methanol and filtered. The filtrate was passed through a column of Amberlite IR-120, and the eluate was concentrated, leaving a yellow oil which was allowed to stand in a vacuum desiccator over phosphorus pentoxide. After standing for approximately 3 weeks, the oil had partially crystallized and was placed on a porous plate. After several days, most of the oil was absorbed leaving 0.38 g. (20%) of colorless crystals, m.p. 125–126.5°. An authentic sample of *cis*-tetra-hydrofuran-2,5-dicarboxylic acid^{4,12} melts at 125–127°. There was no depression of the melting point when the two samples were mixed. In addition, the infrared spectrum was identical with that of the authentic sample.

3-Methylene-2,2,5,5-tetracyanotetrahydrofuran (III). Into a 500-ml. stainless-steel-lined pressure vessel containing 15.0 g. (0.104 mole) of TCNEO and 150 ml. of 1,2-dichloroethane, there was condensed 16 g. (0.4 mole) of allene. The pressure vessel was sealed and heated at 130° for 10 hr. with shaking. The reaction mixture was filtered to remove 0.7 g. of insoluble brown solid, which was discarded. Concentration of the filtrate left a tan solid residue that was recrystallized from benzene using charcoal for clarification to give 10.4 g. of light yellow crystals, m.p. 114-116°. Evaporation of the mother liquors gave an additional 4.4 g. of less pure material, m.p. 105-114°. The total yield of crude crystalline product was 77 %. Further recrystallization from benzene followed by sublimation raised the melting point of III to 116.5-117.5°.

Anal. Calcd. for $C_9H_4N_4O$: C, 58.68; H, 2.19; N, 30.42; mol. wt., 184. Found: C, 58.22; H, 2.42; N, 30.17; mol. wt., 185 (ebullioscopic in ClCH₂-CH₂Cl).

The infrared spectrum determined in KBr showed absorption (μ) at 3.28 (unsaturated CH), 3.37 (saturated CH), 4.44 (unconjugated CN), 5.98 (C=C), and 9.42 (COC).

Tetramethyl Tetrahydrofuran-2,2,5,5-tetracarboxylate from 2,2,5,5-Tetracyanotetrahydrofuran. A solution of 5.00 g. (0.029 mole) of 2,2,5,5-tetracyanotetrahydrofuran in 100 ml. of absolute methanol was cooled in an ice bath and saturated with hydrogen chloride. After 15-20 min. a colorless precipitate began to form. The reaction mixture was allowed to stand overnight at room temperature, and most of the solvent was removed by evaporation under reduced pressure. Ice-water was added to the residue, and the colorless, insoluble solid was collected by filtration, washed with water, and air-dried to give 6.85 g. (77.5%) of colorless crystals, m.p. 102-104°. The sample was recrystallized from methanol to give 5.3 g. of colorless needles, m.p. 78-102°. Repeated recrystallization from methanol failed to sharpen the melting point. However, after the sample had been dried in a vacuum desiccator over concentrated sulfuric acid for 3 days, the melting point was found to be 103-104°.

Anal. Calcd. for $C_{12}H_{16}O_{9}$: C, 47.37; H, 5.30. Found: C, 46.98; H, 5.32.

The infrared absorption spectrum showed saturated CH bonds at 3.3 and 3.5 μ and carbonyl absorption at 5.65 and 5.75 μ . There was also strong ether absorption in the 8–9- μ region.

2,2,5,5-Tetracyano-2,5-dihydrofuran (IV). Into a 400-ml. stainless-steel-lined pressure vessel cooled to

 -78° and containing 25 g. (0.18 mole) of TCNEO and 150 ml. of 1,2-dichloroethane, there was injected 15 g. (0.58 mole) of acetylene. The reaction mixture was heated for 16 hr. at 130° and filtered to give 17.7 g. of pale brown crystals. Concentration of the filtrate gave an additional 9.7 g. of the same product as determined by a comparison of the infrared spectra. The two fractions were combined and recrystallized from 1,2-dichloroethane to give 20.4 g. (71%) of light tan plates, m.p. 159–161°. An analytical sample of IV, m.p. 160–161°, was prepared by further recrystallization from the same solvent.

Anal. Calcd. for $C_8H_2N_4O$: C, 56.50; H, 1.19; N, 32.95. Found: C, 56.73; H, 1.22; N, 32.54.

The infrared spectrum of IV (KBr) shows absorption at 3.20 (unsaturated CH) and 4.42 μ (C=N). There are two weak bands at 5.85 and 6.13 μ , both of which persist in repeatedly purified samples.

Tetramethyl 2,5-Dihydrofuran-2,2,5,5-tetracarboxylate (V). A solution of 3.0 g. (0.018 mole) of IV in 75 ml. of absolute methanol was cooled in an ice bath and saturated with hydrogen chloride. The reaction mixture was allowed to stand at room temperature for 2.5 days, and most of the methanol was removed by evaporation under reduced pressure. The solid residue was washed with water and air-dried to give 4.77 g. (82%) of colorless crystals, m.p. 95.5-97°. The melting point of V was raised to 96.5-97° by recrystallization from methanol.

Anal. Calcd. for $C_{12}H_{14}O_9$: C, 47.69; H, 4.67 Found: C, 47.91; H, 4.88.

The infrared spectrum (KBr) shows absorption at 3.2 (unsaturated CH), 3.35 (saturated CH), and 5.65– 5.75μ (C==O).

Tetramethyl Tetrahydrofuran-2,2,5,5-tetracarboxylate by Reduction of Tetramethyl 2,5-Dihydrofuran-2,2,5,5tetracarboxylate. A solution of 0.5 g. of tetramethyl 2,5-dihydrofuran-2,2,5,5-tetracarboxylate in 15 ml. of methanol was hydrogenated at room temperature and atmospheric pressure in the presence of 50 mg. of 10%palladium on charcoal. After 11 min., 104% of the theoretical amount of hydrogen had been absorbed and the reaction stopped. The reaction mixture was filtered, and the solvent was removed, leaving 0.55 g. of colorless crystals, m.p. 99-101°. After the product had been recrystallized from methanol and dried overnight under vacuum over sulfuric acid, the melting point was 103-104°. There was no depression when the melting point of the sample was determined in admixture with the tetramethyl ester prepared from the ethylene adduct of TCNEO. In addition, the infrared spectra of the two samples were identical.

3-(Pent-4-ynyl)-2,2,5,5-tetracyano-2,5-dihydrofuran (VIII). A mixture of 5.00 g. (0.035 mole) of TCNEO and 9.4 g. (0.10 mole) of 1,6-heptadiyne in 50 ml. of 1bromo-2-chloroethane was heated to reflux for 17 hr. The reaction mixture was cooled to room temperature and concentrated to leave a dark viscous oil which soon solidified to give 6.7 g. of brown solid. The solid was dissolved in ether, and the insoluble solid was separated by filtration. The filtrate was partially evaporated, and petroleum ether was added until a solid precipitated. This solid was collected to give 4.2 g. (51%) of light tan crystalline solid, m.p. 70–73° For further purification the sample was recrystallized

⁽¹²⁾ We are indebted to Professor A. C. Cope, Massachusetts Institute of Technology, for an authentic sample of tetrahydrofuran-cis-2,5-dicarboxylic acid.

from *n*-propyl alcohol to give VIII as colorless crystals, m.p. $73-74^{\circ}$.

Anal. Calcd. for $C_{13}H_8N_4O$: C, 66.10; H, 3.41; N, 23.72. Found: C, 66.27; H, 3.37; N, 23.70.

The infrared spectrum was compatible with a 1:1 adduct showing absorption at 3.04 (acetylenic CH) and 3.23 μ (olefinic CH). There was also absorption (μ) at 4.4 (CN), 4.71 (C=C), and 5.98 (C=C).

3,3'-Trimethylenebis(2,2,5,5-tetracyano-2,5-dihydrofuran) (IX). A suspension of 1.56 g. (0.017 mole) of 1,6-heptadiyne and 5.00 g. (0.034 mole) of TCNEO in 50 ml. of 1-bromo-2-chloroethane was heated to reflux for 21 hr. The reaction mixture was cooled to room temperature and filtered to give 4.4 g. of tan needles. Evaporation of the filtrate gave a small quantity of the product. Recrystallization of the samples from a large volume of dioxane gave 3.0 g. (46%) of glistening needles, m.p. 261-265°. Further recrystallization from dioxane gave an analytical sample of IX which melted sharply at 258° when heated slowly.

Anal. Calcd. for $C_{19}H_8N_8O_2$: C, 60.00; H, 2.12; N, 29.48. Found: C, 60.83; H, 2.03; N, 29.38.

1,1,3,3-Tetracyano-1,3,3a,7a-tetrahydroisobenzofuran (X). A suspension of 15.0 g. (0.014 mole) of TCNEO and 200 ml. of dry benzene was heated and shaken in a stainless-steel pressure vessel for 12 hr. at 150°. The recovered reaction mixture was filtered, and the insoluble portion was digested twice with boiling ethylene dichloride and filtered. The insoluble fraction (the bisadduct of TCNEO and benzene) weighed 3.19 The filtrate from this extract was combined with the g. original filtrate and concentrated to leave 16.9 g. of a tan solid that was dissolved in methylene chloride and passed over a column of acid-washed alumina. The nearly colorless crystalline solid which was recovered by concentration of the methylene chloride eluate weighed 8.77 g. Recrystallization from 1-bromo-2chloroethane gave 7.24 g. (31%) of colorless plates of X, m.p. 165-167°. Further recrystallization of the product raised the melting point to 167-168°.

Anal. Calcd. for $C_{12}H_{0}N_{4}O$: C, 64.84; H, 2.72; N, 25.21; mol. wt., 222. Found: C, 64.95; H, 2.87; N, 24.68; mol. wt., 228 (ebullioscopic in ClCH₂CH₂Cl).

A total of 8.74 g. of crude bisadduct from several runs was recrystallized from a mixture of 1,2-dimethoxyethane and hexane to give 6.07 g. of colorless crystals, which did not melt below 260° and slowly decomposed above that temperature. The recrystallization was repeated three times, and the sample was dried *in vacuo* with the vapors of refluxing xylene to constant weight and analyzed.

Anal. Calcd. for $C_{18}H_6N_8O_2$: C, 59.00; H, 1.65; N, 30.60; mol. wt., 366. Found: C, 58.85; H, 1.74; N, 30.36; mol. wt., 358 (ebullioscopic in ethanol).

Preparation of the Bisadduct of TCNEO and Benzene by the Addition of TCNEO to 1,1,3,3-Tetracyano-1,3,3a,7a-tetrahydroisobenzofuran. A suspension of 1.00 g. (0.0045 mole) of X, 0.65 g. (0.0045 mole) of TCNEO, and 25 ml. of 1,2-dibromoethane was heated to reflux for 18 hr. The reaction mixture was cooled, and the insoluble fraction was air-dried to give 1.23 g. of pale gray solid. The infrared spectrum of this product was identical with that of the 1,2-dimethoxyethane solvate of the above bisadduct. Sublimation of the sample at 200° (0.1 mm.) gave a colorless, crystalline product with the same infrared spectrum as that of the unsolvated material. Solvates were also prepared from tetrahydrofuran and ethyl acetate. These were found to have similar absorption from 9 to 15 μ in the infrared. The ethyl acetate solvate shows a carbonyl band at 5.84 μ and some stronger absorption around 8 μ . Sublimation of the solvates gives the unsolvated product with identical infrared spectra in all cases. The solvates are regenerated by solution of the sublimate in the solvent.

1,1,3,3-Tetracyano-1,3,3a,4,5,6,7,7a-octahydroisobenzofuran (XIII). A suspension of 10.0 g. (0.070 mole) of TCNEO in a solution of 5.80 g. (0.071 mole) of cyclohexene in 150 ml. of toluene was heated to reflux for 10.5 hr. The reaction mixture was cooled to room temperature and filtered to give 3.10 g. of solid. Evaporation of the filtrate gave an additional crop of 10.8 g. of solid which was the same as the first as shown by the identity of their infrared spectra. Recrystallization from absolute ethanol using charcoal for clarification gave 9.43 g. (60%) of light tan crystals, m.p. $116.5-118^{\circ}$. The analytical sample of XIII, m.p. $118-119^{\circ}$, was prepared by recrystallization from benzene.

Anal. Calcd. for $C_{12}H_{10}N_4O$: C, 63.71; H, 4.46; N, 24.77. Found: C, 63.86; H, 4.67; N, 24.73.

The infrared spectrum was consistent with the postulated structure having absorption at 3.37 and 3.46 (saturated CH), at 4.43 (conjugated C \equiv N), and at 9.5 μ (ether).

Tetramethyl 1,3,3a,7a-Tetrahydroisobenzofuran-1,1,-3,3-tetracarboxylate (XI). A solution of 3.00 g. (0.0135 mole) of X in 150 ml. of methanol was stirred and cooled, and hydrogen chloride was added until the solution was saturated. The resulting solution was then refluxed for 16 hr. Most of the methanol was removed by distillation, and ice-water was added to the residue. This caused precipitation of a gummy, insoluble fraction which was dissolved in methylene chloride. The extracts were washed twice with saturated sodium bicarbonate solution and three times with water and dried over "Drierite." The solvent was removed, leaving an oil which crystallized to give 1.36 g. of colorless solid that was recrystallized from methanol to give 0.94 g. (18%) of colorless crystals, m.p. 91–93° Repeated recrystallization from methanol raised the melting point of XI to 93.5–94.5°.

Anal. Calcd. for $C_{16}H_{18}O_{9}$: C, 54.24; H, 5.12. Found: C, 54.38; H, 5.41.

The infrared spectrum of this product was consistent with the proposed structure showing absorption at 3.29 (unsaturated CH) and at 5.61, 5.68, and 5.75 μ (ester carbonyl). In addition, there was absorption at 6.06 and 6.3 μ (C==C). The ultraviolet spectrum in methanol shows λ_{max} 265 m μ (ϵ 3970) and 246 (4180).

Tetramethyl 1,3,3a,4,5,6,7,7a-Octahydroisobenzofuran-1,1,3,3-tetracarboxylate (XII). A solution of 5.00 g. (0.022 mole) of XIII in 150 ml. of methanol was cooled and stirred while being saturated with hydrogen chloride. The resulting solution was allowed to stand overnight at room temperature and was then heated to reflux for 20 hr. Most of the methanol was removed by distillation, and a mixture of ice and water was added to the residue which was then extracted three times with methylene chloride. The combined extracts were washed three times with saturated sodium bicarbonate solution and three times with water and dried over "Drierite." The solvent was removed, leaving an oil which crystallized, giving 1.83 g. of colorless crystals which were recrystallized from diethyl ether to give 1.17 g. (15%) of colorless rhombs, m.p. 114–115°. A subsequent recrystallization from ether and methanol raised the melting point of XII to 115.5–116°.

Anal. Calcd. for $C_{16}H_{22}O_{9}$: C, 53.63; H, 6.19. Found: C, 53.20; H, 6.11.

The infrared spectra shows absorption at 3.37 and 3.46 μ (saturated CH) and at 5.59, 5.62, and 5.69 μ (ester carbonyl).

Tetramethyl 1,3,3a,4,5,6,7,7a-Octahydroisobenzofuran-1,1,3,3-tetracarboxylate (XII) by the Reduction of XI. To a solution of 200 mg. of tetramethyl 1,3,3a,7atetrahydroisobenzofuran-1,1,3,3-tetracarboxylate in 15 ml. of methanol there was added 10 mg. of 10% palladium on charcoal. This suspension was stirred in an atmosphere of hydrogen. The reaction ceased after the addition of 2 molar equiv. of hydrogen. The suspension was filtered and the solvent evaporated to leave a viscous oil that soon crystallized. The colorless solid was recrystallized from diethyl ether to give 160 mg. (80%) of XII as colorless rhombs, m.p. 115–116° alone or admixed with a sample of the tetramethyl ester XII prepared from the cyclohexene–TCNEO adduct.

Reaction of XI with TCNE. A solution of 0.20 g. of tetramethyl 1,3,3a,7a-tetrahydroisobenzofuran-1,1,3,3-tetracarboxylate and 0.072 g. of tetracyanoethylene in 2 ml. of tetrahydrofuran was allowed to stand at room temperature for 3 days. At the end of this time the reaction mixture was nearly a solid mass. This was dried on a porous plate to give 0.26 g. of pale yellow crystals which were recrystallized from ethylene dichloride to give colorless crystals, m.p. $259-260^{\circ}$.

Anal. Calcd. for $C_{22}H_{18}N_4O_9$: C, 54.77; H, 3.76; N, 11.62. Found: C, 54.58; H, 4.12; N, 11.47.

Treatment of 1,1,3,3-Tetracyano-1,3,3a,7a-tetrahydroisobenzofuran with Sodium Amide in Liquid Ammonia. Sodium amide in liquid ammonia was prepared by the addition of 0.46 g. (0.02 g.-atom) of sodium to 75 ml. of liquid ammonia in the presence of a trace of ferric nitrate. When all of the sodium had reacted, a solution of 2.22 g. (0.01 mole) of 1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran in 25 ml. of tetrahydrofuran was added dropwise over a period of 1 hr. An additional 15 ml. of tetrahydrofuran was added, and the ammonia was allowed to evaporate overnight with stirring. To the dark brown reaction mixture there was added slowly a solution of 5.0 ml. of water in 15 ml. of tetrahydrofuran. The reaction mixture was poured into ice-water to give a homogeneous brown solution that was acidified with 4 N sulfuric acid. An oil separated and was extracted three times with methylene chloride. The combined extracts were washed three times with water and dried over "Drierite." The solvent was removed to leave a dark brown oil that soon crystallized to give 0.98 g. of brown solid. The product was recrystallized from carbon tetrachloride using charcoal to give 0.80 g. (56%) of pale

yellow crystals, m.p. 65–66°,¹³ identified as phenylmalononitrile by mixture melting point and comparison of infrared spectra.

4,7-Dimethyl-1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran (XV). A mixture of 25 g. (0.17 mole) of TCNEO and 150 ml. of p-xylene was heated to reflux for 16 hr. The reaction mixture was cooled to room temperature and filtered. The solid product was washed with benzene and air-dried to give 28.0 g. of dark brown crystalline material. This was recrystallized from 1,2-dichloroethane using charcoal to give 19.0 g. (43%) of XV as nearly colorless plates, m.p. 221-221.5°.

Anal. Calcd. for $C_{14}H_{10}N_4O$: C, 67.19; H, 4.12; N, 22.39. Found: C, 67.10; H, 4.02; N, 21.77.

The ultraviolet spectrum in acetonitrile shows a single maximum at 2.67 m μ (ϵ 7160). The infrared spectrum of the adduct shows absorption (μ) at 3.25 (unsaturated CH), 3.35, 3.4, and 3.45 (saturated CH), 4.45 (C=N), 5.95 and 6.1 (C=C), and 9–10 (ether).

Reaction of TCNEO and Toluene. A suspension of 2.3 g. (0.016 mole) of TCNEO in 25 ml. of toluene was heated to reflux for 18 hr. The reaction mixture was filtered to remove a trace of insoluble black solid, and the filtrate was concentrated to give 2.57 g. of pale brown crystalline solid. Recrystallization from 2-propanol gave colorless crystals, m.p. 125–140°, and further recrystallization from the same solvent did not change the melting point.

Anal. Calcd. for $C_{13}H_8N_4O$: C, 66.10; H, 3.41; N, 23.72. Found: C, 66.99; H, 3.84; N, 23.10.

1,1,3,3-Tetracyano-1,3,3a,9b-tetrahydronaphtho[1,2-c]furan (XVI). A suspension of 5.00 g. (0.0347 mole) of TCNEO and 4.45 g. (0.0347 mole) of naphthalene in 50 ml. of 1,2-dibromoethane was heated to reflux for 4.75 hr. The reaction mixture was concentrated under reduced pressure to leave a heavy slush of crystals which was filtered and rinsed with ether. In this manner, there was obtained 7.68 g. of pale tan crystals which were recrystallized from benzene to give 6.89 g. (73%) of XVI as pale yellow crystals, m.p. 173-174°. The analytical sample melted at 172.5-173°.

Anal. Calcd. for $C_{16}H_8N_4O$: C, 70.55; H, 2.96; N, 20.58. Found: C, 71.21; H, 3.27; N, 20.40.

The infrared spectrum showed absorption (μ) at 3.25 and 3.29 (unsaturated CH), 3.39 (saturated CH), 4.42 (C=N), 6.1, 6.22, 6.34, and 6.73 (C=C), and 9–10 (ether).

The ultraviolet absorption spectrum in acetonitrile showed (m μ (log ϵ)) λ_{max} 211 sh (4.35), 216 (4.41), 222 (4.33), 261 (3.90), 286 sh (3.35), 298 (3.5), and 328 (1.27).

6,9-Dibromo-1,1,3,3-tetracyano-1,3,3a,9a-tetrahydronaphtho[1,2-c]furan (XVII). A suspension of 5.00 g. (0.0347 mole) of TCNEO and 9.93 g. (0.0347 mole) of 1,4-dibromonaphthalene in 100 ml. of 1,2-dibromoethane was heated to reflux for 26.5 hr. The reaction mixture was cooled, and the precipitate was collected by filtration. This solid, which weighed 1.1 g., was identified by infrared spectroscopy as recovered TCNEO. The filtrate was concentrated, leaving 13.3 g. of a tan solid which contained some unchanged

(13) The melting point of phenylmalononitrile is reported to be 68-69°: J. C. Hessler, Am. Chem. J., 32, 123 (1904).

1,4-dibromonaphthalene as indicated by the infrared spectrum. The crude product was suspended in diethyl ether and the mixture filtered. The insoluble portion was washed with ether, and the combined filtrates were evaporated. The insoluble fraction weighed 8.61 g. From the ether filtrate there was recovered 4.4 g. of solid which was identified as 1,4-dibromonaphthalene by means of its infrared spectrum. One recrystallization of the insoluble fraction from 1,2-dichloroethane gave 6.08 g. (52.5%) of dense, tan crystals, m.p. 196–198°. Further recrystallization from 1,2-dichloroethane raised the melting point of XVII to $202-203^{\circ}$.

Anal. Calcd. for C_{r6}H₆Br₂N₄O: C, 44.68; H, 1.41; N, 13.03. Found: C, 45.06; H, 1.67; N, 13.02.

The ultraviolet spectrum in acetonitrile showed $(m\mu \ (\log \epsilon)) \ \lambda_{max} \ 320 \ (3.37), \ 259 \ (3.97), \ 267 \ (3.95), \ 278 \ sh \ (3.75), \ 298 \ sh \ (3.09), \ 3.08 \ (3.28), \ and \ 320 \ (3.25).$

4,4,6,6-Tetracyano-3a,4,6,6a-tetrahydrofurano[2,3-c]furan (XVIII). A suspension of 15 g. of TCNEO and 25 ml. of furan in 100 ml. of 1,2-dichloroethane was sealed in a stainless-steel-lined pressure vessel and heated for 16 hr. at 150° with shaking. The recovered reaction mixture was filtered to remove 11.9 g. of black polymeric solid. Evaporation of the residue left a dark solid which was sublimed to give 2.0 g. of reddish brown crystals which were recrystallized from 1,2-dichloroethane to give 1.10 g. of the furan adduct as colorless crystals, m.p. 161–162°. The melting point of the product was unchanged by further recrystallization and sublimation.

Anal. Calcd. for $C_{10}H_4N_4O_2$: C, 56.60; H, 1.90; N, 26.40. Found: C, 56.00; H, 1.95; N, 26.46.

The infrared spectrum showed absorption at 3.18 (unsaturated CH), 4.42 (C=N), and 6.14 μ (C=C). There was also strong 9–10- μ absorption (ether).

4,4,6,6-Tetracyano-3a,4,6,6a-tetrahydrothieno[2,3-c]furan (XIX). A suspension of 15 g. (0.104 mole) of TCNEO in 26 g. (0.31 mole) of thiophene and 150 ml. of 1,2-dichloroethane was heated in a stainlesssteel-lined pressure vessel for 16 hr. at 130°. The reaction mixture was filtered to remove a small amount of suspended black polymeric solid, and the filtrate was evaporated to leave a mass of black crystalline product. The product was dissolved in boiling benzene, treated with charcoal, and filtered. The filtrate deposited 11.8 g. of yellow needles, m.p. 158–162°. Further recrystallization from ethylene dichloride gave XIX with m.p. 159–160°, unchanged by further recrystallizations followed by sublimation, the product retained a faint yellow color.

Anal. Calcd. for $C_{10}H_4N_4SO$: C, 52.62; H, 1.77; S, 14.05. Found: C, 53.42; H, 2.17; S, 14.40.

The infrared spectrum showed absorption (μ) at 3.25 (unsaturated CH), 3.33 and 3.37 (saturated CH), 4.44 (C=N), 6.29 (C=C), and 8-10 (COC).

2-Chloro-4,4,6,6a-tetracyano-3a,4,6,6a-tetrahydrothieno[2,3-c]furan (XX). A suspension of 5.00 g. (0.0347 mole) of TCNEO in 11.9 g. (0.10 mole) of freshly distilled 2-chlorothiophene and 50 ml. of 1,2dibromoethane was heated to reflux for 16 hr. The reaction mixture was cooled to room temperature, and the precipitate was collected by filtration to give 7.18 g. of dark solid which was recrystallized from 1,2dichloroethane with charcoal to give 3.72 g. of nearly colorless crystals, m.p. 178–179°. Another 0.65 g. was obtained by concentration of the mother liquors. Further recrystallization from the same solvent raised the melting point of XX to 179–180°.

Anal. Calcd. for C₁₀H₃ClN₄SO: C, 45.72; H, 1.15; N, 21.33. Found: C, 45.09; H, 1.12; N, 21.25.

The infrared spectrum showed absorption (μ) at 3.23 (saturated CH), 3.33 (saturated CH), 4.41 and 4.44 (C=N), 6.27 (C=C), and 9–10 (COC).

Tetracyanoethylene Oxide. III. Mechanism of the Addition to Olefins¹

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The rate of addition of tetracyanoethylene oxide (TCNEO) to styrene and to trans-stilbene obeys the equation

$$rate = \frac{k_1 k_2 [TCNEO][olefin]}{k_{-1} + k_2 [olefin]}$$

These rate constants are associated with the reaction sequence

(1) This work was presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 20–22, 1964.

$$TCNEO \rightleftharpoons_{k_{-1}}^{k_{1}} TCNEO^{*}$$
$$TCNEO^{*} + olefin \xrightarrow{k_{2}} product$$

Over-all, the reaction is relatively insensitive to solvent and substituent changes. The best formulation of TCNEO* is a hybrid of biradical and zwitterionic species which adds to the olefin by a concerted or near-concerted cyclic process.