Periselective Addition of Nitrile Sulfides, Nitrile Oxides, and Diphenyldiazomethane to Tetracyanoethylene

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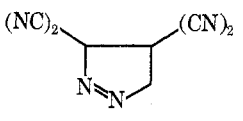
Nitrile sulfides and nitrile oxides underwent periselective 1,3-dipolar addition to the nitrile functions of tetracyanoethylene to form mono and bis thiadiazole and oxadiazole derivatives, respectively. Solvolysis reactions of the thiadiazoles and oxadiazoles were investigated. Diphenyldiazomethane added selectively to the carbon–carbon double bond of tetracyanoethylene to form 1,1-diphenyl-2,2,3,3-tetracyanocyclopropane in high yield.

The formation of Diels–Alder adducts from tetracyanoethylene (TCNE) and 1,3-dienes is a well-known reaction.[1] By contrast, 1,3-dipolar reactions of TCNE have been reported in only two cases. Diazomethane is claimed[2] to undergo exclusive addition to the double bond to yield a pyrazoline **1** which readily lost nitrogen to form 1,1,2,2-tetracyanocyclopropane. Ethyl diazoacetate, however, has been reported[3] to add to the nitrile function of TCNE. The unstable product was postulated to be 4-ethoxycarbonyl-5-tricyanovinyl-1,2,3-triazole (**2**) but was not fully characterized.



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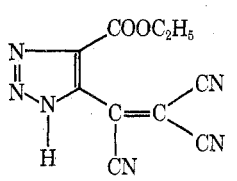


2

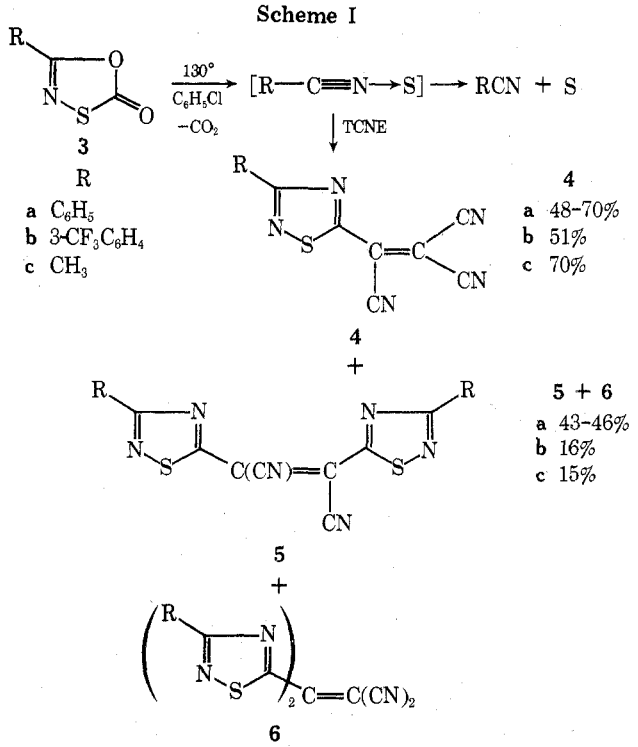
Related nitriles such as acrylonitrile,[4] cyanoacetylene,[5] and dicyanoacetylene[6,7] are reported to react at the unsaturated carbon–carbon bonds with various 1,3-dipoles.[8]

Since the factors which influence the mode of periselective addition of 1,3-dipoles to TCNE have not been studied, we have investigated this type of reaction in more detail.

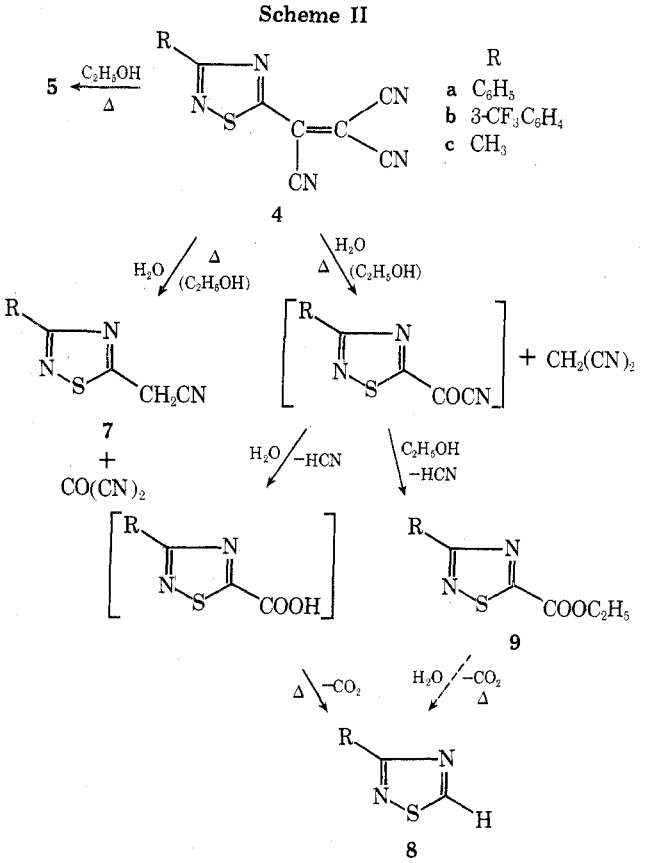
Benzonitrile sulfide,[9-11] obtained by the thermolysis of the oxathiazolone **3a**, reacted with TCNE at 130° to form benzonitrile, sulfur, tricyanoethylene **4a**, and a mixture of dicyanoethylene isomers **5a** (presumably cis and trans) and **6a** as indicated in Scheme I. The yields of dicyanoethylene isomers were substantially increased as the mole ratio of **3a** to TCNE was increased or when **3a** and **4a** were heated at 180°. Similar results were obtained with the oxathiazolone **3b** whereas **3c** produced **4c** and a single dicyanoethylene isomer (presumably trans) **5c**. There was no indication (ir, NMR, GC–mass spectra) that products arising from 1,3-dipolar addition to the carbon–carbon double bond of TCNE were present in significant amounts in any of these reaction mixtures. The major component of the dicyanoethylene mixture was easily separated by selective solvent extraction and is assumed to be the more thermodynamically stable trans isomer of **5**. The structures of **4** and **5** were supported by the elemental analyses, ir, NMR, and mass spectra. The structures of **4** were further supported by the chemical conversions outlined in Scheme II.

The major products **9** from solvolysis of **4** with 95% aqueous ethanol were identified by elemental analyses, spectral data (ir, NMR, mass), and, for **9a** and **9b**, comparison with authentic[11] materials. Malononitrile and the minor prod-

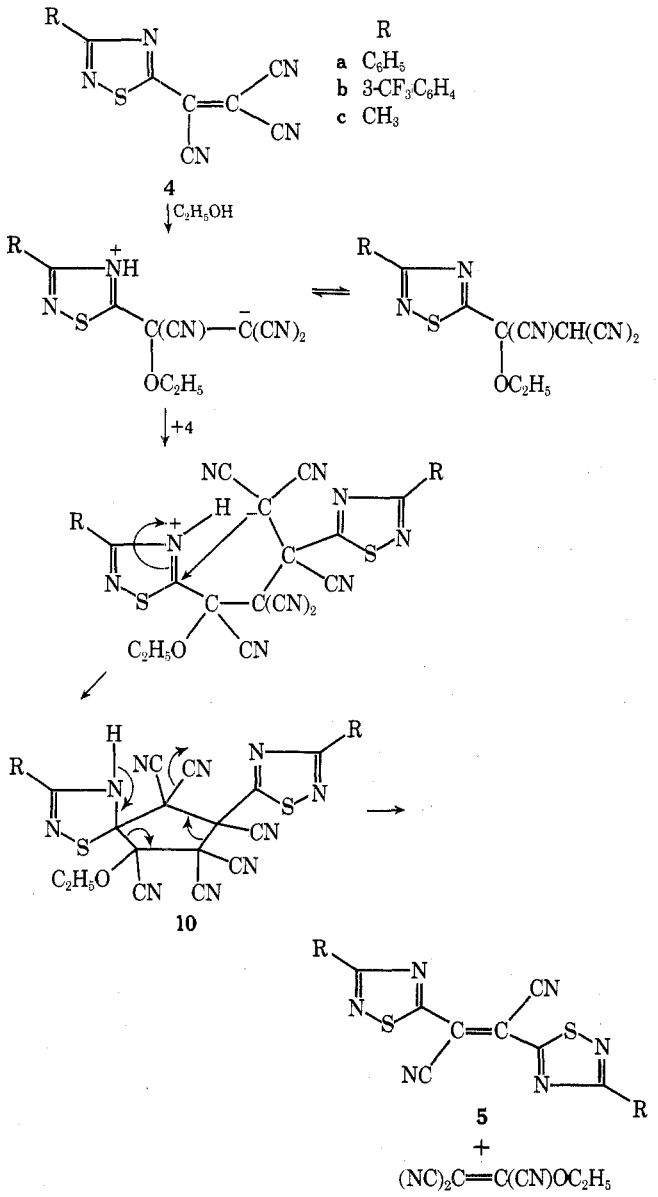
Scheme I



Scheme II



Scheme III

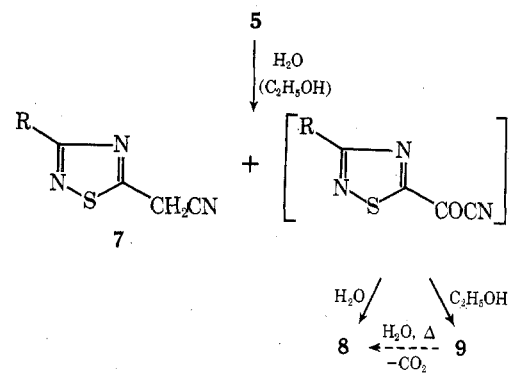


ucts **5**, **7**, and **8** were identified by ir and/or GC–mass spectra. The hydrolytic conversion of tricyanoethylenes to esters has been reported[12] previously. Although the mechanism of this reaction is not known, acyl cyanides[13a] appear to be plausible intermediates with suitable reaction characteristics.

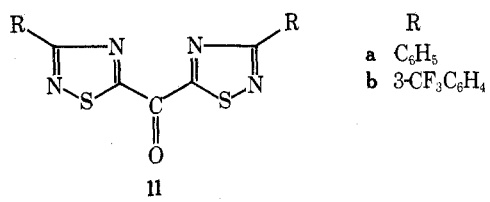
In contrast to 95% aqueous ethanol, dry alcohol converted **4** primarily to the dicyanoethylenes **5**. This unusual transformation is not a thermal reorganization since no change occurs when **4a** is heated in *o*-dichlorobenzene at reflux. Another possibility, the addition of the anion of **8a** to **4a** followed by elimination of cyanide, also did not occur in hot aprotic solvents. The reaction sequence illustrated in Scheme III involving an intermediate spiran **10** is one possible mechanism which is under investigation.[13b]

The hydrolysis of **5a** by 95% aqueous ethanol under various conditions was extremely slow owing to the insolubility of the starting material. The dicyanoethylenes **5b** and **5c**, however, were sufficiently soluble to undergo the expected conversions indicated in Scheme IV. Esters **9b** and **9c** and nitriles **7b** and **7c** were formed in approximately equivalent amounts as indicated by GC–mass spectral data. The thiadiazoles **8b** and **8c** were minor products formed by hydrolysis–decarboxylation of intermediate acyl cyanides

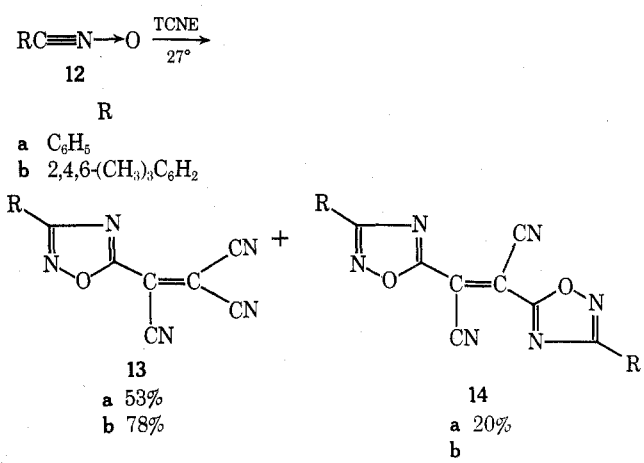
Scheme IV



and/or esters **9** as indicated. Certain fractions consisting of mixtures of **5** and **6**, which were isolated from the hydrocarbon solvent of the TCNE reactions, were also sufficiently soluble in 95% aqueous ethanol to undergo solvolysis. Thus, the GC–mass spectrum of the solvolysis product of **5a** + **6a** indicated the presence of malononitrile, benzonitrile (7%), **7a** (27%), **8a** (9%), **9a** (45%), and bis(3-phenyl-1,2,4-thiadiazol-5-yl) ketone (**11a**, 12%). In a similar manner solvolysis of the mixture **5b** + **6b** yielded malononitrile, **7b** (17%), **8b** (2%), **9b** (24%), and bis[3-(3-trifluoromethylphenyl)-1,2,4-thiadiazol-5-yl)] ketone (**11b**, 54.5%). Product **11b** was isolated and further characterized by elemental analysis and the ir and NMR spectra.



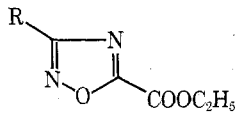
In a manner similar to nitrile sulfides, benzonitrile oxide **12a** and mesitonitrile oxide **12b** reacted with TCNE at room temperature to yield the corresponding 1,2,4-oxadiazole adducts **13** and **14**. In each of these reactions only a single dicyanoethylene was formed and is assumed to be the trans isomer **14**. Product **14b** was initially obtained from the reaction mixture as a yellow powder. This product was converted to a more stable red crystalline form when it was dissolved in chloroform or heated in ether. Another product isolated from the mesitonitrile oxide reaction was an orange powder which had an elemental analysis, cryoscopic molecular weight, mass spectrum, and ir spectrum consistent for a TCNE π complex of **14b**. The orange powder also was formed in nearly quantitative yield when equimolar amounts of **14b** and TCNE were mixed in benzene at room temperature. The π complex could be recrystallized



unchanged from benzene but was converted to **14b** by warm ethanol.

In analogy with the nitrile sulfide reactions, attempts to isolate or identify 1,3-dipolar adducts from nitrile oxides in which the carbon–carbon double bond of TCNE functions as an acceptor were not successful.

Dilute ethanol (95%) converted **13a** to a mixture of products containing ethyl carbamate, benzonitrile, malononitrile, ethyl ester **15a**, nitrile **16a**, and oxadiazole **17a**. The



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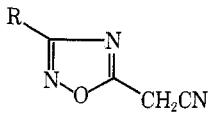

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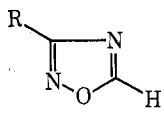
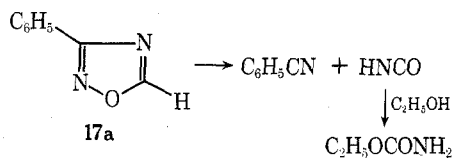


17

a C_6H_5
b 2,4,6-$(CH_3)_3C_6H_2$

products were identified by their GC–mass spectra. The ester **15a** and nitrile **16a** were isolated by column chromatography, and **15a** was shown to be identical (GC retention time, ir spectrum, melting point, mixture melting point) with authentic material.[14] Apparently, benzonitrile and ethyl carbamate result from the ring degradation of **17a**.



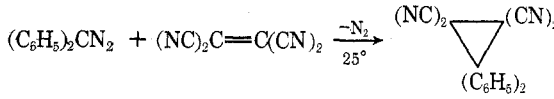
17a

During the solvolysis of **13a** the oxadiazole **17a** may be formed by the hydrolysis–decarboxylation of an intermediate acyl cyanide and/or **15a**. No reaction occurred when **15a** and 95% ethanol were heated at reflux for several hours. In the presence of a catalytic amount of potassium cyanide, however, **15a** was converted to a mixture of **17a**, benzonitrile, and ethyl carbamate. After a reflux period of 48 hr only the latter two components were present in the reaction solution. This result supports the view that ethyl carbamate and benzonitrile are derived from **17a** which in turn may be formed from **15a** during the solvolysis of **13a**. The mesityl analogue **13b** was hydrolyzed by 95% ethanol in a manner similar to the phenyl derivative **13a**. The ester **15b** was isolated and found to be identical with authentic material prepared from ethyl cyanoformate and mesitonitrile oxide. The nitrile **16b** was also isolated and identified by its ir, NMR, and mass spectra.

The 1,2,4-oxadiazolyltricyanoethylenes **13** were similar to the corresponding 1,2,4-thiadiazolyltricyanoethylenes **4** in their activity towards hot *absolute* ethanol. Thus, **13a** was readily converted to **14a** in 85% yield and **13b** yielded **14b** in 79% yield. A mechanism analogous to that outlined in Scheme III would account for these results. Finally, **14b**, like **5b**, was readily solvolyzed by hot 95% aqueous ethanol to yield a mixture of **15b** and **16b**.

Attempts to prepare nitrile imine adducts of TCNE were not successful. Irradiation of mixtures of TCNE and 3,5-diphenyl-1,3,4-oxadiazolin-2-one[15] at 2537 Å produced polymeric materials. Complex mixtures were also obtained when attempts were made to generate nitrile imines from α-halobenzaldehyde phenylhydrazones in the presence of TCNE.

The periselectivity of the TCNE reactions encountered in this work and in the literature may be due to electronic and/or steric factors. To assess the possibility that the contrasting mode of addition of diazomethane and ethyl diazoacetate to TCNE may be significantly influenced by steric effects, we investigated the nature of the diphenyldiazomethane reaction. In a mixed solvent at room temperature a rapid reaction occurred with liberation of nitrogen and precipitation of 1,1-diphenyl-2,2,3,3-tetracyanocyclopropane (**18**) in nearly quantitative yield. The structure of



18

product **18** was supported by the elemental analysis and the ir and mass spectra. The order of steric inhibition to formation of the pyrazoline transition state (i.e., addition to the carbon–carbon double bond of TCNE) is assumed to be in the order diphenyldiazomethane > ethyl diazoacetate > diazomethane. Since diazomethane and diphenyldiazomethane react readily at the double bond of TCNE in contrast to ethyl diazoacetate, however, it would appear that steric effects are somewhat less important than electronic factors in periselective additions of this type.

Our initial attempts to correlate the periselective nature of these diverse TCNE reactions by charge density considerations or frontier electron models have not been successful.

A study of the reactions of other 1,3-dipoles with TCNE is in progress. The reactions of adducts **4**, **5**, **13**, and **14** with a variety of reagents is also under investigation and will be reported at a later date.

Experimental Section

Melting points were taken in open capillaries in a Mel-Temp apparatus and are uncorrected. The tetracyanoethylene used in this work was Eastman white label grade. The 1,3,4-oxathiazol-2-ones were prepared from the corresponding acid amides and chlorocarbonylsulfenyl chloride according to reported procedures.[16] Benzonitrile oxide was prepared from α-chlorobenzaldehyde oxime[17] and mesitonitrile oxide was prepared by the method of Grundman and Dean.[18] Diphenyldiazomethane was prepared[19] by oxidation of benzophenone hydrazone. GC analyses were performed on an F and M Scientific 720 dual column programmed gas chromatograph using 2-ft columns packed with 10% SE-30 or OV-17. Programming was generally carried out from 50 to 300° at 15°/min.

Reaction of 5-Phenyl-1,3,4-oxathiazol-2-one (3a) and TCNE (1:1 Mole Ratio). A mixture of 18 g (0.10 mol) of 5-phenyl-1,3,4-oxathiazol-2-one (**3a**), 12.8 g (0.10 mol) of tetracyanoethylene, and 80 ml of dry chlorobenzene was heated at the reflux temperature (137°) for 16 hr with good agitation. The black reaction mixture was cooled to room temperature under dry nitrogen and diluted with ether and the precipitated solid was collected by filtration. The residue was washed with ether and air dried to yield 20.7 g of yellow powder, mp 200–204°. The ir spectrum indicated that the tricyanoethylene **4a** and the dicyanoethylenes **5a** and **6a** were the only materials present in significant amounts. The crude product (20 g) was extracted with 300 ml of warm tetrahydrofuran and the insoluble dicyanoethylenes (**5a** and **6a**) (1.1 g, 5.5%) collected by filtration. Pure 1,2-bis(3-phenyl-1,2,4-thiadiazol-5-yl)-1,2-ethenedicarbonitrile (**5a**) was partially separated from the mixture as a yellow powder, mp 290–293° dec, by repeated recrystallization from hot tetrahydrofuran: mass spectrum *m/e* (rel intensity, fragment) 398 (44, M^+), 295 (4, $M^+ - C_6H_5CN$), 263 (4, $M^+ - C_6H_5CNS$), 135 (100, $C_6H_5CNS^+$), 103 (36, $C_6H_5CN^+$); ir (Nujol) 4.5 (w), 6.25 (w), 8.85 (s), 11.75 (s), 12.6 (s), 14 μ (s). The ir spectrum of pure **5a** indicates that it is the major constituent of the dicyanoethylene mixture (which also shows weak absorption at 11.35, 11.9, 12.3, and 14.15 μ).

Anal. Calcd for $C_{20}H_{10}N_6S_2$: C, 60.28; H, 2.53; N, 21.09; S, 16.09. Found: C, 60.42; H, 2.54; N, 21.01; S, 16.22.

The tetrahydrofuran extract was concentrated to yield 18.5 g (70%) of tricyanoethylene **4a**. The ir spectrum indicated essentially pure product but the material contained a brown-colored impurity. The impurity was best removed by several recrystallizations from acetonitrile or by chromatography of the benzene solution through Florisil. Pure 2-(3-phenyl-1,2,4-thiadiazol-5-yl)-1,1,2-ethenetricarbonitrile (**4a**) was obtained as a bright yellow, crystalline solid: mp 210–211°; mass spectrum *m/e* (rel intensity, frag-

ment) 263 (58, M^+), 135 (100, $C_6H_5CNS^+$), 103 (50,$C_6H_5CN^+$), 77 (50, $C_6H_5^+$); ir (Nujol) 4.5 (w), 6.5 (w), 6.8 (s), 7.1 (s), 8.4 (s), 11.7 (s), 12.6 (s), 13.95 (s), 14.4 μ (s).

Anal. Calcd for $C_{13}H_5N_5S$: C, 59.30; H, 1.91; N, 26.60; S, 12.18; mol wt, 263.3. Found: C, 59.43; H, 1.81; N, 26.54; S, 12.31; mol wt (tetrahydrofuran), 284.

GC analysis of the chlorobenzene–ether filtrate indicated the presence of benzonitrile, sulfur, tetracyanoethylene, and tricyanoethylene **4a**. Concentration of the filtrate on a hot water bath at 20 mm gave 3.4 g of a mixture containing predominantly tetracyanoethylene, sulfur, and tricyanoethylene **4a**.

Reaction of 5-Phenyl-1,3,4-oxathiazol-2-one (3a) and TCNE (2:1 Mole Ratio). A mixture of 9 g (0.05 mol) of 5-phenyl-1,3,4-oxathiazol-2-one (**3a**), 3.2 g (0.025 mol) of TCNE, and 30 ml of dry chlorobenzene was heated at the reflux temperature (136–138°) for 15 hr. After being cooled to room temperature, the dark mixture was filtered and the residue washed several times with benzene and then ether. The yield of residual green powder was 3.9 g (39%). Gas chromatography and the ir spectrum indicated that the product was primarily a mixture (cis + trans?) of dicyanoethylenes **5a**. The benzene washes were concentrated at reduced pressure to yield 2.5 g of solid. By recrystallization from acetonitrile, the mixture was separated into 2.2 g (33%) of **4a** (mp 209–210°) and 0.4 g (4%) of dicyanoethylene mixture **5a**. The reaction filtrate was concentrated at reduced pressure on a hot water bath to remove solvent (C_6H_5Cl). The residue was washed with ether to yield 1.4 g of a mixture containing **4a**, **5a**, and **6a**. By extraction with acetonitrile the mixture was separated into 1 g (15%) of **4a** and 0.4 g (4%) of a mixture of **5a** and **6a**.

Reaction of 5-Phenyl-1,3,4-oxathiazol-2-one (3a) and 2-(3-Phenyl-1,2,4-thiadiazol-5-yl)-1,1,2-ethanecarbonitrile (4a). A mixture of 2.6 g (0.01 mol) of **4a** and 30 ml of *o*-dichlorobenzene was heated at the reflux temperature (179°) with good agitation under a nitrogen atmosphere. During intervals of 5 min, three 0.7-g portions (2.1 g, 0.012 mol) of **3a** were added to the hot solution. Heating was continued for 0.5 hr and then the mixture was cooled to room temperature. The precipitate (2.3 g, 58%) was collected by filtration and was washed with benzene and ether. The GC and ir spectrum [Nujol, 4.5 (w), 6.25 (w), 7.0 (m), 11.45 (w), 11.85 (s), 12.0 (m), 12.4 (w), 12.75 μ (s)] indicated predominantly a mixture of dicyanoethylenes **5a**. The reaction filtrate and benzene washes were combined and concentrated on a steam bath at 20 mm until most of the *o*-dichlorobenzene had been removed. The residue was washed with ether to yield 1.4 g (30%) of yellow-orange powder. GC analysis and the infrared spectrum [Nujol, 4.5 (w), 6.2 (w), 6.45 (w), 7 (s), 8.35 μ (m)] indicate that this material is predominantly a mixture of isomers **5a** and **6a** (see solvolysis data).

Reaction of 5-(3-Trifluoromethylphenyl-1,3,4-oxathiazol-2-one (3b) and TCNE. A mixture of 13.0 g (0.05 mol) of **3b**, 6.4 g (0.05 mol) of TCNE, 40 ml of dry chlorobenzene, and 20 ml of 1,2,4-trichlorobenzene was heated at the reflux temperature (146°) with stirring for 26 hr. After cooling to room temperature, the black mixture was filtered. The residue was washed with acetonitrile and ether to yield 0.5 g (4%) of **5b** as a yellow powder, mp 224–225°. After recrystallization from hot acetonitrile, 1,2-bis[3-(3-trifluoromethylphenyl)-1,2,4-thiadiazol-5-yl]-1,2-ethenedicarbonitrile (**5b**) was obtained as yellow needles: mp 222–223.5°; ir (Nujol) 4.5 (w), 6.22 (w), 7.6 (s), 8.5 (s), 8.65 (s), 8.85 (s), 8.92 (s), 13.55 (s), 14.4 μ (s); mass spectrum *m/e* (rel intensity, fragment) 534 (35, M^+), 515 (5, $M^+ - F$), 465 (37, $M^+ - CF_3$), 203 (100, $CF_3C_6H_4CNS^+$), 171 (15, $CF_3C_6H_4CN^+$), 145 (19, $CF_3C_6H_4^+$).

Anal. Calcd for $C_{22}H_8F_6N_6S_2$: C, 49.44; H, 1.51; N, 15.73; S, 12.00. Found: C, 49.52; H, 1.48; N, 15.69; S, 12.26.

The reaction filtrate was filtered through a short column of Florisil to remove a black impurity and the column was then washed with benzene. The combined eluate was concentrated at 100° (20 mm) to remove solvent and some unreacted TCNE. The orange residue was mixed with a large volume of petroleum ether and the precipitated powder collected by filtration. The yield of air-dried crude mono adduct was 13.8 g. The crude product (12 g) was heated with acetonitrile and then the mixture was cooled to room temperature and filtered. The residue (1.6 g, 12%) was a mixture of the bis adducts **5b** and **6b** as indicated by the ir spectrum [Nujol, 4.5 (w), 6.2 (w), 6.5 (w), 7.6 (s), 7.8 (m), 11.9 (m), 12.45 (m), 8.5 (s), 8.65 (s), 8.85 (s), 8.95 (s), 13.55 (s), 14.45 μ (s)] and solvolysis products (see solvolysis). The mixture of **5b** and **6b** was extracted with benzene and the benzene solution concentrated. The orange residue was extracted with ether to yield an insoluble orange powder, mp 212.5–216.5°. The ir spectrum [Nujol, 4.5 (w), 6.2 (w), 6.5 (w), 7.55 (s), 7.7 (s), 7.8 (s), 8.5 (s), 8.65 (s), 8.9 (s), 9.15 (s), 9.2 (s), 10.4 (m), 10.9 (s), 11.9 (s), 12.3 (s), 12.4 (s), 13.55 (s), 14.45 μ (s)] indicated primarily **6b**.

The acetonitrile solution was concentrated at reduced pressure. The residue was dissolved in benzene and chromatographed on Florisil. After removal of benzene from the eluate, the residue was agitated with petroleum ether and filtered. The yield of yellow mono adduct **4b** was 8.5 g (51%), mp 118.5–120.5° (sintered at 112° and resolidified). Analytically pure 2-[3-(3-trifluoromethylphenyl)-1,2,4-thiadiazol-5-yl]-1,1,2-ethenetricarbonitrile (**4b**), mp 119.5–121.5°, was obtained by recrystallization from heptane.

Anal. Calcd for $C_{14}H_4F_3N_5S$: C, 50.76; H, 1.22; N, 21.14; S, 9.68. Found: C, 50.83; H, 1.26; N, 20.88; S, 9.45.

The Nujol ir spectra and melting points of **4b** before and after recrystallization from heptane are slightly different. Since the solution ir spectra are the same, however, the differences are presumably due to different crystalline modifications. Ir ($CHCl_3$) 4.5 (m), 6.2 (m), 6.5 (w), 6.8 (m), 6.9 (m), 7.2 (s), 7.6 (s), 7.8 (s), 8.55 (s), 8.85 (s), 9.15 (s), 9.35 (s), 10 (m), 10.5 (m), 10.9 (s) 11.75 μ (s); mass spectrum *m/e* (rel intensity, fragment) 331 (4, M^+), 262 (9, $M^+ - CF_3$), 203 (12, $CF_3C_6H_4CNS^+$), 171 (3, $ArCN^+$), 145 (4, $CF_3C_6H_4^+$).

Reaction of 5-Methyl-1,3,4-oxathiazol-2-one (3c) and TCNE. A mixture of 2.95 g (0.025 mol) of **3c** and 3.2 g (0.025 mol) of TCNE in 25 ml of dry chlorobenzene was heated at 130° under nitrogen for 17 hr. Since some TCNE precipitated when the mixture was cooled to room temperature, an additional 2.95 g (0.025 mol) of **3c** was added and heating at 130° resumed for 24 hr. At the end of this time GC analysis indicated the absence of TCNE and substantial conversion to **4c**. After cooling to room temperature, the dark mixture was filtered to yield 0.6 g (9%) of the bis adduct **5c**. The chlorobenzene filtrate was concentrated on a steam bath at 20 mm and the residue extracted with several portions of hot petroleum ether to yield an additional 0.4 g (6%) of insoluble crude **5c**. Pure 1,2-bis(3-methyl-1,2,4-thiadiazol-5-yl)-1,2-ethenedicarbonitrile, mp 215–216.5°, was obtained by recrystallization of the crude products from tetrahydrofuran–ether: ir (Nujol) 4.5 (w), 6.05 (w), 6.8 (s), 7.0 (s), 7.1 (s), 10.0 (s), 12.0 μ (s); mass spectrum *m/e* (rel intensity, fragment) 274 (23, M^+), 247 (2, $M^+ - HCN$), 233 (12, $M^+ - CH_3CN$), 220 (2, $M^+ - 2HCN$), 192 (2, $M^+ - 2CH_3CN$), 73 (100, CH_3CNS^+), 41 (3, CH_3CN^+); NMR ($CDCl_3$) δ 2.85 (s, 3, CH_3).

Anal. Calcd for $C_{10}H_6N_6S_2$: C, 43.78; H, 2.20; N, 30.64; S, 23.38. Found: C, 43.76; H, 2.12; N, 30.70; S, 23.26.

The petroleum ether extracts were concentrated to yield 4.4 g of a mixture containing predominantly **4c** and sulfur (~11%). An attempt to decolorize the mixture in benzene–hexane with decolorizing carbon was not successful. The recovered material was finally purified by several recrystallizations from methylcyclohexane to yield 2-(3-methyl-1,2,4-thiadiazol-5-yl)-1,1,2-ethenetricarbonitrile (**4c**) as a yellow, crystalline solid: mp 80–81°; ir (Nujol) 4.5 (w), 6.45 (w), 6.9 (s), 7.05 (s), 7.15 (s), 9.85 (s), 11.45 (s), 11.9 μ (s); mass spectrum *m/e* (rel intensity, fragment) 201 (18, M^+), 174 (1, $M^+ - HCN$), 102 [3, $C_2(CN)_3^+$], 76 (10, $C_2(CN)_2^+$), 73 (100, CH_3CNS^+), 41 (4, CH_3CN^+); NMR ($CDCl_3$) δ 2.90 (s, 3, CH_3).

Anal. Calcd for $C_8H_3N_5S$: C, 47.75; H, 1.50; N, 34.81; S, 15.94. Found: C, 47.79; H, 1.46; N, 34.74; S, 16.07.

Reaction of Benzonitrile Oxide (12a) with TCNE. To a cold (0–5°) stirred solution of 1.6 g (0.01 mol) of benzohydroxamyl chloride in 70 ml of ether was added in one portion a cold solution of 1.05 g (0.01 mol) of triethylamine in 5 ml of ether. The precipitated triethylamine hydrochloride (1.3 g) was removed by filtration and the filtrate added to a solution of 1.3 g (0.01 mol) of TCNE in a mixture of 20 ml of benzene and 5 ml of acetonitrile. After about 5 min a yellow precipitate began to form. The mixture was stirred at room temperature for 17 hr and then filtered. The yellow residue of **14a** (0.37 g, 20%), mp 285° dec, was washed with benzene and ether and air dried. An analytical sample of 1,2-bis(3-phenyl-1,2,4-oxadiazol-5-yl)-1,2-ethenedicarbonitrile (**14a**), mp 285° dec, was prepared by recrystallization from *N,N*-dimethylacetamide–ether: ir (Nujol) 4.5 (w), 6.30 (w), 6.35 (w), 6.5 (m), 6.65 (m), 6.95 (s), 7.45 (s), 12.2 (s), 12.65 (s), 13.55 (s), 14.4 μ (s); mass spectrum *m/e* (rel intensity, fragment) 336 (37, M^+), 249 (31, $M^+ - C_6H_5CN_2$), 221 (3, $M^+ - C_6H_5C_2N_2O$), 145 (24, $C_6H_5C_2N_2O^+$), 119 (61, $C_6H_5CNO^+$), 117 (9, $C_6H_5CN_2^+$), 103 (64, $C_6H_5CN^+$), 77 (68, $C_6H_5^+$).

Anal. Calcd for $C_{20}H_{10}N_6O_2$: C, 65.57; H, 2.75; N, 22.94. Found: C, 65.69; H, 2.80; N, 22.98.

The reaction filtrate was concentrated at reduced pressure and the residue (2.25 g) extracted with 40 ml of benzene. GC analysis of the benzene solution using chlorobenzene as a standard indicated

the presence of 1.3 g (53%) of **13a**. The benzene solution was chromatographed on Florisil and the yellow eluate concentrated at reduced pressure. The residue was extracted with petroleum ether and the residue of **13a** (1.35 g) air dried. After recrystallization from acetonitrile, pure 2-(3-phenyl-1,2,4-oxadiazol-5-yl)-1,1,2-ethenetricarbonitrile (**13a**), mp 176.5–178.5°, was obtained as yellow crystals: ir (Nujol) 4.45 (w), 6.25 (m), 6.35 (m), 6.42 (w), 6.6 (s), 6.92 (s), 9.3 (s), 11.3 (s), 12.6 (s), 13.45 (s), 14.2 (s), 14.45 μ (s); mass spectrum *m/e* (rel intensity, fragment) 247 (97, M^+), 221 (3, $M^+ - CN$), 145 (7, $C_6H_5C_2N_2O^+$), 130 (4, $M^+ - C_6H_5CN_2$), 119 (100, $C_6H_5CNO^+$), 117 (99, $C_6H_5CN_2^+$), 103 (39, $C_6H_5CN^+$), 77 (19, $C_6H_5^+$).

Anal. Calcd for $C_{13}H_5N_5O$: C, 63.16; H, 2.04; N, 28.33. Found: C, 63.33; H, 1.94; N, 28.53.

Reaction of Mesitonitrile Oxide (12b) with TCNE. To a solution of 1.2 g (0.0095 mol) of TCNE in 20 ml of benzene and 5 ml of acetonitrile was added a solution of 1.6 g (0.010 mol) of mesitonitrile oxide in 50 ml of ether. After stirring for 3 days at room temperature under dry conditions, the yellow-orange solution was concentrated at reduced pressure. The residue was triturated with petroleum ether to yield 2.4 g of insoluble solid. The crude product was extracted with ether and the insoluble orange powder (0.2 g) recrystallized from benzene to yield a TCNE π complex of **14b**: mp 185–187° dec; ir (Nujol) 4.45 (w), 6.2 (s), 6.5 (s), 6.65 (m), 7.5 (s), 9.15 (s), 11.7 (s), 12.3 μ (s); mass spectrum *m/e* (rel intensity, fragment) 450 (10, M^+), 291 [31, $M^+ - C_6H_2(CH_3)_3CN_2$], 263 [19, $M^+ - C_6H_2(CH_3)_3C_2N_2O$], 187 [20, $C_6H_2(CH_3)_3C_2O^+$], 161 [13, $C_6H_2(CH_3)_3CNO^+$], 159 [80, $C_6H_2(CH_3)_3CN_2^+$], 146 [14, $C_6H_2(CH_3)_3CNO^+-CH_3$], 145 [80, $C_6H_2(CH_3)_3CH^+$], 144 [70, $C_6H_2(CH_3)_3CN_2^+-CH_3$], 130 [100, $C_6H_2(CH_3)_3CN^+-CH_3$], 119 [9, $C_6H_2(CH_3)_3^+$].

Anal. Calcd for $C_{32}H_{22}N_{10}O_2$: C, 66.42; H, 3.84; N, 24.21. Found: C, 66.43; H, 3.82; N, 24.15.

Recrystallization of the π complex from ethanol produced 1,2-bis(3-mesityl-1,2,4-oxadiazol-5-yl)-1,2-ethenedicarbonitrile (**14b**), mp 177.5–178.5° dec, as red crystals: ir (Nujol) 4.5 (w), 6.2 (s), 6.4 (s), 6.65 (s), 11.2 (s), 11.8 μ (s); mass spectrum similar to that of the π complex with some relative intensity differences; NMR ($CDCl_3$) δ 2.28 (s, 12, $ArCH_3$-2), 2.33 (s, 6, $ArCH_3$-4), 6.97 (s, 4, ArH).

Anal. Calcd for $C_{26}H_{22}N_6O_2$: C, 69.31; H, 4.93; N, 18.66. Found: C, 69.43; H, 4.86; N, 18.69.

The orange π complex of **14b** was re-formed in almost quantitative yield when equimolar amounts of **14b** and TCNE were mixed in benzene.

The ether extract of the crude reaction product was concentrated at reduced pressure to yield 2.2 g (78%) of nearly pure **13b** as indicated by the ir spectrum. An analytical sample of 2-(3-mesityl-1,2,4-oxadiazol-5-yl)-1,1,2-ethenetricarbonitrile (**13b**), mp 130.5–131.5°, was prepared by two recrystallizations from heptane: ir (Nujol) 4.5 (w), 6.3 (m), 6.4 (m), 6.65 (s), 9.15 (s), 11.65 μ (s); mass spectrum *m/e* (rel intensity, fragment) 289 (40, M^+), 263 (7, $M^+ - CN$), 235 (37, $M^+ - 2HCN$), 187 (4, $ArC_2N_2O^+$), 159 (78, $ArCN_2^+$), 144 (100, $M^+ - ArCN$), 145 (24, $ArCN^+$), 128 (5, $M^+ - ArCNO$), 119 (2, Ar^+).

Anal. Calcd for $C_{16}H_{11}N_5O$: C, 66.42; H, 3.84; N, 24.21; mol wt, 289. Found: C, 66.23; H, 3.93; N, 23.96; mol wt (C_6H_6), 300.

From the petroleum ether extract of the crude reaction product there was recovered 0.5 g of a gum. Ether extraction of the gum yielded 0.2 g of a yellow powder, mp 187–190° dec. The yellow powder had ir and mass spectra similar to those **14b** and was converted to **14b** when refluxed in ether but was recovered unchanged from hot ethanol.

Solvolysis of 4a with 95% Ethanol. A mixture of 0.53 g (0.002 mol) of **4a** and 20 ml of 95% ethanol was heated with stirring at the reflux temperature for 17 hr. A small amount (0.003 g) of insoluble material was removed by filtration and the filtrate concentrated at reduced pressure. The ir spectrum of the residue (0.5 g) indicated the presence of malononitrile and ethyl ester **9a**. The crude product was dissolved in ether and washed with water and the ether layer was concentrated. The residue was extracted with methanol and the methanol solution concentrated to yield 0.4 g (85%) of nearly pure **9a** as indicated by the ir spectrum. After two recrystallizations from ethanol there was obtained 0.24 g (51%) of pure ethyl 3-phenyl-1,2,4-thiadiazole-5-carboxylate (**9a**), mp 70.0–70.5°. The ir spectrum was identical with that of authentic material[11] and a mixture melting point (70.2–70.8°) was undepressed.

Solvolysis of 4a with Dry Ethanol. A mixture of 0.53 g (0.002 mol) of **4a** and 10 ml of dry ethanol was stirred under a Drierite column at the reflux temperature for 72 hr. After cooling to room temperature, the precipitated yellow solid was collected and washed with ether. The ir spectrum indicated that the product (0.31 g, 77.5%) was pure **5a**.

Solvolysis of 4b with 95% Ethanol. A mixture of 1.0 g (0.003 mol) of **4b** and 30 ml of 95% ethanol was stirred at the reflux temperature for 2 hr. After remaining overnight at room temperature, the solution was concentrated at reduced pressure to yield 1 g of light yellow solid. A GC–mass spectrum of the crude product indicated a mixture containing malononitrile (16%), 3-(3-trifluoromethylphenyl)-1,2,4-thiadiazole (**8b**, 5.5%) [*m/e* (rel intensity, fragment) 230 (73, M^+), 203 (100, $CF_3C_6H_4CNS^+$), 171 (16, $CF_3C_6H_4CN^+$), 145 (17, $CF_3C_6H_4^+$)], ethyl 3-(3-trifluoromethylphenyl)-1,2,4-thiadiazole-5-carboxylate (**9b**, 78%) [*m/e* (rel intensity, fragment) 302 (52, M^+), 283 (4, $M^+ - F$), 274 (2, $M^+ - C_2H_4$), 257 (4, $M^+ - OC_2H_5$), 203 (100, $CF_3C_6H_4CNS^+$)], and 3-(3-trifluoromethylphenyl)-5-cyanomethyl-1,2,4-thiadiazole (**7b** ~1%) [*m/e* (rel intensity, fragment) 269 (100, M^+), 250 (9, $M^+ - F$), 203 (100, $CF_3C_6H_4CNS^+$)].

A solution of the crude product (0.3 g) in benzene was chromatographed on Florisil. The benzene eluate was concentrated and the residue (0.16 g) recrystallized from heptane. The ester **9b**, mp 78–80°, was obtained as white plates and had an ir spectrum identical with that of authentic material[11] (mmp 79–80°).

Solvolysis of 5b with 95% Ethanol. A mixture of 0.1 g (0.0002 mol) of **5b** and 30 ml of 95% ethanol was heated at the reflux temperature with stirring for 6.5 hr. After the mixture cooled to room temperature, precipitated solid (0.01 g) was removed and the solution concentrated at reduced pressure. GC analysis of the viscous residue (0.12 g) indicated the presence of **8b** (3%), **9b** (46.5%), **7b** (46.5%), and starting material **5b** (2%).

Solvolysis of Mixture 5b + 6b with 95% Ethanol. A mixture of 0.2 g of **5b + 6b** (isolated in the reaction of **3b** with TCNE) and 30 ml of 95% ethanol was stirred at the reflux temperature for 4 hr. After cooling to room temperature, the solution was concentrated at reduced pressure to yield 0.2 g of viscous yellow oil. GC analysis indicated a mixture containing **8b** (2%), **9b** (24%), **7b** (17%), the ketone **11** (54.5%), and starting material **5b** (2.5%). The crude product was extracted with hot hexane. Cooling the hexane extract resulted in a light yellow solid. After a second recrystallization from hexane, bis[3-(3-trifluoromethylphenyl)-1,2,4-thiadiazol-5-yl] ketone(**11**) mp 148.5–149.5°, was obtained as light yellow crystals: ir (Nujol) 5.98 (s), 7.55 (s), 8.4 (s), 8.55 (s), 8.9 (s), 9.3 (s), 10.45 (s), 13.55 (s), 14.45 μ (s); mass spectrum *m/e* (rel intensity, fragment) 486 (40, M^+), 467 (4, $M^+ - F$), 257 (2, $M^+ - CF_3C_6H_4C_2N_2S$), 203 (100, $CF_3C_6H_4CNS^+$), 171 (14, $CF_3C_6H_4CN^+$), 145 (11, $CF_3C_6H_4^+$).

Anal. Calcd for $C_{19}H_8N_4F_6OS_2$: C, 46.91; H, 1.66; N, 11.52. Found: C, 47.06; H, 1.60; N, 11.46.

Solvolysis of 5c with 95% Ethanol. A mixture of 0.15 g (0.005 mol) of **5c** and 10 ml of 95% ethanol was stirred at the reflux temperature for 2.5 days and was cooled to room temperature. A small amount of insoluble material was removed by filtration and the filtrate concentrated at reduced pressure. The residue was extracted with ether and the ether solution concentrated to yield 0.1 g of oil. GC–mass spectroscopy indicated two components in a 1:1 ratio with parent ions of *m/e* 172 and 139 consistent for ethyl 3-methyl-1,2,4-thiadiazole-5-carboxylate (**9c**) and 3-methyl-5-cyanomethyl-1,2,4-thiadiazole (**7c**).

Solvolysis of 5a + 6a with 95% Ethanol. A mixture of 0.3 g of **5a + 6a**, prepared from **3a** and **4a** (fraction 2), and 30 ml of 95% ethanol was stirred at the reflux temperature for 24 hr. The mixture was filtered hot and the residue (0.18 g) washed with ethanol and ether. The ir spectrum of the yellow powder was similar to that of the starting mixture except for the absence of a band at 6.5 μ. The ethanol filtrate was concentrated at reduced pressure and the residue (0.15 g) extracted with ether. GC analysis of the ether extract indicated the presence of benzonitrile (7%), 3-phenyl-1,2,4-thiadiazole (**8a**, 9%), ethyl 3-phenyl-1,2,4-thiadiazole-5-carboxylate (**9a**, 45%), 3-phenyl-5-cyanomethyl-1,2,4-thiadiazole (**7a**, 27%) and bis(3-phenyl-1,2,4-thiadiazol-5-yl) ketone (**11a**, 12%): mass spectrum *m/e* (rel intensity, fragment) **8a**, 162 (19, M^+) 135 (29, $C_6H_5CNS^+$), 103 (9, $C_6H_5CN^+$), 77 (11, $C_6H_5^+$); **9a**, 234 (46, M^+), 189 (4, $M^+ - OC_2H_5$), 161 (3, $M^+ - COOC_2H_5$), 135 (100, $C_6H_5CNS^+$), 103 (32, $C_6H_5CN^+$), 77 (16, $C_6H_5^+$); **7a**, 201 (69, M^+), 135 (100, $C_6H_5CNS^+$), 103 (18, $C_6H_5CN^+$), 77 (19, $C_6H_5^+$); **11a**, 350 (41, M^+), 189 (2, $M^+ - C_6H_5C_2N_2S$), 161 (2, $C_6H_5C_2N_2S^+$), 135 (100, $C_6H_5CNS^+$), 103 (31, $C_6H_5CN^+$), 91 (5, $C_6H_5N^+$), 77 (18, $C_6H_5^+$).

Solvolysis of 13a with Dry Ethanol. A mixture of 0.5 g (0.002

mol) of 13a and 20 ml of dry ethanol was heated at the reflux temperature with stirring under anhydrous conditions for 20 hr and was cooled to room temperature. The resultant precipitate was collected by filtration, washed with ethanol and ether, and air dried. The yield of yellow powder was 0.31 g (85%). The ir spectrum of the product was identical with that of 1,2-bis(3-phenyl-1,2,4-oxadiazol-5-yl)-1,2-ethenedicarbonitrile (**14a**) prepared previously. The ethanol filtrate was concentrated at reduced pressure to yield 0.2 g of brown oil. GC–mass spectroscopy indicated that the major constituents of the oil were malononitrile, **15a**, and **16a**.

Solvolysis of 13a with 95% Ethanol. A mixture of 0.45 g (0.002 mol) of 13a and 20 ml of 95% ethanol was stirred at the reflux temperature for 20 hr. After being cooled to room temperature, the solution was concentrated at reduced pressure to yield 0.4 g of viscous oil. GC–mass spectral analysis indicated the presence of malononitrile, benzonitrile, ethyl carbamate, 3-phenyl-1,2,4-oxadiazole (**17a**), ethyl ester 15a, and nitrile **16a**. A benzene solution of crude product (0.3 g) was chromatographed on Florisil. From the benzene eluate there was recovered 0.26 g of colorless oil. After being stored overnight under petroleum ether, the oil deposited white crystals of 3-phenyl-5-cyanomethyl-1,2,4-oxadiazole[20] (**16a**): mp 74.5–76.0°; ir (Nujol) 4.4 (w), 6.25 (s), 6.35 (m), 7.5 (s), 8.3 (s), 11.15 (s), 13.9 (s), 14.4 μ (m); NMR (CD_3CN) δ 4.4 (s, 2, $-CH_2CN$), 7.8–8.2 (m, 5, ArH); mass spectrum *m/e* (rel intensity, fragment) 185 (93, M^+), 145 (2, $M^+ - CH_2CN$), 119 (100, $C_6H_5CNO^+$), 103 (8, $C_6H_5CN^+$). A single sharp peak was observed on GC. The petroleum ether soluble product slowly crystallized at room temperature. The material was recrystallized from dilute ethanol to yield ethyl 3-phenyl-1,2,4-oxadiazole-5-carboxylate (**15a**), mp 54.5–55.0°, as white plates. The product gave a single sharp peak on GC. The ir spectrum was identical with that of authentic material[14] and the mixture melting point was undepressed.

Solvolysis of 15a with 95% Ethanol. A mixture of 0.22 g (0.001 mol) of **15a** and 10 ml of 95% ethanol was heated at the reflux temperature with stirring for 26 hr. GC analysis indicated that a reaction had not occurred. A catalytic quantity of potassium cyanide was added and heating resumed for 5 hr. GC analysis then indicated the emergence of small peaks due to benzonitrile and 3-phenyl-1,2,4-oxadiazole (17a) [ethyl carbamate was decomposed in the injector block (300°) during these analyses]. After the reaction mixture was held at the reflux temperature for 19 hr, the GC peak due to 15a was greatly reduced and the peaks due to benzonitrile and 17a proportionally increased. Finally, after the reaction mixture was heated at reflux for another 29 hr, the only component detected by GC was benzonitrile. After being cooled to room temperature, the ethanol solution was dried over magnesium sulfate and then concentrated at reduced pressure. The ir spectrum of the semisolid residue (0.15 g) indicated that benzonitrile and ethyl carbamate were the major components.

Solvolysis of 13b with Dry Ethanol. A mixture of 1 g (0.0034 mol) of **13b** and 10 ml of dry ethanol was stirred at the reflux temperature for 8 hr and was cooled to room temperature. The precipitate of red, crystalline **14b** (0.5 g, 65%) was collected, washed with ethanol and ether, and air dried. The ir spectrum of the product was identical with that of **14b** prepared previously from **12b** and TCNE.

Solvolysis of 13b with 95% Ethanol. A mixture of 0.5 g (0.002 mol) of **13b** and 20 ml of 95% ethanol was stirred at the reflux temperature for 1.5 hr. After being cooled to room temperature, the yellow solution was concentrated on a warm water bath at 20 mm. The residual yellow oil (0.55 g) was analyzed by GC–mass spectroscopy. Besides malononitrile and ethyl carbamate, the following products were detected [product, mass spectrum, *m/e* (rel intensity, fragment)]: mesityl isocyanate (2%), 161 (100, M^+), 146 (49, $M^+ - CH_3$), 133 (18, $M^+ - CO$), 132 (15, $M^+ - HCO$), 119 (8, $M^+ - NCO$); mesityl cyanide (20%), 145 (92, M^+), 130 (100, $M^+ - CH_3$), 115 (10, $M^+ - 2CH_3$); 3-mesityl-1,2,4-oxadiazole (**17b**, 1%), 188 (2, M^+), 161 (14, $M^+ - HCN$), 145 (85, $M^+ - HCNO$), 130 [100, $C_6H_2(CH_3)_3^+-CH_3$]; ethyl 3-mesityl-1,2,4-oxadiazole-5-carboxylate (**15b**, 35%), 260 (28, M^+), 187 (100, $M^+ - COOC_2H_5$), 161 (9, $M^+ - CNCOOC_2H_5$), 159 (47, $M^+ - COCOOC_2H_5$), 145 (28, $M^+ - CNOCOOC_2H_5$), 130 [18, $C_6H_2(CH_3)_3^+-CH_3$); 3-mesityl-5-cyanomethyl-1,2,4-oxadiazole (**16b**, 42%), 227 (23, M^+), 187 (26, $M^+ - CH_2CN$), 161 [47, $M^+ - CH_2(CN)_2$], 159 (70, $M^+ - COCH_2CN$), 145 (100, $M^+ - CNOCH_2CN$), 130 [85, $C_6H_2(CH_3)_3^+-CH_3$].

Ethyl 3-Phenyl-1,2,4-oxadiazole-5-carboxylate (15a). The method of Huisgen et al.[14] was employed with slight modifications.

A solution of 1.5 ml (10.5 mmol) of triethylamine in 20 ml of ether was added with stirring to a mixture of 1.25 g (8 mmol) of phenyl hydroxamyl chloride[17] and 4 ml (20 mmol) of ethyl cyanoformate in a water bath. After 1 hr the precipitated triethylamine hydrochloride was removed by filtration and the ether solution was concentrated at reduced pressure. The residual yellow oil (1.7 g) was extracted with petroleum ether. From the extract there was recovered 1.5 g of oil which crystallized when seeded with **15a**. The crude product was recrystallized twice from ethanol to yield 0.9 g (52%) of white needles, mp 54–55.5° (lit. mp 53–54°).

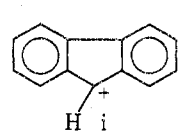
Ethyl 3-Mesityl-1,2,4-oxadiazole-5-carboxylate (15b). To a solution of 1.0 g (0.010 mol) of ethyl cyanoformate in 10 ml of dry ether was added 0.3 g (0.002 mol) of mesitonitrile oxide. The colorless solution was stirred at room temperature for 23 hr and then was concentrated at reduced pressure (0.5 mm) on a warm water bath. The residual oil (0.52 g, 100%) was essentially pure **15b** as indicated by the ir spectrum and a single peak eluting from the gas chromatogram.

Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.59; H, 6.21; N, 10.76. Found: C, 64.71; H, 6.20; N, 10.74.

3-Mesityl-5-cyanomethyl-1,2,4-oxadiazole (16b). A solution of 1.3 g (0.02 mol) of malononitrile and 0.32 g (0.002 mol) of mesitonitrile oxide in 25 ml of dry ether was stirred at room temperature for 48 hr. The solution was then washed several times with water and finally dried over magnesium sulfate. After the ether was removed at reduced pressure, there was recovered 0.42 g (92%) of viscous oil. The product crystallized after a short time (mp 61–64°) and GC analysis indicated a single material: ir (Nujol) 4.42 (w), 6.2 (m), 6.3 (s), 7.6 (s), 9.2 (s), 11.35 (s), 11.8 μ (s); NMR (CD_3CN) δ 2.11 [s, 6, $Ar(CH_3)_2$-2,6] 2.27 (s, 3, $ArCH_3$-4), δ 4.27 (s, 2, $-CH_2CN$), 6.95 (s, 2, ArH).

Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.69; H, 5.78; N, 18.49. Found: C, 68.76; H, 5.76; N, 18.32.

1,1-Diphenyl-2,2,3,3-tetracyanocyclopropane (18). To a stirred solution of 1.3 g (0.01 mol) of TCNE in 20 ml of benzene and 5 ml of acetonitrile cooled in an ice bath was added dropwise a solution of 2 g (0.01 mol) of diphenyldiazomethane in 50 ml of ether. The purple color of the diazo compound disappeared immediately during addition and nitrogen was continuously liberated. Eventually a white precipitate began to form. After being stirred overnight at room temperature, the mixture was filtered and the residue (2.9 g, 100%), mp 274–276° dec, washed with ether: ir (Nujol) 4.45 (w), 6.3 (w), 6.75 (m), 13.05 (s), 13.37 (s), 14.1 (s), 14.4 μ (s); NMR (CD_3CN) δ 7.4 (m, 3, ArH), 7.8 (m, 2, ArH); mass spectrum *m/e* (rel intensity, fragment) 294 (69, M^+), 268 (36, $M^+ - CN$), 267 (65, $M^+ - HCN$), 241 (16, $M^+ - HCN - CN$), 230 [8, $M^+ - C(CN)_2$], 166 [29, $(C_6H_5)_2C^+$], 165 (100, i), 77 (18, $C_6H_5^+$). An



H i

analytical sample, mp 276–278° dec, was prepared by recrystallization from ethanol.

Anal. Calcd for $C_{19}H_{10}N_4$: C, 77.53; H, 3.43; N, 19.04. Found: C, 77.80; H, 3.62; N, 19.07.

Registry No.—**3a**, 5852-49-3; **3b**, 57459-15-1; **3c**, 17452-74-3; **4a**, 57459-16-2; **4b**, 57459-17-3; **4c**, 57459-18-4; *cis*-**5a**, 57459-19-5; *trans*-**5a**, 57459-20-8; *cis*-**5b**, 57459-21-9; *trans*-**5b**, 57459-22-0; **5c**, 57459-23-1; **6a**, 57459-24-2; **6b**, 57459-25-3; **7a**, 57459-26-4; **7b**, 57459-27-5; **8a**, 50483-82-4; **8b**, 57459-28-6; **9a**, 50483-79-9; **9b**, 50483-80-2; **11a**, 57459-29-7; **11b**, 57459-30-0; **12a**, 873-67-6; **12b**, 2904-57-6; **13a**, 57459-31-1; **13b**, 57459-32-2; **14a**, 57459-33-3; **14b**, 57459-34-4; **14b** TCNE π complex, 57474-16-5; **15a**, 37760-54-6; **15b**, 57459-35-5; **16a**, 57459-36-6; **16b**, 57459-37-7; **17b**, 57459-38-8; **18**, 57459-39-9; TCNE, 670-54-2; ethanol, 64-17-5; mesityl isocyanate, 2958-62-5; mesityl cyanide, 2571-52-0; ethyl cyanoformate, 623-49-4; malononitrile, 109-77-3; diphenyldiazemethane, 883-40-9.

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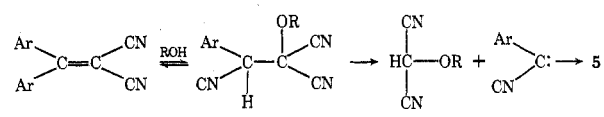

If one assumes that solvolysis of the carbene by ethanol is not a rapid reaction, this suggestion certainly appears feasible. Information to be presented in a future publication, however, will show that the formation of **5** is inhibited when a base is present in the reaction mixture.

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Electrochemical Reduction of Ethylene Trithiocarbonate. Reactions of Trithiocarbonyl Radical Anions

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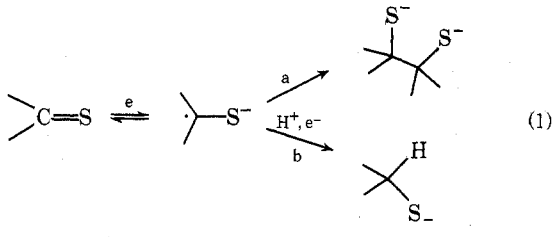
The electrochemical reduction of ethylene trithiocarbonate (1) has been studied in *N,N*-dimethylformamide–tetra-*n*-butylammonium bromide solutions at a platinum electrode. Reduction proceeds through the radical anion of 1 which reacts via anionic elimination of a molecule of ethylene. At potentials on the foot of the voltammetric wave the major electrolysis product is a bis(trithiocarbonate) dianion which was isolated as the methyl or ethyl ester after aklylation with the alkyl iodide. Alkylation with either 1,2-dibromoethane or 1,2-diiodoethane produced 1,4,6,9-tetrathiospiro[4.4]nonane as the major product. Reduction with sodium metal gives larger amounts of products derived from trithiocarbonate dianions. A mechanism is proposed for the reduction which accounts for the observed potential dependence of the electrolysis products.

Previous work in this laboratory has shown that several cyclic trithiocarbonates are electrochemically reduced under voltammetric conditions via an ECE pathway.[1] For ethylene trithiocarbonate cyclic voltammograms at fast sweep rates (ca. 75 V sec^{-1}) demonstrated the presence of a reversible one-electron couple in acetonitrile solutions at −1.76 V vs. a saturated calomel electrode (SCE). As the rate of the potential scan was decreased, the one-electron wave was transformed into an irreversible two-electron wave with a peak width of ca. 50 mV. This type of behavior has become familiar in recent years and is characteristic of an electrode process for which Nernstian electron transfer reactions are maintained and the irreversibility is caused by a chemical step involving the radical anion intermediate (an ECE pathway).[2]

By analogy to the well-studied electroreduction of carbonyl compounds, two possible pathways are suggested for the radical anion of thiocarbonyl groups: thiopinacol and mercaptan formation. In aqueous 2-propanol buffers two-



(1)

electron reductions of the thiocarbonyl group have been observed for a variety of thiones.[3] In nonaqueous solvents, however, the low proton availability would favor pathway a in eq 1 over b. In fact addition of proton donors such as phenol or water to DMF solutions did not appreciably decrease the lifetime of the radical anion in the voltammetric experiments,[1] a result which suggests pathway a. Further support for this pathway comes from work of Astruc et al.,[4] in which a dimeric product was obtained from the electroreduction of a 1,2-dithiole-3-thione.

The dimercaptide dianion which would result from the 2,2′ coupling of two ethylene trithiocarbonate radical anions represents a potentially useful synthetic intermediate as a ligand or a nucleophile for the preparation of new transition metal complexes or multisulfur heterocycles. Electrogenerated mecaptides have been used successfully for the preparation of compounds in the tetrathiofulvalene series[5] and it was our hope to carry out similar reactions using ethylene trithiocarbonate (1) instead of carbon disulfide. However, the radical anion of 1 was found to react by an unexpected pathway which is described below.

Results

Alkylation with Alkyl Iodides. Electrolyses in DMF–TBABr solutions of ca. 1-g quantities of 1 at potentials between −1.4 and −1.6 V vs. SCE consumed an average of 0.98 F/mol of electricity. Usually the electrolysis was complete within 1 hr, at which point the solution had acquired a light brown color. Addition of an excess of alkylating agent, e.g., CH_3I, caused the color to change from brown to yellow. Product isolation gave yellow needles, mp 59.0–59.8°, in greater than 50% current yield (based on 1 F/mol) after two recrystallizations from acetonitrile. No attempt was made to maximize the yield of the major product. In