Acknowledgment. This investigation was made possible in part by the financial support of the National Institutes of Health (Grants CA-12115 and AI-11490). The authors thank Dr. J. M. Gardlik, Dr. J. A. Jenkins, and Ms. C. Murowski for their early efforts in the development of a viable synthesis of **13**, Dr. Sean Traynor for a large sample of **16*** and for certain experimental details, Professor Robert Bates for a generous gift of (*S*)-(−)-α-phellandrene, and Mr. C. R. Weisenberger for the high-resolution mass spectral data.

Thiacyanocarbons. 5. Reactions of Tetracyano-1,4-dithiin and Tetracyanothiophene with Nucleophiles: Synthesis of Tetracyanopyrrole and Tetracyanocyclopentadiene Salts†

H. E. Simmons,* R. D. Vest, S. A. Vladuchick, and O. W. Webster

Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

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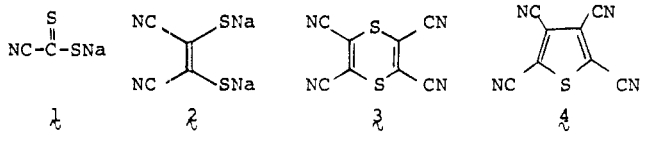
Reactions at the double bonds of tetracyano-1,4-dithiin and tetracyanothiophene have been explored. Generally, nucleophiles attack the dithiin by an addition–elimination mechanism to produce divinyl sulfides. The resulting anions are stable, experience fragmentation, or undergo further condensation reactions to produce heterocyclic structures. For example, tetracyano-1,4-dithiin is converted by thiocyanate ion to a thiophenopyrimidine. In fragmentation reactions, the dithiin acts as a masked maleonitrile and as such is useful for the synthesis of tetracyanoethylene. Remarkably, the dithiin reacts with sodium azide to give tetracyanopyrrole and with reactive methyl compounds to give substituted tetracyanocyclopentadienide ions. Tetracyanothiophene reacts with nucleophiles in a manner similar to tetracyanodithiin but at higher temperatures.

The synthesis of sodium cyanodithioformate (**1**) and its oxidative dimerization to disodium dimercaptomaleonitrile (**2**) have been described by Bähr and Schleitzer[1] and in greater detail in previous papers of this series.[2-5]



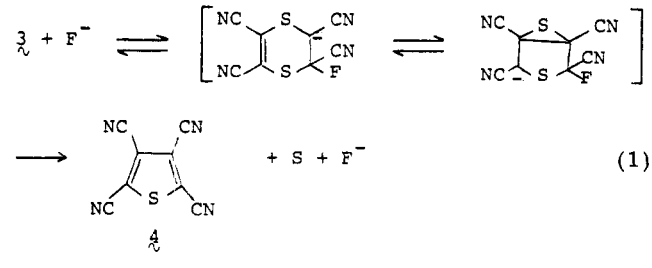
The oxidation of **1** or **2** gives tetracyano-1,4-dithiin (**3**) in high yield. The mechanism of these oxidations and the properties of **3** have been discussed.[3] Tetracyano-1,4-dithiin undergoes facile addition reactions with many ionic nucleophiles at one of the carbon–carbon double bonds followed by ring opening. The fate of the resulting anions depends strongly on the specific reactant and conditions.

Tetracyano-1,4-dithiin extrudes sulfur at 210 °C to give tetracyanothiophene (**4**).[3] Tetracyanothiophene is less reactive than the dithiin, but certain nucleophiles will open the ring.

This paper discusses reactions of **3** and **4** which give vinyl sulfide salts, heterocycles, and cyanocyclopentadienides.

Results and Discussion

Catalysis of Sulfur Extrusion. Cesium fluoride in diethylene glycol dimethyl ether catalyzes the extrusion of sulfur from **3** at 60 °C to give **4**. The course of the reaction is probably as shown in eq 1. This is one of a

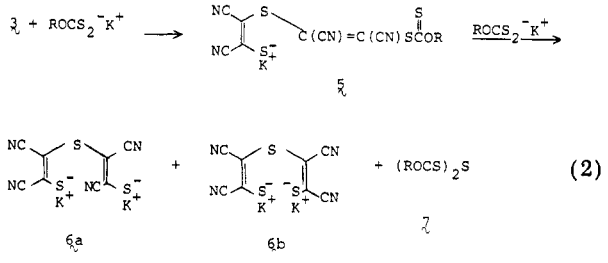


(1)

† Contribution No. 2642.

few non-ring-opening reactions of **3** with a nucleophile.

Ring-Opening Reactions. Potassium alkyl xanthates react with **3** in acetone to give a mixture of the cis,cis and cis,trans dipotassium salts of bis(2-mercapto-1,2-dicyanovinyl) sulfide (**6a,b**)[6] and the thioanhydride **7** in good yields (eq 2). The intermediate **5** cannot be isolated since it



(2)

reacts rapidly with a second mole of xanthate ion. In large-scale runs, small quantities of **2** were isolated, suggesting that addition of a second mole of xanthate ion to a double bond of **5** competes inefficiently with the cleavage reaction.

The thiolate groups on **6a** and **6b** are easily methylated with methyl iodide or dimethyl sulfate. In fact, by quenching the reaction of **3** with potassium ethyl xanthate in acetonitrile after 5 min at −10 °C with dimethyl sulfate, one can determine the stereochemistry of the reaction. Proton NMR showed that the reaction was approximately 90% complete based on ethyl *S*-methyl dithiocarbonate produced from unreacted xanthate. If one assumes that

(1) G. Bähr and G. Schleitzer, *Chem. Ber.*, **88**, 1771 (1955); **90**, 438 (1957); G. Bahr, *Angew. Chem.*, **68**, 525 (1956).
(2) H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4746 (1962).
(3) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962).
(4) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4772 (1962).
(5) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4782 (1962).
(6) Robert D. Vest, U.S. Patent 3 226 423 (1965); *Chem. Abstr.*, **64**, 6504*f* (1966).

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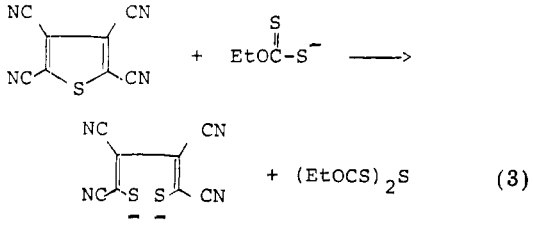
the double bond in 3 which is not undergoing attack retains its stereochemistry (remains cis), then the equal-intensity peaks found at δ 2.80 and 2.75 must arise from the cis,trans dimethyl derivative of **6a**, and the singlet at 2.77 ppm must arise from the cis,cis dimethyl derivative of **6b**. Integration showed that the yields of the cis,trans and cis,cis isomers were 50% and 35%, respectively. A peak at 2.63 ppm corresponded to bis(methylthio)maleonitrile (5%). In runs conducted at higher temperatures and longer times, a singlet appeared at 2.78 ppm which is attributed to further isomerization to the trans,trans isomer. Thus, ring opening of **3** by xanthate ion is not stereospecific, and without evidence to the contrary, we assume ring opening by other nucleophiles will also be nonstereospecific.

In an analogous reaction (eq 3) potassium ethyl xanthate reacts with **4** to open the ring, but heating is required.



(3)

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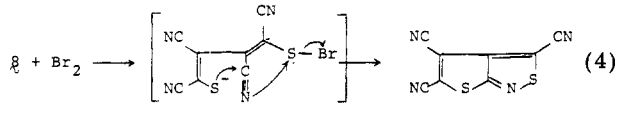
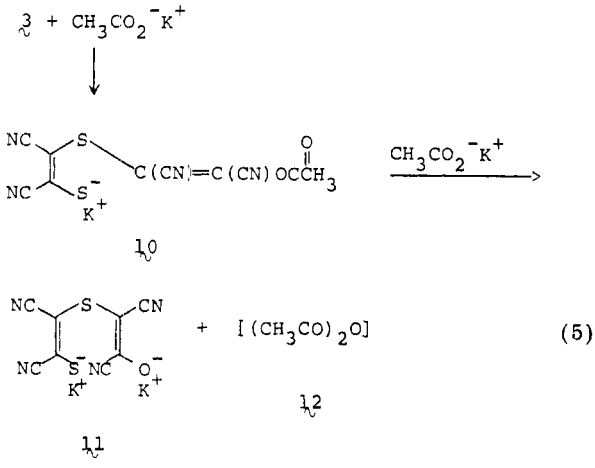
On treatment of 8 with bromine, the fused heterocyclic compound **9**, 3,4,5-tricyanothieno[2,3-*c*]isothiazole, is produced (eq 4). The structure of **9** is based on elemental analysis, infrared and ^{13}C NMR (Table I) spectra, and mechanistic considerations.



(4)

9

Potassium acetate in tetrahydrofuran is sufficiently nucleophilic to add to dithiin **3**. The intermediate vinyl acetate **10** (which cannot be isolated) is readily cleaved to the mixed mercaptide oxide cyanocarbon ion **11**. Although necessary to balance the equation, acetic anhydride **12** was not identified as a product (eq 5).

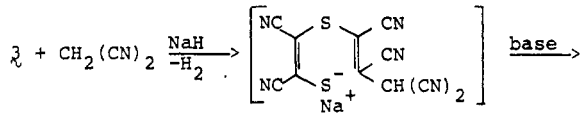


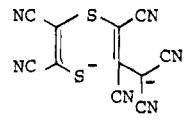
(5)

11 **12**

Sodium dicyanomethanide ring opens **3** to give the resonance-stabilized dianion **13**[7] (eq 6).

Sodium dicyanomethanide also reacts with 4 to open the ring (eq 7). The thiolate dianion **14** which is produced





(6)

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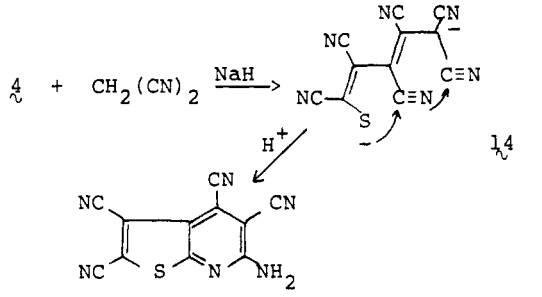
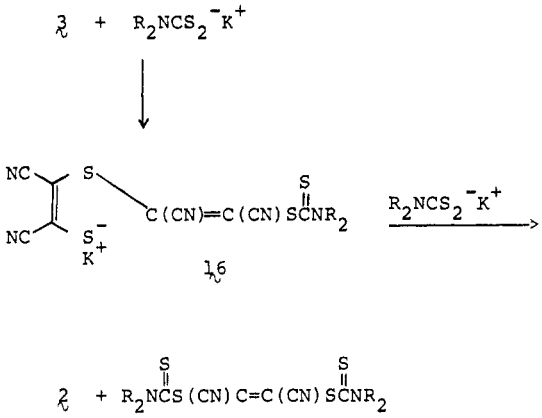


(7)

14 **15**

readily ring closes on treatment with acid to give 6-amino-2,3,4,5-tetracyanothieno[2,3-*b*]pyridine (**15**). The structure of **15** follows from elemental analysis, infrared and ^{13}C NMR (Table I) spectra, and mechanistic considerations.

Fragmentation Reactions. Another reaction mode of **3** is addition of 2 mol of nucleophile to a double bond followed by heterolytic fragmentation to a tetrasubstituted ethylene and dimercaptomaleonitrile ion. An example is provided by the reaction of **3** with excess potassium dialkyl dithiocarbamates in acetone which produces mixtures of bis[(dialkylthiocarboxy)thio]maleo- and -fumaronitriles **17**[8] (eq 8).



(8)

16

17

Reaction 8 was conducted with *N,N*-dimethyl- and *N,N*-diethyldithiocarbamate and 2,6-dimethyl-1-morpholine- and 1-piperidinecarbodithioate. The cis and trans isomers are generally separated readily by fractional crystallization. Their structures are assigned from infrared spectra (the nitrile absorption at 4.5–4.6 μm is strong in the cis and missing in the trans isomer). The pure isomer *cis*-**17** is synthesized unequivocally in good yield by the reaction of **2** with the appropriate dialkylthiocarbamyl chloride. The mode of addition of excess dialkyldithio-

(7) Robert D. Vest, U.S. Patent 3088968 (1963); *Chem. Abstr.*, **60**, 699*h* (1964).

(8) Robert D. Vest, U.S. Patent 3197472 (1965); *Chem. Abstr.*, **63**, 11576*g* (1965).

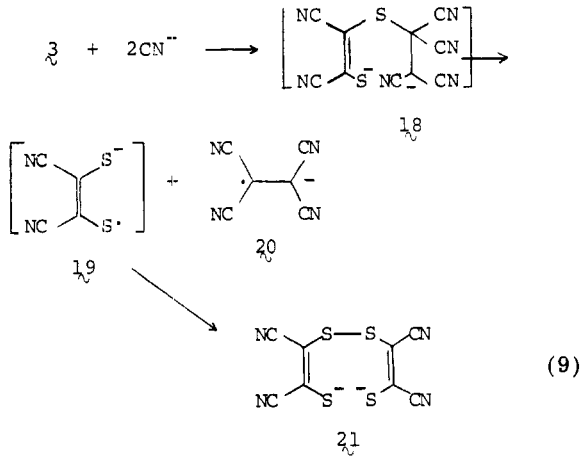
Table I. ^{13}C Chemical Shifts[a]

9	15	34	40	56
163.3	164.5	168.3	167.3	119.8
138.5	157.7	156.4	164.8	114.6
128.2	120.8	132.6	118.8	112.5
127.4	116.4	117.4 (2)	116.0	102.0
111.1	115.1	113.0	112.5	
110.8	113.1 (2)	111.8	112.1	
109.7	111.3	107.9	111.5	
108.7	111.0	105.0	110.5 (2)	
	110.3		107.8	
	96.2		103.0	

[a] Downfield from Me_4Si in parts per million, solvent Me_2SO-d_6, chromium acetylacetonate added as relaxation agent.

carbamate ion to 3 does not affect the product or yield. When a limited quantity (1 mol) of the nucleophile is used, however, the intermediate monoanion 16 can be isolated as its solid silver salt.

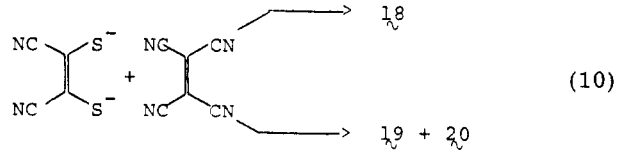
A homolytic mode of fragmentation involving the anion radical 19 has been observed following addition of 2 mol of cyanide to 3 (eq 9). This course of fragmentation is



(9)

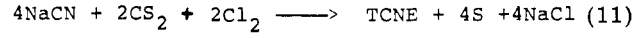
favored because 20 is a relatively stable anion radical. It is known that 19 is configurationally stable and rapidly dimerizes to *cis,cis*-bis(2-mercapto-1,2-dicyanovinyl) disulfide ion 21.[3,4]

At completion of the reaction with sodium or potassium cyanide in acetonitrile, the solution shows the strong characteristic ESR (nine lines with a spacing of 1.56 G)[10] and visible (complex absorption centered at 425 nm)[9] spectra of tetracyanoethylene anion radical 20. The dimerization 19 → 21 occurs too rapidly for 19 to be observed directly by spectral methods.[3] The disulfide salt 21 is characterized by its ultraviolet spectra (λ_{max} 382 nm). Strong evidence for this interpretation is provided by the observation that TCNE reacts with 2 to form a mixture that is identical in spectral and chemical aspects with that from the former process (eq 10). It is not known whether



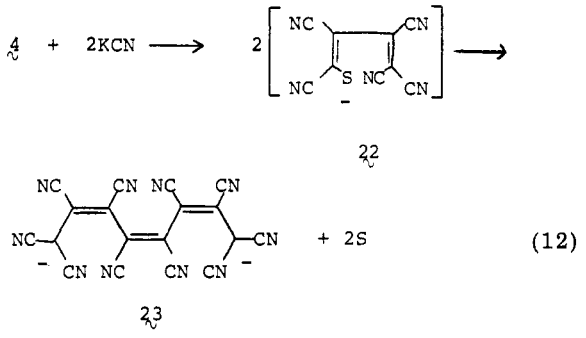
(10)

TCNE functions as a one-electron oxidant to form 19 directly or by addition to give 18 which subsequently fragments. The essential identity of the final mixtures from the independent reactions suggests, however, that 18 may be involved in both. Oxidation of the reaction mixture from sodium cyanide and dithiin 3 with chlorine gives moderate yields of TCNE and regenerated 3.[4] In effect, dithiin 3 (2 mol) yields TCNE (2 mol), and 3 (1 mol) is reformed. Since 3 is prepared from sodium cyanide, carbon disulfide, and chlorine, this route to TCNE is attractive for large-scale synthesis (eq 11).



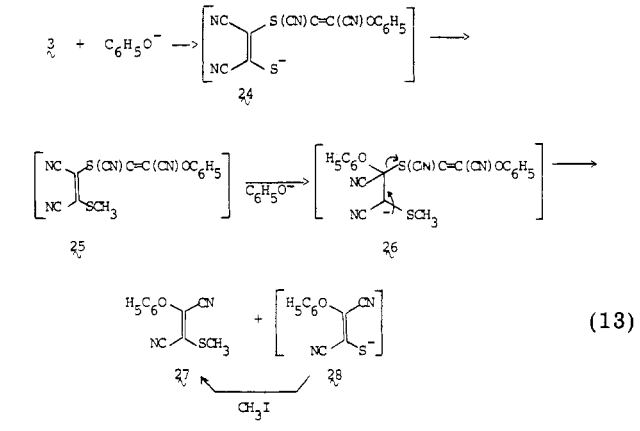
(11)

Potassium cyanide reacts with tetracyanothiophene in refluxing acetonitrile to yield a sulfur-free dipotassium salt (λ_{max} 512 nm, CH_3CN). On the basis of the analytical data and mechanistic considerations, structure 23 (or a stereoisomer) is assigned to this product. This unusual transformation can be interpreted in terms of ring opening of 4 by the nucleophilic cyanide ion to form anion 22, followed by dimerization with sulfur loss (eq 12). The latter reaction is quite analogous to the oxidative dimerization of sodium cyanodithioformate (1) with sulfur loss to yield Bähr's salt 2.[1-3]



(12)

Fragmentation of 3 can also be facilitated by alkylation of the first-formed thio anion which produces a neutral divinyl sulfide intermediate susceptible to further attack by nucleophiles. Thus, when 3 is treated with sodium phenoxide (2 mol) in THF in the presence of excess methyl iodide, 1-(methylthio)-2-phenoxyfumaronitrile (27) is isolated in 40% yield. The reaction probably proceeds through intermediates 24–26 and 28 which were not isolated (eq 13). Under the reaction conditions, 24 is rapidly

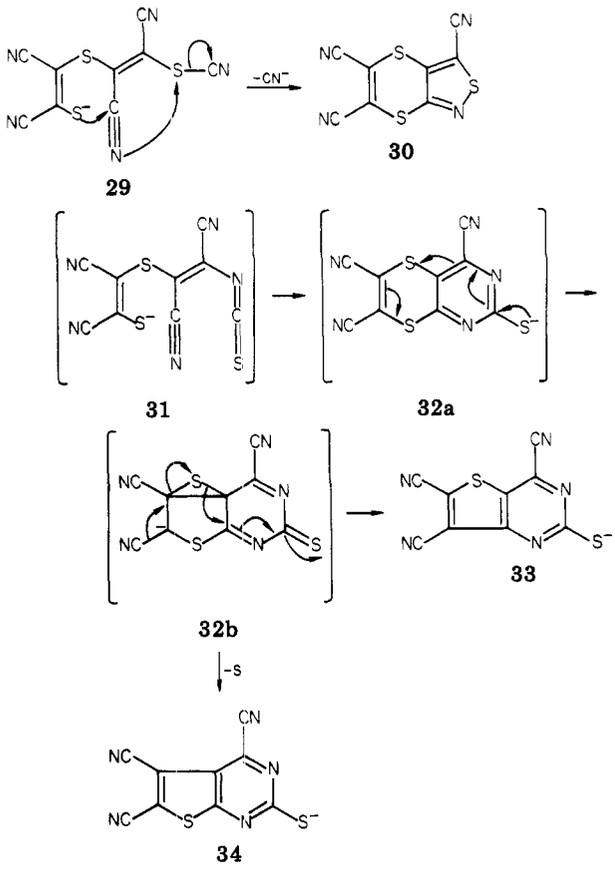


(13)

methylated, and the resulting divinyl sulfide (25) reacts primarily with a second mole of phenoxide ion at the double bond bearing the methylthio group to form intermediate 26. This mode of addition is expected to be favored, judging by the greater stabilization of carbanions by an adjacent methylthio group compared to a phenoxy group (the latter arising if addition occurred at the other double bond). Fragmentation followed by methylation

(9) O. W. Webster, W. Mahler, and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).
(10) W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

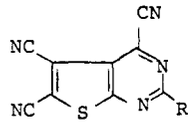
Scheme I



results in conversion of both double bonds of **3** to fumaronitrile **27**. Dithiin **3** can be thus considered a masked fumaronitrile. The product is homogeneous, and its structure was assigned primarily on the basis of the known stability of the fumaronitrile in related fumaro- and maleonitrile pairs.

Heterocyclic Systems. Perhaps the most important reactions of **3** or **4** with nucleophiles are those that lead to new heterocyclic ring systems. For example **3** reacts with thiocyanate ion to form a mixture of two heterocyclic compounds, tricyano-1,4-dithiino[*c*]isothiazole (**30**)[2] and 2-mercapto-4,5,6-tricyanothieno[2,3-*d*]pyrimdine (**34**). These products are postulated to arise in the manner shown in Scheme I. Sodium thiocyanate in THF functions as an ambient anion and adds to a double bond of **3** in both senses to give a mixture of vinyl thiocyanate and a vinyl isothiocyanate (not isolated). Intermediate **29** cyclizes rapidly to dithiinoisothiazole **30**. In the isomeric intermediate, there is no convenient leaving group, and yet cyclization occurs. The driving force is formation of the aromatic dithiinopyrimidine **32a** which cannot, however, be isolated. The mercaptide ion in **32a** is appropriately located to induce sulfur extrusion (**32a,b** → **34**). The product is the sodium salt of 2-mercapto-4,5,6-tricyanothieno[2,3-*d*]pyridimidine (**34**) which is isolated in 30% yield as the crystalline tetramethylammonium salt. The structure of **34** is based on mechanistic arguments, spectral data, and chemical behavior. The ^{13}C NMR spectrum of **34** exhibits eight peaks. Like **15** the ^{13}C resonance arising from two cyano groups on the thiophene ring occurs at the same chemical shift. The analysis clearly shows that a sulfur atom has been extruded. The ^{13}C NMR shows that the sulfur atom indicated in structure **32b** has been extruded. Structure **34** has two low-field peaks at δ 168.3 and 156.4 due to the ring-junction carbon with a sulfur atom on one side and a nitrogen on the other and the carbon between the two nitrogens on the pyrimidine ring. Compare this spectrum with that of the similar structure **15**. The alternative structure **33** would have only one low-field resonance as in **9**.

Methylation of **34** gives a crystalline *S*-methyl derivative **35** which loses methyl mercaptan when treated with strong base, proving that methylation occurs on sulfur. The *S*-methyl derivative **35** is a useful synthetic intermediate

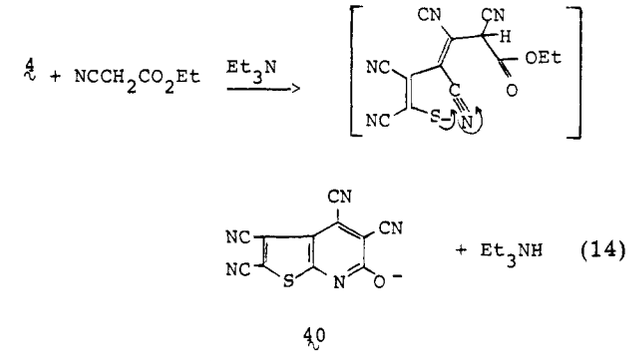


35, R = CH_3S
36, R = $(CN)_2C^-(CH_3)_4N^+$
37, R = C_6H_5NHNH
38, R = Br
39, R = p-$(CH_3)_2NC_6H_4$

by virtue of its susceptibility to attack by nucleophiles. Thus **35** reacts readily with sodium dicyanomethanide and with phenylhydrazine to give thiacyanocarbon anion **36** and the hydrazine **37**, respectively, with liberation of methyl mercaptan. Bromination of the sodium salt **34** gives the highly reactive 2-bromopyrimidine **38**, which condenses readily with aromatic amines to produce intense, highly colored dyes; for example, **38** and dimethylaniline gave **39** [λ_{max} 568 nm (ϵ 39 000)].

Thiocyanate forms a bright purple charge-transfer complex with **4**, but no reaction occurs even on prolonged reflux in acetonitrile.

A heterocyclic compound similar to **34** is produced by reaction of cyanoacetic ester with **4** (eq 14). The structure



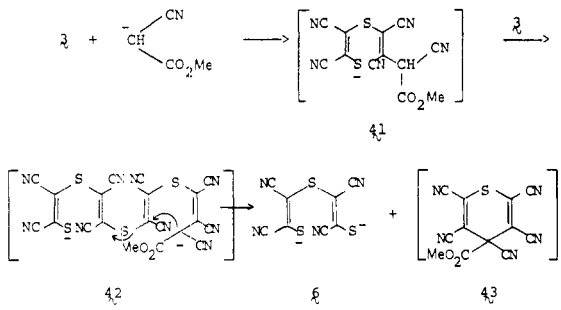
40 is based on its ^{13}C NMR spectrum, which compares nicely with those of **15** and **34** (Table I), and on its elemental analysis. The mechanism of its formation is no doubt similar to that for the formation of **15** and **34**.

Cyanocyclopentadiene Synthesis. The reaction of cyanoacetic ester with **3** takes a different course from that of its reaction with **4**. Pentacyanocyclopentadienide (**44**)[17] is produced in high yield. The isolation of **6** in equal amounts would seem to indicate the reaction is proceeding as shown in eq 15.

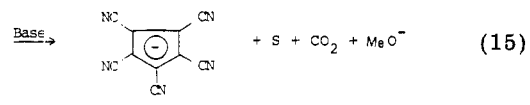
The role of the second mole of **3** is to remove the negative charge on the sulfur in **41** so that **42** can ring close. The base-catalyzed decarboxylation and sulfur extrusion of **43** is driven by the great stability of the polycyanocyclopentadienide ion.[11-13]

Malonic ester, methoxyacetic ester, and nitromethane undergo similar condensation reactions with **3** to give (methoxycarbonyl)tetracyanocyclopentadienide (**45**),

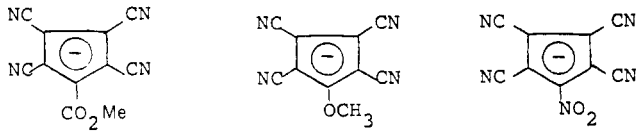
(11) O. W. Webster, *J. Am. Chem. Soc.*, 88, 4055 (1966).
(12) O. W. Webster, *J. Org. Chem.*, 32, 39 (1967).
(13) O. W. Webster, *J. Am. Chem. Soc.*, 88, 3046 (1966).



41 42 6 43



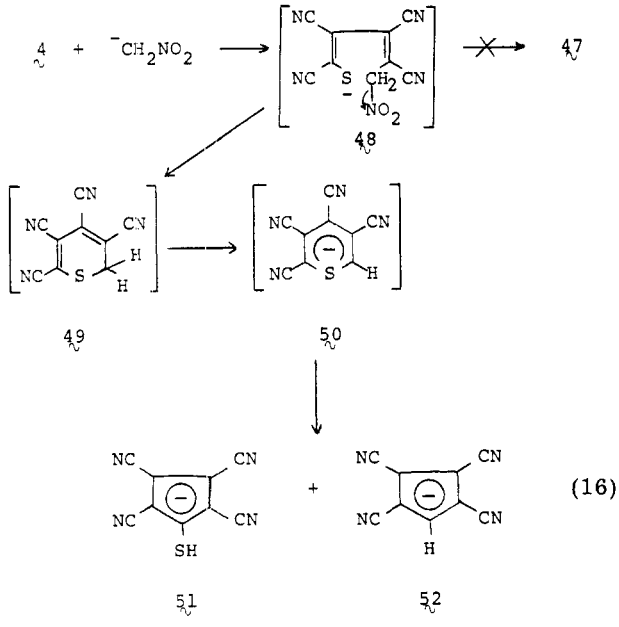
44 (15)



45 46 47

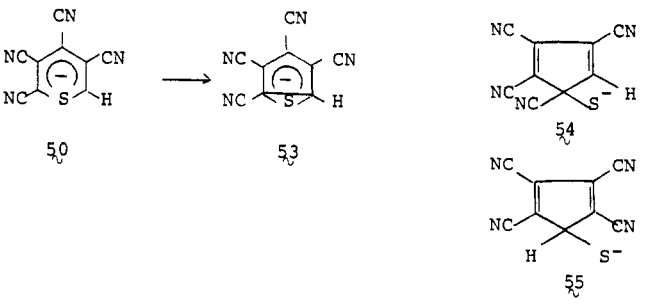
methoxytetracyanocyclopentadienide (**46**), and nitrotetracyanocyclopentadienide (**47**).[11,14] Since **6** can be converted back to **3** by various oxidizing agents, the overall process is an attractive route to tetracyanocyclopentadienide compounds.

Nitromethane anion reacts with **4** in refluxing acetonitrile to give, surprisingly, mercaptotetracyanocyclopentadienide ion (**51**)[11] as the major product along with tetracyanocyclopentadienide ion (**52**) in the ratio 85:15 (eq 16). It might have been expected that the nitrocyclo-



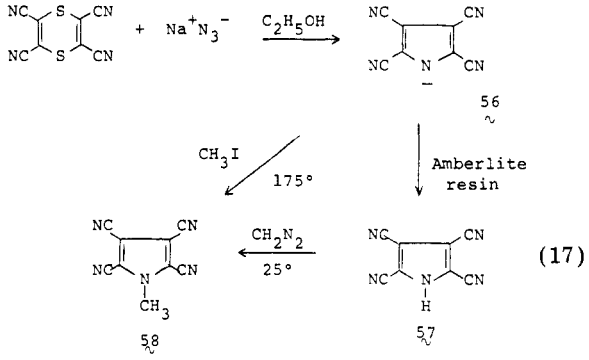
48 49 50 51 52 (16)

pentadienide ion **47** would be formed. A possible mechanism involves expulsion of nitrite ion from the ring-opened intermediate **48** to form the thiacyclohexadiene **49**, which would be converted to the dienide ion **50** under the conditions of the reaction. The dienide **50** is a reasonable precursor to the cyclopentadienides since it is a formal 8-π-electron monocycle that may undergo thermal disrotatory ring closure. The intermediate allyl anion **53** is expected to undergo facile aromatization. The unsymmetrical **53** can undergo thiirane ring opening to give both **54** and **55**. Sulfur extrusion from **54** then gives **52**, whereas a lower energy path is open to **55**, i.e., deprotonation–protonation to give **51** directly. The product ratio is in accord with this interpretation. Independent experiments establish that **51** does not arise from reaction of **52** with elemental sulfur in the presence of nucleophiles.



50 53 54 55

Tetracyanopyrrole.[15] Dithiin **3** undergoes a remarkable reaction with sodium azide in ethanol at 25 °C to form the sodium salt **56** of the previously unknown tetracyanopyrrole (**57**), the other products being elemental nitrogen and sulfur (eq 17). Another surprising feature of the reaction is that a small amount of pentacyanocyclopentadienide (**44**) is always produced.



56 58 57 (17)

Since the two ions are very similar in size and solubility, they cannot be separated by recrystallization. However, separations can be made by high-performance liquid chromatography. The pyrrole anion is most readily isolated as the tetramethylammonium salt in 72% yield. The colorless pyrrole anion **56** is a very weak base and forms crystalline salts with tetraalkylammonium and metal ions. Tetracyanopyrrole anion is also produced by treatment of tetracyanothiophene with ammonia.

The mechanism of the reaction of **3** with azide ion is not known and has not yielded readily to experiment. Clearly, several steps are involved in the transformation, and a variety of paths seem plausible. Tetracyanothiophene (**4**) is not an intermediate since it is inert to sodium azide under the conditions of reaction 17. The structure of **56** is confirmed by its ^{13}C NMR which has four resonances, two kinds of nitrile carbons and two kinds of ring carbons (Table I).

Tetracyanopyrrole (**57**) can be obtained by passing an acetonitrile solution of tetramethylammonium tetracyanopyrrolate through an Amberlite ion-exchange column

(14) O. W. Webster, U.S. Patent 3 591 619 (1971); *Chem. Abstr.*, **75**, 88199 (1971).

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(16) O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).

(17) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

(18) C. D. Weis, *J. Org. Chem.*, **27**, 3514 (1962).

(acid form). The free pyrrole is a colorless, crystalline solid, moderately soluble in water, whose aqueous solutions are very acidic (pK_a = 2.7). Methylation of tetracyanopyrrolate salts with methyl iodide at 175 °C gives *N*-methyltetracyanopyrrole (**58**) in low yields. A more convenient preparation is reaction of the free pyrrole **57** with diazomethane in acetonitrile/ether. The ultraviolet spectra of tetracyanopyrrolate ion, the free pyrrole, and the *N*-methyl derivative are very similar, suggesting that the π electrons are as extensively delocalized in the free pyrrole as in its anion.

Summary

Tetracyanodithiin and tetracyanothiophene undergo reaction with a wide variety of nucleophiles to provide facile synthetic routes to a number of compounds difficult to obtain by other means.

A related reaction of tetracyanodithian with sulfur under nucleophilic conditions is described in the following paper in this series.[19]

Experimental Section

All melting points are corrected. Infrared spectra were determined on a Perkin-Elmer Model 21 double-beam spectrometer using NaCl optics. The visible and ultraviolet spectra were obtained by means of a Cary Model 11 recording spectrometer. The ^{13}C NMR were obtained on a Bruker WH90, 22.63-MHz instrument. The ^1H NMR spectra were run on a Varian A60D. The multifunctional and reactive nature of thiacyanocarbons coupled with the nonvolatility of the ionic products makes purification a special problem. Therefore, some of the elemental analyses differ from the calculated values by more than the "satisfactory" ±0.4%.

Tetracyano-1,4-dithiin (3). The chlorine oxidation of sodium cyanodithioformate to give tetracyano-1,4-dithiin has been described.[2] The dithiin was recrystallized from ethylene dichloride as bright yellow crystals, mp 200–205 °C dec.

Conversion of 3 to 4 under Fluoride Ion Catalysis. Cesium fluoride (4.7 g, 32 mmol) was added over a period of 1 h to a solution of **3** (5.0 g, 23 mmol) in diglyme at 60 °C and then warmed to 90 °C for 1 h. The mixture was cooled, diluted with an equal volume of water, and filtered. The water-insoluble material was crystallized from benzene to give 1.76 g (41%) of tetracyanothiophene (mp 198 °C) characterized by a comparison of its infrared spectrum with that of authentic material.[2]

Bis(2-mercapto-1,2-dicyanovinyl) Sulfide (6). Reaction of 3 with Potassium Ethyl Xanthate. Tetracyanodithiin (10.8 g, 0.05 mol) in 200 mL of acetone was added over 0.5 h to 16.0 g (0.1 mol) of potassium ethyl xanthate in 500 mL of acetone. After 0.5 h of additional stirring, the solvents were removed in vacuo, and the residue was extracted several times with 50-mL portions of low-boiling petroleum ether under reflux. On evaporation to dryness, the petroleum ether extracts gave 6.1 g (58%) of the anhydro sulfide of ethyl xanthic acid (**7**),[20] mp 55 °C. Anal. Calcd for $C_6H_{10}O_2S_3$: C, 34.26; H, 4.79. Found: C, 34.11; H, 4.74. The petroleum ether insoluble residue (19 g) was dissolved in 300 mL of acetone and filtered to remove 2.21 g of insoluble material. The addition of 1 L of chloroform to the acetone solution gave 11 g (65%) of the dipotassium salt of bis(2-mercapto-1,2-dicyanovinyl) sulfide (**6**) as a yellow solid which melted with decomposition at 280–285 °C. The ^1H NMR of the methylated product shows this material to be a mixture of isomers. The infrared spectrum showed characteristic bands at 4.53 (C≡N) and 6.76 μm (C=C), and the ultraviolet spectrum showed λ_{max} (EtOH) 380 nm (ϵ 18400) and 218 (16950). Anal. Calcd for $C_8N_4S_3K_2$: C, 29.4; N, 17.2; S, 29.5. Found: C, 28.7; N, 17.3; S, 29.5.

Tetra-*n*-propylammonium Salt of 6. A solution of 6.26 g (0.02 mol) of tetra-*n*-propylammonium iodide in 100 mL of water was added slowly to an aqueous solution (100 mL) of 3.26 g (0.01 mol) of the dipotassium salt **6**. The solid (5.90 g, 95%, mp 160–196 °C) which precipitated was removed by filtration, dried, and recrystallized from ethanol to give bright orange crystals, mp 207–212 °C. Recrystallization from ethanol did not change the melting point. The infrared spectrum was consistent with the tetra-*n*-propylammonium salt of a cyanocarbon anion, and the ultraviolet spectrum showed λ_{max} (EtOH) 378 nm (ϵ 18940) and a shoulder at 220 nm (ϵ 16400). Anal. Calcd for $C_{32}H_{56}N_6S_3$: C, 61.99; H, 9.09. Found: C, 61.6; H, 8.92.

Dimethyl Derivative of 6. Methyl iodide (30 mL) was added at room temperature over 1 h to a suspension of 9.3 g (0.02 mol) of the finely ground silver salt of **6** in 200 mL of acetonitrile, and the mixture was then heated under reflux for 2.5 h. The color gradually became yellow. The insoluble material was removed by filtration, and the filtrate was evaporated to dryness. Recrystallization of the residue from methylene chloride/methylcyclohexane and ethanol/methylcyclohexane gave 3.72 g (67%) of the dimethyl derivative of **6**, which, on repeated recrystallization from ethyl ether/methylcyclohexane, gave an analytical sample, mp 123.0–123.5 °C. The infrared spectrum showed absorptions at 4.45, 4.50 (C≡N), 6.56, 6.64 (C=C), and 7.01, 7.54 μm (SCH_3), and the ultraviolet spectrum had λ_{max} (EtOH) 339 nm (ϵ 5250) and 200 (9500). Anal. Calcd for $C_{10}H_6N_4S_3$: C, 43.1; H, 2.16; S, 34.6. Found: C, 43.2; H, 2.39; S, 34.7.

Bis(tetrapropylammonium) 1,2,3,4-Tetracyano-1,3-butadiene-1,4-dithiolate (8). Reaction of 4 with Potassium Ethyl Xanthate. A solution of 1.84 g (10 mmol) of **4** and 3.20 g (20 mmol) of potassium ethyl xanthate in 200 mL of acetonitrile was heated under reflux for 4 h. The solution was evaporated to dryness, and the residue extracted with 100 mL of water. Tetrapropylammonium chloride (3.0 g, 13.5 mmol) was added to the extract to precipitate 1.62 g (28%) of bis(tetrapropylammonium)-1,2,3,4-tetracyanobutadiene-1,4-dithiolate (**8**). An analytical sample was recrystallized from ethanol: mp 197–198 °C dec; IR (KBr) 3.36, 3.46, 4.55, 4.60, 6.32, 6.8, 7.1, 7.2, 9.08, 9.7, 10.1, 10.3, 13.25 μm; λ_{max} (CH_2Cl_2) 280 nm (sh, ϵ 4570), 360 (8820), 447 (14700). Anal. Calcd for $C_{32}H_{56}N_6S_2$: C, 65.3; H, 9.6; N, 14.3; S, 10.9. Found: C, 65.2; H, 9.6; N, 14.3; S, 10.1.

3,4,5-Tricyanothieno[2,3-*c*]isothiazole (9). A solution of 0.59 g (1.00 mmol) of **8** in 50 mL of acetonitrile was treated with 0.05 mL (1 mmol) of bromine. After 2 h, the solution was concentrated to dryness, and the residue washed with water. The water-insoluble fraction was extracted with benzene, and the extract concentrated to dryness to give 100 mg (46%) of **9**: mp 155 °C dec (from cyclohexane); IR (Nujol) 2230, 1550, 1240, 1180, 1070, 945, 812 cm^{-1}; ^{13}C NMR (Me_2SO-d_6) δ 163.3, 138.5, 128.2, 127.4, 111.1, 110.8, 109.7, 108.7. Anal. Calcd for $C_8N_4S_2$: C, 44.5; N, 26.0. Found: C, 44.4; N, 26.1.

Dipotassium 2-Mercapto-1,2-dicyanovinyl 2-Hydroxy-1,2-dicyanovinyl Sulfide (11). Reaction of 3 with Potassium Acetate. A mixture of 10.8 g (0.05 mol) of **3** and 0.8 g (0.1 mol) of potassium acetate in 100 mL of THF was stirred at room temperature for 16 h during which time a yellow solid precipitated from the dark red solution. Dilution with an equal volume of ethyl acetate and filtration gave 11.05 g (71%) of a yellow solid (**11**). Reprecipitation of the yellow solid from acetone by addition of chloroform afforded an analytical sample of the yellow crystalline dipotassium 2-mercapto-1,2-dicyanovinyl 2-hydroxy-1,2-dicyanovinyl sulfide (**11**), mp 241–242 °C. Anal. Calcd for $C_8N_4S_2OK_2$: C, 31.0; S, 20.7. Found: C, 30.6; S, 20.6.

A small sample of the dipotassium salt was converted to the bis(tetra-*n*-propylammonium) salt by conventional techniques and twice recrystallized from isopropyl alcohol. An analytical sample melted at 203–204 °C. Anal. Calcd for $C_{32}H_{56}N_6S_2O$: C, 63.5; H, 9.33; S, 11.6. Found: C, 63.4; H, 9.38; S, 11.5.

Bis(tetramethylammonium) 2-Mercapto-1,2-dicyanovinyl 1,2,3,3-Tetracyanopropenido Sulfide (13). Reaction of 3 with Malononitrile. Sodium hydride in mineral oil (0.05 mol), malononitrile (3.3 g, 0.05 mol), and tetrahydrofuran (400 mL) were mixed in a predried flask under nitrogen. To the sodium salt that is formed was added 5.4 g (0.025 mol) of **3** dissolved in 50 mL of tetrahydrofuran over a perid of 0.5 h. The red solution was stirred for 10 min, and the solvents were removed under diminished pressure at room temperature to give an orange paste. The paste was dissolved in 100 mL of water and extracted with pe-

(19) S. A. Vladuchick, T. Fukunaga, H. E. Simmons, and O. W. Webster, *J. Org. Chem.*, following paper in this issue.

(20) G. Borony, B. W. Fulpins, and T. P. King, *J. Org. Chem.*, **43**, 2930 (1978).

troleum ether to remove mineral oil. The addition of an aqueous solution of 10.5 g (excess) of tetramethylammonium chloride precipitated 7.3 g (72%) of the crystalline bis(tetramethylammonium) 2-mercapto-1,2-dicyanovinyl 1,2,3,3-tetracyanopropenido sulfide (13), mp 210–212 °C. The ultraviolet spectrum showed λ_{max} (EtOH) 407 nm (ϵ 17 500), 215 (9200). Anal. Calcd for $C_{19}H_{24}N_8S_2$: C, 53.2; H, 5.65; N, 26.2; S, 15.0. Found: C, 53.0; H, 5.45; N, 25.5; S, 14.7.

Bis(tetra-*n*-propylammonium) 1,2,3,4,5,5-Hexacyano-1-mercaptopentadienediide (14). Reaction of 4 with Malononitrile. To a suspension of sodium hydride (4.8 g, 50% dispersion in mineral oil, 0.1 mol) in 150 mL of 1,2-dimethoxyethane at 0 °C was added 3.3 g (0.05 mol) of malononitrile. After hydrogn evolution had ceased, 9.1 g (0.0495 mol) of 4 was added. More hydrogen was given off, and a deep orange solution resulted. After 2 h the solvent was removed by distillation, the residue was dissolved in 100 mL of water, and 30 g (.135 mol) of tetra-*n*-propylammonium chloride was added. Orange 14 (23.8 g, 78%) precipitated and was recrystallized from methylene chloride–ether: mp 215 °C dec; UV λ_{max} 454 nm (ϵ 13 900), 354 (17 000); IR (KBr) 3.35, 3.45, 4.58, 6.6, 6.66, 6.77, 6.95, 7.0, 7.33, 9.05, 10.3, 13.2 μm. Anal. Calcd for $C_{35}H_{56}N_8S$: C, 67.7; H, 9.1; N, 18.1; S, 5.2. Found: C, 67.9; H, 8.8; N, 18.2; S, 5.2.

6-Amino-2,3,4,5-tetracyanothieno[2,3-*b*]pyridine (15). A solution of 14.0 g (22.5 mmol) of 14 in 300 mL of acetonitrile was treated with 100 mL of 6 N sulfuric acid and allowed to stand 1 h. Orange 15 (3.05 g, 54%) precipitated: mp >315 °C from acetonitrile; IR (KBr) 2.95, 3.0, 3.1, 4.45, 6.1, 6.35, 6.51, 6.7, 6.0, 6.65, 11.15, 12.95 μm; ^{13}C NMR (Me_2SO-d_6) δ 164.5, 167.7, 120.8, 116.4, 115.1, 113.1 (2 C, nitrile), 111.3 (nitrile), 111.0 (nitrile), 110.3, 96.2. Anal. Calcd for $C_{11}H_2N_6S$: C, 52.8; H, 0.8; N, 34.3; S, 12.8. Found: C, 52.8; H, 0.8; N, 33.8; S, 12.7.

1,2-Dicyanovinylene 1,2-Bis(dimethyldithiocarbamate) (17, R = CH_3). Reaction of 3 with Potassium *N,N*-Dimethyldithiocarbamate. A solution of 21.6 g (0.1 mol) of 3 in 400 mL of acetone was added slowly over 1.5 h to a stirred solution of 31.4 g (0.22 mol) of potassium dimethyldithiocarbamate in 500 mL of acetone. After an additional 1.5 h at room temperature, the solvents were removed in vacuo, and the resulting thick paste was extracted with 700 mL of hot benzene. Filtration removed 19.0 g (theory 21.8 g) of dipotassium dimercaptomaleonitrile, and concentration and cooling of the filtrate afforded 11.1 g (35%) of bis(1,2-dimethyldithiocarbamyl)-1,2-dicyanoethylene (17, R = CH_3) as a mixture of cis and trans isomers.

The yield of 17 was improved by the following modification. After the volatile material was removed from the reaction mixture, the thick paste was poured with vigorous stirring into 2 L of water to give 22.5 g (71%) of 17, mp 141.0–141.5 °C. An analytical sample (mp 164–165 °C) was prepared by recrystallization from benzene. The infrared spectrum showed absorptions at 3.42 (CH), 4.5 (very weak, C≡N), and 6.60 μm (C=C), and the ultraviolet spectrum showed λ_{max} (EtOH) 236 nm (ϵ 24 070) and 277 (17 800) and shoulders at 300 nm (ϵ 6300) and at 400 nm (ϵ 2035).

An authentic cis sample of 17 was prepared in the following manner. A solution of 12.3 g (0.1 mol) of dimethylthiocarbamyl chloride in 50 mL of acetonitrile was added over 30 min to a stirred suspension of 9.3 g (0.05 mol) of 2 in 100 mL of acetonitrile at 0 °C. The mixture was allowed to warm to room temperature and was then heated at 40–50 °C for 2 h. After the mixture cooled, the insoluble material was removed by filtration, washed well with water, and recrystallized from benzene to give 5.97 g (37.5%) of a yellow solid, mp 161–162 °C. The infrared spectrum of this compound was essentially identical with that of the ethylene isolated from the reaction of 3 and potassium dimethyldithiocarbamate. The filtrate from the above mixture on evaporation to dryness and crystallization from benzene gave a 1.22 g of yellow crystals (mp 149–154 °C) whose infrared was very similar except for a stronger C≡N absorption. It was evident from the infrared spectra that the product was a mixture of cis and trans isomers.

1,2-Dicyanovinylene 1,2-Bis(diethyldithiocarbamate) (17, R = C_2H_5). A solution of 4.32 g (0.02 mol) of 3 in 100 mL of acetone was added dropwise to a stirred solution of 9 g (0.04 mol) of sodium diethyldithiocarbamate in 100 mL of acetone over 0.5 h. After the mixture was stirred for an additonal hour, the solvent was removed and the residue extracted with refluxing benzene for 4 h. The insoluble residue was discarded. The benzene solution, on concentration and dilution with 10 mL of ethanol, afforded 4.05 g (55%) of bright orange 17 (R = C_2H_5), mp 106–108 °C. An analytical sample (from ethyl ether) melted over a wide range (119.5–128.0 °C) and was apparently a mixture of isomers. The infrared spectrum was, in general, similar to that of the methyl analogue, and the ultraviolet spectrum showed λ_{max} (EtOH) 241 nm (ϵ 21 032) and 280 (16 900) and shoulders at 390 nm (ϵ 2920) and 325 (6250). Anal. Calcd for $C_{14}H_{20}N_4S_4$: C, 45.1; H, 5.4; N, 15.0; S, 34.4. Found: C, 45.5; H, 5.78; N, 15.0; S, 34.4.

1,2-Dicyanovinylene 1,2-Bis(2,6-dimethylmorpholine-1-carbodithioate). The 2,6-dimethylmorpholine derivative was prepared in 69.5% yield by the procedure described above and was separated into cis and trans isomers by fractional crystallization; the trans isomer had a melting point of 160–163 °C. The infrared spectrum showed almost no absorption at 4.5 or 6.4 μm for C≡N and C=C but otherwise was very similar to that of the cis isomer. The ultraviolet spectrum showed λ_{max} (EtOH) 450 nm (ϵ 3190), 372 (6750) and 250 (6850). Anal. Calcd for $C_{18}H_{24}O_2N_4S_4$: C, 47.4; H, 5.30. Found: C, 47.9; H, 5.41. The cis isomer had a melting point of 147–151 °C. The infrared spectrum showed a strong absorption at 4.58 (C≡N) and 6.35 μm (C=C). The ultraviolet spectrum showed λ_{max} (EtOH) 388 nm (ϵ 7050) and 264 (14 750).

1,2-Dicyanovinylene 1,2-Bis(piperidine-1-carbodithioate). This ethylene was prepared in 72% yield in a similar manner and melted at 199–202 °C after recrystallization from toluene. Anal. Calcd for $C_{16}H_{20}N_4S_4$: C, 54.5; H, 3.66. Found: C, 55.0; H, 3.38.

Tetracyanoethylene Anion Radical (20). Reaction of 3 with Potassium Cyanide. Under a nitrogen atmosphere, a suspension of 1.68 g (0.025 mol) of potassium cyanide in 50 mL of acetonitrile was added over a 5-min period to a stirred solution of 2.16 g (0.01 mol) of 3 in 200 mL of acetonitrile containing 2.0 mL of water. The cyanide dissolved in a few minutes, giving a dark solution. The ESR spectrum (nine-line pattern with a spacing of 1.6 G) and visible spectrum (characteristic fine structure centered around 425 nm) indicated a high concentration of tetracyanoethylene ion radical (20).[16] The reaction mixture was cooled to −5 °C, and gaseous chlorine was added slowly by means of a gas-inlet tube until the dark brown color was replaced by a light yellow solution containing suspended potassium chloride and sulfur. After removal of the inorganic solids (1.71 g) by filtration and the solvents by evaporation under diminished pressure, the residue was sublimed at 100–200 °C (0.1 torr) to obtain 0.307 g of tetracyanoethylene (24%) characterized by its color reactions with *N,N*-dimethylaniline[17] and with anthracene.

Bis(tetraethylammonium) 1,1,2,3,4,5,6,7,8,8-Decacyanooctatriene-1,8-diide (23). Reaction of 4 with Potassium Cyanide. A solution of 5.00 g (27.1 mmol) of 4 in 50 mL of acetonitrile was added in a slow stream to a suspension of 5.00 g (76 mmol) of potassium cyanide in 100 mL of acetonitrile under reflux. After 16 h the mixture was filtered, and the filtrate was concentrated to dryness. The residue was chromatographed on alumina with acetonitrile as eluant. The red second band was dissolved in water and was treated with excess tetraethylammonium chloride to give 3.06 g (18%) of insoluble bis(tetraethylammonium) 1,1,2,3,4,5,6,7,8,8-decacyanooctatriene-1,8-diide (23): mp 273–275 °C (from CH_3CN and then 1,2-dichloroethane); IR (KBr) 3.34, 4.55, 6.73, 6.86, 7.20, 7.81, 8.55, 10.0 and 12.76 μm; UV (CH_3CN) λ_{max} 512 nm (ϵ 17 600) 400 (18 800), 348 (8500), 298 (45 800). Anal. Calcd for $C_{34}H_{40}N_{12}$: C, 66.2; H, 6.5; N, 27.3. Found: C, 66.0; H, 6.6; N, 27.4.

1-(Methylthio)-2-phenoxydicyanoethylene (27). Reaction of 3 with Sodium Phenoxide. Under anhydrous conditions, a solution of sodium phenoxide was prepared from 1.9 g (0.02 mol) of phenol and 1.0 g (0.02 mol) of a 50% sodium hydride dispersion in 100 mL of dry tetrahydrofuran. A solution of 2.2 g (0.01 mol) of 3 in 25 mL of tetrahydrofuran was added rapidly through a dropping funnel at 34–40 °C. The mixture was stirred for 15 min, and 30 mL of methyl iodide was added. After the mixture was heated under reflux for 3.5 h, the solvent was removed at room temperature and the residue extracted with hot chloroform (100 mL). After an activated carbon treatment and filtration, the chloroform solution was diluted with petroleum ether and cooled overnight. Crystalline 1-(methylthio)-2-phenoxydicyanoethylene (27; 1.7 g, 39.5%, mp 183–186 °C) was collected in two crops. The ultraviolet spectrum has λ_{max} 317 nm (ϵ 1570) and 220 (920). Anal.

Calcd for $C_{11}H_3OSN_2$: C, 61.2; H, 3.73; N, 13.0; S, 14.9. Found: C, 61.2; H, 3.69; N, 12.5; S, 15.0.

Tetramethylammonium 2-Mercapto-4,5,6-tricyanothieno[2,3-*d*]pyrimidine (34). Reaction of 3 with Sodium Thiocyanate. A solution of 2.43 g (0.03 mol) of sodium thiocyanate in 200 mL of dry tetrahydrofuran was added to a solution of 6.48 g (0.03 mol) of **3** dissolved in 100 mL of tetrahydrofuran, and the mixture was stirred at room temperature for 1 h. Removal of the solvent from the deep orange-brown solution gave an orange solid, which was stirred for 30 min with 100 mL of water. The water-insoluble material was removed by filtration and characterized as a mixture of 0.9 g of **30**[2] and 0.4 g of sulfur. The aqueous filtrate was divided into two portions.

One portion (25 mL) of the aqueous filtrate was treated with excess tetramethylammonium chloride, and the yellow solid which precipitated was collected, dried, and recrystallized from methanol. There was obtained 0.72 g (30%) of tetramethylammonium 2-mercapto-4,5,6-tricyanothieno[2,3-*d*]pyrimidine (**34**) as yellow needles, mp 293–294 °C. The infrared spectrum had absorptions at 4.5 (CN), 6.73, 6.83 (C=CS and/or C=N), and 10.55 μm (Me_4N^+), and the ultraviolet spectrum showed 7 maxima, the strongest of which were 438 nm (ε 18 300) and 241 (22 900); ^{13}C NMR (Me_2SO-d_6) δ 168.3, 156.4, 132.6, 117.4 (2 C, nitrile), 113.0, 111.8, 107.9, 105.0. Anal. Calcd for $C_{13}H_{12}N_6S_2$: C, 49.3; H, 3.83; S, 20.3. Found: C, 49.5; H, 3.67; S, 20.5.

The remainder of the aqueous solution containing **34** was heated with 6.7 g (excess) of dimethyl sulfate for 3 h, and the yellow solid was collected, dried, and recrystallized from methanol to obtain 3.54 g (54%) of yellow-brown 2-(methylthio)-4,5,6-tricyanothieno[2,3-*d*]pyrimidine (**35**), mp 150–152 °C. The infrared spectrum had absorptions at 4.50 (CN), 6.60, 6.70 (C=CS and/or C=N) and 7.04, 754 μm (SCH_3). The ultraviolet spectrum exhibited absorption maxima at 287 nm (ε 8000), 3.87 (21 000), and 401 (20 000). Repeated crystallizations from methanol gave a yellow solid which melted at 151–152 °C but was not analytically pure. Chromatography on acid-washed alumina gave the bright yellow **35** as hexagonal plates, mp 151–152 °C. Anal. Calcd for $C_{10}H_3N_5S_2$: C, 46.7; H, 1.17; N, 27.2; S, 24.9. Found: C, 46.5; H, 1.4; N, 26.3; S, 24.8.

Tetramethylammonium 2-Dicyanomethyl-4,5,6-tricyanothieno[2,3-*d*]pyrimidinide (36). To a tetrahydrofuran solution (50 mL) of sodium dicyanomethanide (0.44 g, 5 mmol) was added 128 g (5 mmol) of **35** in 20 mL of tetrahydrofuran. The solution turned deep red and methyl mercaptan evolved. After the mixture was stirred overnight, the solvents were removed, and 30 mL of water was added. On addition of 0.6 g of tetramethylammonium chloride, 1.05 g (58.5%) of **36** precipitated. The product was purified by dissolution in ethyl acetate and precipitation with ether. The red needles thus obtained melted at 218–220 °C: IR 4.55, 4.57, 6.74, 6.95, 10.59 μm; UV λ_{max} 487 nm (ε 38 600). Anal. Calcd for $C_{16}H_{12}N_8S$: C, 55.2; H, 3.48; N, 32.2; S, 9.20. Found: C, 55.8; H, 3.63; N, 32.0; S, 9.28.

2-(2-Phenylhydrazino)-4,5,6-tricyanothieno[2,3-*d*]pyrimidine (37). A solution of 1.29 g (5 mmol) of **35** in 100 mL of ethanol was heated to reflux temperature, and 0.54 g (5 mmol) of phenylhydrazine in 10 mL of ethanol was added dropwise. Methyl mercaptan evolved, and after an additional 20 min, the solution was cooled in ice. Tan crystals of **37** (1.24 g, 78%) formed and were recrystallized from ethanol: mp 236–237 °C, resolidified and melted at 241–242 °C; IR 2.93, 3.02, 4.50, 6.20, 6.49, 6.70, 13.05, 14.45 μm. Anal. Calcd for $C_{15}H_7N_7S$: C, 56.8; H, 2.24; N, 30.9; S, 10.1. Found: C, 57.36; H, 2.44; N, 30.3; S, 10.2.

2-Bromo-4,5,6-tricyanothieno[2,3-*d*]pyrimidine (38). An aqueous solution (35 mL) of **34** was prepared as described above from 0.81 g (10 mmol) sodium thiocyanate and 2.16 g (10 mmol) of **3**. Bromine was added to the solution until an excess was present. Tan **38** (2.38 g, 82%) precipitated and was collected by filtration, dried, and recrystallized from methylene chloride: mp 219–220 °C; IR 4.46 (CN), 6.41, 6.76 (C=N or C=C); UV λ_{max} 253 nm (ε 15 700), 315 (sh, 9750), 330 (13 200), 346 (12 000). Anal. Calcd for C_9N_5BrS: C, 37.2; N, 24.1; S, 11.1; Br, 27.6. Found: C, 37.3; N, 23.7; S, 11.4; Br, 27.6.

2-[*p*-(*N*,*N*-Dimethylamino)phenyl]-4,5,6-tricyanothieno[2,3-*d*]pyrimidine (39). A suspension of 0.58 g (2 mmol) of **38** in 30 mL of ethanol was stirred at 35–45 °C, and a solution of 0.36 g (3 mmol) of *N*,*N*-dimethylaniline in 10 mL of ethanol was added dropwise over 15 min. The solution turned purple, and solid product began to crystallize. After an additional 30 min at 40 °C, the mixture was heated at reflux for 5 min and was cooled in ice. Purple needles of **39** (0.40 g, 61%) formed; mp 270–272 °C. After repeated recrystallizations from ethanol and then ethyl acetate, the melting point was found to be 275–276 °C. The elemental analysis indicates the presence of an impurity with higher carbon and lower nitrogen content than **39**: λ_{max} 568 nm (ε 39 000), 330 (6500), 307 (7150), 256 (15 200). Anal. Calcd for $C_{17}H_{10}N_6S$: C, 61.8; H, 3.05; N, 25.4; S, 9.70. Found: C, 62.6; H, 3.26; N, 23.9; S, 9.74.

6-Hydroxy-2,3,4,5-tetracyanothieno[2,3-*b*]pyridine (40) Triethylammonium Salt. Reaction of 4 with Ethyl Cyanoacetate. A solution of 1.84 g (10 mmol) of **4** and 1.13 g (10 mmol) of ethyl cyanoacetate in 50 mL of 1,2-dichloroethane was treated with 2.00 g (20 mmol) of triethylamine at room temperature. After the mixture was allowed to stand overnight, 1.67 g (47%) of yellow-green **40** was collected and recrystallized from 1-chlorobutane; mp 174–175 °C. Anal. Calcd for $C_{17}H_{16}N_6OS$: C, 58.0; H, 4.58; N, 23.9. Found: C, 58.3; H, 5.03; N, 23.5. A small amount of the above salt was dissolved in hot water and treated with tetra-*n*-propylammonium chloride, and when the solution cooled the tetra-*n*-propylammonium salt of **40** crystallized. A sample was recrystallized from 1-chlorobutane: mp 159.5–161 °C; ^{13}C NMR (Me_2SO-d_6; Pr_4N^+ not given) δ 167.3, 164.8, 118.8, 116.0, 112.5, 112.1, 111.5, 110.5 (2 C), 107.8, 103. Anal. Calcd for $C_{23}H_{28}N_6OS$: C, 63.3; H, 6.47; N, 19.3. Found: C, 63.3; H, 6.50; N, 19.0.

Tetraethylammonium Pentacyanocyclopentadienide (44). Reaction of 3 with Methyl Cyanoacetate. To a suspension of sodium hydride (0.8 g, 20 mmol, of 60% dispersion in mineral oil) in 70 mL of 1,2-dimethoxyethane at 0 °C was added 0.99 g (10 mmol) of methyl cyanoacetate. After hydrogen evolution had ceased, 2.16 g (10 mmol) of **3** was added, and the mixture was stirred at room temperature until hydrogen evolution had again ceased (about 2 h). The mixture was then heated under reflux for 3 h, cooled, and concentrated to dryness under reduced pressure. The residue was extracted with 108 mL of water, and the extract treated with 1.65 g (10 mmol) of tetraethylammonium chloride. Light yellow **44** (1.58 g, 99%) precipitated and was purified by being dissolved in 50 mL of cold concentrated nitric acid. Compound **44** was reprecipitated with ice–water and was recrystallized from ethanol; mp 355–358 °C. The IR of the product was identical with that of the product prepared from diazotetracyanocyclopentadiene and cuprous cyanide.[11]

The filtrate remaining after the collection of the crude **44** was treated with 2.21 g (10 mmol) of tetra-*n*-propylammonium chloride to precipitate 2.71 g (87%) of **6**. The IR was identical with that of **6** prepared from **3** and potassium ethyl xanthate.

Tetraethylammonium (Methoxycarbonyl)tetracyanocyclopentadienide (45). The above procedure for preparing **44** was repeated with 1.32 g (10 mmol) of dimethyl malonate and 2.16 g (10 mmol) of **3** to give 1.32 g (57%) of **45**. An analytical sample (mp 142–143 °C) was recrystallized from ethanol: IR (KBr) 2.75, 3.3, 3.58, 4.49, 5.83, 6.23, 6.90, 7.0, 7.16, 7.28, 7.90, 8.40, 8.51, 8.95, 9.48, 9.99, 11.90, 12.25 μm. Anal. Calcd for $C_{19}H_{23}N_5O_2$: C, 64.6; H, 6.56; N, 19.8. Found: C, 64.3; H, 6.69; N, 19.8.

Tetraethylammonium Methoxytetracyanocyclopentadienide (46). The above procedure for preparing **44** was repeated with 2.6 g (25 mmol) of methyl methoxyacetate and 10.8 g (50 mmol) **3** to give 3.33 g (41%) of **46**. An analytical sample was recrystallized from water: mp 148–151 °C; ^1H NMR (CD_3CN) δ 4.0 (s, OMe); IR (KBr) 3.3, 4.53, 5.83, 6.60, 6.75, 7.0, 7.16, 7.37, 8.14, 8.53, 9.53, 9.99, 11.28, 12.75, 14.55 μm. Anal. Calcd for $C_{18}H_{23}N_5O$: C, 66.4; H, 7.12; N, 21.5. Found: C, 66.1; H, 7.04; N, 21.8.

Tetraethylammonium Nitrotetracyanocyclopentadienide[11] (47). A suspension of 12.5 g (0.15 mol) of sodium nitromethide (from nitromethane and sodium methoxide in methanol) in 1 L of tetrahydrofuran was cooled to −70 °C, and a solution of 10.8 g (0.05 mol) of **3** in 500 mL of tetrahydrofuran was added in a slow stream. The reaction mixture was slowly warmed. At −20 °C it turned deep red. After 1 h at room temperature, the mixture was filtered, and the filtrate was concentrated to dryness. The residue which remained (19.1 g) was dissolved in 1400 mL of water, and a solution of 20 g (0.12 mol) of tetraethylammonium chloride

in 100 mL of water was added over 20 min. Tetraethylammonium nitrotetracyanocyclopentadienide (47; 8.02 g, 94%) crystallized. The IR of product was identical with that of the product prepared from diazotetracyanocyclopentadiene and sodium nitrite.

To the filtrate was then added 30 g (0.11 mol) of tetra-*n*-propylammonium bromide in 100 mL of water. Bis(tetrapropylammonium) bis(2-mercapto-1,2-dicyanovinyl) sulfide (6; 13.38 g, 86%) was isolated.

Tetraethylammonium Mercaptotetracyanocyclopentadienide (51). Reaction of 4 with Nitromethanide. A suspension of 2.4 g (0.10 mol) of sodium hydride (from a 60% mineral oil dispersion) in 500 mL of tetrahydrofuran was treated with 4.44 mL of methanol and heated under reflux to generate sodium methoxide. At room temperature, 6.0 g (0.10 mol) of nitromethane was added and the mixture again refluxed a few minutes. The reaction mixture was concentrated to 100 mL to remove methanol and then diluted with 500 mL of tetrahydrofuran and cooled to −75 °C. Tetracyanothiophene (9.2 g, 0.050 mol) was added, and the temperature was allowed to come to room temperature. The deep red solution was stirred overnight and was concentrated to dryness. The residue was extracted with 200 mL of water, and 10 g (0.060 mol) of tetraethylammonium chloride was added to the extract. The crude **51** which precipitated (11.86 g) was shown to contain 15% tetracyanocyclopentadienide (**52**)[11] by ^{1}H NMR (ArH at δ 6.76 integrated against Et_4N^+); thus the yield of **51** was 62%. The IR of the product, recrystallized from ethanol, was identical with **51** prepared from diazotetracyanocyclopentadiene and potassium xanthate.[11]

Tetramethylammonium Tetracyanopyrrolide (56). Reaction of 3 with Sodium Azide. Tetracyanodithiin (10.8 g, 0.05 mol), sodium azide (3.25 g, 0.05 mol), and 200 mL of ethanol were mixed and stirred overnight, while nitrogen was slowly evolved. The dark red reaction mixture was filtered to remove 1.15 g of elemental sulfur, and the filtrate was evaporated to dryness under reduced pressure. Water (200 Ml) was added, and 1.1 g of a brown solid which contained appreciable amounts of elemental sulfur was removed by filtration. The aqueous filtrate was decolorized with "Darco" and stirred at 0 °C, while 11 g of tetramethylammonium chloride was added as a saturated aqueous solution. Reddish brown tetramethylammonium pyrrolide (**56**; 7.25 g, 62.5%) was removed by filtration, washed with water, and dried under reduced pressure. An analytical sample (from isopropyl alcohol) melted at 282–283 °C: IR of 4.52 (C≡N), 6.78 and 6.90 (C=C/C=N), 3.33, 6.76, 10.55 (tetramethylammonium) and 9.33 μm; UV (EtOH) λ_{max} 268 nm (ϵ 10800), 254 (10400), 235 (38600), 227 (31900). In comparison, tetracyanofuran[18] has ultraviolet absorptions at 310 nm (ϵ 33700), 258 (12400), and 220 (23400). Tetracyanothiophene[2] has the following: λ_{max} (EtOH) 281 nm (ϵ 10850), 239 (24600); ^{13}C NMR (Me_2SO-d_6) δ 119.8, 114.6, 112.5, 102.0. Anal. Calcd for $C_{12}H_{12}N_6$: C, 60.0; H, 5.04; N, 35.0. Found: C, 61.2; H, 5.14; N, 34.3. High-pressure LC analysis showed the sample was contaminated with tetramethylammonium pentacyanocyclopentadienide.

Tetramethylammonium Tetracyanopyrrolide (56). Reaction of 3 with Ammonia. To a solution of 2.16 g (10 mmol) of **3** in 25 mL of tetrahydrofuran at 0 °C were added 0.33 mL (5 mmol) of concentrated ammonium hydroxide and 1.5 mL of triethylamine. The red solution which formed was allowed to stir at room temperature overnight and was concentrated to dryness. The residue was extracted with 100 mL of water, and the extract was treated with 3 g of tetramethylammonium chloride to precipitate 0.21 g (13%) of **56**. After recrystallization from 2-propanol, the melting point was 280 °C, and the IR and UV were the same as those of the material prepared from **3** and sodium azide.

Tetracyanopyrrole (57). A column containing 200 g of Amberlite IR-120H ion-exchange resin which had been thoroughly washed with acetonitrile was prepared. A solution of 1.94 g of tetramethylammonium tetracyanopyrrolate in 25 mL of acetonitrile was slowly added to the top of the column while acetonitrile was removed from the bottom. The free pyrrole was eluted with acetonitrile and the eluant evaporated to dryness under a stream of dry nitrogen. The residue was sublimed at 0.1 torr (200 °C) to give an off-white solid which melted with decomposition at 193–209 °C. Resublimation did not change the melting point: IR 3.15 (NH), 6.38, 6.69 (C=C/C=N), 4.45 μm (C≡N); UV (EtOH) λ_{max} 269 nm (ϵ 10500), 236 (37000). Another sample of tetracyanopyrrole (**57**) was conveniently purified by recrystallization from methylene chloride as tan crystals, mp 202–212 °C dec. The isolated yield was about 20%. Anal. Calcd for C_8HN_5: C, 57.5; H, 0.60; N, 41.9; neutralization equivalent 167. Found: C, 57.4; H, 0.88; N, 41.7; neutralization equivalent 170.0; pK_a = 2.7 (water).

***N*-Methyltetracyanopyrrole (58).** Tetramethylammonium tetracyanopyrrolate (2.40 g, 0.01 mol) was acidified in acetonitrile as described in the above section. The eluant was added slowly to a solution of about 0.02 mol of diazomethane and the resulting solution allowed to stand overnight. Removal of the solvent gave a semicrystalline mass which was recrystallized several times from methylene chloride/methyl cyclohexane to afford off-white crystals of *N*-methyltetracyanopyrrole (**58**): mp 186–188.5 °C; overall yield 0.45 g (25%); IR 3.4, 3.55 (CH), 4.46 (C≡N), 6.65 μm (C=C, C=N), but no absorption at 3.14 (NH); UV (EtOH) λ_{max} 262 nm (ϵ 11000), 283 (2850, sh), 230 (34500), 223 (35500). Anal. Calcd for $C_9H_3N_5$: C, 59.7; H, 1.67; N, 38.7; mol wt 181. Found: C, 59.6; H, 1.95; N, 40.5; mol wt 176 (ethylene dichloride).

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Registry No. **1**, 33498-03-2; **2**, 18820-77-4; **3**, 2448-55-7; **4**, 4506-96-1; **6** bis(tetra-*n*-propylammonium) salt, 75111-66-9; **6** dimethyl derivative, 75111-67-0; **6a**/**6b**, 75111-68-1; **7** (R = C_2H_5), 2905-52-4; **8**, 75111-70-5; **9**, 75111-71-6; **11** bis(tetra-*n*-propylammonium) salt, 75111-73-8; **11** dipotassium salt, 75111-74-9; **13**, 75111-76-1; **14**, 75111-78-3; **15**, 75111-79-4; *cis*-**17** (R = CH_3), 75111-80-7; *trans*-**17** (R = CH_3), 75111-81-8; *cis*-**17** (R = C_2H_5), 75111-82-9; *trans*-**17** (R = C_2H_5), 75111-83-0; **17** (R_2 = $CH_2CH(CH_3)OCH(CH_3)CH_2$), 75111-84-1; **17** ($R_2$ = $(CH_2)_5$), 3438-41-3; **20**, 670-54-2; **23**, 75111-86-3; **27**, 75111-87-4; **30**, 4656-27-3; **34**, 75125-10-9; **35**, 75125-11-0; **36**, 75125-13-2; **37**, 75111-88-5; **38**, 75111-89-6; **39**, 75111-90-9; **40** triethylammonium salt, 75111-92-1; **40** tetra-*n*-propylammonium salt, 75111-94-3; **44**, 75149-54-1; **45**, 75149-56-3; **46**, 75149-58-5; **47**, 75149-60-9; **51**, 75149-62-1; **52**, 75149-64-3; **56**, 49719-48-4; **57**, 5231-17-4; **58**, 5217-34-5; potassium ethyl xanthate, 140-89-6; potassium acetate, 127-08-2; malononitrile, 109-77-3; potassium dimethyldithiocarbamate, 128-03-0; dimethylthiocarbamyl chloride, 16420-13-6; sodium diethyldithiocarbamate, 148-18-5; tetracyanoethylene, 670-54-2; sodium phenoxide, 139-02-6; sodium thiocyanate, 540-72-7; sodium dicyanomethanide, 20334-42-3; phenylhydrazine, 100-63-0; *N*,*N*-dimethylaniline, 121-69-7; ethyl cyanoacetate, 105-56-6; methyl cyanoacetate, 105-34-0; dimethyl malonate, 108-59-8; methyl methoxyacetate, 6290-49-9; sodium nitromethide, 25854-38-0; sodium azide, 26628-22-8.