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# Thiacyanocarbons. III. Mechanism of the Oxidation of Disodium Dimercaptomaleonitrile to Tetracyano-1,4-dithiin

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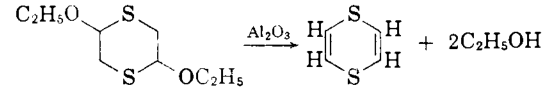
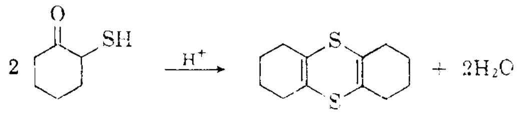
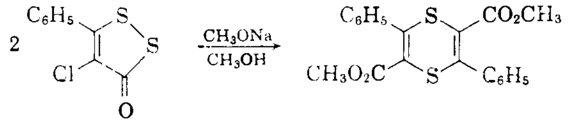
The reaction of disodium dimercaptomaleonitrile with thionyl chloride in 1,2-dimethoxyethane gives tetracyano-1,4-dithiin in nearly quantitative yield. A study of the mechanism of this oxidation has revealed a complicated sequence of reactions, which were identified by isolation or trapping of the various intermediates. A scheme is proposed to account for the over-all oxidation process, all of whose intermediate steps can be demonstrated in separate reactions. Some consideration is also given to the processes which occur when disodium dimercaptomaleonitrile is converted to tetracyano-1,4-dithiin with halogens and tetracyanoethylene.

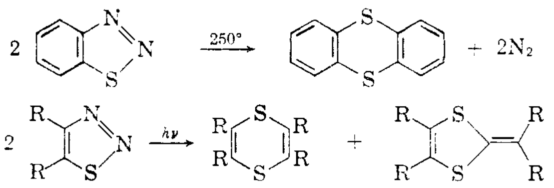
**Introduction.**—In papers I[1] and II[2] the chemistry of disodium dimercaptomaleonitrile (**1**)[3] was studied and the utility of this salt in the synthesis of thiacyanocarbons was demonstrated. Of particular interest is the oxidation of **1** to tetracyano-1,4-dithiin (**2**),[2,4] and some observations on the mechanism of this transformation are the subject of the present paper.

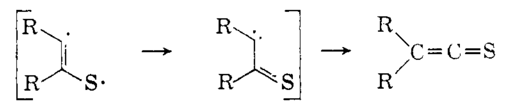
Although substituted 1,4-dithiins have been known for many years, the parent, 1,4-dithin, was only recently prepared by Parham, Wynberg and Ramp[5] by the alumina-catalyzed elimination of ethanol from 2,5-diethoxytetrahydro-1,4-dithiin.[6] The ring system has also been formed in acid-catalyzed condensations of appropriate mercaptoketones; *e.g.*, 2-mercaptocyclohexanone gave an octahydrothianthrene.[7] Recently, Boberg has reported a base-catalyzed conversion of a dithiolenone to a tetrasubstituted dithiin.[8] The mechanism of this transformation is unknown but can be rationalized in terms of multiple addition–elimination sequences. Thermal[9] and ultraviolet light induced[10] transformations of 1,2,3-thiadiazoles have given 1,4-dithiins (and 1,3-dithioles in the light reaction). In the latter reaction Kirmse and Horner postulated an intermediate diradical or carbene, which dimerized to a 1,4-dithiin or rearranged to a thioketene which subsequently reacted with unrearranged diradical to give the corresponding 1,3-dithiole.











None of these observations shed much light on the interpretation of the present studies of the oxidation of an ethylenic 1,2-dimercaptan to a 1,4-dithiin by a process which involves an electrically neutral intermediate containing two sulfur atoms, dicyano-1,2-dithiete.

**Mechanism of Oxidation of Disodium Dimercaptomaleonitrile (1) with Thionyl Chloride.**—At the outset, it is striking to note that when one mole of disodium dimercaptomaleonitrile (**1**) was treated with one mole of oxidizing agents as diverse as chlorine, bromine, iodine, perchloryl fluoride, sulfur monochloride, sulfur dichloride, thionyl chloride, sulfuryl chloride, potassium ferricyanide, potassium persulfate, hydrogen peroxide, ferric chloride and tetracyanoethylene, the primary oxidation product was tetracyano-1,4-dithiin (**2**) in yields of 30–100% in all cases.[1] A second product, tricyano-1,4-dithiino-[c]-isothiazole, isolated in some oxidations was shown[1] to result from a subsequent reaction of dithiin **2** with elemental sulfur.

The variety of reagents and conditions by which salt **1** was oxidized to dithin **2** suggested initially that similar mechanisms and possibly common intermediates were involved. Preliminary experiments with oxidizing agents that varied widely chemically, *e.g.*, potassium ferricyanide, the halogens, tetracyanoethylene and thionyl chloride, indicated that certain features of the oxidations were indeed the same for all the systems. Some of the isolated intermediates, however, depended strictly

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[1] H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4756 (1962).

[2] H. E. Simmons, D. C. Blomstrom and R. D. Vest, *ibid.*, **84**, 4782 (1962).

[3] G. Bähr, G. Schleitzer and H. Bieling, *Chem. Tech.*, **8**, 596 (1956); G. Bähr, *Angew. Chem.*, **68**, 525 (1956).

[4] G. Bähr, *ibid.*, **70**, 606 (1958); **73**, 628 (1961).

[5] W. E. Parham, H. Wynberg and F. L. Ramp, *J. Am. Chem. Soc.*, **75**, 2065 (1953). For a review of the work of Parham in the dithiin field, see W. E. Parham in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Editor, Pergamon Press, New York, N. Y., 1961, p. 248.

[6] Some interesting chemical and physical studies of 1,4-dithiin are reported by W. E. Parham, B. Gadsby and R. A. Mikulec, *J. Org. Chem.*, **24**, 1819 (1959).

[7] F. Asinger, M. Thiel, H. Usbeck, C.-H. Gröbe, H. Grudmann and S. Tränkner, *Ann.*, **634**, 144 (1960).

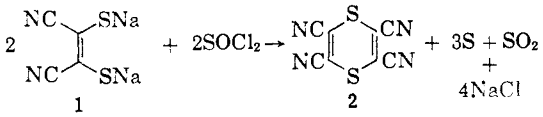
[8] F. Boberg, *Angew. Chem.*, **73**, 579 (1961).

[9] P. Jacobson and E. Ney, *Ber.*, **22**, 904 (1889).

[10] W. Kirmse and L. Horner, *Angew. Chem.*, **69**, 721 (1957).

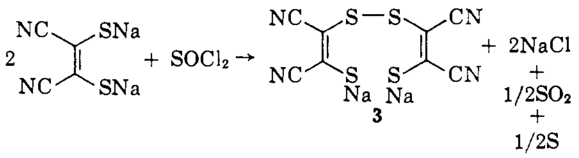
on the oxidizing agent, and the mechanism cannot be discussed with complete generality. Since oxidation of **1** with thionyl chloride gave nearly quantitative yields of **2** under easily studied conditions and since thionyl chloride as an oxidizing agent poses some questions of wider interest, most of the detailed studies were carried out with this system.

Salt **1** has low solubility in 1,2-dimethoxyethane (DME), and, although the reaction with thionyl chloride is carried out for synthetic purposes in a heterogeneous system, it was first determined that the reaction takes the same course when carried out in a dilute, homogeneous system. Two of the products, sulfur and sodium chloride, have low solubility in DME and precipitate during the reaction, while dithiin **2** and sulfur dioxide are very soluble in this medium. The stoichiometry of the oxidation was easily confirmed to be



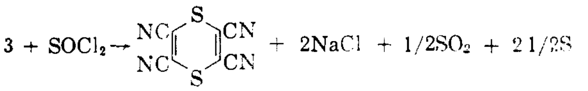
Clues to the mechanism were obtained from a study of intermediates and the conditions under which they formed and reacted. The salient observations which bear on the interpretation of the oxidation of **1** by thionyl chloride are first outlined below. From these considerations a reasonable mechanism can be developed and tested.

1. When one-half mole of thionyl chloride was added slowly to one mole of salt **1** in DME at 0°, a deep orange-red color formed as **1** dissolved. From this homogeneous solution, there was isolated in moderate yield a crystalline salt of empirical formula $C_8N_4S_4Na_2$,[11] whose structure was shown to be disodium *trans-trans*-bis-(2-mercapto-1,2-dicyanovinyl) disulfide.[2] At this stage the amount of dithiin **2** formed was negligible. Spectral studies showed[2] that the initially formed salt was the *cis-cis* isomer **3**, although the *trans-trans* isomer was usually the only product isolated because of facile isomerization. *cis-cis*-**3**, synthesized by oxidation of **1** with tetrabromethane,[2] underwent all of the reactions of *trans-trans*-**3** which was used in most of these studies.

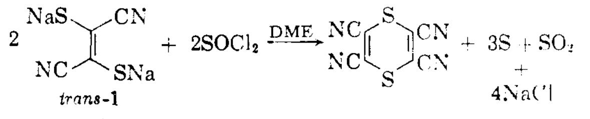


2. When a second one-half mole of thionyl chloride was added to the reaction mixture in (1), the color faded and dithiin **2** formed in nearly quantitative yield. The only other products isolated were elemental sulfur (>90%), sodium chloride (>90%) and sulfur dioxide. No inorganic products containing sulfur of oxidation state less than 0 were detected.

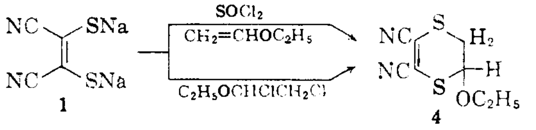
In separate experiments, *cis-cis*-**3** and *trans-trans*-**3** were treated with one mole of thionyl chloride under the conditions employed in (1). Both isomers gave dithiin **2** in nearly quantitative yield, and the stereochemistry of **3** had no detectable effect on the course of the oxidation.



It was also determined that disodium *trans*-**1**[2] was oxidized by thionyl chloride in DME solution in a completely analogous manner. The crude yield of dithiin **2** was quantitative and 69% after recrystallization.

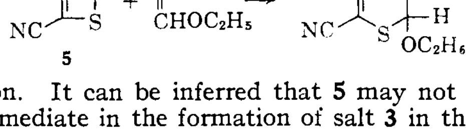


3. When one mole of salt **1** was treated with one mole of thionyl chloride in DME containing excess (3 moles) ethyl vinyl ether, the yield of dithiin **2** decreased to 15% and the major product isolated in 63% yield was 2,3-dicyano-5-ethoxy-5,6-dihydro-1,4-dithiin (**4**), which was synthesized independently from **1** and α,β-dichloroethyl ethyl ether. The stereochemistry of 1 did not affect the oxidation, since disodium *trans*-**1**[2] gave 53% of **4** under the same conditions. Other electron-rich olefins were trapped in a similar manner during oxidation of salt **1**, and adduct **4** was formed using other oxidizing reagents, such as iodine in DME and potassium ferricyanide in water.



Repetition of the initial experiment using one-half mole of thionyl chloride resulted in the formation of **4** in only 5% yield, and the major product was *trans-trans*-**3**; *i.e.*, ethyl vinyl ether showed virtually no effect on the first stage of the oxidation. When one mole of *trans-trans*-**3** was treated with one mole of thionyl chloride in DME containing ethyl vinyl ether, the yield of pure **4** was 58.7% showing that *both* halves of **3** were utilized in the formation of **4** in the second stage of the oxidation.[12]

These results show that the oxidation proceeds in two rather discrete steps: **1** → **3** and **3** → **2**. It is also evident that ethyl vinyl ether interrupts the oxidation sequence by trapping some intermediate primarily during **3** → **2**. The structure of the product, dihydrodithiin **4**, suggests the intermediacy of the unknown, electrically neutral dicyano-1,2-dithiete (**5**) which functions similar to a diene component in a Diels-Alder addition with the vinyl ether during the second stage of the oxidation. It can be inferred that **5** may not be an intermediate in the formation of salt **3** in the first

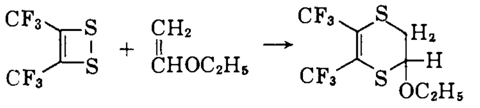


(11) This salt was not very stable to manipulation and considerable losses were encountered during isolation and recrystallization. Quantitative spectral analysis before isolation indicated it was formed in high yield.[2]

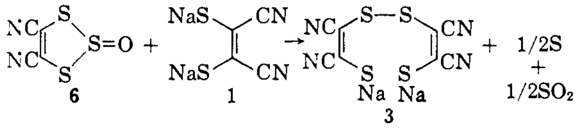
(12) These observations (3) are complicated by a slow reaction of thionyl chloride with ethyl vinyl ether to give a sulfinyl chloride by addition. It will be shown in a subsequent publication[13] that the conclusions below are not altered by this side reaction.

stage of the reaction, since only a low yield of adduct **4** was obtained and because of the evidence in observation (4). This distinction is not, however, completely clear-cut and will be discussed further below.

The proposed addition of dicyano-1,2-dithiete (**5**) to ethyl vinyl ether to form adduct **4** receives strong support from the observation that bis-(trifluoromethyl)-1,2-dithiete[29] has been found to undergo this type of addition reaction.

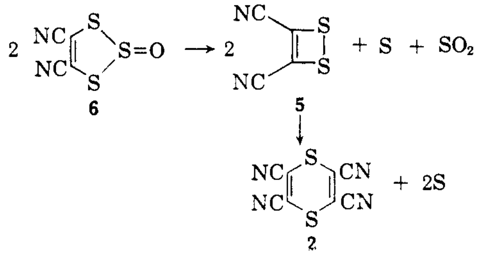


4. Dicyano-1,2,3-trithiole-2-oxide (**6**),[4] previously prepared from **1** and excess thionyl chloride as solvent,[2] underwent the reactions anticipated for an intermediate in the first half of the thionyl chloride oxidation of **1** in DME (observation 1). Thus: (a) Trithiole oxide **6** reacted instantaneously with salt **1** under the reaction conditions to give *trans-trans*-**3** (46%), sulfur and sulfur dioxide. Spectral studies showed that the first-formed product was *cis-cis*-**3** which isomerized during isolation.[2]

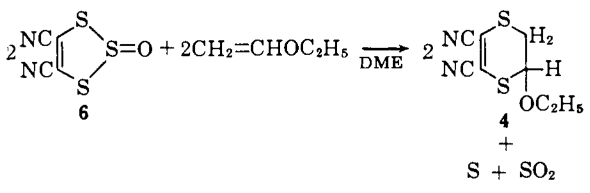


In confirmation, the product was treated with methyl sulfate before isolation, and a mixture of the *cis-cis* and *trans-trans* dimethyl derivatives of **3**[2] was obtained in which the *cis-cis* isomer predominated.

(b) Trithiole oxide **6** is stable in methylene chloride solution, but in basic solvents, such as dimethoxyethane, slow conversion to dithiin **2** (95%), sulfur and sulfur dioxide occurred. That dicyano-1,2-dithiete (**5**) is formed in the spontaneous decomposition of **6** and is indeed the precursor of **2** was inferred by the following observation and by the kinetic studies described below.



(c) Trithiole oxide **6** reacted slowly in DME containing ethyl vinyl ether to give a 78% yield of **4** along with a small amount of **2**.

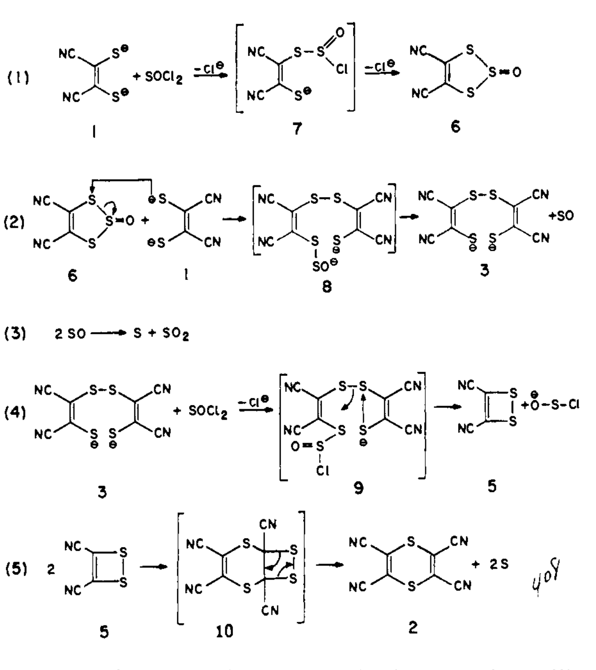


Although radical intermediates may be involved in oxidations of **1** by some reagents, the conditions of the reaction with thionyl chloride and the nature of the reactants suggest an ionic interpretation for observations 1–4. Some evidence for this view was gained by noting that when the oxidation was carried out in the presence of styrene, no polystyrene was formed and the monomer was recovered unchanged. Further, no transient radicals could be detected when the oxidation was carried out in an e.p.r. spectrometer probe.

A mechanism incorporating the above experimental observations is outlined in Chart I and discussed below. It is proposed that nucleophilic displacement by the mercaptide **1** on thionyl chloride is the first step to form an intermediate salt **7** (eq. 1). Intramolecular ring closure to give trithiole oxide **6** would be expected to be facile, since half-acylated derivatives of **1** have previously been shown to retain their *cis* configuration.[2] The reaction of trithiole oxide **6** with salt **1** which is present in excess during oxidation (eq. 2) has been shown to be a very rapid reaction in DME leading directly to disulfide salt **3** (observation 4a). In contrast, the slow, direct conversion of **6** to dithiin **2** (observation 4b) cannot be responsible for the formation of **2** under the reaction conditions, since salt **1** is present in large excess as **6** is being formed. The relative rates of these two reactions are not accurately known, but it can be estimated that the former process (**6** → **2**) is several orders of magnitude slower than the latter (**6** + **1** → **3**).

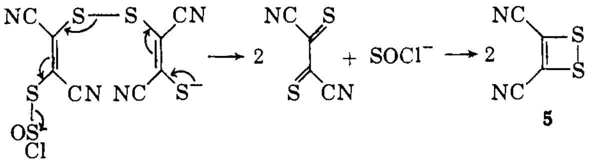
CHART I

OXIDATION OF SALT 1



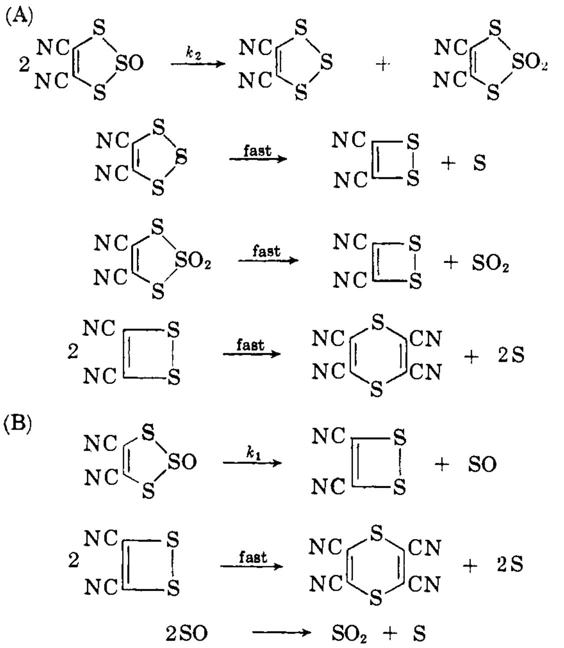
It was further shown that addition of one mole of thionyl chloride to one mole of salt **3** in DME gave dithiin **2**, sulfur and sulfur dioxide (observation 2). It is proposed that the intermediate chlorosulfinyl salt **9**, aided by the high energy of the disulfide bond, undergoes "unzippering" as shown in eq. 4 with the simultaneous formation of two moles of dicyano-1,2-dithiete (**5**) and the ion $SOCl^-$ (or sulfur monoxide and chloride ion).[18]

The unzippering reaction also occurs with *trans-trans*-**3** on treatment with thionyl chloride. In this case because of stereochemical considerations, it may be that the bis-(thiocarbonyl) isomer is actually formed and reverts rapidly to the more stable dithiete structure **5**.[16]



The presence of dithiete **5** in the second stage of the reaction (eq. 4 and 5) has been demonstrated in observations 3 and 4c by trapping experiments, and it was further found that both halves of salt **3** were utilized. Subsequent dimerization of **5** to form dithiin **2** completes the over-all oxidation.[14]

Further support for the existence of dicyano-1,2-dithiete (**5**) as a highly reactive intermediate was provided by a brief study of the kinetics of the conversion of dicyano-1,2,3-trithiole-2-oxide (**6**) in ether solvents to tetracyano-1,4-dithiin (**2**), sulfur and sulfur dioxide. The above observations suggest two interpretations providing for the intermediacy of **5**: (A) bimolecular disproportionation and (B) unimolecular expulsion of sulfur monoxide.



In some solvents, such as methylene chloride and ethanol, trithiole oxide **6** was stable for several hours. In solvents containing ether groups, however, conversion to **2** occurred smoothly and could be followed by periodically obtaining the ultraviolet spectrum. The progress of the reaction was determined by measuring the appearance of the absorption band of dithiin **2** at 327 mμ. It was difficult to measure the disappearance of the characteristic band of trithiole oxide **6** at 273 mμ because of interference by the strong sulfur dioxide absorption at 278 mμ. Sulfur dioxide absorbs only weakly in the 327 mμ region, and this effect was compensated for by a small correction. The appearance of **2** was followed to 90% completion and where possible the disappearance of **6** was followed to *ca.* 25% completion. In DME, diethyl ether and tetrahydrofuran, the reaction showed first-order kinetics, and the first-order rate constant was invariant to fourfold changes in the initial concentration of **6**. The reaction was very sensitive to traces of impurities, especially bases, and in some runs at low concentrations the reaction began normally and then accelerated erratically in the fashion of a superimposed zero-order reaction which may have been due to traces of impurity on the cell walls. Some typical data are presented in Table I. The data from runs 1–5 show the reaction to have a specific first-order rate constant in DME of $k_1 = 0.022 \pm 0.004$ sec.$^{-1}$ ($t_{1/2}$ 32 min.). In several experiments there was good agreement within the experimental error between the rate constants based on the appearance of **2** and on the disappearance of **6** in the early part of the measurements (*ca.* 25% reaction) before absorption from sulfur dioxide became a significant factor. The same rate constant should be obtained by following the appearance of **2** as by following the disappearance of **6** provided the disappearance of **6** is rate

TABLE I

CONVERSION OF TRITHIOLE OXIDE **6** TO DITHIIN **2**[a]

| Run | Solvent | Initial concn. of **6**, mole/l. | $k_1$, sec.$^{-1}$ |
|---|---|---|---|
| 1 | Dimethoxyethane | 0.00888 | 0.018 |
| 2 | Dimethoxyethane | .00872 | .025 |
| 3 | Dimethoxyethane | .00309 | .026 |
| 4 | Dimethoxyethane | .00258 | .021[c] |
| 5 | Dimethoxyethane | .00255 | .022[d] |
| 6 | Dimethoxyethane | .00052 | .154[b] |
| 7 | Tetrahydrofuran | .00372 | .0086 |
| 8 | Diethyl ether | .00430 | .0012 |

[a] All data were obtained at 33°. [b] Typical erratic run showing superimposed zero-order decomposition. [c] Disappearance of **6**. [d] Appearance of **2**.

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(13) Displacement on chlorine in thionyl chloride by nucleophiles would lead to expulsion of the ion SOCl⁻. Such a process may occur in the reaction with iodide ion where the products are chloroiodate(I) ion, sulfur, and sulfur dioxide (N. B. Brownell and L. C. King, *J. Am. Chem. Soc.*, **71**, 2929 (1949)). Alternatively, it is possible that dissocia-

$$\mathrm{SOCl_2 + I^- \longrightarrow ICl + \bar{O}SCl}$$

$$\mathrm{SOCl_2 + \bar{O}SCl \longrightarrow Cl\overset{\overset{O}{\|}}{S}OSCl + Cl^-}$$

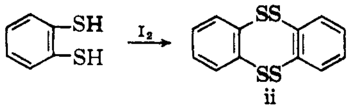
$$\mathrm{Cl\overset{\overset{O}{\|}}{S}OSCl + I^- \longrightarrow ICl + SO_2 + \bar{S}Cl}$$

$$\mathrm{ICl + Cl^- \longrightarrow ICl_2^-}$$

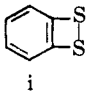
$$\mathrm{^-SCl \longrightarrow S + Cl^-}$$

tion of ⁻O–S–Cl to sulfur monoxide and chloride ion may occur in basic solvents. At any rate, further reaction of this ion produced in eq. 4 with thionyl chloride would lead to the observed products.

(14) The oxidation of a 1,2-dimercaptan has been claimed to give a dithiete. P. C. Guha and M. N. Chakladar, *Quart. J. Indian Chem. Soc.*, **2**, 3181 (1925), reported the oxidation of dithiocatechol with iodine in ethanol gave **i**. Recently L. Field, W. D. Stephens and E. L. Lippert, Jr., *J. Org. Chem.*, **26**, 4782 (1961), have shown that the product of this reaction is a polymer containing disulfide bonds. At high dilution the eight-membered ring dimer **ii** was obtained.



ii



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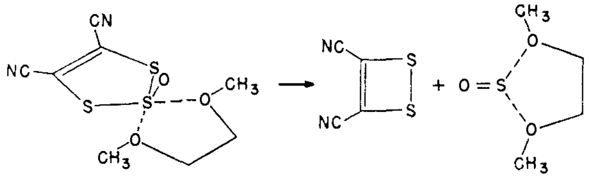
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determining and is followed by rapid conversion of any intermediate to product.

Mechanism B meets the requirement of unimolecular kinetics found for the disappearance of trithiole oxide **6**. The suggestion that sulfur monoxide is a chemically significant species under these conditions requires support which is provided later in the text. The reaction is accelerated in ether solvents, the rate depending on the base strength of the ether and its coördinating ability. Complexes such as **11** in DME may be the species preceding unimolecular dissociation to **5** and solvated sulfur monoxide **12**. Evidence for this view was sought by studying the conversion **6** → **2** in methylene chloride solution in the presence of kinetically significant concentrations of DME. The kinetics were complicated and did not allow detailed analysis; however, it was evident that the rate was dependent on DME concentration with an order greater than one. Finally, disproportionation of the strongly solvated sulfur monoxide **12** would then give sulfur and sulfur dioxide, the observed products.[15]

The kinetics of the decomposition of trithiole oxide **6** in DME containing ethyl vinyl ether were examined briefly. Over the first 60% reaction, the rate was largely independent of vinyl ether concentration and very nearly first-order with $k_1$ = 0.079 ± 0.006 sec.$^{-1}$, compared to $k_1$ = 0.022 ± 0.004 sec.$^{-1}$ in the absence of ethyl vinyl ether. During the last 40% of the reaction the rate was erratic in two runs. The fourfold increase in rate could be a solvent effect in this system which is sensitive to changes in the medium (Table I). The conversion **6** → **2** is extremely slow in methylene chloride and qualitatively the rate increased several orders of magnitude on the addition of 10% ethyl ether, but was only slightly greater when ethyl vinyl ether was used in place of ethyl ether.

The limited data support the view that dicyano-1,2-dithiete (**5**) is formed unimolecularly from **6** in a slow reaction followed by rapid dimerization to **2** or by rapid scavenging reactions. Direct reaction between trithiole oxide **6** and ethyl vinyl ether to give **4** must be slow, and it was further shown above that **4** was formed under conditions where no **6** was present, *e.g.*, the oxidation of *cis-cis*-**3** with thionyl chloride.

Attempts to isolate or identify dithiete **5** spectrally have not yet been successful. Further support for the intermediacy of electrically neutral dithiete **5** will be found in a later publication.[16]

Sulfur monoxide has not often been postulated by organic chemists as an intermediate in reactions carried out in solution at moderate temperatures, but there seems to be no good grounds for its exclusion.[17]

The preparations of sulfur monoxide originally described by Schenk and co-workers[18] have more recently been questioned,[19] but its existence as a transient, reactive intermediate has not been excluded.[20] Sulfur monoxide is known spectroscopically[21] and has been studied at high temperatures,[22] where the following reactions were established.

$$2SO \longrightarrow S + SO_2$$

$$S_2 + 2SO_2 \longrightarrow 4SO$$

In systems shown to be free of $S_2O$,[22b] the experimental heat of formation of sulfur monoxide was determined to be $\Delta H_0^0 = -15{,}400 \pm 300$ cal./mole, a value in good agreement with the previously derived spectroscopic value.[21]

The mechanism proposed in Chart I is in accord with observations 1–4 and with the conclusions drawn from the kinetic studies, and additional support was provided by the following observations. Equations 1 and 2 reflect observation 3 in which the addition of one-half mole of thionyl chloride to one mole of salt **1** in DME containing three moles of ethyl vinyl ether gave largely salt **3** and only a low yield of adduct **4**. However, when this experiment was repeated with ethyl vinyl ether present in large excess (15 moles), salt **3** and dithiin **2** were detected in low yield and the dihydrodithiin **4** was now isolated in 44% yield.

This last result can be interpreted by considering the relative rates of eq. 1–4. Salt **3** is soluble in DME and its effective concentration rapidly be-

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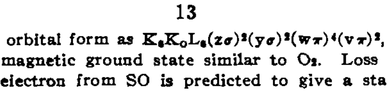
[15] An alternative dissociation of **6** to the anion-radical **13** was considered unlikely, although the associated cation-radical $(SO\cdot)^+$ may be energetically feasible. Sulfur monoxide (SO) can be described


13

in molecular orbital form as $K_sK_OL_s(z\sigma)^2(y\sigma)^2(w\pi)^4(v\pi)^2$, which predicts a paramagnetic ground state similar to $O_2$. Loss of an antibonding $v\pi$-electron from SO is predicted to give a stable species, $(SO\cdot)^+$.

When the conversion **6** → **2** was carried out in an e.p.r. spectrometer, a transient signal was indeed observed, but sufficient resolution of the weak, broad spectrum could not be obtained for identification. It is not known at the present time if complexes of presumably paramagnetic SO, such as **12**, its decomposition products or $(SO\cdot)^+$ is the source of the observed signal.

[16] Paper IV, H. E. Simmons, D. C. Blomstrom and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4782 (1962).

[17] See, for example, A. C. Poshkus and J. E. Herweh, *ibid.*, **84**, 555 (1962), who present evidence that sulfur monoxide is formed directly in the reaction of triethyl phosphite and thionyl chloride.

[18] Some pertinent references on the incomplete combustion of sulfur are P. W. Schenk, *Z. anorg. allgem. Chem.*, **220**, 268 (1934); **248**, 297 (1949); *Chem. Zentr.*, **114**, 251 (1943). Preparation of SO from thionyl chloride and metals is described by P. W. Schenk and H. Platz, *Z. anorg. allgem. Chem.*, **215**, 113 (1933); also see E. Gruner, *ibid.*, **212**, 393 (1933), and R. A. Hubbard and W. F. Luder, *J. Am. Chem. Soc.*, **73**, 1327 (1951).

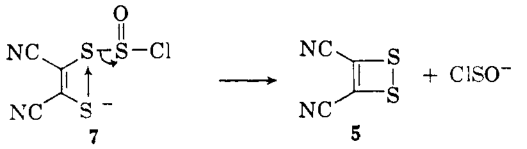
[19] M. Goering and K.-D. Wiebusch, *Z. anorg. allgem. Chem.*, **257**, 227 (1948); D. J. Meschi and R. J. Meyers, *J. Am. Chem. Soc.*, **78**, 6220 (1956); E. A. Evans, A. B. Scott and J. L. Huston, *ibid.*, **74**, 5525 (1952).

[20] A. V. Jones, *J. Chem. Phys.*, **18**, 1263 (1950).

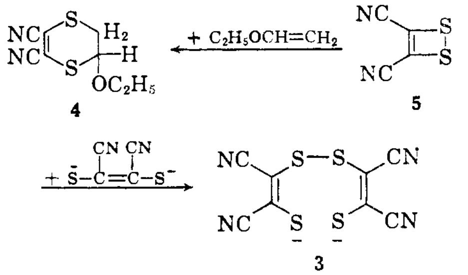
[21] G. Herzberg, "Molecular Spectra and Molecular Structures 1: Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 573.

[22] (a) N. P. Diev, A. I. Okunev, V. V. Paduchev, V. V. Toporova and V. S. Mokronosov, *Trudy Inst. Met., Akad. Nauk S.S.S.R. Ural, Filial, Skornik Rabot*, **1**, 17 (1957); (b) E. W. Dewing and F. D. Richardson, *Trans. Faraday Soc.*, **54**, 679 (1958).

comes greater than that of the slightly soluble salt **1**. Since salts **1** and **3** react with thionyl chloride at similar rates in solution, it would be expected that the reaction **3** + $SOCl_2$ → 2 **5** (eq. 4) would continually produce dithiete **5** even during the early part of the addition of thionyl chloride. An alternative source of dithiete **5** is the direct expulsion of $Cl–S–O^-$ from intermediate **7**, but this is shown below to be unlikely.

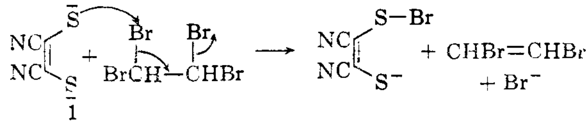


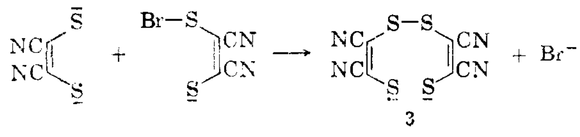
Regardless of whether the process **7** → **5** or **3** + $SOCl_2$ → **5** is the source of dithiete 5, both ethyl vinyl ether and unreacted salt **1** compete for **5**, the latter reaction simply forming salt **3**. When the concentration of ethyl vinyl ether is very high, the formation of 4 competes effectively with the fast reaction **5** + **1** → **3**, even when only one-half mole of thionyl chloride is employed.



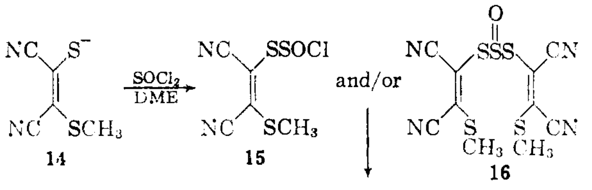
It has been assumed in the foregoing discussion that adduct **4** arises only in a Diels–Alder type addition of dithiete **5** to ethyl vinyl ether, but it is conceivable that trithiole oxide **6** and ethyl vinyl ether react directly to give adduct 4. This point was considered in the kinetic studies above; however, a simple competition experiment showed that the direct reaction was too slow to account for more than a minor portion of adduct **4** formed *under the usual oxidation conditions* (*presence of* **1**). When one mole of salt **1** and 15 moles of ethyl vinyl ether competed for one mole of trithiole oxide **6**, the main product was salt **3**. The yield of adduct **4** was only 13% compared to 44% for the experiment in which thionyl chloride was added to the salt and ethyl vinyl ether.

In connection with the question of the possible intermediacy of dithiete **5** in the first part of the oxidation of salt **1** with thionyl chloride, it is interesting to note that salt 1 was oxidized by tetrabromoethane to *cis-cis*-3, *cis*- and *trans*-dibromoethylene and sodium bromide.[2] One interpretation involves the following reactions. Displacement on sulfenyl bromides by mercaptide ions to give disulfides is well known.[23] When this oxidation was carried out in the presence of six moles of ethyl vinyl ether, no adduct **4** was detected and salt **3** was the only product isolated. Apparently bromide ion is not expelled rapidly from the intermediate sulfenyl bromide to give dithiete **5**, and reaction of the sulfenyl bromide with a second molecule of salt **1** must be very rapid. It is therefore reasonable that the ion **7** would undergo cyclization to trithiole oxide **6** rather than expel O–S–Cl ion in the first half of the oxidation reaction, since $Cl–S–O^-$ should not be an exceptionally good leaving group relative to bromide ion.





The formation of disulfide bonds in the oxidation of mercaptans with thionyl chloride is old,[24] but no detailed mechanism studies have been made of these reactions. In the present case, it is not known whether displacement by salt **1** on trithiole oxide **6** occurs at sulfide sulfur or at the thionyl sulfur. It is considered likely that the former occurs with the formation of the disulfide bond directly (eq. 2, Chart II). Such a mechanism is in accord with the *cis-cis* geometry observed in salt **3**. It was previously found[2] that 1-sodiomercapto-2-methylmercaptomaleonitrile (**14**) was oxidized in high yield by thionyl chloride in DME to a mixture of *cis-cis*- and *trans-trans*-bis-(2-methylmercapto-1,2-dicyanovinyl) disulfide (**17**). Exclusive of the stereochemistry, it seems that **15** and/or **16** were intermediates which underwent displacement at sulfide sulfur by **14** to form the disulfide bond.



$NC(CH_3S)C{=}C(CN){-}SS{-}C(CN){=}C(SCH_3)CN$

17

In eq. 2, Chart I, intermediate salt **8** is postulated to lose the elements of sulfur monoxide to give *cis-cis*-3. Although little is known concerning sulfur monoxide as a leaving group from an anion, strong solvation by basic solvents such as DME was shown above to facilitate such a reaction. The proposed intermediate **8** is structurally similar to the trisulfide ion, $R–S_3^-$, which is known to be unstable and rapidly degrades to mercaptide ion and elemental sulfur.[25]

Finally, dimerization of **5**, depicted as a Diels–Alder addition in Chart I, would give an adduct **10** from which loss of sulfur should be facile under the reaction conditions (presence of weak nucleophiles). An alternative head-to-tail dimerization of the type known to occur with certain electronegatively substituted thiocarbonyl com-

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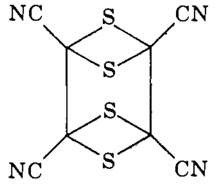
[23] See the extensive review article by A. J. Parker and N. Kharasch, *Chem. Revs.*, **59**, 583 (1959).

[24] B. Holmberg, *Ann.*, **359**, 81 (1908); *Ber.*, **43**, 226 (1910); also see S. F. Birch, T. V. Cullum and R. A. Dean, *J. Inst. Petr. Tech.*, **39**, 206 (1953).

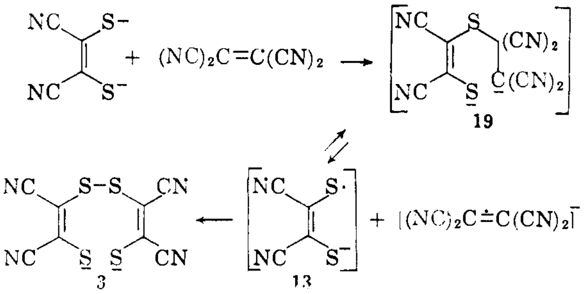
[25] See H. Böhme, in Houben-Weyl, "Methoden der Organischen Chemie," 4th Ed., Vol. IX, Stuttgart, 1955, p. 54.

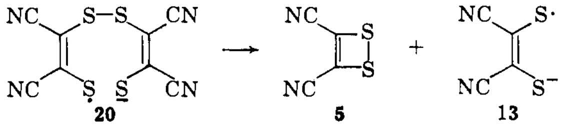
pounds[26] to give the adduct **18** should also be considered.



**18**

**Other Oxidations of Salt 1.**—No detailed investigations have been made of the oxidation of salt **1** with other oxidizing agents. Some facets of the thionyl chloride oxidation are clearly unique to this system, such as the occurrence of trithiole oxide **6** as an intermediate and the mode of decomposition of the disulfide salt **3** (eq. 4). Salt **3** has been isolated or detected in the oxidations of salt **1** by bromine in DME or methanol, iodine in ethanol and tetracyanoethylene in DME as well as by thionyl chloride in DME, and it seems reasonable that dithiete **5** may be an intermediate in the subsequent oxidations of salt **3** by most or all of these reagents by reactions similar to those discussed for the thionyl chloride oxidation. With a one-electron transfer reagent, *e.g.*, tetracyanoethylene, the transient anion-radical **13** provides a ready precursor of salt **3** by simple dimerization. When solutions of tetracyanoethylene and salt **1** in DME were mixed at 0° at approximately equal rates, spectral analyses showed only disulfide salt **3** and tetracyanoethylene anion-radical.[27] A reasonable interpretation in accord with the known chemistry of tetracyanoethylene would involve nucleophilic addition of the mercaptide ion to tetracyanoethylene to give an intermediate salt **19**, which is in equilibrium with the two anion-radicals. The equilibrium is displaced by rapid dimerization of **13** to **3**. One - electron oxidation of salt **3** by tetracyanoethylene is postulated to give an anion-radical **20** that decomposes to **5** and **13**. Evidence for an analogous sequence in the oxidation of the monomethyl derivative **14** was given previously.[2]

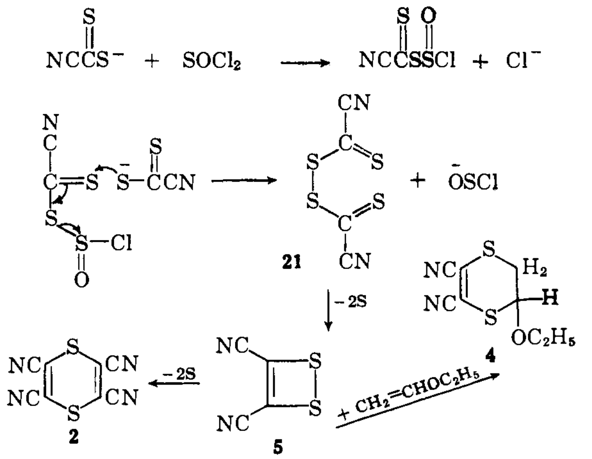




Oxidation of salt **1** to salt **3** with potassium ferricyanide probably proceeds *via* ion-radical **13**, which on subsequent one-electron oxidation gives dithiete **5** by a process (**20** → **5** + **13**) analogous to that described for tetracyanoethylene. Oxidation of salt **1** by chlorine, bromine and iodine may also occur in the first step through the intermediate **13**, although it is more probable that sulfenyl halides are intermediates by analogy with many known mercaptide ion–halogen oxidations.[23] A similar course was proposed above for the oxidation of salt **1** with 1,1,2,2-tetrabromoethane. Nothing is known with certainty concerning the mechanism of oxidation of salt **1** with sulfuryl chloride, sulfur monochloride and sulfur dichloride,[1] but it is probable that a sulfenyl chloride is the first intermediate formed.

In summary, it seems evident that in one-electron oxidations, salt **1** is converted to salt **3** *via* an anion-radical **13**. In the more usual two-electron oxidations, salt **1** is converted to an intermediate, such as **7**, or the corresponding sulfenyl halide mentioned above from which salt **3** is formed. Similar processes are thought to be involved in the subsequent oxidation of salt **3** to dithiin **2**, the crucial common intermediate being dithiete **5**. Even oxidation of **1** by potassium ferricyanide *in aqueous solution* alone gave dithiin **2** and adduct **4** in the presence of ethyl vinyl ether.

**Oxidation of Sodium Cyanodithioformate.**—Sodium cyanodithioformate·3DMF, the precursor of sodium dimercaptomaleonitrile (**1**),[3] undergoes many oxidation reactions to give ultimately the same products as salt **1**. It was previously noted that direct oxidation of sodium cyanodithioformate·3DMF with chlorine gave tetracyano-1,4-dithiin (**2**).[1] Similarly, the cyanodithioformate ion was oxidized to **2** by thionyl chloride in acetonitrile in 19.5% yield. When the latter reaction was carried out in the presence of ethyl vinyl ether, the adduct **4** was isolated in 34% yield. It is known that sodium cyanodithioformate·3DMF does not dimerize spontaneously[2] to salt **1** in acetonitrile, but it is not known with certainty that reaction with thionyl chloride gives salt **1**. An interpretation based on the preceding chemistry and not involving formation of salt **1** follows. The loss of sulfur from the postulated intermediate **21** in the presence of nucleophiles[1,2] to give dithiete **5** is not unusual in view of the ready dimerization with



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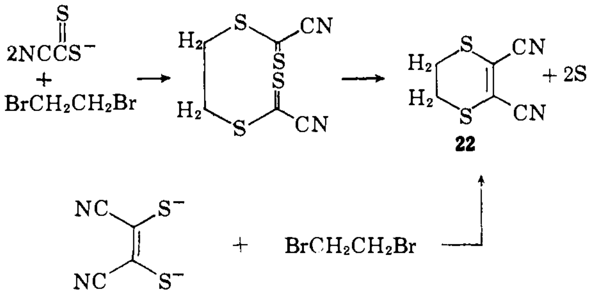
(26) W. J. Middleton, E. G. Howard and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 2589 (1961).

(27) O. W. Webster, W. Mahler and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).

sulfur loss of covalent cyanodithioformates.[2] A similar reaction of tetraethylammonium cyanodithioformate ion with ethylene dibromide gave an unstable, red diester which readily lost sulfur to give 2,3-dicyano-5,6-dihydro-1,4-dithiin (22). Authentic 22 was prepared from salt 1 and ethylene dibromide.



## Experimental[28]

**Materials.**—The preparation and purification of the compounds used in this study have been reported previously[1,2] or else are described in the sections below.

**Oxidation of *cis*-1 with Thionyl Chloride.**—The details of this reaction were reported in paper I of this series.[1] It was determined that the sole reaction products in DME solution were dithiin 2, sulfur, sulfur dioxide and sodium chloride. No trace of sulfide ion was found in the precipitate of sodium chloride and sulfur which was removed at completion. The polymerization of styrene was not initiated when the oxidation was carried out in the presence of added styrene, and no transient radical intermediates were detected when the oxidation was performed in a tube mounted in an e.p.r. spectrometer probe.

**Reaction of *trans-trans*-3 with Thionyl Chloride.**—A solution of recrystallized *trans-trans*-3[2] (0.30 g., 0.00093 mole) in DME (5 ml.) was treated at 0° with thionyl chloride (0.11 g., 0.00093 mole) in DME (3 ml.) over 5 minutes. The reaction mixture was filtered, and the filtrate was evaporated *in vacuo*. The dry residue was extracted with DME (5 ml.), and the extract was evaporated to dryness in a stream of nitrogen. The tan solid obtained weighed 0.19 g. (95%) and melted at 169–193° (lit.[1] m.p. 207–208° dec.). The infrared spectrum showed the product to be essentially pure dithiin 2. A similar result was observed starting with *cis-cis*-3.

**Oxidation of Disodium *trans*-1.**—A suspension of disodium *trans*-1 (0.20 g., 0.001 mole) in DME (5 ml.) was stirred and cooled in an ice-bath. Over 5 minutes a solution of thionyl chloride (0.12 g., 0.0010 mole) in DME (2 ml.) was added. The same color changes which occur when the *cis* isomer was employed were noted. The reaction mixture was evaporated to dryness under reduced pressure, extracted with a small volume of DME at 25°, and the extract again evaporated to dryness. There was obtained 0.13 g. of crude dithiin 2. Recrystallization from ethylene dichloride ("Darco") gave 0.08 g. (69%) of pure tetracyano-1,4-dithiin (2), m.p. 189–197°. The infrared spectrum was identical with that of an authentic sample.

**Oxidation of Salt 1 in the Presence of Ethyl Vinyl Ether. A. Thionyl Chloride (One Mole).**—A suspension of 1 (5.0 g., 0.027 mole) in DME (30 ml.) which contained ethyl vinyl ether (5.8 g., 0.081 mole) was cooled in an ice-bath to 0°. A solution of thionyl chloride (3.20 g., 0.027 mole) in DME (10 ml.) was added dropwise with stirring over 20 minutes. The characteristic deep red color formed during the thionyl chloride addition and increased to a maximum near the halfway point. At this time the solution was nearly homogeneous. During the second half of the addition, sodium chloride began to separate and the color changed to a light yellow. The reaction mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The yellow residue was extracted with hot methylene chloride (50 ml.) leaving behind 0.45 g. (15%) of dithiin 2. After one treatment with Darco, the hot methylene chloride extract was diluted with methylcyclohexane until crystallization began. After chilling the solution in Dry Ice there was obtained 3.56 g. (63%) of crystalline 2,3-dicyano-5-ethoxy-4,5-dihydro-1,4-dithiin (4), m.p. 103.5–105°.

*Anal.* Calcd. for $C_8H_8N_2OS_2$: C, 45.32; H, 3.80; N, 13.22; S, 30.25. Found: C, 45.41; H, 4.02; N, 13.26; S, 30.30.

The infrared, ultraviolet and n.m.r. spectra were in complete accord with the assigned structure. The proton n.m.r. spectrum of 4 was extremely similar to that of the adduct from bis-(trifluoromethyl)-1,2-dithiete and ethyl vinyl ether.[29] The synthesis of authentic 4 is described below.

**B. Thionyl Chloride (One-half Mole).**—The procedure used above was employed varying only the amount of thionyl chloride added. In three separate experiments 0.50, 0.75 and 1.0 mole of thionyl chloride were added to a solution containing 1.0 mole of salt 1 in DME. Methylene chloride extracts of the crude reaction product were passed through a column of acid-washed alumina for partial purification. The solutions were then concentrated to known volume and the infrared spectra were determined and compared to spectra of adduct 4 in methylene chloride solutions of known concentration. Four bands were used in the comparison (4.5, 6.6, 7.6 and 8.6 μ). The adduct 4 was then isolated from solution to determine yields; the results are

| Mole of $SOCl_2$ added | Yield, % 4 (infrared) | Yield, % 4 (isolation) | Yield, % 3 |
|---|---|---|---|
| 0.50 | 4 | 4 | *ca.* 50 |
| 0.75 | 45 | 49 | .. |
| 1.00 | 59 | 63 | 0 |

These results clearly show that the Diels–Alder adduct 4 was formed largely during the addition of the second one-half mole of thionyl chloride.

No product was obtained when the reaction was carried out using thionyl chloride in ether as solvent.

When the oxidation was repeated employing salt 1 (1 mole), thionyl chloride (0.5 mole) and ethyl vinyl ether (15 mole) in DME, work up in the usual manner led to isolation of adduct 4 in 44% yield. Only a trace of dithiin 2 was detected. This experiment clearly suggests that competition between the vinyl ether and salt 1 is occurring for some reactive intermediate, presumably dithiete 5.

**C. Potassium Ferricyanide.**—A mixture of salt 1 (5.0 g., 0.027 mole) and ethyl vinyl ether (6.0 g., 0.083 mole) in water (50 ml.) and methanol (20 ml.) was stirred and cooled at 0° while a solution of potassium ferricyanide (17.7 g., 0.054 mole) in water (125 ml.) was added over 10 minutes. After 30 minutes the solid was removed by filtration and washed with water. Recrystallization of the dried residue from ether gave 1.44 g. (25%) of adduct 4. When the order of addition was reversed the yield was 27%.

**Oxidation of *trans-trans*-3 in the Presence of Ethyl Vinyl Ether. A. Thionyl Chloride (One Mole).**—A solution of recrystallized *trans-trans*-3 (0.30 g., 0.00093 mole) and ethyl vinyl ether (0.44 g., 0.0061 mole) in DME (5 ml.) was cooled in an ice-bath and treated by dropwise addition with thionyl chloride (0.11 g., 0.00093 mole) in DME (3 ml.) over 5 minutes. The reaction mixture was filtered and the filtrate was evaporated *in vacuo*. The dark residue was chromatographed on acid-washed alumina using 80:20 ether–methylene chloride as eluent. The infrared spectrum of the yellow solid (0.19 g., 49%) melting at 100–105° was identical to that of authentic 2,3-dicyano-5-ethoxy-5,6-dihydro-1,4-dithiin (4).

In a second run on a larger scale (3 g. of salt 3), adduct 4 was obtained in 58.7% yield after purification by chromatography. Recrystallization gave 50.3% pure product. This proves that both halves of the salt 3 are utilized in trapping the vinyl ether.

**B. Iodine.**—A solution of recrystallized *trans-trans*-3 (0.50 g., 0.0015 mole) in DME (4 ml.) and ethyl vinyl ether (0.40 g., 0.0056 mole) was stirred and cooled to 0°. Over a 10-minute period a solution of iodine (0.78 g., 0.0031 mole)

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[28] All melting points are corrected and boiling points are uncorrected. Infrared spectra were determined on a Perkin–Elmer model 21 double beam infrared spectrometer equipped with NaCl optics (2–15 μ). Spectra were obtained in potassium bromide wafers and Nujol mulls. The visible and ultraviolet spectra were obtained by means of a Cary model 14 recording spectrophotometer.

[29] C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).

in DME (4 ml.) was added. The residue obtained by evaporation of the reaction mixture *in vacuo* was extracted with methylene chloride (50 ml.). The extract was washed with dilute sodium bisulfite solution and dried. After removal of the solvent, the infrared spectrum of the dark residue showed it to be largely adduct 4 contaminated with a small amount of tricyano-1,4-dithiino[c]isothiazole. Chromatography of a solution of the solid in methylene chloride on acid-washed alumina yielded 0.27 g. (42%) of pure **4**.

**Oxidation of Disodium *trans*-1 with Thionyl Chloride in the Presence of Ethyl Vinyl Ether.**—Disodium *trans*-1[2] (0.20 g., 0.0011 mole) was added to a solution of ethyl vinyl ether (0.46 g., 0.0063 mole) in DME (5 ml.), and the suspension was stirred and cooled at 0°. Over 5 minutes thionyl chloride (0.12 g., 0.0010 mole) in DME (2 ml.) was added dropwise. After 10 minutes the mixture was filtered and the filtrate was evaporated to a sirup *in vacuo*. The residue was dissolved in 1:1 ether–methylene chloride and the resulting solution was chromatographed on acid-washed alumina. Elution with the same solvent gave 0.12 g. (53%) of crude adduct **4**, m.p. 102–106°. Infrared analysis of the product showed it to be essentially pure **4**.

**2,3-Dicyano-5,6-dihydro-5-ethoxy-1,4-dithiin (4).**—An authentic sample of this compound was prepared by the following metathetical reaction. Salt **1** (3.00 g., 0.0161 mole) in DME (30 ml.) was stirred and cooled in an ice-bath. A solution of $\alpha,\beta$-dichloroethyl ethyl ether (2.31 g., 0.0163 mole) in DME (8 ml.) was added over 10 minutes. After the mixture was stirred for 30 minutes at 0°, the solids were filtered, and the filtrate was diluted with cold water. The oil which separated crystallized rapidly. The yield of crude product was 2.47 g. (72%). Recrystallization from methylene chloride–methylcyclohexane gave 1.46 g. (43%) of pure 2,3-dicyano-5,6-dihydro-5-ethoxy-1,4-dithiin (**4**), m.p. 104–106°. The infrared spectrum was identical to that of the product isolated in the trapping experiments above.

**Reaction of Trithiole Oxide 6 with Salt 1.**—A solution of freshly prepared **6**[1] (0.05 g., 0.00027 mole) in 0.5 ml. of DME was added immediately to a suspension of salt 1 (0.05 g., 0.00027 mole) in 0.5 ml. of DME. The mixture instantaneously became deep red in color and the suspended solid dissolved rapidly. A visible spectrum of the solution taken at this point showed the same absorption peaks as those of disulfide salt **3** obtained from salt 1 and thionyl chloride (398 $m\mu$, sh. at 415 $m\mu$). The solution was evaporated to dryness under reduced pressure and the residue was taken up in the minimum amount of acetonitrile. The salt was precipitated by the slow addition of methylene chloride to the acetonitrile solution. The yield of crude *trans-trans*-**3** was 0.04 g. (46%). After the product was dried *in vacuo* at 56°, its infrared spectrum was identical to that of the half-oxidized intermediate previously prepared from 1 and thionyl chloride.

A similar experiment employing **6** (0.101 g., 0.00054 mole) and salt 1 (0.100 g., 0.00054 mole) in DME (3 ml.) was carried out. Five minutes after mixing, methyl sulfate (0.14 g., 0.0011 mole) was added, and the mixture was worked up as previously described.[2] There was obtained 0.12 g. (70%) of a mixture of *trans-trans*- and *cis-cis*-bis-(2-methylmercapto-1,2-dicyanovinyl) disulfide.[2] The infrared spectrum indicated that the *cis-cis* isomer was formed in the larger amount, but a quantitative ratio was not determined.

**Conversion of Trithiole Oxide 6 to Dithiin 2.**—A solution of **6** (0.050 g., 0.00027 mole) in 1 ml. of DME was allowed to stand at room temperature for 1 hour. After about 20 minutes turbidity developed and a yellow solid separated. The precipitated sulfur was filtered off and the filtrate was evaporated to dryness at room temperature. The crystalline residue melted at 184–189°, and the infrared spectrum showed that it was essentially pure **2**. No trace of the strong chracteristic absorptions of tricyano-1,4-dithiino[c]-isothiazole[1] was observed. Although the sulfur dioxide was not determined, its presence was inferred by the strong characteristic odor of the reaction mixture before evaporation. The yield of dithiin **2** was 0.028 g. (95%).

Trithiole oxide **6** was also unstable in diethyl ether and tetrahydrofuran solutions, and ether solvents in general gave high yields of dithiin **2**, sulfur and sulfur dioxide. Solutions of **6** in methylene chloride were only decomposed to the extent of 50% in 24 hours.

**Reaction of Trithiole Oxide 6 with Ethyl Vinyl Ether.**—Trithiole oxide **6** (0.10 g., 0.00053 mole) was added in portions over 5 minutes to a solution of ethyl vinyl ether (0.23 g., 0.0032 mole) in 3 ml. of DME. The mixture was allowed to stand overnight at room temperature and was then evaporated to dryness. The slightly oily crystals were dissolved in 80:20 ether–methylene chloride and the solution was chromatographed on a column of acid-washed alumina. The eluate was evaporated to give 0.088 g. (78%) of cream colored crystals melting at 106–106.5°. The infrared spectrum of the product was identical to that of authentic adduct **4**.

**Addition of Trithiole Oxide 6 to Salt 1 and Ethyl Vinyl Ether.**—Freshly sublimed trithiole oxide 6 (0.061 g., 0.00032 mole) was added in portions over 15 minutes to a mixture of salt 1 (0.069 g., 0.00037 mole) and ethyl vinyl ether (0.40 g., 0.0056 mole) in DME (1.5 ml.) at 0°. The solution was evaporated to dryness *in vacuo*. The residue was extracted thoroughly with methylene chloride. The extract was concentrated and chromatographed on acid-washed alumina. From the eluate was obtained 0.0089 g. (13%) of adduct **4**, identified by its infrared spectrum. An insoluble orange solid was recovered from the methylene chloride extraction in 80% yield and was shown to be *trans-trans* **3**.

**Oxidation of Salt 1 with 1,1,2,2-Tetrabromethane in the Presence of Ethyl Vinyl Ether.**—A mixture of salt 1 (1.86 g., 0.0100 mole) and ethyl vinyl ether (5.30 g., 0.074 mole) in DME (25 ml.) was stirred at 25°, and over 10 minutes solid 1,1,2,2-tetrabromoethane (3.48 g., 0.010 mole) was added. After 30 minutes the red-orange suspension was filtered and the filtrate was evaporated to dryness *in vacuo*. The residue was extracted thoroughly with methylene chloride. Evaporation of the methylene chloride extract gave 0.02 g. of a gummy material whose infrared spectrum was different from that of adduct **4**. The maximum yield of **4** would, therefore, have been <1%. The red-orange solid removed in the initial filtration was shown to be disodium *trans-trans*-**3**[2] which was formed in 55% yield.

**Kinetic Studies.**—A brief study of the kinetics of the decomposition of trithiole oxide **6** in ether solvents was carried out by periodically obtaining the ultraviolet spectrum. Trithiole oxide **6** was prepared as previously described[1] and was twice sublimed rapidly at 105° (0.2 mm.) for immediate use in a kinetics experiment. It was essential that the solvents employed be as pure as possible. In DME, which had been stored and distilled from sodium, erratic reaction rates were observed and often it was not possible to reproduce in successive runs the initial spectrum of freshly mixed solutions of **6**. The best method found for purification of DME was distillation through a 15″ column packed with glass helices from lithium aluminum hydride in a nitrogen atmosphere. This procedure was superior to distillation from sodium, passage through molecular sieves or even to gas chromatographic separation. The transparency in the ultraviolet spectrum was used as a criterion of purity. DME purified in the preferred manner showed a gradual increase of absorption from 0 at 276 $m\mu$ to 0.1 at 220 $m\mu$ (measured in a 1-cm. cell *vs.* air). Tetrahydrofuran and diethyl ether were also purified by distillation from lithium aluminum hydride.

The progress of the reaction was followed by measuring the appearance of the absorption band of tetracyano-1,4-dithiin (**2**) at 327 $m\mu$. It would have been better to measure the disappearance of the trithiole oxide **6** band at 273 $m\mu$, but sulfur dioxide, a reaction product, absorbs strongly at 278 $m\mu$. Sulfur dioxide absorbs only weakly at 327 $m\mu$, and a small correction was applied in treating the data. In some runs the disappearance of **6** was followed over the early stages of the reaction, and good agreement was found between this rate and the rate of appearance of **2**.

In a typical kinetics run, freshly sublimed trithiole oxide **6** (0.0164 g., 0.0000872 mole) was placed in a clean 50-ml. erlenmeyer flask fitted with a serum stopper. The flask was purged with nitrogen by means of syringe needles which pierced the stopper. 1,2-Dimethoxyethane (10.0 ml.) was transferred as rapidly as possible by syringe from a serum-stoppered container into the sample flask. The sample dissolved in a few seconds and a second syringe was used to fill a 0.5-mm. ultraviolet cell with the solution. The cell temperature was 33°. The first reading was taken quickly, usually 2 minutes after mixing. The data for this run are given in Table II. Specific first-order rate constants were calculated using the expression $k_1 = 2.303/t \times \log C_0/C$, where $C$ refers to the concentration of trithiole oxide **6**.

Similar kinetics runs were attempted on this system with ethyl vinyl ether added to the reaction mixture. For the first 60% reaction the kinetics were largely first order, but it

TABLE II

RATE OF CONVERSION OF 0.00872 *M* SOLUTION OF DICYANO-1,2,3-TRITHIOLE-2-OXIDE TO TETRACYANO-1,4-DITHIIN IN 1,2-DIMETHOXYETHANE AT 33°

| Time, min. | Absorbance at 327 mμ | Concn. **6**, g./l.[b] | $k_1$, sec.$^{-1}$ |
|---|---|---|---|
| 0 | 0.523[a] | 1.640 | .... |
| 1.83 | .572 | 1.572 | 0.0230 |
| 2.75 | .598 | 1.538 | .0232 |
| 3.42 | .612 | 1.519 | .0225 |
| 4.25 | .635 | 1.488 | .0229 |
| 5.17 | .660 | 1.452 | .0235 |
| 8.00 | .738 | 1.346 | .0247 |
| 12.0 | .836 | 1.212 | .0252 |
| 18.0 | .963 | 1.041 | .0252 |
| 28.0 | 1.135 | 0.807 | .0253 |
| 39.0 | 1.294 | .591 | .0262 |
| 52.0 | 1.414 | .426 | .0259 |
| 67.0 | 1.504 | .303 | .0252 |
| 82.0 | 1.578 | .205 | .0254 |
| 102 | 1.652 | .105 | .0270 |
| 172 | 1.728 | 0 | .... |
| | | Av. | 0.0247 ± 0.0023 |

[a] Extrapolated. [b] Trithiole oxide **6** concn. = [1-(abs. −0.523/1.728−0.523)] × 1.640.

was evident that the reaction was more complicated than before, since during the last 40% reaction the rate accelerated erratically in two runs. The implication of an imposed catalytic zero-order reaction was evident, and this system was not studied in detail. The crude data gave $k_1$ = 0.079 sec.$^{-1}$ in the presence of ethyl vinyl ether (*ca.* 0.00872 mole) under the same conditions (solvent, DME) over the first 25% reaction.

**Oxidation of Sodium Cyanodithioformate·3DMF with Thionyl Chloride.**—A freshly prepared solution of sodium cyanodithioformate·3DMF[2] (68.8 g., 0.200 mole) in dimethylformamide (50 ml.) was stirred and cooled. The temperature was maintained at 10–20° while thionyl chloride (11.8 g., 0.100 mole) was added dropwise over 15 minutes. The red mixture was poured into water (400 ml.) and the precipitated solid was removed by filtration. The solid was dissolved in acetone (150 ml.), the resulting solution was filtered, and water (150 ml.) was added. There was obtained 2.11 g. (19.5%) of crude tetracyano-1,4-dithiin (**2**). The infrared spectrum of the product showed no contamination by tricyano-1,4-dithiino[c]isothiazole.[1]

**Oxidation of Sodium Cyanodithioformate·3DMF with Thionyl Chloride in the Presence of Ethyl Vinyl Ether.**—A solution of sodium cyanodithioformate·3DMF was prepared in the usual manner[2] from sodium cyanide (4.9 g., 0.10 mole) and carbon disulfide (8.2 g., 0.11 mole) in dimethyl formamide (30 ml.). The suspension was diluted with dry acetonitrile (40 ml.) and ethyl vinyl ether (11.0 g., 0.15 mole) was added. The mixture was stirred in an ice-bath while a solution of thionyl chloride (5.95 g., 0.050 mole) in acetonitrile (5 ml.) was added dropwise over 10 minutes. The dark brown color lightened to amber, and the reaction mixture was poured into water (300 ml.). The gummy red mass was removed by filtration and taken up in methylene chloride. The methylene chloride solution was washed three times with water, dried over sodium sulfate and evaporated to dryness *in vacuo*. The residue was chromatographed on acid-washed alumina using ether as eluent. There was obtained 3.64 g. (34%) of 2,3-dicyano-5-ethoxy-5,6-dihydro-1,4-dithiin (**4**), m.p. 98–102°. The infrared spectrum was identical with that of an authentic sample.

**Reaction of Tetraethylammonium Cyanodithioformate with Ethylene Dibromide.**—A mixture of tetraethylammonium cyanodithioformate[2] (4.64 g., 0.020 mole) and ethylene dibromide (1.87 g., 0.010 mole) in DME (50 ml.) was stirred for 30 minutes at 25° and then for 1 hour under reflux. The precipitated tetraethylammonium bromide was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The residue was chromatographed on acid-washed-alumina using methylene chloride as eluent. There was obtained 0.29 g. (17%) of 2,3-dicyano-5,6-dihydro-1,4-dithiin (**22**), m.p. 135–137°, whose infrared spectrum was identical with that of an authentic sample.[2] Subsequent fractions from the chromatogram afforded an unstable orange oil which could not be characterized but may have been 1,2-bis-(cyanodithioformato)-ethane.

**Oxidation of Salt 1 with Tetracyanoethylene.**—Under anhydrous and oxygen-free conditions a solution of tetracyanoethylene (0.128 g., 0.0010 mole) in acetonitrile (20 ml.) was added dropwise over 15 minutes to a stirred solution of **1** (0.186 g., 0.0010 mole) in acetonitrile (60 ml.). After the mixture had stirred for 5 minutes, the ultraviolet and visible spectra were obtained. The ultraviolet spectrum showed the presence of a trace of dithiin **2** (242, 315, 329 mμ), no significant amount of salt **1** and traces of tetracyanoethylene. The visible spectrum was consonant with the presence of sodium tetracyanoethylene anion-radical and disodium *cis-cis*-**3** (389 mμ). Both products were isolated in other oxidation experiments.

A second portion of tetracyanoethylene (0.128 g., 0.0010 mole) in acetonitrile (20 ml.) was added dropwise over 10 minutes. After the mixture had stirred for an additional 5 minutes, the ultraviolet and visible spectra were again obtained. The ultraviolet spectrum showed dithiin **2** (315, 329 mμ), tetracyanoethylene and no tricyano-1,4-dithiino-[c]-isothiazole.[1] The visible spectrum showed the well-defined absorption maxima of sodium tetracyanoethylene anion-radical and indicated the absence of *cis-cis*-**3**. The reaction mixture was stoppered and allowed to stir at 25° for an additional 2 days and the spectra were again determined. The ultraviolet region showed bands at 285 and 240 mμ indicating the presence of the isothiazole.[1] Weak absorption at 329, 271 and at 263 mμ showed traces of dithiin **2** and tetracyanoethylene, respectively.