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Alkyl-Substituted s-Trithianes Containing Functional Groups in the Side Chain[1]

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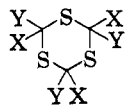
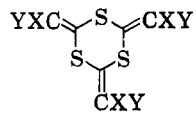
2,4,6-Tris(chloromethyl)-s-trithiane (I) has been prepared from chloroacetaldehyde and hydrogen sulfide. The two geometrical isomers have been isolated and structures have been assigned from proton magnetic resonance data. Dehydrohalogenation has yielded 2,4,6-tris(methylene)-s-trithiane (II), an unusual ketene thioacetal. The reactions of these two compounds have been investigated. *cis*-2,4,6-Tris(2-chloroethyl)-s-trithiane (XI) has been prepared from acrolein and dehydrohalogenated to 2,4,6-triethylidene-s-trithiane (XIII). The conformation of s-trithiane derivatives is discussed.

The objective of this work was the preparation of 2,4,6-tris(chloromethyl)-s-trithiane (I) and 2,4,6-tris(methylene)-s-trithiane (II), and an investigation of their reactions. I is related to mustard gas in structure, while II is structurally similar to a





I. X = $ClCH_2$, Y = H
II. X = Y = H
III. X = Cl_3C, Y = H
IV. X = Y = Cl
V. X = Cl_3C, Y = Cl
XIII. X = CH_3, Y = H
VI. X = $(CH_2)_nNHCH_3 \cdot HCl$, Y = H
IX. X = $C_6H_5SCH_2$, Y = H
XI. X = $ClCH_2CH_2$, Y = H
XII. X = $C_6H_5SCH_2CH_2$, Y = H
XIV. X = $CH_2=CH$, Y = H

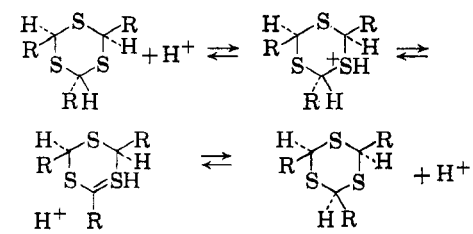
ketene thioacetal, being the cyclic trimer of thioketene, which has not been reported in a monomeric form. It was of interest to see if their reactions parallel those of their noncyclic analogs.

Although numerous s-trithianes are known, there are very few examples of 2,4,6-trialkyl-s-trithianes with functional groups in the side chain.[2] Chattaway and Kellett[3] prepared 2,4,6-tris(trichloromethyl)-s-trithiane (III) in very low yield from chloral and hydrogen sulfide; only one of the two possible isomers was isolated.

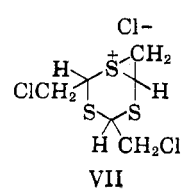
Dehydrohalogenation yielded 2,4,6-tris(dichloromethylene)-s-trithiane (IV), which was chlorinated to 2,4,6-trichloro-2,4,6-tris(trichloromethyl)-s-trithiane (V); here, too, only one isomer was isolated. More recently Leonard and Musker[4] prepared several 2,4,6-tris(methylaminoalkyl)-s-trithiane trihydrochlorides (VI, n = 5–7) by mercuric acetate oxidation of 1-methyl-1-azacycloalkanes followed by treatment with hydrogen sulfide and hydrogen chloride.

The reaction of chloroacetaldehyde with hydrogen sulfide in acetic acid, using hydrogen chloride as the catalyst, gave a 27% yield of 2,4,6-tris(chloromethyl)-s-trithiane (I). The product consisted of 84% of the β-isomer, m.p. 162°, and 16% of the α-isomer, m.p. 100.0–100.5°. In 75% aqueous sulfuric acid the yield was improved slightly (35%), and the ratio of α-isomer to β-isomer was 2:1. It is not readily apparent why the change in reaction conditions led to a change in the isomer distribution, but the more stable β-isomer predominated when hydrogen chloride was used as the catalyst under all the conditions investigated (see Table II). This phenomenon is not a general one, however. Douglass and Hydro[5] obtained predominantly the α-isomer of 2,4,6-tribenzyl-s-trithiane using hydrogen chloride in absolute ethanol.

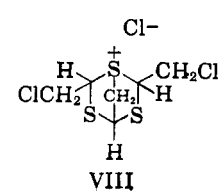
Although acidic reagents generally isomerize α-2,4,6-trialkyl-s-trithianes to the β-isomers, we were unable to isomerize α-I to the β-isomer with iodine or zinc chloride under the conditions used by Suyver with the trimethyl derivative.[6] Isomerization may be considered to take place in the following manner:



Since it appears rather unlikely that in the case of I the α-isomer is more stable than the β, the lack of isomerization must be attributed to decreased electron density on the sulfur atoms, perhaps by the contribution of structures such as VII or VIII to the structure of I.



VII



VIII

(1) Presented in part at the Delaware Science Symposium, Wilmington, Del., Jan. 13, 1960, and before the Division of Organic Chemistry at the 137th Meeting of the Amer. Chem. Soc., Cleveland, Apr. 5–14, 1960.

(2) E. E. Campaigne, *Chem. Revs.*, **39**, 1 (1946).

(3) F. D. Chattaway and E. G. Kellett, *J. Chem. Soc.*, 2908 (1929).

(4) N. J. Leonard and W. K. Musker, *J. Am. Chem. Soc.*, **81**, 5631 (1959).

TABLE I

PROTON MAGNETIC RESONANCE[a] SPECTRA OF *s*-TRITHIANE DERIVATIVES

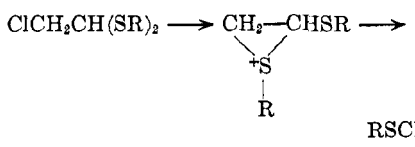
Compound	Solvent	Chem. Shift,[b] c.p.s.	Coupling Const., c.p.s.	No. Protons	Assignment
cis-I	DMF	138 (triplet)	5.3	3	Ring H
		196 (doublet)	5.3	6	$-CH_2Cl$
trans-I	DMF	136 (triplet)	5.9	2	Ring H
		149 (triplet)	5.9	1	Ring H
		186 (doublet)	6.7	2	$-CH_2Cl$
		199 (doublet)	5.4	4	$-CH_2Cl$
cis-IX	CCl_4	−42		15	C_6H_5
		149 (triplet)	7.0	3	Ring H
		198 (doublet)	7.0	6	$-CH_2S-$
trans-IX	CCl_4	−46		15	C_6H_5
		132 (triplet)	6.9	2	Ring H
		150 (triplet)	6.9	1	Ring H
		194 (unresolved)		6	$-CH_2S-$
cis-XI	DMF	103 (triplet)	5.9	3	Ring H
		153 (triplet)	5.4	6	$-CH_2Cl$
		238 (unresolved)			$-CH_2-$
cis-XII	CCl_4	−40		15	C_6H_5
		131 (unresolved)		3	Ring H
		197 (triplet)		6	$-CH_2S-$
		250 (2 sets of triplets)		6	$-CH_2-$

[a] 60-Mc. high resolution spectrometer. [b] With respect to benzene.

In most cases assignment of the *cis*-structure to the β-isomer and *trans* to the α-isomer of trisubstituted *s*-trithianes has been by analogy with Chattaway and Kellett's work on 2,4,6-trimethyl-*s*-trithiane.[7] These authors found that the α-isomer is *trans*, since it gave two monosulfones upon oxidation, while the β-isomer is *cis*, since it gave only one monosulfone. Proton magnetic resonance (Table I) has confirmed these assignments for α- and β-2,4,6-tris(chloromethyl)-*s*-trithiane. The β-isomer must be *cis*, since it showed only two kinds of protons in the ratio of 2:1, a doublet representing the methylenic hydrogens and a triplet representing the ring hydrogens. The α-isomer showed two sets each of doublets and triplets in the ratio of 4:2:1:2, in complete accord with expectations for a *trans*-isomer. It would appear reasonable, therefore, to conclude that in all cases the less soluble, higher melting 2,4,6-trisubstituted-*s*-trithiane is the *cis*-isomer, while the more soluble, lower melting isomer is the *trans*.

cis-I was oxidized with hydrogen peroxide in acetone at room temperature. A low yield of a dioxide, which was shown by infrared analysis to be a disulfoxide, was obtained. No attempt was made to determine which of the two geometrical isomers of the disulfoxide had been isolated; other oxidation products were undoubtedly present in the reaction mixture.

Treatment of either *cis*- or *trans*-I with sodium *t*-butoxide gave a 62% yield of 2,4,6-tris(methylene)-*s*-trithiane (II) as an unstable, yellow oil. Other nucleophilic reagents appeared to give the same results. Trimethylamine gave a 50% yield of trimethylammonium hydrochloride (isolated as the hydroiodide) after eighteen hours at 100°, and sodium 3,5-dinitrobenzoate gave a 69% yield of the free acid after seven days in boiling ethanol. Thus, it would appear that the compound is much less prone to dehydrohalogenate than is 2,4,6-tris(trichloromethyl)-*s*-trithiane (III), which loses hydrogen chloride even with alcoholic potassium acetate at room temperature. I is much more stable than α-halomercaptals, which are reported to eliminate hydrogen chloride spontaneously.[8-10] In this reaction a rearrangement takes place, presumably *via* the formation of an intermediate sulfonium ion.[10]



Since the rearrangement of I is unlikely, it apparently undergoes a normal E_2 elimination, the elimination being more difficult than in III because of the lower acidity of the ring hydrogens.

In only one instance did I undergo a nucleophilic displacement rather than elimination. *cis*-I reacted with sodium thiophenoxide to give a 66% yield of the *cis*-isomer of 2,4,6-tris(phenylthiomethyl)-*s*-

(5) I. B. Douglass and W. R. Hydro, *J. Am. Chem. Soc.*, **73**, 3507 (1951).

(6) J. F. Suyver, *Rec. trav. chim.*, **24**, 377 (1905).

(7) F. D. Chattaway and E. G. Kellett, *J. Chem. Soc.*, 1352 (1930).

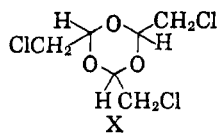
(8) E. Rothstein, *J. Chem. Soc.*, 1553 (1940).

(9) E. Rothstein and R. Whitely, *J. Chem. Soc.*, 4012 (1953).

(10) J. W. Heberling and Hans Wynberg, *J. Am. Chem. Soc.*, **77**, 1169 (1955).

trithiane (IX). The same compound was isolated in 24% yield by the photochemical addition of thiophenol to 2,4,6-tris(methylene)-*s*-trithiane (II).[11] The absence of a methyl band in the infrared spectrum of the pure compound indicated the correctness of the assigned structure. This was confirmed by the proton magnetic resonance spectrum of *cis*-IX, which showed that substitution had occurred without isomerization, since the spectrum showed two kinds of hydrogen, in addition to the aromatic hydrogens, in the ratio of 2:1. Similarly, *trans*-I reacted with sodium thiophenoxide under the same conditions. Although the *trans*-tris-(phenylthiomethyl) derivative could not be crystallized, proton magnetic resonance showed that here too substitution took place without rearrangement, *trans*-IX showing three kinds of hydrogen, in addition to the aromatic hydrogens, in a ratio of 2:1:6; the two different kinds of methylene hydrogens were not resolved. Inasmuch as both *cis*- and *trans*-I reacted without rearrangement, there can be little doubt that the reaction involved a nucleophilic displacement and not an elimination reaction followed by addition.

Although these reactions appear to be normal nucleophilic displacements, a comparison of the reactivity of I with its oxygen analog, 2,4,6-tris(chloromethyl)-*s*-trioxane (X), casts some doubt on this conclusion. One would expect comparable rates for I and X in a straight nucleophilic displacement. However, both *cis*- and *trans*-I reacted



X

completely with sodium thiophenoxide in less than an hour in refluxing ethanol, as evidenced by sodium chloride formation, whereas X precipitated only 13% of the calculated quantity of sodium chloride in two hours under the same conditions, and even after five days the reaction was incomplete. In an attempt to determine if there is any SN1 character to the reaction of I with thiophenoxide, presumably involving sulfonium intermediates such as VII or VIII,[12] the reaction of *cis*-I with ethanol was investigated. Although chloride ion was liberated in refluxing ethanol, the reaction was considerably slower than in the presence of thiophenoxide, and the infrared spectrum of the residue indicated considerable decomposition of the molecule. It appears, therefore, that a detailed kinetic investigation would be required to determine the course of this interesting substitution reaction.

The structure of 2,4,6-tris(methylene)-*s*-trithiane (II) was assigned on the basis of its analysis, its spectrum, and its chemical properties. Acid hydrolysis gave acetic acid in 63% yield, while aniline gave thioacetanilide and *N,N'*-diphenylacetamidine; 1,1-bis(ethylthio)ethene is reported to give the same products.[15] These reactions, plus the photochemical addition of thiophenol,[16] leave little doubt as to the correctness of the assigned structure. II was isolated as a pale yellow liquid with a fruity odor. It polymerized on standing, even at −40°, but was considerably more stable in solution and in the presence of potassium hydroxide. It copolymerized with styrene in the presence of a free radical catalyst to yield, as expected, an insoluble, cross-linked polymer.

2,4,6-Tris(2-chloroethyl)-*s*-trithiane (XI) was prepared in low yield from acrolein, hydrogen chloride, and hydrogen sulfide; no attempt was made to determine optimum conditions for the reaction, and only one isomer was isolated. Although the analysis was slightly off, presumably because of some loss of hydrogen chloride during recrystallization, proton magnetic resonance confirmed the structure and showed that the compound isolated was the *cis*-isomer. Reaction of XI with sodium thiophenoxide yielded 2,4,6-tris(2-phenylthioethyl)-*s*-trithiane (XII), very probably the *cis*-isomer according to proton magnetic resonance, while reaction with potassium *t*-butoxide yielded 2,4,6-triethylidene-*s*-trithiane (XIII) rather than the expected trivinyl compound (XIV). The ethylidene structure was assigned to XIII on the basis of a strong 7.28-μ band in the infrared spectrum assignable to a methyl group. 3-Chloro-1,1-bis(ethylthio)propane is reported to react analogously, giving 1,1-bis(ethylthio)-1-propene on dehydrohalogenation instead of the 2-propene.[18]

The conformation of the *s*-trithiane ring is very interesting, since there is no possibility of hydrogen eclipsing, even in the boat form. There is little doubt, from the electron diffraction investigation

(11) The low yield in this reaction may be attributable to the simultaneous formation of the *trans*-isomer, which was not isolated. Apparently some reverse addition also took place, since methyl bands were found in the infrared spectrum of the crude reaction mixture.

(12) Roberts and Cheng[13] postulated a sulfonium ion intermediate similar to VII to explain the formation of 2-ethyl-2-methyl-4-chloromethyl-1,3-dithiolane from methyl ethyl ketone and 2,3-dimercapto-1-propanol in the presence of hydrogen chloride, and the conversion of this to a mixture of 4-hydroxymethyl- and 4-ethoxymethyl-1,3-dithiolanes with aqueous ethanolic sodium hydroxide. However, Miles and Owen[14] reported that 2-phenyl-4-bromomethyl-1,3-dithiolane yielded the 4-methylene compound with sodium ethoxide.

(13) R. M. Roberts and C. G. Cheng, *J. Org. Chem.*, **23**, 983 (1958).

(14) L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 2938 (1950).

(15) H. C. Volger and J. F. Arens, *Rec. trav. chim.*, **76**, 847 (1957).

(16) The radical-catalyzed addition of ethyl mercaptan to 1,1-bis(ethylthio)ethene follows a similar course, yielding 1,1,2-tris(ethylthio)ethane.[17]

(17) L. C. Rinzema, J. Stoffelsma, and J. F. Arens, *Rec. trav. chim.*, **78**, 354 (1959).

(18) E. Rothstein, *J. Chem. Soc.*, 1550 (1940).

of Hassel and Viervoll,[19] that *s*-trithiane itself exists predominantly in the chair form. From the evidence in the literature and our proton magnetic resonance work it appears quite reasonable that *cis*-2,4,6-trialkyl-*s*-trithianes should exist in the chair form with three equatorial substituents. The situation with respect to the *trans*-isomers is less clear, however. The spectra of the *cis*- and *trans*-chloromethyl (I) and phenylthiomethyl (IX) derivatives are listed in Table I. In *trans*-I one ring hydrogen is 13 c.p.s. to the high field side of the other two. Lemieux and co-workers[20] found that the signals for axial protons occur at higher field than those for equatorial protons in a number of substituted cyclohexanes. In particular, the axial proton shift was 17 c.p.s. higher than the equatorial shift in the closely related compound, *trans*-2,4,6-tris(trichloromethyl)-*s*-trioxane, which has been shown rather unequivocally by dipole moment studies to exist in the chair form.[21] In order for *trans*-I to agree with Lemieux's findings and to exist in the chair conformation, it would have to have two equatorial hydrogens and one axial, *i.e.*, two axial chloromethyl groups and one equatorial. Inasmuch as this is highly unlikely, it is tempting to reason that the molecule exists in the boat form. An inspection of molecular models shows that the one *trans*-axial hydrogen in this conformation would be expected to be shifted to the high field side of the two *cis*-axial hydrogens. The same reasoning applies to the phenylthiomethyl compound (IX); here one ring hydrogen appears at 18 c.p.s. to the high field side of the other two.

There is a fundamental difference, however, between the spectra of I and IX. A comparison of *cis*- and *trans*-I shows that the environment of the odd hydrogen in the *trans*-isomer has changed, the two presumably axial hydrogens showing the same chemical shift as in the *cis*-isomer. The reverse is true in IX, however, since here the odd hydrogen in the *trans*-isomer has the same chemical shift as the three axial hydrogens in the *cis*-isomer, whereas the two presumably axial hydrogens in the *trans*-isomer have shifted. No reason for this discrepancy is apparent, and we are inclined to believe that an insufficient number of examples exist for proton magnetic resonance to be used to make unequivocal structural assignments in this area. It is unfortunate that the moment of a freely rotating chloromethyl group is so small that dipole moment measurements of *cis*- and *trans*-I would not serve to distinguish between chair and boat forms.[22]

(19) O. Hassel and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947).

(20) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

(21) A. Novak and E. Whalley, *Can. J. Chem.*, **36**, 1116 (1958).

(22) We are indebted to Prof. J. G. Miller of the University of Pennsylvania for this observation.

EXPERIMENTAL[23]

Spectral determinations. The proton magnetic resonance spectra were obtained with a Varian Associates' high resolution spectrometer operating at 60 Mc. and a magnetic field of about 14,100 gauss. The samples were dissolved in dimethylformamide or carbon tetrachloride. Benzene in a capillary tube was introduced as the reference. Most of the infrared absorption spectra were determined by a Perkin-Elmer Model 21 infrared spectrophotometer. The few taken with a Perkin-Elmer Infracord, without solvent, are so indicated. The ultraviolet spectral determination was made in isooctane using a Cary (Model 11) ultraviolet spectrophotometer.

2,4,6-Tris(chloromethyl)-s-trithiane (I). After passing hydrogen sulfide through 200 ml. of 75% (by volume) sulfuric acid at 0° for 30 min., chloroacetaldehyde (49.3 g. of 37% aqueous solution, 0.232 mole) was added dropwise with stirring over 2 hr., the hydrogen sulfide flow being continued for 20 hr. before the mixture was allowed to warm up overnight. After cooling to 0°, the addition of excess water yielded an oily solid, which was recrystallized from methylene chloride, then from benzene to give 2.62 g. of *cis*-I, m.p. 157.0–158.0°. An analytical sample was recrystallized several times from benzene, m.p. 160.5–161.0°; the melting point depended on the rate of heating.

Anal. Calcd. for $C_6H_9Cl_3S_3$: C, 25.40; H, 3.20; S, 33.90. Found: C, 25.54; H, 3.39; S, 34.20.

Addition of *n*-hexane to the benzene mother liquors gave 2.46 g. of *trans*-I as colorless needles, m.p. 100.0–100.5°, unchanged by recrystallization from benzene and from ether. An additional 2.63 g. was recovered from the mother liquors, making a total yield of 35% for both isomers.

Anal. Found: C, 25.51; H, 3.33; S, 33.90.

The infrared absorption spectrum of the *cis*-isomer (taken on a Nujol mull) had major bands at 7.77, 8.27, 9.35, 9.90, 10.43, 12.85, 13.62, and 14.35 μ. The *trans*-isomer had bands at 7.77, 8.25, 8.70, 9.71, 9.84, 9.98, 10.45, 10.65, 10.85, 13.23, 13.70, and 14.10 μ.

The use of other reaction media at −10° is summarized in Table II.

TABLE II

EFFECT OF REACTION MEDIUM ON YIELD OF 2,4,6-TRIS(CHLOROMETHYL)-*s*-TRITHIANE

Reaction Medium	Total Yield, %	Ratio *cis*- to *trans*-Isomers
60:40 95% H_2SO_4–CH_3COOH	35	38:62
Acetic acid saturated with HCl	27	84:16
Ether saturated with HCl	27	76:24
95% Ethanol saturated with HCl	10	[a]

[a] No *trans*-isomer was isolated.

2,4,6-Tris(chloromethyl)-s-trithiane-1,3-dioxide. A mixture of *cis*-2,4,6-tris(chloromethyl)-*s*-trithiane (0.50 g., 1.8 millimoles), hydrogen peroxide (5 ml. of 30% aqueous solution, 44 mmoles), and acetone (30 ml.) was stirred 3 days at 25°, then poured into water to give 1.09 g. of a colorless solid, m.p. 194–196°. Repeated crystallization from ethanol gave colorless needles melting at 250° with decomposition.

Anal. Calcd. for $C_6H_9Cl_3O_2S_3$: C, 22.83; H, 2.87; S, 30.47. Found: C, 23.05; H, 3.11; S, 31.20.

The infrared absorption spectrum (taken with a potassium bromide disk) had major bands at 7.01, 9.35, 9.55 (sulfoxide), and 12.21 μ. No band due to a sulfone was present.

(23) Analyses were carried out by the Analytical Division of the Research Center. All melting points are corrected.

2,4,6-Tris(methylene)-s-trithiane (II). *cis*-2,4,6-Tris-(chloromethyl)-*s*-trithiane (4.00 g., 14 mmoles) was added to a solution of sodium (1.00 g., 0.044 g.-atom) in 50 ml. of *t*-butyl alcohol. The mixture was heated to boiling and was then stirred 3 days at 25°. After removal of the solvent by distillation *in vacuo* at 25°, the residue was taken up in *n*-hexane, filtered to remove sodium chloride, and distilled to give 1.53 g. of II as a pale yellow liquid with a slight fruity odor, b.p. 73–74° at 0.25 mm. (62% yield).

Anal. Calcd. for $C_6H_6S_3$: C, 41.35; H, 3.47; S, 55.18. Found: C, 41.38; H, 3.80; S, 55.27.

The infrared absorption spectrum (taken partly in carbon tetrachloride, partly in carbon disulfide) showed bands at 6.29, 6.44 (exocyclic double bond),[24] 8.91, 11.27, 11.81 (exocyclic double bond), and 12.47 μ.[25] The ultraviolet absorption spectrum (in isooctane) showed bands at 240–244 mμ ($\epsilon \times 10^{-3} = 14.6$, —S—C—S—)[26] and 267 m$\mu$ (shoulder, $\epsilon \times 10^{-3} = 10.5$).

The product soon started to polymerize even at −40°, turning brown and developing a mercaptan-like odor in a day or two. Dilution with solvent, addition of a little potassium hydroxide, and storage under nitrogen reduced the tendency to decompose.

Application of this procedure to *trans*-I gave a product identical in boiling point and infrared absorption spectrum.

When *cis*-I was treated with trimethylamine in aqueous dioxane for 18 hr. at 100° in a sealed tube, the solvent evaporated, and the residue recrystallized from anhydrous ethanol, a 50% yield was obtained of trimethylamine hydrochloride, isolated by conversion to the hydriodide[27] with alcoholic potassium iodide. Aqueous sodium picrate converted it to a picrate, m.p. 221° with decomposition. A mixed melting point with authentic material[28] showed no depression.

Heating *cis*-I with sodium 3,5-dinitrobenzoate in boiling anhydrous ethanol for 7 days, followed by evaporation and recrystallization from ethyl acetate (with hot filtration) gave a 69% yield of 3,5-dinitrobenzoic acid, m.p. 203–204°.[29]

cis-2,4,6-Tris(phenylthiomethyl)-s-trithiane (IX) *from* I. Thiophenol (1.18 g., 11 mmoles) was added to a solution of sodium (0.25 g., 0.011 g.-atom) in 62 ml. of anhydrous ethanol. *cis*-I (1.00 g., 3.5 mmoles) was then added. After the mixture was heated at reflux (with occasional shaking) for 50 min., it was filtered to remove the sodium chloride (0.57 g., 92%). Cooling the mixture gradually to −20° gave 1.02 g. (66%) of *cis*-IX, m.p. 73.5–77.5°. Further recrystallization from ethanol gave colorless needles, m.p. 82.0–82.5°.

Anal. Calcd. for $C_{24}H_{24}S_6$: C, 57.10; H, 4.79; S, 38.11. Found: C, 57.29; H, 4.96; S, 38.32.

The infrared absorption spectrum (taken partly in carbon tetrachloride, partly in carbon disulfide) showed bands at 6.30, 6.78, 6.98, 9.76, 13.6, and 14.5 μ. No bands assignable to methyl or thiocarbonyl groups were present.

Application of this procedure to the *trans*-isomer gave an oil that could not be induced to crystallize; a satisfactory analysis could not be obtained. Its infrared spectrum was identical to that of the *cis*-isomer. However, its proton magnetic resonance spectrum (Table I) showed unequivocally that it was the *trans*-isomer.

Application of this procedure (with the calculated amount of sodium thiophenoxide) to 2,4,6-tris(chloromethyl)-*s*-trioxane[30] gave 0.08 g. (13%) of sodium chloride in 2.5 hr. After 5 days a total of 0.53 g. (86%) of sodium chloride had formed.

cis-2,4,6-Tris(phenylthiomethyl)-s-trithiane (IX) *from II.* After irradiating a mixture of II (0.75 g., 4.3 mmoles) and thiophenol (5.4 g., 49 mmoles) in a Vycor tube with an ultraviolet lamp (Hanovia 16106) for 20 hr., the excess thiophenol was removed by distillation, heating finally to 100° at 0.2 mm., and the residue was taken up in ethyl acetate–*n*-hexane. The oily crystals that formed on standing several days at −40° were separated by decanting the supernatant liquid and were recrystallized from ethanol to give 0.53 g. *cis*-IX, m.p. 74.0–75.0° (24% yield). Several recrystallizations from ethanol raised the melting point to 81.5–82.0°. The residue from the mother liquor showed a weak band at 7.35 μ in the infrared spectrum (taken on an Infracord) assignable to a methyl group.

Alcoholysis of cis-I. A solution of *cis*-I (0.14 g., 0.49 mmole) in 50 ml. of anhydrous ethanol was heated 4 hr. at 70°. After the mixture cooled gradually to −20°, filtration removed unchanged *cis*-I (0.08 g., 57% recovery). Titration of an aliquot of the mother liquor with 0.1*N* sodium hydroxide (using phenolphthalein) showed 0.50 mmole (34%) of hydrogen chloride to have formed. A control run showed no reaction between ethanol and hydrogen chloride under these conditions. The infrared spectrum of the residue from the remaining mother liquor (taken on an Infracord) showed 2,4,6-tris(methylene)-*s*-trithiane (II) to be absent. Bands at 5.81 μ (assignable to a carbonyl group) and at 8.99 and 9.29 μ (assignable to ethers) were present.

Acid hydrolysis of 2,4,6-tris(methylene)-s-trithiane (II). A mixture of II (1.66 g., 9.5 mmoles), dioxane (12 ml.), and 5% hydrochloric acid (8 ml.) was refluxed with stirring for 10 hr. Concentrated hydrochloric acid (1 ml.) was added, and heating was continued for 3 hr.; a 38% yield of hydrogen sulfide was obtained (determined as cadmium sulfide). The reaction mixture was steam-distilled. The distillate was neutralized with sodium hydroxide, extracted with ether to remove some orange oil, reduced in volume to 30 ml., and a solution of 2-benzyl-2-thiopseudourea hydrochloride (5.5 g., 29 mmoles) in water (35 ml.) added. The mixture was seeded, cooled overnight at 0–5°, and filtered to recover 3.82 g. (63%) of 2-benzyl-2-thiopseudourea acetate, m.p. 132–133°. A mixed melting point with an authentic sample[31] showed no depression.

Reaction of aniline with 2,4,6-tris(methylene)-s-trithiane (II). After standing for 4 weeks, a solution of II (0.20 g., 1.1 mmoles), aniline (0.32 g., 3.4 mmoles), and *N*-phenyl-2-naphthylamine (0.01 g.) in benzene (1.0 ml.) was extracted several times with boiling *n*-hexane. Yellow crystals of an unknown compound (0.05 g., m.p. 140–141°) insoluble in both 10% hydrochloric acid and 5% sodium hydroxide formed in the concentrated extract on standing 4 weeks. After two crystallizations from *n*-hexane, yellow needles, m.p. 144.0–144.5°, were obtained.

Anal. Found: C, 65.86; H, 5.01; N, 9.39.

Extraction of the combined residue from evaporation of the filtrate and from the extraction with 5% sodium hydroxide followed by addition of carbon dioxide gave 0.17 g. (33%) of thioacetanilide, m.p. 67–68°. Crystallization from *n*-hexane and from water raised the melting point to 74.5–76.0°, a mixed melting point with authentic material[32] showing no depression.

Further extraction of the oil with 5% hydrochloric acid, followed by addition of ammonia to the extract, gave 0.08 g. (11%) of *N,N'*-diphenylacetamidine, m.p. 122.0–123.5°. Further crystallization from *n*-hexane raised the melting point to 131.5–132.5°, a mixed melting point with authentic material[32] showing no depression.

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Polymerization of II *with styrene.* A solution of II (0.05 g.), styrene (0.5 ml.), and α,α'-azodiisobutyronitrile (0.01 g.) in 2 ml. of benzene under nitrogen set to a gel on heating overnight at 60°. After filtration and washing with benzene, 0.30 g. of golden-brown polymer was obtained. It was swollen by boiling carbon tetrachloride, and by toluene and butyl acetate at 100°, but did not dissolve.

cis-2,4,6-Tris(2-chloroethyl)-s-trithiane (XI). Hydrogen sulfide was passed into a solution of 33.6 g. (0.60 mole) of acrolein in 200 ml. of ether, previously saturated with hydrogen chloride, for 20 hr. at −20 to −10°. After warming to room temperature overnight, the mixture was treated with benzene and water, the benzene layer was separated, dried over magnesium sulfate, and freed of solvent by distillation. The residue was crystallized from ethyl acetate, then from ethyl acetate—*n*-hexane to give 5.08 g. of XI (8%), m.p. 115.0–116.0°. Further recrystallization from ethyl acetate raised the melting point to 130.0–131.5°.

Anal. Calcd. for $C_9H_{15}Cl_3S_3$: C, 33.18; H, 4.64; S, 29.52. Found: C, 33.94; H, 5.14; S, 30.20.

The rather unsatisfactory analysis probably resulted from loss of chloride during recrystallization. However, both its proton magnetic resonance spectrum and formation of the phenylthio derivative (XII) served to confirm the assigned structure.

cis-2,4,6-Tris(2-phenylthioethyl)-s-trithiane (XII). A sample (0.20 g., 0.62 mmole) of XI was treated with sodium thiophenoxide as described above for I. Since the product did not crystallize from the filtered reaction mixture, the solvent was removed by distillation and the residue was crystallized from ether to give 0.20 g. (59%) of XII, m.p. 70.0–74.0°. Further crystallization from *n*-hexane gave colorless needles, m.p. 82.5–83.0°.

Anal. Calcd. for $C_{27}H_{30}S_6$: C, 59.30; H, 5.53; S, 35.17. Found: C, 59.39; H, 5.95; S, 35.48.

2,4,6-Triethylidene-s-trithiane (XIII). To a solution of 0.18 g. (0.0046 g.-atom) of potassium in 10 ml. of *t*-butyl alcohol was added 0.50 g. (1.5 mmoles) of XI and 0.01 g. of 2,6-di-*t*-butyl-4-methylphenol. The solution was refluxed for 1 hr. The next day the solvent was removed *in vacuo* at 25°, and the residue was distilled to give 0.25 g. (76%) of an orange liquid, b.p. 109° at 0.15 mm.

Anal. Calcd. for $C_9H_{12}S_3$: C, 49.96; H, 5.59. Found: C, 49.56; H, 5.95.

The infrared spectrum (taken on an Infracord) had a band at 7.28 μ assignable to a methyl group.

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Reaction of Thiocyanates with Trialkyl Phosphites

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Trialkyl phosphites, $(RO)_3P$, react with alkyl and aryl thiocyanates, R'SCN, to give the alkylnitrile, RCN, and the corresponding thiophosphate, $(RO)_2P(=O)SR'$. The reaction is believed to occur by an ionic mechanism involving displacement of the cyanide ion by nucleophilic attack of the phosphorus on sulfur.

Trivalent phosphorus compounds, such as the trialkyl phosphites, are strong nucleophiles and will readily displace halide from an alkyl halide. The intermediate quasiphosphonium salt subsequently eliminates alkyl halide with simultaneous formation of the corresponding dialkyl alkylphosphonate. This reaction, first observed by Arbuzov,

$$(RO)_3P + R'Cl \longrightarrow [(RO)_3\overset{\oplus}{P}R'Cl^{\ominus}] \longrightarrow (RO)_2P(=O)R' + RCl$$

has received the attention of numerous experimenters[1] and has been extended to the displacement of groups other than halides.

Recently, nucleophilic attack of trialkyl phosphites on alkyl disulfides and sulfenyl chlorides has been reported[2] and discussed in a review.[3] In the case of ethyl disulfide, the reaction is a typical displacement of ethyl mercaptide ion from the sulfur of the disulfide followed by deethylation of the quasiphosphonium salt by ethyl mercaptide

$$(C_2H_5O)_3P + C_2H_5SSC_2H_5 \longrightarrow \left[\begin{matrix} C_2H_5S\overset{\oplus}{P}(OC_2H_5)_3 \\ C_2H_5S^{\ominus} \end{matrix}\right] \downarrow \; C_2H_5SC_2H_5 + C_2H_5SP(=O)(OC_2H_5)_2$$

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