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Binary Carbon Sulfides Based on the α-C_3S_5 Subunit and Related C—S—O, C—S—Cl, and C—S—N Compounds

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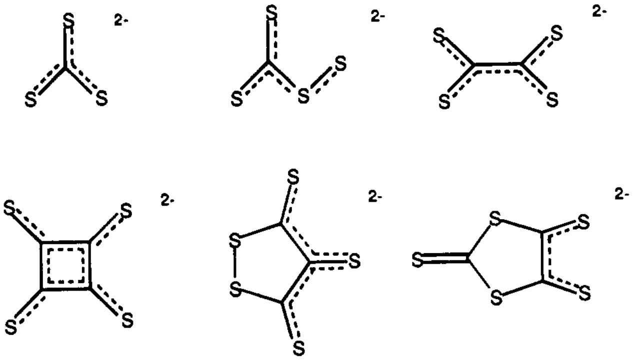
The synthesis and characterization of molecular carbon sulfides including C_3S_8, C_6S_8, C_6S_{10}, and C_6S_{12} are described. The reaction of 2 equivs of S_2Cl_2 with $(NBu_4)_2[Zn(C_3S_5)_2]$ (**1**) affords a 2:1 mixture of C_3S_8 and C_6S_{12}. Treatment of this mixture with excess $Hg(OAc)_2$ gives the soluble yellow species C_3S_7O. This compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 4.204(2)$ Å, $b = 8.942(5)$ Å, $c = 12.017(6)$ Å, $\alpha = 103.02(4)°$, $\beta = 96.64(4)°$, $\gamma = 90.47(4)°$, and $Z = 2$. The oxidation of **1** with 2 equiv of SO_2Cl_2 and subsequent extraction of the orange solid with CS_2 yielded the dimer C_6S_{10}. Raman spectra indicate that the crude oxidation product is modified upon extraction, possibly by break-up of the polymer $(C_3S_5)_n$. Treatment of C_6S_{10} with 2 equivs of $Hg(OAc)_2$ results in rearrangement of the central C_4S_4 ring in addition to a C═S to C═O exchange, to give a 1,4,5,6-tetrathiacycloheptadiene ring. $C_6S_8O_2$ crystallizes in the monoclinic space group $P2_1/c$, with $a = 15.461$ (6) Å, $b = 9.648(3)$ Å, $c = 7.852(1)$ Å, $\beta = 98.71(2)°$, and $Z = 4$. The ^{13}C NMR spectrum of $C_6S_8O_2$ exhibits resonances at δ 187.0, 137.5, and 130.8 in agreement with the crystal structure. Treatment of **1** with 4 equivs of HCl at −78 °C gave the metastable $C_3S_5H_2$ as characterized by ^1H NMR, FDMS, and IR spectroscopies, as well as its conversion to $C_3S_5Me_2$. This dithiol evolves H_2S, giving a new compound of the formula C_6S_8. This species was converted with $Hg(OAc)_2$ to $C_6S_6O_2$, which is formulated as a derivative of a c-1,2-S_2C_4 compound based on spectroscopic and elemental analysis data. Treatment of $(Bu_4N)_2[Zn(C_3S_5)_2]$ with 4 equiv of SO_2Cl_2 gave the sulfenyl chloride $C_3S_5Cl_2$, which in turn reacts with $LiN(SiMe_3)_2$ and Me_3SiN_3 to give $C_3S_5[N(SiMe_3)_2]_2$ and C_3S_5NCl, respectively.

Introduction

Compositions of two elements are among the most fundamental classes of matter.[1] Binary *molecular* phases are common for the hydrides of the main group elements, e.g., hydrocarbons and boranes, but otherwise such stoichiometrically simple families of molecules remain quite rare. In this context, the potential scope of carbon sulfide chemistry is considerable, given the fact that C—C, S—S, and C—S bonds are thermochemically robust. The C—C, C—S, and S—S (divalent sulfur) bond dissociation energies are 356 (diamond), 272 (C_2H_5SH), and 226 kJ/mol (S_8), respectively.[2,3] Not only are carbon sulfides expected to enjoy significant thermal stability, but they are also derived from abundant and inexpensive resources. These general considerations motivated our interest in the preparation of new carbon sulfides.

C—S cores are found in a variety of electronic materials, prominent representatives being the tetrathiafulvalenes and metallodithiolenes.[4] Poly(carbon subsulfide) displays high electrical conductivity, reminiscent of $(SN)_x$, and there would be interest in the development of more processible analogues of $(C_3S_2)_n$.[5] The carbon sulfides are thus promising precursors to new inorganic polymers. Carbon sulfides also have an important place in coordination chemistry;[6] thiocarbon ligands which have received study include CS_3^{2-} and its perthiolate CS_4^{2-},[7] tetrathiaoxalate $C_2S_4^{2-}$,[8,9] C_2S_6,[6-10] two isomers of $C_3S_5^{2-}$,[11] and tetrathiosquarate[12] $C_4S_4^{2-}$ (Chart 1). As we show in this paper, the coordination complexes of these species could be employed for the the preparation of new carbon sulfides.

Chart 1



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Most known binary carbon sulfides are comprised of three subunits: the two-connecting thiocarbonyl (CS), two-connecting S_x units ($x \geq 1$), and the four-connecting C=C fragment; i.e., they can be classified with the formula $S_x(CS)_y(C_2)_z$. One isomer of C_9S_9 does not conform to this pattern, as it features hypervalent 3-coordinated sulfur centers.[13] Tetrahedral carbon has not yet been observed in binary carbon sulfides although a complex of "$C_2S_6^{6-}$" has been described.[10] Mass spectrometric experiments, especially those utilizing neutralization–reionization techniques, have identified the linear molecules C_2S_2 and C_4S_2, as well as benzotrithiete (C_6S_6) and two isomers of CS_3.[14]

A major breakthrough in thiocarbon chemistry resulted from the development of an efficient synthesis of 2-thioxo-1,3-dithiole-4,5-dithiolate[10,15] (eq 1). In two preliminary reports, we

$$4e^- + 4\,CS_2 \longrightarrow CS_3^{2-} + C_3S_5^{2-} \qquad (1)$$

have shown how this anion can be converted to C_3S_8, C_6S_{10}, and C_6S_{12} via oxidative coupling and electrophilic sulfiding.[16] A more recent paper summarizes the syntheses of carbon sulfides from the second ("β") form of $C_3S_5^{2-}$.[17] In this paper, we describe new or improved syntheses of four carbon sulfides derived from α-$C_3S_5^{2-}$. These results are complemented by the preparation of a series of oxo derivatives of carbon sulfides. These new C–S–O compounds exhibit improved solubility, which has allowed a more complete characterization than is possible with the binary systems. Finally, we report the preparation of $C_3S_5Cl_2$ and its conversion to nitrogen-containing heterocycles.

Results and Discussion

C_3S_8 and C_6S_{12}. The reaction of $Cp_2TiC_3S_5$ with S_2Cl_2 affords a mixture of C_3S_8 and C_6S_{12}, along with poorly soluble yellow solids, which we assume are polymeric.[16] For this application, the Ti-containing reagent is prepared from Cp_2TiCl_2 by a chelate transfer reaction with $[Zn(C_3S_5)_2]^{2-}$. A still more efficient route to carbon sulfides uses this zinc complex directly. In this procedure, the precipitated product consists only of carbon sulfides, as established by the absence of ν_{CH} bands in its IR spectrum. It has the stoichiometry "C_3S_7" on the basis of elemental analysis, corresponding to a 2:1 mixture of C_3S_8 and C_6S_{12} (eq 2). The utility of the Zn reagent rests in the high

$$[Zn(C_3S_5)_2]^{2-} + 2\,S_2Cl_2 \longrightarrow C_3S_8 + {}^1/_2\,C_6S_{12} + ZnCl_4^{2-} \qquad (2)$$

solubility of $(NBu_4)_2ZnCl_4$ in the reaction medium, which allows easy separation from the precipitated carbon sulfides.

The mixture of C_3S_8 and C_6S_{12} from eq 2 can be separated by virtue of the greater solubility of the octasulfide in CH_2Cl_2. Solutions of C_3S_8 are slightly unstable with respect to C_6S_{12} via a photochemical process that can be easily minimized. The EI mass spectra of C_3S_8 and C_6S_{12} are similar, but the fragmentation patterns differ in important details. The molecular ion for C_3S_8 was observed along with the fragments $C_3S_6^+$ and S_8^+ and several smaller fragments. In the case of C_6S_{12}, the molecular ion was not observed, but a *m/z* 328 peak, corresponding to $C_6S_8^+$, is present in its mass spectrum, while it is absent in the spectrum for C_3S_8. The mass spectra of C_3S_8 and C_6S_{12} both feature strong peaks corresponding to $C_3S_6^+$. This ion is seen in the mass spectrum of other C–S compounds derived from α-$C_3S_5^{2-}$, such as C_6S_{10}. We speculate that $C_3S_6^+$ has a bicyclic structure and is related to other cyclic 7-π-e^- systems such as $S_3C_2(CF_3)_2^+$ and $S_3C_2(CO_2Me)_2^+$:[18]

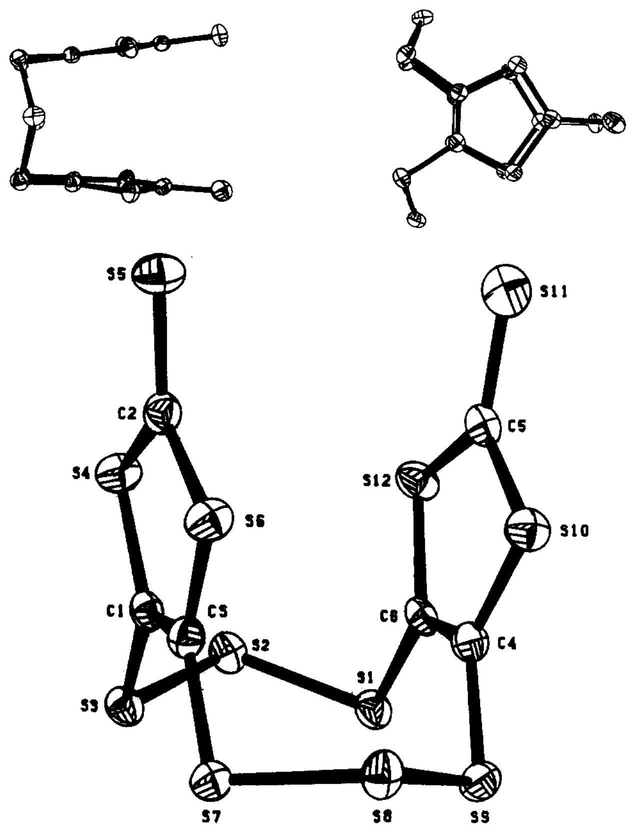
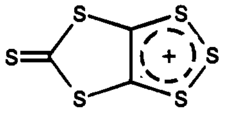
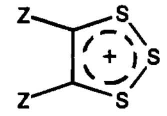


Figure 1. The structure of C_6S_{12} (three views).





The IR spectra of C_3S_8 and C_6S_{12} are quite similar and are dominated by strong $\nu_{C=S}$ bands at 1055 and 1064 cm^{-1}, respectively. The greatest difference appears in the ν_{SS} region. Bands attributable to $\nu_{C=C}$ were not observed, nor were they seen in the IR spectra of 1,3,4,6-tetrathiapentalene-2,5-dithione (D_{2h} symmetry) and $C_3S_5Me_2$, although they were observed in their Raman spectra.[19]

The structure of C_6S_{12} was determined by single-crystal X-ray diffraction (Figure 1). The molecule adopts a crown structure reminiscent of S_8 wherein the two C=C units replace S atoms. Thus, the S_6C_4 core adopts a crown conformation of approximate C_{2v} symmetry. The average S–S bond distance (2.061 Å) and S–S–S angle (106.8°) are very similar to the corresponding values for many forms of elemental sulfur, e.g. orthorhombic S_8 (2.051 Å, 108.1°) and S_6 (2.057 Å, 102.2°).[20] The most striking aspect of the structure is the presence of nearly eclipsed

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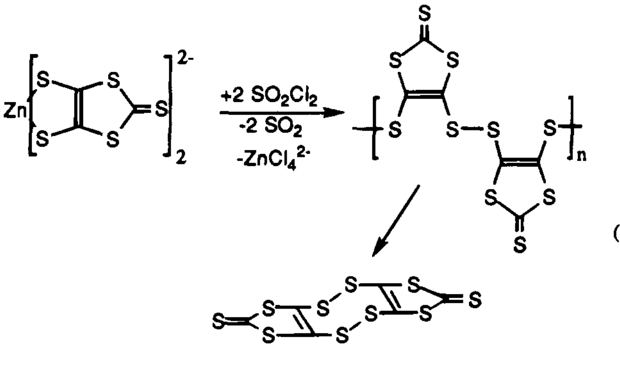
and mutually parallel (11.85°) C_3S_5 units with an interplanar distance of 3.88 Å for S(6) and S(10). The two C_3S_5 subunits are well suited for van der Waals interactions in view of the similar (Pauling) electronegativities of carbon (2.55) and sulfur (2.58).[2] The delocalized bonding in the C_3S_5 moieties should enhance the polarizability of its constituent atoms which in turn would strengthen this interaction. The intramolecular $\pi-\pi$ interaction in C_6S_{12} is reminiscent of the *inter*molecular $\pi-\pi$ interactions seen in partially oxidized complexes of the type $M(C_3S_5)_2^{n-}$.[21]

C_6S_{10}. Sulfuryl chloride readily converts $(NBu_4)_2[Zn(C_3S_5)_2]$ to a yellow-orange solid analyzing as $[C_3S_5]_n$. The precipitated solid is transparent in the range 2500–3500 cm^{-1}, demonstrating the absence of hydrocarbons. The solid is insoluble in most organic solvents but is slightly soluble in CS_2. In fact, this crude solid crystallizes upon being slurried in CS_2. We suggest that the initial precipitate is largely polymeric and that recrystallization in CS_2 promotes the conversion to the dimer (eq 3). The Raman spectrum of the product after extraction exhibits a new band in the ν_{SS} region at 512 cm^{-1}. The rate of dissolution of the polymer in CS_2 appears to decrease when the SO_2Cl_2 reaction is conducted at higher temperatures, indicating a greater proportion of the polymer. The EIMS of C_6S_{10} and C_6S_{12} are similar in that the $C_3S_6^+$ and $C_6S_8^+$ peaks were observed but no molecular ion was present. However, in contrast to the spectra of C_6S_{12} and C_3S_8, only a weak S_8^+ peak was observed in the mass spectrum of C_6S_{10}, indicating the absence of polysulfide linkages. We found that samples of $[C_3S_5]_n$ that had not been slurried with CS_2 were less reactive toward $Hg(OAc)_2$ (see below).



(3)

The molecular structure of the CS_2 solvate of C_6S_{10} (Figures 2 and 3) confirms the presence of two planar C_3S_5 subunits interconnected by persulfide bonds. Centrosymmetry is crystallographically imposed. The S_4 and the C_3S_5 planes are connected by 101° angles (Table 1). The monoclinic lattice of C_6S_{10}·$0.5CS_2$ consists of layers formed by stacking of C_3S_5 rings (distance between C_3S_5 rings is *ca.* 3.5 Å) such that each C_6S_{10} molecule engages in $\pi-\pi$ interactions with four other C_6S_{10} molecules. The sheets thus formed are joined by S···S contacts (3.83 Å) between thione groups. This interconnection pattern defines an array of infinite channels along the *c* axis which are partially occupied by CS_2 molecules.

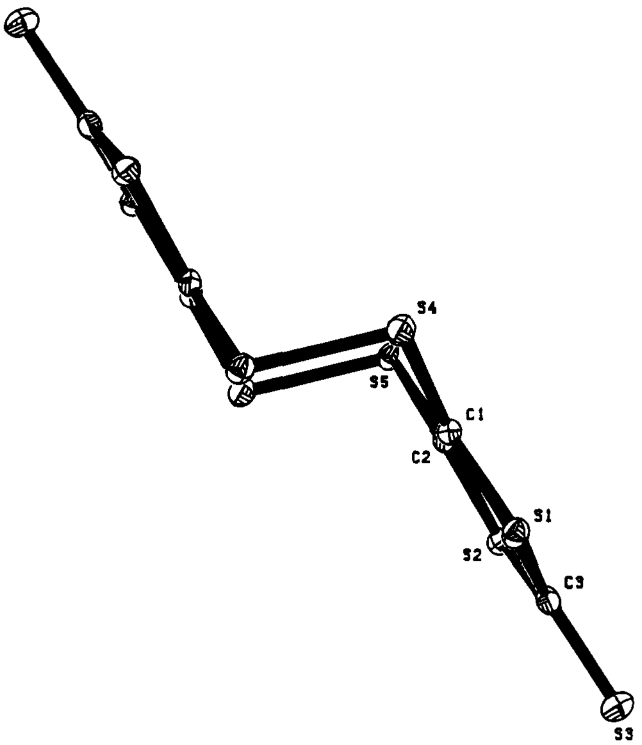


Figure 2. A side view of the structure of C_6S_{10}.

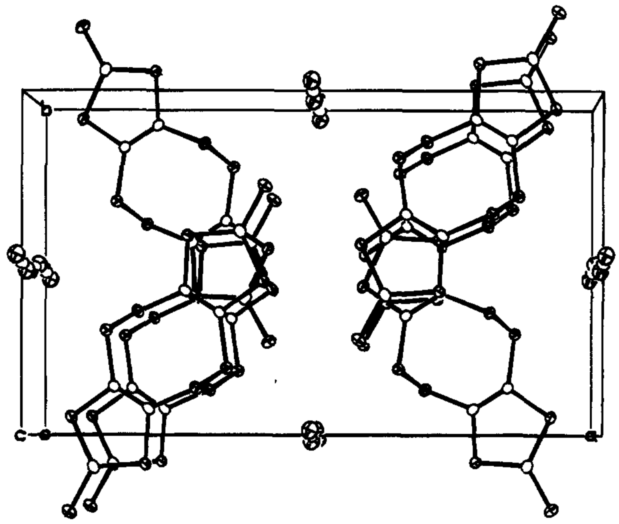
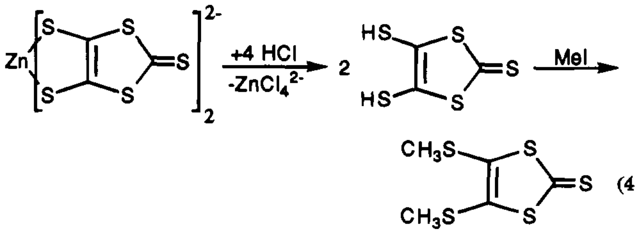


Figure 3. View of a portion of the C_6S_{10} unit cell.

C_6S_8. Given the high reactivity of $[Zn(C_3S_5)_2]^{2-}$ toward electrophiles, we investigated its protonation. A red dichloromethane slurry of $(NBu_4)_2[Zn(C_3S_5)_2]$ reacts rapidly with anhydrous hydrogen chloride, even at −78 °C. After sufficient hydrogen chloride was used to discharge the deep red color of the starting zinc complex, we obtained a bright yellow precipitate of the dithiol $C_3S_5H_2$. This species exhibits a weak IR band at 2498 cm^{-1} assigned to ν_{SH} and a molecular ion in its FD mass spectrum. The ^1H NMR spectrum of *fresh* $CDCl_3$ solutions of this species features a single line at 3.75 ppm. Solutions of $C_3S_5H_2$ in the presence of base react with methyl iodide to give the known $C_3S_5Me_2$ in high yield (eq 4).



(4)

The thermal lability of $C_3S_5H_2$ was indicated by the appearance of several new peaks in its ^1H NMR spectrum after several

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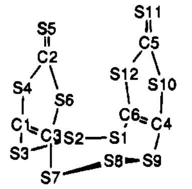
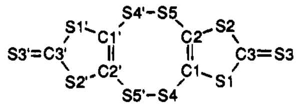
Table 1. Selected Bond Distances (Å) and Angles (deg) for C_6S_{12}, C_6S_{10}, $C_6S_8O_2$, and C_3S_7O

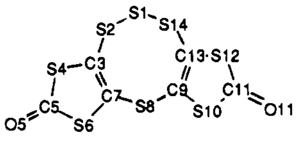
C_6S_{12}	S5—C2	1.634(5)	C1—S4—C2	97.3(2)
	C1—C3	1.340(6)	C1—S3—S2	102.0(1)
	S3—C1	1.754(5)	S3—C1—C3	124.7(4)
	S1—S2	2.061(2)	S1—S2—S3	105.62(7)
C_6S_{10}	S3—C3	1.635(3)	C1—S1—C3	97.7(1)
	C1—C2	1.349(3)	S5′—S4—C1	101.52(8)
	S4—C1	1.757(2)	S4—C1—C2	127.7(2)
	S4—S5′	2.0757(9)		
$C_6S_8O_2$	O5—C5	1.207(3)	C3—S4—C5	96.6(1)
	C3—C7	1.346(3)	S1—S2—C3	101.73(9)
	S2—C3	1.762(2)	S2—C3—C7	126.1(2)
	S8—C7	1.768(2)	C7—S8—C9	99.4(1)
	S1—S2	2.0479(9)	S2—S1—S14	106.31(4)
C_3S_7O	S1—S2	2.0529(14)	S6—C3—57	111.93(14)
	S2—S3	2.0620(14)	C1—C2—S1	126.44(14)
	S5—C1	1.769(26)	C2—S1—S2	104.35(9)
	C1—C2	1.3518(32)	S1—S2—S3	103.78(6)
	C2—S1	1.7651(25)		
	C2—S7	1.7501(26)		
	S7—C3	1.7811(27)		



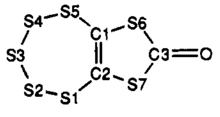
C_6S_{12}



C_6S_{10}



$C_6S_8O_2$



C_3S_7O

minutes at room temperature. *cis*-Dimercaptoethylene, a compound similar to $C_3S_5H_2$, is also thermally unstable.[22] Solid samples of $C_3S_5H_2$ darken after 1−2 days, concomitant with evolution of hydrogen sulfide. When the protonation of $[Zn(C_3S_5)_2]^{2-}$ was conducted at room temperature, followed by heating, we obtained a red-brown powder analyzing as C_6S_8 (eq 5).

$$2C_3S_5H_2 \xrightarrow{\Delta} C_6S_8 + 2H_2S \qquad (5)$$

Characteristic of other binary carbon sulfides, this species is noticeably soluble only in CS_2. Its formula is supported by microanalysis and the observation of a strong molecular ion in the EI mass spectrum. Unlike the aforementioned C_6S_{10} and C_6S_{12}, C_6S_8 does not undergo fragmentation to $C_3S_6^+$. This observation indicates that the C_3S_4 subunits are not joined by persulfide linkages. The IR spectrum of C_6S_8 is dominated by a strong $\nu_{C=S}$ band at 1050 cm^{-1}, while its Raman spectrum shows an intense ν_{SS} absorption at 499 cm^{-1}. On the basis of the structure of its dioxo derivative $C_6S_6O_2$ (vide infra), we suggest that C_6S_8 adopts structure **I**, rather than structure **II**. Attempts to react C_6S_8 with reagents known to cleave S—S bonds such as $LiBHEt_3$ and $Cp_2Ti(CO)_2$ led to complex reaction mixtures.

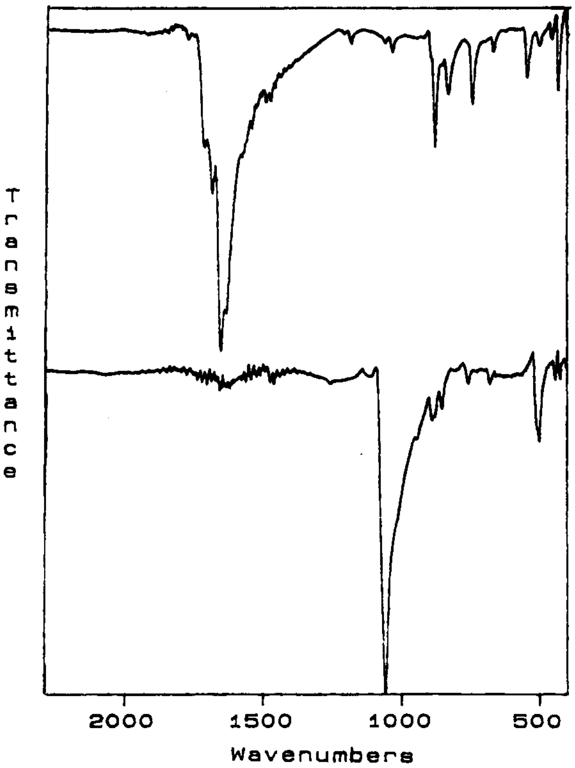
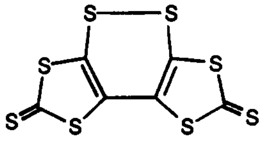
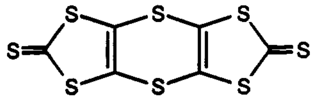


Figure 4. IR spectra of C_6S_{10} and $C_6S_8O_2$ (top).

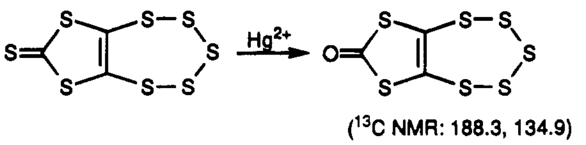


I



II

C_3S_7O. The simplest of the new C—S—O compounds is that derived from C_3S_8. It proved convenient to start with "C_3S_7", the mixture of C_3S_8 and C_6S_{12} described in eq 2. Treatment of this mixture with acetic acid solutions of Hg^{2+} led to the steady dissolution of the carbon sulfide concomitant with the deposition of a brown solid which likely contains HgS.[23] The yield from this reaction is ~60% on the basis of the percent C_3S_8 in "C_3S_7" (eq 6). As for the other C—S—O compounds described below,



(6)

C_3S_7O proved to be quite soluble in chlorinated solvents. It crystallizes easily as lemon-yellow cubes. This compound was also characterized by elemental analysis and mass spectrometry. In the ν_{SS} region of its IR spectrum (550−400 cm^{-1}), we observed a band at 465 cm^{-1}. The ^{13}C NMR spectrum of C_3S_7O showed resonances at 188.3 and 134.9 ppm, in the range expected for dithiocarbonates and tetrathiaethylenes.[24] For reference, we present the ^{13}C NMR shifts for tetrathiapentalenedione (TPD),[25] which we recorded, and a tricyclic derivative of dithiasquarate.[26] The data for TPD clearly support the assignments for C_3S_7O.

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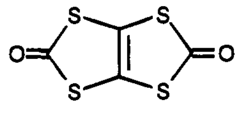
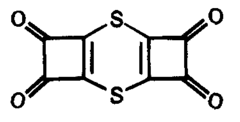
(28) Possible rearrangement pathways for converting C_6S_{10} to $C_6S_8O_2$ are discussed (but not experimentally evaluated) in: Galloway, C. P. Ph.D. Thesis, University of Illinois, Urbana-Champaign, IL, 1994.



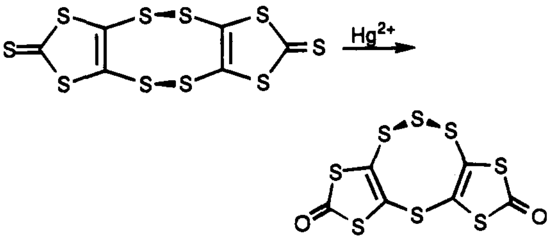
(^{13}C NMR: 188.7, 112.1)



(^{13}C NMR: 187.2, 184.1)

The structure of C_3S_7O was confirmed by single crystal X-ray diffraction. The C_2S_5 ring adopts a chair conformation like S_7, while the C_3S_4O fragment is planar (Figure 5). The S—S distances of the C_2S_5 ring correspond to normal unstrained single bonds, and the C=C distance of 1.35 Å is appropriate for a double bond. The long S—S bond distance of 2.18 Å in S_7 is thought to indicate a repulsive interaction between the pair of S atoms associated with the 0° dihedral angle.[29] In the C_2S_5 ring of C_3S_7O, the C=C subunit is ideally suited for the sites associated with the 0° dihedral angle since carbon vertices, with one less valence electron than sulfur, experience diminished intervertex repulsion. Of course, similar arguments can be applied to other pentathiepins (i.e., species with the formula $S_5C_2R_2$). This avoidance of 0° dihedral angles at sulfur may explain the scarcity of the cyclic species of the type *c*-$S_4C_2R_2$.

$C_6S_8O_2$. The Hg^{2+}-promoted hydrolysis of the thiocarbonyl groups in C_6S_{10} gave a good yield of pale orange crystals analyzing as $C_6S_8O_2$. In contrast to its precursor, this C—S—O compound exhibits good solubility in organic solvents. Microanalysis and mass spectrometry confirm the formula. Its IR spectrum features strong $\nu_{C=O}$ bands at 1723 and 1661 cm^{-1}, and there are no bands in the $\nu_{C=S}$ region. We were surprised that the ^{13}C NMR spectrum of $C_6S_8O_2$ showed *three* resonances instead of the two expected for an uncomplicated C=O for C=S replacement. Whereas the CO groups appear equivalent, we observed two ethylenic carbon signals. These data point to the structure shown in eq 7. This structure was confirmed by single-crystal X-ray diffraction (Figure 6). Salient features are the planar C_3S_2O subunits and the strongly folded central 1,4,5,6-C_4S_4 ring which adopts a chair conformation (Table 1). The synthesis of $C_6S_8O_2$ thus provides an unexpected isomer resulting from a rearrangement of the central C_4S_4 ring.[28] An alternative approach to the symmetrical isomer of $C_6S_8O_2$ could proceed via the desulfurization of C_3S_7O, although this opportunity was not explored.



(7)

(^{13}C NMR: 187.0, 137.5, 130.8)

$C_6S_6O_2$. A chloroform–acetic acid slurry of C_6S_8 was also found to react efficiently with mercuric acetate to give red $C_6S_6O_2$. The solubility of this compound in organic solvents is far greater than for the parent C_6S_8. Its IR spectrum shows several bands near 1600 cm^{-1}, two of which are quite strong and are assigned to $\nu_{C=O}$. The ^{13}C NMR spectrum of this compound shows three bands in positions similar to those for $C_6S_8O_2$, suggestive of the noncentrosymmetric structure shown in eq 8. We propose that the conversion of C_6S_8 to $C_6S_6O_2$ proceeds without any skeletal rearrangement, in contrast to the situation for C_6S_{10}/$C_6S_8O_2$.

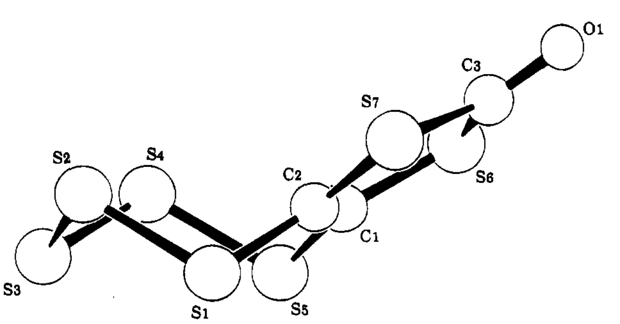


Figure 5. The structure of C_3S_7O.

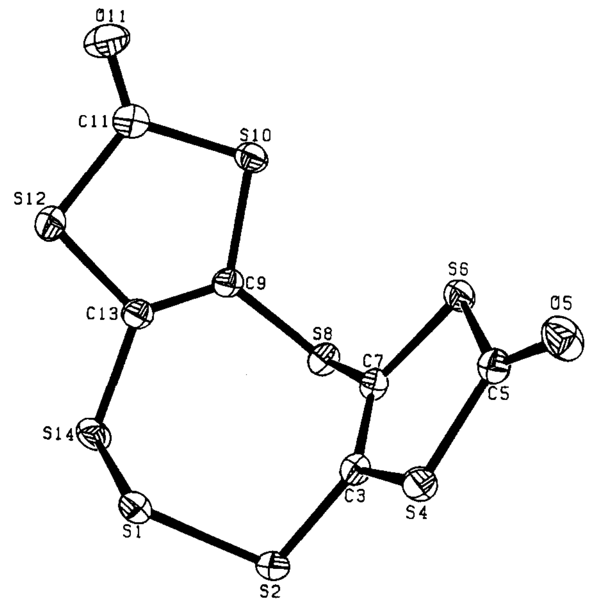
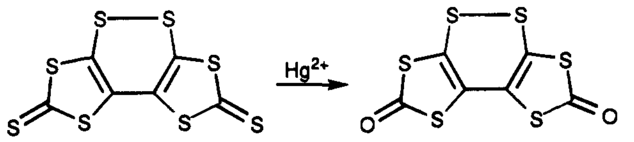


Figure 6. The structure of $C_6S_8O_2$.



(^{13}C NMR: 186.6, 124.5, 114.8)

(8)

Synthesis of C—S—N Compounds. Many methods for making S—N bonds involve the addition of nitrogenous nucleophiles to electrophilic sulfur centers.[29] Our experiments show that this approach is applicable to the α-C_3S_5 system. Preliminary experiments showed that SO_2Cl_2 attacks $[C_3S_5]_n$ to give $C_3S_5Cl_2$. A more practical method involves treatment of $Zn(C_3S_5)_2^{2-}$ with 4 equiv of SO_2Cl_2 according to eq 9. The bis(sulfenyl chloride) was obtained in good yield as bright yellow, moisture-sensitive crystals which were characterized by IR spectroscopy (ν_{CS} = 1059 cm^{-1}, ν_{SCl} = 535 cm^{-1}) and microanalysis. Further support for the structural assignment comes from its conversions to two derivatives.

$$\mathrm{Zn(C_3S_5)_2^{2-} + 4SO_2Cl_2 \longrightarrow 2C_3S_5Cl_2 + ZnCl_4^{2-} + 4SO_2} \qquad (9)$$

Treatment of $C_3S_5Cl_2$ with 2 equiv of $LiN(SiMe_3)_2$ gave $C_3S_5[N(SiMe_3)_2]_2$, isolated as analytically pure red microcrystals. This bis(sulfenamide) is soluble in organic solvents, allowing NMR characterization; the compound was further characterized

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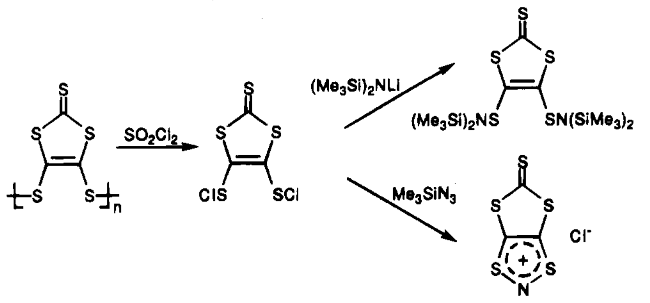
(29) Wolmerhäuser, G.; Johann, R. *Angew Chem., Int. Ed. Engl.* **1989**, *28*, 920; *Angew. Chem.* **1989**, *101*, 952. Wolmerhäuser, G.; Kraft, G. *Chem. Ber.* **1989**, *122*, 385 and references therein.

Scheme 1



by IR and EI mass spectrometry (molecular ion). The synthesis of an inorganic C—S—N species was accomplished by treatment of $C_3S_5Cl_2$ with Me_3SiN_3. This affords a poorly soluble brown solid analyzing as C_3S_5NCl. On the basis of its IR spectrum and microanalysis, as well as crystallographically-confirmed precedents,[29] we suggest that this is the chloride salt of the bicyclic dithiazolium species shown in Scheme 1.

Conclusions

Several new carbon sulfides have been prepared by starting from the kinetic isomer of $C_3S_5^{2-}$. The conversion of this anion to neutral carbon sulfides has been effected by four types of electrophilic reactions: (i) electrophilic sulfiding which employs sulfur chlorides as a source of S_x^{2+}, illustrated by the synthesis of C_6S_{12} and C_3S_8; (ii) oxidation employing SO_2Cl_2, such as the synthesis of C_6S_{10}; (iii) protonation, followed by H_2S elimination, as in the synthesis of C_6S_8; (iv) reaction with $CSCl_2$, as in the synthesis of the D_{2h} isomer of C_4S_6 from $C_3S_5^{2-}$.[15] These methods could be profitably applied to other thioanions, some of which are listed in Chart 1.

The recurring difficulty in this area is the low solubility of the neutral carbon sulfides. The enhanced solubility of the carbonyl analogues of these thiocarbonyls facilitates their purification as well as their analysis. The favorable solubility is considered to result from the diminished strength of the intermolecular van der Waals interactions for carbonyls vs thiocarbonyls. We have shown that in at least one case the thiocarbonyl-to-carbonyl transformation can be accompanied by substantial structural changes in the heterocyclic framework.

The binary carbon sulfides are of interest as easily prepared precursors to more complex molecules and polymers. The utilization of these molecular building blocks hinges on the availability of functional groups which are reactive under mild conditions. One such functionality is the S—S bond, which can be cleaved using hydride and chlorinating agents. The dithiocarbonate function, several examples of which are described in this report, represents another reactive functional group. Studies on the base hydrolysis of these C—S—O compounds should lead to a new generation of thiocarbon anions.[30,31] Our studies also establish that $C_3S_5^{2-}$ salts can serve as precursors to C—S—N species.[32]

Experimental Section

Materials and Methods. Preparative reactions were performed under an atmosphere of nitrogen. $Cp_2TiC_3S_5$ was prepared as described previously.[16] CH_2Cl_2 was distilled from P_2O_5 or CaH_2, THF from Na—Ph_2CO, toluene from Na, Me_3CN from CaH_2, and MeOH from BaO or $Mg(OMe)_2$. The HPLC setup consists of a Varian 2510 pump, a Varian 2550 variable-wavelength detector (set at 300 nm), and a Spectraphysics recorder/integrator. Samples were eluted with HPLC grade MeOH (Baxter) on a reverse-phase column consisting of C18 bonded onto 5 μ silica gel (MicroPak MCH-5, 15 cm × 4 mm). The flow rate was 0.5 mL/min.

$(NBu_4)_2[Zn(C_3S_5)_2]$. This procedure was adapted from that in ref 15. To 10 g of Na spheres (0.4348 mol) were added 200 mL of DMF and 100 mL of CS_2 (excess). The slurry was stirred under a blanket of dinitrogen for 6 h at 0 °C. The resulting dark red viscous mixture was treated with 20 mL of MeOH to destroy unreacted sodium, and the volatiles were removed *in vacuo*. The following were added in succession to the residue: a solution of 14.85 g of $ZnSO_4{\cdot}7H_2O$ (51.63 mmol) in 75 mL of H_2O, a solution of 33.29 g (103.26 mmol) of NBu_4Br in 75 mL of MeOH, and 100 mL of H_2O. The purple solid was washed with three 50 mL portions of water and air-dried. The product was recrystallized by extraction into 300 mL of CH_2Cl_2, followed by filtration to remove solids if necessary. The dark red solution was concentrated to 150 mL and diluted with 100 mL of Et_2O to give 46.5 g of red crystals (90% based on Na). Anal. Calcd for $C_{38}H_{72}N_2S_{10}Zn$: C, 48.40; H, 7.70; N, 2.97. Found: C, 48.27; H, 7.72; N, 2.98.

Reaction of S_2Cl_2 with $(NBu_4)_2[Zn(C_3S_5)_2]$. A solution of 0.317 g of S_2Cl_2 (0.35 mmol) in 50 mL of CH_2Cl_2 was slowly added at 0 °C to a solution of 1.105 g of $(NBu_4)_2[Zn(C_3S_5)_2]$ (1.17 mmol) in *ca.* 100 mL of CH_2Cl_2. The addition was completed after 3 h, and the mixture was warmed to room temperature and stirred for a further 2 h. The yellow crystalline solid was washed with 50 mL of CH_2Cl_2. Yield: 530 mg of "C_3S_7" (87% based on S_2Cl_2). HPLC (CS_2): R_f = 7.64 min (C_3S_8), 9.08 min (C_6S_{12}). Anal. Calcd for C_3S_7: C, 13.9; S, 86.2. Found: C, 13.9; S, 86.0.

$(C_3S_5)_n$ from $(Bu_4N)_2[Zn(C_3S_5)_2]$. A solution of 3.00 g of $(Bu_4N)_2[Zn(C_3S_5)_2]$ (3.18 mmol) in 150 mL of CH_2Cl_2 was cooled with an acetone–dry ice bath and treated dropwise with a solution of 510 μL of SO_2Cl_2 (6.36 mmol) in 100 mL of CH_2Cl_2 over a 2-h period. The orange precipitate was filtered off, washed with CH_2Cl_2, and dried in air. Yield: 0.927 g (74%). The IR spectrum of the crude product showed the absence of ν_{CH} bands (2900–3100 cm^{-1}). The solid was extracted twice with ~200 mL of CS_2. Evaporation of this extract gave an orange-brown solid. Yield: 353 mg (28%). Anal. Calcd for C_6S_{10}: C, 18.35; S, 81.65. Found: C, 18.25; S, 81.87.

$C_6S_8O_2$. A rapidly stirred slurry of 1.456 g of C_6S_{10} (3.71 mmol) in 200 mL of $CHCl_3$–glacial acetic acid (5:3) was treated with 4.72 g of $Hg(OAc)_2$ (14.81 mmol). After 2.5 h, the milky slurry was filtered to give a pale orange filtrate. The filtrate was washed in a separatory funnel with two 200-mL portions of H_2O, one 200-mL portion of a 3% Na_2CO_3 solution, and again two 200-mL portions of H_2O. The chloroform solution was dried over Na_2SO_4, and the solvent was removed on a rotary evaporator. The crude pale orange solid was recrystallized from chloroform by the addition of hexane. Yield: 0.713 g (53%). Anal. Calcd for $C_6O_2S_8$: C, 19.99; S, 71.14. Found: C, 19.90; S, 70.87. EIMS *m/z* (intensity): 360 (M^+, 3), 296 (M^+ − 2S, 24). IR (KBr): $\nu_{C=O}$ = 1723 (m), 1661 (vs) cm^{-1}. ^{13}C NMR (CD_2Cl_2, 2.9×10^{-3} M $Cr(acac)_3$, 25 °C): δ 187.0 (s), 137.5 (s), 130.8 (s).

$C_3S_5H_2$. A solution of 3.0 g of $(NBu_4)_2[Zn(C_3S_5)_2]$ (3.18 mmol) in 30 mL of CH_2Cl_2 was treated dropwise over 30 min with 13 mL of 1.0 M HCl in Et_2O (Aldrich) at −78 °C. The supernatant was filtered from the resulting yellow solid while a temperature of −78 °C was maintained. The solid was washed with two 15-mL portions of CH_2Cl_2 followed by two 15 mL portions of cold (0 °C) Et_2O. This afforded 0.96 g of a bright yellow, thermally unstable powder. Yield: 76%. IR (KBr): ν_{SH} = 2498 (w), $\nu_{C=S}$ = 1053 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.75 (br, s, −S*H*). FDMS *m/z*: 198 (M^+).

C_6S_8. A solution of 3.00 g of $(NBu_4)_2[Zn(C_3S_5)_2]$ (3.18 mmol) in 30 mL of CH_2Cl_2 was treated with 13 mL of a 1.0 M solution of HCl in Et_2O. The resulting yellow solution was heated under reflux for 24 h to give a dark red-brown precipitate, which was collected and washed with CH_2Cl_2. Yield: 0.616 g (59%). Anal. Calcd for C_6S_8: C, 21.94; S, 78.06. Found: C, 21.80; S, 77.73. EIMS *m/z* (intensity): 328 (M^+, 20), 296 (M^+ − S, 5). IR (KBr): $\nu_{C=S}$ = 1060 (vs) cm^{-1}. Raman (514 nm, solid sample): ν_{SS} = 499 (s) cm^{-1}.

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(30) Other interesting C—S—O speices include $C_3S_3O_2$ (Krebs, B.; Gattow, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 618; *Angew. Chem.* **1963**, *75*, 978), $C_8S_6O_4$ (Demetriadis, N. G.; Huang, S. J.; Samulski, E. T. *Tetrahedron Lett.* **1977**, 2223), $C_8S_4O_4$ and $C_8S_3O_4$ (Scherer, O.; Kluge, F. *Chem. Ber.* **1966**, *99*, 1973), and $C_8S_8O_2$.[25]

(31) Zheng, Y.; Galloway, C. P.; Rauchfuss, T. B.; Rheingold, A. L., Wilson, S. R. Unpublished results.

(32) Recent work on C—S—N heterocycles: (a) Boyle, P. D.; Parsons, S.; Passmore, J.; Wood, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 199. Banister, A. J.; Lavender, I.; Rawson, J. M.; Clegg, W.; Tanner, B. K.; Whitehead, R. J. *J. Chem. Soc., Dalton Trans.* **1993**, 1421.

Table 2. Crystallographic Data for C_3S_7O and $C_6S_8O_2$

	C_3S_7O	$C_6S_8O_2$
mol wt	276.45(2)	360.54
a, Å	4.204(2)	15.461(6)
b, Å	8.942(5)	9.648(3)
c, Å	12.017(6)	7.852(1)
α, deg	103.02(4)	90
β, deg	96.64(4)	98.71(2)
γ, deg	90.47(4)	90
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
V, Å	436.91(4)	1158(1)
Z	2	4
ϱ_{calcd}, g/cm^3	2.101	2.068
cryst dimens, mm^3	0.2 × 0.3 × 0.4	0.2 × 0.4 × 0.5
collecn temp, °C	−78	−75
radiation (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2*θ* range, deg		2−58
no. of measd reflns		3417
no. of unique reflns	1658	3063
no. of obsd reflns ($I > 2.58\sigma(I)$)	1513	2569
R, %	2.3	3.0
R_w, %	2.1	3.9

$C_6S_6O_2$. A slurry of 1.27 g of C_6S_8 (3.86 mmol) in 120 mL of $CHCl_3$−glacial acetic acid (5:1) was treated with 2.46 g of $Hg(OAc)_2$ (7.72 mmol). After 16 h, the dark red solution was filtered from the cloudy orange slurry. Following extraction with three 200 mL portions of H_2O, the organic phase was then dried over Na_2SO_4, concentrated to ~50 mL, and chilled. The red microcrystals were washed with hexane. Yield: 0.710 g (62%). Anal. Calcd for $C_6O_2S_6$: C, 24.31; S, 64.89. Found: C, 24.07; S, 64.84. EIMS *m/z* (intensity): 296 (M$^+$, 39), 268 (M$^+$ − CO, 22), 240 (M$^+$ − 2CO, 37). IR (KBr): $\nu_{C=O}$ = 1689, 1656 (vs) cm^{-1}. ^{13}C NMR ($CDCl_3$, 3.6 × 10^{-3} M Cr(acac)$_3$, 25 °C): *δ* 186.6 (s), 124.5 (s), 114.8 (s).

C_6S_{12}. A solution of 0.585 mL of S_2Cl_2 (7.32 mmol) in 20 mL of CH_2Cl_2 was added to a solution of 1.37 g (3.66 mmol) of $Cp_2TiC_3S_5$ in 100 mL of CH_2Cl_2. The addition was completed in 1 h and resulted in a color change from green to orange. After the mixture was stirred at room temperature for 12 h, the yellow-brown solid was collected. The solid was extracted with *ca.* 300 mL of CS_2, and the extracts were taken to dryness to give orange crystals. Yield: 450 mg (54%). Anal. Calcd for C_6S_{12}: C, 15.8; S, 84.2. Found: C, 16.1; S, 84.4. EIMS *m/z* (intensity): 328 (M$^+$ − 4S, 20), 292 ($C_3S_8^+$, 20), 256 (S_8^+, 17), 240 ($C_4S_6^+$, 65); IR (KI): $\nu_{C=S}$ = 1067, 1060 (vs) cm^{-1}.

C_3S_8. Solutions of 1 g of $Cp_2TiC_3S_5$ (2.67 mmol) and 0.216 mL of S_2Cl_2 (2.67 mmol), each in 20 mL of CH_2Cl_2, were simultaneously added dropwise to 300 mL of stirred CH_2Cl_2 over a period of 6 h at room temperature. The resulting yellow-orange suspension was filtered, and the yellow solids were washed with 50 mL of CH_2Cl_2 to give 400 mg of yellow solids. The CH_2Cl_2-soluble portion of the reaction mixture and CH_2Cl_2 washings were combined and filtered through a thick pad of silica gel to remove $(C_5H_5)_2TiCl_2$. Concentration of this filtrate gave yellow crystals. Yield: 120 mg (31%). Anal. Calcd for C_3S_8: C, 12.3; S, 87.7. Found: C, 12.6; S, 86.2. EIMS *m/z* (intensity): 292 (M$^+$, 20), 256 (S_8^+, 7), 228 (M$^+$ − 2S). IR (KI): $\nu_{C=S}$ = 1056 (vs) cm^{-1}.

C_3S_7O. To a slurry of 0.5 g of "C_3S_7" (1.92 mmol) in 100 mL of 3:1 $CHCl_3$−glacial acetic acid was added 0.611 g (1.92 mmol) of $Hg(OAc)_2$. After 5 min of stirring at room temperature, most of the solids had dissolved. With continued stirring, a brown solid began to precipitate. The reaction mixture was filtered after 0.5 h, and the solid was washed with an additional 50 mL of $CHCl_3$. The $CHCl_3$ extracts were washed with two 50-mL portions of H_2O, 50 mL of a 5% $NaHCO_3$ solution, and again with 50 mL of H_2O. The pale yellow $CHCl_3$ solution was dried over Na_2SO_4. Evaporation of the solvent gave 175 mg yellow microcrystals (33% based on starting "C_3S_7"). Anal. Calcd for C_3OS_7: C, 13.03; S, 81.18. Found: C, 13.10; S, 80.25. EIMS *m/z* (intensity): 276 (M$^+$, 19), 256 (S_8^+, 8), 212 (M − 2S$^+$, 90). IR (KBr): $\nu_{C=O}$ = 1662 (vs), ν_{ss} = 461 (m) cm^{-1}. ^{13}C NMR (CD_2Cl_2, 4.2 × 10^{-3} M Cr(acac)$_3$, 25 °C): *δ* 188.3, 134.9.

Table 3. Atomic Coordinates for $C_6S_8O_2$

	x/*a*	*y*/*b*	*z*/*c*
S1	0.15844(4)	0.35109(7)	0.06260(9)
S2	0.27333(4)	0.27080(6)	0.00582(8)
C3	0.3467(2)	0.4085(3)	0.0643(3)
S4	0.41172(4)	0.39726(7)	0.26450(8)
C5	0.4701(2)	0.5532(3)	0.2489(3)
O5	0.5298(1)	0.5919(2)	0.3555(3)
S6	0.43073(4)	0.64676(6)	0.05763(8)
C7	0.3549(2)	0.5234(3)	−0.0291(3)
S8	0.29617(4)	0.55593(7)	−0.23642(8)
C9	0.2123(2)	0.6623(3)	−0.1791(3)
S10	0.23016(4)	0.84101(7)	−0.17065(9)
C11	0.1271(2)	0.8880(3)	−0.1125(3)
O11	0.1048(2)	1.0046(2)	−0.0901(3)
S12	0.06115(4)	0.73997(7)	−0.09173(9)
C13	0.1347(2)	0.6167(3)	−0.1453(3)
S14	0.09769(5)	0.44392(7)	−0.15907(9)

Table 4. Atomic Coordinates for C_3S_7O

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}, Å^2
S1	0.8290(2)	0.11671(6)	0.61648(5)	0.0239(2)
S2	0.5904(2)	−0.05598(6)	0.66371(5)	0.0256(2)
S3	0.8398(2)	−0.06855(6)	0.81932(5)	0.0266(2)
S4	0.6821(2)	0.11828(7)	0.93094(5)	0.0272(2)
S5	0.9269(2)	0.30326(7)	0.90289(5)	0.0267(2)
S6	0.5026(2)	0.53700(7)	0.82737(5)	0.0282(2)
S7	0.4091(2)	0.37403(6)	0.58282(5)	0.0256(2)
O	0.1629(5)	0.6426(2)	0.6631(2)	0.0423(7)
C1	0.6837(6)	0.3608(2)	0.7907(2)	0.0209(7)
C2	0.6430(6)	0.2864(2)	0.6786(2)	0.0200(7)
C3	0.3269(7)	0.5414(3)	0.6862(2)	0.028(1)

$C_3S_5Cl_2$. A solution of 3.05 g of $[Bu_4N]_2[Zn(C_3S_5)_2]$ (3.24 mmol) in 100 mL of dry CH_2Cl_2 was cooled to −78 °C and treated with 1.04 mL of SO_2Cl_2 (12.96 mmol) via syringe. The initially dark purple color quickly became bright yellow, with formation of a bright yellow precipitate. The mixture was stirred at −78 °C for 10 min and then allowed to warm to room temperature. After 1 h, the precipitate was collected by filtration under N_2, washed with 100 mL of dry CH_2Cl_2, and dried *in vacuo*. Yield: 1.54 g (89%). Anal. Calcd for $C_3Cl_2S_5$: C, 13.48; Cl, 26.53; S, 59.99. Found: C, 13.83; Cl, 26.34; S, 59.54. IR: 1059 (m), 981 (s), 792 (m), 535 (m) cm^{-1}.

$C_3S_5[N(SiMe_3)_2]_2$. A solution of 5.229 g of $LiN(SiMe_3)_2$ (13.3 mmol) in 100 mL of dry THF was added to a slurry of 4.176 g of $C_3S_5Cl_2$ (15.6 mol) in 100 mL of THF via cannula. The initial slurry immediately became deep red, and most of the yellow solid dissolved. The reaction was mildly exothermic. The mixture was stirred for 1 h, the solution was decanted to a second flask via cannula, and the solvent was removed *in vacuo*. The product was extracted with two 50-mL portions of CH_2Cl_2, and the extracts were filtered through a bed of Celite. The solvent was removed, and the residue was dried overnight *in vacuo* (16 h) to afford a dark red-brown solid. Yield: 6.535 g (81%). Anal. Calcd for $C_{15}H_{36}N_2S_5Si_4$: C, 34.83; H, 7.03; N, 5.42; S, 30.99. Found: C, 34.76; H, 6.96; N, 5.27; S, 31.14. ^{1}H NMR ($CDCl_3$): *δ* 0.26, $^2J(^1H-^{29}Si)$ = 3 Hz). EIMS *m/z* (70 eV): 516 (M$^+$).

C_3S_5NCl. A slurry of 4.37 g of α-$C_3S_5Cl_2$ (16.35 mmol) in 200 mL of dry THF was cooled to −78 °C and treated with 2.6 mL of Me_3SiN_3 (19.62 mmol) via syringe. After 5 min, the cold bath was removed and the mixture was stirred for a further 90 min, during which time the bright yellow color slowly changed to brown. The flask was then fitted with a condenser, and the mixture was refluxed for 21 h. The resultant deep brown solid was allowed to settle, isolated via filter cannula, washed with 300 mL of THF, and dried *in vacuo*. Yield: 3.52 g (88%). Anal. Calcd for C_3NClS_5: C, 14.66; N, 5.70; S, 65.22; Cl, 14.42. Found: C, 14.36; N, 5.55; S, 67.72; Cl, 14.31. IR: 1064 (s), 1271 (br, m), 1460 (m br).

X-ray Crystallography of C_3S_7O. A yellow, transparent cuboidal crystal was mounted on a glass fiber with epoxy and cooled to −75 °C for data collection on a STOE II diffractometer. Cell dimensions were obtained as fit from 20 reflections. The space group $P\bar{1}$ was indicated by systematic absences and the successful refinement. Absorption corrections were not applied. The structure was solved by direct methods using SHELX 76. Correct positions of all 11 atoms were readily determined from the *E* map, and the atoms were refined anisotropically. The final difference Fourier map had no significant features. Crystal data are presented in Table 2.

X-ray Crystallography of $C_6S_8O_2$. The yellow, transparent, prismatic crystal was mounted using epoxy to a thin glass fiber and cooled to −75 °C for data collection. Final cell dimensions were obtained from the least squares fit of 25 reflections ($26.9° < 2\theta < 34.9°$). The space group $P2_1/c$ was unambiguously determined from the systematic absences. Absorption corrections were applied to the data set with maximum and minimum transmission factors of 0.735 and 0.456, respectively. The structure was solved by direct methods. Correct positions for all atoms were deduced from the *E* map. In the final cycle of least-squares refinement, all atoms were anisotropically refined and an empirical isotropic extinction parameter was varied. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed a slight dependence on sin θ. Crystal data are presented in Table 2.

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Supplementary Material Available: Tables of thermal parameters, bond distances, and bond angles for $C_6S_8O_2$ and C_3S_7O (3 pages). Ordering information is given on any current masthead page.