

Chiroptical Properties of Cyclic Esters and Ketals Derived from (*S*)-1,2-Propylene Glycol and (*S,S*)- and (*R,R*)-2,3-Butylene Glycol

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The optically pure five-membered ring thionocarbonates (**1a-3a**), carbonates (**1b-3b**), sulfites (*cis*- and *trans*-**1c**, **2c**, **3c**), phosphite (**2d**), and 2-bromo- and 2-chloromethyl-1,3-dioxolanes (*cis*- and *trans*-**1e**, **2e**, **2f**) were prepared from the three title diols by standard methods and their uv and CD spectra were measured in various solvents over the range 185–400 m μ at room temperature. The CD spectra of **1a-3a** display two well-defined Cotton effects of opposite signs and of diverse intensities centered at 222–235 and 325 m μ , related to the uv $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The sign of the long-wavelength Cotton effect is associated with the chirality of the heterocycle ring. A positive ellipticity for the $n \rightarrow \pi^*$ transition is assigned to thionocarbonates of *R* configuration, and vice versa, a negative one for the *S* series. Cyclic carbonates do not show CD maxima above 185 m μ ; the curves of dichroic absorption for the *R* and *S* forms are antipodal and their signs correlate with those of the long-wavelength Cotton effect of the corresponding thionocarbonates. The condensation of (*S*)-1,2-propylene glycol with thionyl chloride gave rise to the expected isomers of opposite rotations, assigned the *cis*- and *trans*-**1c** structures, exhibiting similar dichroic bands centered at 212–225 and 195–200 m μ . The complex chiroptical properties of **1c-3c** and **2d** are discussed in terms of ring conformation and asymmetric solvation of the chromophore. The condensation of (*S*)-1,2-propylene glycol with bromoacetaldehyde again led to the expected *cis* and *trans* isomers. The dichroic curves of the geometric isomers and of **2e** do not correspond to those of the uv spectra. A CD study of the title glycols is herein included.

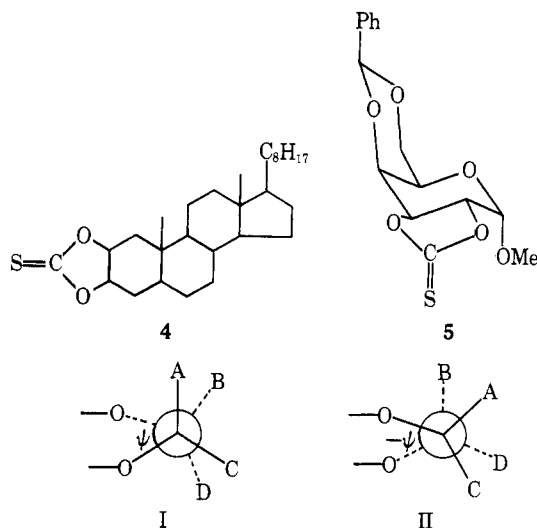
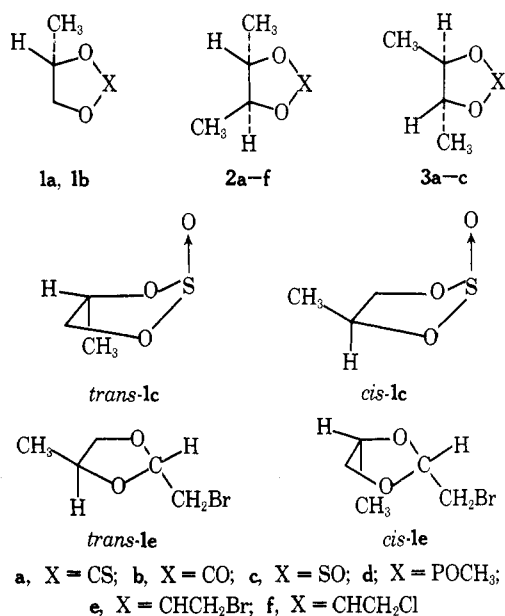
There is considerable interest in the application of chiroptical methods of configurational assignments in chiral alcohols and polyols.¹ The uv absorption of an oxy chromophore at a saturated carbon occurs below 200 m μ , and thus it is not expected to observe maxima in their CD spectra in this region. This was borne out in the cases of optically active acetals, ethers, and alcohols.^{1a,2} However, recently^{1b} it has been demonstrated that some secondary and tertiary alcohols show well-defined Cotton effects in the region of 185–192 m μ . It is worthy of note that the production of CD and ORD data of saturated oxy compounds is more readily obtained *via* derivatization of these compounds to form new chromophores such as carboxyl,³ thionocarbonate,^{4,5} and mono- and dioxycarbonylbenzenes,⁶ and also by complex formation.⁷

Following our concern in structural effects on reactivity in organic carbonates⁸ and sulfites,^{9,10} we became interested in exploring the possibility of deduction of stereochemistry in optically active diols by chiroptical methods. We thought that this goal could successfully be obtained if the oxy chromophore is part of a cyclic ester, such as thionocarbonate, carbonate, sulfite, and phosphite, or of a dioxolane system. For this purpose we converted the optically pure forms of the three known compounds (*S*)-(+)-1,2-propylene glycol (**1**), (*S,S*)-(-)-2,3-butylene glycol (**2**), and (*R,R*)-(+)-2,3-butylene glycol (**3**) into their corresponding optically pure five-membered ring thionocarbonates (**1a-3a**), carbonates (**1b-3b**), sulfites (*cis*- and *trans*-**1c**, **2c**, and **3c**), phosphite (**2d**), 2-bromomethyl-1,3-dioxolanes (*cis*- and *trans*-**1e**, **2e**), and a 2-chloromethyl-1,3-dioxolane (**2f**), and measured their circular dichroism spectra in various solvents.

Results and Discussion

Cyclic Thionocarbonates and Carbonates. Chiral cyclic thionocarbonates^{4,5} have been reported to exhibit one $n \rightarrow \pi^*$ and one $\pi \rightarrow \pi^*$ dichroic band. The signs of the Cotton effects associated with these bands were related to the chirality of the ring. For the $n \rightarrow \pi^*$ transition it was shown, using rigid systems, that conformation I causes a positive Cotton effect, while conformation II exhibits a negative one.

In flexible systems, where conformational equilibrium



between two limiting conformations resembling the above given I and II exists, a decrease in the absolute value of

Table I
Spectral Properties of Cyclic Thionocarbonates

Compd	Solvent	$n \rightarrow \pi^*$			$\pi \rightarrow \pi^*$		
		$\lambda_{\max}, m\mu$	$\Delta\epsilon$	$10^{40} R^2$	$\lambda_{\max}, m\mu$	$\Delta\epsilon$	$10^{40} R^2$
1a	Hexane	325	-0.047	-0.12	222	+0.83	+2.56
2a	Hexane	325	-0.73	-2.75	235	+3.13	+10.06
	Dioxane ^b	315	-1.21		240	+3.33	
	Methanol	307	-0.55				
3a	Hexane	324	+0.75	+2.46	235	-3.33	-8.86
4^c	Dioxane	315	+2.3	+6.1	238	-14.12	
5^c	Dioxane	323	+2.8	+7.6			

^a R in cgs units. ^b In ref 5; $\lambda_{\max} = 313 m\mu$; $\Delta\epsilon = -0.8$. ^c Reference 4.

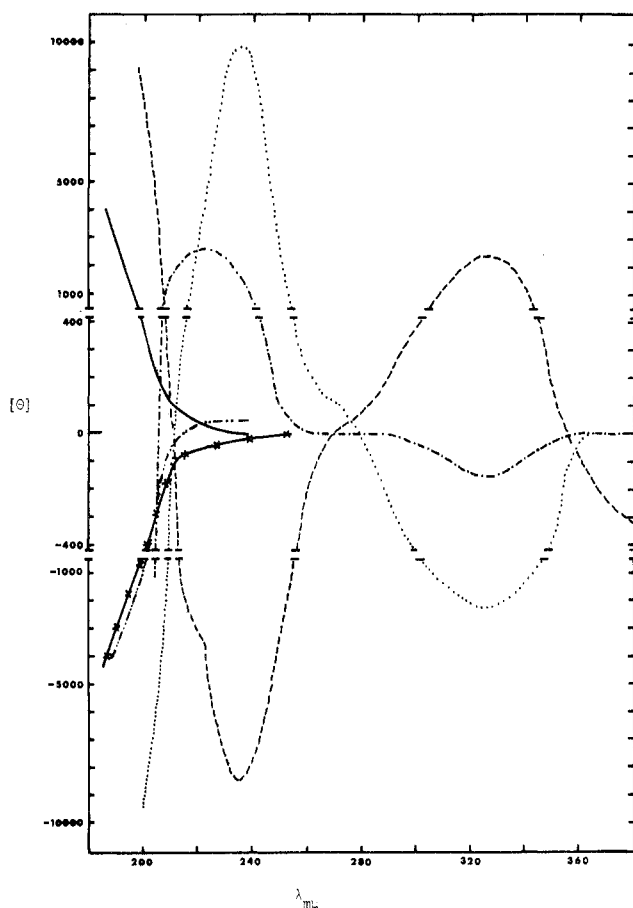


Figure 1. CD curves of (a) (*S*)-methylethylene thionocarbonate (**1a**) (---); (b) (*S,S*)-1,2-dimethylethylene thionocarbonate (**2a**) (....); (c) (*R,R*)-1,2-dimethylethylene thionocarbonate (**3a**) (-.-.-); (d) (*S*)-methylethylene carbonate (**1b**) (-.-.-.-); (e) (*S,S*)-1,2-dimethylethylene carbonate (**2b**) (x-x-x); (f) (*R,R*)-1,2-dimethylethylene carbonate (**3b**) (—) in hexane.

the rotational strength R and in $\Delta\epsilon$ would be expected compared to rigid systems. Thus, the pseudorotation of the five-membered ring thionocarbonates should decrease the chiroptical properties of both the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi$ transitions. The low rotational strength observed in compounds **2a** and **3a** (see Figure 1 and Table I) is in accordance with this assumption when compared to the R and $\Delta\epsilon$ values reported by Haines and Jenkins⁴ for the two puckered five-membered ring thionocarbonates 5 α -cholestane-2 β ,3 β -diol thionocarbonate (**4**) and 4,6-*O*-benzylidene- α -D-galactopyranoside 2,3-thionocarbonate (**5**).

In spite of pseudorotation, substitution on the ring carbons undoubtedly causes the cyclic thionocarbonates to attain a preferred conformation. For both **2a** and **3a** the anti form seems more stable than the gauche one; *i.e.*, conformation II ($B = C = \text{Me}$; $A = D = \text{H}$) should be more populated in the case of **2a** and I ($A = D = \text{Me}$; $B = C = \text{H}$) in the case of **3a**. This implies a negative Cotton effect in **2a**, and a positive one in **3a**.

Table II
Coupling Constants and Calculated Dihedral Angles of Cyclic Carbonates

Cyclic carbonate	$J_{\text{H-H}}$ (cis)	$J_{\text{H-H}}$ (trans)	ψ , deg
Ethylene ^a	8.9	7.4	18.5
1-Methylethylene ^b	7.6	7.1	28.8
1-Phenylethylene ^c	8.07	7.78	25.4
<i>trans</i> -2,3-Dimethylethylene ^d		7.2	31.5
<i>cis</i> -2,3-Dimethylethylene ^d	7.35		30.5

^a Reference 14. ^b Reference 8. ^c Reference 15. ^d Reference 16; the methyls were assumed to be in an axial conformation and therefore the constant for $J_{\text{H-H}}$ (cis) was used in the calculation.

Compound **1a** shows an even greater decrease in the R and $\Delta\epsilon$ values than that shown by **2a** and **3a**. However, unlike the latter, in **1a** the chiroptical properties of the $n \rightarrow \pi^*$ transition and those of the $\pi \rightarrow \pi^*$ transition are unevenly affected. This will be explained later in the discussion.

Because of the flexibility of five-membered rings, conformational assignments based on nmr analysis in such systems should be taken with care. However, valuable information concerning conformational preference or time-averaged conformation of five-membered ring cyclic phosphites, dioxolanes, and dithiolanes has been obtained by nmr measurements.¹¹⁻¹³ It seems that even if absolute values of the dihedral angle, ψ , of five-membered ring carbonates cannot be calculated from the Karplus equation, using Haake's parameters¹² and nmr coupling constants, the influence of substituents on ψ could nevertheless be estimated by this method. The results obtained for some carbonates are presented in Table II. Calculation of the dihedral angles of the same cyclic carbonates by another method based on the R values¹⁷ shows a degree of skewness higher by at least 10°, but the influence of the substituents on ψ is similar to that observed in Table II. X-Ray analysis of ethylene carbonate in the solid state¹⁸ gave a value of 26.2° for the dihedral angle ψ , which is also higher than the value appearing in Table II. The results represented in Table II indicate only a small change in the puckering of 1-methylethylene carbonate compared to that of *trans*-2,3-dimethylethylene carbonate. The torsional angles of the analogous thionocarbonates **1a** and **2a** are similarly assumed to differ from each other to a small extent only, *i.e.*, by $\sim 3^\circ$. This shows that the difference in the chiroptical properties between the monosubstituted thionocarbonate **1a** and the disubstituted thionocarbonates **2a** and **3a** could not originate from differences in their conformation alone. It seems that the low intensity of the dichroic band of **1a** results also from the low chirality of the chromophore in this molecule which contains only one asymmetric carbon. While differences in the degree of puckering should affect the intensity of the CD $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions to the same extent, the number of asymmetric centers should influence each transition in a different manner.

Table III
Spectral Properties of Five-Membered Ring Sulfites

Compd	Solvent	λ_{\max} , m μ	ϵ	λ_{\max} , m μ	$10^2 \Delta\epsilon$	λ_{\max} , m μ	$10^2 \Delta\epsilon$
<i>cis</i> -1c	Hexane	215	300	217.5	+6.1	197.5	-130.3
	Isooctane	216	296	217.5	+5.5	197.5	-130.3
		217 ^a	122 ^a				
<i>trans</i> -1c	Acetonitrile	217	182	212	+12.1	192	-125.0
	Ethanol	217	77	212	+9.1		
	Hexane	218	114	226	+1.5		
	Isooctane	218	112	225	+1.4	197	-121.2
		216 ^a	49 ^a				
2c	Acetonitrile	216	83	222	+1.3	195	-112.4
	Ethanol	218	61	222	+1.2		
	Hexane	214	240	225	-2.4	198	+266.6
				220 ^a	-3.2 ^a	195 ^a	+236.3 ^a
	Isooctane	214	238	223	-2.6	198	+263.6
		214 ^a	58 ^a	221 ^a	-3.8 ^a	193 ^a	+245.4 ^a
	Acetonitrile	213	177	217	-2.6	197	+242.4
3c	Ethanol	214 ^a	124 ^a	220 ^a	-2.6 ^a	195 ^a	+236.3 ^a
		213	137	222	-2.6		
		215 ^a	67 ^a				
	Hexane	214	240	225	+2.5	197.5	-303.7

^a Data obtained for samples containing 3 μ l of TFA.

Addition of 5 μ l of TFA to 3a in 3 ml of hexane causes a decrease of the $\Delta\epsilon$ values of both transitions by a factor of 1.8. This could suggest that the main effect of TFA is not a consequence of its asymmetrical solvation of the chromophore, but probably results from its influence on the equilibrium of the conformers in solution.

The cyclic five-membered ring carbonates 1b and 2b show uv absorption in hexane at 215 m μ with molar extinction coefficients of 5 and 8, respectively. A shift in λ_{\max} to 207 m μ is observed in ethanol. This is in accord with the calculation of Pople¹⁹ for the $n \rightarrow \pi^*$ transition of carbonic acid.

The CD curves of 1b, 2b, and 3b (Figure 1) show no maxima at 215 m μ . However, an absorption is observed up to 185 m μ for the three compounds which could be attributed to an $n \rightarrow \sigma^*$ transition. An $n \rightarrow \pi^*$ dichroic band is perhaps submerged in this absorption. Thionocarbonates show in addition to the two CD absorptions mentioned earlier another absorption below 200 m μ (see Figure 1) which presumably corresponds to an $n \rightarrow \sigma^*$ transition. The sign of the Cotton effect in this region is identical with that of the $n \rightarrow \pi^*$ transition of the same molecule. As the short-wavelength CD absorption of the thionocarbonates and that of carbonates have the same sign for a given chirality, it seems that the same effects influence the chiroptical properties of the electronic transitions in both cyclic thionocarbonates and cyclic carbonates.

Cyclic Sulfites. We deemed it of interest to compare the uv spectra of the sulfites 1c, 2c, and 3c with those of saturated dialkyl sulfoxides and sulfinates. Unlike the sulfoxides, which exhibit two absorption bands, a shoulder at 210–220 m μ and a maximum below 210 m μ (ethanol),^{20,21} the cyclic sulfites show only one maximum at 213–218 m μ (see Table III). The short-wavelength absorption band in sulfoxides, attributed to an $n \rightarrow \pi^*$ transition, exhibits a blue shift with increasing polarity of the solvent,²⁰ and the molar extinction coefficients (ϵ) are much larger than those in cyclic sulfites. It seems that the electronic transition of the cyclic sulfites resembles more the long-wavelength absorption band of dialkyl sulfoxides, which is characterized by a low ϵ and is less sensitive to solvent effects. Dialkyl sulfinates, like cyclic sulfites, show only one maximum (at 215 m μ , in ethanol), but in contrast to cyclic sulfites this transition is sensitive to a solvent effect.²⁰

In dissymmetric dialkyl sulfoxides only the Cotton effect at long wavelength was assumed to be associated with

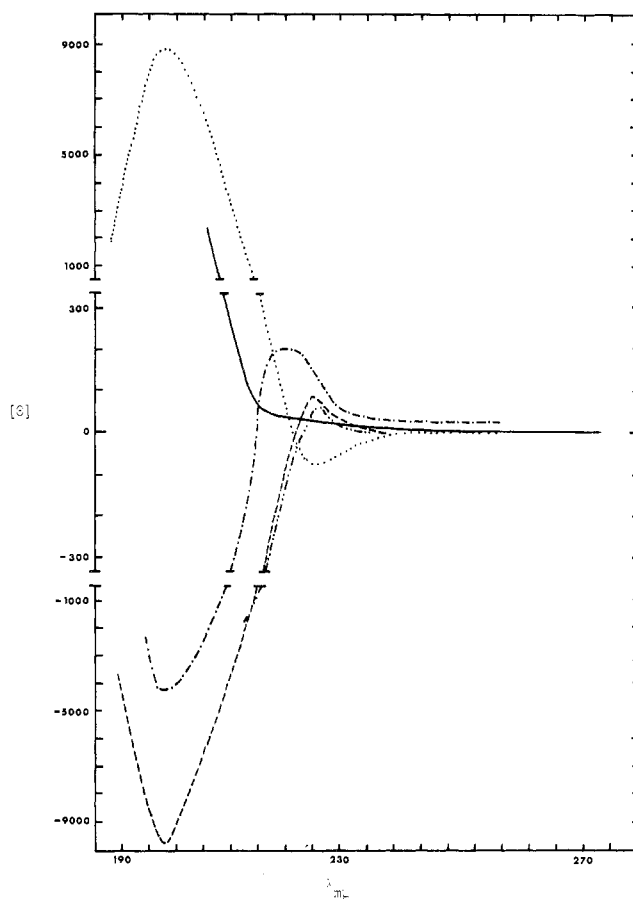


Figure 2. CD curves of (a) *cis*-(*S*)-methylethylene sulfite (*cis*-1c) (---); (b) *trans*-(*S*)-methylethylene sulfite (*trans*-1c) (- · - · -); (c) (*S,S*)-1,2-dimethylethylene sulfite (2c) (·····); (d) (*R,R*)-1,2-dimethylethylene sulfite (3c) (----); (e) (*S,S*)-1,2-dimethylethylene methyl phosphite (2d) (—) in benzene.

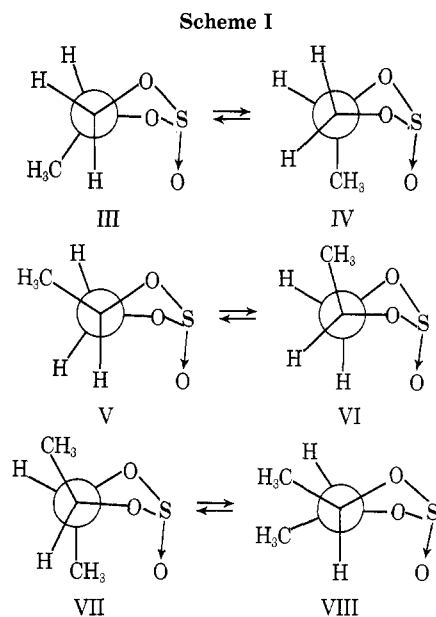
the dissymmetric alkyl group, while the short-wavelength band is attributed to the chirality of the sulfur atom.²² In contrast, in cyclic sulfites both transitions seem to be associated with the asymmetric perturbation of the chromophores caused by the chiral alkyl moiety of the ring. This is indicated by the CD curves of 2c and 3c (Figure 2). When S \rightarrow O becomes a chiral center, as in *cis*- and *trans*-1c, an essential change in the CD spectra is observed. The two 1c isomers, although identical with 2c in the alkyl moiety configuration, differ from 2c in their chiroptical

properties. Also, in contrast to **2c** and **3c**, *trans*-**1c** and *cis*-**1c** do not exhibit an antipodal relationship. This is not surprising, as the two are in fact diastereoisomers: they possess the same dissymmetric alkyl moiety but differ from each other by the S→O configuration, which is *S* in *trans*-**1c** and *R* in *cis*-**1c**. Even so, none of the CD bands of one compound is antipodal to the respective band in the spectrum of the other compound. Comparison of the two spectra shows that the effect of the asymmetric center at the sulfur atom is reflected mainly in the long-wavelength band of the CD spectra. In this region the spectra of the two diastereoisomers differ from each other in λ_{\max} as well as intensity, the *cis* isomer showing the dichroic band of shorter wavelength and higher intensity, yet the sign of the Cotton effect is positive in both. As in other ring systems^{5,23-25} the chirality of the ring may be the factor determining the sign of the Cotton effect in cyclic sulfites. In the **1c** isomers the change in the configuration at the sulfur atom may bring about conformational changes in the molecules, from which a correlation between the conformation of the cyclic sulfites and the signs of Cotton effects displayed by them could result. This would be in analogy to cyclic and open-chain sulfoxides,^{22,26} where restriction in rotation around the C-S bond and spatial interaction of the chromophore with the surrounding alkyl groups influence the Cotton effect.

Nmr analysis of ethylene sulfite¹² and sultones²⁷ has shown that these rings are not planar. Recently it was suggested by Green and Hellier, on the basis of nmr and ir analysis, that in ethylene sulfite as well as in other five-membered ring sulfites the S→O bond is axially orientated to the ring.²⁸ This is in analogy to six-membered ring sulfites, such as trimethylene²⁹ and 4-methyltrimethylene sulfite,⁹ where the preference of rigid chair conformation with axial S→O orientation is clearly demonstrated. Average *cis* and *trans* vicinal coupling constants obtained for the five-membered ring sulfites²⁸ could indicate that the substituents on the two ring carbons are not eclipsed. On this basis and in analogy to five-membered ring phosphites, which are believed to exist in a twist-envelope conformation,^{11,12} it can be assumed that the preferred conformation for **1c**, **2c**, and **3c** is the twist-envelope with S→O axial.

Since in the synthesis of **1c** the *cis* and *trans* isomers are obtained in a 1:2 mixture, it is clear that the two differ greatly in the steric interaction between the methyl and S→O groups. Therefore, it is expected that each of the isomers will attain different twist-envelope forms. In the case of *cis*-**1c** it seems that as a result of strain due to CH₃...S→O interaction, conformation IV is of higher energy than conformation III (Scheme I). If the chirality of the five-membered ring is defined as positive in conformation III and negative in IV, then *cis*-**1c** should exhibit a positive Cotton effect. In *trans*-**1c** similar steric interactions should considerably be diminished and therefore almost equal population of conformers of structures V and VI is to be expected. The observed small positive Cotton effect in this case suggests a slight preference of conformation V over VI. Looking at models reveals that the nonbonded interaction between the sulfur atom and the methyl group is greater in VI than in V.³⁰

Compound **2c** can be described by the two limiting twist-envelope conformations VII and VIII. In the latter there is an increase in energy due to the gauche form, while in VII there exists nonbonded interaction between methyl and S→O groups. However, since nonbonded interaction is strongly dependent on the distance between the interacting groups, the energy would be lowered if the molecule attained a less puckered form with the S→O



group farther removed from the methyl group. Thus conformation VII seems to be the more populated form of **2c**. Since the sign of the dihedral angle of VII is opposite to that of the dihedral angle of III and V, the CD absorption bands of **2c** are expected to be of opposite signs to those of the **1c** isomers, as found experimentally.

On the basis of conformational equilibrium it seems reasonable that increasing solvent polarity should lead to an increase in the intensity of the long-wavelength dichroic band in *cis*-**1c**, since owing to solvation of the chromophore there is a stronger nonbonded interaction between the S→O and the methyl group, and the dihedral angle is increased. This is indeed observed. In *trans*-**1c** no solvent effect is observed, since steric hindrance even in the solvated molecule is very small.

The effect of solvent in **2c** is not clear. No effect is observed on increasing solvent polarity, while addition of TFA causes an increase in the negative absorbance of the long-wavelength band and a small decrease in the dichroic band at short wavelength. A very small decrease in the absorbance at short wavelength is observed also in *cis*- and *trans*-**1c** on increasing the solvent polarity. It seems that the solvent effect in cyclic sulfites can be attributed not only to conformational changes but also to an asymmetric solvation of the chromophore which affects the two dichroic bands differently.

It is important to note that cyclic sulfites are highly associated in solution.³¹ However, neither in a concentration range of $3.5\text{--}35 \times 10^{-3} M$ (*n*-hexane), used for measuring the long-wavelength band, nor in a concentration range of $6\text{--}17 \times 10^{-4} M$, used for the short-wavelength band, could any significant changes in the CD spectra be observed on changing the sulfite concentration.

The phosphite **2d** exhibits a Cotton effect in the short-wavelength range of the same sign as that of the respective cyclic sulfite, **2c**. No absorption was found in the long-wavelength region.

Diols and Dioxolanes. Kirk, Mose, and Scopes have lately demonstrated the existence of well-defined Cotton effects in a long series of secondary and tertiary steroidal and terpene alcohols in the region 185–203 μ .^{1b} The ellipticity values ($\Delta\epsilon$) of these alcohols vary remarkably, from 0.12 in 3α -hydroxy- 5α -cholestane up to 4.19 in the case of $5\alpha,17\beta H$ -pregnan- 20β -ol. The situation differs, however, when the oxy chromophore is attached to the side chain carbon 20, in which case the epimeric diols

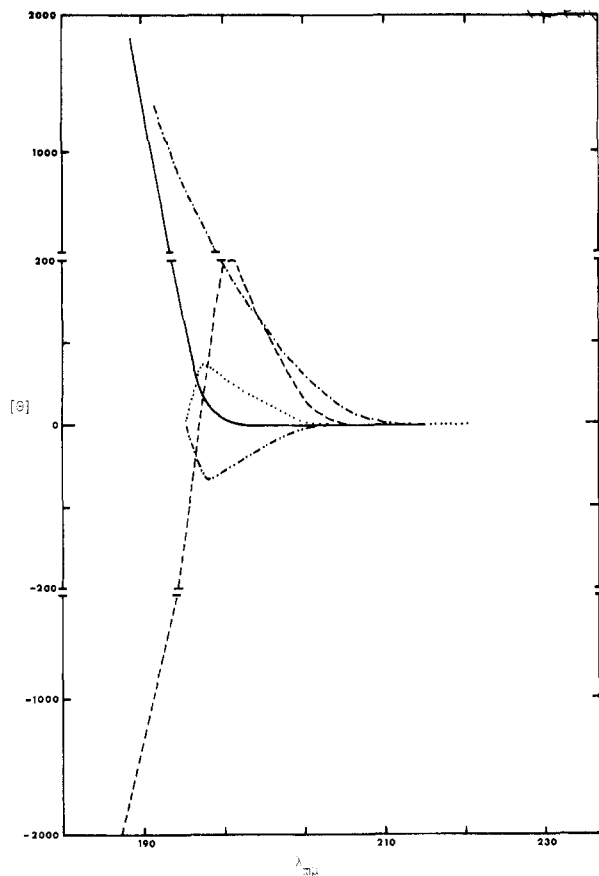


Figure 3. CD curves of (a) (-)-(S,S)-2,3-butylene glycol (**2**) (---); (b) (+)-(R,R)-2,3-butylene glycol (**3**) (-·-·-); (c) *trans*-(-)-(S)-2-bromomethyl-4-methyl-1,3-dioxolane (*trans*-**1e**) (—); (d) *cis*-(-)-(S)-2-bromomethyl-4-methyl-1,3-dioxolane (*cis*-**1e**) (-·-·-); (e) (-)-(S,S)-2-bromomethyl-4,5-dimethyl-1,3-dioxolane (**2e**) (----) in hexane.

(2*R*)- and (2*S*),24-dihydroxycholeane display at 190–200 $m\mu$ only "end absorptions" of negative and positive signs, respectively.³² By variance, the corresponding cyclic ethers, (2*R*)- and (2*S*),24-oxidocholeane, exhibit well-defined Cotton effects of opposite signs in the 195–200- $m\mu$ region. The $\Delta\epsilon$ values of these ethers vary significantly from -0.085 in the 2*R* case to +0.291 in the case of (2*S*),24-oxidocholeanes.³³

In the saturated diols 1–3 we observed Cotton effects in the region of 198 $m\mu$ only in the cases of **2** and **3** and none in the case of **1**. Moreover, in contrast to the steroidal monofunctional alcohols the $\Delta\epsilon$ values found for **2** and **3** were notably low (0.022).

On the basis of prevailing views, the above variances could be explained in terms of conformational effects. Thus, the preferred conformation for both **2** and **3** is most likely with the methyls anti, the dihedral angle between the two oxy groups in **2** would assume an opposite sign to that of **3**, and they should obviously give rise to antipodal CD curves, as is the case. In analogy to (*R*)-phenylethylene glycol,³⁴ the lack of Cotton effect in **1** could reasonably be attributed to a near to zero value of the dihedral angle between the oxygen atoms owing to hydrogen bonding. In diols **2** and **3**, by contrast, a small but significant dihedral angle does exist owing to torsional effects stemming from Me...Me interactions.

The uv curves of the bromodioxolanes *cis*-**1e**, *trans*-**1e**, and **2e** in hexane show maxima at 220–235 $m\mu$ with normal absorption coefficients of 47–105. The appearance of the uv maximum in the chlorodioxolane **2f** at 212.5 $m\mu$ (ϵ 38) is in line with maxima shown by halogenoalkanes in which the $n \rightarrow \sigma^*$ transition of the chlorine chromophore

occurs at a lower wavelength than that of bromine.³⁵ The bathochromic shift in the uv absorption of the dioxolanes compared to that of alkyl halides³⁵ can be explained in terms of electronic or dipole-dipole interactions between the halogen and the ring oxygen atoms.

The dichroic curves of *cis*-**1e**, *trans*-**1e**, and **2e** (Figure 3) do not correspond to those of the uv spectra. Thus, **2e** exhibits a positive Cotton effect at 203 $m\mu$ ($\Delta\epsilon$ 0.06) and an absorption of opposite sign at lower wavelength. Significantly, both *cis*- and *trans*-**1e** display only such an absorption, of positive sign. The *cis* isomer, however, shows the beginning of a positive Cotton effect below 220 $m\mu$, while in *trans*-**1e** there is no absorption above 200 $m\mu$. The absorption in *cis*-**1e** could be related to two positive superimposed Cotton effects. This then implies that (a) the long-wavelength absorption is not due to an additional asymmetric center in the dioxolane ring (at position 2 in the monomethyl dioxolanes); and (b) the dichroic band at longer wavelength originates from an $n \rightarrow \sigma^*$ transition of the halogen.

The differences in the CD spectra of *cis*-**1e**, *trans*-**1e**, and **2e** could also be explained by different preferred conformations of these compounds *per se*, or by a different net overlap of the nonbonding 2p orbitals of oxygen resulting from conformational changes.³⁶ The nmr chemical shift data of these compounds are, however, very similar and do not allow any conclusion concerning differences in conformation.

The chiral five-membered ring sulfites and dioxolane systems included in this study display significant variations in their dichroic properties when an asymmetric center other than those of the diol residue is introduced into the molecule. In sulfites these differences are pronounced both in the shorter and in the longer wavelengths, whereas in the case of the dioxolanes they are noticed in the short wavelengths only.

Experimental Section

The optically active 1,2-glycols used were (+)-(S)-1,2-propylene glycol (Aldrich), (-)-(S,S)-2,3-butylene glycol (Burdick and Jackson), and (+)-(R,R)-2,3-butylene glycol prepared from dibutyl L-tartrate according to literature procedures, by way of 2,3-O-isopropylidene-L-threitol 1,4-bis(methanesulfonate)³⁷ and subsequent reduction and hydrolysis.³⁸

Ir spectra were recorded on a Perkin-Elmer Model 237 spectrometer, uv spectra on a Unicam Model Sp 800 A spectrometer, nmr spectra on a JEOL C-60-H spectrometer, and mass spectra on a Varian MAT CH-5 spectrometer. Optical rotations were measured with a Perkin-Elmer 141 polarimeter and CD spectra with a Cary 60 recording spectropolarimeter.

Thionocarbonates. The thionocarbonates were prepared according to the method of Staab and Walther.³⁹ To a solution of *N,N*-thiocarbonyldiimidazole (10–13 mmol) in toluene (10 ml) an equimolar amount of the glycol was added, and the reaction mixture was refluxed under nitrogen for 2 hr. The solvent was partially evaporated and the product was separated from the reaction mixture and purified by preparative vpc (2 ft \times 0.25 in. 10% SE-30 column).

(*S*)-Methylethylene thionocarbonate (**1a**) was a colorless liquid: retention time 4.5 min on the above-mentioned column at 110° (gas flow rate 40 ml/min); n_D^{20} 1.520; ν_{\max} 1250 (C=S) and 1400 cm^{-1} ; λ_{\max} (hexane) 235 $m\mu$ (ϵ 6150) and 315 (54); nmr (CCl₄) δ 1.5 (3 H, d, J = 6 Hz, CH₃), 4.18 and 4.66 (2 H, dd, dd, CH₂), 5.0 ppm (1 H, m, CH); mass spectrum M^+ 118.

Anal. Calcd for C₄H₆O₂S: C, 40.68; H, 5.085; S, 27.12. Found: C, 40.50; H, 5.06; S, 27.20.

(*S,S*)-1,2-Dimethylethylene thionocarbonate (**2a**)⁵ was a colorless liquid: retention time 5 min on the above-mentioned column at 120° (gas flow rate 45 ml/min); n_D^{20} 1.512; ν_{\max} 1250 and 1400 cm^{-1} ; λ_{\max} (hexane) 230 $m\mu$ (ϵ 6000) and 325 (20); nmr (CCl₄) δ 1.5 (6 H, d, J = 6 Hz, CH₃), 4.50 ppm (2 H, m, CH); mass spectrum M^+ 132.

(*R,R*)-1,2-Dimethylethylene thionocarbonate (**3a**) had vpc, ir, nmr, and mass spectral data identical with those of **2a**.

Anal. Calcd for $C_5H_8O_2S$: C, 45.45; H, 6.06; S, 24.24. Found: C, 45.37; H, 6.08; S, 24.30.

Carbonates. The carbonates were prepared by a transesterification reaction of the diol with diethyl carbonate.⁴⁰ A mixture of glycol (13 mmol) and diethyl carbonate (1.7 g, 14 mmol) was kept at 100° overnight, while ethanol was slowly distilled. The reaction mixture was then fractionally distilled under low pressure.

(-)-(S)-**Methylethylene carbonate (1b)** was obtained in a yield of 87%: bp 100–105° (25 mm); ν_{\max} 1800 (C=O), 1100 cm^{-1} (CO); λ_{\max} (dioxane) 215 $m\mu$ (ϵ 5); nmr (CCl_4) δ 1.49 (3 H, d, J = 6 Hz, CH_3), 4.04 and 4.57 (2 H, dd, dd, CH_2), 4.87 ppm (1 H, m, CH); mass spectrum M^+ 102; $[\alpha]^{25}_D$ -1.7° (c 0.92, EtOH).

Anal. Calcd for $C_4H_6O_3$: C, 47.06; H, 5.88. Found: C, 47.20; H, 5.94.

(+)-(S,S)-**1,2-Dimethylethylene carbonate (2b)** was obtained in a yield of 70%: bp 68° (0.5 mm); retention time 12 min on a column of 100% Carbowax 1500 M on Chromosorb P 60–80 (6 ft \times 0.25 in.) at 150° (gas flow rate 60 ml/min); n^{20}_D 1.4185; ν_{\max} 1800 (C=O), 1050 cm^{-1} (CO); λ_{\max} (dioxane) 215 $m\mu$ (ϵ 8); nmr (CCl_4) δ 1.41 (6 H, d, J = 6 Hz, CH_3), 4.36 ppm (2 H, m, CH); mass spectrum M^+ 116; $[\alpha]^{25}_D$ +35° (c 1.09, EtOH). For data of the racemic compound see ref 21.

Anal. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.90. Found: C, 51.82; H, 6.92.

(-)-(R,R)-**1,2-Dimethylethylene carbonate (3b)** had boiling point, vpc, ir, nmr, and mass spectral data identical with those of **2b**, and $[\alpha]^{25}_D$ -36.2° (c 1.0, EtOH).

Anal. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.90. Found: C, 51.80; H, 6.95.

Sulfites. The sulfites were obtained by the reaction of thionyl chloride and the appropriate diol without solvent.⁴¹ To the glycol (13 mmol) freshly distilled thionyl chloride (2.2 g, 18 mmol) was slowly added dropwise at room temperature. The reaction mixture was kept at 60° for 30 min and then fractionally distilled under low pressure.

(S)-**1-Methylethylene Sulfite (1c)**. A 0.73-g (45%) yield of a 1:2 mixture of the cis and trans sulfite isomers was obtained, bp 68° (25 mm).⁴² The isomers were separated by vpc (20 ft \times 0.25 in. 10% Carbowax 1500 M at 120°, gas flow rate 50 ml/min). *cis*-(+)-(S)-Methylethylene sulfite (*cis*-**1c**) had retention time 83 min; n^{20}_D 1.4380; ν_{\max} 1200 cm^{-1} (S=O); λ_{\max} (EtOH) 215 $m\mu$ (ϵ 55); nmr (CCl_4) δ 1.59 (3 H, d, J = 6 Hz, CH_3), 4.2–4.7 ppm (3 H, m, CH_2 and CH); mass spectrum M^+ 122; $[\alpha]^{25}_D$ +3.0° (c 0.275, hexane). *trans*-(-)-Methylethylene sulfite (*trans*-**1c**) had retention time 91.7 min; n^{20}_D 1.4383; ν_{\max} 1200 cm^{-1} (S=O); λ_{\max} (EtOH) 215 $m\mu$ (ϵ 61); nmr (CCl_4) δ 1.41 (3 H, d, J = 6 Hz, CH_3), 3.8 (1 H, q, one of the CH_2 protons), 4.63 (1 H, four lines, one of the CH_2 protons), 5.07 ppm (1 H, sextet, CH); mass spectrum M^+ 122; $[\alpha]^{25}_D$ -3.5° (c 0.73, hexane).

Anal. Calcd for $C_3H_6O_3S$: C, 29.51; H, 4.92; S, 26.23. Found (for isomeric mixture): C, 29.38; H, 4.90; S, 26.40.

(+)-(S,S)-**1,2-Dimethylethylene sulfite (2c)** had bp 70° (25 mm); n^{20}_D 1.4332; ν_{\max} 1200 cm^{-1} (S=O); λ_{\max} (dioxane) 225 $m\mu$ (ϵ 17); nmr (CCl_4) δ 1.47 and 1.55 (6 H, two d, J = 5 Hz, CH_3), 3.98 (1 H, m, CH), 4.60 ppm (1 H, m, CH); mass spectrum M^+ 136; $[\alpha]^{25}_D$ +20.1° (c 0.54, hexane).

Anal. Calcd for $C_4H_8O_3S$: C, 35.29; H, 5.88; S, 23.53. Found: C, 35.13; H, 5.90; S, 23.62.

(-)-(R,R)-**1,2-Dimethylethylene sulfite (3c)** had boiling point, ir, uv, nmr, and mass spectral data identical with those of **2c** and $[\alpha]^{25}_D$ -20.3° (c 0.55, hexane).

Anal. Calcd for $C_4H_8O_3S$: C, 35.29; H, 5.88; S, 23.53. Found: C, 35.40; H, 5.84; S, 23.60.

(+)-(S,S)-**1,2-Dimethylethylene methyl phosphite (2d)** was prepared by transesterification according to the following. A mixture of (-)-(S,S)-2,3-butylene glycol (2 g, 22 mmol) and trimethyl phosphite (3.2 g, 26 mmol) was kept at 100° overnight, while methanol was slowly distilled. The cyclic phosphite (1.8 g, 54% yield) was separated from the reaction mixture by fractional distillation, bp 55° (25 mm), and was further purified by vpc (10 ft \times 0.25 in. 10% Carbowax 20 M at 110°, gas flow rate 40 ml/min): retention time 10 min; n^{20}_D 1.4375; ν_{\max} 1200 ($POCH_3$), 1000 cm^{-1} (O-P-O); λ_{\max} (hexane) 210 $m\mu$ (ϵ 41); nmr (CCl_4) δ 1.29 and 1.37 (6 H, two d, J = 5 Hz, CH_3), 3.45 (3 H, d, J = 11 Hz, $POCH_3$), 3.8 ppm (2 H, m, CH); $[\alpha]^{25}_D$ +42° (c 0.97, dioxane), $[\alpha]^{25}_D$ +65° (c 0.67, hexane).

Anal. Calcd for $C_5H_{11}O_3P$: C, 40.0; H, 7.33. Found: C, 39.8; H, 7.30.

1,3-Dioxolanes were prepared by the transacetalation method of Paquette and Houser.⁴³

2-Bromomethyl-1,3-dioxolanes. A mixture of glycol (26 mmol), bromoacetaldehyde diethyl acetal (5.0 g, 26 mmol), and a few drops of concentrated sulfuric acid was kept at 120° for 4 hr, while ethanol was slowly distilled. The reaction mixture was cooled, diluted with ether, and washed twice with water and then with concentrated bicarbonate solution. After the ether solution was dried (Na_2SO_4) and evaporated the dioxolane was separated from the residue by fractional distillation at low pressure. Further purification of the dioxolane was carried out by preparative vpc (6 ft \times 0.25 in. 10% Carbowax 20 M).

trans-(-)-(S)-**2-Bromomethyl-4-methyl-1,3-dioxolane (trans-1e)** had retention time at 85° 25 min; n^{25}_D 1.4662; ν_{\max} 1100 (O-C-O), 750 cm^{-1} (CBr); λ_{\max} (hexane) 225 $m\mu$ (ϵ 47); nmr (CCl_4) δ 1.27 (3 H, d, J = 5 Hz, CH_3), 3.23 (2 H, d, J = 4.5 Hz, CH_2Br), 3.37 and 4.15 (3 H, two m, O-CH- CH_2 -O), 5.15 ppm (1 H, t, J = 6 Hz, O-CH-O); mass spectrum M^+ 181 and 183; $[\alpha]^{25}_D$ -30.6° (c 0.78, hexane).

Anal. Calcd for $C_5H_9BrO_2$: C, 32.97; H, 4.95; Br, 44.51. Found: C, 33.20; H, 4.95; Br, 44.26.

cis-(-)-(S)-**2-Bromomethyl-4-methyl-1,3-dioxolane (cis-1e)** had retention time at 85° 27 min; n^{25}_D 1.4658; ir and uv data identical with those of *trans*-**1e**; nmr (CCl_4) δ 1.3 (3 H, d, J = 5 Hz, CH_3), 3.26 (2 H, d, J = 4 Hz, CH_2Br), 3.2–4.4 (3 H, two m, O-CH- CH_2 -O), 4.99 ppm (1 H, t, J = 5 Hz, O-CH-O); mass spectrum M^+ 181 and 183; $[\alpha]^{25}_D$ -24° (c 1.170, hexane).

Anal. Calcd for $C_5H_9BrO_2$: C, 32.97; H, 4.95; Br, 44.51. Found: C, 33.10; H, 4.93; Br, 44.30.

(-)-(S,S)-**2-Bromomethyl-4,5-dimethyl-1,3-dioxolane (2e)** had bp 80° (25 mm); n^{25}_D 1.4597; retention time 10 min at 120° (6 ft \times 0.25 in. 10% Carbowax 20 M, flow rate 70 ml/min); ν_{\max} 1100 (O-C-O) and 770 cm^{-1} (CBr); λ_{\max} (hexane) 225 $m\mu$ (ϵ 85) and 275 (65); nmr (CCl_4) δ 1.20 and 1.25 (6 H, two d, J = 6 Hz, CH_3), 3.21 (2 H, d, J = 4 Hz, CH_2Br), 3.58 (2 H, m, O-CH- CH_2 -O), 5.07 ppm (1 H, t, J = 5 Hz, O-CH-O); mass spectrum M^+ 195 and 197; $[\alpha]^{25}_D$ -10° (c 0.975, hexane).

Anal. Calcd for $C_6H_{11}BrO_2$: C, 36.73; H, 5.61; Br, 41.32. Found: C, 36.56; H, 5.62; Br, 41.02.

(S,S)-**2-Chloromethyl-4,5-dimethyl-1,3-dioxolane (2f)** was prepared from (S,S)-2,3-butylene glycol and chloroacetaldehyde diethyl acetal by a procedure identical with that given for the 2-bromomethyl-1,3-dioxolanes: retention time at 120° 12 min (6 ft \times 0.25 in. 10% Carbowax 20 M, flow rate 70 ml/min); λ_{\max} (hexane) 213 $m\mu$ (ϵ 38); λ_{\max} (AcCN) 217 $m\mu$ (ϵ 119); nmr (CCl_4) δ 1.22 and 1.27 (6 H, two d, J = 6 Hz, CH_3), 3.40 (2 H, d, J = 4 Hz, CH_2Cl), 3.62 (m, 2 H, O-CH- CH_2 -O), and 5.13 ppm (1 H, t, J = 4.5 Hz, O-CH-O).

Anal. Calcd for $C_6H_{11}O_2Cl$: C, 47.84; H, 7.30; Cl, 23.58. Found: C, 47.62; H, 7.51; Cl, 23.34.

Registry No.—**1a**, 51175-86-1; **1b**, 51260-39-0; *cis*-**1c**, 51260-40-3; *trans*-**1c**, 51260-41-4; *cis*-**1e**, 51260-42-5; *trans*-**1e**, 51260-43-6; **2a**, 51175-87-2; **2b**, 51261-82-6; **2c**, 51260-44-7; **2d**, 51260-45-8; **2e**, 51260-46-9; **2f**, 51175-88-3; **3a**, 35677-60-2; **3b**, 51260-48-1; **3c**, 51260-47-0; **4**, 24410-91-1; **5**, 32588-95-7.

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Synthesis of Macrocylic Polythiaethers¹

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Macrocylic polythiaethers have been synthesized and some of their properties have been determined. The compounds reported comprise a homologous series containing two, four, or six sulfur atoms in the macrocylic ring. One example of a five sulfur atom macrocylic is included. The synthetic methods allow for symmetrical or unsymmetrical bridging of the ring sulfur atoms by ethylene, tri-, tetra-, penta-, and hexamethylene bridges. These methods are contrasted to previously reported methods for macrocylic polyoxaether and mixed polyoxa-polythiaether synthesis.

The preparation and properties of numerous macrocylic polyoxaethers have been previously reported.² In addition, a limited number of macrocylic polythiaethers^{3,4} and mixed azo-oxa-thia macrocylic^{2b,3a} and macrobicyclic⁵ polyethers containing four or more sulfur atoms in the macrocylic ring have been described.

The macrocylic polyoxaethers have generated particular interest through stable complex formation with cations of the alkali and alkaline earths, ammonium, and silver.^{2,6} As model compounds, they have allowed extensive thermodynamic correlations to structurally related macrocylics, both biological and synthetic in origin, which exhibit varying degrees of biological activity in the processes of active ion transport.⁷ Relative to the oxoethers, the thia and mixed oxo-thia macrocylics exhibit lower selectivity and coordinatability of active metal ions.^{2c,6} To date, macrocylic polythiaethers have not been given consideration as possible ion transport agents owing to their less discriminating coordination chemistry and lack of defined biologically related macrocylics. However, in the absence of other ring heteroatoms, macrocylic polythiaethers exhibit substantial coordinatability^{3a,5} and selectivity^{1,8} toward posttransitional element cations in agreement with hard and soft acids and bases theory.⁹ On the basis of the established correlations between biological activity and macrocylic structure,^{7,10} more detailed selectivity and coordinatability studies and chemotherapeutic evaluations of macrocylic polythiaethers, as related to purging of Hg(II) from test animals, are presently in progress in our labora-

tories. The scope and purpose of this paper is to report on the convenient preparation of a series of new and some previously reported macrocylic polythiaethers containing no azo- or oxoether functionality which may be exploited for other than active metal coordination chemistry.

Results and Discussion

A search of the literature has disclosed only several references to macrocylic polythiaethers containing four or more sulfur atoms. With the exception of thioformaldehyde polymerization,¹¹ all other methods of thiaether ring closure were based on α -mercaptide displacement of an ω -halide function. The α -mercapto- ω -halopolythiamethylene intermediates are available only by *in situ* generation from condensation of α,ω -dihaloalkanes with active metal sulfide,^{4a} α,ω -polymethylene dimercaptides,^{4b} or precondensed α,ω -polythiapolymethylene dimercaptides.³

Unlike the strong template effect and corresponding high yields of macrocylic polyoxaethers offered by oxygen coordination of alkali metal ion during cyclization of polyoxa units,^{2,12} low sulfur-active metal ion coordination renders template effects of little consequence. Thus, the competition between cyclization and predominant linear polymerization is more statistically defined, entropy constraints of cyclization favoring linear polymerization whereas high dilution favors cyclization kinetically.¹³ However, no prior study has elaborated the specific factors effecting relative distribution of cyclic products for the present reaction. By the methods outlined in Scheme