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The Synthesis, Structure, and Reactions of 1,3-Oxathiacycloalkanes

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Data concerning the methods of synthesis, structure, and properties of 1,3-oxathiacycloalkanes are discussed. The modern ideas about steric structure, reactivity, and mechanisms of the reactions of 1,3-oxathiacycloalkanes in the liquid phase are surveyed and described systematically.
The bibliography includes 102 references.

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I. INTRODUCTION

The chemistry of 1,3-oxathiacycloalkanes has been developing vigorously during the last 10–15 years. These compounds proved to be of interest for stereochemical studies and are used in fine organic synthesis and in the synthesis of biologically active preparations.

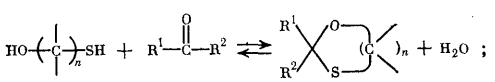
The problems associated with the chemistry of 1,3-oxathiacycloalkanes include selective methods of their synthesis from carbonyl compounds and mercaptoalkanols of different structure, the characteristics of their electronic and steric structure determined by the presence of oxygen and sulphur atoms in the 1- and 3-positions in the heterocycle, and their behaviour in reactions accompanied by the homolytic and heterolytic dissociation of the carbon–sulphur and carbon–oxygen bonds.

The aim of the present review is to give a systematic account and to survey the principal data concerning the synthesis, structure, and reactivity of 1,3-oxathiacycloalkanes in the liquid phase.

The gas-phase reactions of 1,3-oxathiacycloalkanes have been hardly investigated and the available data concern specific problems of heterogeneous catalysis and we have not considered them.

II. THE SYNTHESIS OF 1,3-OXATHIACYCLOALKANES

At the present time 1,3-oxathiacycloalkanes have been less thoroughly investigated than 1,3-dioxacycloalkanes and 1,3-oxazacycloalkanes. This is apparently due to the greater availability of diols and aminoalcohols compared with mercaptoalkanols. The vast majority of the 1,3-oxathiacycloalkanes described in the literature have been synthesised by the interaction of mercaptoalkanols with carbonyl compounds[1-21]:

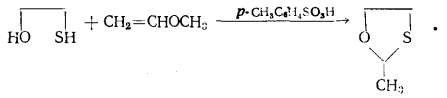


$n = 2, 3$.

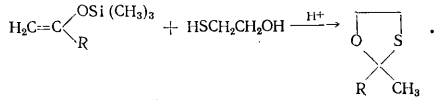
Various 1,3-oxathiolans[1-9] have been obtained by this method from 1,2-mercaptoalkanols and aldehydes or ketones[1-9] and 1,3-oxathianes have been obtained from 1,3-mercaptoalkanols[10-21].

Mercaptoalcohols condense in the presence of catalysts such as toluene-*p*-sulphonic acids, inorganic acids, and P_2O_5. Aldehydes and particularly formaldehyde give rise to 1,3-oxathiacycloalkanes in yields up to 90%, while in the case of ketones the yields are 30–70%.

Vinyl ethers can be used instead of carbonyl compounds[22,23]. Thus the condensation of mercaptoethanol with methyl vinyl ether yielded 2-methyl-1,3-oxathiolan[22]:

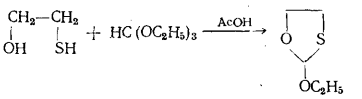


The reaction of trimethylsilyl vinyl ethers with 2-mercaptoethanol also leads to 1,3-oxathiolans[23]:



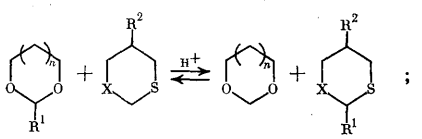
The yields reach 62–75% and are determined by the structure of the initial ether.

2-Ethoxy-1,3-oxathiolan has been synthesised by the reaction of 2-mercaptoethanol with ethyl orthoformate in the presence of acetic acid[24]:



2-Butyl-1,3-oxathiolan has been synthesised by the reaction of 2-ethoxy-1,3-oxathiolan with C_4H_9MgBr.[24]

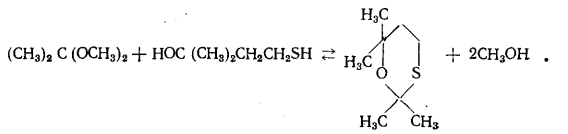
The possibility of obtaining 1,3-oxathianes as a result of the exchange reaction with 1,3-dioxacyclanes has been demonstrated[25-27]. This method makes it possible to obtain substituted 1,3-oxathianes which are difficult to synthesise by other methods:



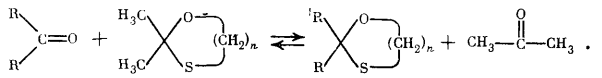
$n = 0, 1, 2$; X = O, S; $R^1 = CH_3$, C_2H_5, *n*-C_3H_7; $R^2 = H$, CH_3, iso-C_3H_7, iso-C_5H_{11}.

The yields are fairly high (79–95%). The reaction is catalysed by hydrochloric, sulphuric, and toluene-*p*-sulphonic acids and also by the KU-2 cation-exchange resin.

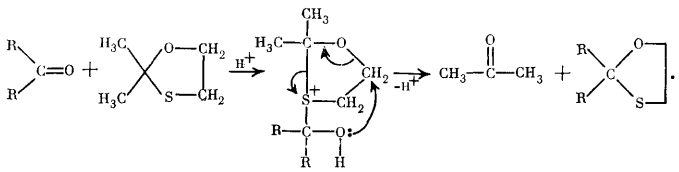
2,2,6,6-Tetramethyl-1,3-oxathiane has been obtained by the exchange acetalisation using the Dowex-50 catalyst[12]:



The synthesis of 2,2-disubstituted 1,3-oxathiacycloalkanes by the exchange reaction of 2,2-dimethyl-1,3-oxathiolan (or 2,2-dimethyl-1,3-oxathiane) with higher ketones has been described[1]:

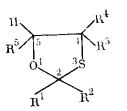


The yields reach 90%. The following reaction mechanism has been proposed:



The properties of certain five- and six-membered 1,3-oxathiacycloalkanes are presented in Tables 1 and 2.

Table 1. The properties of 1,3-oxathiolans



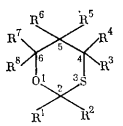
No.	R^1	R^2	R^3	R^4	R^5	B.p. °C (mmHg)	n_D^{20}	d_4^{20}	Refs.
1	H	H	H	H	H	55 (55)	1.5085	1.1656	[6]
2	CH_3	H	H	H	H	50 (30)	1.4852	1.0649	[6]
3	CH_3	CH_3	H	H	H	60 (67)	1.4724	—	[1, 6, 29]
4	C_2H_5	H	H	H	H	69—71 (43)	1.4828	1.0383	[6]
5	C_3H_7	H	H	H	H	85 (40)	1.4802	1.0129	[6]
6	iso-C_3H_7	H	H	H	H	83 (43)	1.4776	1.0090	[6]
7	C_6H_5	H	H	H	H	98—100 (1.3)	1.5850	—	[29]
8	C_2H_5	C_2H_5	H	H	H	105 (80)	1.4834	1.0039	[6]
9	CH_3	C_2H_5	H	H	H	12 (8)	1.4751	0.9776	[1]
10	H	H	CH_3	H	CH_3	75—78 (8)	1.4784	1.0444	[30]
11	CH_3	H	CH_3	H	CH_3	60—70 (9)*	1.466	0.9926	[30]
12	CH_3	CH_3	CH_3	H	CH_3	70—72 (9)*	1.4578	0.9531	[30]
13	CH_3	H	CH_3	CH_3	CH_3	80 (10)*	1.4603	—	[30]
14	H	H	H	H	CH_3	62—64 (64)	1.4877	1.0810	[28]
15	CH_3	H	H	H	CH_3	40—42 (35)*	1.434	1.0189	[28]
16	C_2H_5	H	H	H	CH_3	79—80 (58)*	1.4714	0.9900	[28]
17	C_3H_7	H	H	H	CH_3	88—89 (55)*	1.4654	0.9699	[28]
18	CH_3	CH_3	H	H	CH_3	42—44 (29)	1.4648	0.9788	[28]
19	C_2H_5	CH_3	H	H	CH_3	84—85 (74)*	1.4648	0.9825	[28]
20	iso-C_3H_7	CH_3	H	H	CH_3	95—97 (63)*	1.4670	0.9635	[28]
21	C_4H_9	CH_3	H	H	CH_3	106—108 (61)*	1.4700	0.9566	[28]
22	—$(CH_2)_5$—		H	H	H	106—107 (21)	1.5152	—	[23]
23	—$(CH_2)_6$—		H	H	H	135—140 (15)	1.5219	—	[23]
24	—$(CH_2)_4$—		H	H	H	103—107 (28)	1.5115	—	[23]
25	C_6H_5	CH_3	H	H	H	98 (1.3)	1.5640	—	[23, 29]
26	C_6H_5	C_6H_5	H	H	H	42—43	—	—	[1]
27	CH_3	C_2H_5	H	H	C_6H_5	104—105**	—	—	[9]
28	—$(CH_2)_5$—		H	H	C_6H_5	36—37**	—	—	[9]
29	—$(CH_2)_5$—		H	C_6H_5	C_6H_5	93—94**	—	—	[9]

* Mixture of isomers.
** Melting point.

III. THE STRUCTURE OF 1,3-OXATHIACYCLOALKANES

1,3-Oxathiacycloalkanes proved to be of interest for structural and kinetic studies. Firstly, the ring in these compounds is asymmetric, which increases the number of isomers. Secondly, the conformational effects in these compounds differ significiantly from those in symmetrical 1,3-dioxoacyclanes, since the bond lengths differ greatly: the lengths of the C—S, C—C, and C—O bonds are 1.82, 1.54, and 1.43 Å respectively. Thirdly, the electronegativity of the sulphur atom is much lower than that of the oxygen atom. The structure of 1,3-oxathiacycloalkanes has been investigated by ^1H NMR and the acid-catalysed equilibrium method.

Table 2. The properties of 1,3-oxathianes



No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	B.p., °C (mmHg)	n_D^{20}	Refs.
1	H	H	H	H	H	H	H	H	48 (11)	1.5026	[12]
2	CH_3	H	H	H	H	H	H	H	66—70 (24)	1.4922	[12]
3	H	H	H	H	H	H	CH_3	H	52—54 (13)	1.4920	[12]
4	H	H	H	CH_3	H	H	H	H	50—62 (12)	1.4903	[15]
5	H	H	H	H	CH_3	H	H	H	49—51 (8)	1.4939	[12]
6	C_2H_5	H	H	H	H	H	H	H	75—78 (19)	1.4856	[12]
7	iso-C_3H_7	H	H	H	H	H	H	H	75—78 (16)	1.4853	[12]
8	CH_3	CH_3	H	H	H	H	H	H	65—68 (17)	1.4890	[12]
9	H	H	CH_3	CH_3	H	H	H	H	73—75 (20)	—	[12]
10	H	H	H	H	H	H	CH_3	CH_3	53—55 (6)	1.4918	[12]
11	CH_3	CH_3	H	H	H	CH_3	H	H	55—57 (12)	1.4789	[12]
12	CH_3	CH_3	CH_3	H	H	H	H	H	60—63 (12)	1.4763	[15]
13	CH_3	H	H	H	CH_3	CH_3	H	H	70—72 (20)	1.4763	[15]
14	CH_3	CH_3	H	H	CH_3	H	H	H	57—58 (8)	1.4797	[12]
15	CH_3	H	CH_3	CH_3	H	H	H	H	70—72 (19)	1.4747	[12]
16	CH_3	H	CH_3	H	H	H	H	H	65—75 (20)*	1.4766	[15]
17	CH_3	H	H	H	H	H	CH_3	CH_3	68 (17)	1.4818	[15]
18	iso-C_3H_7	H	CH_3	H	H	H	H	H	73—85 (7)	1.4766	[15]
19	t-C_4H_9	CH_3	CH_3	CH_3	H	H	H	H	75—83 (8)	1.4835	[15]
20	H	H	H	H	H	CH_3	CH_3	H	54—64 (10)*	1.4898	[15]
21	CH_3	CH_3	CH_3	H	H	H	CH_3	H	59—70 (13)*	1.4695	[15]
22	CH_3	H	H	CH_3	H	H	H	H	67 (8)*	1.4810	[25]
23	C_2H_5	H	H	H	CH_3	H	H	H	70—74 (12)	1.4845	[25]
24	C_3H_7	H	H	H	CH_3	H	H	H	67—68 (2)	1.4810	[25]
25	CH_3	H	H	H	iso-C_3H_7	H	H	H	81—81 (9)	1.4821	[25]
26	C_3H_7	H	H	H	iso-C_3H_7	H	H	H	80 (1)	1.4806	[25]

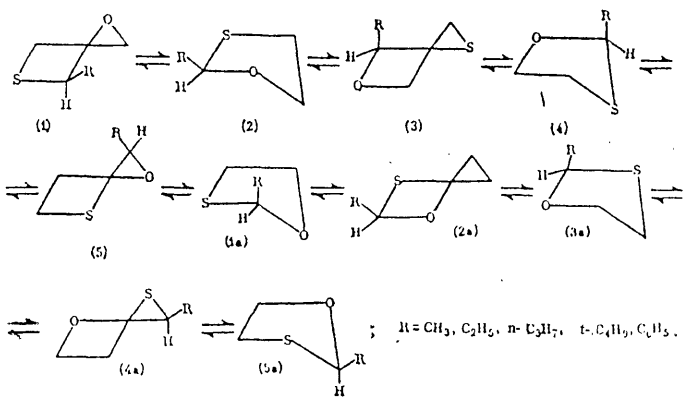
* Mixture of isomers.

1. The Stereochemistry of 1,3-Oxathiolans

The conformational analysis of five-membered rings has developed more slowly, despite their greater abundance in nature, than that of the corresponding six-membered rings. This is a consequence of the conformational mobility of the five-membered rings, for which there is a lower barrier to pseudorotation and a greater number of conformations with similar energies. The stereochemistry of 1,3-oxathiolans has been investigated by ^1H NMR[6,28-42].

It has been concluded[28,32,33] that the most probable conformation of 2-substituted 1,3-oxathiolans is that of a flexible "envelope". There is a possibility of nine different conformations, among which those with O (1 and 1a) or C^5 (2 and 2a) atoms on the "flap" are preferred and agree best with the

observed spin–spin coupling constants:



There is a possibility of the alternative half-chair conformations, where the C(4) or C(5) atoms and one of the heteroatoms lie respectively above and below the plane of the three other atoms; these conformations are in essence energetically equivalent to the corresponding conformations of the "envelope" type[32]. Three main factors determining the conformation of 2-substituted 1,3-oxathiolans have been pointed out[33]. The most important is the decrease of the *trans*-annular van der Waals interactions between the substituents at the C(2) atom and the methylene groups in the 4- and 5-positions. The second important factor is the minimisation of the torsional energies which is achieved when the heteroatom is in the β-position relative to the atom on the "flap" of the "envelope". The third factor is the increase in the size of the groups vibrating about the carbon atom on the "flap". This is attained in oxathiolans having conformations (1) and (2), which has been confirmed by calculations of the free energy change as a function of the changes in the torsional angles[33]. It has been shown that the conformational energy minima for oxathiolan and 2-methyloxathiolan are fairly close. The lowest pseudorotation energy is 12 kJ mol^{-1}.

Thus the conformational behaviour of 2-substituted 1,3-oxathiolans has been investigated in extremely great detail, although it is insufficient for the determination of the overall pattern of the conformational effects. The stereochemistry of 2,4- and 2,5-dialkyl-, 2,4,5-trialkyl-, and 2,4,4,5-tetraalkyl-1,3-oxathiolans has been investigated[6,29–31,37]. It has been confirmed that conformations (1) and (2) are most preferred. Certain thermodynamic constants of the isomeric equilibrium involving substituted 1,3-oxathiolans have also been determined (Table 3); the conformational energies of the alkyl substituents in the 2-position are in the range 5–8 kJ mol^{-1}.[28,36]

Table 3. Thermodynamic constants for the isomeric equilibria involving substituted 1,3-oxathiolans at 25 °C.[29,36]

Equilibrium	$-\Delta H^\circ$, kJ mol^{-1}	ΔS°, J mol^{-1} K	$-\Delta G^\circ$, kJ mol^{-1}
trans-2,5-di-CH_3 ⇄ *cis*-2,5-di-CH_3	4.67	5.65	2.99
trans-C_2H_5-5-CH_3 ⇄ *cis*-2-C_2H_5-5-CH_3	4.87	7.60	2.60
trans-2-iso-C_3H_7-5-CH_3 ⇄ *cis*-2-iso-C_3H_7-5-CH_3	3.03	3.06	2.11
2-C_2H_5-*cis*-2,5-di-CH_3 ⇄ 2-C_2H_5-*trans*-2,5-di-CH_3	1.11	0.21	1.05
2-t-C_4H_9-*cis*-2,5-di-CH_3 ⇄ 2-t-C_4H_9-*trans*-2,5-di-CH_3	—	—	3.99
trans-2,4-di-CH_3 ⇄ *cis*-2,4-di-CH_3	0.18	0.11	0.15

2. Stereochemistry of 1,3-Oxathianes

The structure of 1,3-oxathianes has been studied by ^{1}H NMR and by measuring their dipole moments[10,12,15,16,42–48]. The different bond lengths (1.41 Å for C–O, 1.54 Å for C–C, and 1.82 Å for C–S) and valence angles (110° for O–C–C, 111.7° for C–O–C, and 100° for C–S–C) in 1,3-oxathiane resulting in an unusual geometry of its ring. The "ether" part of the molecule (C^4–O–C^2) is more bent than the "thioether" part (C^6–S–C^2) and the axial valence angles are not rigorously parallel. The non-bonding 1,3-interactions are therefore appreciably weakened[10,12].

The main form of the 1,3-oxathiane ring is the chair conformation, although other conformations are also possible[12,48], the torsional and ring strains in 1,3-oxathianes having a greater influence on the energy parameters of different reactions than in the case of more symmetrical molecules[10,42–48]. Two conformations of the chair type are possible for 1,3-oxathianes[12]:

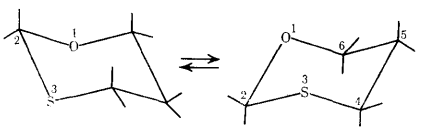


Table 4. Conformational energies* of axial alkyl groups in 1,3-oxathianes, 1,3-dioxanes, and 1,3-dithianes (kJ mol^{-1}).

Alkyl group	Position and orientation				Refs.
	2a	4a	5a	6a	
1,3-Dioxane					
CH_3	16.65	12.2	3.55—4.1	12.2	[39, 41, 42]
C_2H_5	16.9	—	2.90—3.09	—	[12, 39, 42]
iso-C_3H_7	17.45	—	4.1	—	[12, 39, 42]
1,3-Oxathiane					
CH_3	13.6	7.4	2.85—3.1	12.3	[12, 43]
C_2H_5	13.6	—	—	—	[12, 43]
iso-C_3H_7	14.85	—	—	—	[12, 43]
1,3-Dithiane					
CH_3	8.0	6.5	4.9	6.5	[12]
C_2H_5	7.0	—	3.4	—	[12]
iso-C_3H_7	9.7	—	4.4	—	[12]

* The values obtained from data for an acid-catalysed chemical equilibrium.

Table 5. Energies of the 1,3-diaxial interactions (H–CH_3, CH_3–heteroatom) in methyl-substituted 1,3-oxathianes, 1,3-dioxanes, and 1,3-dithianes (kJ mol^{-1})[12,39,42,43].

Compounds	Positions				
	2,1	2,6	4,6	5,1	5,3
1,3-Dioxane	8.5	8.5	3.7	2.0	2.0
1,3-Oxathiane	4.4	9.2	3.1	2.85	—
1,3-Dithiane	4.0	4.0	2.5	2.4	2.4

The free energies of ring inversion in certain *gem*-substituted derivatives are in the range 33.5–48.5 kJ mol^{-1}.[12] These values are quite usual for six-membered rings and are responsible for the ease of inversion close to room temperature. The energy parameters (Tables 4 and 5) show that the energies of the conformational interactions in the 1,3-oxathiane ring are intermediate between those of 1,3-dioxanes and 1,3-dithianes.

As mentioned above, the 1,3-oxathiane molecules exist preferentially in the chair conformation but, owing to the marked ring asymmetry, the chair is distorted and other conformations become possible[48] (Table 6).

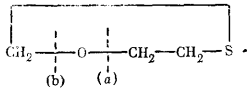
Table 6. Thermodynamic parameters of the chair–"twist" transformations in 1,3-diheterocycloalkanes[48].

Compound	ΔG°, kJ mol^{-1}	ΔH°, kJ mol^{-1}	ΔS°, J mol^{-1} K^{-1}
1,3-Di-t-butylcyolohexane	21.3	25.0	13.4
1,3-Dioxane	33.3	35.9	9.2
1,3-Oxathiane	23.0	25.0	9.2
1,3-Dithiane	7.5	14.2	22.2

Since all four carbon atoms in the 1,3-oxathiane ring are magnetically non-equivalent, these compounds are convenient objects for studies by ^{13}C NMR. The results of ^{13}C NMR measurements for various methyl-substituted 1,3-oxathianes have been reported, the influence of substituents on the chemical shifts of the carbon atom signals have been discussed, and a comparative analysis with 1,3-dioxanes and cyclohexanes has been carried out[55]; the dependence of the influence of the substituents on the nature of the heteroatom has been demonstrated. The chemical shifts for 1,3-oxathianes are in the following ranges: 68–81 p.p.m. for C(2); 23–27 p.p.m. for C(4); 25–42 p.p.m. for C(5); 62–75 p.p.m. for C(6).[55] It has also been shown that the α-effect is very considerable for all the compounds investigated, the equatorial methyl group having a greater deshielding influence than the axial group; this effect is manifested to a greater extent in 1,3-oxathianes than in 1,3-dioxanes and cyclohexanes; the $|\delta|$- and $|j|$-effects are smaller.

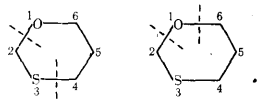
3. The Mass Spectra of 1,3-Oxathiolans and 1,3-Oxathianes

The fragmentation of 1,3-oxathiolans under the influence of electron impact has been investigated[51,52]. It has been found that, among all the possible ring fragmentation pathways, the decompositions (*a*) and (*b*) are the most probable:



It has been concluded that the dominant process (*a*) takes place as a result of the splitting off of an electron from the ring O atom despite the fact that the removal of a non-bonding electron from the S atom requires less energy. In substituted 1,3-oxathiolans the alkyl side group is eliminated from the 2-position more readily than from the 4- and 5-positions. The elimination of an H atom from the 2-, 4-, and 5-position is unlikely[51,52].

The characteristic features of the mass spectra of 1,3-oxathianes are a relatively high intensity of the molecular ion, the absence of metastable transitions, and the preferential shift of the charge to the sulphur-containing fragments[50]. There is a possibility of two main mechanisms of ring opening involving the dissociation of the C^4–S and C^6–O bonds:



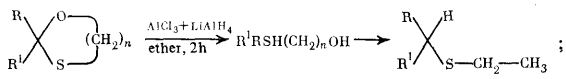
The intensity of the molecular ion peak diminishes with increase of the contribution by the 2-alkyl substituent[50].

IV. THE REACTIONS OF 1,3-OXATHIACYCLOALKANES

The reactions of 1,3-oxathiacycloalkanes have been comparatively little investigated. The heterolytic processes involving the opening of the 1,3-oxathiacycloalkane ring have been studied in greatest detail. Data have been obtained recently on the radical-chain reactions of compounds of this class.

1. Heterolytic Reactions of 1,3-Oxathiacycloalkanes

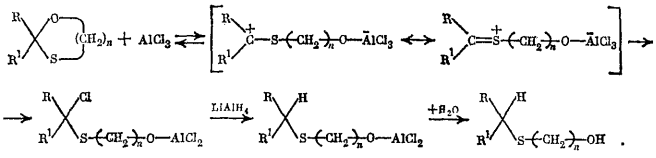
1,3-Oxathiolans and 1,3-oxathianes have been reduced[53,54] with lithium tetrahydroaluminate and aluminium chloride in ether:



$n=2,3$.

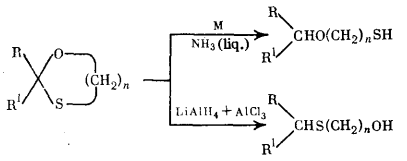
It has been shown that the reductive cleavage involves mainly the C–O bond. Thus the above reaction makes it possible to obtain thioethers from aldehydes and ketones.

On hydrogenolysis with a mixture of $LiAlH_4$ and BF_3 for 2 h, less than 1% of 1,3-oxathiolan reacted, while the $AlCl_3$ + $LiAlH_4$ mixture gives rise under the same conditions to 85–90% of hydrogenation products, mainly the hydroxythioether together with a small amount of a dialkyl sulphide. A mechanism involving the formation of a resonance-stabilised cation in the first stage has been proposed; on reaction with the nucleophilic chloride ion (from $AlCl_3$), this cation gives rise to an α-halogenothioether, which is readily reduced to the thioether[53]:

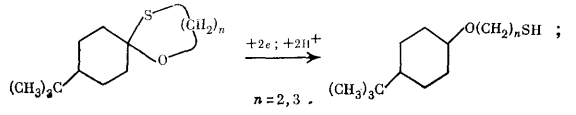


The study of the reductive cleavage of the 1,3-oxathiolan ring with a mixture of lithium tetrahydroaluminate and aluminium chloride or with boron trifluoride in ether[55] confirmed data[53,54] concerning the preferential opening of the 1,3-oxathiolan ring at the C–O bond and not the C–S bond (1,3-dithiolan does not undergo hydrogenolysis). The yields of the reduction products depend greatly on the order of mixing of the reactants. The addition of a Lewis acid to a mixture of oxathiolan and the hydride makes it possible to achieve better yields and to avoid the charring of the products and also permits reduction with the BF_3–$LiAlH_4$ system. The addition of a solution of a 1,3-oxathiacycloalkane to the $AlCl_3$–$LiAlH_4$ or BF_3–$LiAlH_4$ mixture[53,54] results in partial charring of the products in the former case and in the decomposition of $LiAlH_4$ even before it reacts with the oxathiacycloalkane in the latter case[55].

The cleavage of the oxathiacycloalkane ring at the C–S bond can be achieved when 1,3-oxathianes and 1,3-oxathiolans are treated with metals in liquid ammonia. In contrast to the effect of the $LiAlH_4$–$AlCl_3$ mixture, this results in the formation of the corresponding β- or γ-alkoxymercaptans[56–59]:

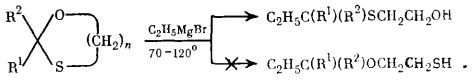


This reaction is widely used in peptide synthesis. Sometimes the reductive cleavage involves both bonds (C–O and C–S), which leads to sulphur-free products. Thus treatment of 2-methyl-2-phenyl-1,3-oxathiolan with sodium in liquid ammonia yields ethylbenzene as the main reaction product[59]. In general 1,3-oxathiolans with the phenyl substituent in the 2-position produce the corresponding alkylbenzenes on reduction[63]. The reduction of various substituted 1,3-oxathiolans and 1,3-oxathianes with metals in liquid ammonia has been studied. It has been shown that the reduction proceeds via the transfer of two electrons and the addition of a proton (from ammonia) to a carbon atom[57]:



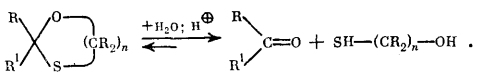
In the reactions of cyclic ketones the yields are 60–90%. For aldehyde derivatives, the yields of alkoxythiols are lower owing to the formation of thiols and olefins in side reactions[57]. The effectiveness of metals in the reduction decreases in the sequence Ca > Li > Na > K. The addition of proton-donating solvents (t-C_4H_9OH, C_2H_5OH) does not increase the yield of the reduction products. In the series of 1,3-oxathianes the yields are higher than for 1,3-oxathiolans.

The cleavage of 1,3-oxathiolans by a Grignard reagent has been investigated[59]:



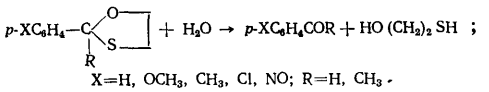
The reaction proceeds with dissociation of the C–O bond, i.e. via the first pathway. The reactivity of 1,3-oxathiolans increases in the sequence 1,3-oxathiolan < 2-ethyl-2-methyl-1,3-oxathiolan ≦ 2-propyl-1,3-oxathiolan ≦ 2-methyl-1,3-oxathiolan. The decrease of reactivity on passing from dioxolans to oxathiolans is associated with the increase of electron density at the C(2) atom[59].

1,3-Oxathiacycloalkanes react with water in the presence of acid catalysts to form the corresponding aldehydes (or ketones) and mercaptoalcohols[60–66]:



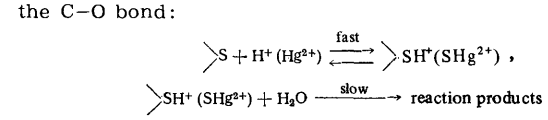
The hydrolysis of 1,3-oxathiolans has been studied in greatest detail, while extremely few data are available for 1,3-oxathianes.

The hydrolysis of 2-aryl-1,3-oxathiolans catalysed by the H_3O^+ and Hg^{2+} ions has been investigated[60]:



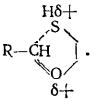
X=H, OCH_3, CH_3, Cl, NO; R=H, CH_3.

It has been shown that 2-aryl-1,3-oxathiolans hydrolyse more slowly than the corresponding 1,3-dioxolans. This has been explained by the fact that oxygen stabilises the α-carbenium ion more effectively than does sulphur[60]. On the basis of the study of the isotope effects and the determination of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for 1,3-oxathiolans relative to 1,3-dioxalans, it was concluded that the acid hydrolysis of 2-phenyl-1,3-oxathiolans proceeds via the *A*2 mechanism with rupture of the C–O bond:



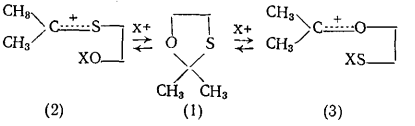
The activation entropies for the hydrolysis of 1,3-oxathiolans are in the range from −17.8 to −24.4 e.u., which is less than the values for 2-phenyl-1,3-oxathiolan (−8.9 e.u.) and 2-methyl-2-phenyl-1,3-dioxolan (−8.9 e.u.), which have been shown to hydrolyse via the *A*1 mechanism and are close to the $\Delta S^{\neq}$ for 4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolan (−14.2 e.u.), which has been shown to involve the *A*2 mechanism. The ratios k_D/k_H for 1,3-oxathiolans are also smaller than the values corresponding to the *A*1 mechanism.

The acid hydrolysis of 2-aryl-1,3-oxathiolans in HCl solutions in water and in a 50:50(%) dioxan–water mixture has been investigated[61]. The study of the isotope effect of the solvent and also the comparative analysis of 1,3-oxathiolans and 1,3-dioxolans led to the conclusion that the hydrolysis proceeds via the *A*1 mechanism with dissociation of the C–S bond and the formation of the intermediate ion:



The isotope effect of the solvent ($k_D/k_H < 2$) is smaller than that usually observed for the *A*1 mechanism ($k_D/k_H > 2$). The low isotope effect of the solvent may be a result of the more intense protonation of the sulphur atom than the oxygen atom and this can be accounted for in its turn by the difference between the S–H and O–H bond lengths[61]. These conclusions have been confirmed by the comparative analysis of oxathiolans and the thioacetals $C_6H_5CH(OCH_3)SC_6H_4R$.[62]

The ^1H NMR study of 1,3-oxathiolans in a solution of the 1:1 FSO_3H + SbF_5 mixture in liquid SO_2 at −60 °C showed[63,64] that protonation leads mainly to the cation (2)(X=H), while the formation of the cation (3) (X=H) is unlikely:



(2) (1) (3)

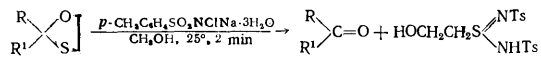
These results have been confirmed by the ^1H NMR study of 2,2-dimethyl-1,3-dithiolan under the same conditions. It was concluded that the hydrolysis of 1,3-oxathiolans proceeds with the dissociation of the C–O bond via the *A*1 mechanism. The preferential dissociation of the C–O bond on protonation and on formation of compound (6) in the kinetic stage can be explained mainly by the lower basicity of the S atom in relation to the proton compared with the O atom. It has been suggested that the intermediate product is formed without the participation of the nucleophile. The opening of the 1,3-oxathiolan rings on bromination has also been investigated[63,64]. It was shown that the basicity factor does not play here a major role and that in this instance there is a possibility of the dissociation of the C–O and C–S bonds with formation of the corresponding ions (6)(X=Br) and (7)(X=Br).

The study of the hydrolysis of 1,3-oxathiolan, 2-methyl-1,3-oxathiolan, and 2,2-dimethyloxathiolan in aqueous solutions of $HClO_4$ and $DClO_4$ showed[65] that the rate of reaction depends on the substituents in the 2-position. For 2-methyl-1,3-oxathiolan, it is approximately 2250 times higher than for the unsubstituted 1,3-oxathiolan and for 2,2-dimethyl-1,3-oxathiolan is 57 times higher than for 2-methyl-1,3-oxathiolan[71]. It is believed[65] that the hydrolysis proceeds via the *A*1 mechanism with dissociation of the C–O bond.

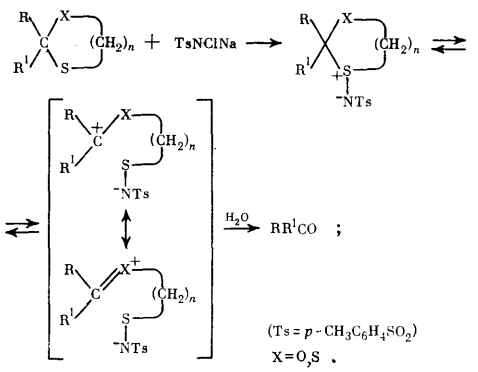
It is seen from the data considered that the mechanism of the hydrolysis of 1,3-oxathiolan has still not been determined unambiguously.

The hydrolysis of 2-substituted 1,3-oxathianes by $HClO_4$ in a H_2O/D_2O mixture has been studied[66] and it has been found that the relative rates of the acid hydrolysis of 1,3-oxathianes, 2-methyl-1,3-oxathiane, and 2,2-dimethyl-1,3-oxathiane are 1, 45, and 8×10^6 respectively. The rate of hydrolysis of 2-methyl-1,3-oxathiane proved to be much lower than was assumed. This can be explained by the fact that only the isomer with the axial conformation is hydrolysed; if account is taken of the mole fraction of the axial conformation, then the rate of hydrolysis of 2-methyl-1,3-oxathiane increases approximately by a factor of 300.[66] The hydrolysis of 1,3-oxathiacycloalkanes makes it possible to synthesise various aldehydes or ketones or to regenerate them when thioacetal or thioketal protecting groups are used.

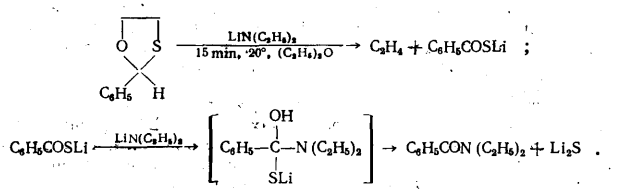
A convenient and rapid method of regenerating ketones and aldehydes by treating 1,3-oxathiacycloalkanes with chloramine T has been proposed[67,68]:



The reaction proceeds under mild conditions, the yields reaching 90–100%. Apart from the carbonyl compound, 2-hydroxyethyltoluene-p-sulphonimidosulphine-toluene-p-sulphonylimine and bis(2-hydroxyethyl) disulphide are formed (the latter product is obtained when less than 2 moles of chloramine T per mole of the oxathiolan are used in the reaction). The intermediate formation of a carboxonium ion has been postulated:

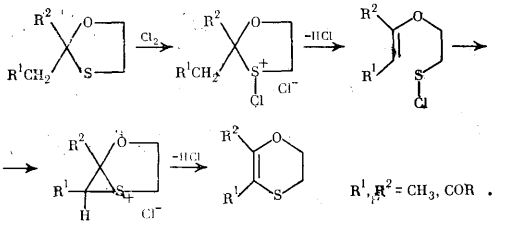


Olefins which are difficult to obtain by other methods can be synthesised by treating 1,3-oxathiacycloalkanes with alkaline reagents, for example, lithium dialkylamides. The reaction of 2-phenyl-1,3-oxathiolan with lithium diethylamide in ether has been studied in detail[69]:



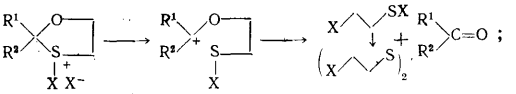
The yields of the olefins were nearly quantitative. Olefins can be obtained analogously also from the more readily available 1,3-dioxolans. However, olefins which are difficult to obtain, such as *trans*-cyclo-octene, *cis*- and *trans*-cyclo-octa-1,5-dienes, and also tetrasubstituted olefins can be synthesised more conveniently from 1,3-oxathiolans[69–71].

The chlorination of 1,3-oxathiolans having α-methylene groups leads to 5,6-dihydro-1,4-oxathi-ines[72–75]:

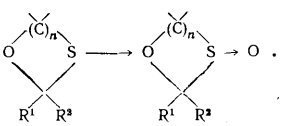


The reaction is carried out at low temperatures (between −20° and −70 °C) and the yields are 55–60%.

In the absence of α-methylene group, *C*-halogenation takes place instead. For example, the chlorination and bromination of certain substituted 1,3-oxathiolans lead to the formation of the corresponding ketones and disulphides[75]:



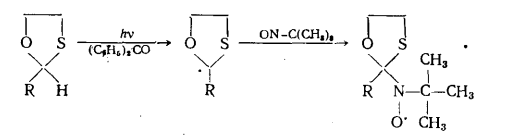
The oxidation of 1,3-oxathianes[75] and 1,3-oxathiolans[77,78] constitutes the main method of synthesis of cyclic sulphoxides:



The study of the oxidation of 1,3-dithiane and 1,3-oxathiane[76] showed that the content of isomers with an axial or equatorial SO group depends both on the cyclic sulphide being oxidised and on the oxidant. The content of the 1,3-oxathiane isomer with an axial SO group increases in the following sequence of oxidants: t-BuOCl > $NaIO_4$ > H_2O_2 > N_2O_4.

2. Homolytic Reactions of 1,3-Oxathiacycloalkanes and 1,3-Dithiacycloalkanes

When 1,3-oxathiacycloalkanes and 1,3-dithiacycloalkanes interact with sources of free radicals, the abstraction of hydrogen atoms results in the formation of 1,3-diheterocycloalkyl radicals. Thus the benzophenone-sensitised ultraviolet irradiation of 1,3-oxathiolans leads to the formation of 1,3-oxathia-2-cyclopentyl radicals, which in the presence of a spin-trapping agent (2-methyl-2-nitrosopropane) yield fairly stable spin-adducts (nitroxy-radicals) whose signals have been detected in the EPR spectra[79–82]:

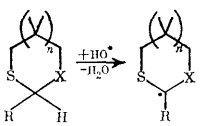


Nitroxy-radicals containing 1,3-oxathia- and 1,3-dithia-2-cycloalkyl residues are formed on photolytic decomposition of t-butyl peroxide in 1,3-diheterocycloalkanes in the presence of 2-methyl-2-nitrosopropane[80–82]. The spectroscopic

characteristics of the nitroxy-radicals containing the 1,3-diheterocycloalkane residue show that the formation of radicals with an unpaired electron at the ring C(2) atom is the dominant process[79-82]. Consequently, under the conditions investigated (20–25 °C), the *t*-butoxy-radicals arising on photolysis of t-butyl peroxide attack very selectively the carbon–hydrogen bonds located between the two heteroatoms.

The increase of the hyperfine coupling constant a_n on passing from 1,3-dioxacycloalkane to 1,3-oxathia- and 1,3-dithia-cycloalkanes is evidently associated with the increase of electron density at the N atom of the nitroxy-group as a consequence of the decrease of the negative inductive effect following the replacement of the ring oxygen atoms by the less electronegative sulphur atoms[79-82]. In all the examples investigated the EPR spectra did not reveal signals due to nitroxy-radicals which might have been formed from the acyclic acylheteroalkyl radicals. This shows that the 1,3-oxathiacycloalkyl radicals do not undergo a rearrangement under the conditions investigated[79-82].

The structure of the radicals arising from 1,3-oxathia- and 1,3-dithiacycloalkanes under the influence of hydroxy- and t-butoxy-radicals has been studied directly[82,83,86-89]. When the hydroxy-radicals generated by the reaction Ti(III) + H_2O_2 → Ti(IV) + HO^- + $\dot{O}H$ react with 1,3-oxathia- and 1,3-dithiacycloalkanes in water at 25 °C, 1,3-dihetero-2-cycloalkyl radicals are formed more selectively (Table 7)[82,83,87], in contrast to 1,3-dioxacycloalkanes[84,85]:



;

n = 0, 1; X = O, S; R = H, CH_3, n-C_3H_7, $CH(CH_3)_2$.

Under the same conditions, cyclic acetals give rise to di- and mono-alkoxycycloalkyl radicals[82,84,85]. The replacement of the oxygen atom by the sulphur atom either greatly activates the hydrogen atom adjoining the two heteroatoms or increases the lifetime of the 1,3-dihetero-2-cycloalkyl radicals formed compared with other types of radicals.

An analogous picture has been observed in the interaction of sulphur-containing 1,3-oxaheterocycloalkanes with t-butoxy-radicals[89]. In the analysis of the EPR spectra and in the study of the configurations of sulphur-containing 1,3-dihetero-2-cycloalkyl radicals in combination with calculations by quantum-chemical methods[86-89], it was established that the sulphur atom exhibits a fairly large delocalising effect (~ 19% of the spin density) and flattens the pyramidal structure of the paramagnetic centre, which is characteristic of 1,3-dioxa-2-cycloalkyl radicals[85,90].

Thus the configuration of the tervalent carbon atom is flattened on passing from 1,3-dioxa-2-cycloalkyl radicals, via 1,3-oxathia-2-cycloalkyl radicals, to 1,3-dithia-2-cycloalkyl radicals.

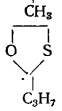
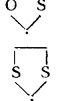
1,3-Oxathia- and 1,3-dithia-cycloalkanes are extremely active donors of a hydrogen atom in the reaction with t-butoxy-radicals. The activities of 1,3-diheterocycloalkanes in the reaction involving the abstraction of a hydrogen atom by t-butoxy-radicals have been determined by the method of competing reactions[82,91,92]:

$$[(CH_3)_3CO]_2 \rightarrow 2\,(CH_3)_3CO^{\bullet};$$

$$(CH_3)_3CO^{\bullet} \begin{cases} \xrightarrow[+RH]{k_a} (CH_3)_3COH + R^{\bullet} \\ \xrightarrow{k_d} CH_3COCH_3 + CH_3^{\bullet} \end{cases}.$$

At a constant temperature the parameter k_a/k_d is a measure of the reactivity of 1,3-diheterocycloalkanes in the abstraction of a hydrogen atom by t-butoxy-radicals. At 130 °C the ratio k_a/k_d is 5.0–8.0 litre mol^{-1} for 1,3-oxathiacycloalkanes and 7.0–10.0 litre $mole^{-1}$ for the corresponding dithia-derivatives[82,91,92].

Table 7. EPR parameters of the radicals generated from 1,3-oxathia- and 1,3-dithia-cycloalkanes by treatment with hydroxy-radicals in water[79,83,87].

Radical	HFI constant, G			*g*-Factor
	$a_{\alpha\text{-H}}$	$a_{\beta\text{-H}}$	$a_{\gamma\text{-H}}$	
	—	16.6 (q)	0.5 (m)	2.0037
	—	15.5 (t)	0.5 (m)	2.0037
	—	15.2 (d)	0.5 (m)	2.0037
	—	17.7 (q)	0.5 (m)	2.0047
	—	9.0 (t)	0.5 (m)	2.0077
	5.1 (d)	—	1.1 (m)	2.0051
	14.4 (d)	—	1.0 (m)	2.0039
	13.5 (d)	—	1.3 (m)	2.0050
	15.2 (d)	—	1.5 (m)	2.0054

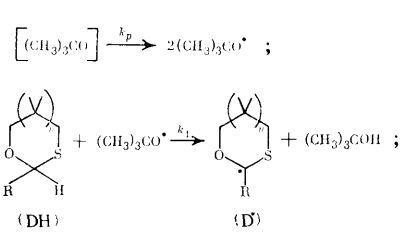
The increase of the reactivity of 1,3-diheterocycloalkanes as the oxygen atoms are substituted by sulphur atoms is common to five-, six-, and seven-membered rings. There is a greater increase of activity on passing from 1,3-dioxacycloalkanes to 1,3-oxathiacycloalkanes than on passing from 1,3-oxathiacycloalkanes to 1,3-dithiacycloalkanes. The alkyl substituents in 1,3-diheteroanalogues of cycloalkanes have little influence on their reactivity. The partial rate constants for the OCH(R)S and SCH(R)S (R = CH, n-C_3H_7, or iso-C_3H_7) fragments found by an additive scheme[92] are in the ranges $(k_a/k_d)^{130^\circ}_{OCH(R)S}$ = 5.3–8.2 litre mol^{-1} and $(k_a/k_d)_{SCH(R)S}$ = 6.3–9.6 litre mol^{-1} for heterocycles with different numbers of carbon atoms in the ring.

The partial contributions of the OCH(R)S and SCH(R)S groups are more than 80% of the effective rate constant and the hydrogen atom is therefore mainly abstracted at 130 °C from the carbon atom adjoining the two heteroatoms[82,92]. It

is striking that the following dependence of the reactivity on ring size is common to the oxygen- and sulphur-containing 1,3-diheterocycloalkanes: 1,3-diheterocyclohexanes < 1,3-diheterocycloheptanes < 1,3-diheterocyclopentanes[92].

The results have been interpreted[82,91,92] within the framework of ideas concerning the polar effects in the homolytic abstraction of a hydrogen atom by free radicals. Evidently the higher reactivity of 1,3-oxathia- and 1,3-dithia-cycloalkanes compared with that of 1,3-dioxacycloalkanes is due to a more favourable combination of polar factors in the transition state of the reaction involving the abstraction of a hydrogen atom by the electrophilic radical $(CH_3)_3CO^{\bullet}$[82,91,92].

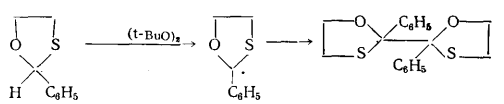
In the reaction initiated by t-butyl peroxide, 1,3-oxathiacycloalkanes are converted at 120–150 °C into esters of thiolocarboxylic acids[82,93]. The initial rate of formation of the thioesters varies linearly with the substrate concentration and is directly proportional to the square root of the initiator concentration[82,93], which suggested a radical-chain unbranched mechanism of the isomerisation of 1,3-oxathiacycloalkanes with quadratic chain termination by the rearranged radicals (A·):



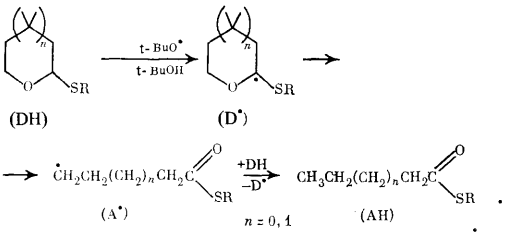
The rate-limiting stage of the reaction is the abstraction of a hydrogen atom from the substrate by the rearranged radical A·. The values of the kinetic parameter $(k_3/\sqrt{k_4})^{130^\circ}$ found, which are a measure of the reactivity of 1,3-oxathiacycloalkanes in the free radical isomerisation reaction, have shown[82,89] that 1,3-oxathiacycloalkanes are 2–3 times less reactive than 1,3-dioxacycloalkanes[82,93]. This was confirmed by the method of competing reactions[94].

The reduced reactivity of 1,3-oxathiacycloalkanes in the free radical isomerisation reaction compared with 1,3-dioxacycloalkanes is in direct contrast with their higher reactivity in the abstraction of a hydrogen atom by t-butoxy-radicals and is evidently associated with the less favourable combination of polar factors in the stage involving the abstraction of a hydrogen atom by the relatively nucleophilic carbon-centred acylheteroalkyl radical A· in the case where the ring contains a sulphur atom, which is less electronegative than oxygen.

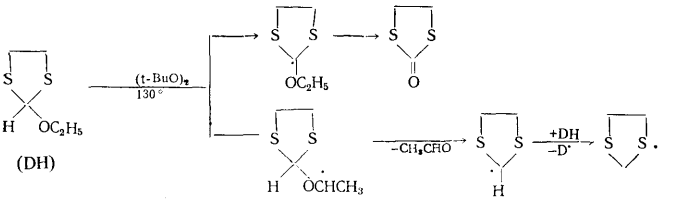
If the 1,3-oxathia-2-cycloalkyl radicals formed are fairly stable and do not undergo a unimolecular rearrangement, they recombine with formation of the corresponding dimeric product. Thus the reaction of 2-phenyl-1,3-oxathiolan with t-butyl peroxide at 130 °C results in the formation of a mixture of the *threo*- and *erythro*-isomers of bis-2-phenyl-1,3-oxathiolan[96]:



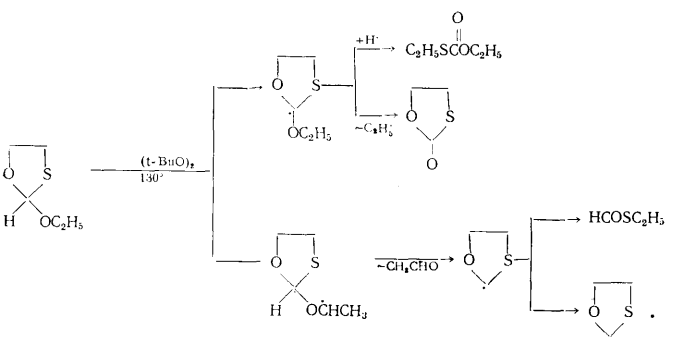
2-Alkylthiotetrahydropyrans and 2-alkylthiotetrahydrofurans isomerise analogously to 1,3-dithiolan[97–100]:



The reaction involving 2-ethoxy-1,3-dithiolan, in which only the cleavage products, namely ethylene dithiocarbonate and 1,3-dithiolan, are formed is somewhat more complex[101]:

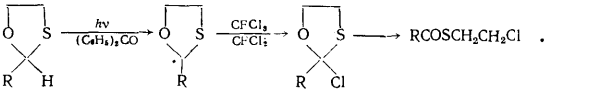


It has been suggested that the former product is formed via the 2-ethoxy-1,3-dithia-2-cyclopentyl radical and that the latter product arises as a result of the abstraction of a hydrogen atom from the α-position in the ethoxy-group via a stage involving the formation and fragmentation of the α-1,3-dithiacyclopentyl-2-hydroxyethyl radical[101]. Isomerisation and cleavage products are formed simultaneously from 2-ethoxy-1,3-oxathiolan[102]:



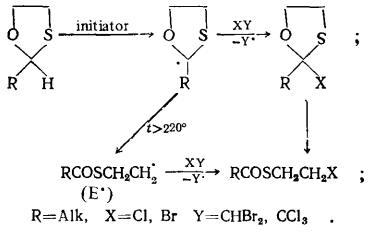
Linear and cyclic thiocarbonates are formed via the 2-ethoxy-1,3-oxathia-2-cyclopentyl radical and 1,3-oxathiolan and ethyl thioformate are formed via the 1,3-oxathiacyclopentyl-2-hydroxyethyl radical arising as a result of the abstraction of a hydrogen atom from the α-position in the ethoxy-group[102].

In polyhalogenomethanes in the presence of free-radical initiators, 1,3-oxathiolans are selectively converted into halogenothioethers, which has been attributed to the involvement of the solvent in the chain propagation stage[79,97–99]. Thus the photolysis of 2-alkyl-1,3-oxathiolans in $CFCl_3$ in the presence of benzophenone results in the formation of chloroethyl esters of thiolocarboxylic acids probably via the corresponding cyclic chlorides, which are unimolecularly converted into chlorothioethers under the reaction conditions:

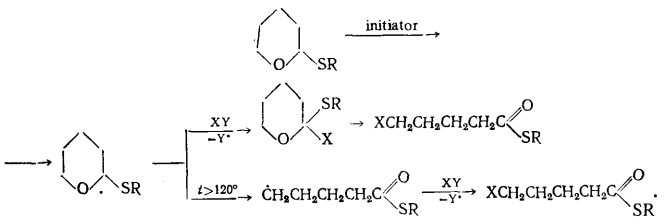


In the reaction initiated by lauroyl peroxide (at 80 °C) or

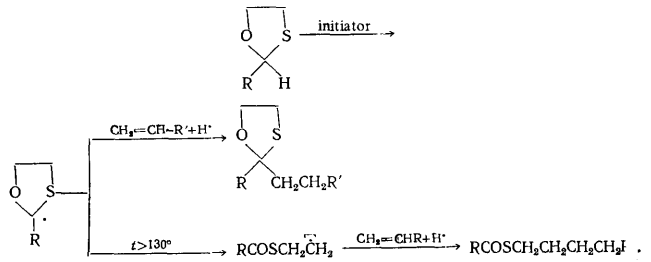
t-butyl peroxide (at 120–150 °C) in polyhalogenomethanes (CCl_4, CCl_3Br, and $CHBr_3$) 1,3-oxathiolans are converted into chloro- and bromo-thioethers[98,99]



The authors[98,99] do not rule out the possibility of the formation of halogenothioethers at relatively high temperatures (> 120 °C) via a stage in which a halogen atom is obstructed by the rearranged acylthioethyl radical E·. Under analogous conditions (80–150 °C), 2-alkylthiotetrahydropyrans give rise to esters of δ-halogenothiolovaleric acids[99], whose formation can be represented as proceeding both via a cyclic halogeno-derivative and via a stage in which a halogen atom is obstructed by the rearranged radical E·:



On interaction with terminal olefins in the presence of radical initiators, 1,3-oxathiolans yield 2-alkyl-1,3-oxathiolans and alkyl thioacylates, whose formation is regarded as proceeding via a stage in which the 1,3-oxathia-2-cyclopentyl and the isomeric acylthioethyl radicals add to the double bond of the olefin[99]:



At relatively low temperatures (≤ 70°) only 2-alkyl-1,3-oxathiolans are formed[99]

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On the basis of the data considered, one may reach definite conclusions concerning the methods of synthesis, structure, and types of reactions of 1,3-oxathiacycloalkanes.

The general and most effective methods of synthesis of 1,3-oxathiacycloalkanes involve acid-catalysed reactions of mercaptoalkanols with aldehydes, ketones, alkyl vinyl ethers, and orthoesters.

The main conformation of 1,3-oxathiolans is that of an inverted envelope. The 1,3-oxathiane ring exists preferentially in the chair conformation but the asymmetry of the ring gives rise to an increased probability of other conformations compared with 1,3-dioxanes.

The majority of the heterolytic reactions of 1,3-oxathiocycloalkanes proceed with the opening of the ring at the C–O or C–S bonds. Five-membered 1,3-oxathiacycloalkanes are the most reactive.

The high reactivity of the hydrogen atoms at the carbon atom linked to the two heteroatoms is responsible for the high selectivity of the attack by free radicals on the 2-position in the heterocycle. The mode of the homolytic reactions of substituted 1,3-oxathiacycloalkanes is therefore determined mainly by the rate of formation of the 1,3-oxathia-2-cycloalkyl radicals and the ability of the latter to participate in a unimolecular rearrangement with formation of a thioester, in addition to carbon–carbon double bonds, or in the abstraction of a halogen from polyhalogenoalkanes.

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