THIETANES

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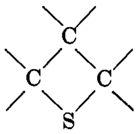
CONTENTS

I. INTRODUCTION

The present review covers the chemistry of four-membered heterocyclic compounds containing one sulfur atom in the ring of the basic structure



The official designation of compounds of this type is thietanes; the terms trimethylene sulfide and thiacyclobutane are used as well. If the ring has one C=C double bond, it is named thiete or thietene.

Compared with other heterocyclic systems, thietanes have so far been investigated only on a small scale, although their higher reactivity makes this group of compounds appear more attractive than the open-chain sulfides. In a patent (46) Lilienfeld claimed in 1911 to have obtained 3-hydroxythietane as a not isolated component of a reaction mixture. However, credit for the first isolation and identification of thietane and some of its homologs is due to Grishkevich-Trochimovskii in 1916 (35). There is no evidence of any systematic scientific research in the field of thietanes. This might be due to the fact that thietanes are not yet applied on an industrial scale, and previous methods of synthesis were intricate and expensive. Since various improved methods for the synthesis of such compounds have been proposed in recent years, it is expected that greater attention will be given to the chemistry of thietanes in the near future.

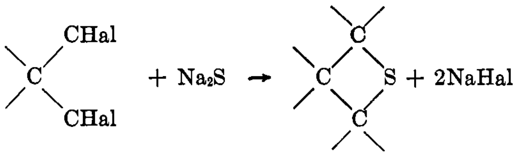
Potential industrial applications of thietane derivatives as proposed so far are in the insecticidal field (30, 51).

The following review comprises the literature on preparation, properties, and reactions of thietanes up to 1963 and partly up to 1964.

II. METHODS OF PREPARATION (TABLE I)

A. FROM 1,3-DIHALIDES

The earliest and so far the most general method for the synthesis of thietanes comprises the reaction of 1,3-dihaloalkanes with alkali sulfides. In most instances 1,3-dibromo compounds were used; however, the

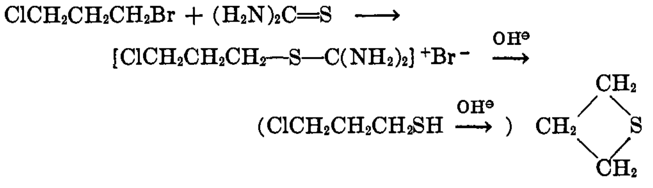


yields obtained with 1,3-dichloro compounds are quite similar (18). Suitable sulfides include sodium sulfide or potassium sulfide. Also potassium hydrosulfide may be used in large excess; this does not entail the formation of bisthiols (4, 6). Principal by-products are the corresponding polymeric thioethers. According to Bost and Conn (18), polymerization is more intense with a 20% excess of Na_2S instead of stoichiometric quantities; other authors obtained the highest yields of thietanes with an excess of alkali sulfide between 50 and 100%. In general, the reaction is carried out in alcohol, alcohol–water, or dioxane–water solutions with heating the mixture for several hours at 70–100°. Yields range between 30 and 55%. Carrying out the reaction in liquid ammonia furnishes no advantage (18a).

The method was used to make thietane itself (9, 17, 18, 35, 63), 2-methylthietane (35), 2,4-dimethylthietane (35), 3,3-dimethylthietane (6), 2-(α-hydroxyethyl)-thietane (68), 3-hydroxythietane (46, 49, 57), 3,3-bis-(chloromethyl)thietane (60), spirodithietane (4, 45, 60), 3,3-pentamethylenethietane (8), and thietanylcarboxylic acids and their derivatives (68a, 71, 72).

α,α′-Dihalo ketones or their ketals yield the corresponding thietan-3-one derivatives (22, 23, 50).

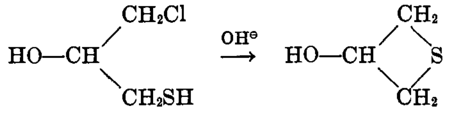
A modified version of this reaction is the reaction of 1,3-dihalides with thiourea, and the subsequent alkaline cleavage of the thiuronium salt (13, 37).



In the alkaline medium the intermediate 3-chloro mercaptan is immediately cyclized to form the thietane (see section IIB).

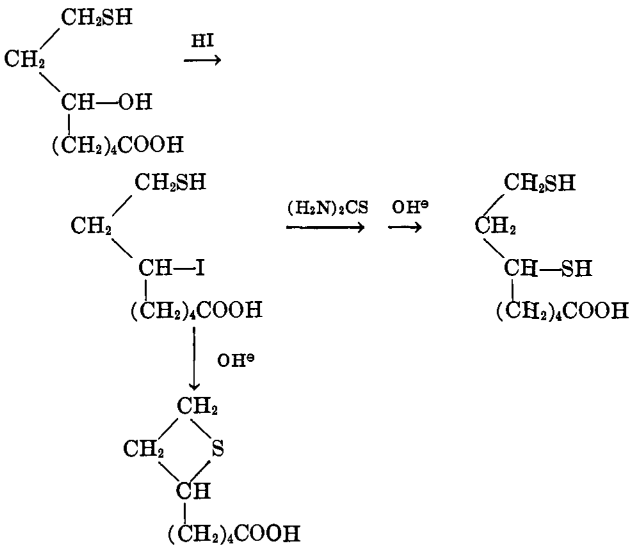
B. FROM 3-HALO MERCAPTANS AND THEIR DERIVATIVES

3-Halo mercaptans can be readily converted to thietanes by alkali; however, the synthesis of these halo compounds is rather intricate. In alkaline medium 2-hydroxy-3-chloropropyl mercaptan is converted at 50–60° to 3-hydroxythietane in yields of 80% (1, 62).

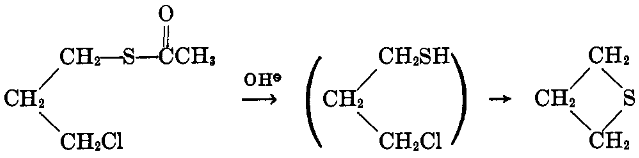


Since 2-hydroxy-3-chloropropyl mercaptan is formed from epichlorohydrin and hydrogen sulfide, 3-hydroxythietane is obtained from epichlorohydrin and H_2S in alkaline medium (27). The same 3-hydroxythietane is derived by alkaline hydrolysis of 3-chloropropene sulfide. Apparently, this reaction is accompanied by the intermediate formation of 2-hydroxy-3-chloropropyl mercaptan (1).

Moreover, 3-halo mercaptans are hypothetical intermediates in the reaction of dihalides with thiourea and alkali as referred to in section IIA (13, 37) and in the reaction of 3-hydroxy mercaptans with thiourea and hydriodic acid with subsequent alkaline hydrolysis (19) or with hydrochloric acid and alkali (29).

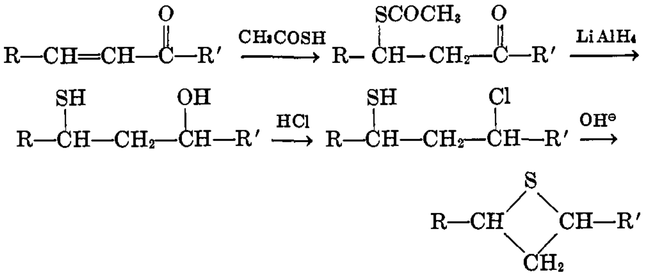


Finally, also the synthesis of thietanes from 3-chlorothiol esters and alkali is assumed to involve 3-chloro mercaptans as intermediates (10, 15, 21, 26).



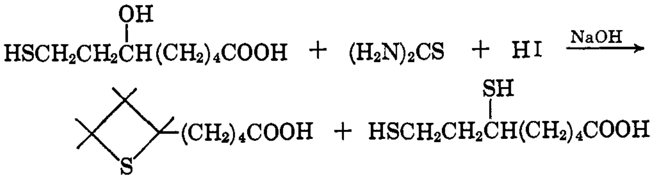
Since 3-halothiol acetates are readily obtained in high yield from allyl halides and thiolacetic acid, this reaction represents one of the best routes for the synthesis of thietanes. The cyclization reaction is reported to yield 24% thietane (26), while a yield of 80% is indicated for 3-methylthietane (15).

An alternative route is the addition of thiolacetic acid to α,β-unsaturated ketones, reduction of the β-acetylthio ketones, and stepwise reaction of the resulting hydroxy mercaptans with hydrochloric acid and then with alkali (29). The yields of the individual steps are high.

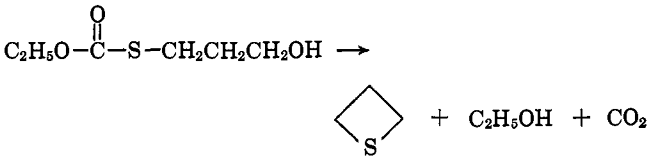


C. FROM 3-HYDROXY MERCAPTANS AND THEIR DERIVATIVES

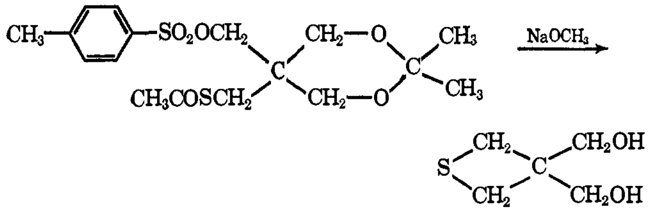
3-Hydroxy mercaptans themselves are comparatively stable compounds. Their conversion with thiourea in the presence of hydriodic acid and subsequent alkaline hydrolysis results in thietane compounds in addition to 1,3-dithiols. This has been described for thietanylcarboxylic acid derivatives (19). This reaction is assumed to involve 3-iodo mercaptan as the first intermediate step.



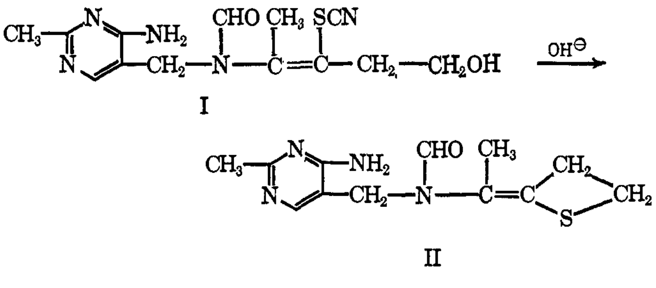
The pyrolysis of ethyl 3-hydroxypropylthiolcarbonate in the presence of catalytic amounts of sodium hydroxide at 200° furnished thietane (57a). The yield could not be stated as the product was a mixture.



Upon treamtent of O-tosyl-S-acetyl-O,O-isopropylidene monothiopentaerethrytol with sodium ethylate, a thietane was isolated in low yield (11).



By hydrolysis of cyanothiamine (I) or O-diphenylmethanesulfonylthiamine disulfide the thietane compound II was obtained (68).

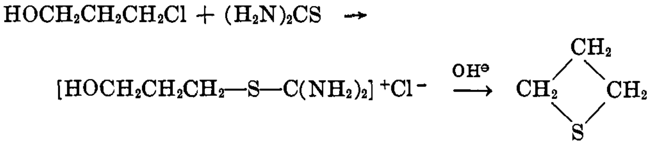


I

II

D. FROM 3-HYDROXYALKYL HALIDES

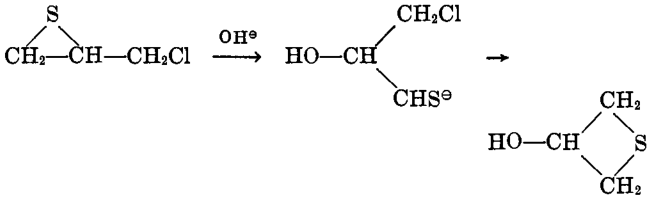
Interaction of 3-chloropropanol-1 with thiourea yields the corresponding S-thiuronium salt. Treatment of this salt with aqueous potassium carbonate at room temperature gives thietane (43).



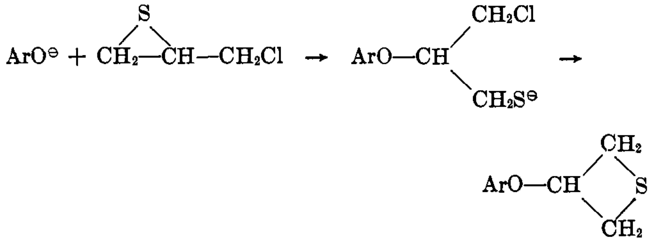
The second product of the alkaline degradation of the thiuronium salt is claimed to be dicyandiamide. The exact mechanism of this reaction is not known, and yields are not disclosed.

E. FROM CHLOROMETHYLTHIIRANE (3-CHLOROPROPENE SULFIDE)

Alkaline hydrolysis of chloromethylthiirane (3-chloropropene sulfide) yields 3-hydroxythietane (1). This ring enlargement may be explained by "abnormal" opening of the thiirane ring, followed by cyclization of the resultant 3-chloro-2-hydroxypropyl mercaptan.



In a similar manner 3-aryloxythietanes are formed by reaction with alkali phenoxides in aqueous medium (58).



By this method a number of different 3-aryloxythietanes have been prepared in yields of about 30–60%. The corresponding aryl thioglycidyl ethers are formed as by-products, which become the main products if the reaction is carried out in anhydrous polar solvents (58).

F. FROM CYCLIC CARBONATES OF 1,3-DIOLS

Cyclic carbonates of 1,3-diols (1,3-dioxan-2-ones) give thietanes upon heating with alkali thiocyanates (60, 61). The reaction mechanism is similar to that of the conversion of oxiranes with thiocyanates (Scheme I).

TABLE I

PREPARATION OF THIETANES

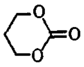
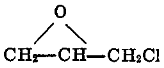
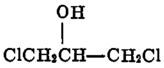
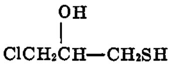
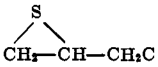
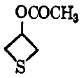
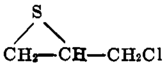
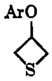
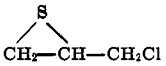
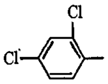
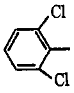
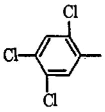
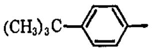
Thietane	Ref	Starting material	Reactant	Yield, %	Derivatives	Ref	Mp, °C
	35	$Br(CH_2)_3Br$	Na_2S	Low	$HgCl_2$ adduct	35	93–95 dec
	9			38–48		16	92–95
	63			45	CH_3I adduct	35	99
	18			16.5		9	97–98
	18a		$Na–S–NH_3$ (liq)	32		16	98–100
	17	$Cl(CH_2)_3Cl$	Na_2S	30		26	97–98
	18			23			
	37	$Cl(CH_2)_3Br$	$(H_2N)_2CS–NaOH$	53.5	Sulfone	35	76
	14			45		16	75
	26	$CH_3COS(CH_2)_3Cl$	KOH	24		21	77–78
	21		NaOH				
	57a	$C_2H_5OCOS(OH_2)_3OH$	Pyrolysis		Sulfoxide	21	Bp 91.2 (14 mm)
	43	$HO(CH_2)_3Cl$	$(H_2N)_2CS–Na_2CO_3$				n^{20}_{D} 1.5156
	60		KSCN	3			
	62		H_2S–alkali		CH_3I adduct	1	114
	27		$H_2S–Ba(OH)_2$	39		27	110–110.5
	46	 $ClCH_2\overset{OH}{\overset{\vert}{C}}H{-}CH_2Cl$	Na_2S		Sulfone	27	101–102
	49, 57		Na_2S	*Ca.* 40	Dinitrobenzoate	27	112–113
	1	 $ClCH_2\overset{OH}{\overset{\vert}{C}}H{-}CH_2SH$	$NaHCO_3$	90			
	1		Na_2CO_3	45			
	50		$NaBH_4$				
	1		$(CH_3CO)_2O$				
	1		CH_3COOK				
 Ar = C_6H_5	58		ArONa	26	Sulfoxide Sulfone	58 58	90–95 147
p-ClC_6H_4	58			23	Sulfone	58	190
o-ClC_6H_4	58			41.5			
	58			46.8	Sulfoxide Sulfone	58 58	124–281 134
	58			61			
	58			38.4			
p-$NO_2C_6H_4$	58			49	Sulfoxide Sulfone	58 58	118–122 154
		58			25		
p-$CH_3OC_6H_4$	58			19			
1-Naphthyl	58			12			
1-Br-2-naphthyl	58			19			

TABLE I (*Continued*)

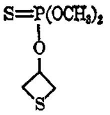
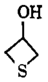
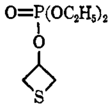
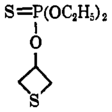
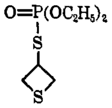
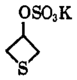
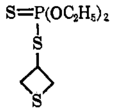
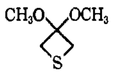
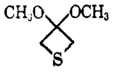
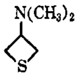
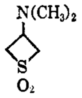
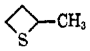
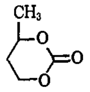
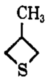
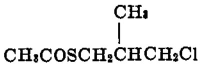
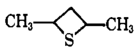
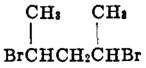
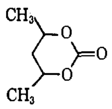
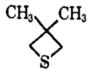
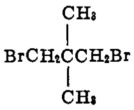
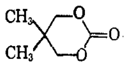
Thietane	Ref	Starting material	Reactant	Yield, %	Derivatives	Ref	Mp, °C
	30		$(CH_3O)_2P(S)Cl$				
	30		$(C_2H_5O)_2P(O)Cl$				
	30		$(C_2H_5O)_2P(S)Cl$				
	30		$(C_2H_5O)_2P(O)SK$				
	30		$(C_2H_5O)_2P(S)SK$				
	57		$Al(OC_4H_9)_3$	18–25	Semicarbazone	57	188–189
	50		$H_2O–H^+$	Quant	2,4-Dinitrophenylhydrazone	50	175–176
	50	$(BrCH_2)_2C(OCH_3)_2$	Na_2S	75–80			
	28		$LiAlH_4$	30	Hydrochloride Picrate	28 28	180.5–182.5 210–212
	35	$BrCH_2CH_2CH(CH_3)Br$	Na_2S	30	HgCl₂ adduct	35	103–104 dec
			KSCN	16	CH_3I adduct Sulfone	35 35	113–124 Bp 251.5–253.5
	60						
	2	?	?				
	15	 $CH_3COSCH_2CH(CH_3)CH_2Cl$	NaOH	80	$HgCl_2$ adduct	15	*Ca.* 85
	35	 $BrCH(CH_3)CH_2CH(CH_3)Br$	Na_2S		$HgCl_2$ adduct Sulfone	35 35	90–91 Bp 255–255.5
cis	60		KSCN	4			
trans	60		KSCN	3			
	6	 $BrCH_2C(CH_3)_2CH_2Br$	KHS	55 60 56	$HgCl_2$ adduct CH_3I adduct Sulfone	6 6 6	118 130 54–55
	6		K_2S				
	60		KSCN				

TABLE I (*Continued*)

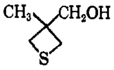
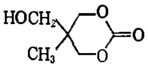
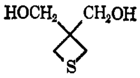
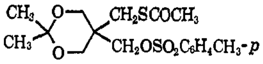
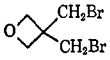
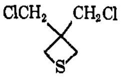
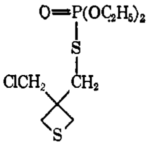
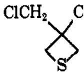
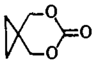
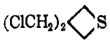
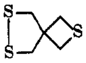
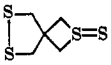
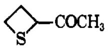
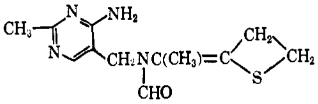
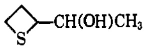
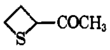
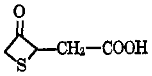
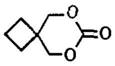
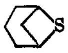
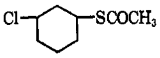
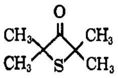
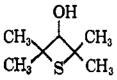
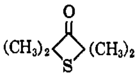
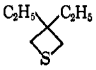
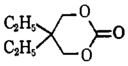
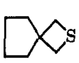
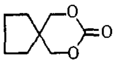
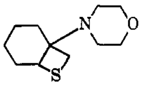
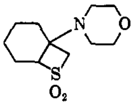
Thietane	Ref	Starting material	Reactant	Yield, %	Derivatives	Ref	Mp, °C
	60		KSCN	50			
	11		CH_3ONa	Low			
	33		K_2S	70	Sulfoxide Sulfone	33 33	71 150–151
	60	$(ClCH_2)_3CCH_2Br$	K_2S	30			
	51		$(CH_3O)_2P(O)SNa$				
	4	$(BrCH_2)_2C(CH_2Br)_2$	K_2S		CH$_3$I adduct	4 45	143 dec 135
	45		Na_2S	37	Disulfone	4 45	244.5 136–137
					Disulfoxide	4	144
	60	$(ClCH_2)_3CCH_2Br$	K_2S	24			
	60		KSCN	8			
	60		Zn–Na_2CO_3	10			
	7		Cu (powder)				
	68		HCl				
	68		$NaBH_4$				
	68	$CH_3CH(OH)CH(Cl)CH_2CH_2Cl$	K_2S	54			
	23	$ClCH_2COCHClCH_2COOH$	Na_2S	15			
	60		KSCN	33			
	10		KOH		Sulfone		171.5–172.5
	22	$(CH_3)_2CHBr—CO—CHBr(CH_3)_2$	NaSH	70			
	22		$NaBH_4$		3,5-Dinitrobenzoate		91–92.5
	60		KSCN	63			
	60		KSCN	50			
	64		$LiAlH_4$				

TABLE I (*Continued*)

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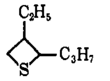
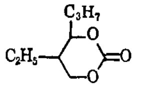
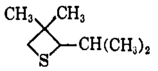
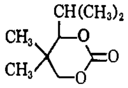
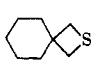
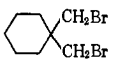
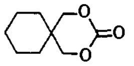
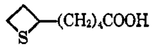
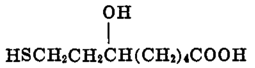
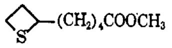
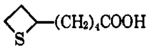
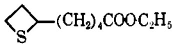
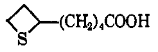
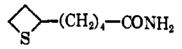
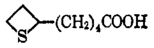
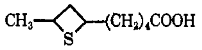
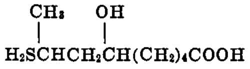
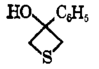
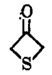
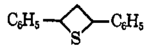
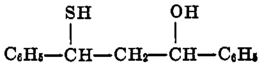
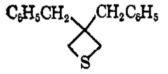
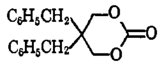
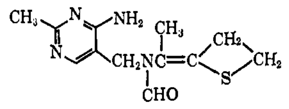
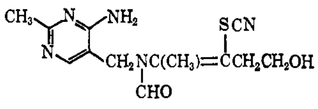
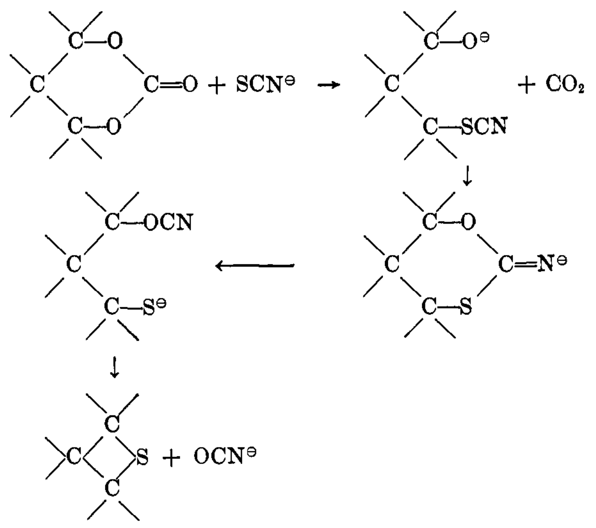
						
cis	60		KSCN	9		
trans	60		KSCN	7		
	60		KSCN	13		
	8		K_2S	54	$HgCl_2$ adduct Sulfone I_2 adduct	161 72.5–73 83–84
	60		KSCN	57		
	19	 $HSCH_2CH_2\overset{OH}{C}H(CH_2)_4COOH$	$(H_2N)_2CS$-HI-NaOH	15		
	71	$ClCH_2CH_2CHCl(CH_2)_4COOCH_3$	K_2S-KOH	48		
	71		Na_2S-NaOH	43		
	71	$BrCH_2CH_2CHBr(CH_2)_4COOC_2H_5$	Na_2S-NaOH	57		
	71	$HOCH_2CH_2CHBr(CH_2)_4COOH$	$(H_2N)_2CS$-$SOCl_2$-NaOH			
	72	$ClCH_2CH_2CHCl(CH_2)_4COOCH_3$	Na_2S			
	71		CH_2N_2			
	72	$ClCH_2CH_2CHCl(CH_2)_4COOC_2H_5$	Na_2S			
	71		C_2H_5OH/H_2SO_4			
	68a	$ClCH_2CH_2CHCl(CH_2)_4CONH_2$	Na_2S			
	68a		$ClCOOC_2H_5$-NH_4OH			
	19	 $H_2S\overset{CH_3}{C}HCH_2\overset{OH}{C}H(CH_2)_4COOH$	$(H_2N)_2CS$-HI-NaOH			
	71	$CH_3CHBrCH_2CHBr(CH_2)_4COOC_2H_5$	Na_2S-NaOH			
	49		C_6H_5MgBr			
	29	 $C_6H_5-\overset{SH}{C}H-CH_2-\overset{OH}{C}H-C_6H_5$	HCl-NaOH			
cis	29				Sulfone	163–164
trans	29				Sulfone	166–167
	60		KSCN	29		
	68		Na_2CO_3	11		

The assumption that the first step involves nucleophilic attack of the thiocyanate ion at the carbon atom in the 4-position is in agreement with the observation that the reactivity decreases upon substitution of the dioxanones in the 4-position and also with the fact that the less nucleophilic thiourea does not react with dioxanones (61).

The reaction is carried out without solvent by heating the components at 170–220°, the resultant thietane distilling off at the same time. At present this is the best method for making 3,3-disubstituted thietanes. Yields range between 30 and 65%; the purity of the crude products is high. Only poor yields are reported for thietanes unsubstituted in the 3-position or substituted in the 2-position. In these cases elimination of β-hydrogen atoms to form unsaturated alcohols becomes a competing reaction, which may even dominate as in the example of 4,4,6-trimethyl-1,3-dioxan-2-one.

If the reaction temperature is too high, the formation of oxetanes from the dioxanones is another competitive reaction. These oxetanes obviously do not react with the thiocyanate ion. Large substituents decrease the

SCHEME I

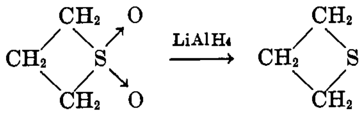


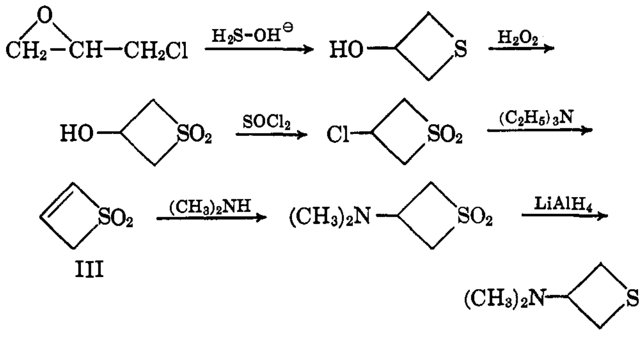
reactivity of the cyclic carbonates by steric hindrance. However, with 5,5-cycloalkylidenedioxanones the yield of spirothietanes drops with decreasing ring size.

The reaction has been studied extensively with many different cyclic carbonates (60, 61).

G. FROM THIETANE DIOXIDES (TRIMETHYLENE SULFONES)

Thietane dioxides can be reduced with lithium aluminum hydride to give the corresponding thietanes in high yield (12). However, this reaction is more of analytical rather than synthetic value. Dittmer and Christy (27, 28) used this reaction for the preparation of 3-dimethylaminothietane *via* the sulfone, since the former compound cannot be obtained by direct methods.

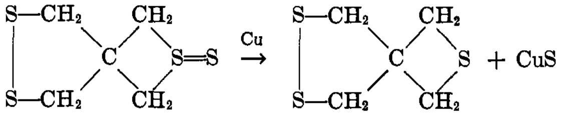




On the other hand, reduction of the thietene dioxide (III) with $LiAlH_4$ entails ring cleavage (28).

Thietane dioxides can be prepared either by oxidation of thietanes (see section IVD) or by direct syntheses on the basis of sulfenes and enamines (54, 55, 64), or from sulfenes and ketene acetals (67). Addition of sulfenes to ketene O,N-acetals, or aminals yields thietene dioxides which on hydrolysis form thietan-3-one dioxides (39, 56).

Thietane monoxides (trimethylene sulfoxides) can be reduced to thietanes by using zinc in hydrochloric acid (3). There is a certain resemblance between the reduction of thietane oxides and the desulfurization of thietane sulfides described in one paper (7).



III. PHYSICAL PROPERTIES

Many physical properties of thietane are known; the more important are listed below.

		Ref
Melting point (triple point)	−73.25°	37, 59
Crystalline transition temperature	−93°	59
Boiling point at 760 mm	94.97°	59
	95.0°	37
Molar heat of fusion	1971 cal	59
Cryoscopic constant (calcd)	0.0248 deg⁻¹	59
	0.023 deg⁻¹	37
Molar heat capacity of the liquid at 21°	26.9 cal/deg	59
Molar heat of vaporization	8234 cal	59
Molar heat capacity of the vapor at 104° and 190 mm	20.8 cal/deg	59
Molar entropy of the vapor at 25°	68.17 cal/deg	59
Molar entropy of the liquid at 25°	44.72 cal/deg	59
Molar heat of formation at 25°, liquid	6.20 kcal	40, 59
Molar heat of formation at 25°, gas	14.7 kcal	40
	−0.80 kcal	53
Density at 20°	1.0200	37
	1.0228	42
at 40°	1.0017	42
Viscosity at 20°	0.638 cp	37
Surface tension at 20°	36.3 dynes cm⁻¹	37
	34.6 dynes cm⁻¹	42
Refractive index n^{20}_D	1.51020	37
	1.50887	42
Molar refraction	21.71	37
	21.51	24
	21.64	42
Parachor	178.1	37
	177.0	42
Molar polarization	86.21	24
Dipole moment	1.78 D.	24

The vapor pressure at various temperatures may be expressed by the equation

$$\log p = 7.01667 - 1321.331/(t + 224.513) \quad (59)$$

The thermodynamic functions $-(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$, and C_p° were calculated from spectroscopic data for temperatures between 0 and 730° (59). Spectrophotometric analysis of thietane showed a planar ring structure with C_{2v} symmetry. The following atomic distances and atomic angles were reported (59): C–C distance 1.54 A, C–S distance 1.82 A, C–H distance 1.09 A; $\angle$C–S–C 79°. From this the product of the moments of inertia is calculated to be 1.925×10^{-114} g^3 cm^6 (59).

Orientation polarization and dipole moment of thietane and thietane dioxide were determined from the dielectric constants, specific volumes, and specific refraction of these compounds (24). The ionization potential of thietane has been determinated from the electron impact spectrum to be 8.9 ± 0.15 ev (32, 44).

The Raman spectra of thietane (2, 59) and 2-methylthietane (3) were measured. The lines of the C–S bond are in the range 600–740 cm^{-1}. The infrared spectrum of thietane (37) shows two C–S bands between 650 and 720 cm^{-1} (14 to 15 μ). Infrared absorption at 8.5 ± 0.1 μ has been found characteristic of thietanes (24). The individual vibrational bands of thietane have been interpreted (48).

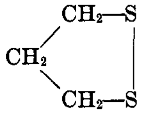
In addition to the maximum at 215–220 μ, which is typical of cyclic sulfides, the ultraviolet spectrum of thietane (37) shows a sharp minimum at 235 μ. Comparison of the ultraviolet spectra of cyclic sulfides of different ring size shows that the weak absorption maximum of trimethylene sulfide (275 mμ) is found at a longer wavelength than that of ethylene sulfide and tetra- and pentamethylene sulfide (25). This seems to be due to the electron density at the sulfur atom. The electron density at the sulfur atom (electron donor ability) of cyclic sulfides of different ring size has been determined by different methods: (1) Measurement of the dissociation of boron trifluoride complexes showed the order: four > five > six > three-membered rings (65). (2) Chemical shift of the α-CH_2 in the nmr spectra showed the order: four > three > five > six-membered rings (36). (3) Spectrophotometric measurement of the dissociation of the iodine complexes showed the order: five > six > four > three-membered rings (52, 66). (4) Measurement of the donor ability against phenol showed the order: five > six > four > three-membered rings (47).

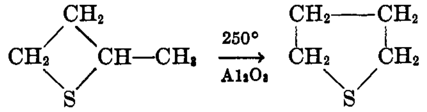
IV. REACTIONS OF THIETANES

A. GENERAL—STABILITY, PYROLYSIS

Thietanes hold an intermediate position between the highly reactive thiiranes and the more inert thiophanes. While the reaction of thiiranes always entails opening of the ring, the five-membered thiophane ring remains intact in most reactions. Thietanes, on the other hand, can be caused to react in either way. In general, the ring remains intact in addition reactions at the free electron pair of the sulfur; however, certain electrophilic addition reactions may entail ring opening. Although little information is available on the mechanism of ring-opening reactions of thietanes, there should be a relationship between ring-opening reactions of symmetrical thietanes and those of thiiranes which have been investigated in greater detail (58a). For lack of information no inferences can be made on the ring-opening mechanism of asymmetrical substituted thietanes. However, this reaction seems to involve two possible mechanisms, whereas only one single product has been isolated in the case of asymmetrical thiiranes. The principal reason for the much lower reactivity of thietanes compared with thiiranes is the lower strain of four-membered rings compared with three-membered ring systems. Correspondingly, thietanes have a higher resistance to heat or light. The low thiirane members polymerize even on storing, whereas thietanes are stable over extended periods of time if stored in the dark at room temperature; they can be distilled almost undecomposed up to temperatures of 150°.

At 250° thietane decomposes over aluminum oxide to give hydrogen sulfide, olefins, and hydrogen. In an atmosphere of hydrogen sulfide the pyrolysis on Al_2O_3 at 250° yields small quantities of 1,2-dithiolane (69). Under these conditions, at temperatures between 350 and 400°, 2-methylthietane is converted to thiophane (tetramethylene sulfide); that is, isomerization occurs with ring enlargement rearrangement (70).





Slow polymerization was observed upon exposure to sunlight. This became evident after 2 weeks; a thick white slurry was formed after 1 year (37). Exposure to ultraviolet radiation for 65 hr at 50° resulted in 1.7 mole % ethylene in addition to the corresponding quantity of a white solid (38).

Exceptional instability is exhibited by thietanes with a strained polycyclic structure. Thus, 6-thiabicyclo-[3.1.1]heptane polymerizes in sunlight or under the action of sulfuric acid (10).

B. POLYMERIZATION

Several authors report the formation of solid polymers as by-products of the synthesis of thietane from trimethylene dihalides and alkali sulfides. Bost and Conn (18) examined these polymers and, by cryoscopic analysis in camphor, determined a molecular weight of 440; this suggests the presence of a hexamer $(C_3H_6S)_6$. In view of the absence of thiol groups and the sulfur content determined by analysis, the hexamer is assumed to have a cyclic structure. The substance melts at 51–52°; it is insoluble or difficultly soluble in most conventional solvents and readily soluble in chloroform, tetrachloromethane, and bromobenzene. Vigorous reduction of the hexamer with Zn–HCl results in hydrogen sulfide and propane but fails to give propyl mercaptan or trimethylenedithiol. Oxidation of the hexamer with $KMnO_4$ leads to an insoluble solid substance which could not be purified but probably constitutes a polymeric sulfone.

Solid polymers (mp 83–84°) are obtained by heating thietane with water at 120–125°, or with dilute sulfuric acid at 105–110° (70). Low-melting crystalline polymers containing halogen and sulfur were derived from thietane upon interaction with gaseous hydrogen chloride or heating with concentrated hydrochloric acid. Cryoscopic determination in camphor showed a molecular weight of 890 (70). Similar polymers fused completely at 100° were also obtained upon interaction of concentrated hydrochloric acid with thietane at room temperature (16).

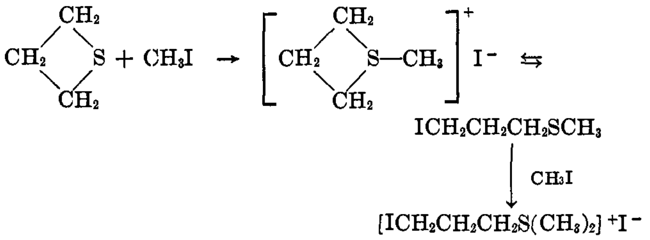
Thietane failed to react with diethylamine, dibutylamine, or potassium hydrosulfide. On the other hand, the addition of aluminum chloride or tin chloride to 2-methylthietane at room temperature entailed vigorous polymerization. The resultant polymers are white rubberlike substances which are partially soluble in pyridine and insoluble in most other solvents (70). Thietane and 2,2-dimethyl-, 2,2-diethyl-, and 2,2-pentamethylenethietane could be polymerized at 25° using boron fluoride etherate as catalyst. Oxidation of the soft or rubbery polysulfides furnished the high-melting polysulfones, which decompose below their melting temperature and are degraded on boiling with alkali (30a).

Poly(trimethylene sulfide) prepared by routes other than polymerization of thietane is reported to melt at 56 (41) or 61° (20).

C. ADDITION COMPOUNDS

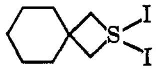
Contrary to thiiranes, thietanes are capable of forming addition compounds similar to those known for open-chain sulfides, without involving ring cleavage. Thus, the addition of mercury dichloride solution results in the crystalline 1:1 complexes that are often used for the characterization of thietanes (4, 6, 15, 16, 35). Interaction of mercury diiodide with thietane does not yield a crystalline adduct (16).

Interaction with methyl iodide gives crystalline 1:2 adducts which are likewise used in many instances for the characterization of thietanes (6, 8, 9, 16, 26, 27, 35). According to Bennet and Hock (9), these adducts represent sulfonium salts of open-chain sulfides, where one iodine atom is linked by an ionic bond.



The addition compound of iodine and thietane is stable in highly dilute carbon tetrachloride solution, in which the dissociation constant of this complex has been determined by spectrophotometric analysis. In more concentrated solutions a brown solid precipitates which is an iodine adduct of polymeric trimethylene sulfide (37). A black crystalline iodine adduct comprising two iodine atoms for each sulfur atom has been obtained from spirodithietane. However, the constitution of this product has not been examined in detail (4).

A crystalline stable iodine adduct has been obtained from 3,3-pentamethylenethietane (8). Reportedly, it has the structure



Thietane combines with bromine at low temperatures to form an orange-yellow dibromide which decomposes at room temperature (16).

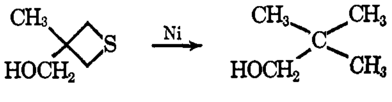
D. OXIDATION

Unlike thiiranes, the ring of thietanes remains intact if oxidized to sulfoxides and sulfones, a reaction which implies the addition of oxygen to the sulfur atom. Reaction with 1 mole of hydrogen peroxide, with nitrous acid or with chromic acid in glacial acetic acid yields cyclic sulfoxides (4, 21, 58). Cyclic sulfones are obtained by interaction with excess hydrogen peroxide (4, 6, 16, 58) or potassium permanganate (4, 16, 35) or peracetic acid (6). The oxidation of thietane by H_2O_2 has been found to be a second-order reaction (21). Oxidation of thietane with nitric acid furnished polymers which could not be identified (13). Both the sulfones and the sulfoxides are crystalline compounds which can be used for the characterization of thietanes. The sulfoxides give crystalline 1:1 adducts with mercury dichloride (4) or other salts (5).

Since the oxidation of cyclic disulfides with $KMnO_4$ yields disulfonic acids, the oxidation can be used for distinguishing this group of substances from thietanes (7).

E. DESULFURIZATION

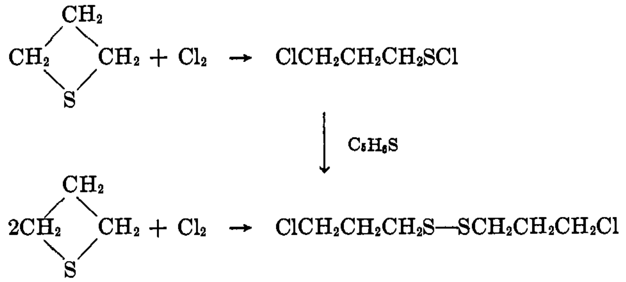
Reductive desulfurization with ring splitting is effected by treating the thietanes with Raney nickel in boiling benzene (60), for instance



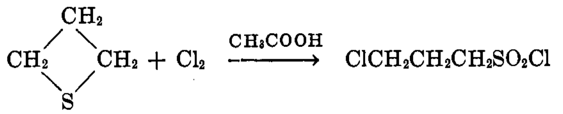
This reaction is of importance in identifying the structure of thietanes (1). In certain cases it is also a convenient method of synthesis as in the above example regarding the preparation of neopentyl alcohol (60).

F. REACTION WITH HALOGENS

If 0.5 mole of chlorine or bromine is added to 1 mole of thietane, γ-halopropyl disulfides are obtained as the main product. If thietane is added dropwise with intense cooling to a chloroform solution of chlorine (molar ratio 1:1), 3-chloropropanesulfenyl chloride-1 is obtained which combines with a further mole of thietane to form the disulfide (63).



3-Chloropropanesulfenyl chloride is also formed upon interaction of sulfuryl chloride with thietane (13). Reaction of thietane with excess chlorine in 75% acetic acid gives 3-chloropropanesulfonyl chloride in high yield (63).

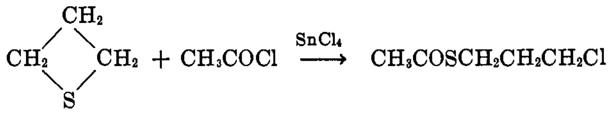


Analogously, from spirodithietane the bis(sulfonyl chloride), $(ClCH_2)_2C(CH_2SO_2Cl)_2$, is obtained by chlorination in aqueous acetic acid solution (34).

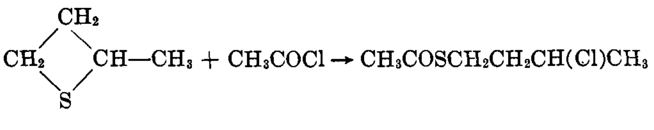
These halogenation reactions proceed analogous to the halogenation of thiiranes, except that the reaction rate and yields are somewhat smaller in the case of thietanes.

G. REACTION WITH ACETYL CHLORIDE AND WITH SULFURYL CHLORIDE

Interaction of acetyl chloride with thietane in the presence of tin tetrachloride at room temperature entails ring opening to give the thioacetate (70).

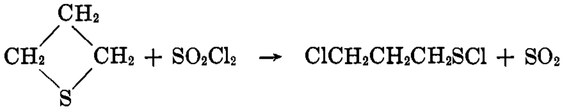


The same reaction occurs with 2-methylthietane; in this case the ring is split preferably between the sulfur and the secondary C atom



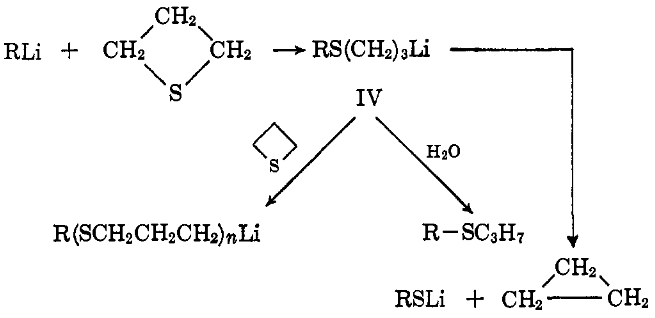
In addition, this reaction seems to yield a minor proportion of the isomer $CH_3COSCH(CH_3)CH_2CH_2Cl$ (70).

Heating of a solution of thietane with molar quantities of sulfuryl chloride gives 3-chloropropanesulfenyl chloride-1 in high yield (13). This reaction is catalyzed by traces of iodine.



H. REACTION WITH ORGANOLITHIUM COMPOUNDS

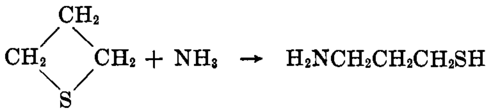
Butyllithium and phenyllithium react with thietane at room temperature. Products isolated from this reaction include mercaptans, thioethers, and polymeric thioethers. Hence, the reaction is quite heterogeneous. Bordwell, and Pitt (14) propose a possible explanation for the formation of various products by an addition reaction involving ring cleavage in the first step.



The generation of the primary adduct (IV) has been confirmed by carboxylation and isolation of γ-(butylthio)butyric acid in a yield of 30%.

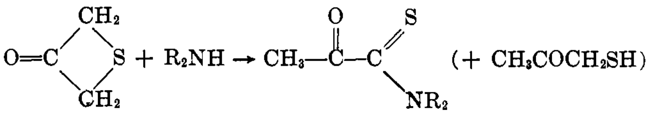
I. REACTION WITH AMINES

Grishkevich-Trochimovskii (35) investigated the reaction of thietane with ammonia and reported the formation of 3-aminopropyl mercaptan.



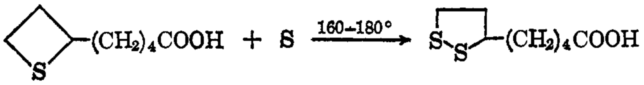
Yuriev, *et al.* (70), on the other hand, did not observe a reaction upon boiling thietane with equimolar amounts of dibutylamine for 22 hr, or upon heating with diethylamine at 110°.

Thietan-3-one is readily split by secondary amines under formation of thiopyruvic amides *via* several unstable intermediates (31). Mercaptoacetone is claimed to be a by-product.



J. REACTION WITH SULFUR

Ring enlargement of thietanes to 1,2-dithiolanes is possible by heating the thietanes with elemental sulfur. In this way, α-lipoic acid can be prepared from 5-(2-thiethanyl)valeric acid (71).



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