THIIRANES

MANFRED SANDER

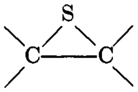
Battelle-Institut e.V., Frankfurt a. Main, Germany

Received August 30, 1965

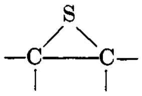
CONTENTS

I. INTRODUCTION

Thiirane is the official term for three-membered rings comprising one sulfur atom.



Other designations used for these compounds include olefin sulfides, alkene sulfides, ethylene sulfides, episulfides, thioalkylene oxides, thiacyclopropanes. In the present report the individual representatives are designated as the corresponding olefin sulfides, since these names are easy to construct from the name of the corresponding olefin and enable the structure to be readily understood. The term cyclohexene sulfide, for example, is simpler and clearer than the respective designations 2,3-tetramethylenethiirane or 2,3-tetramethylenethylene sulfide or episulfidocyclohexane or 7-thiabicyclo[4.1.0]heptane. However, for certain complicated structures, such as carbohydrates, the prefix epithio attached to the name of the sulfur-free saturated hydrocarbon derivative may be the more convenient nomenclature, which is generally used in *Chemical Abstracts*. For the entire class the name thiiranes or thiirane compounds will be adopted, and for the atomic grouping



the term thiirane group is used.

Thiirane compounds have been known for a relatively short period of time. In 1916 Staudinger and Pfenninger (222) mentioned the synthesis of tetraphenylethylene sulfide and its thermal decomposition to tetraphenylethylene and sulfur; a more detailed description of this reaction was published in 1920 (223). In the same year Delépine (50) prepared ethylene sulfide, the first pure aliphatic thiirane, and recognized the importance of this group of compounds as reactive substances suitable for a variety of reactions. When in 1934 Dachlauer and Jackel discovered a method for the synthesis of thiiranes from olefin oxides and alkali thiocyanates or thiourea (42), thiiranes started gaining technical interest. The most important scientific knowledge on the chemistry of thiiranes is due to studies conducted by Culvenor and Davies between 1949 and 1952 (37–40, 43, 44).

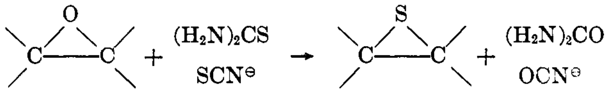
In 1951, Tarbell and Harnish (237) presented the first summarizing review on ring-opening reactions of thiiranes; in 1953 the first general review on thiiranes was published in Japanese (166). A review in German was given by Schönberg in 1955 (200); a Russian review appeared in 1957 (107). Short summaries on the chemistry of thiiranes have been published by Reid (179) and by Kaufmann and Schickel (113).

The present review comprises the literature on preparation, properties, and reactions of thiiranes up to 1964.

II. METHODS OF PREPARATION

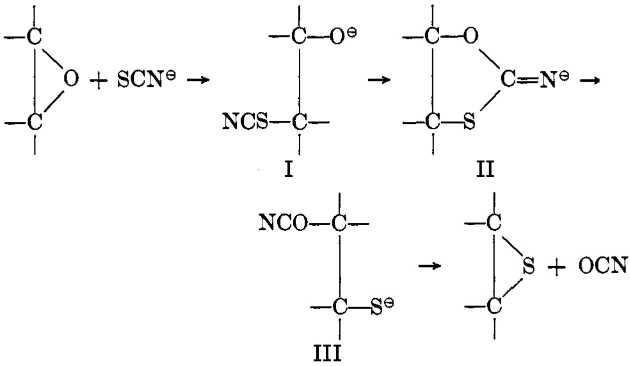
A. FROM ALKENE OXIDES (OXIRANES)

The most important method for the synthesis of thiiranes is the conversion of alkene oxides (epoxides) with *thiourea* or *inorganic thiocyanates* as described for the first time in a patent specification (42).



The reaction of ethylene oxide with thiourea was studied some years ago, but only intermediates and no thiiranes were isolated (169). In general, the reaction is carried out at 0 to 20° in aqueous or alcoholic solution, in the simplest case, by storing an aqueous solution of potassium thiocyanate and ethylene oxide. Reaction temperatures above 60° entail appreciable polymerization.[1] Since all thiiranes are insoluble in water, whereas the low alkene oxides are water-soluble, no difficulties are encountered in controlling the reaction and in isolating the reaction products if water is used as solvent. If water-insoluble alkene oxides are used, the reaction is carried out either in a mixture of water and alcohol or dioxane, or in methanol or ethanol alone. No cooling is required if cyclohexane is used as solvent (250). The inexpensive alkene oxides are used in excess to give conversions of thiocyanate or thiourea up to 98% (42). The expensive epoxides, on the other hand, are treated with excess thio reagent. The yields obtained at the conventional molar ratio of 1:1 generally range between 40 and 75%. Individual references reporting yields above 90% are assumed to relate to crude products. Even if the alkene oxides used are soluble in water, they are partially extracted by the resultant thiiranes, so that the crude products usually contain a certain proportion of the original reactants. The thiiranes are commonly purified by fractional distillation. For subsequent conversions it is also possible to use the crude products extracted from the reaction mixture. If the reaction is carried out at room temperature or lower temperatures, there is hardly any difference in yields, no matter if thiourea, potassium thiocyanate, or ammonium thiocyanate is used. Temperatures involving more substantial polymerization of the thiiranes make the yields drop in the foregoing order of the individual thio reagents (37). Most probably, this has to be attributed to the basicity of the reagents, since the pH value of the aqueous solution increases rapidly during the reaction. If ethylene oxide is replaced by a mixture of ethylene chlorohydrin and alkali, ethylene sulfide is obtained in low yield (167).

According to the unanimous reports of several authors (21, 69, 175, 246), the reaction of alkene oxides with thiocyanates proceeds according to the mechanism



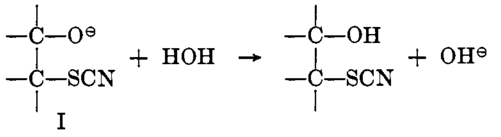
The first two steps are very fast, while the last two steps take place at a very slow rate. The oxathiolanimine intermediate (II) was isolated as nitrobenzoate (175). The entire reaction is accompanied by Walden

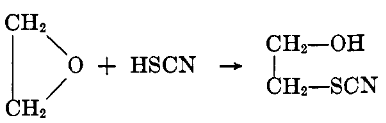
---

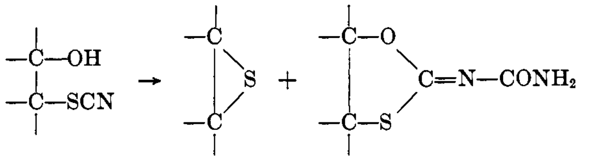
[1] Higher thiiranes which do not tend to polymerize are dimerized if the temperature exceeds 60° (181).

inversion at both of the two C atoms of the ring, so that L-(−)-2-butene sulfide results from D-(+)-2-butene oxide (175). Both the oxathiolane ring and the thiirane ring may be closed only in the *trans* position, just as the ring opening of thiiranes by nucleophilic reagents—analogous to that of oxiranes—always results in *trans* derivatives.

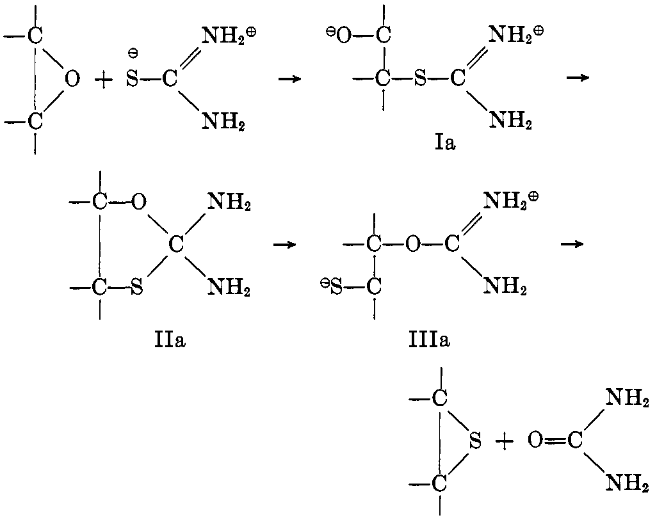
The rapid increase of the pH value in the early stage of the reaction may be explained by hydrolysis of I. The formation of β-hydroxy isothiocyanates turns out to be the main reaction if ethylene oxide is converted with thiocyanic acid at low temperature (175, 208, 249). Those hydroxy isothiocyanates decompose in acid solution at room temperature to give primarily oxathiolane derivatives and thiiranes (175), but other by-products are obtained as well. Hence, it has been proposed to carry out the reaction in weakly alkaline medium (addition of K_2CO_3).


I





A similar reaction mechanism has been proposed for the reaction with thiourea (21, 40).


Ia

IIa

IIIa

Owing to the possible mesomeric forms of Ia and IIIa, these intermediates are relatively stable. This applies particularly to Ia which, in the presence of at least 1 equiv of aqueous mineral acid, may be isolated as the β-hydroxyisothiuronium salt (5, 21, 115). Addition of alkali to the isothiuronium salt or heating of the salt with weak acids gives the desired thiiranes. The best yields were obtained by neutralization with sodium carbonate (21). Excessive pH values encountered upon pouring the isothiuronium salt solution into alkali has an adverse effect on the yield, since this results in the corresponding hydroxythiol, as well as polymers.

In the absence of acid or alkali, the pH value of the solution increases strongly in the early stage of the reaction. This may be attributed either to hydrolysis of the intermediate Ia or to hydrolysis of the resultant urea to ammonia. At any rate, this increase of the pH value has an adverse effect on the yields of cyclic sulfides.

Cyclopentene sulfide is not obtained by reaction of cyclopentene oxide either with thiocyanates or with thiourea, despite the fact that the corresponding thiuronium salt is obtained in satisfactory yield if the reaction is carried out in acidic medium (21, 246). This may be rated as evidence indicating that also in the case of the reaction with thiourea cyclization takes place in the *trans* position. However, this assumption was disproved by Goodman and Baker (84) who obtained cyclopentene sulfide in a yield of 20% by treating cyclopentene oxide with KSCN.

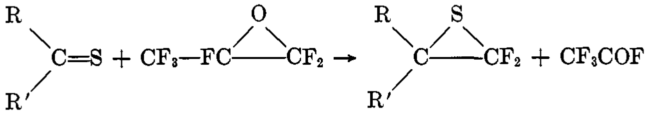
The above mechanism applies to all thio reagents; the last step—cleavage of III or IIIa followed by cyclization—is feasible only if the O–C bond is weakened by electron-attracting groups, as in the case of O-uronium salts or cyanates. However, cyclization does not occur if a hydrogen atom or an alkyl group is attached to the oxygen atom; this includes compounds of the type $HS–CH_2–CH_2–OH$ or $HS–CH_2–CH_2–O–alkyl$ (40).

By interaction of the corresponding alkene oxides with thiourea the following thiiranes have been prepared: ethylene sulfide (42, 76, 91), propene sulfide (18, 21, 37, 43, 46, 92), chloropropene sulfide (37, 44, 46, 75), 2-butene sulfide (96), isobutene sulfide (37), butadiene monosulfide (38), 1-hexene sulfide (22), 1-octene sulfide (153), cyclohexene sulfide (37), 4-methylcyclohexene sulfide (38), stilbene sulfides (115), thioglycidyl ethers (5, 205), thioglycidyl sulfides and thioglycidyl amines (5, 204), various bis(thioglycidyl) ethers (135), thiirane fatty acids, fatty esters, and fatty alcohols (60, 113, 172). Thiiranes could not be prepared from the following alkene oxides by means of thiourea: glycidol (5, 37), styrene oxide (37), ethyl dimethylglycidate (37), ethyl phenylglycidate (39), other glycidates (29, 60), glycidamides (243), benzylideneacetone oxide (37), stilbene oxide (37), cyclopentene oxide (21).

By converting epoxides with potassium thiocyanate (or ammonium thiocyanate), the following alkene sulfides were obtained: ethylene sulfide (24, 42, 46, 75, 148, 212, 250), propene sulfide (212, 225), 3-chloropropene sulfide (42, 37), 2-butene sulfide (163, 175), isobutene sulfide (212), cyclopentene sulfide (84), cyclohexene sulfide (37, 46, 212, 246, 247), styrene sulfide (87, 165, 228), various 3-alkoxypropene sulfides and 3-phenoxypropene sulfide (122, 168, 205). Only small yields of thiiranes have been obtained from sugar epoxides (89) and epoxysterines (127). Thiiranes were not obtained from cyclopentene oxide (246) and glycidol (37).

Other thio reagents which are less or not suitable for the synthesis of thiiranes from epoxides include: diphenylthiourea (37), xanthamide, thioacetamide, thiobenzamide, thiobarbituric acid (39). Interaction of alkene oxides with alkali dithio- and polythiocarbonates gives cyclic thiocarbonates (37); the same applies to the reaction with carbon disulfide (61, 178). Some types of cyclic thiocarbonates can be converted to thiiranes (see section IIB). Reactions with alkali mercaptides yield β-hydroxy mercaptans (39, 158) and those with thioacetic acid furnish the acetyl derivatives of hydroxy mercaptans which can be converted to thiiranes (see section IIC). Interaction of epoxides with alkali thiosulfates gives β-hydroxysulfonic acids (39), whereas only polymers were obtained from P_2S_5 (158). Durden (62) investigated the reaction of alkene oxides with carbonyl sulfide which in general furnished only small yields of thiiranes. Treatment of epoxides with sulfur dioxide in the presence of quaternary ammonium salts yields copolymers which are reported to give thiiranes upon pyrolysis (68).

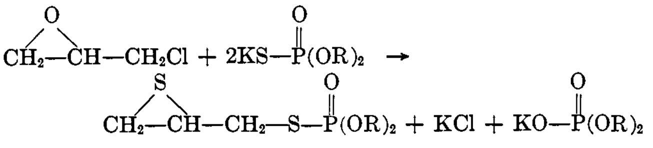
Hexafluoropropene oxide reacts with perhalogenated thiocarbonyl compounds in a unique reaction affording a perhalogenated thiirane and trifluoroacetyl fluoride (147). The reaction is carried out at 175 to 400°



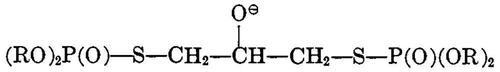
R, R′ = F, Cl, CF_3, or other highy fluorinated alkyl groups

under pressure or in vapor phase without catalysts. The yields are about 50%. In this way, tetrafluoroethylene sulfide, hexafluoropropene sulfide, chlorotrifluoroethylene sulfide, and octafluoroisobutene sulfide (147) have been prepared.

Worth mentioning is the generation of thioglycidyl thiophosphates by conversion of epichlorohydrin with 2 moles of the alkali salt of dialkyl thiophosphates (203).



The authors interpret this result by postulating substitution of an SH group for the OH group of an intermediate chlorohydrin ester. However, it seems more probable that the reaction involves the substitution of a thiophosphate group for the chlorine atom of the chlorohydrin ester or an oxygen–sulfur exchange in an intermediate epoxy ester; in both instances the reaction may proceed *via* the anion

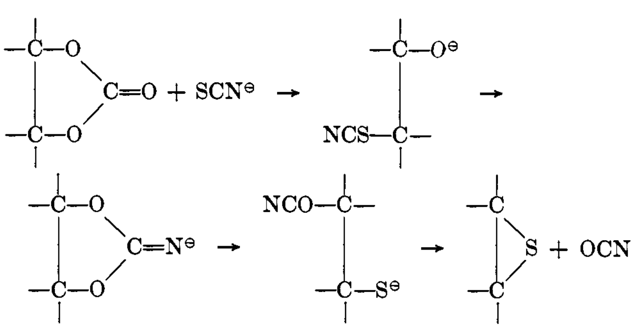


$$(RO)_2P(O){-}S{-}CH_2{-}\underset{}{\overset{O^{\ominus}}{\overset{|}{C}}}H{-}CH_2{-}S{-}P(O)(OR)_2$$

an analog to intermediates I or Ia, in the sulfuration with thiourea and thiocyanates.

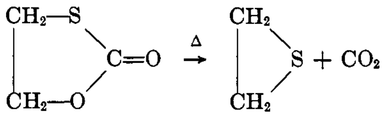
B. FROM CYCLIC CARBONATES

Reaction between the cyclic carbonates of 1,2-diols (1,3-dioxolones) with alkali thiocyanates at 100 to 200° furnishes the corresponding thiiranes according to a four-step mechanism including two Walden inversions analogous to the reaction with alkene oxides (206). Yields are high if the reaction occurs below 150°

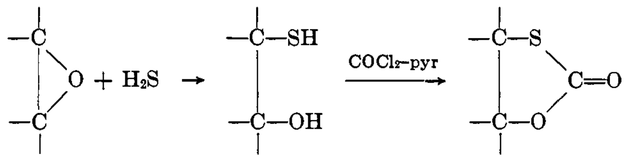


and if the resultant thiirane distils off quickly. This is both the case with low-molecular-weight compounds. The yield of ethylene sulfide obtained in this way is 80–85% (reaction temperature 95–100°); the yield of propene sulfide (reaction temperature 140–150°) is only 51% whereas higher substituted dioxolones react slowly to give polymers as main product. Cyclic carbonates of diols with tertiary hydroxyl groups showed no reaction. Only low yields are obtained by using thiourea instead of thiocyanates. Some years after the first publication (206) a patent protecting this reaction was issued in France (220).

Another important process is the synthesis of thiiranes by heating cyclic monothiol carbonates (184, 185).



These starting compounds are readily prepared by the following route or by heating open-chain β-mer-

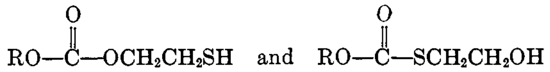


captoethyl carbonates in the presence of sulfonic acids (111).

The advantage inherent in this method is to be seen in the fact that cyclic carbonates are storable for extended periods of time. The thiirane is prepared immediately before it is used by heating the thiol carbonate, or else the thiol carbonate is used itself instead of the thiirane (186).

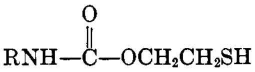
The decomposition is prompted by small amounts of alkali and inhibited by acids. For example, the decomposition of ethylene monothiol carbonate in the presence of 1% Na_2CO_3 at 200° gives ethylene sulfide in a yield of 88% (184).

The cyclic thiol carbonates may be replaced by the open-chain O- and S-carbonates (73, 186)



$$RO{-}\overset{O}{\overset{\|}{C}}{-}OCH_2CH_2SH \quad \text{and} \quad RO{-}\overset{O}{\overset{\|}{C}}{-}SCH_2CH_2OH$$

(likewise obtainable from 2-hydroxy mercaptans) or by mercaptocarbaminates



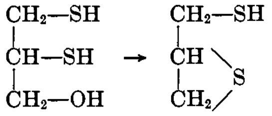
$$RNH{-}\overset{O}{\overset{\|}{C}}{-}OCH_2CH_2SH$$

This method may also be used for the synthesis of hydroxyalkylthiiranes (73, 186).

Cyclic trithiocarbonates, which are available from epoxides by reaction with alkali alkylxanthates, can be converted to thiiranes by alkaline hydrolysis. The method is restricted to the synthesis of such thiiranes which show low tendency to polymerization. Yields of 50–60% are reported (145).

C. FROM HYDROXY MERCAPTANS AND THEIR DERIVATIVES

Signaigo (210) described the synthesis of dithioglycidol (yield 32%) by heating of dithioglycerol (BAL).



This is the only reference dealing with the preparation of a thiirane by dehydration of a hydroxy mercaptan. Miles and Owen (151) observed that 2-mercaptoethanol (2-hydroxyethyl mercaptan) and 2-mercaptocyclohexanol fail to give thiiranes upon treatment with alkali. 2-Hydroxy mercaptans are reported to be comparatively stable distillable compounds: cyclization generally is possible *via* derivatives only. Such derivatives include S-acetyl (93, 94, 151), O-acetyl (93, 94, 151), and O,S-diacetyl derivatives (70, 83, 93, 94, 151) of 2-hydroxy mercaptans. By heating these derivatives with aqueous alkali solutions, such as KOH or $NaHCO_3$, they are converted into thiiranes. The latter should be continuously distilled off during the reaction in order to reduce the tendency to ring opening or polymerization by the alkali.

Yields between 25 and 80% are reported for this process; differences between the individual derivatives were not observed. This method was used for making ethylene sulfide (93, 151), cyclohexene sulfide (93, 151), cyclopentene sulfide (83, 94), cholestene sulfide (234, 235), dithioglycidol (93, 151), hydroxymethyldithioglycidol (70), and dithioglycidyl acetate (151) and its homologs (57). However, there are 1,2-diacetates which do not give thiirane upon treatment with alkalies (57).

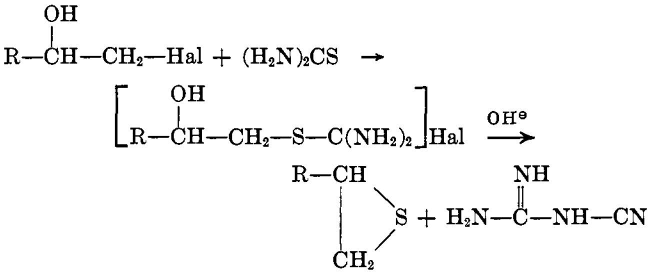
Further derivatives of 2-mercaptoethanol which can be readily converted in high yield by alkali-catalyzed pyrolysis in ethylene sulfide include the respective O-carbamates, O-carbonates, and S-carbonates (186). The conversion of cyclic carbonates of 2-hydroxy mercaptans (184, 185) to thiiranes has been discussed in section IIB.

2-Thiocyanatocyclopentanol mesylate, in the presence of aqueous NaOH, furnished cyclopentene sulfide in a yield of 63%, whereas the corresponding tosylate furnished only small quantities of that thiirane (84). Equally negative was the treatment of 2-acetylthiocyclohexyl tosylate with alkali (94); however, from a sugar-α-thiocyanomesylate the thiirane was obtained in high yield (30, 31), whereas the direct conversion of the corresponding epoxide is difficult (30, 89).

For steroidal thiiranes the alkaline treatment of mesyloxy thiocyanates or even hydroxy thiocyanates seems to be the best method of preparation (121, 127, 234, 235). The yields are reported to be nearly quantitative.

D. FROM HYDROXYALKYL HALIDES

Interaction of 2-hydroxyalkyl halides with thiourea in a polar solvent results in the corresponding isothiouronium salts which in turn yield the respective thiiranes upon treatment with alkali (117).



In general, the thiuronium salt is not isolated but decomposed by adding a concentrated solution of alkali carbonate. Yields are reported to be "very high"; detailed figures are not available.

Ethylene sulfide, propene sulfide, 1-butene sulfide, 2-butene sulfide, and isobutene sulfide were prepared by this method (117). Conversion of 2-thiocyanocyclopentanol with aqueous potassium carbonate solution gave cyclopentene sulfide in very low yields (84).

TABLE I
PREPARATION OF THIIRANES

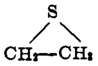
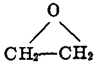
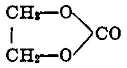
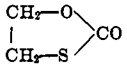
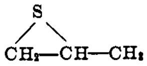
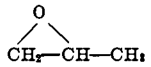
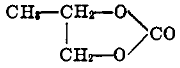
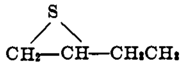
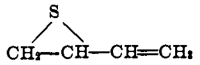
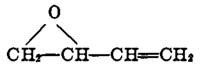
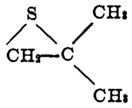
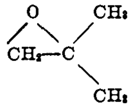
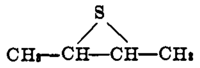
Thiirane	Starting material	Reagent	Yield, %	Ref
A. Aliphatic Thiiranes without Functional Groups				
		KSCN	97	42
		KSCN	*Ca.* 50	212
		KSCN	27	148
		KSCN	50	24
		KSCN	...	75
		KSCN	...	46
		KSCN	...	85
		NH_4SCN	48	250
		$(H_2N)_2CS$	...	42
		$(H_2N)_2CS$	50–60	76
		$(H_2N)_2CS$	48	91
		COS	Max. 40	62
		KSCN	64.5	206, 207
		KSCN	80–85	206
		Heating (+Na_2CO_3)	88	184–186
	$ClCH_2CH_2SCN$	Na_2S	...	50
	$NCSCH_2CH_2SCN$	Na_2S		50
	$ClCH_2CH_2SH$	$NaHCO_3$ or Na_2S	*Ca.* 90	32
	$ClCH_2CH_2SH$	NaOH	*Ca.* 50	32
	$ClCH_2CH_2OH$	$(H_2N)_2CS$	Very good	117
	$ClCH_2CH_2OH$	NaOH-KSCN	27	167
	$CH_3COOCH_2CH_2SH$ or $HOCH_2CH_2SCOCH_3$ or $CH_3COOCH_2CH_2SCOCH_3$	NaOH	*Ca.* 25	93, 151
	$C_6H_5NHCOOCH_2CH_2SH$	Heating	High	186
	$C_2H_5OCOSCH_2CH_2OH$	Heating	High	186
	$C_2H_2OCOOCH_2CH_2SH$	Heating	High	186
		$(H_2N)_2CS$	61	37
		$(H_2N)_2CS$	70	43
		$(H_2N)_2CS$	63	21
		$(H_2N)_2CS$	...	140
		$(H_2N)_2CS$	...	46
		$(H_2N)_2CS$	58	92
		$(H_2N)_2CS$	65	18
		$(H_2N)_2CS$	...	190
		KSCN	...	212
		KSCN	65	225
		KSCN	65	18
			51	206
	$ClCH(CH_3)CH_2SCN$	Na_2S	...	51
	$NCSCH(CH_3)CH_2SCN$	Na_2S	...	51
	$ClCH(CH_3)CH_2OH$	$(H_2N)_2CS$	Good	117
	$CH_3CH_2SCH_2Cl$	HF–KF		173
	$CH_3CH{=}CH_2$	$C_2H_5S_4C_2H_5$	15	112
	$BrCH(C_2H_5)CH_2SCN$	Na_2S	...	51
	$NCSCH(C_2H_5)CH_2SCN$	Na_2S	...	51
	$ClCH_2CH(OH)CH_2CH_3$	$(H_2N)_2CS$–K_2CO_3	Good	117
		$(H_2N)_2CS$	50	38
		$(H_2N)_2CS$	57	37
		KSCN	73	212
		$(H_2N)_2CS/K_2CO_3$	Good	117
	$ClCH(CH_3)CH(CH_3)SH$	$NaHCO_3$	80	32
	$ClCH(CH_3)CH(CH_3)OH$	$(H_2N)_2CS/K_2CO_3$	Good	117

TABLE I (*Continued*)

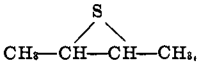
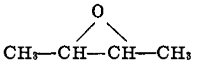
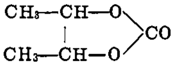
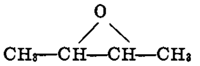
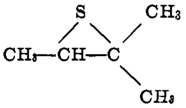
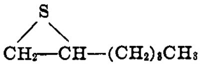
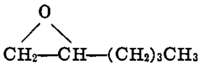
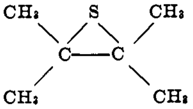
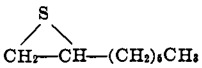
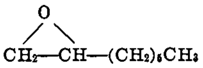
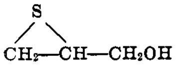
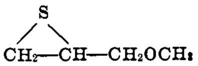
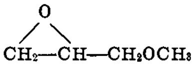
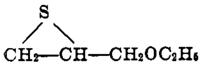
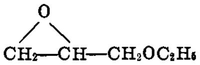
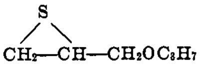
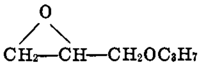
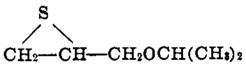
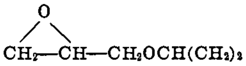
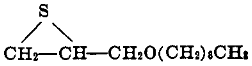
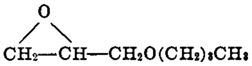
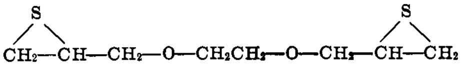
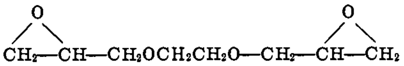
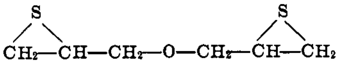
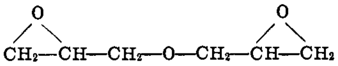
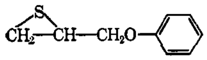
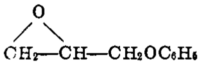
Thiirane	Starting material	Reagent	Yield, %	Ref
, *cis*	 *cis*	KSCN	...	163
cis	 *meso*	KSCN	31	206
trans	 *trans*	KSCN	...	163
L-(−)	D-(+)	KSCN	76	175
SS	*RR*	$(NH_2)_2CS$	73	96
	$NCSCH(CH_3)C(CH_3)(CH_3)SCN$	Na_2S	...	26
		$(H_2N)_2CS$	52	22
	$C_4H_9CHBrCH_2Br$	$(H_2N)_2CS/NaOH$	64	252
	$NCSC(CH_3)_2C(CH_3)_2SCN$	Na_2S	90–95	256
		$(H_2N)_2CS$	78	153
B. Aliphatic Thiiranes with Functional Groups 1. Hydroxyl Compounds and Their Ether and Ester Derivatives				
	$C_2H_5OOCSCH_2CH(OH)CH_2OH$	Pyrolysis	77	186
		KSCN	80	168
		KSCN	92.5	205
		$(H_2N)_2CS$	85.5	205
		KSCN	65	168
		KSCN	90	205
		$(H_2N)_2CS$	...	5
		$(H_2N)_2CS$	83	205
		KSCN	59	205
		$(H_2N)_2CS$	90	205
		KSCN	53	168
		KSCN	38	205
		$(H_2N)_2CS$	81	205
		KSCN	50	168
		KSCN	40	205
		$(H_2N)_2CS$	90	205
		$(H_2N)_2CS$	...	135
		$(H_2N)_2CS$	...	135
		KSCN	65	168
		KSCN	...	122
		KSCN	61	205

TABLE I (*Continued*)

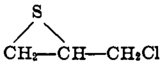
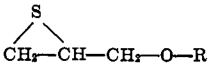
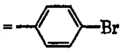
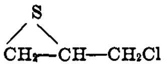
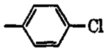
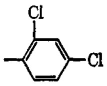
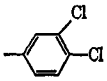
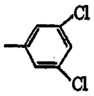
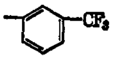
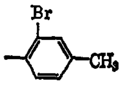
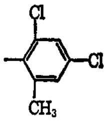
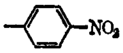
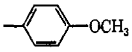
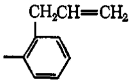
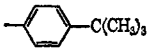
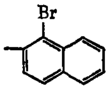
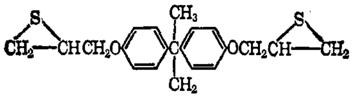
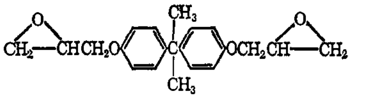
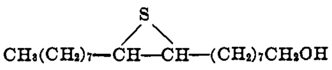
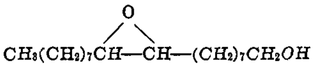
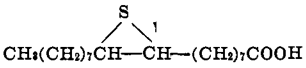
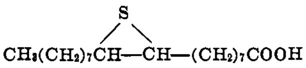
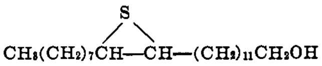
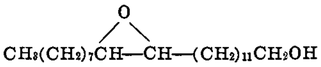
Thiirane	Starting material	Reagent	Yield, %	Ref
		C_6H_5ONa		192
				
R = 		RONa	...	192
			...	192
			...	192
			..	192
			...	192
			...	192
			..	192
			...	192
			...	192
			...	192
			...	192
			...	192
			...	192
		$(H_2N)_2CS$	...	135
 cis	 cis	$(H_2N)_2CS$	64	113
cis	 cis	$LiAlH_4$	...	144
trans	 trans	$LiAlH_4$	...	144
 cis		$(H_2N)_2CS$	62.5	113

TABLE I (*Continued*)

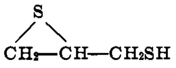
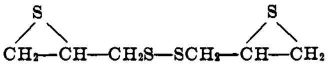
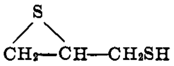
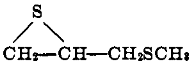
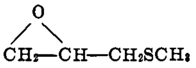
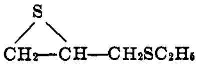
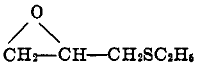
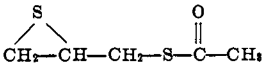
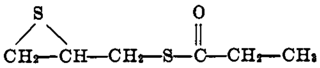
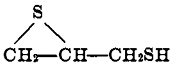
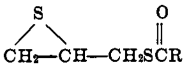
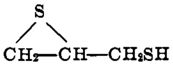
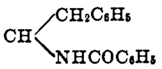
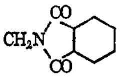
Thiirane	Starting material	Reagent	Yield, %	Ref
2. Thiol Compounds and Their S-Alkyl, Aryl, Acyl, and Phosphoryl Derivatives				
	$HOCH_2CH(SH)CH_2SH$	Heating	32	210
	$HOCH_2CH(OH)CH_2SH$	HCl-$NaHCO_3$	57	57
	$CH_3COOCH_2CH(SH)CH_2SH$	$NaHCO_3$	27	93, 151
		I_2-KI	...	5
		$(H_2N)_2CS$	Low	5
		$(H_2N)_2CS$	60	5
	$CH_3COOCH_2CH(SCOCH_3)CH_2SCOCH_2$	$NaHCO_3$	80	151
	$HOCH_2CH(SCOCH_3)CH_2SCOCH_3$	$NaHCO_3$	55	151
	$C_2H_5COOCH_2CH(SCOC_2H_5)CH_2SCOC_2H_5$	$NaHCO_3$	38	57
		C_2H_5COBr-$NaHCO_3$	24	176
				
R = C_3H_7		RCOCl-$NaHCO_3$	35	5, 176
CH_2Cl		RCOCl-$NaHCO_3$	49	5, 176
$CHCl_2$		RCOCl-$NaHCO_3$	29	5, 176
CCl_3		RCOCl-$NaHCO_3$	40	5, 176
		$RCOOCOOC_2H_5$	15	58
CH_2CH_2Cl		RCOCl	41	5, 176
C_6H_{11}		RCOCl	53	5, 176
$C_{15}H_{21}$		RCOCl	81	5, 176
$CH_2SC_2H_5$		RCOCl	9	5, 176
$CH_2CH_2SCH_3$		RCOCl-$NaHCO_3$	5	5, 176
$CH_2CH_2COOCH_3$		RCOCl-$NaHCO_3$	39	5, 176
		$RCOOCOOC_2H_5$	25	58
$CH_2COOC_2H_5$		RCOCl	45	5, 176
$CH_2CH_2COCH_3$		$RCOOCOOC_2H_5$	63	5, 58
C_6H_5		RCOCl	22	5, 176
$C_6H_4NHCOCH_3$-*p*		$RCOOCOOC_2H_5$	54	5, 58
$C_6H_4N(CH_3)_2$-*p*		RCOCl	13	5, 176
$C_6H_4N{=}NC_6H_5$-*p*		RCOCl	83	5, 176
$CH_2C_6H_5$		RCOCl	38	5, 176
$CH(C_6H_5)_2$		RCOCl	65	5, 176
		$RCOOCOOC_2H_5$	17	58
$CHClC_6H_5$		RCOCl	2	5, 176
$CH_2C_6H_4Cl$-*p*		RCOCl	77	5, 176
$CH_2OC_6H_4Cl$-*p*		RCOCl	34	5, 176
$CH_2NHCOOCH_2C_6H_5$		$RCOOCOOC_2H_5$	46	5, 58
$CH_2NHCOC_6H_5$		RCOCl	21	5, 176
		$RCOOCOOC_2H_5$	30	5, 58
 $CH\begin{cases}CH_2C_6H_5\\NHCOC_6H_5\end{cases}$		$RCOOCOOC_2H_5$	29	5, 58
$C_6H_4NO_2$-*p*		RCOCl	84	5, 176
		$RCOOCOOC_2H_5$	59	5, 58
C_6H_4Cl-*p*		RCOCl	99	5, 176
C_4H_4O (furyl)		RCOCl	56	5, 176
		$RCOOCOOC_2H_5$	49	58
		RCOCl	74	58
OCH_3		RCOCl	67	58
OC_2H_5		RCOCl	50	58
OC_4H_9		RCOCl	19	58
$OCH_2C_6H_5$		RCOCl	20	58

TABLE I (*Continued*)

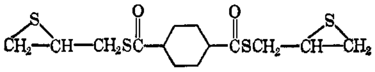
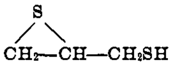
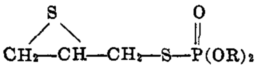
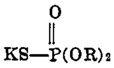
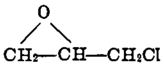
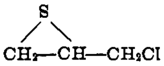
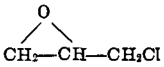
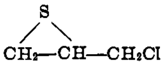
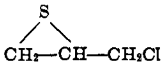
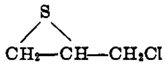
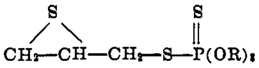
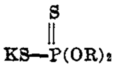
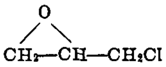
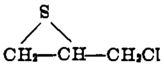
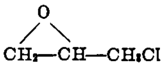
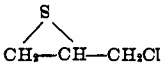
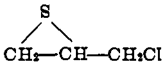
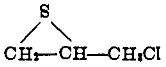
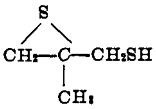
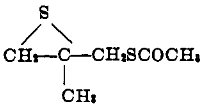
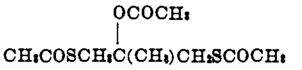
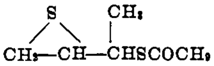
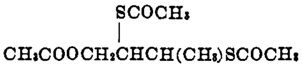
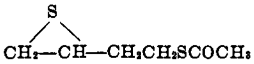
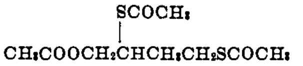
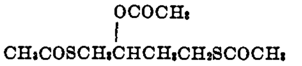
Thiirane	Starting material	Reagent	Yield, %	Ref
		$(C_2H_5OCOOCO)_2C_6H_4$	50	5, 58
				
R = CH_3	 $KS{-}\overset{\overset{O}{\parallel}}{P}(OR)_2$		51	203
			58.5	133
C_2H_5			55	203
			83.3	133
n-C_3H_7			100	133
i-C_3H_7			98	133
				
R = CH_3	 $KS{-}\overset{\overset{S}{\parallel}}{P}(OR)_2$		70	203
			89.5	133
C_2H_5			86.8	203
			95	133
n-C_3H_7			100	133
i-C_3H_7			96.5	133
	$HSCH_2C(OH)(CH_3)CH_2SH$	HCl-$NaHCO_3$	54	57
	 $CH_3COSCH_2\overset{\overset{OCOCH_3}{\vert}}{C}(CH_3)CH_2SCOCH_3$	$NaHCO_3$	53	57
	 $CH_3COOCH_2\overset{\overset{SCOCH_3}{\vert}}{CH}CH(CH_3)SCOCH_3$	$NaHCO_3$	69	57
	 $CH_3COOCH_2\overset{\overset{SCOCH_3}{\vert}}{CH}CH_2CH_2SCOCH_3$	$NaHCO_3$	65	57
	 $CH_3COSCH_2\overset{\overset{OCOCH_3}{\vert}}{CH}CH_2CH_2SCOCH_3$	$NaHCO_3$	62	57

TABLE I (*Continued*)

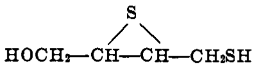
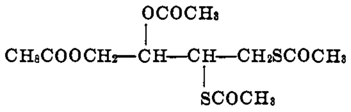
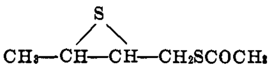
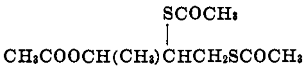
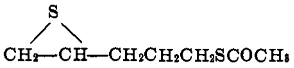
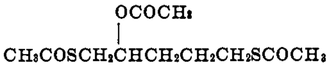
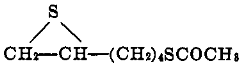
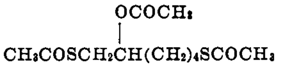
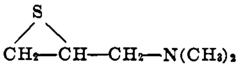
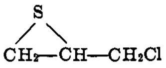
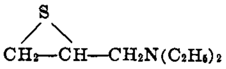
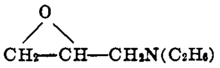
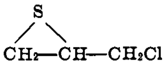
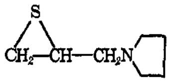
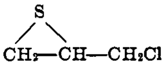
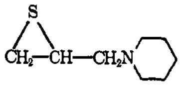
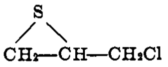
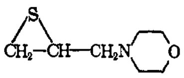
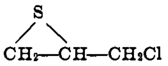
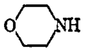
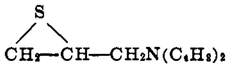
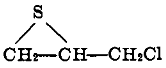
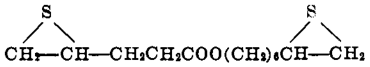
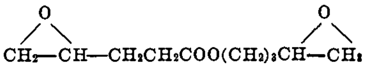
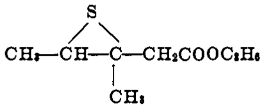
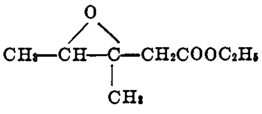
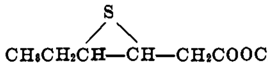
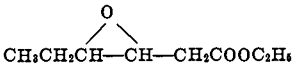
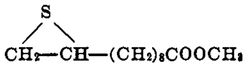
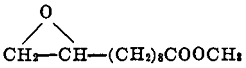
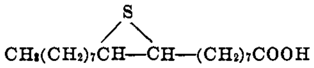
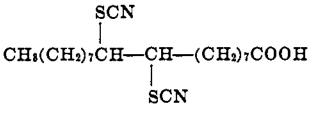
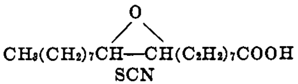
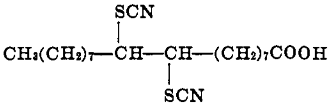
Thiirane	Starting material	Reagent	Yield, %	Ref
	 $CH_3COOCH_2-\overset{OCOCH_3}{CH}-\underset{SCOCH_3}{CH}-CH_2SCOCH_3$	HCl		70
	 $CH_3COOCH(CH_3)\overset{SCOCH_3}{CH}CH_2SCOCH_3$	$NaHCO_3$	59	57
	 $CH_3COSCH_2\overset{OCOCH_3}{CH}CH_2CH_2CH_2SCOCH_3$	$NaHCO_3$	46	57
	 $CH_3COSCH_2\overset{OCOCH_3}{CH}(CH_2)_4SCOCH_3$	$NaHCO_3$	56	57
	3. Amines			
		$(CH_3)_2NH$	37	229
		$(H_2N)_2CS$	29	5
		$(H_2N)_2CS$	60	204
		$(C_2H_5)_2NH$	35	229
			48	229
			75	229
			62.5	229
		$(C_4H_9)_2NH$	72	229
	4. Carboxylic Acids and Their Derivatives			
		$(H_2N)_2CS$	...	135
		$(H_2N)_2CS$	17	60
		$(H_2N)_2CS$	58	172
 *cis*	 *cis*	$(H_2N)_2CS$	54	113
		$(H_2N)_2CS$	55.3	113
	 $CH_3(CH_2)_7\overset{SCN}{CH}-\underset{SCN}{CH}-(CH_2)_7COOH$	KOH	...	191
cis	 *cis*	$(H_2N)_2CS$	81	113
	 $CH_3(CH_2)_7-\overset{SCN}{CH}-\underset{SCN}{CH}-(CH_2)_7COOH$ *threo*	Na_2S	51	145

TABLE I (*Continued*)

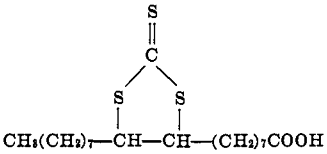
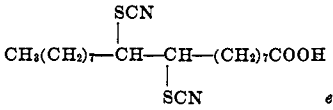
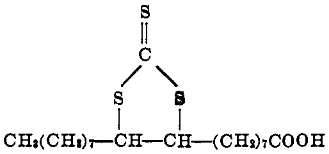
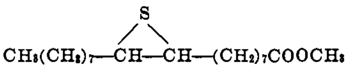
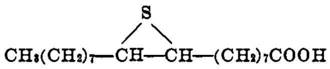
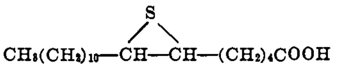
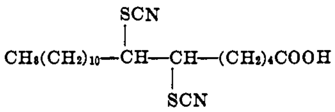
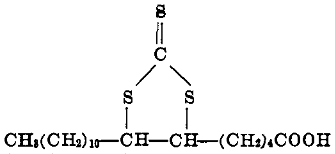
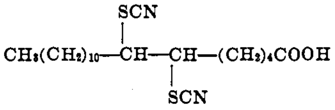
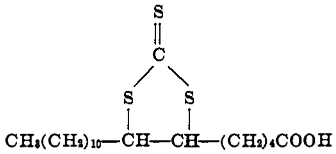
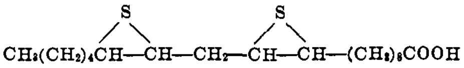
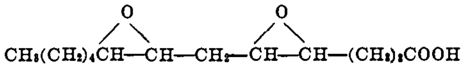
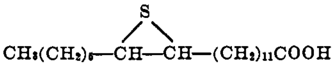
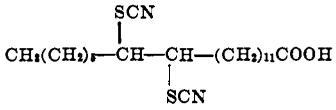
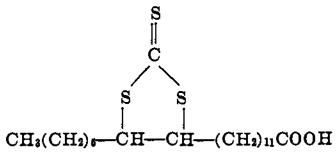
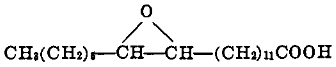
Thiirane	Starting material	Reagent	Yield, %	Ref
		KOH	51	145
	 *threo*	KOH	68	145
	$\mathrm{CH_3(CH_2)_7{-}CH{=}CH{-}(CH_2)_7COOH}$ *cis*	ClSCN/KOH	41	145
trans	 $\mathrm{CH_3(CH_2)_7{-}\overset{SCN}{CH}{-}\underset{SCN}{CH}{-}(CH_2)_7COOH}$ *erythro*	Na$_2$S	51	145
		KOH	63	145
	 *erythro*	KOH	68	145
	$\mathrm{CH_3(CH_2)_7{-}CH{=}CH{-}(CH_2)_7COOH}$ *trans*	ClSCN-KOH	59	145
 *cis*	 *cis*	CH$_2$N$_2$	92.5	113
 *cis*	 $\mathrm{CH_3(CH_2)_{10}{-}\overset{SCN}{CH}{-}\underset{SCN}{CH}{-}(CH_2)_4COOH}$ *threo*	Na$_2$S	64	145
		KOH	63	145
	 *threo*	KOH	56	145
	$\mathrm{CH_3(CH_2)_{10}{-}CH{=}CH{-}(CH_2)_4COOH}$ *cis*	ClSCN-KOH	48	145
trans	 $\mathrm{CH_3(CH_2)_{10}{-}\overset{SCN}{CH}{-}\underset{SCN}{CH}{-}(CH_2)_4COOH}$ *erythro*	Na$_2$S	53	145
		KOH	66	145
	 *erythro*	KOH	75	145
	$\mathrm{CH_3(CH_2)_{10}{-}CH{=}CH{-}(CH_2)_4COOH}$ *trans*	ClSCN-KOH	51	145
 *cis–cis*	 *cis–cis*	(H$_2$N)$_2$CS	68.5	113
 *cis*	 $\mathrm{CH_3(CH_2)_5{-}\overset{SCN}{CH}{-}\underset{SCN}{CH}{-}(CH_2)_{11}COOH}$ *threo*	Na$_2$S	61	145
		KOH	62	145
	 *threo*	KOH	72	145
	$\mathrm{CH_3(CH_2)_5{-}CH{=}CH{-}(CH_2)_{11}COOH}$ *cis*	ClSCN-KOH	49	145
trans	 *trans*	(H$_2$N)$_2$CS	71.5	113

TABLE I (*Continued*)

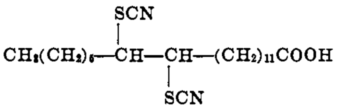
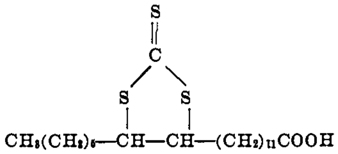
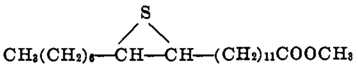
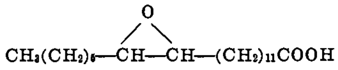
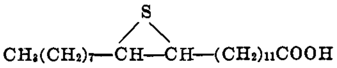
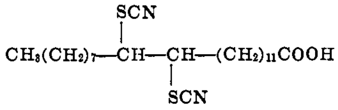
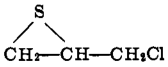
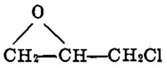
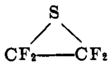
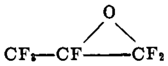
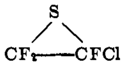
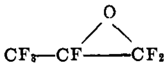
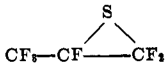
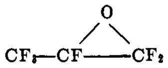
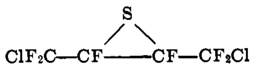
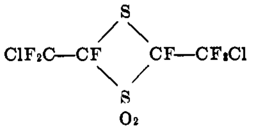
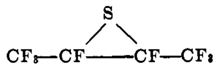
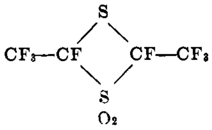
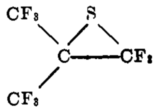
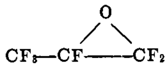
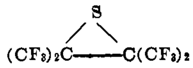
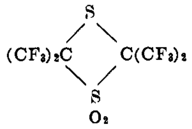
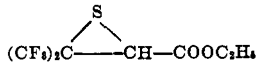
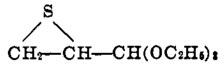
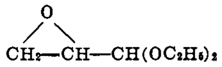
Thiirane	Starting material	Reagent	Yield, %	Ref
	 $\mathrm{CH_3(CH_2)_6{-}\overset{SCN}{CH}{-}\underset{SCN}{CH}{-}(CH_2)_{11}COOH}$ *erythro*	Na_2S	74	145
		KOH	74	145
	 *erythro*	KOH	78	145
	$CH_3(CH_2)_6{-}CH{=}CH{-}(CH_2)_{11}COOH$ *trans*	ClSCN-KOH	54	145
 *trans*	 *trans*	CH_2N_2	72.5	113
	 $\mathrm{CH_3(CH_2)_7{-}\overset{SCN}{CH}{-}\underset{SCN}{CH}{-}(CH_2)_{11}COOH}$	NaOH	30–60	191
	5. Other Functional Groups			
		KSCN	Good	42
		KSCN	47	37
		NH_4SCN	38	37
		$(H_2N)_2CS$	67	37
		$(H_2N)_2CS$	...	44
		$(H_2N)_2CS$	46.5	75
		$(H_2N)_2CS$	50–60	46
		$F_2C{=}S$	15	147
		ClFC=S	...	147
		$F(CF_3)C{=}S$	42.5	147
		Pyrolysis	...	150
		Pyrolysis	...	150
		$(CF_3)_2C{=}S$	56	147
		Pyrolysis	...	150
	$N_2CHCOOC_2H_5$	$(CF_3)_2C{=}S$	...	150
		KSCN	57	255

TABLE I (*Continued*)

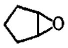
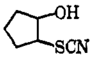
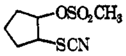
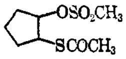
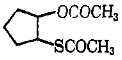
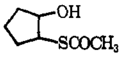
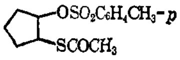
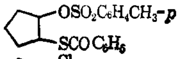
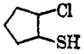
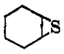
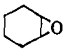
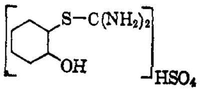
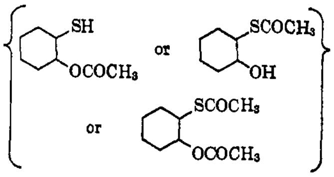
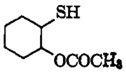
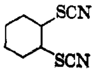
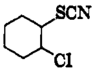
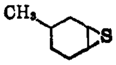
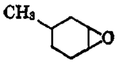
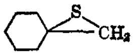
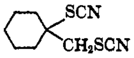
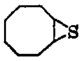
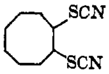
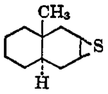
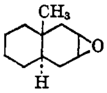
Thiirane	Starting material	Reagent	Yield, %	Ref
C. Cycloaliphatic Thiiranes				
		KSCN	20	84
		K_2CO_3	Low	84
		NaOH	63	84
		NaOH	66	83
		NaOH	82	83
		$NaHCO_3$	20	94
		NaOH in $CH_3O(C_2H_4O)_2CH_3$	35	83
		NaOH in $CH_3O(C_2H_4O)_2CH_3$	25	83
		$NaHCO_3$	75	246
		KSCN, NH_4SCN, or $(H_2N)_2CS$	43-61	37
		KSCN	60	212
		KSCN	71-73	246, 247
		KSCN	...	46
		Na_2CO_3	69	21
		KOH	*Ca.* 55	93, 151
		$NaHCO_3$	70	151
		Na_2S-H_2S	...	158
		Na_2S	...	71
		C_2H_5-S_4-C_2H_5	8	112
		$(H_2N)_2CS$	60	38
		Na_2S-H_2S	...	158
		Na_2S	50	174
 *trans*	 *trans*	KSCN	...	127

TABLE I (*Continued*)

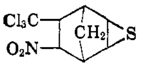
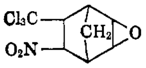
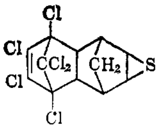
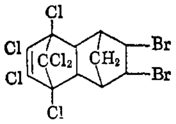
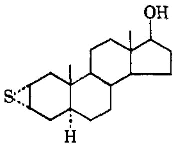
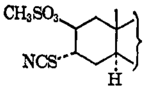
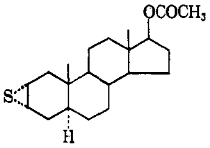
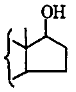
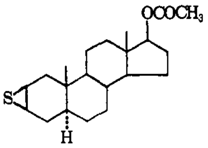
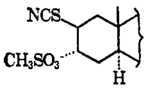
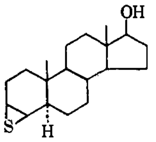
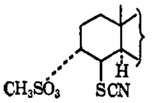
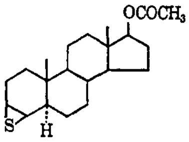
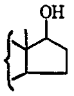
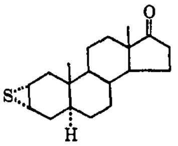
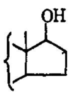
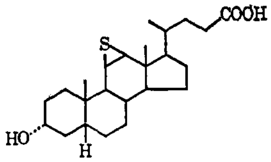
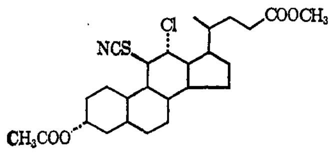
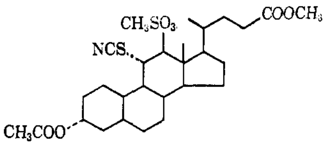
Thiirane	Starting material	Reagent	Yield, %	Ref
		KSCN	...	139
		Na_2S	...	221
	D. Steroids and Carbohydrates			
 17β-Hydroxyandrostene 2α,3α-sulfide		KOH	64	235
 17β-Acetoxyandrostene 2α,3α-sulfide		$(CH_3CO)_2O$	...	235
 17β-Acetoxyandrostene 2β,3β-sulfide		KOH or Al_2O_3	77	235
 17β-Hydroxyandrostene 3β,4β-sulfide		KOH	...	235
 17β-Acetoxyandrostene 3β,4β-sulfide		$(CH_3CO)_2O$	...	235
 17β-Oxoandrostene 2α,3β-sulfide		CrO_3	62	235
 3α-Hydroxycholenic acid 11β,12β-sulfide		KOH	...	233
		KOH	...	233

TABLE I (*Continued*)

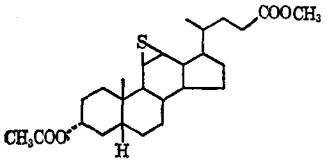
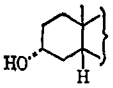
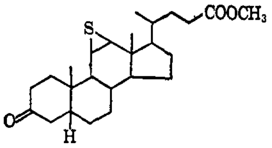
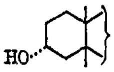
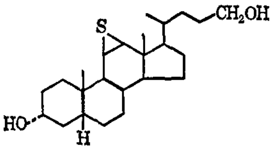
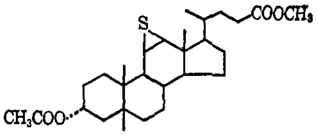
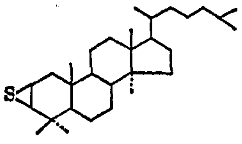
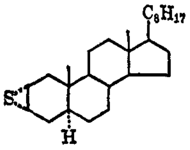
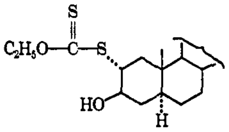
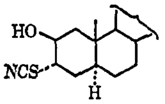
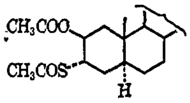
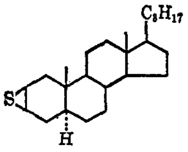
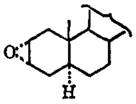
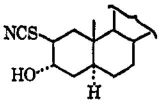
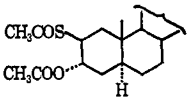
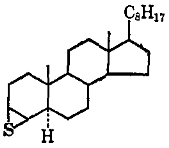
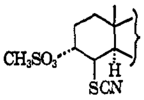
Thiirane	Starting material	Reagent	Yield, %	Ref
 Methyl 3α-acetoxycholenate 11β,12β-sulfide		$(CH_3CO)_2O$	. . .	233
 Methyl 3-oxocholenate 11β,12β-sulfide		CrO_3	. . .	233
 3α-Hydroxycholen-24-ol 11β,12β-sulfide		$LiAlH_4$	. . .	233
 Lanostene 2β,3β-sulfide	?	?	. . .	53
 Cholestene 2α,3α-sulfide		$NaOC_2H_5$	72	127
		KOH	High	234, 235
		KOH	High	234
 Cholestene 2β,3β-sulfide		KSCN	15	127
		KOH	High	234, 235
		KOH	High	234, 235
 Cholestene 3β,4β-sulfide		KOH	68.5	128
		Al_2O_3	. . .	235

TABLE I (*Continued*)

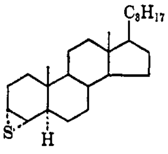
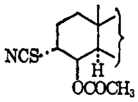
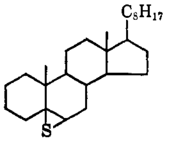
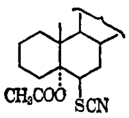
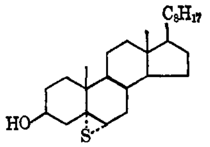
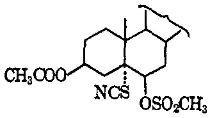
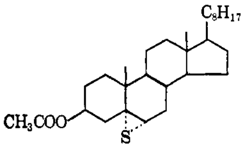
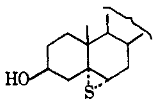
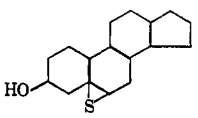
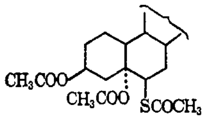
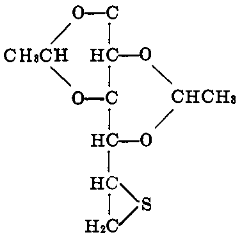
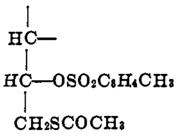
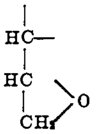
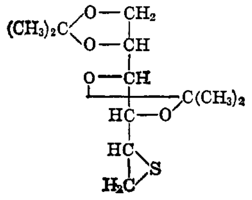
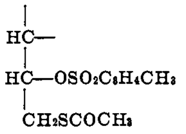
Thiirane	Starting material	Reagent	Yield, %	Ref
 Cholestene 3α,4α-sulfide		KOH	...	235
 Cholestene 5β,6β-sulfide		KOH	76	128
 3β-Hydroxycholestene 5α,6α-sulfide		KOH	...	121
 3β-Acetoxycholestene 5α,6α-sulfide		$(CH_3CO)_2O$	...	121
 3β-Hydroxycoprostene 5β,6β-sulfide		KOH	...	235
 5,6-Dideoxy-5,6-epithio-1,3:2,4-di-O-ethylidene-L-iditol		$NaOCH_3$	89	36
		$(H_2N)_2CS$	...	36
 5,6-Dideoxy-5,6-epithio-1,2:3,4-di-O-isopropylidene-L-gulitol		$NaOCH_3$	72	36

TABLE I (*Continued*)

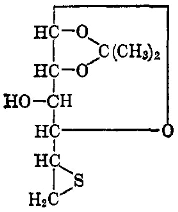
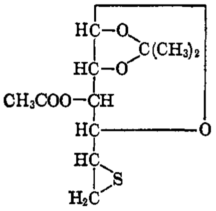
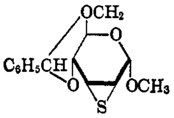
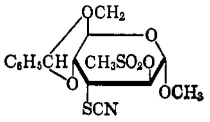
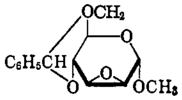
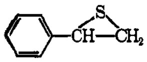
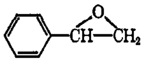
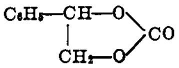
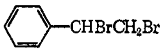
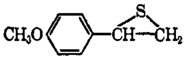
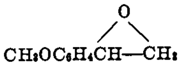
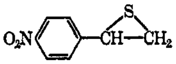
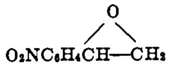
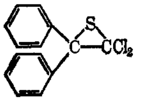
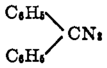
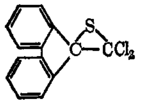
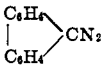
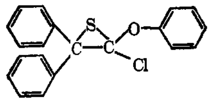
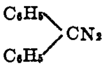
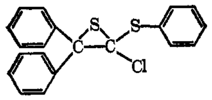
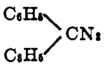
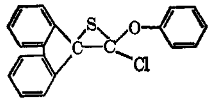
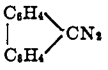
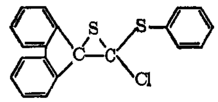
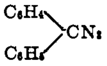
Thiirane	Starting material	Reagent	Yield, %	Ref
 5,6-Dideoxy-5,6-epithio-1,2-O-isopropylidene-α-D-idose		$NaOCH_3$	73	36
 Methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epithio-α-D-alloside		KOH	62	30, 31
		NH_4SCN	20	89
E. Thiiranes Substituted with Aromatic Groups				
		KSCN	47-59	87
		KSCN	55	165
		KSCN	72	228
		KSCN	34	206
		$(H_2N)_2CS$-NaOH	38	252
	 $CH_3OC_6H_4\overset{O}{CH{-}CH_2}$	$(H_2N)_2CS$	...	116
	 $O_2NC_6H_4\overset{O}{CH{-}CH_2}$	$(H_2N)_2CS$	...	116
	 $\begin{matrix}C_6H_5\\C_6H_5\end{matrix}>CN_2$	$S{=}CCl_2$	...	224
	 $\begin{matrix}C_6H_4\\ \vert \\C_6H_4\end{matrix}>CN_2$	$S{=}CCl_2$	...	224
	 $\begin{matrix}C_6H_5\\C_6H_5\end{matrix}>CN_2$	$C_6H_5O\overset{\overset{S}{\Vert}}{C}Cl$	70	196
	 $\begin{matrix}C_6H_5\\C_6H_5\end{matrix}>CN_2$	$C_6H_5S\overset{\overset{S}{\Vert}}{C}Cl$	70	196
	 $\begin{matrix}C_6H_4\\ \vert \\C_6H_4\end{matrix}>CN_2$	$C_6H_5O\overset{\overset{S}{\Vert}}{C}Cl$	30	195
	 $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CN_2$	$C_6H_5S\overset{\overset{S}{\Vert}}{C}Cl$	*Ca.* 70	195

TABLE I (*Continued*)

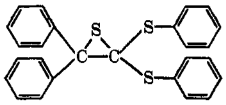
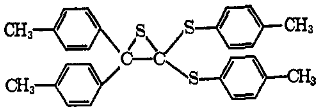
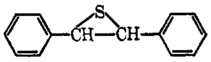
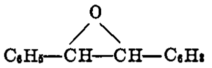
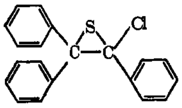
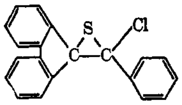
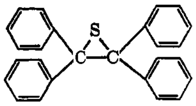
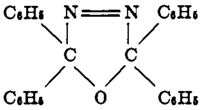
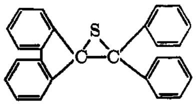
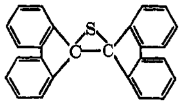
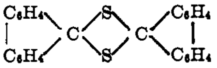
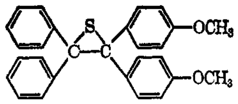
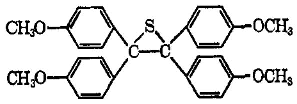
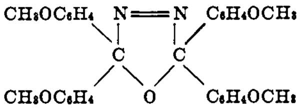
Thiirane	Starting material	Reagent	Yield, %	Ref
	$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>CN_2$	$(C_6H_5S)_2C{=}S$	*Ca.* 60	195
	$\begin{matrix}CH_3C_6H_4\\CH_3C_6H_4\end{matrix}\!>CN_2$	$(CH_3C_6H_5S)_2C{=}S$	...	195
 *trans*	 *trans*	$(H_2N)_2CS$	86	115
cis	*cis*	$(H_2N)_2CS$	64	115
	$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>CN_2$	$C_6H_5\overset{\overset{S}{\|}}{C}Cl$	...	224
	$\begin{matrix}C_6H_4\\\vert\\C_6H_4\end{matrix}\!>CN_2$	$C_6H_5\overset{\overset{S}{\|}}{C}Cl$	...	224
		H_2S	85	199
	$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>CN_2$	$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>C{=}S$	...	223
	$(C_6H_5)_2CN_2$	S		125
		S	90–95	202
	$\begin{matrix}C_6H_4\\\vert\\C_6H_4\end{matrix}\!>CN_2$	$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>C{=}S$	...	223
	$(C_6H_5)_2CN_2$	$\begin{matrix}C_6H_4\\\vert\\C_6H_4\end{matrix}\!>CS$	...	125
	$\begin{matrix}C_6H_4\\\vert\\C_6H_4\end{matrix}\!>C{=}S$	$NaC{\equiv}CH$	...	187
		Raney Ni	90	187
	$\begin{matrix}C_6H_4\\\vert\\C_6H_4\end{matrix}\!>CN_2$	$\begin{matrix}C_6H_4\\\vert\\C_6H_4\end{matrix}\!>C{=}S$	68	125
		S	60	125
	$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>CN_2$	$\begin{matrix}CH_3OC_6H_5\\CH_3OC_6H_5\end{matrix}\!>C{=}S$	...	223
	$\begin{matrix}CH_3OC_6H_4\\CH_3OC_6H_4\end{matrix}\!>C{=}S$	$\left\{\begin{matrix}C_6H_5MgBr & \text{or}\\C_6H_5MgI & \text{or}\\C_{10}H_{10}MgBr & \text{or}\\CH_3OC_6H_4MgBr & \end{matrix}\right\}$	70	193
	$\begin{matrix}CH_3OC_6H_4\\CH_3OC_6H_4\end{matrix}\!>C{=}S$	$Mg + MgI_2$	40	194
		H_2S	...	199

TABLE I (*Continued*)

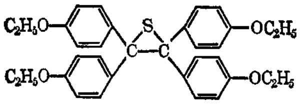
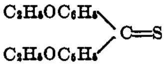
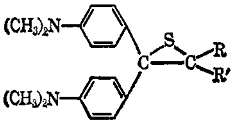
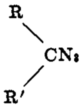
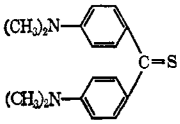
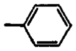
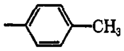
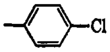
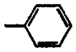
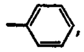
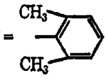
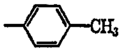
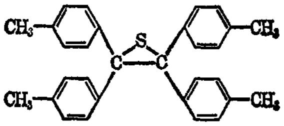
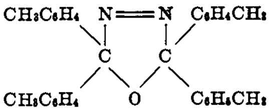
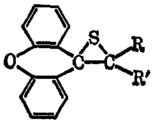
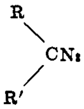
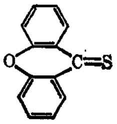
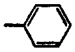
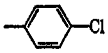
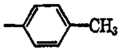
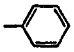
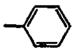
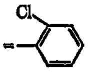
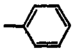
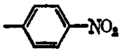
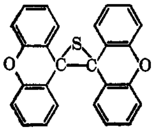
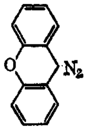
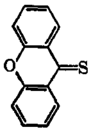
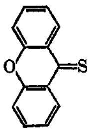
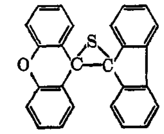
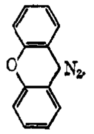
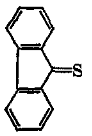
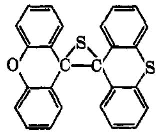
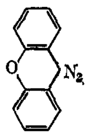
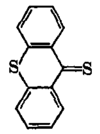
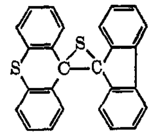
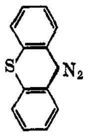
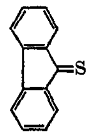
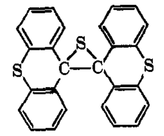
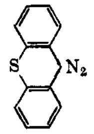
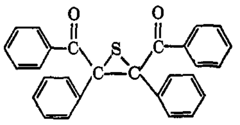
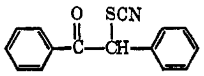
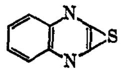
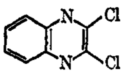
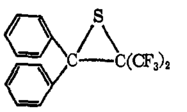
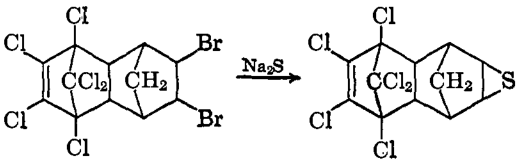
Thiirane	Starting material	Reagent	Yield, %	Ref
	$(CH_3OC_6H_4)_2CN_2$	S	90-95	202
	 $(C_2H_5OC_6H_4)_2C{=}S$	C_6H_5MgBr	...	193
	 $RR'CN_2$			
R = R′ = 			...	223
			Very good	201
			Very good	201
R = CH_3, R′ = 			Very good	201
R = , R′ = 			Very good	201
R = CH_3, R′ = 			Very good	201
		H_2S	...	199
	 $RR'CN_2$		...	
R = R′ = 			...	197
			Very good	201
			Very good	201
R = CH_3, R′ = 			Very good	201
R = , R′ = 			Very good	201
R = , R′ = 			Very good	201
			85	125
		S	70	125
		S	93	202
		$NaC{=}CH$	...	187

TABLE I (*Continued*)

Thiirane	Starting material	Reagent	Yield, %	Ref
			...	125
			80	125
			...	125
		S	60	125
		NaH	85	55
		$(H_2N)_2CS$		242
	$(C_6H_5)_2CN_2$	$(CF_3)_2C{=}S$	...	150

E. FROM DIHALOALKANES

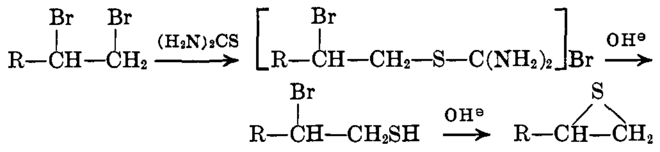
Direct conversion of ethylene dichloride, ethylene dibromide, or similar 1,2-dihaloalkanes with alkali sulfides leads to polymeric ethylene sulfides (50). The only example described in the literature for the direct synthesis of a thiirane from a dihalide and alkali sulfide is the following reaction (221)



In this case, polymerization is probably suppressed for steric reasons. Four-, five- and six-membered thiacycloalkanes, on the other hand, are readily formed from the corresponding α,ω-dihaloalkanes upon treatment with sodium sulfide.

The formation of ethylene sulfide in a yield of 20% has been observed on reaction of 1,2-dibromoethane with hexamethylcyclotrisilthiane (1).

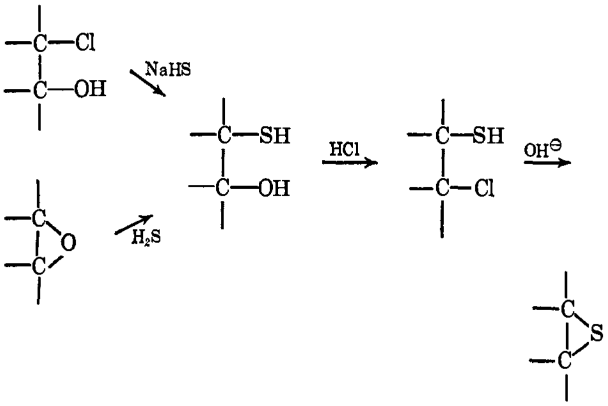
An indirect route for making thiiranes consists in the reaction of 1,2-dihalides with thiourea to give the monothiuronium salt and the decomposition of the latter by alkali (252). It may be assumed that the generation of the thiiranes entails the intermediate formation of 2-halo mercaptans which are not isolated.



The reaction cannot be carried out with ethylene dibromide, since this results in the bisthiuronium salt yielding dithioethylene glycol upon hydrolysis. It is true that a monothiouronium salt is obtained from 1,2-dibromopropane; however, allyl mercaptan is obtained upon hydrolysis. The method was successfully applied to the synthesis of 1-hexene sulfide (yield 64%), styrene sulfide (yield 34%) (252), and quinoxaline 2,3-sulfide (242).

F. FROM HALO MERCAPTANS

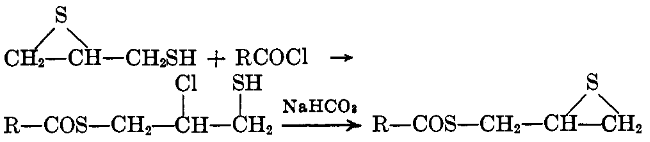
Just as epoxides are obtainable from 2-halo alcohols (chlorohydrins) and alkali, thiiranes are derived by treatment of 2-halo mercaptans with alkali. 2-Halo mercaptans are preferably prepared from 2-hydroxy mercaptans which in turn can be made from 1,2-halohydrins or epoxides.



In the presence of strong alkalies such as NaOH, 2-chlororoethyl mercaptan is merely converted to polymeric ethylene sulfide; treatment with water has the same effect (16); *i.e.*, too high or too low pH values lead to polymerization of the ethylene sulfide formed as intermediate. However, if the pH value is kept in a range between 5.5 and 11.5, preferably between 7.5 and 9.5, ethylene sulfide is obtained in high yield. For this purpose, weak alkalies such as $NaHCO_3$, CH_3COONa, NaH_2PO_4 or Na_2HPO_4, and NaHS are recommended (32); the most common reagent is $NaHCO_3$. Since 2-halo mercaptans are fairly unstable, they are usually not isolated; instead the crude product from the conversion of 2-hydroxy mercaptans with hydrochloric acid is treated with aqueous $NaHCO_3$ solution after the excess acid has been removed (57, 175). Yields between 35 and 90% are reported.

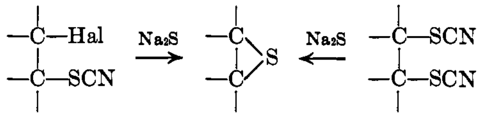
The following compounds were prepared by this method: ethylene sulfide (32), 2-butene sulfide (32, 175), dithioglycidol (57), 2-methyldithioglycidol (57).

A specific variation of this method comprises the reaction of dithioglycidol with carboxylic chlorides and subsequent treatment, without isolation, with sodium hydrogen carbonate to give S-acyl derivatives of dithioglycidol. Yields between 35 and 99% are reported (5).



G. FROM HALO THIOCYANATES OR DITHIOCYANATES

Thiiranes are also obtained by interaction of 2-halo thiocyanates or of 1,2-bisthiocyanates with sodium sulfide (50, 51). This reaction is of historical importance, since it represents the first method for making alkylene sulfides (Delépine, 1920). The starting compounds are obtainable by conversion of 1,2-dihalides with alkali thiocyanates or by addition of thiocyanogen or thiocyanogen chloride to olefins. As both of the reactions are not very convenient, Delépine's method today is of importance only in special cases. The reaction involves Walden inversion caused by *trans* addition of the reagent (145).



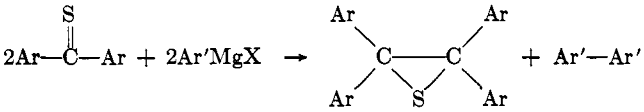
The conversion is generally carried out with aqueous sodium sulfide solution and preferably alcohol is added as solubilizer. The reaction takes place at room temperature or with gentle heating. In a modified method alkali is used instead of Na_2S (145, 191).

The yields of this reaction are reported to be relatively high, although exact figures are not disclosed. The following compounds were prepared on the basis of 2-halo thiocyanates: ethylene sulfide (50), propene sulfide (51), 1-butene sulfide (51), cyclohexene sulfide (71); on the basis of 1,2-bisthiocyanates: ethylene sulfide (50), propene sulfide (51), 1-butene sulfide (51), trimethylethylene sulfide (26), tetramethylethylene sulfide (256), cyclohexene sulfide (158), cyclooctene sulfide (174), 2,2-pentamethylenethylene sulfide (158), and various thiiranylcarboxylic acids (145, 191).

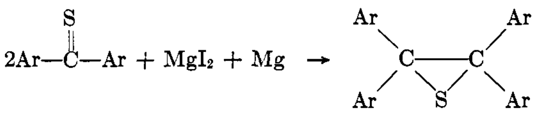
The conversion of thiocyanato alcohols and their sulfonic esters to thiiranes has been mentioned in sections C and D, respectively. In one case the conversion of an α-thiocyanoketone to a thiirane has been accomplished by means of sodium hydride (55). The reaction seems to proceed *via* several steps.

H. FROM THIOKETONES, THIOESTERS, AND THIOCARBOXYLIC CHLORIDES

Aromatic thioketones, upon interaction with Grignard compounds, give tetraarylethylene sulfides (193).



A modification of the method comprises the conversion of aromatic thioketones with magnesium subiodide (194). The yields of this procedure are inferior to those of the Grignard reaction. Since aromatically substituted ethylene sulfides split off sulfur at elevated temperatures with simultaneous conversion

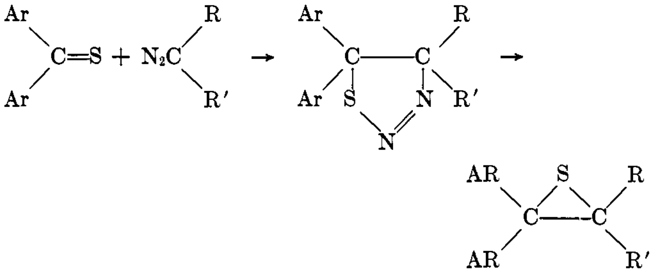


to the corresponding olefins, unnecessary heating has to be avoided when the mixture is worked up.

This method was used for making compounds of the above structure, where Ar = p-$CH_3OC_6H_5$– and p-$C_2H_5OC_6H_4$– (193, 194).

Also treatment of thioketones with sodium acetylide results in the formation of thiiranes besides furnishing dimeric thioketones as the main product (187).

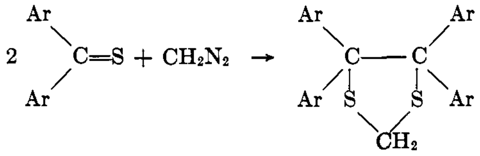
Interaction of diazoalkanes with thioketones is another route for making thiiranes (223). An unstable five-membered ring is postulated as intermediate product. Only aromatic thioketones have been investigated so far.



Diphenyldiazomethane, diazofluorene, and phenyldiazomethane react readily with thiobenzophenone. Ethyl diazoacetate and phenylbenzoyldiazomethane react slowly. No reaction was observed with diethyl diazomalonate and ethylbenzoyl diazoacetate (223).

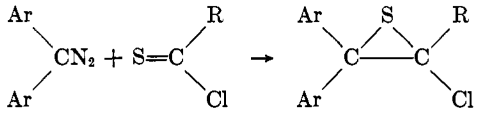
p,p'-Dimethoxythiobenzophenone and bis(*p*-dimethylamino)thiobenzophenone react with diphenyldiazomethane at a lower rate than does thiobenzophenone (223). Interaction of various aryldiazomethanes with bis(*p*-dimethylamino)thiobenzophenone furnished the corresponding thiiranes in excellent yields (201). Xanthione (201), thiofluorenone, and thiaxanthione (125) may be likewise converted to the corresponding thiiranes in high yields.

In contrast to the assumptions of Staudinger (223), Schönberg (198) postulates 1,3-dithiolanes as intermediates, since the reaction of thiobenzophenone with diazomethane, diazoethane, and ethyl diazoacetate furnished only dithiolanes instead of thiiranes (198).



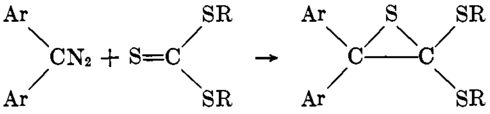
The only exception among aliphatic compounds are highly fluorinated thiocarbonyl compounds which react in the same manner with diazoalkanes. Examples include the reaction of hexafluorothioacetone with diphenyldiazomethane or with ethyl diazoacetate (150).

Chloro-substituted aromatic thiiranes were obtained by conversion of aromatically substituted diazoalkanes with thiocarboxylic acid chlorides, thiophosgene, dithiocarbonic ester chlorides, and thiocarbonic ester chlorides.



The following thiiranes were synthesized: Ar = C_6H_5, R = Cl and C_6H_5 (224); R = OC_6H_5 and SC_6H_5 (196); Ar, Ar = diphenylene, R = Cl and C_6H_5 (224), R = OC_6H_5 and SC_6H_5 (195).

The use of trithiocarbonates in an analogous process resulted in thiirane disulfides.

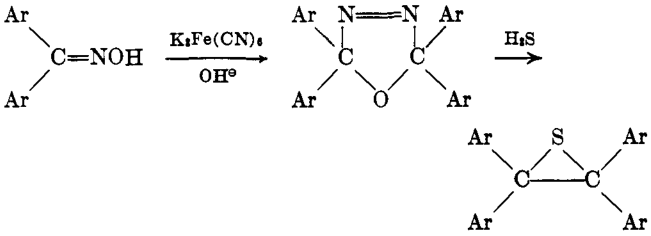


The synthesis covered: Ar = C_6H_5, R = C_6H_6 (195); Ar = p-$CH_3C_6H_4$, R = p-$CH_3C_6H_4$ (195).

Thiiranes were not obtained from the conversion of phenylbenzoyldiazomethane with thiophosgene, ethyl diazoacetate with thiobenzoyl chloride (224), diphenyldiazomethane with thiourea, thiobenzamide, ethyl dithiobenzoate, carbon disulfide, and phenylisothiocyanate (223), and from diazofluorene with phenylthiocarbonyl chloride (195).

I. FROM OXADIAZOLINES

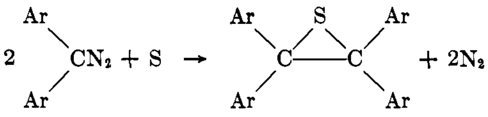
By interaction with H_2S, 2,2,5,5-tetraaryl-Δ^3-1,3,4-oxadiazolines (obtained by oxidation of aromatic ketoximes) are converted to the corresponding tetraarylthiiranes (199).



The following compounds were prepared: Ar = C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$ (199).

J. FROM DIAZOALKANES AND SULFUR

Diaryldiazomethanes can be converted to symmetric tetraarylthiiranes by treatment with elemental sulfur.



The reaction, which has been discovered simultaneously by two different research groups (125, 202), takes place at room temperature; it gives high yields and is accelerated by ultraviolet light.

Besides diphenyldiazomethane (125, 202) and bis-(4-methoxyphenyl)diazomethane (202) the condensed ring compounds 9-diazofluorene (125), 9-diazoxanthene (125), and 9-diazooxanthrene (125, 202) have been converted in this way.

K. FROM OLEFINS

Attempts at the direct addition of elemental sulfur to olefins, analogous to the synthesis of ethylene oxide from ethylene and oxygen, have so far not furnished thiiranes. It is reported in various patents (48, 171) that the conversion of unsaturated ketones, unsaturated carboxylic acids, or unsaturated carboxylic esters with sulfur results in thiirane compounds. However, definite compounds have not been isolated so far, nor is there any evidence establishing the presence of thiirane groups. The assumption that thiirane compounds are formed is based exclusively on the observation that hydrogen sulfide does not evolve during the reaction. Yet this might also be interpreted in terms of an intermolecular addition of sulfur. It becomes apparent from reliable scientific investigations that the reaction of sulfur with unsaturated compounds leads primarily to disulfides and polysulfides, in addition to a number of by-products not containing thiirane groups (9, 13, 71). A review on the reaction of sulfur with olefins has recently been published by Bateman and Moore (14).

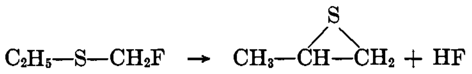
Evidence contradicting the statement of the mentioned patents is given involuntarily by the inventor himself. Dearborn (49) claims the addition of halogen to such "thiirane carboxylic esters" to give thiirane dihalides and thiirane tetrahalides. Yet compounds of this type are not capable of existence. Culvenor, Davis, and Heath (39) treated cyclohexene with sulfur under various conditions without obtaining cyclohexene sulfide.

Similar results are reported for the conversion of olefins with hydrogen sulfide and mercaptans (59, 137) which failed to yield any thiirane products. On the other hand, small yields of thiiranes were isolated as by-products after causing ethylene, propylene, and cyclohexene to react with diethyl tetrasulfide at 150° (112). In this case, the diethyl tetrasulfide apparently gives off monoatomic sulfur on heating.

If carbonyl sulfide is irradiated by light of a wavelength of 2550 to 2290 A in the presence of ethylene or propylene in vapor phase at 25°, the formation of ethylene sulfide and propene sulfide, respectively, is observed (230). The yield is high, but the reaction rate is extremely low; within 60 min, conversions of less than 0.1% have been measured. These experiments, too, show that monoatomic sulfur would readily react with olefins to give thiiranes and that the problem in the "direct synthesis" lies in the difficulty of obtaining monoatomic sulfur. In fact, the formation of cyclohexene sulfide from cyclohexene has recently be used as a means for detecting monatomic sulfur (192a).

L. FROM CHLOROMETHYL SULFIDES

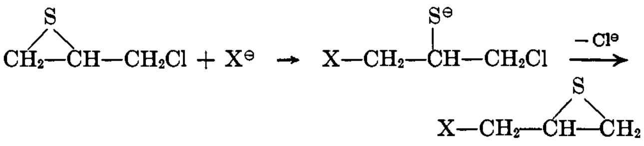
Petrov and Sokolskii (173) made the observation that the reaction of ethylchloromethyl sulfide with HF–KF at −15° gives propene sulfide instead of the expected fluoromethyl compound. Apparently, this is due to a decomposition of the fluoromethyl sulfide.



Other fluoromethyl sulfides, too, decompose at room temperature or elevated temperatures with the splitting off of HF; however, thiiranes were not isolated in those cases (173).

M. FROM 3-CHLOROPROPENE SULFIDE AND FROM DITHIOGLYCIDOL

Reaction of 3-chloropropene sulfide with nucleophilic reagents may open the thiirane ring to yield a derivative of 1-chloropropane-2-thiol which, on treatment with alkali, is converted to a new thiirane compound.

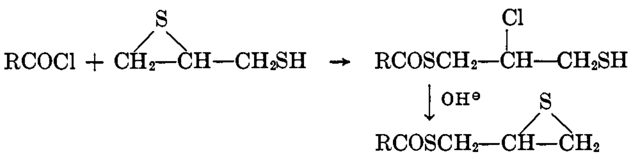


This type of reaction has been realized with thiophosphates (X = $(RO)_2P(O)S$–) and with dithiophosphates (X = $(RO)_2P(S)S$–) (133). Interaction with the ammonium salts of thiophosphates gives nearly quantitative yields of thioglycidyl thiophosphates.

From secondary amines (X = R_2N–) the corresponding tertiary glycidylamines are formed (229). In this case no alkali is required, since the amine itself acts as a base.

Alkali phenoxides (X = ArO–), on reaction with chloropropene sulfide, furnish the corresponding aryl thioglycidyl ethers, as well as aryloxythietanes and polymers, depending on the solvent and reaction conditions used (192). Direct chlorine displacement is supposed in this case rather than a ring-opening mechanism.

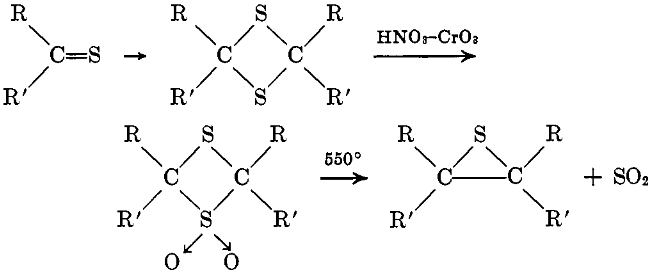
A similar ring opening and new ring-closing reaction is the treatment of dithioglycidol (3-mercaptopropene sulfide) with carboxylic halides or with chlorocarbonates



(5). Aqueous sodium hydrogen carbonate is recommended as a suitable base.

N. FROM DITHIETANE DIOXIDES

Highly fluorinated thioketones are easily dimerized to dithietanes, which can be oxidized to their asymmetric dioxides. On pyrolysis these dioxides split off sulfur dioxide yielding highly fluorinated thiiranes (150).



R, R' = F, CF_3, CF_2Cl

A summary of the preparation of thiiranes is given in Table I.

III. PHYSICAL PROPERTIES

The structure of ethylene sulfide was calculated by Cunningham and his co-workers (41) on the basis of microwave measurements. As reported, ethylene sulfide has the following atomic distances and angles: C–C 1.492, C–S 1.819, C–H 1.078 A, ∠H–C–H 116° 00′, ∠C–S–C 65° 48′. These values suggest a partial double bond character of the C–C bond of ethylene sulfide. This applies to an even greater extent to ethylene oxide (41). Reported values for propene sulfide are: C–H 1.09, $C–C_{methyl}$ 1.513 A, ∠H–C–H 109° 28′ (25). The strain energy of ethylene sulfide was estimated from the difference between the heat of formation and the individual bond energies (162). It amounts to 9 kcal/mole, compared with 13 kcal/mole for ethylene oxide and 25 kcal/mole for cyclopropane. More recent determinations of the strain energy from the difference between the measured and the calculated heat of formation show 18.6 for ethylene sulfide, about 28 for ethylene oxide, about 23 for ethylenimine, and 27.5 kcal/mole for cyclopropane (34). In any case, ethylene sulfide features a lower ring strain than other saturated three-membered rings. Difficult to explain is the strong difference of the proton–proton coupling constants of propene oxide and propene sulfide—measured from nmr spectra—whereas no difference in this respect is found between ethylene oxide and ethylene sulfide (161). However, large differences have been reported for the C^{13}–H couplings of ethylene oxide, sulfide, and imine (157).

The electron donor ability of different saturated hetero rings toward phenol has been determined by infrared measurements at different temperatures. Cyclic sulfides have been found to be weaker donors than cyclic ethers and these are weaker than cyclic imines. From the cyclic sulfides the five-membered rings form the strongest hydrogen bridges, thiiranes the weakest. A similar relationship between ring strain and donor ability is found with the cyclic ethers and imines showing increased s character of the free electrons at the heteroatom with increasing ring strain (129). Analogous spectroscopic measurements on the iodine complexes of different cyclic sulfides also indicate a decrease in electron donor ability in the order: five- > six- > four- > three-membered rings (236).

A further measure for the electron density at the heteroatom is the chemical shift of the α- and β-CH_2 groups in the magnetic proton resonance spectrum. According to these measurements, the electron density at the heteroatom of saturated heterocycles decreases in the order: N > O > S. With all three types the three-membered compounds show the lowest electron density at the heteroatom (90, 130).

The infrared absorption of ethylene sulfide was measured in the gaseous phase (240) and in the liquid phase (88); the infrared absorption of polyethylene sulfide (in Nujol) was measured as well (88). The Raman spectrum of ethylene sulfide is likewise known (239, 240). Sheppard (209) measured the infrared absorption of cyclohexene sulfide but did not assign a specific band to the C–S bond. Guthrie, *et al.* (88), assigned the bands at 625 and 660 cm^{-1} to the C–S stretching vibration of ethylene sulfide. The force constants of ethylene sulfide have been calculated from spectroscopic data and have been found to be very similar to the known constants of ethylene oxide (248).

Ultraviolet absorption of ethylene sulfide, propene sulfide, and cyclohexene sulfide in solution and gaseous phase was measured by Davis (46). In isooctane solution, a peak at 2610–2625 A and a minimum at approximately 2370 A were found to be characteristic of thiiranes. The ultraviolet spectra of styrene sulfides substituted in the *para* position indicate that there is a certain conjugation of the thiirane ring with the benzene ring suggesting a pseudo-unsaturated character or electron-attracting properties of the thiirane ring (231). Optical rotatory dispersion and circular dichroism of optical active thiiranes have been measured (15, 56).

The potential functions for hindered internal rotation of the methyl group in propene sulfide has been determined from the far-infrared spectrum (72).

From the electron impact spectrum of ethylene sulfide its molar ionization potential has been determined to be 8.87 ± 0.15 (80) and 8.9–9.1 ev (118).

The influence of molecular configuration on the chemical shift of thiirane protons has been studied by nmr spectroscopy of steroidal thiiranes (241).

The dipole moment of ethylene sulfide totals 1.66 D. (85), that of ethylene oxide 1.88 D., that of propene sulfide 1.95 D. (25). The molar refraction of ethylene sulfide was found to be 17.33 (85), while the equation $R_D = 17.33 + 4.635Z$ (Z = number of C atoms of the alkyl group) applies to alkyl-substituted thiiranes (141). The refractive indices of the individual thiiranes are always larger than those of their oxygen analogs.

Corresponding to their higher molecular weight thiiranes always have lower vapor pressures than the equivalent oxiranes. The vapor pressure of ethylene sulfide was measured between 18 and 88° and the equation $\log p = 7.03725 - 1194.37(t + 232.42)$ derived (88). From this, the heat of vaporization (at 25°) is calculated to be 7240 ± 5 cal/mole (88). The heat of formation of ethylene sulfide, determined from its heat of combustion, was found to be 19.29 ± 0.16 kcal/mole for the real gas under saturation pressure (88). The thermodynamic functions $(F_T^\circ - H_0^\circ)T$, $H_T^\circ - H_0^\circ$, S°, and C_p° were calculated from microwave spectra and infrared spectra of ethylene sulfide (88).

Calorimetric determinations of heat of combustion and heat of formation of a number of thiiranes—at 25° in liquid phase—furnished the following values (232).

	H_c, kcal/mole	H_f, kcal/mole
Ethylene sulfide	−481.02	+12.38
Propene sulfide	−633.75	+2.74
Isobutene sulfide	−787.56	−5.82
2-Butene sulfide, *cis*	−787.56	−5.82
2-Butene sulfide, *trans*	−786.32	−7.06
2-Methyl-2-butene sulfide	−941.26	−14.49
2,3-Dimethyl-2-butene sulfide	−1098.24	−19.88

The corresponding values for about 100 organic sulfur compounds, including some thiiranes, have been tabulated by Mackle and O'Hara (136).

IV. REACTIONS

Considering the multitude of reactions which thiiranes are able to undergo, fundamental information is still scarce in this field. Much of the information is published in patents or short communications. Some statements reported in the earlier literature have later been found incorrect, and sometimes even those corrections were later disproved. It has only been in the last few years that more fundamental investigations on the reactivity of thiiranes were conducted. This lack of information may be attributed to the difficult availability of thiiranes and the limited storability and the unpleasant odor of the lower representatives of this class. In view of the recent development of more convenient methods of synthesis, further basic studies on the reactions of thiiranes may be expected in the future.

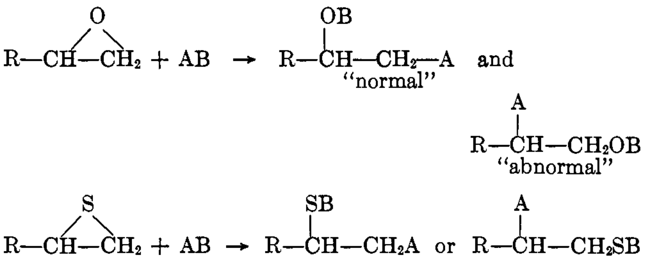
Similar to oxiranes, all reactions of thiiranes involve ring opening. The polarity of the C–S bond is smaller than that of the C–O bond, as is demonstrated also by the difference in the dipole moments of ethylene sulfide and ethylene oxide. The electron density at the oxygen atom in oxiranes is higher than that at the sulfur atom in thiiranes.

Hence, thiiranes are expected to be less reactive toward electrophilic reagents than oxiranes, which seems to be true in some cases. No clear rule can be outlined about the reactivity of thiiranes toward nucleophilic reactants in comparison with oxiranes; in practice thiiranes seem to have about the same or a little higher reactivity.

In non-ionic reactions involving ring cleavage thiiranes are more reactive than oxiranes. Obviously the lower ring strain is overruled by the lower bond energy of C–S compared with C–O bonds. Thus thermal desulfurization of thiiranes is much more readily achieved than deoxygenation of oxiranes. In reactions of this type electron-attracting substituents enhance the reactivity of thiiranes drastically. Little is known about radical reactions with thiiranes.

The most important reactions from the point of view of organic syntheses are the additions of ethylene sulfide to compounds with active hydrogen atoms, which always involve mercaptoethylation. Mercaptoethylation may be catalyzed by acids or bases; the latter are preferred and involve a nucleophilic mechanism. Polymerization may be considered as a special case of mercaptoethylation.

While reactions of asymmetric oxiranes entailing ring opening frequently yield a mixture of the two possible isomers, with the product of the ring-opening reaction at the primary C atom prevailing (this mechanism is therefore referred to as "normal addition"), the two possible isomers could never be definitely isolated from reactions of asymmetric thiiranes. The predominant or exclusive formation of the product of the "normal" or "abnormal" addition has been observed in each instance. (Some authors who report to have obtained a mixture of isomers failed to prove this statement.) The reaction scheme is



For anionic (nucelophilic) additions the "normal" ring opening at the primary carbon atom seems to be preferred, whereas the "abnormal" opening at the secondary (or tertiary) carbon atom has usually been observed for cationic (electrophilic) additions. However, no systematic studies have been conducted on this subject; also the effect of different substituents on addition reactions of thiiranes is largely unexplored.

A. POLYMERIZATION

A review on poly(alkylene sulfides) has been presented by Davis and Fettes (45).

Ethylene sulfide polymerizes so readily (without initiator) that poly(ethylene sulfide) had been known 80 years before the monomer was synthesized (132). Various attempts made in the 19th century to convert ethylene chloride or ethylene bromide with K_2S or Na_2S furnished poly(ethylene sulfide) described as a white, amorphous, insoluble substance of the composition $(C_2H_4S)_x$ (35, 104, 138, 142). The earlier authors distinguished between a modification (mp 145°) which does not depolymerize upon heating and a modification (mp 113°) which is converted to dithiane upon heating. Crafts demonstrated that poly(ethylene sulfides) of this type contain organically combined halogen in substantial proportion even if excess sodium sulfide is used (35). In more recent papers the polymers from ethylene bromide and sodium sulfide are reported not to melt below 180° (79) or 187–190°, respectively (124). The polymer $(C_2H_4S)_x$ was also obtained from 2,2′-dichlorodiethyl sulfide and potassium sulfide or from disodium ethylenedithiolate and ethylene dibromide (149). 2,2′-Dichlorodiethyl sulfide on treatment with sodium metal is split to gaseous ethylene and a poly(ethylene sulfide) melting at 158–160° (103). This polymer is reported to be soluble in aniline, nitrobenzene, or camphor at 170° and could be oxidized by treatment with H_2O_2 in acetic acid to a substance melting at 312°, whose analysis agrees approximately with poly(ethylene sulfone). In 1863 already poly(propene sulfide) was prepared from 1,2-dibromopropane; this product was described to constitute a white, amorphous, insoluble powder (104, 149). On heating it did not depolymerize to form the corresponding dimer—dimethyldithiane (104, 149).

Bennett (16) obtained poly(ethylene sulfide) by interaction of 2-hydroxyethyl mercaptan with 50% sulfuric acid at boiling temperature. Somewhat different modifications, A and B, were reported which were insoluble in conventional solvents but soluble in fused camphor. Fraction A melted at around 193–197°; its molecular weight determined by cryoscopic analysis in camphor ranged between 1400 and 1700. Fraction B melted at approximately 177–180° and showed a molecular weight of 1720. Dry heating of A furnished a yellow oil of unpleasant odor, while heating of B gave substantial quantities of crystalline dithiane. On heating in phenol both substances failed to give dithiane. Similar polymers not described in detail were obtained from the dehydration of 2-hydroxyethyl mercaptan with phosphoric acid, zinc chloride, or phosphorus pentoxide. Another sample of poly(ethylene sulfide) which Bennett obtained by causing 2-chloroethyl mercaptan to react with caustic soda solution melted at 170–175°. More recent repetition of Bennett's work furnished poly(ethylene sulfide) which melted at 158–165° (103). It was not before 1920, when Delépine was successful in making the monomer in pure form, that the actual research on the polymerization of ethylene sulfide and its homologs started.

According to Delépine (52) *ethylene sulfide*, on storing at room temperature, gradually polymerizes to form a white mass. This was confirmed by all later investigations. Delépine reports (50, 52) that the polymerization is accelerated by the addition of hydrochloric acid, nitric acid, sulfuric acid, aqueous or alcoholic ammonia solutions, concentrated caustic soda solution, and to a lesser extent by acetic acid or calcium chloride. While all of these polymers are colorless, the addition of pyridine results in a dark brown resin. Analysis of the terminal groups of some of these polymers showed that they had a low degree of polymerization. The product polymerized with acetic acid, for example, had a degree of polymerization of $n = 12$ (52), while polymerization with ammonia furnished a product with $n = 6$ (50).

After Delépine's work, poly(ethylene sulfide) was neglected almost completely for 30 years. Only the more recent polymer science has taken a more or less superficial interest in the polymerization of ethylene sulfide.

Braz (24) made the statement that the reaction of ethylene sulfide with molar quantities of primary or secondary amines to give the corresponding 2-mercaptoethylamines is always accompanied by polymerization. The use of polar solvents and strongly basic amines such as diethylamine makes the polymerization become the main reaction.

Furukawa, Nomura, and Oda (76) described the poly(ethylene sulfide) obtained in the absence of catalysts as a white powder of mp 140–150°, which is insoluble in conventional solvents.

Ohta, Kondo, and Ohi (167) used aqueous caustic soda solution in methanol for making a polymer of mp 182–185°. Initiation with ammonia, piperidine, pyridine, methylamine, hydrazine, ethylenediamine, and hydrochloric acid furnished polymers whose molecular weights, calculated from the N or Cl content, ranged between 419 and 960. Variation of the NH_3 concentration did not affect the molecular weight of the products. The rate of polymerization is higher in base-catalyzed reactions than in the presence of acids.

Boileau and Sigwalt (18) polymerized ethylene sulfide by means of NaOH, C_2H_5ONa, and primary amines. The resultant polymers melted below 180°. The molecular weights determined by cryoscopic analysis in camphor were below 1000. A product polymerized in the presence of small quantities of NaOH was insoluble in chloroform, ether, dioxane, benzene, CS_2, and the like. Apparently this insolubility is due to pronounced crystallinity, since the polymer shows a distinct X-ray diffraction pattern. In a second paper the same authors describe the polymerization in tetrahydrofuran at −50° (19). By using naphthalenesodium as catalyst they obtained polymers which melt at 208–210°, whereas reactions catalyzed by boron fluoride etherate furnished a polymer melting at 192–195°. The polymers could be melt-spun to fibers, for which the crystallographic constants have been determined by X-ray analysis.

Propene sulfide and *1-butene sulfide* have a much lower tendency to polymerization. On storing these compounds for 6 months Delépine did not note any change (51). After adding concentrated H_2SO_4, a transparent gel is formed rapidly; the use of alkali or ammonia involves slow polymerization to viscous products; no reaction is observed with acetic acid; HNO_3, HCl, and pyridine react without polymerization (51).

For comparison, Marvel and Weil (140) prepared poly(propene sulfide) by heating the monomer with catalytic amounts of sodium ethoxide. The polymer was viscous soluble in dioxane and chloroform, and insoluble in ether and methanol. Carrying out the polymerization in dioxane furnished a solid polymer. Oxidation with peracetic acid leads to the corresponding polysulfone.

Boileau and Sigwalt (18) described a more elaborate study of the polymerization of propene sulfide. Cationic catalysts such as $TiCl_4$ and $AlCl_3$ yielded low-molecular-weight polymers; anionic catalysts including $NaNH_2$, KOH, and Na gave high-molecular-weight products upon polymerization with quantities of about 2% of catalyst at room temperature. Other anionic catalysts such as $Al(C_2H_5)_3$ or butyllithium were unsuccessful. All samples were soluble in organic solvents such as chloroform, CH_2Cl_2, CCl_4, dioxane, THF, benzene, etc., and insoluble in ether, acetone, alcohols, cyclohexane, and water. Relative molecular weight determinations were made by viscosimetry. The highest viscosity totaling $[\eta] = 2.65$ was determined for a specimen polymerized with sodium metal. Products of $[\eta] > 1$ are elastic polymers; products of $[\eta] < 1$ constitute viscous oils.

In an excellent paper the same authors refer to polymerization studies using naphthalenesodium in tetrahydrofuran (20). By using ultrahigh purity reagents in a hermetically sealed apparatus they were able to obtain polymers of a very low dispersity ($M_n/M_w \approx 1$) and molecular weights of 70,000 to 320,000. The molecular weights of these polymers determined by osmometry, light scattering, and end group analysis agreed very well with the molecular weights calculated from the monomer/catalyst ratio. Thus, this system represents a classical type of "living polymers" without the possibility of chain transfer to the monomer.

In the presence of a complex salt of $CdCl_2$, NH_4Cl, and K_2S as catalyst propene sulfide can be polymerized to give high-molecular-weight products (63). While zinc catalysts tend to produce amorphous, largely atactic poly(propene sulfide), cadmium salts tend to produce a crystalline polymer, which is believed to be the isotactic modification melting at 40–41° (3). The glass transition temperature lies at −52.5°.

Copolymers of propene sulfide containing about 25–30% ethylene sulfide and about 5% of an unsaturated thiirane are tough white gums, which can be vulcanized with sulfur in the presence of conventional vulcanization accelerators and fillers. The resulting polysulfide rubber shows promising technological elastomer properties (3).

Polymerization of *3-chloropropene sulfide* in the presence of catalytic quantities of sulfuric acid was reported by Furukawa, Nomura, and Oda (77, 78). At room temperature a colorless, soft resin is formed which is soluble in chloroform. Conversion of the product with aniline yielded a brittle resin showing 63% of the calculated nitrogen content. Polymerization with H_2SO_4 at elevated temperature furnished a dark brown, soft resin which is soluble in benzene. A molecular weight or approximately 1000 was determined by cryoscopy.

Polymeric *cyclohexene sulfide* was obtained by Mousseron (158) who tried to prepare the monomer. The polymer is soluble in benzene, insoluble in ether, and decomposes roughly at 165–170°. Culvenor, *et al.* (39), obtained viscous to solid polymers on treatment of cyclohexene sulfide with hydrazine, hydroxylamine, guanidine, *o*-aminophenol, sulfuric acid, alkali, or ammonia. A polymer melting at 71° has been obtained by using triethylaluminum as catalyst (10).

1-Octene sulfide, which is completely stable at room temperature and polymerizes only to a very low degree even at 140°, polymerizes rapidly on addition of lithium aluminum hydride, a typical anionic catalyst (153).

Styrene sulfide polymerizes slowly at room temperature. The polymerization can be catalytically accelerated by aluminum trialkyls or heavy-metal mercaptides. The polymers melt at 50–120°, are soluble in organic solvents, and have a noncrystalline structure. Their thermal stability is low; at 200° strong decomposition occurs; one of the resultant decomposition products is 2,5-diphenyldithiane. Oxidation with hydrogen peroxide leads to the corresponding polysulfones (165). Polymerization of styrene sulfide in the presence of basic or acidic catalysts furnishes solid or viscous products with molecular weights of 1000 to 2000 (134).

Polymerization of a *sugar episulfide* has been effected by using a boron fluoride catalyst. The soluble polymer is reported to have a number-average molecular weight of 72,000 (253).

Highly fluorinated thiiranes are capable of undergoing radical polymerization. By irradiation or with dinitrogen difluoride or organic peroxides as catalysts tetrafluoroethylene sulfide can be polymerized to a solid polythioether melting at 174–176°. Monochlorotrifluoroethylene sulfide under the same conditions yields oily polymers. In this way also copolymers of fluorinated thiiranes and other vinyl monomers have been obtained (147).

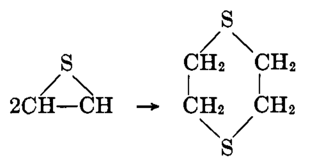
Copolymers of alkene sulfides and alkene oxides are claimed in a patent (11). Propene sulfide is used in the examples. Copolymerization is effected in the autoclave with alkali metal hydroxide at 25–175°. The resultant oils have a high stability to oxidation and are recommended as additives to lubricating oils or greases. Another patent teaches how to make block copolymers from alkene sulfides and alkene oxides by mathematical manipulation (131).

Copolymers of trioxane with small amounts of thiiranes show higher thermostability than the homopolymer or other copolymers of trioxane. Boron fluoride etherate is used as polymerization catalyst (119). However, the requirement of high amounts of catalyst and the low space-time yield are disadvantages of this copolymerization (251).

No copolymers could be obtained from propene sulfide and β-propiolactone (54).

B. DIMERIZATION

If a mixture of ethylene sulfide vapor and hydrogen sulfide is passed over Al_2O_3 at 220°, dithiane is obtained in a yield of 94% (257).



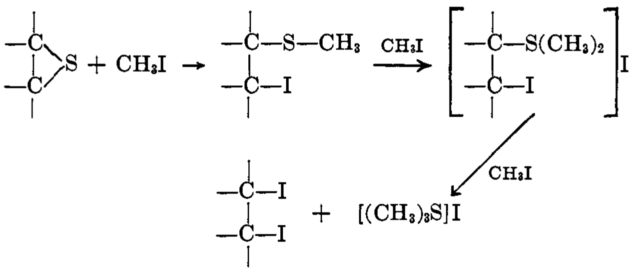
Dithiane is also formed on thermal decomposition of poly(ethylene sulfide) and especially on heating of the polymer in phenol at 160–180° (35, 104, 137). Treatment of styrene sulfide with dimethyl sulfate at 0–20° yields approximately 15% 2,5-diphenyldithiane (165). Heating of propene sulfide in the presence of toluenesulfonic acid yields 2,5-dimethyldithiane (180). Similarly, on refluxing dodecene-1 sulfide with potassium thiocyanate the 2,5-didecyldithiane is obtained (181).

C. ADDUCTS WITH HEAVY METAL SALTS

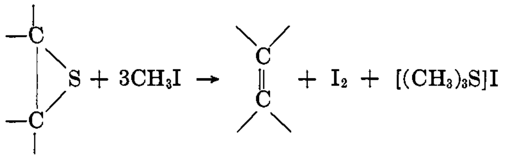
$AgNO_3$, $HgCl_2$, $PtCl_4$, K_2PtCl_6, and $AuCl_3$ combine with ethylene sulfide, propene sulfide, and 1-butene sulfide to form solid adducts which are insoluble in water, alcohol, or ether (50, 51). Closer examination of the yellow silver adduct of ethylene sulfide showed an approximate composition of $Ag(C_2H_4S)_3$. On storing it decomposes slowly to give free ethylene sulfide (52). Later investigations (39) confirmed that the precipitates of ethylene sulfide with Hg(II) salts cannot be purified.

D. REACTION WITH METHYL IODIDE

Cyclohexene sulfide, chloropropene sulfide, and propene sulfide combine with excess methyl iodide to give trimethylsulfonium iodide (39), *i.e.*, the *two* C–S bonds of the thiirane ring are split, probably *via* an intermediate methyl sulfide.



However, Schuetz and Jacobs could not isolate a 1,2-diiodide as intermediate (205). Helmkamp and Pettitt also failed to obtain the diiodide from the reaction of 2-butene sulfide and methyl iodide; however, on heating the solution butene is formed while iodine is set free.



The reaction is stereospecific; an unstable cyclic sulfonium salt is assumed as intermediate (97). Open-chain sulfonium salts as intermediates have been isolated in the reaction of butene sulfide or cyclohexene sulfide with methyl bromide (99).

Delépine, *et al.* (50, 51), reported that the reaction of methyl iodide with ethylene sulfide yields a crystalline salt of the approximate composition $C_2H_4S \cdot CH_3I$, while unstable salts are obtained with propene and butene sulfide. The lower is the thiirane; the higher is the excess of CH_3I that has to be used in order to obtain trimethylsulfonium iodide (39). Also alkoxypropene sulfides require a large excess of methyl iodide; if used in 30-fold excess, yields of 65–70% of trimethylsulfonium iodide were obtained (205).

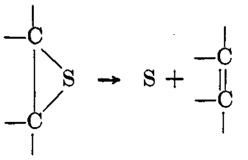
Since methyl iodide splits only *one* C–S bond of trimethylene sulfides (thietanes) and ring opening is not encountered with tetra- and pentamethylene sulfides, the reaction with CH_3I and the subsequent isolation and identification of the resultant quaternary salt provides a convenient way of distinguishing sulfur-containing ring systems of different size.

Formation of a cyclic sulfonium salt has recently been observed upon interaction of cyclooctene sulfide and trimethyloxonium 2,4,6-trinitrobenzenesulfonate, but not in the case of cyclohexene sulfide or 2-butene sulfide (174). Intermediate formation of cyclic sulfonium compounds of thiiranes is assumed for a number of reactions involving sulfides substituted in β position. A review on such reactions has been published recently (86).

E. DESULFURIZATION TO OLEFINS

1. *By Thermal Decomposition*

Aromatically substituted thiiranes split off elemental sulfur on heating and are converted to the corresponding olefins.

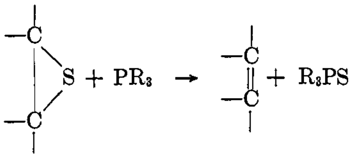


This is true especially if the thiirane is substituted by more than one aromatic nucleus. Electron-attracting groups such as C=O, COOR, and Cl likewise promote the abstraction of sulfur. Thus, styrene sulfide can still be distilled undecomposed under vacuum (87), while attempts to prepare stilbene sulfide or ethyl phenylthioglycidate furnished stilbene or ethyl cinnamate and sulfur at room temperature (38). Consequently, thiiranes with two or more aryl groups can only be isolated and purified by crystallization. To a small extent, olefin formation was also observed on extended heating of 1-octene sulfide (153) and cyclohexene sulfide (158).

Thermal decomposition of polyarylthiiranes to olefins occurs so easily that this reaction is regarded as one of the best methods to prepare certain arylolefins (223, 224). It is promoted by the addition of copper bronze and then requires temperatures below 100° (195, 196 174).

2. By Organophosphorus Compounds

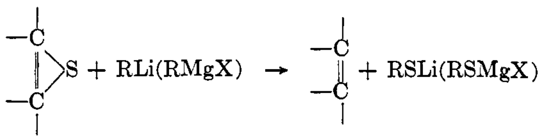
Aliphatic thiiranes which, on heating, tend to polymerize or dimerize rather than to decompose to olefin and sulfur can be desulfurized by interaction with trivalent organophosphorus compounds.



The following phosphorus compounds are used: triphenylphosphine (39, 47, 53), triethylphosphine (39), triethyl phosphite (31, 39, 47, 163, 204, 205), and tributylphosphine (53). With tertiary phosphines the reaction takes place readily at room temperature; gentle heating is recommended if phosphites are used. The yields of olefins and of phosphine sulfides range between 85 and 99%. The reaction is stereospecific (53, 163). The kinetics of the reaction were investigated (53); it is a first-order reaction with respect to the two reactants. This suggests a nucleophilic attack of the phosphorus at the sulfur atom. The following thiiranes were subjected to the reaction: ethylene sulfide (39, 205), propene sulfide (39, 204, 205), 1-butene sulfide (53), 2-butene sulfide (163, 53), isobutene sulfide (39), 3-chloropropene sulfide (39, 204, 205), styrene sulfide (205), cyclohexene sulfide (39, 47, 205), methoxypropene sulfide (204, 205), ethoxypropene sulfide (205), propoxypropene sulfide (205), isopropoxypropene sulfide (205), butoxypropene sulfide (205), phenoxypropene sulfide (205), and diethoxypropene sulfide (205), as well as a sugar episulfide (31).

3. By Organometallic Compounds

A further possibility of desulfurizing aliphatic thiiranes is their reaction with organometallic compounds, especially organolithium and Grignard compounds (22, 163, 205). The reaction yields olefin on the one hand and metal thiolate on the other.



The yields of olefins are lower than those obtained from the conversion with organophosphorus compounds. However, this reaction is important for the synthesis of certain thiophenols which are difficult to prepare by other methods (22); the yields total around 60%. With Grignard compounds the reaction is more complex; Bordwell, *et al.* (22), isolated only low yields (5–13%) of the corresponding thiols. Japanese authors (75) reported that β-phenylethyl mercaptan is formed upon interaction of ethylene sulfide with phenylmagnesium bromide. This suggests that the addition mechanism known for epoxides may also occur as a side reaction with thiiranes.

The following substances were subjected to the reaction: ethylene sulfide (22, 75), propene sulfide (22), 2-butene sulfide (163), cyclohexene sulfide (22), and a number of 2-alkoxypropene sulfides (205).

4. By Other Reagents

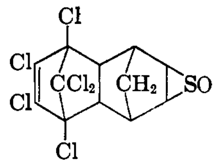
Stereospecific desulfurization of 2-butene sulfide has been observed on treatment with methyl iodide in boiling acetone (97, 99) or with catalytic amounts of iodine in benzene (98).

Certain thiiranes could be desulfurized quantitatively on treatment with lithium aluminum hydride (127, 144) or with potassium butoxide (146). Reaction of arylthiiranes with nascent hydrogen (Zn–CH_3COOH) also gives the corresponding olefins besides hydrogen sulfide (199).

F. OXIDATION

Nearly all attempts to oxidize ethylene sulfides to cyclic sulfones or sulfoxides failed. Any oxidation reaction entails ring opening (39). Sulfonic acids and sulfuric acid are formed (39). Thus, the carboxysulfonic acids, HO_3SCH_2COOH and $HO_3SCH_2CH_2SCH_2COOH$, were isolated on oxidation of ethylene sulfide with nitric acid (52). Oxidation with $KMnO_4$ also yields sulfuric acid (50). Hydrogen peroxide reacts vigorously with ethylene sulfide (39, 100); 2-hydroxypropanesulfonic acid, $CH_3CH(OH)CH_2SO_3H$, was obtained from propene sulfide (225). Oxidation of ethylene sulfide with perbenzoic acid or dibenzoyl peroxide furnished insoluble polymers, probably poly(ethylene sulfone) (100).

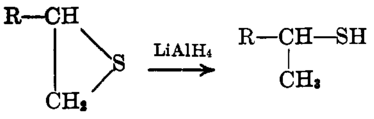
One exception is the synthesis of the sulfoxide



by oxidation of the corresponding thiirane compound with peracetic acid, as described in a patent (221). Recently dibenzoylstilbene sulfide has been oxidized to the corresponding sulfoxide or sulfone, depending on the amount of hydrogen peroxide used (55). However, thiirane dioxides can be synthesized by routes other than oxidation. Thus tetraphenylethylene sulfone has been prepared by causing diphenyldiazomethane to interact with sulfur dioxide, whereas no stable sulfones could be obtained by analogous reaction with monoaryldiazomethanes (222). Monomeric ethylene sulfone was recently isolated upon conversion of diazomethane with SO_2 (100) or with sulfene (170). This substance (mp 19°, bp 64° (0.3 mm)) is rather stable at room temperature, but tends to polymerize to poly(ethylene sulfone) at temperatures above 60°. *cis*-2-Butene sulfone has been synthesized in an analogous way from diazoethane and sulfur dioxide (164).

G. REDUCTION

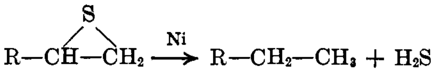
It has already been mentioned that the reduction of aromatic ethylene sulfides with nascent hydrogen is accompanied by the formation of the corresponding olefin and H_2S (199). Reduction of alkene sulfides with lithium aluminum hydride yields secondary mercaptans under ring opening.



The yields of mercaptans amounted to 72% for propene sulfide (22), 73% for 1-hexene sulfide (22), 20% for 1-octene sulfide (153), and 75–85% for a number of 3-alkoxypropene sulfides (110). The reduction of cyclohexene sulfide (22, 159) and carbohydrate thiiranes (36) with $LiAlH_4$ was also reported. By-products of the reduction are solid polymers and sulfur-containing liquids, but not hydrogen sulfide (153). By the use of lithium aluminum deuteride it was demonstrated that the reduction of 2-butene sulfide involves inversion of the configuration (96).

Relatively resistant to reduction by $LiAlH_4$ are steroidal thiiranes and some higher thiiranyl carboxylic esters. Such esters may be reduced to the alcohols without affecting the thiirane group (144, 233). At higher temperature desulfurization occurs with formation of olefins (127, 144, 234).

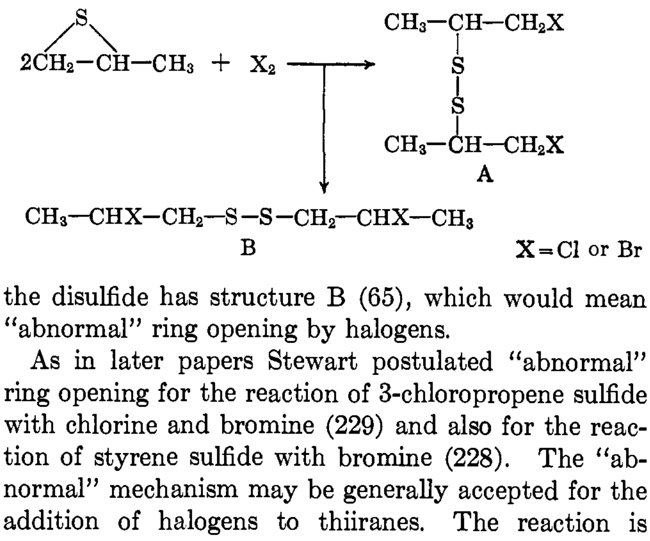
Reductive desulfurization may be accomplished with Raney nickel in ethanol (36, 229, 233).



$$R{-}\overset{S}{\overline{CH{-}CH_2}} \xrightarrow{Ni} R{-}CH_2{-}CH_3 + H_2S$$

H. REACTION WITH HALOGENS

Bromine reacts with ethylene sulfide to form a viscous, colored substance (50). Interaction of chlorine (in CCl_4) with cyclohexene sulfide yields 1,2-dichlorocyclohexane in addition to a large proportion of polymers (39). If a solution of chlorine or bromine (molar ratio 1:2) is slowly added to a nonaqueous solution of propene sulfide, a bis(halopropyl) disulfide results, which according to Stewart and Cordts (225, 227) has the structure A. Other authors recently showed that

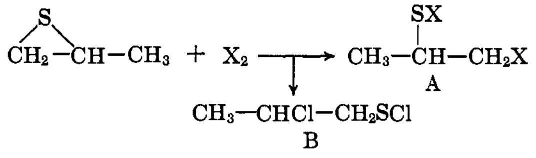


the disulfide has structure B (65), which would mean "abnormal" ring opening by halogens.

As in later papers Stewart postulated "abnormal" ring opening for the reaction of 3-chloropropene sulfide with chlorine and bromine (229) and also for the reaction of styrene sulfide with bromine (228). The "abnormal" mechanism may be generally accepted for the addition of halogens to thiiranes. The reaction is quantitative and fast, so that thiiranes can be titrated with bromine solution. Chloroform or carbon tetrachloride may be used as solvent.

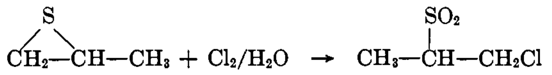
Treatment of 2-butene sulfide with iodine solution at room temperature gives the diiodo disulfide, which on further treatment with warm iodine solution decomposes with desulfurization (98).

If propene sulfide is added to a solution of chlorine or bromine in a molar ratio of 1:1, β-halosulfenyl halides are obtained (225).

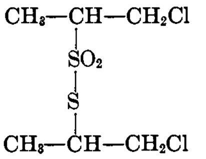


Here again an earlier report (225) claimed structure A, whereas in a more recent publication (65) structure B has been proved. The yields are about 45%, and sulfuryl chloride may be used instead of chlorine.

Interaction of aqueous chlorine solution with propene sulfide gives the corresponding β-chlorosulfonyl chloride (226).

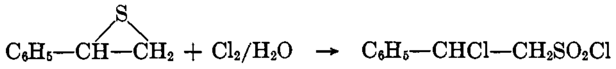


The same compound is formed if an aqueous chlorine solution is permitted to act on the sulfenyl chloride, or by interaction of chlorine in acetic acid with bis(β-chloroalkyl) disulfide (225). On addition of limited quantities of chlorine to an acetic acid solution of propene sulfide a product was isolated whose analysis suggests the following structure (225).



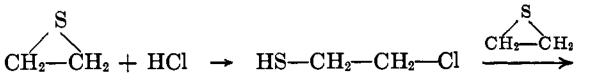
$$\begin{array}{c} CH_3\text{—}CH\text{—}CH_2Cl \\ | \\ SO_2 \\ | \\ S \\ | \\ CH_3\text{—}CH\text{—}CH_2Cl \end{array}$$

"Abnormal" ring opening is reported for the reaction of chlorine in aqueous acetic acid with styrene sulfide (228). The analogous structure is assumed for the reaction product of 3-chloropropene sulfide and aqueous chlorine (229).

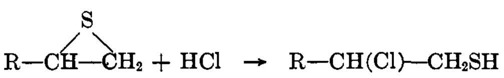


I. REACTION WITH HYDROGEN HALIDES

Dilute aqueous hydrochloric acid yields polymers as exclusive products (50, 228), which, however, contain chlorine as terminal groups. If ethylene sulfide is added to an excess of concentrated hydrochloric acid, the monomeric and the dimeric adduct can be isolated (52).



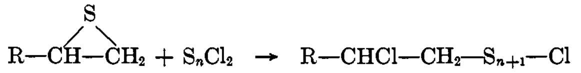
With gaseous hydrogen chloride in ethereal solution only β-chloroethyl mercaptan was obtained (148); interaction with hydrogen bromide gave β-bromoethyl mercaptan (52). Only polymeric products were obtained from cyclohexene sulfide and boiling concentrated hydrochloric acid, while 2-chlorocyclohexyl mercaptan was formed in a yield of 57% by shaking cyclohexene sulfide with hydrochloric acid in great excess at room temperature. Analogous to this, a yield of 72% of the corresponding dichloropropyl mercaptan is obtained from 3-chloropropene sulfide-1 (39). Based on the example of propene sulfide and chloropropene sulfide Davies and Savige demonstrated that hydrogen halides add to asymmetric thiiranes under ring opening at the secondary carbon atom (43, 44).

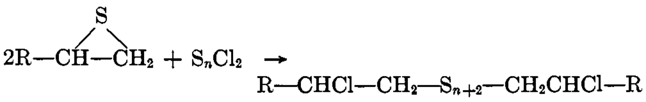


The same "abnormal" mechanism is assumed for the addition of hydrogen chloride to styrene sulfide (228). Not even traces of the isomeric 1-chloro-2-thiols could be detected. Contrary to this, the "normal" addition product is always present in the few known cases of "abnormal" ring opening of ethylene oxides. Therefore, the authors assume that ring opening proceeds *via* an intermediate ethylenesulfonium ion, which would correspond to an electrophilic attack by the hydrogen halides (44). A further proof for the "abnormal" addition of HCl to propene sulfide has been provided recently (64).

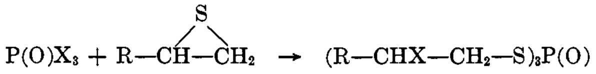
J. REACTION WITH SULFUR HALIDES AND PHOSPHORUS HALIDES

The additions of sulfur dichloride and disulfur dichloride to thiiranes obey the same mechanism as does the addition of halogens to thiiranes (66). While dimeric products are formed at a molar ratio of sulfur halide to thiirane of 1:2, monomeric polythiochlorides are isolated at a ratio of 1:1.



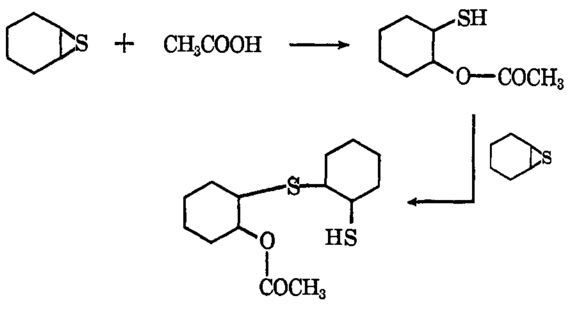


Ring opening again is "abnormal" in nature. For reactions carried out in carbon tetrachloride yields of 40–85% have been reported (66). Sulfuryl chloride reacts with thiiranes in a manner similar to chlorine (see section IVH); sulfur dioxide is split off (65). Phosphoric or phosphorous halides react with thiiranes to form β-halothiol esters (120). No proof has been given for the structure of the products. PCl_3, PF_3, and POF_3 were used in the examples. Tertiary amines served as catalysts.



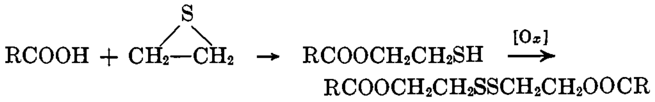
K. REACTION WITH CARBOXYLIC ACIDS

Acetic acid causes slow polymerization of ethylene sulfide, while propene sulfide and 1-butene sulfide show no change (50, 51). On boiling with excess glacial acetic acid, cyclohexene sulfide forms 26% monomeric and 48% dimeric acetoxy mercaptan (96).



Treatment of thiiranes with excess iodine in glacial acetic acid results in quantitative formation of the acetoxy disulfide so that this reaction can be used for iodometric determination of thiiranes (192).

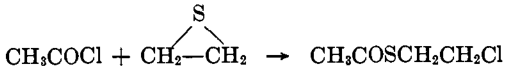
Conversion of technical grade fatty acids with a solution of ethylene sulfide in benzene at 100° yields β-mercaptoethyl esters which can be oxidized to give the corresponding disulfide diesters.



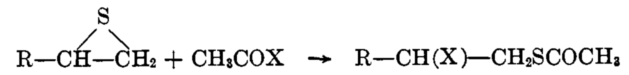
The latter products, added to lubricating oils in quantities of 5–10%, increase the film stability and reduce abrasion (211).

L. REACTION WITH CARBOXYLIC HALIDES AND CHLOROMETHYL ETHERS

At room temperature, acetyl chloride and ethylene sulfide furnish β-chloroethyl thiolacetate in a yield of 75% (7).



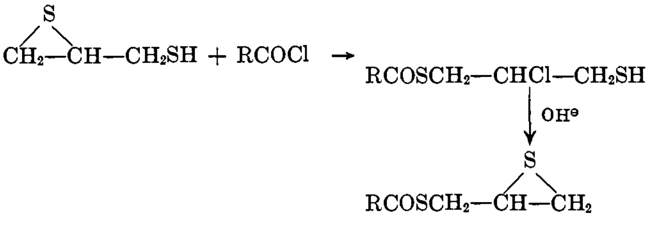
This reaction also gives high yields with propene sulfide. chloropropene sulfide, and cyclohexene sulfide (39), as well as with styrene sulfide (228). In the case of asymmetrical thiiranes, ring opening is "abnormal;" *i.e.*, it occurs at the secondary C atom (43, 44, 109).



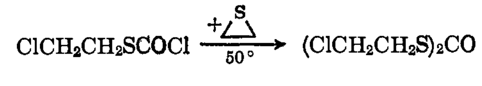
$R = CH_3, ClCH_2;\ X = Cl, Br$

Acetyl bromide (43, 91, 109), acetyl iodide (108, 109), chloroacetyl chloride (109, 148, 173), chloroacetyl bromide (148), propionyl bromide (91, 109), butyryl bromide (91, 109), benzoyl chloride (39), and benzoyl bromide (91, 109) react in the same manner as acetyl chloride; the reactions furnish yields up to 90%.

Accordingly, 3-mercaptopropene sulfide reacts with carboxylic chlorides to yield 1-acylthio-2-chloropropane-3-thiols, which can be converted to 3-acylthiopropene sulfides by treatment with alkali (5).



Phosgene reacts with ethylene sulfide in two steps (188). Tertiary amines act as catalysts.

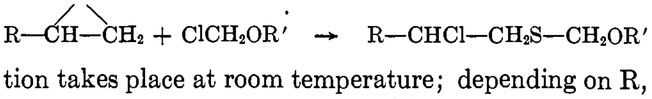


In the case of propene sulfide the addition of phosgene follows the "abnormal" way (67).

Chlorocarbonates react with thiiranes analogous to phosgene (67).

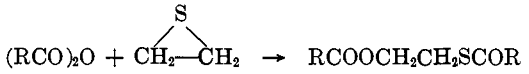
Benzoyl fluoride, picryl chloride, dinitrobenzoyl chloride, triphenylmethyl chloride, p-toluenesulfonyl chloride, and p-toluenesulfonyl fluoride react with propene sulfide or cyclohexene sulfide according to a different mechanism, giving polymers as principal products (39).

The reactivity of the chlorine atom in α-chloroalkyl ethers is generally very high. Hence the reaction of these compounds with thiiranes gives β-chloroalkyl sulfides. As observed with propene sulfide, ring opening is "abnormal" (8). Catalyzed by $HgCl_2$ the reaction takes place at room temperature; depending on R, the yields vary between 23 and 78% (8).

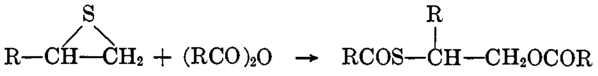


M. REACTION WITH CARBOXYLIC ANHYDRIDES

Ethylene sulfide reacts with carboxylic anhydrides to give the diester of β-mercaptoethanol (7).

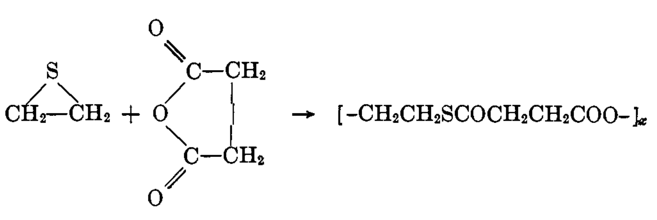


The reaction is catalyzed by pyridine (7), and in the case of asymmetrical thiiranes involves "normal" ring opening at the primary C atom (43, 44).



These two facts are indications of a nucleophilic reaction mechanism. Normally, the reaction is carried out at 130°, furnishing the diester in yields of approximately 50–80%. Thiirane groups in some steroidal thiiranes are not affected by acetic anhydride even in pyridine (233, 121).

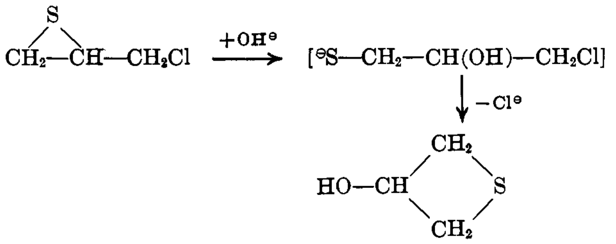
The use of dicarboxylic anhydrides results in polymeric esters (7).



N. REACTION WITH HYDROXY COMPOUNDS

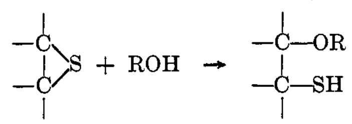
Water. At room temperature no reaction with thiiranes is noticed. Nevertheless, a spot test proved minor ring opening (39). At 100° propene sulfide reacts with water to form different unidentified products (39). Kinetic measurements of the hydrolysis of styrene sulfide catalyzed by sulfuric acid did not furnish conclusive information on the reaction order (123).

Alkaline hydrolysis of 3-chloropropene sulfide yields 3-hydroxythietane suggesting an exceptionally "abnormal" ring opening by nucleophilic attack at the secondary carbon atom (5).

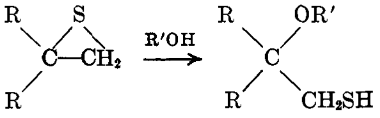


Alcohols. Propene sulfide reacts with ethanol at 100° to form different unidentified products (39).

β-Alkoxy mercaptans are obtained by conversion of thiiranes with alcohols in the presence of catalytic quantities of boron trifluoride (213, 218). The reaction



is carried out at around 100°; with isobutene sulfide the yields are 20–40% if primary alcohols are used (213), but very small upon use of secondary alcohols. Propene sulfide or cyclohexene sulfide yield no or only small amounts of alkoxy mercaptans even with primary alcohols (213). The use of excess quantities of the thiirane results in products of high boiling points (213). The alkoxy group adds in "abnormal" manner to the secondary or tertiary C atom of asymmetrical thiiranes (213, 218).

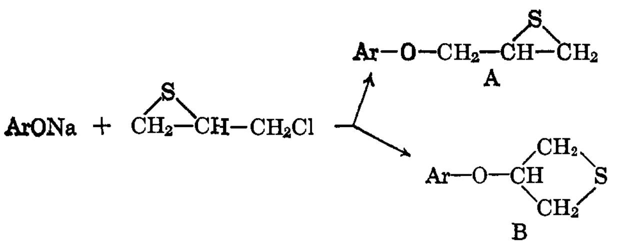


The same direction of ring opening has been reported for the addition of ethanol to styrene sulfide catalyzed by sulfuric acid (123).

Reaction of thiiranecarboxylic acids with potassium butoxide resulted in desulfurization affording the olefinic acids (146).

Phenols. According a Japanese paper (75) ethylene sulfide reacts with phenol to form β-phenoxyethyl mercaptan.

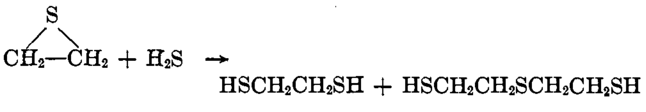
Alkali phenoxides react with 3-chloropropene sulfide in a twofold way: besides polymers, arylthioglycidyl ethers A are formed as well as 3-aryloxythietanes B (192).



In protic solvents such as water or alcohol the formation of A is preferred, whereas the formation of B is preferred in polar aprotic solvents such as diglyme, dimethyl sulfoxide, or methyl ethyl ketone. However, in any solvent both the products A and B are formed. The formation of B clearly shows attack of the phenoxide ion at the secondary carbon atom; this is evidence seldom observed for a nucleophilic thiirane ring scission in the "abnormal" way. The formation of A may be explained either by "normal" ring opening or by direct exchange of chlorine. The first explanation would imply that in this reaction the thiirane ring is opened both in the "normal" and in the "abnormal" way. This has never been observed in other cases and thus the direct chlorine exchange is the more probable explanation.

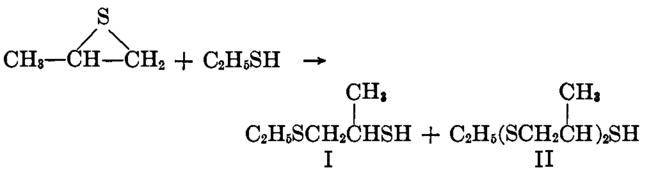
O. REACTION WIYH THIOL COMPOUNDS

Hydrogen Sulfide. The reaction of ethylene sulfide with excess hydrogen sulfide at 45–60° yields approximately 50% dithioglycol (ethylenedithiol) and about 16% trithiodiglycol (148).



The corresponding 1,2-dithiols are also formed upon interaction of potassium hydrogen sulfide with cyclohexene sulfide, propene sulfide (39), and 1-octene sulfide (153). The yields are lower than those obtained with hydrogen sulfide, since polymers are formed in greater proportion. Chloropropene sulfide and KHS furnish a small amount of trithioglycerol (39).

Mercaptans. In the absence of catalysts, thiiranes react rather sluggishly with mercaptans. Thus, upon heating cyclohexene sulfide with ethyl mercaptan for 6 hr at 120°, almost all of the starting material was recovered unchanged (39).[2] In a patent recommending a reaction temperature of 100 to 200° and the use of excess quantities of mercaptan, a yield of 56% of the 1:1 addition product (I) and 24% of the 2:1 addition product (II) is indicated for the conversion of propene sulfide with ethyl mercaptan. The conversion of ethylene



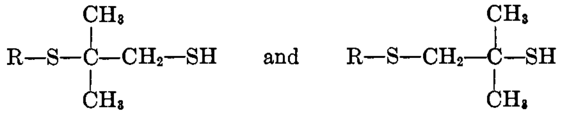
sulfide with ethyl mercaptan gives yields of 22% of the 1:1 addition product and 6% of the 2:1 addition product (183).

Snyder, Stewart, and Ziegler (213) reported that the addition of mercaptans to thiiranes was successful only in the presence of catalysts. The reaction of isobutene

---

(2) Mercaptans or H_2S are claimed to stablize ethylene sulfide on storage, preventing it from polymerization (33).

sulfide with the equivalent quantity of mercaptans in the presence of sodium ethoxide as catalyst (*ca.* 10%), furnished approximately 40% of the 1:1 addition product; a 100% excess of mercaptans supplied the 1:1 addition product in a yield of 75%. This reaction is claimed to yield a mixture of the two isomers



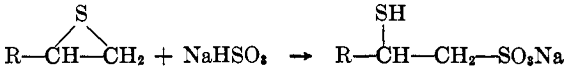
$R{-}S{-}C(CH_3)_2{-}CH_2{-}SH$ and $R{-}S{-}CH_2{-}C(CH_3)_2{-}SH$

with the primary mercaptans prevailing; this would correspond to a preference of the "abnormal" ring opening. In the presence of boron fluoride etherate as catalyst, the yields are about the same; however, the tertiary mercaptan dominates in the mixture ("normal" ring opening). Yet, this statement (213) is supported by only one single experiment, and in a patent (216) the same authors state just the contrary structures. In no case have the isomers been isolated; the tertiary mercaptans were identified by amperometric titration of the mixture.

In the presence of C_2H_5ONa as catalyst, cyclohexene sulfide and mercaptans furnished a yield of 30–40% of the 1:1 addition product (213, 216). Tetramethylethylene sulfide does not react as desired (213). Styrene sulfide reacts with *n*-butyl mercaptan in the presence of BF_3 yielding 33% of a 1:1 addition product of unidentified structure (228). Also the catalyzed addition of mercaptans yields 2:1, 3:1, and higher products. Analogous to simple mercaptans, alkoxy mercaptans, such as β-ethoxyethyl mercaptan, react with ethylene sulfides (213, 217). Additions of different hydroxy mercaptans and dithiols to propene sulfide in the presence of catalytic quantities of sodium ethoxide furnished the corresponding 1:1 addition products in a yield of approximately 50% besides 2:1 addition products. Products from the addition of thiols to dithioglycidol were obtained only in small quantities (4).

The use of molar amounts of alkali, or the reaction of thiiranes with alkali mercaptides, does not improve or impair the result obtained with catalytic quantities of alkali. The reaction of cyclohexene sulfide with sodium ethyl mercaptide, for example, gives 55% of the 1:1 addition product and 30% of the 2:1 addition product; 25% of the 1:1 product and 25% of the 2:1 product are obtained with sodium *t*-butyl mercaptide (39). Ethylene sulfide and sodium methyl mercaptide (50% excess) yield 40% of the 1:1 product; the reaction with sodium amyl mercaptide is similar (148).

Bisulfites. Reaction of thiiranes with aqueous solutions of sodium hydrogen sulfite at 50–100° furnishes good yields of salts of β-mercaptosulfonic acid (245).



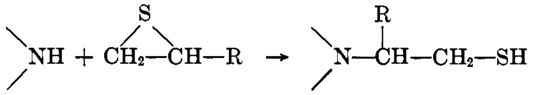
Thiophosphates. Dialkyl dithiophosphates, $(RO)_2P(S)SH$, add ethylene sulfide at 70–80° in the absence of catalysts, the reaction obviously stopping at the stage of 1:1 adduct $(RO)_2P(S)SCH_2CH_2SH$. In the presence of NaOH, higher adducts, $(RO)_2P(S)S(CH_2CH_2S)_nP(S)(OR)_2$, are formed (143). The conversion of thiiranes with dialkyl dithiophosphates is also claimed in a patent, but the products are not described in detail (101).

Alkali xanthates react with thiiranes under formation of cyclic trithiocarbonates (see section IVS).

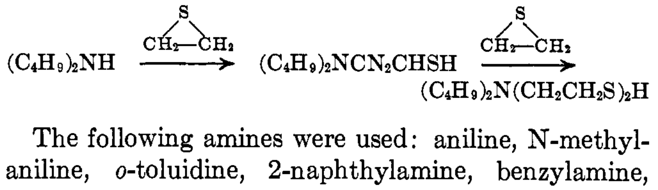
P. REACTION WITH AMINO COMPOUNDS

Ammonia. Aqueous ammonia solution causes quick polymerization of ethylene sulfide (50), while propene sulfide and butene sulfide polymerize slowly with this reagent (51). The reaction of anhydrous ammonia with thiiranes has not yet been described.

Primary and Secondary Amines. According to Reppe and Nicolai (182), primary and secondary amines react with ethylene sulfide or propene sulfide at 100–200°, in the absence of catalysts, to give β-mercaptoalkylamines.



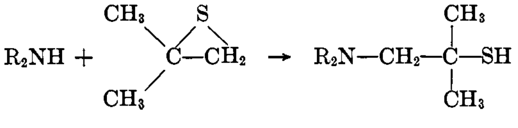
No evidence supporting the assumed "abnormal" mechanism of the reaction is given by the authors. The higher the basicity of the amines, the higher is the rate of the addition. In general, primary amines merely furnish the monomercaptan, $RNHCH_2CH_2SH$; if the thiirane is used in large excess and in the case of strongly basic amines, the dimercaptans, $RN(CH_2CH_2SH)_2$, are obtained as well. But even the strongly basic piperidine furnishes the monomercaptan as principal product upon conversion with 1 mole of ethylene sulfide. Conversion of a primary amine to the dimercaptan is best performed in two steps. In this way 1:2 addition products can be obtained in the case of strongly basic secondary amines (even in the absence of a catalyst). Here, the mercaptoamine itself obviously acts as a basic catalyst.



The following amines were used: aniline, N-methylaniline, *o*-toluidine, 2-naphthylamine, benzylamine, cyclohexylamine, dodecylamine, N-methyldodecylamine, butylamine, dibutylamine, piperazine. The yields are up to 90% (182).

In an analogous way, Culvenor, *et al.* (39), obtained 2-methylanilinocyclohexyl mercaptan (yield 50%) from methylaniline and cyclohexene sulfide in boiling 80% ethanol. It is interesting to note that no reaction occurred upon heating of the two components at 100° in the absence of solvent. Furukawa, *et al.* (75), described the formation of β-anilinoethyl mercaptan from aniline and ethylene sulfide.

Snyder, *et al.* (212), studied the reaction of equimolar quantities of secondary and primary amines and thiiranes at 100°. The results obtained by these authors agree essentially with those obtained by Reppe and Nicolai (182). The reaction rate drops not only with decreasing basicity, but also in the case of steric hindrance. Thus, the strongly basic, but sterically hindered dicyclohexylamine does not form an adduct under the reaction conditions applied. Contrary to Reppe and Nicolai, Snyder, *et al.*, maintain that the addition of asymmetric thiiranes involves "normal" ring opening, since in this reaction the tertiary mercaptan is practically the only product obtained from isobutene sulfide.



$$R_2NH + (CH_3)_2\overset{S}{C}{-}CH_2 \rightarrow R_2N{-}CH_2{-}C(CH_3)_2{-}SH$$

This view is based on a color test and the conversion into sulfenyl iodides by means of iodine.

The authors state that the reaction is catalytically accelerated neither by phenol or aluminum chloride, nor by the sodium derivative of amines. This is in agreement with the findings of Gilman and Woods (82) who, from diethylaminelithium and ethylene sulfide, obtained similar yields of β-diethylaminoethyl mercaptan as did Braz (24) later on in the absence of alkali.

Snyder, *et al.* (212), used the following substances as thiirane compounds: ethylene sulfide, propene sulfide, isobutene sulfide, cyclohexene sulfide; as amines: dibutylamine, diamylamine, diheptylamine, dioctylamine, dicyclohexylamine, diphenylamine, piperidine, 3-methylpiperidine, 4-ethylpiperidine, morpholine, piperazine, as well as the primary amines: heptylamine, dodecylamine, and aniline. The yields of β-amino mercaptan ranged between 50 and 80%. Only small amounts of 1:2 or higher molecular weight addition products were obtained. In spite of Reppe's patent (182) issued in 1934, Snyder and Stewart were granted a patent for the conversion of amines and thiiranes without catalysts in 1950 (219).

Braz (24) studied the reaction of ethylene sulfide with secondary and primary amines in benzene solution at 100°. He observed that the differences in the basicity of the amines have a strong effect on the yield of β-amino mercaptan. In the case of strongly basic amines (diethylamine) in polar solvents (methanol), polymerization becomes the main reaction. It can be suppressed by using a large excess of amine, or nonpolar solvents, or no solvents at all.

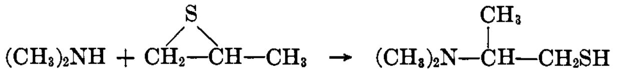
The investigated amines include diethylamine, diisoamylamine, diallylamine, N,N-diethylethylenediamine, morpholine, hexylamine, benzylamine, and aniline. The yields ranged between 50 and 80% (24).

Rachinskii, Slavachevskaya, and Ioffe (177) carried out the reaction of ethylene sulfide with amines in benzene at room temperature and obtained similar yields.

In a series of publications Yuriev and Dyatlovitskaya, (258) reported on the preparation of β-mercaptoethylamines from primary amino compounds and ethylene sulfide, and their conversion to heterocyclic compounds containing sulfur and nitrogen. The mercaptoethylation takes place at approximately 100° in the absence of catalysts; the yields amount to approximately 60–70%.

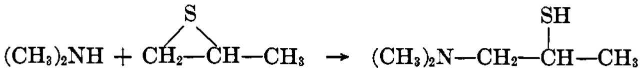
A detailed study on the mercaptoethylation of aliphatic amines has been reported by Wineman, Gollis, James, and Pomponi (254). They recommend adding a benzene solution of ethylene sulfide slowly to a boiling benzene solution of the amine. The amines—particularly primary amines—should by used in excess. Strongly polar amines tend to telomerization; addition of ethanol may suppress this side reaction. In this way the monomercaptoethyl derivatives are obtained in yields of 40–70% except in the case of branched amines. Two secondary and 27 primary amines have been investigated, including hydroxyalkyl-, alkoxyalkyl-, *t*-aminoalkylamines, and di-primary diamines (254).

Using an ethereal solution at room temperature, Hansen (91) obtained β-dimethylaminoethyl mercaptan from dimethylamine and ethylene sulfide in a yield of 70%, and 2-dimethylaminopropanethiol-1 from dimethylamine and propene sulfide in a yield of 69% (92). The structure of this product was proved by acetylation and comparison with material synthesized separately. Accordingly, amines seem to add to asymmetric thiiranes with "abnormal" ring opening, as assumed by Reppe and Nicolai.



$$(CH_3)_2NH + CH_2\overset{S}{-}CH{-}CH_3 \rightarrow (CH_3)_2N{-}\overset{CH_3}{CH}{-}CH_2SH$$

Contradictory results have been reported by Turk, Louthan, Cobb, and Bresson (244) on repetition of Hansen's work. The reaction product of dimethylamine and propene sulfide has been found to be identical with 1-dimethylaminopropanethiol-2 synthesized in an unambiguous way. Also the two other isomers, 2-dimethylaminopropanethiol-1 and 1-dimethylaminopropanethiol-3, have been synthesized and were not identical with the mercaptoalkylation product. Further structural evidence has been furnished by nmr spectra. Accordingly the addition of amine involves "normal" ring opening.



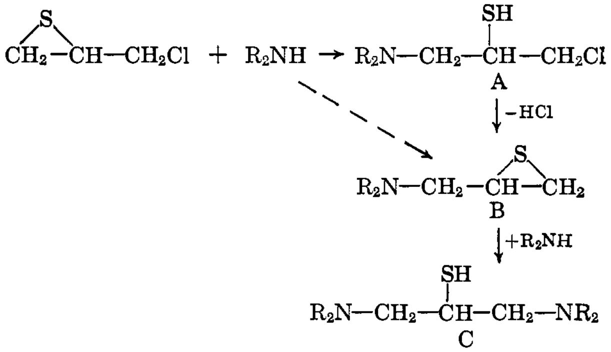
$$(CH_3)_2NH + CH_2\overset{S}{-}CH{-}CH_3 \rightarrow (CH_3)_2N{-}CH_2{-}\overset{SH}{CH}{-}CH_3$$

An analogous structure has been proved by nmr for the reaction product of isobutene sulfide and piperidine (244) thus confirming the earlier assumption of Snyder, Stewart, and Ziegler (212). For analogy the addition of octylamine and decylamine to isobutene sulfide is formulated according to the "normal" mechanism (244).

Upon reaction of methoxy- and ethoxypropene sulfide with a 100% excess of piperidine or morpholine in boiling benzene, Jacobs and Schuetz (110) obtained yields of 80–92% amino mercaptans, whereas only the starting materials were recovered upon interaction of alkoxypropene sulfides with diethylamine under the same conditions. This is attributed by the authors to a renewed cleavage of the resultant diethylamino mercaptans during distillation. Aqueous solutions of diethylamine exclusively involve polymerization of the thiirane. The authors assume "normal" ring opening without proving the structure.

Reaction of styrene sulfide with piperidine and morpholine only yields sulfur-free products (87). However, in solvents styrene sulfide could be added to secondary amines (dimethylamine, piperidine, morpholine) under "normal" ring opening (228). The structure of the products has been proved by desulfurization furnishing β-phenylethylamines. The addition is not influenced by basic or acidic catalysts but is sterically hindered by larger substituents at the nitrogen atom. The yields are about 60% (228).

Special attention should be given to the recently published results on the reaction of 3-chloropropene sulfide with secondary amines (229). Three alternative products may be expected if the amine is used in excess.



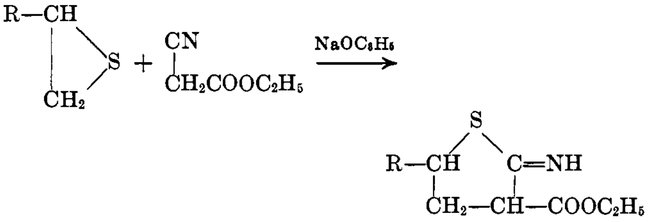
However, in no case has it been possible to isolate type A. If the reaction is carried out in ether or petroleum ether in a molar ratio of 1:1, mainly B is obtained, whereas a mixture of B and C is formed from the reactants used in a 1:2 ratio. The structure of type B and C has been established by desulfurization evidencing "normal" ring opening. Although the possibility that B may be formed by direct halogen displacement (dotted line) instead of an addition mechanism is not completely ruled out, such a displacement is highly improbable according to the author. Only polymeric materials could be obtained by converting chloropropene sulfide with primary amines (229).

From all these papers, particularly from the more recent literature, a clear picture can be obtained on the reaction of thiiranes with primary and secondary amines, which may be summarized as follows. (1) The reaction involves mercaptoalkylation and needs no catalyst. (2) Ring opening of asymmetrical thiiranes obeys the "normal" mechanism with nucleophilic attack at the primary carbon atom. (3) In primary amines the two hydrogen atoms at the nitrogen atom may react under mercaptoalkylation. (4) The thiol group of the resultant mercaptoalkylamine may be subjected to a further mercaptoalkylation. (Side-reactions according to (3) and (4) can be suppressed by using the amine in large molar excess.) (5) High basicity of the amine and high polarity of the solvent promote polymerization of the thiirane.

Other NH Compounds. The β-mercaptoethylation of cyanamide (154), guanylurea (155), and biguanide (156) is described in patent specifications. Details of the non-uniform products obtained are not reported.

Q. REACTION WITH CH-ACIDIC COMPOUNDS

Ethyl malonate and ethyl acetoacetate do not react with simple thiiranes in the presence of sodium ethoxide (214). In the presence of $NaOC_2H_5$, ethyl 2-iminothiophane-3-carboxylate is obtained from ethyl cyanoacetate.

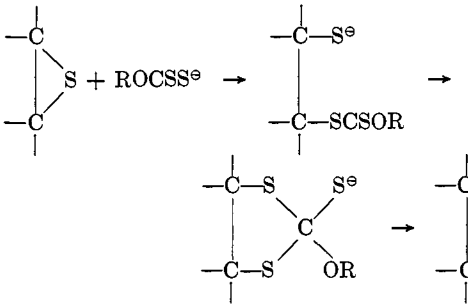


The constitution of the products and thus the mechanism of the reaction involving "normal" ring opening was definitely identified by Snyder and Alexander. In the case of ethylene sulfide the yields are low (23%) in view of substantial polymerization; from propene sulfide and isobutene sulfide which polymerize less readily, the imino ester was obtained in respective yields of 30 and 60% (214). The corresponding imino ester was also obtained from styrene sulfide, in addition to polymeric material (87).

R. REACTION WITH CARBON DISULFIDE

An American patent claims the formation of cyclic trithiocarbonates from thiiranes and carbon disulfide at 200° under pressure in the presence of quaternary salts (152). No yields are reported. The reaction was simultaneously found by Russian authors (178) who used trimethylamine as catalyst at temperatures of 100–120°. In this way the trithiocarbonates have been obtained from ethylene sulfide and propene sulfide in a yield of about 90%.

The formation of cyclic trithiocarbonates by interaction of thiiranes with carbon disulfide in the presence of alkali hydroxide in alcoholic solution is assumed to involve addition of the resultant xanthate ion, followed by abstraction of an alkoxide ion (36, 38, 105, 146).



V. USES

The high reactivity and most disagreeable odor of thiiranes are obstacles to the direct technological application of this group of compounds. On the other hand, their high reactivity makes thiiranes valuable materials, either for the finishing of natural or synthetic polymers or as intermediates for the manufacture of other sulfur-containing compounds.

A. DIRECT APPLICATION OF THIIRANES

Ethylene sulfide vapors have a higher disinfecting effect than ethylene oxide (114). At a concentration of 0.27 mmole/l., 90% of the spores of an aerosol comprising *Bacterium globigii* are destroyed within 65 min. The use of thiiranes as insecticidal and fungicidal constituents of sprays is described in a patent (238). In a comparative study covering the evaluation of 6155 substances for their toxic effect on insects thiiranes proved to belong to the most active groups (74). Chloropropene sulfide has been claimed to be an effective nematocide (95).

Dithioglycidyl thiophosphates have a strong contact insecticidal effect (133, 203). S-Acyl derivatives of dithioglycidol inhibit tuberculosis (5, 57, 176). Among a number of S-acyldithioglycidols the furanoyl compound showed the highest tuberculostatic activity in mice; however, the activity of these compounds decreases upon more extended application as the bacteria soon become resistant (2).

Aryloxypropene sulfides have been proposed as light and heat stabilizers for polyvinyl chloride and copolymers of vinyl chloride (122). They are claimed to be more effective than the conventional aryloxypropene oxides. Episulfidized soy bean oil is a suitable plasticizer for polyvinyl chloride (113).

Combined with a polymerization catalyst for thiiranes (*e.g.*, amines), bisthiiranes are vulcanizers for natural or synthetic rubber at low temperatures (135). It is assumed that the terminal SH groups of the resultant thiirane polymers add to the double bonds of rubber, thus giving rise to cross linking. Thiiranecarboxylic acids may be used in the manufacture of Factices (191).

Addition of small amounts of dithioglycidol (3-mercaptopropene sulfide) to the polymerization of acrylonitrile yields polymers of increased thermal stability (106). The dithioglycidol apparently acts as transfer agent, similar to dodecyl mercaptan, a well-known regulator.

Fluorinated thiiranes may be used as refrigerants or as fire extinguisher agents (147).

B. TREATMENT OF POLYMERS WITH THIIRANES

Attempts to make wool unshrinkable by a treatment with ethylene sulfide were successful only if comparatively large amounts of ethylene sulfide are polymerized within the fiber. However, the handle of the fabric is impaired by this treatment (12). According to Barr and Speakman (12), the terminal SH groups of polyethylene sulfide react with the disulfide bridges of keratin. According to Blackburn and Phillips (17), the disulfide bridges are reduced in a first step, whereupon the resultant cysteine groups combined with ethylene sulfide to form long side chains.

Similar studies were performed on collagen (81). On incorporation of substantial amounts of polyethylene sulfide, the shrinkage of raw and tanned hides is reduced, and the percentage of soluble components approaches zero.

Champetier and Hennequin-Lucas (27) investigated the grafting of cellulose with ethylene sulfide and propene sulfide. Reaction occurs on using cellulose containing benzene inclusions in the presence of catalysts like BF_3, $HClO_4$, or piperidine, and on using alkali cellulose without catalysts. After extraction with xylene the products obtained show a sulfur content corresponding to 4 moles of C_2H_4S per glucose unit and a substitution of up to 2.5 OH groups per glucose unit. According to the authors, the growth of the side chains is stopped soon (maximum degree of polymerization of the side chain 6.3) by oxidation of the terminal SH groups to disulfide bridges with cross linking of the cellulose. It appears probable that the cellulose treated with ethylene sulfide also contains polyethylene sulfide as the latter can hardly be extracted with xylene. Films from cellulose or partially acetylated cellulose, which have been treated with ethylene sulfide, can be grafted with styrene at 65° in the presence of radicals (28). The styrene side chains are linked to the cellulose by the mercaptoethyl groups.

The treatment of polymers of any type with dithioglycidol (3-mercaptopropene sulfide) is claimed in a patent (126). Examples are the treatment of rayon yarn, alkali cellulose, polyamides, and styrene–butadiene copolymers. This treatment may involve chemical linkage with the polymer (*via* the OH, NH, or olefin group) or polymerization within the substrate. In any case the materials contain organically combined sulfur after the treatment, which cannot be extracted by solvents. Grafting of unreactive synthetic fibers such as polypropylene or polyvinyl chloride fibers with thiranes is possible by exposure to a γ source (160).

C. THIIRANES AS INTERMEDIATES

The reactions described in section IV yield products of a more or less defined chemical structure; for the major part they are mercapto compounds. Potential applications have been indicated for almost all of these products; however, it would be beyond the scope of this review to discuss the practical potential of these products in greater detail. Nevertheless, some reactions of thiiranes are discussed in the following which furnish undefined products of commercial usefulness.

Treatment of halogen-containing lubricant additives, *e.g.*, ethyl tetrachlorothiobutyrate, with ethylene sulfide yields products which are less corrosive at the same lubricity (102). Further lubricant additives described in the literature include the undefined products of the reaction of dialkyldithiophosphoric acids with thiiranes (101). The reaction products of hydroxycarboxylic acids with ethylene sulfide are also recommended as lubricant additives (6).[3] The reaction products of cyanamide, of guanylurea, and of biguanide can be used as dehairing agents, as insecticides, as vulcanization accelerators, as plasticizers, or for the production of resins (154–156). The addition of polyethylene sulfide to mixtures of synthetic elastomers is described in a patent (189), while copolymers of alkylene oxides and alkylene sulfides are recommended as additives to lubricating oils, greases, or cutting oils (11).

Copolymers from ethylene sulfide and propene sulfide are—after vulcanization—elastomers of potential technical interest (3). Polymers of fluorinated thiiranes are usable as packaging films, as coatings and as water-repellent impregnation (147).

VI. REFERENCES

(1) Abel, E. W., Armitage, D. A., and Bush, R. P., *J. Chem. Soc.*, 2455 (1964).
(2) Acred, P., and Brown, D. M., *Brit. J. Pharmacol.*, **15**, 485, 496 (1960); *Chem. Abstr.*, **55**, 8670 (1961).
(3) Adamek, S., Wood, B. B. J., and Woodhams, R. T., *Rubber Age*, **96**, 581 (1965).
(4) Adams, E. P., Doyle, E. P., Hatt, D. L., Holland, D. O., Hunter, W. H., Mansford, K. R. L., Nayler, J. H. C., and Queen, A., *J. Chem. Soc.*, 2649 (1960).
(5) Adams, E. P., Ayad, K. N., Doyle, F. P., Holland, D. O., Hunter, W. H., Nayler, J. H. C., and Queen, A., *J. Chem. Soc.*, 2665 (1960).
(6) Adelson, D. E., Perry, G. L., and Pritzker, G. G., U. S. Patent 2,628,941 (1953); *Chem. Abstr.*, **47**, 4600 (1953).
(7) Alderman, V. V., Brubaker, M. M., and Hanford, W. E., U. S. Patent 2,212,141 (1940); *Chem. Abstr.*, **35**, 463 (1941).
(8) Arbuzov, B. A., and Nuretdinova, O. N., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 927 (1963); *Chem. Abstr.*, **59**, 7384 (1963).
(9) Armstrong, R. T., Little, J. R., and Doak, K. W., *Ind. Eng. Chem.*, **36**, 628, 2866 (1944).
(10) Bacskai, R., *J. Polymer Sci.*, **A1**, 2777 (1963).
(11) Ballard, S. A., Morris, R. C., and Van Winkle, J. L., U. S. Patent 2,484,370 (1949); *Chem. Abstr.*, 44, 1255 (1950).
(12) Barr, T., and Speakman, J. B., *J. Soc. Dyers Colourists*, **60**, 238 (1944).
(13) Bateman, L., Glazebrook, R. W., Moore, C. G., Porter, M., Ross, G. W., and Saville, R. W., *J. Chem. Soc.*, 2838 (1958).
(14) Bateman, L., and Moore, C. G., in "Organic Sulfur Compounds," Vol. I, N. Kharash, Ed., Pergamon Press, Oxford, 1961, pp 210–228.
(15) Bays, D. E., Cookson, R. C., Hill, R. R., McGhie, J. F., and Usher, G. E., *J. Chem. Soc.*, 1563 (1964).
(16) Bennett, G. M., *J. Chem. Soc.*, **121**, 2139 (1922).
(17) Blackburn, S., and Phillips, H., *J. Soc. Dyers Colourists*, **61**, 203 (1922).
(18) Boileau, S., and Sigwalt, P., *Compt. Rend.*, **252**, 882 (1961).
(19) Boileau, S., Coste, J., Raynal, J., and Sigwalt, P., *Compt. Rend.*, **254**, 2774 (1962).
(20) Boileau, S., Champtetier, G., and Sigwalt, P., *Makromol. Chem.*, **69**, 180 (1963).
(21) Bordwell, F. G., and Andersen, H. M., *J. Am. Chem. Soc.*, **75**, 4959 (1953).
(22) Bordwell, F. G., Andersen, H. M., and Pitt, B. M., *J. Am. Chem. Soc.*, **76**, 1082 (1954).
(23) Reference deleted in revision.
(24) Braz, G. I., *Zh. Obshch. Khim.*, **21**, 688 (1951); *Chem. Abstr.*, **45**, 9473 (1951).
(25) Butcher, S. S., *J. Chem. Phys.*, **38**, 2310 (1963).
(26) Calingaert, C., *Bull. Soc. Chim. Belges*, **31**, 109 (1922); *Chem. Abstr.*, 16, 3870 (1922).
(27) Champetier, G., and Hennequin-Lucas, F., *Compt. Rend.*, **252**, 2785 (1961).
(28) Chaudhuri, D. K., and Hermans, J. J., *J. Polymer Sci.*, **48**, 159 (1960).
(29) Choughuley, A. S. V., and Chadha, M. S., *Indian J. Chem.*, **1**, 437 (1963); *Chem. Abstr.*, **60**, 4126 (1964).
(30) Christensen, J. E., and Goodman, L., *J. Am. Chem. Soc.*, **82**, 4738 (1960).
(31) Christensen, J. E., and Goodman, L., *J. Am. Chem. Soc.*, **83**, 3827 (1961).
(32) Coltoff, W., U. S. Patent 2,183,860 (1939); *Chem. Abstr.*, **34**, 2395 (1940); British Patent 508,932; Netherlands Patent 47,835 (1940).
(33) Coltoff, W., and Langedijk, S. L., U. S Patent 2,185,660 (1940); *Chem. Abstr.*, **34**, 2865 (1940).
(34) Cox, J. D., *Tetrahedron*, **19**, 1175 (1963).
(35) Crafts, J. M., *Ann.*, 124, 110 (1862); **128**, 220 (1863).
(36) Creighton, A. M., and Owen, L. N., *J. Chem. Soc.*, 1024 (1960).
(37) Culvenor, C. C. J., Davies, W., and Pausacker, K. H., *J. Chem. Soc.*, 1050 (1946).
(38) Culvenor, C. C. J., Davies, W., and Heath, N. S., *J. Chem. Soc.*, 278 (1949).
(39) Culvenor, C. C. J., Davies, W., and Heath, N. S., *J. Chem. Soc.*, 282 (1949).
(40) Culvenor, C. C. J., Davies, W., and Savige, W. E., *J. Chem. Soc.*, 4480 (1952).
(41) Cunningham, G. L., Boyd, A. W., Myers, R. J., and Gwinn, W. D., *J. Chem. Phys.*, **19**, 676 (1951).

---

[3] As well as the oxidized reaction products from ethylene sulfide and fatty acids (211).

(42) Dachlauer, K., and Jackel, L., French Patent 797,621 (1936); German Patent 636,708 (1936); British Patent 465,662 (1937); U. S. Patents 2,094,837 and 2,094,914 (1937); *Chem. Abstr.*, **30**, 7122 (1936).

(43) Davies, W., and Savige, W. E., *J. Chem. Soc.*, 317 (1950).

(44) Davies, W., and Savige, W. E., *J. Chem. Soc.*, 774 (1951).

(45) Davis, F. O., and Fettes, E. M., in "Polyethers," Part III, N. G. Gaylord, Ed., Interscience, New York, N. Y., 1962, pp 1–37.

(46) Davis, R. E., *J. Org. Chem.*, **23**, 216, 1380 (1958).

(47) Davis, R. E., *J. Org. Chem.*, **23**, 1767 (1958).

(48) Dearborn, F. E., U. S. Patent 2,169,793 (1940); 2,237,096 (1941); 2,333,093 (1943); 2,427,717 (1947); 2,845,438 (1958); *Chem. Abstr.*, **34**, 214 (1940); **35**, 5305 (1941); **38**, 2170 (1944); **42**, 330 (1948); **53**, 4299 (1959).

(49) Dearborn, F. E., U. S. Patent 2,695,286 (1954); *Chem. Abstr.*, **49**, 2488 (1955).

(50) Delépine, M., *Compt. Rend.*, **171**, 36 (1920); *Bull. Soc. Chim. France*, (4) **27**, 740 (1920).

(51) Delépine, M., and Jaffeux, P., *Compt. Rend.*, **172**, 158 (1921); *Bull. Soc. Chim. France*, (4) **29**, 136 (1921).

(52) Delépine, M., and Eschenbrenner, S., *Bull. Soc. Chim. France*, (4) **33**, 703 (1923).

(53) Denney, D. D., and Boskin, M. J., *J. Am. Chem. Soc.*, **82**, 4736 (1960); *Chem. Ind.* (London), 330 (1959).

(54) Dermer, O. C., and Ames, W. A., *J. Polymer Sci.*, **A2**, 4145 (1964).

(55) Dittmer, D. C., and Levy, G. C., *J. Org. Chem.*, **30**, 636 (1965).

(56) Djerassi, C., Wolf, H., Lightner, D. A., Bunnenberg, E., Takeda, K., Komeno, T., and Kuriyama, K., *Tetrahedron*, **19**, 1547 (1963).

(57) Doyle, F. P., Holland, D. O., Mansford, K. R. L., Nayler, J. H., and Queen, A., *J. Chem. Soc.*, 2660 (1960).

(58) Doyle, F. P., and Ayad, K. N., British Patent 819,688 (1960); *Chem. Abstr.*, **54**, 8849 (1960); German Patent 1,131,695 (1962); Swiss Patent 358,794 (1962).

(59) Duffey, H. R., Snow, R. D., and Keyes, D. B., *Ind. Eng. Chem.*, **26**, 91 (1934).

(60) Durden, J. A., Stansbury, H. A., and Catlette, W. H., *J. Am. Chem. Soc.*, **81**, 1943 (1959).

(61) Durden, J. A., Stansbury, H. A., and Catlette, W. H., *J. Am. Chem. Soc.*, **82**, 3082 (1960).

(62) Durden, J. A., Stansbury, H. A., and Catlette, W. H., *J. Org. Chem.*, **26**, 836 (1961).

(63) Endo, K., and Kojima, H., Japanese Patent 21,496 (1963); *Chem. Abstr.*, **60**, 3122 (1964).

(64) Epshtein, G. Y., Usov, I. A., and Ivin, S. Z., *Zh. Obshch. Khim.*, **33**, 3638 (1963); *Chem. Abstr.*, **60**, 7909 (1964).

(65) Epshtein, G. Y., Usov, I. A., and Ivin, S. Z., *Zh. Obshch. Khim.*, **34**, 1948 (1964); *Chem. Abstr.*, **61**, 8178 (1964).

(66) Epshtein, G. Y., Usov, I. A., and Ivin, S. Z., *Zh. Obshch. Khim.*, **34**, 1951 (1964); *Chem. Abstr.*, **61**, 8178 (1964).

(67) Epshtein, G. Y., Usov, I. A., and Ivin, S. Z., *Zh. Obshch. Khim.*, **34**, 1954 (1964); *Chem. Abstr.*, **61**, 8178 (1964).

(68) Etlis, V. S., and Grobov, L. N., USSR Patent 128,462 (1960); *Chem. Abstr.*, **55**, 1650 (1961).

(69) Ettlinger, M. G., *J. Am. Chem. Soc.*, **72**, 4792 (1950).

(70) Evans, R. M., Fraser, J. B., and Owen, L. N., *J. Chem. Soc.*, 248 (1949).

(71) Farmer, E. H., and Shipley, F. W., *J. Chem. Soc.*, 1519 (1947).

(72) Fately, W. G., and Miller, F. A., *Spectrochim. Acta*, **19**, 611 (1963).

(73) Fields, D. L., and Reynolds, D. D., Belgian Patent 616,671 (1962); *Chem. Abstr.*, **60**, 2890 (1964).

(74) Frear, D. E., and Seiferle, E. J., *J. Econ. Entomol.*, **40**, 736 (1947); *Chem. Abstr.*, **42**, 2045 (1948).

(75) Furukawa, K., Nomura, M., and Oda, R., *J. Chem. Soc. Japan*, **55**, 671 (1952); *Chem. Abstr.*, **49**, 1626 (1955).

(76) Furukawa, K., Nomura, M., and Oda, R., *Bull. Inst. Chem. Res. Kyoto Univ.*, **28**, 74 (1952); *Chem. Abstr.*, **46**, 11105 (1952).

(77) Furukawa, K., and Oda, R., *Bull. Inst. Chem. Res. Kyoto Univ.*, **30**, 50 (1952); *Chem. Abstr.*, **47**, 3611 (1953).

(78) Furukawa, K., Nomura, M., and Oda, R., *J. Chem. Soc. Japan*, **56**, 189 (1953); *Chem. Abstr.*, **49**, 4581 (1955).

(79) Fuson, R. C., Lipscomb, R. D., McKusick, B. C., and Reed, L. J., *J. Org. Chem.*, **11**, 513 (1946).

(80) Gallegos, E., and Kiser, R. W., *J. Phys. Chem.*, **65**, 1177 (1961).

(81) Gill, A., *J. Soc. Leather Trades' Chemists*, **42**, 394 (1958); *Chem. Abstr.*, **53**, 11867 (1959).

(82) Gilman, H., and Woods, L. A., *J. Am. Chem. Soc.*, **67**, 1843 (1945).

(83) Goodman, L., Benitez, A., and Baker, B. R., *J. Am. Chem. Soc.*, **80**, 1680 (1958).

(84) Goodman, L., and Baker, B. R., *J. Am. Chem. Soc.*, **81**, 4924 (1959).

(85) Günthard, H. H., and Gäumann, T., *Helv. Chim. Acta*, **33**, 1958 (1950).

(86) Gundermann, K. D., *Angew. Chem.*, **75**, 1194 (1963).

(87) Guss, C. O., and Chamberlain, D. L., *J. Am. Chem. Soc.*, **74**, 1342 (1952).

(88) Guthrie, G. B., Scott, D. W., and Waddington, G., *J. Am. Chem. Soc.*, **74**, 2795 (1952).

(89) Guthrie, R. D., *Chem. Ind.* (London), 2121 (1962).

(90) Gutowsky, H. S., Ritedge, R. L., Tamres, M., and Searles, S., *J. Am. Chem. Soc.*, **76**, 4242 (1954).

(91) Hansen, B., *Acta Chem. Scand.*, **11**, 537 (1957).

(92) Hansen, B., *Acta Chem. Scand.*, **13**, 151, 159 (1959).

(93) Harding, J. S., Miles, L. W. C., and Owen, L. N., *Chem. Ind.* (London), 887 (1951).

(94) Harding, J. S., and Owen, L. N., *J. Chem. Soc.*, 1528 (1954).

(95) Harukawa, Ch., Sakai, M., and Konishi, K., Japanese Patent 9997 (1962); *Chem. Abstr.*, **60**, 3440 (1964).

(96) Helmkamp, G. K., and Schnautz, N., *Tetrahedron*, **2**, 304 (1958).

(97) Helmkamp, G. K., and Pettitt, D. J., *J. Org. Chem.*, **25**, 1754 (1960).

(98) Helmkamp, G. K., and Pettitt, D. J., *J. Org. Chem.*, **27**, 2942 (1962).

(99) Helmkamp, G. K., and Pettitt, D. J., *J. Org. Chem.*, **29**, 3258 (1964).

(100) Hesse, G., Reichold, E., and Majmudar, S., *Chem. Ber.*, **90**, 2106 (1957); see also *Chem. Ber.*, **93**, 1129 (1960).

(101) Hopkins, T. R., Rhodes, A., and Arakelian, A. N., German Patent 1,012,416 (1958); British Patent 818,962 (1959); *Chem. Abstr.*, **54**, 15917 (1960).

(102) Hrubesch, A., German Patents 964,772 and 1,002,329 (1957); *Chem. Abstr.*, **53**, 22893 (1959).

(103) Hurd, C. D., and Wilkinson, K., *J. Am. Chem. Soc.*, **71**, 3429 (1949).

(104) Husemann, A., *Ann.*, **126**, 269 (1863).

(105) Igbal, S. M., and Owen, L. N., *J. Chem. Soc.*, 1030 (1960).

(106) Imperial Chemical Industries Ltd., British Patent 597,368 (1948); *Chem. Abstr.*, **42**, 7573 (1948).

(107) Ioffe, D. V., and Rachinskii, F. Yn., *Usp. Khim.*, **26**, 678 (1957); *Chem. Abstr.*, **52**, 1133 (1958).

(108) Ivin, S. Z., *Zh. Obshch. Khim.*, **22**, 267 (1952); *Chem. Abstr.*, **46**, 10103 (1952).

(109) Ivin, S. Z., *Zh. Obshch. Khim.*, **28**, 177 (1958); *Chem. Abstr.*, **52**, 12829 (1958).

(110) Jacobs, R. L., and Schuetz, R. D., *J. Org. Chem.*, **26**, 3472 (1961).

(111) Johnson, D. L., and Fields, D. L., U. S. Patent 3,072,676 (1963); *Chem. Abstr.*, **58**, 12426 (1963).

(112) Jones, S. G., and Reid, E. E., *J. Am. Chem. Soc.*, **60**, 2452 (1938).

(113) Kaufmann, H. P., and Schickel, R., *Fette, Seifen, Anstrichmittel*, 65, 625 (1963); *Chem. Abstr.*, **60**, 5757 (1964); see also Schickel, R., Dissertation, Münster, 1961.

(114) Kaye, S., *Am. J. Hyg.*, **50**, 289 (1949); *Chem. Abstr.*, **44**, 6578 (1950).

(115) Ketcham, R., and Shah, V. P., *J. Org. Chem.*, **28**, 229 (1963).

(116) Ketcham, R., Shah, V. P., and Strait, L. A., Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., 1964, p 42N.

(117) Kienle, R. N., U. S. Patent 2,766,256 (1956); *Chem. Abstr.*, **51**, 3302 (1957).

(118) Kiser, R. W., and Gallegos, E. J., *J. Phys. Chem.*, 66, 947 (1962).

(119) Köcher, E. U., Wagner, K., Emden, v. d. W., and Dankert, G., German Patent 1,176,862 (1964).

(120) Kolka, A. J., U. S. Patent 2,866,808 (1958); *Chem. Abstr.*, **53**, 12176 (1959).

(121) Komeno, T., *Chem. Pharm. Bull.* (Tokyo), **8**, 672 (1960); *Chem. Abstr.*, **55**, 17685 (1961).

(122) Kosmin, M., U. S. Patent 2,824,845 (1958); *Chem. Abstr.*, **52**, 9667 (1958); U. S. Patent 2,965,651 (1960); *Chem. Abstr.*, **55**, 10468 (1961).

(123) Kwart, H., and Herwig. J. A., *J. Am. Chem. Soc.*, **85**, 1508 (1963).

(124) Lal, J., and Trick, G. S., *J. Polymer Sci.*, **50**, 13 (1961).

(125) Latif, N., and Fathy, I., *J. Org. Chem.*, **27**, 1633 (1962).

(126) Lazier, W. A., and Signaigo, F. K., U. S. Patent 2,396,957 (1946); *Chem. Abstr.*, **40**, 3935 (1946).

(127) Lightner, D. A., and Djerassi, C., *Chem. Ind.* (London), 1236 (1962).

(128) Lightner, D. A., and Djerassi, C., *Tetrahedron*, **21**, 583 (1965).

(129) Lippert, E., and Prigge, H., *Ann.*, **659**, 81 (1962).

(130) Lippert, E., and Prigge, H., *Ber. Bunsenges. Phys. Chem.*, **67**, 415 (1963).

(131) Lissant, K. J., U. S. Patent 3,083,232 (1963); *Chem. Abstr.*, **59**, 5277 (1963).

(132) Loewig, C., and Weidmann, S., *Poggendorffs Ann.*, **46**, 81 (1839); **49**, 128 (1839).

(133) Lorenz, W., German Patent 1,086,712 (1960).

(134) Lüssi, H., and Zahner, H., German Patent 1,122,710 (1962); *Chem. Abstr.*, **56**, 15684 (1962); British Patent 898,314 (1962).

(135) Mackinney, H. W., U. S. Patent 2,962,457 (1960); *Chem. Abstr.*, **55**, 6009 (1961).

(136) Mackle, H., and O'Hara, P. A. G., *Tetrahedron*, **19**, 961 (1963).

(137) Mailhe, A., and Renaudie, M., *Compt. Rend.*, **195**, 391 (1932).

(138) Mansfeld, W., *Chem. Ber.*, **19**, 693 (1886).

(139) Mark, V., U. S. Patent 2,771,470 (1956); *Chem. Abstr.*, **51**, 6686 (1957).

(140) Marvel, C. S., and Weil, E. D., *J. Am. Chem. Soc.*, **76**, 61 (1954).

(141) Maslov, P. G., and Kolchikhin, A. A., *Zh. Obshch. Khim.*, **28**, 835 (1958); *Chem. Abstr.*, **52**, 17229 (1958).

(142) Masson, O., *J. Chem. Soc.*, **49**, 234 (1886).

(143) Mastryukova, T. A., Odnoralova, V. N., and Kabachnik, M. I., *Zh. Obshch. Khim.*, **28**, 1563 (1958); *Chem. Abstr.*, **53**, 1117 (1959).

(144) McGhie, J. F., Ross, W. A., Julietti, F. J., Grimwood, B. E., Usher, G., and Waldron, N. W., *Chem. Ind.* (London), 1980 (1962).

(145) McGhie, J. F., Ross, W. A., Julietti, F. J., and Grimwood, B. E., *J. Chem. Soc.*, 4638 (1962).

(146) McGhie, J. F., Ross, W. A., Julietti, F. J., Swift, G., Usher, G., Waldron, N. M., and Grimwood, B. E., *Chem. Ind.* (London), 460 (1964).

(147) McGrew, F. C., U. S. Patent 3,136,744 (1964); *Chem. Abstr.*, **61**, 4312 (1964); British Patent 943,373 (1963).

(148) Meade, E. M., and Woodward, F. N., *J. Chem. Soc.*, 1894 (1948).

(149) Meyer, V., *Ber.*, **19**, 3259 (1886).

(150) Middleton, W. J., U. S. Patent 3,136,781 (1964); *Chem. Abstr.*, **61**, 5612 (1964).

(151) Miles, L. W. C., and Owen, L. N., *J. Chem. Soc.*, 817 (1952).

(152) Millikan, A. F., U. S. Patent 3,073,846 (1963); *Chem. Abstr.*, **58**, 13794 (1963).

(153) Moore, C. G., and Porter, M., *J. Chem. Soc.*, 2062 (1958).

(154) Moore, L. P., and Ericks, W. P., U. S. Patent 2,323,409 (1943); *Chem. Abstr.*, **38**, 212 (1944).

(155) Moore, L. P., and Ericks, W. P., U. S. Patent 2,442,957 (1948); *Chem. Abstr.*, **42**, 7328 (1948).

(156) Moore, L. P., and Ericks, W. P., U. S. Patent 2,453,333 (1948); *Chem. Abstr.*, **43**, 1799 (1949).

(157) Mortimer, F. S., *J. Mol. Spectry.*, **5**, 199 (1960).

(158) Mousseron, M., Bousquet, M., and Marret, O., *Bull. Soc. Chim. France*, 84 (1948).

(159) Mousseron, M., Jacquier, R., Mousseron-Canet, M., and Zagdoun, R., *Bull. Soc. Chim. France*, 1042 (1952).

(160) Muroi, T., Morimoto, S., and Yamaouchi, A., Japanese Patent 9891/61; *Chem. Abstr.*, **56**, 3682 (1962); German Patent 1,129,925 (1962).

(161) Musher, J. J., and Gordon, R. G., *J. Chem. Phys.*, **36**, 3097 (1962).

(162) Nelson, R. A., and Jessup, R. S., *J. Res. Natl. Bur. Std.*, **48**, 206 (1952).

(163) Neureiter, N. P., and Bordwell, F. G., *J. Am. Chem. Soc.*, **81**, 578 (1959); Neureiter, N. P., U. S. Patent 2,950,337 (1960); *Chem. Abstr.*, **55**, 1440 (1960).

(164) Neureiter, N. P., and Bordwell, F. G., *J. Am. Chem. Soc.*, **85**, 1209 (1963).

(165) Noshay, A., and Price, C. C., *J. Polymer Sci.*, **54**, 533 (1961).

(166) Ohta, M., *J. Japan. Chem.*, **7**, 756, 801 (1953); *Chem. Abstr.*, **48**, 13615 (1954).

(167) Ohta, M., Kondo, A., and Ohi, R., *Nippon Kagaku Zasshi*, **75**, 985 (1954); *Chem. Abstr.*, **51**, 14668 (1957).

(168) Ohta, H., and Ohta, M., *Nippon Kagaku Zasshi*, **77**, 198 (1956); *Chem. Abstr.*, **52**, 253 (1958).

(169) Olin, J. F., and Dains, F. B., *J. Am. Chem. Soc.*, **52**, 3322 (1930).

(170) Opitz, G., and Fischer, K., *Z. Naturforsch.*, **18b**, 775 (1963).

(171) Otto, F. P., and Meyer, R. E., U. S. Patent 2,520,101 (1950); *Chem. Abstr.*, 44, 10314 (1950).

(172) Owen, T. C., Gladys, C. L., and Field, L., *J. Chem. Soc.*, 501 (1962).

(173) Petrov, K. A., and Sokolskii, G. A., *Zh. Obshch. Khim.*, **27**, 2711 (1957); *Chem. Abstr.*, **52**, 7198 (1958).

(174) Pettitt, D. J., and Helmkamp, G. K., *J. Org. Chem.*, **28**, 2932 (1963); **29**, 2702 (1964).

(175) Price, C. C., and Kirk, P. F., *J. Am. Chem. Soc.*, **75**, 2396 (1953).

(176) Queen, A., British Patent 810,389 (1959); *Chem. Abstr.*,

54, 2360 (1960); U. S. Patent 2,918,476 (1959); German Patent 1,090,227 (1961); Swiss Patent 353,002 (1961).

(177) Rachinskii, F. Y., Slavachevskaya, N. M., and Ioffe, D. V., *Zh. Obshch. Khim.*, **28**, 2998 (1958); *Chem. Abstr.*, **53**, 9045 (1959).

(178) Razuvaev, G. A., Etlis, V. S., and Grobov, L. N., *Zh. Obshch. Khim.*, **33**, 1366 (1963); *Chem. Abstr.*, **59**, 9827 (1963).

(179) Reid, E. E., "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1960, pp 11–19.

(180) Remes, N. L., and Krewer, W. A., U. S. Patent 2,891,072 (1959); *Chem. Abstr.*, **53**, 20099 (1951).

(181) Remes, N. L., and Krewer, W. A., U. S. Patent 2,900,392 (1959); *Chem. Abstr.*, **54**, 587 (1960).

(182) Reppe, W., and Nicolai, F., German Patent 631,016 (1936); *Chem. Abstr.*, **30**, 6008 (1936); U. S. Patent 2,105,843 (1938).

(183) Reppe, W., and Freytag, A., German Patent 696,774 (1940); *Chem. Abstr.*, **35**, 5909 (1941).

(184) Reynolds, D. D., *J. Am. Chem. Soc.*, **79**, 4951 (1957).

(185) Reynolds, D. D., U. S. Patent 2,828,318 (1958); *Chem. Abstr.*, **52**, 14651 (1958).

(186) Reynolds, D. D., Fields, D. L., and Johnson, D. L., *J. Org. Chem.*, **26**, 5130 (1961).

(187) Ried, W., and Klug, H., *Chem. Ber.*, **94**, 368 (1961).

(188) Ringsdorf, H., and Overberger, C. G., *Makromol. Chem.*, **44–46**, 418 (1961).

(189) Romeyn, H., and Petras, J. F., German Patent 925,314 (1955); *Chem. Abstr.*, **52**, 2443 (1958).

(190) Sabatino, E. C., and Grittner, R. J., *J. Org. Chem.*, **28**, 3437 (1963).

(191) Salchow, R., *Kautschuk*, 14, 12 (1938); *Chem. Abstr.*, **32**, 4007 (1938); *Kautschuk*, **13**, 119 (1937); *Chem. Abstr.*, **31**, 8991 (1937).

(192) Sander, M., *Monatsh.*, **96**, 896 (1965).

(192a) Schmidt, U., and Osterroth, Ch., *Angew. Chem.*, **77**, 455 (1965).

(193) Schönberg, A., *Ann.*, **454**, 37 (1927).

(194) Schönberg, A., and Schütz, O., *Chem. Ber.*, **60**, 2351 (1927).

(195) Schönberg, A., and Vargha, v. L., *Ann.*, **483**, 176 (1930).

(196) Schönberg, A., and Vargha, v. L., *Chem. Ber.*, **64**, 1390 (1931).

(197) Schönberg, A., and Nickel, S., *Chem. Ber.*, **64**, 2323 (1931).

(198) Schönberg, A., Cernik, D., and Urban, W., *Chem. Ber.*, **64**, 2579 (1931).

(199) Schönberg, A., and Barakat, M. Z., *J. Chem. Soc.*, 1074 (1939).

(200) Schönberg, A., in Houben-Weyl, "Methoden der organischen Chemie," Vol. 9, Stuttgart, 1955, p 153.

(201) Schönberg, A., Fateen, A. K., and Sammour, A. M. A., *J. Am. Chem. Soc.*, **79**, 6020 (1957).

(202) Schönberg, A., and Frese, E., *Chem. Ber.*, **95**, 2810 (1962).

(203) Schrader, G., and Lorenz, W., German Patent 1,082,915 (1960); *Chem. Abstr.*, **55**, 25983 (1961).

(204) Schuetz, R. D., and Jacobs, R. L., *J. Org. Chem.*, **23**, 1799 (1958).

(205) Schuetz, R. D., and Jacobs, R. L., *J. Org. Chem.*, **26**, 3467 (1961).

(206) Searles, S., Hays, H. R., and Lutz, E. F., *J. Org. Chem.*, **27**, 2832 (1962); *J. Am. Chem. Soc.*, **80**, 3168 (1958).

(207) Searles, S., Lutz, E. F., Hays, H. R., and Mortensen, H. E., *Org. Syn.*, **42**, 59 (1962).

(208) Sergeev, P. G., and Kolychev, B. S., *Zh. Obshch. Khim.*, **7**, 2600 (1937); *Chem. Abstr.*, **32**, 2534 (1938).

(209) Sheppard, N., *Trans. Faraday Soc.*, **46**, 429 (1950).

(210) Signaigo, F. K., U. S. Patent 2,436,233 (1948); *Chem. Abstr.*, **42**, 3775 (1948).

(211) Slobodin, Y. M., Altmann, S. S., and Tammik, K. D., *Proizv. Smaz. Materialov*, **5**, 58 (1959); *Chem. Abstr.*, **54**, 12559 (1960).

(212) Snyder, H. R., Stewart, J. M., and Ziegler, J. B., *J. Am. Chem. Soc.*, **69**, 2672 (1947).

(213) Snyder, H. R., Stewart, J. M., and Ziegler, J. B., *J. Am. Chem. Soc.*, **69**, 2675 (1947).

(214) Snyder, H. R., and Alexander, W., *J. Am. Soc. Chem.*, **70**, 217 (1948).

(215) Snyder, H. R., and Eliel, E. L., *J. Am. Chem. Soc.*, **70**, 2825 (1948).

(216) Snyder, H. R., and Stewart, J. M., U. S. Patents 2,490,984 and 2,490,985 (1949); *Chem. Abstr.*, **44**, 2550 (1950).

(217) Snyder, H. R., and Stewart, J. M., U. S. Patent 2,497,100 (1950); *Chem. Abstr.*, **44**, 4025 (1950).

(218) Snyder, H. R., and Stewart, J. M., U. S. Patent 2,497,422 (1950); *Chem. Abstr.*, **44**, 4025 (1950).

(219) Snyder, H. R., and Stewart, J. M., U. S. Patent 2,505,870 (1950); *Chem. Abstr.*, **44**, 7352 (1950).

(220) Societe Nationale des Petroles d'Aquitaine, French Patent 1,307,385 (1962); *Chem. Abstr.*, **58**, 9027 (1963).

(221) Soloway, S. B., U. S. Patent 2,694,073 (1954); *Chem. Abstr.*, **49**, 3465 (1955).

(222) Staudinger, H., and Pfenninger, F., *Chem. Ber.*, **49**, 1941 (1916).

(223) Staudinger, H., and Siegwart, J., *Helv. Chim. Acta*, **3**, 833 (1920).

(224) Staudinger, H., and Siegwart, J., *Helv. Chim. Acta*, **3**, 840 (1920).

(225) Stewart, J. M., and Cordts, H. P., *J. Am. Chem. Soc.*, **74**, 5880 (1952).

(226) Stewart, J. M., U. S. Patent 2,743,290 (1956); *Chem. Abstr.*, **51**, 456 (1957).

(227) Stewart, J. M., U. S. Patent 2,774,794 (1956); *Chem. Abstr.*, **51**, 7400 (1957).

(228) Stewart, J. M., *J. Org. Chem.*, **28**, 596 (1963).

(229) Stewart, J. M., *J. Org. Chem.*, **29**, 1655 (1964).

(230) Strausz, O. P., and Gunning, H. E., *J. Am. Chem. Soc.*, **84**, 4080 (1962).

(231) Strait, L. A., Ketcham, R., Jambotkav, D., and Shah, V. P., *J. Am. Chem. Soc.*, **86**, 4628 (1964).

(232) Sunner, S., *Acta Chem. Scand.*, **17**, 728 (1963).

(233) Takeda, K., Komeno, T., and Kawanami, J., *Chem. Pharm. Bull.* (Tokyo), **8**, 621 (1960); *Chem. Abstr.*, **55**, 12451 (1960).

(234) Takeda, K., and Komeno, T., *Chem. Ind.* (London), 1793 (1962).

(235) Takeda, K., Komeno, T., Kawanami, J., Ishihara, S., Kadokawa, H., Tokura, H., and Itani, H., *Tetrahedron*, **21**, 329 (1965).

(236) Tamres, M., and Searles, S., *J. Phys. Chem.*, **66**, 1099 (1962).

(237) Tarbell, D. S., and Harnish, D. P., *Chem. Rev.*, **49**, 1 (1951).

(238) Tendeloo, H. J. C., U. S. Patent 2,225,573 (1940); *Chem. Abstr.*, **35**, 2269 (1941).

(239) Thompson, H. W., and Dupre, D. J., *Trans. Faraday Soc.*, **36**, 805 (1940).

(240) Thompson, H. W., and Cave, W. T., *Trans. Faraday Soc.*, **47**, 951 (1951).

(241) Tori, K., Komeno, T., and Nakagawa, T., *J. Org. Chem.*, **29**, 1136 (1964).

(242) Traeger, E., and Hewehi, Z. El., *J. Prakt. Chem.*, (4) **18**, 255 (1962).

(243) Tung, C. C., and Speziale, A. J., *J. Org. Chem.*, **29**, 1577 (1964).

(244) Turk, S. D., Louthan, R. P., Cobb, R. L., and Bresson, C. R., *J. Org. Chem.*, **29**, 974 (1964).

(245) Ufer, H., and Freytag, A., German Patent 696,773 (1940); *Chem. Abstr.*, **35**, 5909 (1941).

(246) Van Tamelen, E. E., *J. Am. Chem. Soc.*, **73**, 3444 (1951).

(247) Van Tamelen, E. E., *Org. Syn.*, **32**, 39 (1952).

(248) Venkateswarin, K., and Thyagarjan, G., *Proc. Indian Acad. Sci., Sect. A*, **52**, 101 (1960); *Chem. Abstr.*, **55**, 5123 (1961).

(249) Wagner-Jauregg, T., *Ann.*, **561**, 87 (1949).

(250) Warner, P. F., U. S. Patent 3,071,593 (1963); *Chem. Abstr.*, **58**, 11329 (1963).

(251) Weissermel, K., Fischer, E., Gutweiler, K., and Hermann, H. D., *Kunststoffe*, **54**, 410 (1964).

(252) Wenisch, W. J., Dissertation, New York, 1955.

(253) Whistler, R. L., *J. Polymer Sci.*, **A2**, 2595 (1964).

(254) Wineman, R. J., Gollis, M. H., James, J. C., and Pomponi, A. M., *J. Org. Chem.*, **27**, 4222 (1962).

(255) Wright, J. B., *J. Am. Chem. Soc.*, **79**, 1694 (1957).

(256) Youtz, M. A., and Perkins, P. P., *J. Am. Chem. Soc.*, **51**, 3508 (1929).

(257) Yuriev, Y. K., and German, L. S., *Zh. Obshch. Khim.*, **25**, 2527 (1955); *Chem. Abstr.*, **50**, 9428 (1956).

(258) Yuriev, Y. K., and Dyatlovitskaja, S. V., Part II, *Zh. Obshch. Khim.*, **27**, 1787 (1957); *Chem. Abstr.*, **52**, 4603 (1958); Part X, *Zh. Obshch. Khim.*, **29**, 3885 (1959); *Chem. Abstr.*, **54**, 21049 (1960).