

## DIHYDROTHIOPHENES. SYNTHESIS AND PROPERTIES (REVIEW)

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*The literature data on the methods of synthesis and properties of 2,3-dihydrothiophene and 2,5-dihydrothiophene have been correlated for the first time.*

### INTRODUCTION

The considerable interest of investigators in thiophene and its derivatives is explained by the fact that these compounds play an important role in the solution of many theoretical and practical problems of organic chemistry. Compounds containing the thiophene ring display a marked aromatic character, and in addition their ability to be desulfurized with ring fission and the formation of acyclic products is very important. Consequently they are promising subjects for studying certain reactions and for the synthesis of numerous compounds of practical interest. A very large number of publications has appeared on the synthesis and study of the properties of thiophene and its derivatives, including a vast amount of material correlated in reviews and monographs such as [1-7]. In the main, methods of synthesis and the properties of thiophene and its derivatives have been considered in the review articles. There are significantly fewer data on the chemistry of their hydrogenated analogs and there is practically no information on the synthesis and properties of the simplest representatives of the partially hydrogenated thiophene derivatives 2,3-dihydrothiophene and 2,5-dihydrothiophene. It must be said that some attention is paid in monographs [6, 7] to the reduction of thiophene to dihydrothiophenes.

The fully available 2,3-dihydrothiophene and 2,5-dihydrothiophene have a rich synthetic potential. They contain a reactive double bond and a sulfur atom and may readily react with fission of the heterocyclic ring. The study of dihydrothiophenes as intermediates in the conversion of thiophene and its derivatives into alicyclic compounds plays a significant role in the creation of theoretical bases for the desulfurization of petroleum derivatives.

In spite of the fact that the study of dihydrothiophenes began more than half a century ago, undeservedly little attention has been paid to the actual parent compounds of this series, viz. 2,3-dihydrothiophene and 2,5-dihydrothiophene. Less than a hundred papers and patents have been published in all, a significant portion of which is devoted to the study of the physicochemical characteristics and desulfurization of dihydrothiophenes, and their synthetic possibilities have undeservedly been investigated insufficiently.

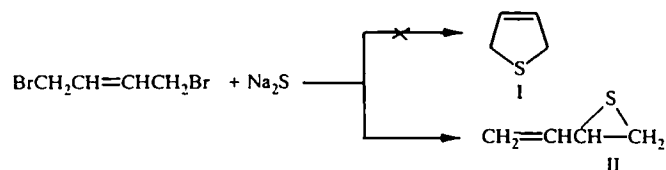
### 1. METHODS OF OBTAINING 2,3-DIHYDROTHIOPHENE AND 2,5-DIHYDROTHIOPHENE

#### 1.1. From Alkenes or Alkynes

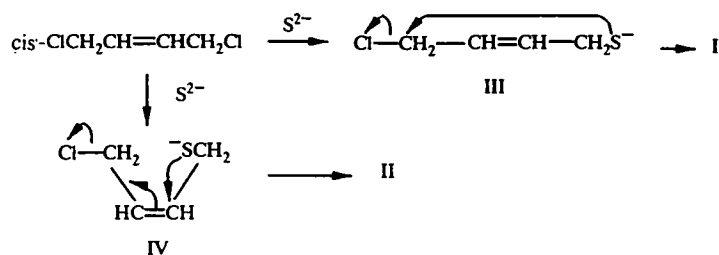
Attempts to obtain dihydrothiophene by the reaction of 1,4-dibromobut-2-ene with sodium sulfide at 25-30°C in alcohol were undertaken even in 1938 [8]. The authors assumed that the reaction product was 2,5-dihydrothiophene (3-thiolene) (I). However it was later established that vinylthiirane (II) was formed under these conditions and not thiolene (I) [9, 10].

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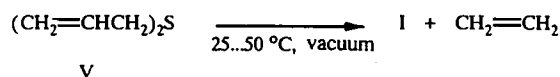
A. N. Kosygin Moscow State Textile Academy, Moscow 117918, Russia. Translated from *Khimiya Geterotsiklicheskich Soedinenii*, No. 10, pp. 1299-1324, October, 1998. Original article submitted June 5, 1997.



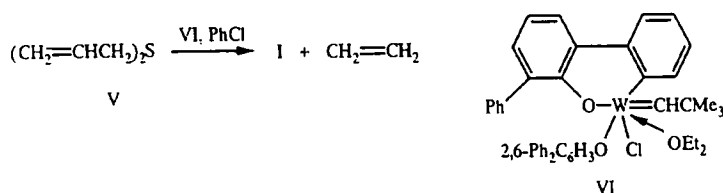
Thiolene (I) was synthesized by the cyclocondensation of 1,4-dichlorobut-2-ene with sodium sulfide conducted in dimethyl sulfoxide at 35-38°C for 30 min [10]. It was established thereby that the vinylthiirane (II) together with dihydrothiophene (I) were formed as a result of the intramolecular nucleophilic substitution reaction of the anions [(III) or (IV)] formed as intermediates.



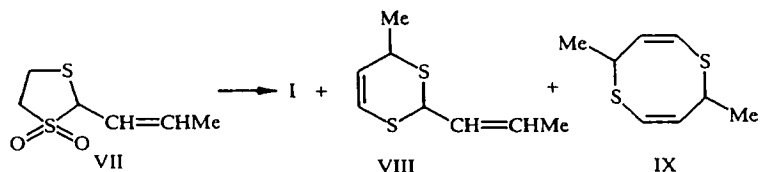
Diallyl disulfide (V) undergoes an intramolecular change in the presence of a molybdenum-containing complex with the formation of thiolene (I) and ethylene [11]. It is interesting that other acyclic  $\alpha,\omega$ -dienes polymerize under these conditions [11].



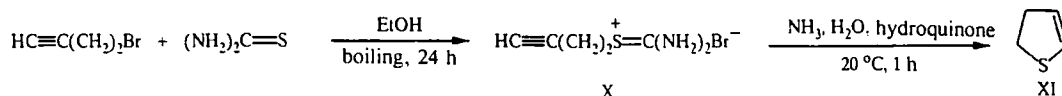
The authors of [12] have investigated in detail the conversion of sulfide (V) in the presence of complex (VI) at various ratios of sulfide:catalyst (VI) (100:1 and 250:1), temperatures (50 and 80°C), and reaction times (3, 6, 8 h) and determined the conversion of sulfide and also the yield of thiolene (I). High conversions of sulfide (V) (88-98%) and yield of product (78-88%) were achieved in all cases.



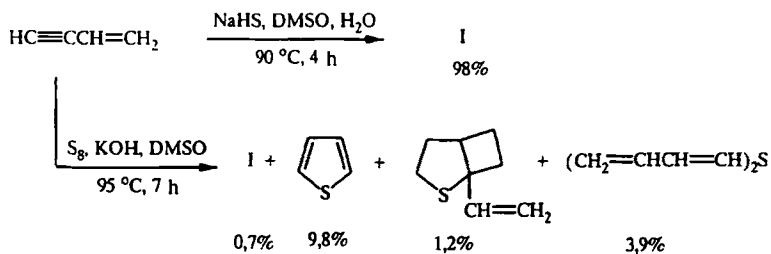
2-Propenyl-1,3-dithiolane 1,1-dioxide (VII) is converted under conditions of vacuum flame pyrolysis into a mixture of thiolene (I), thiophene, and the thioaldehyde  $\text{MeCH}=\text{CHC}(\text{S})\text{H}$  and the latter is converted by [4+2]- or [4+4]-dimerization into products (VIII) or (IX) respectively [13].



Compound (X), formed from 4-bromo-1-butyne and thiourea, is converted in aqueous ammonia solution at room temperature in 45% yield into 2,3-dihydrothiophene (2-thiolene) (XI) [14].



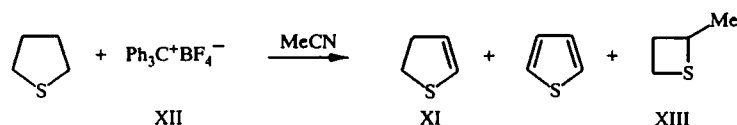
Dihydrothiophene (I) is formed in practically quantitative yield on treating vinylacetylene with sodium hydrosulfide in water and dimethyl sulfoxide. A complex mixture of products is obtained by the reaction of vinylacetylene with elementary sulfur in dimethyl sulfoxide in the presence of potassium hydroxide but the overall yield of thiolene (I) was 0.7% [15].



## 1.2. From Five-Membered Sulfur-Containing Compounds

Tetrahydrothiophene (thiophane) or its derivatives are frequently used to obtain dihydrothiophenes.

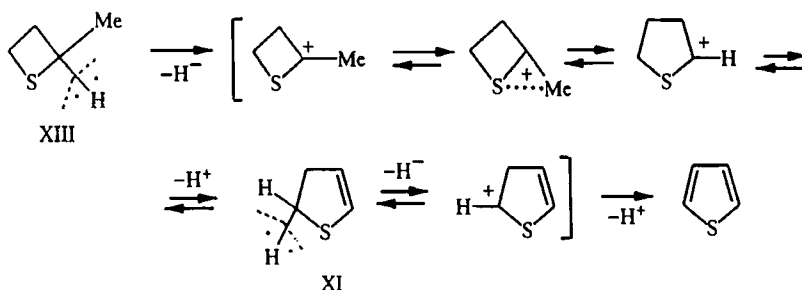
A mixture of 2-thiophene (XI), thiophene, and 2-methylthiacyclobutane (XIII) is formed on treating thiophane with triphenyl tetrafluoroborate (XII) in acetonitrile. The yields of these compounds depended on the ratio of thiolane:salt (XII), temperature, and on reaction time [16].



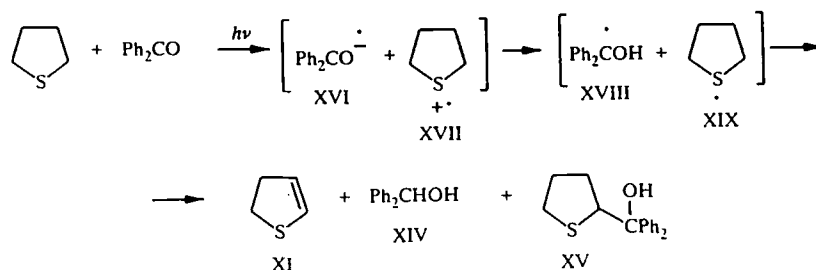
Ratio of thiophane:salt (XII), T, °C, duration (h), yields of (XI), thiophene, and (XIII), %:  
 1 : 2; 20; 1, (1, —, —); 1 : 2; 30, (1, 8, 29, 2); 1 : 2; 40, 1, (—, 2, —); 1 : 1; 30, 2, (20, 2, 8); 1 : 2,  
 30, 2, (6, 50, 2); 1 : 3, 30, 2 (13, 3, 6)

If chloranil is used as oxidizing agent in this reaction in place of salt (XII) (ratio of thiophane:chloranil = 1:22, reaction temperature 80°C, time 3-30 h) then the process occurs to an insignificant extent. The yields of thiolene (XI) were 1-3%, of thiophene 4-8%, and of product (XIII) 1-2%.

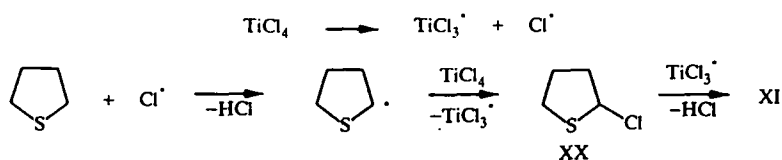
The authors of [16] considered that the conversion of compound (XIII) into thiophene occurs through the stage of forming thiolene (XI) by the following scheme:



Irradiation (UV) of a mixture of thiolane and benzophenone in deuterobenzene (Philips SP 1000 lamp) and removal of gases at  $10^{-5}$  mm gave a mixture of thiolene (XI), secondary alcohol (XIV), and tertiary alcohol (XV) [17]. A scheme was proposed in this work for the conversion of thiolane and benzophenone into compounds (XI), (XIV), and (XV). This included the intermediate formation of the radical-anion (XVI) and the radical-cation (XVII), and then radicals (XVIII) and (XIX). The direct formation of radicals (XVIII) and (XIX) from thiolane and benzophenone was not excluded.



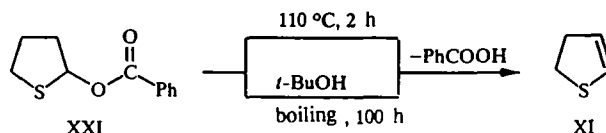
The formation of thiolene (XI) from 2-chloro-tetrahydrothiophene (XX) by treatment of the thiolane with titanium tetrachloride was established in [18].



Dihydrothiophene (XI) may also be obtained by the reaction of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with chloro derivative (XX) [19].

A fairly common method of synthesizing thiolene (XI) is the fission of benzoic acid from 2-benzoyloxy-tetrahydrothiophene (XXI). The latter may be obtained by heating tetrahydrothiophene with tert-butyl perbenzoate (95-105°C, 4 h) [20] or by the reaction of tetrahydrothiophene S-oxide (XXII) with benzoic anhydride (boiling in benzene for 5 h) [21].

This method of obtaining thiolene (XI) was published for the first time by G. Sosnovsky in 1961 [22]. Two modifications of it were proposed, 1) pyrolysis of the benzoyloxy derivative (XXI) at 110°C (80% yield) and 2) prolonged boiling of compound (XXI) in tert-butyl alcohol (64% yield).

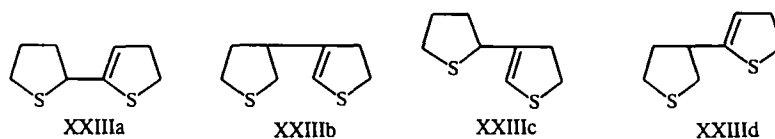


Later the same author synthesized dihydrothiophene (XI) in yields of 60 and 82% by keeping ester (XXI) at 750 [23] or at 10 mm Hg [20] and 110-140°C for 2 h.

The thiolene is also formed in 53% yield by passing vapors of compound (XXI) in a current of nitrogen through a pyrex tube packed with glass wool at 300°C and 300 mm Hg for 2 h [18].

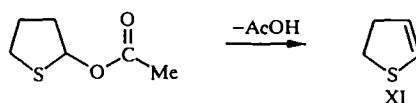
Compound (XI) was obtained in lower yield (23%) by heating ester (XXI) in a flask with a Vigreux column at 80°C and atmospheric pressure [21].

The dimeric product (XXIIIa) was obtained in 45% yield by the pyrolysis of the benzoyloxy derivative (XXI) at 160-170°C and atmospheric pressure [24, 25]. The structure of (XXIIIa) [structures (XXIIIb-d) are also possible for the thiolene dimer] was demonstrated by the formation of normal octane on desulfurizing it by boiling in 80% ethanol in the presence of Raney Ni for 5 h. Data of IR and NMR spectra also confirmed (XXIIIa) [25].

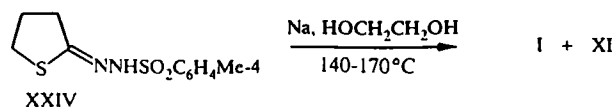


Pure monomeric thiolene (XI) was successfully obtained in 60% yield when compound (XXI) was decomposed in high vacuum and the distilled product collected in a trap cooled in liquid nitrogen [26, 27]. Monomer (XI) is preserved for 2-3 weeks in an atmosphere of nitrogen at the temperature of a solid CO<sub>2</sub>-isopropyl alcohol bath [14].

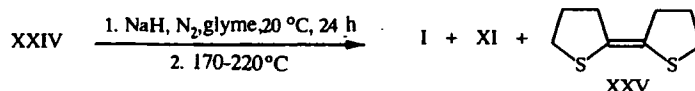
Dihydrothiophene (XI) was also obtained in 17% yield by the pyrolysis of 2-acetyloxetetrahydrothiophene at 150°C for 1 h [28]. Thiolene (XI) (20% yield) and its dimer (73.5% yield) were obtained in 1 h at 130-155°C and atmospheric pressure from the same acetoxy derivative [23]. A significantly higher yield of monomer (XI) (up to 86%) was achieved if the process was carried out in a nitrogen atmosphere at 400°C in a vacuum of 10<sup>-4</sup> mm Hg for 2 h [27].



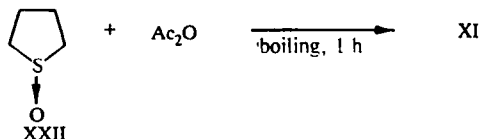
Treating sulfonylhydrazone (XXIV) with sodium at 140-170°C leads to a mixture of thioleues (I) and (XI) [total yield 66%, ratio of (I):(XI) 35:65] [29].



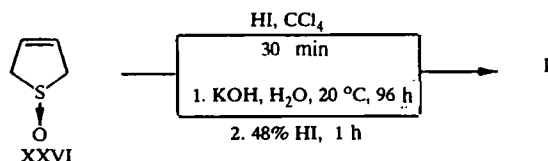
The sulfonylhydrazone (XXIV) was converted into the sodium salt by the action of sodium hydride [30]. Pyrolysis of this salt at 170-220°C gave a mixture of thiolenes (I) (11% yield) and (XI) (39% yield) with compound (XXV) as a contaminant.



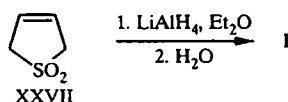
On boiling in acetic anhydride tetrahydrothiophene S-oxide (XXII) is converted into dihydrothiophene (XI) [30].



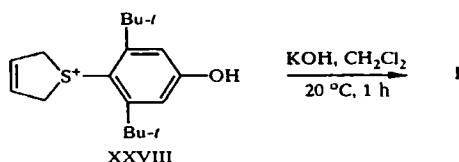
Two methods have been described for converting 2,5-dihydrothiophene S-oxide (XXVI) into thiolenes (I), 1) by treatment with 48% hydriodic acid in carbon tetrachloride, and 2) by the action of potassium hydroxide and subsequent reaction with 48% hydriodic acid [31].



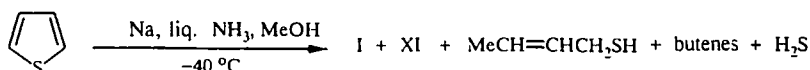
Using the inability of lithium aluminum hydride to reduce an unactivated double bond, the authors of [30] effected the conversion of  $\Delta^3$ -sulfolene (XXVII) into dihydrothiophene (I) by the action of this reducing agent.



The reduction of  $\Delta^3$ -sulfolene (XXVII) was effected in [32, 33] by the action of diisobutylaluminum in mineral oil at 20-25°C during 1.5 h. The thiolenes formed were distilled from the reaction mixture immediately after the end of the reaction. The yield was 12%. The preparation of dihydrothiophene (I) in 59% yield has been described by the treatment of cation (XXVIII) with potassium hydroxide in dichloromethane at room temperature [34].



A report of the reduction of thiophene by metallic sodium and liquid ammonia in methanol appeared for the first time in 1950 [9]. It was established that under these conditions 2,3-dihydrothiophene (XI) was formed as a result of 1,2 addition of hydrogen to thiophene, and 2,5-dihydrothiophene (I) as a result of 1,4 addition. It was discovered that as well as the addition reactions there also took place a splitting of the heterocyclic nucleus and hydrodesulfurization with the formation of but-2-enethiol, a mixture of butenes, and hydrogen sulfide.

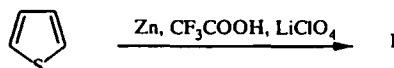


This process was studied in more detail in [35]. By carrying out the reaction at  $-40^{\circ}\text{C}$  for 8 h and subsequently keeping the reaction mixture at  $-40^{\circ}\text{C} \rightarrow 20^{\circ}\text{C}$  during 12 h there was obtained dihydrothiophene (XI), dihydrothiophene (I), and but-2-enethiol in yields of 12.3, 26.2, and 17% respectively.

The conversions of thiophene under the action of sodium and ammonia in methanol have also been reported in [31, 36, 37].

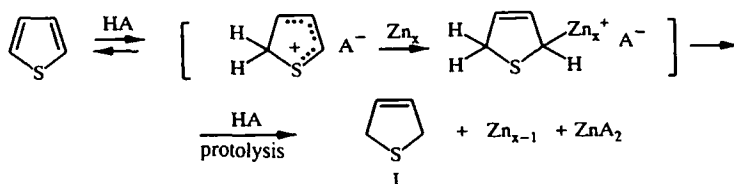
On investigating the reduction of thiophene by the action of metallic sodium in liquid ammonia and also metallic lithium in liquid ammonia and ammonium salts  $\text{NH}_4^+\text{X}^-$  ( $\text{X} = \text{SO}_4, \text{Cl}, \text{Br}$ ), it was established that thiolene formation was observed only on using sodium in the presence of ammonium bromide. The dihydrothiophenes were obtained in 86% yield overall, calculated on the thiophene converted (conversion 48%). The mixture of products contained 57% initial thiophene, 37% dihydro-thiophene mixture, and the remainder consisted of unidentified products [38].

The authors of [39] have reported that only thiolene (I) was obtained on reducing thiophene with metallic zinc in trifluoroacetic acid (in certain cases in the presence of lithium perchlorate).

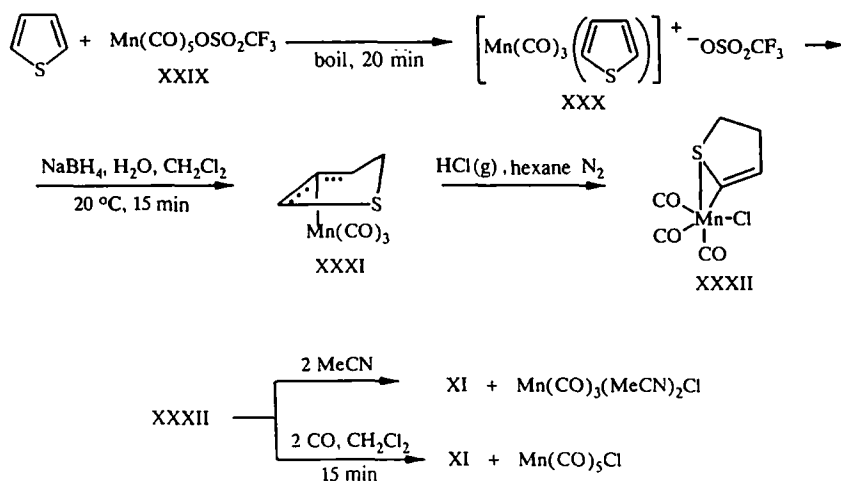


Reaction conditions, yield of (I), %: boiling for 10 h,  $20^{\circ}\text{C}$ , PhH, 7; boiling for 3.5 h,  $20^{\circ}\text{C}$ , 0.5 h, 16-22; boiling for 3.5 h + 0.5 h, at  $20^{\circ}\text{C}$ , 42; boiling for 14 h + 11 h, at  $20^{\circ}\text{C}$ , 46.

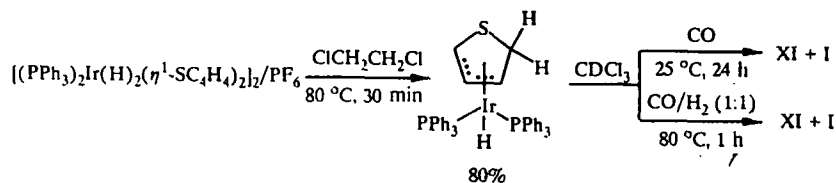
A mechanism for the process was proposed in the same paper, comprising the intermediate formation of a thio-phenium ion.



A multistage process for converting thiophene into thiolene (XI) has been reported [40]. Thiophene was reacted with pentacarbonylmanganese trifluoromethane-sulfonate (XXIX) and compound (XXX) was obtained in 74% yield. The latter was reduced with sodium borohydride to complex (XXXI) (86% yield). Complex (XXXI) was converted by treatment with hydrogen chloride into complex (XXXII) (63% yield). Thiolene (XI) was obtained by the action of acetonitrile or carbon monoxide on complex (XXXII) (in the case of CO the yield was quantitative).

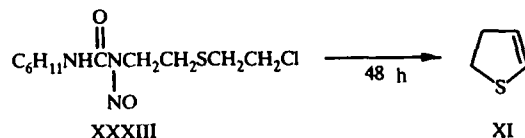


A mixture of thioenes (I) and (XI) in a ratio of 5:1 is formed as a result of the following conversions of an iridium hydride complex containing thiophene ligands [41]:

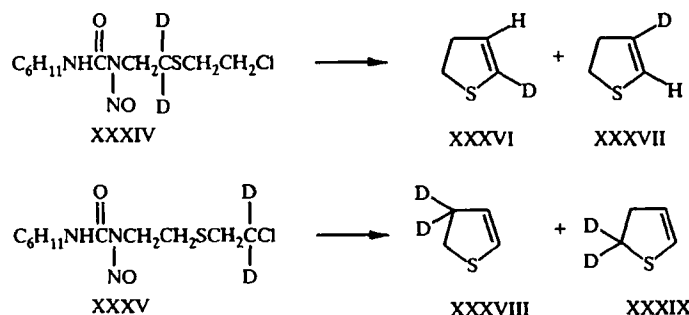


### 1.3. Other Methods

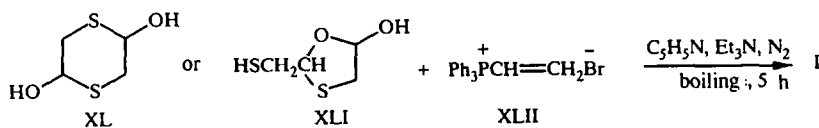
Thiolenes (XI) is formed in 4% yield from compound (XXXIII) under physiological conditions (potassium phosphate buffer pH 7.2, 37°C) [42].



Deuterated thiolenes (XXXVI) and (XXXVII) or (XXXVIII) and (XXXIX) were obtained from the corresponding deuterated N-nitroso compounds (XXXIV) or (XXXV) under the same conditions [42].

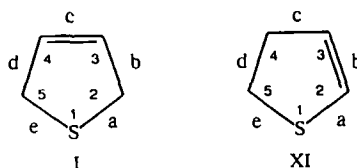


The reaction of the two dimeric forms of mercaptoacetaldehyde (XL) and (XLI) with vinyltriphenylphosphonium bromide (XLII) on boiling in the presence of pyridine and triethylamine in an inert atmosphere has been described. As a result dihydrothiophene (I) was formed in 44% yield [43].





## 2. STRUCTURE AND PHYSICAL PROPERTIES OF DIHYDROTHIOPHENES

The IR spectra of thiolenes (I) and (XI) have been studied in the range 2600-2900  $\text{cm}^{-1}$  [44]. The observed bands were assigned to the different combinations of symmetric stretching vibrations of  $\text{CH}_2$  groups and the deformation vibrations of the ring. Results obtained were in agreement with the following values of the internal angles and bond lengths of thiolenes assumed by the authors on the basis of standard values for related molecules: (I)  $\angle = 95^\circ$ ;  $a = 1.82 \text{ \AA}$ ;  $b = 1.518 \text{ \AA}$ ;  $c = 1.34 \text{ \AA}$ ;  $d = 1.518 \text{ \AA}$ ;  $e = 1.82 \text{ \AA}$ ; (XI)  $\angle = 95^\circ$ ;  $a = 1.77 \text{ \AA}$ ;  $b = 1.34 \text{ \AA}$ ;  $c = 1.518 \text{ \AA}$ ;  $d = 1.54 \text{ \AA}$ ;  $e = 1.82 \text{ \AA}$ .





Calculations on the thiolenes (I) molecule have been carried out by the method of molecular mechanics and the barriers for pseudorotation and compression have been estimated. It was shown that the calculated and experimentally determined

TABLE 1. Physical Properties of Dihydrothiophenes

Thiolene	bp, °C/mm Hg	mp, °C	$n_D^{20}$	$d_4^{20}$
 XI	48/100 [22]	-110,2 [35]	1,5268* [22]	1,0361 [9, 35, 36]
	112/760 [9, 35, 36]	-108,7 [36]	1,5311 [9, 35, 36]	1,0391 [49]
	64,8...65/160 [49]		1,5301 [49]	
	90/0,5 † [22]		1,6006 ‡ [22]	
	88...90/0,2 † [23]		1,6023 ‡ [23]	
 I	122/760 [33]	-50,3 [9, 35]	1,5300 [31]	1,0591 [9, 35, 36]
	122,3/760 [9, 35, 36]	-49,3 [36]	1,5206 [9, 36]	1,0589 [49]
	116...119/711 [31]		1,5298 [49]	
	76,2/185 [49]			

\*  $n_D^{25}$ .†  $T_{Bp}$  of dimer.‡  $n_D^{20}$  of dimer.

TABLE 2. Thermodynamic Characteristics of Dihydrothiophenes

Thiolene	Heat of formation, kcal/mole, 25°C	$\Delta E_c^\circ$ , kcal/mole <sup>-1</sup> [36]	$\Delta H_c^\circ$ , kcal/mole <sup>-1</sup> [36]	$\Delta H_f^\circ$ , kcal/mole <sup>-1</sup> [36]	$\Delta H_v$ , kcal/mole <sup>-1</sup> [36]	$\Delta P(\text{gas})$ , kcal/mole <sup>-1</sup> [36]
 XI	12,76* [49] 21,78 † [44, 49]	735,99±0,25	737,85±0,25	12,76±0,28	9,02±0,10	21,78±0,30
 I	11,31* [49] 20,86 † [44, 49]	734,57±0,25	736,40±0,25	11,31±0,28	9,55±0,06	20,86±0,28

\*Liquid.

†Gas.

dihedral angle for the ring of thiolene (I) was 0, consequently 2,5-dihydrothiophene (I) is a planar conformer [45]. Data were given in the same study for the internal angles (1 = 96.2°; 2 = 5 = 104.2°; 3 = 4 = 117.7°) and for the bond lengths (a = e = 1.84 Å; b = d = 1.506 Å; c = 1.34 Å).

Data of IR and Raman spectra confirmed the planar structure of the thiolene (I) ring [46]. Such a structure for the thiolene (I) ring is a result of little ring strain and weak repulsion of atoms not bonded by valency [47].

On the other hand, in compound (XLIII), formed from dihydrothiophenes and the chromium carbonyl (XLIV), the dihydrothiophene ring has the conformation of an envelope with a dihedral angle of 22.5° and the C-S bond in a pseudo-axial position [48].

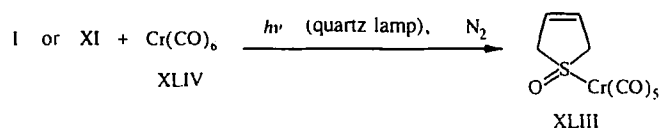






TABLE 3. Spectral Characteristics of Dihydrothiophenes\*

Thiolenes	IR spectrum, $\text{cm}^{-1}$	UV spectrum, $\lambda_{\text{max}}$ , nm [49]	PMR spectrum, $\delta$ , ppm	Mass spectrum, $m/z$ [29]
 XI	2793,0 2784,5 2778,7 2766,9 2757,6 2750,7 2737,2 [44]	236 <sup>†</sup> 262 <sup>†</sup> 237 <sup>‡</sup> 263 <sup>‡</sup>	2-H 6,06 3-H 5,48 4-H 3,08 5-H 2,62 [37] $J_{2,3}$ 5,98 [53] 6,01 [37] $J_{2,4}$ 2,23 [53] 2,2 [37] 2,78 [53] $J_{3,4}$ 2,5 [37] 9,99 [53] $J_{4,5}$ 9,2 [37]	86 (50%) ** 85 (100%) 45 (30%) 39 (14%) 38 (12%)
 I	3049, 2914, 2445, 1637, 1440, 1335, 1259, 1221, 1118, 1112, 1024, 958, 945, 891, 814, 711, 672, 665, 610, 510 [46]	211 <sup>†</sup> 208 <sup>‡</sup>	2-H 3,66 [54] 3,67 [37] 4-H 5,79 [54] 5,81 [37] 5-H 3,66 [54] $J_{2,4}$ 2,25 [54] $J_{2,5}$ 3,24 [54] $J_{4,5}$ 2,52 [54]	86 (87%) ** 85 (100%) 45 (57%) 27 (21%) 39 (21%)

\*For vibrational IR and Raman spectra see [46, 50]; for microwave spectra see [51, 52].

<sup>†</sup>In MeOH.

<sup>‡</sup>In cyclohexane.

\*\*Molecular ion.

The dihydrothiophenes are liquid substances under ordinary conditions with low melting points. Boiling and melting points, densities, and refractive indices of the dihydrothiophenes are given in Table 1.

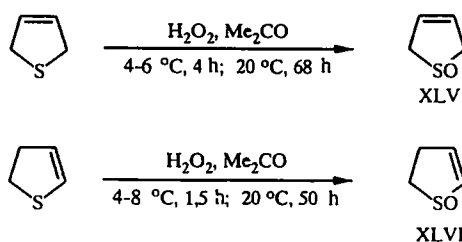
The thermodynamic characteristics of the dihydrothiophenes are given in Table 2.

The principal data obtained when studying the spectra of dihydrothiophenes are brought together in Table 3.

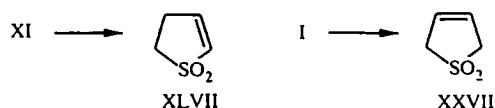
### 3. CHEMICAL CONVERSIONS OF DIHYDROTHIOPHENES

#### 3.1. Oxidation of Dihydrothiophenes

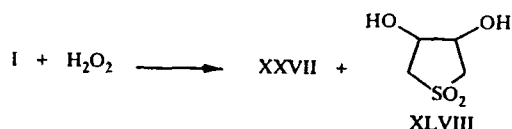
Treating thiolenes (I) or (XI) with 30% hydrogen peroxide in acetone at low temperature and subsequently keeping the reaction mixture at 20°C forms the corresponding sulfoxide (XLV) or (XLVI) each in 48% yield.



The action of 30% hydrogen peroxide on the dihydrothiophenes in acetic acid at 20°C (24 h) and subsequent boiling of the reaction mixture (3 h) leads to the corresponding sulfolene (XLVII) or (XXVII) [35].



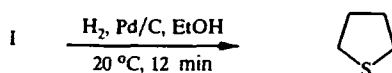
If a 100% excess of hydrogen peroxide is used when oxidizing thiolene (I) then a mixture of  $\Delta^3$ -sulfolene (XXVII) and 3,4-dihydroxytetrahydrothiophene S,S-dioxide (XLVIII) is formed at a ratio of (XXVII):(XLVIII) equal to 1:4 [35].



### 3.2. Addition Reactions to the Double Bond of Dihydrothiophene

#### 3.2.1. Addition of Hydrogen

2,5-Dihydrothiophene (I) is converted quantitatively into tetrahydrothiophene on hydrogenation over Pd/C treated with concentrated hydrochloric acid [55].

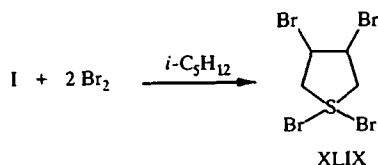


It was established that (I) reacts with hydrogen more rapidly than acyclic sulfides. Thus the sulfides  $\text{MeCH}=\text{CHCH}_2\text{SR}$  ( $R = \text{Bu, Ph}$ ) are converted under analogous conditions into the saturated compounds  $\text{MeCH}_2\text{CH}_2\text{CH}_2\text{SBu}$  or  $\text{MeCH}_2\text{CH}_2\text{CH}_2\text{SPh}$  after 35-45 h or 120 h respectively [55].

#### 3.2.2. Addition of Hydrogen Chloride and Halogens

2,3-Dihydrothiophene (XI) readily adds hydrogen chloride in carbon tetrachloride with the formation of 2-chlorotetrahydrothiophene (XX) [21].

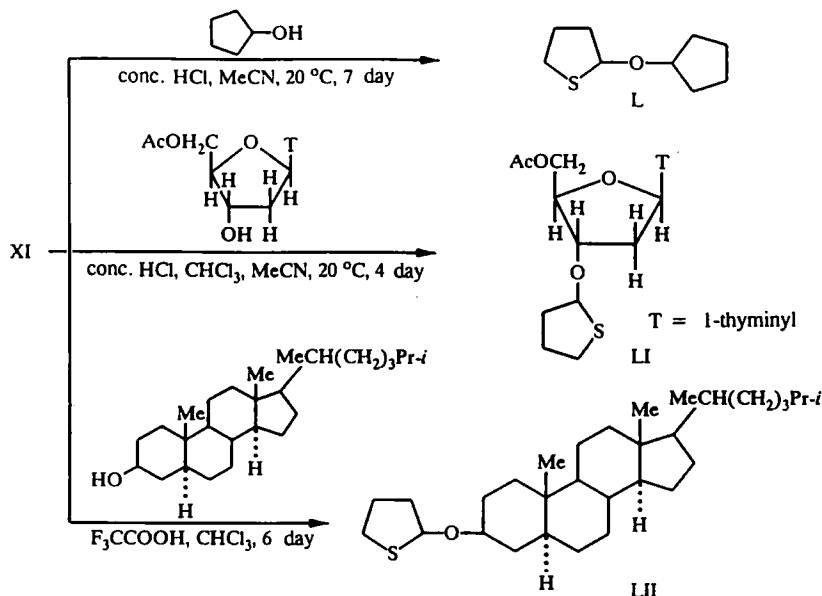
A yellow crystalline compound was obtained by the action of bromine on thiolene (XI) but was not identified as a result of rapid decomposition with the liberation of hydrogen bromide [35]. However, the quantity of bromine absorbed afforded a basis for the authors to assert that this substance was the product of addition of bromine to the double bond of the initial thiolene (XI). The tetrabromide (XLIX) was obtained in 85% yield in the same work [35] from the same reactants.



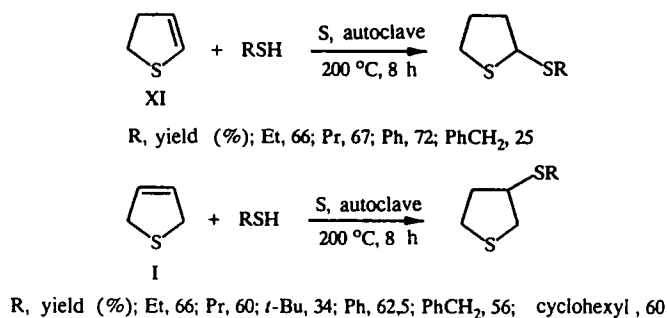
The preparation and identification of 2,3-dichlorotetrahydrothiophene and of 2,3-dibromotetrahydrothiophene has been described more recently by the reaction of thiolene (XI) with chlorine or bromine in carbon tetrachloride or in deuteriochloroform at 40°C [21]. The yields of the addition products were not mentioned.

#### 3.2.3. Addition of Alcohols and Thioalcohols

Dihydrothiophene (XI) adds cyclopentanol, 5<sup>1</sup>-O-acetylthymidine, or cholestanol in the presence of strong acid at room temperature with the formation of the corresponding compound (L) in 11% yield, (LI) in 57% yield, and (LII) in 75% yield [56].



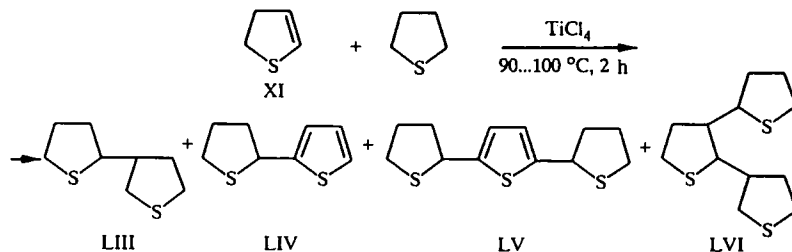
Thioalcohols RSH add to dihydrothiophene in the presence of elementary sulfur at high temperature in an autoclave [57].



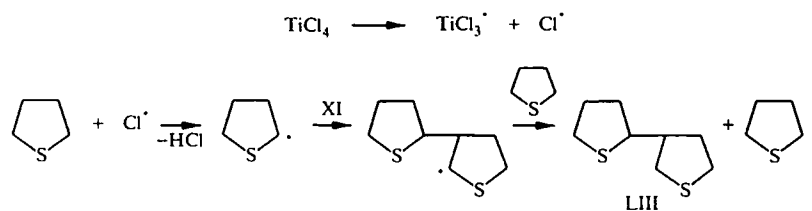
The addition products of thioglycolic acid HSCH<sub>2</sub>COOH under the same conditions were not identified since they were obtained in low yield and decomposed on attempted distillation [57].

### 3.2.4. Reaction with Tetrahydrothiophene

Compounds (LIV), (LV), and (LVI) were isolated in yields of 3.1, 0.6, and 1.4% respectively, as well as the addition product (LIII) (0.4% yield), on heating thiolene (XI) with tetrahydrothiophene in the presence of titanium chloride [18].

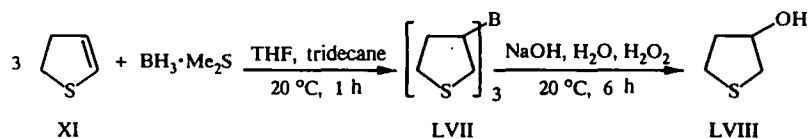


In the opinion of the authors, the addition product (LIII) is formed by a radical chain process.

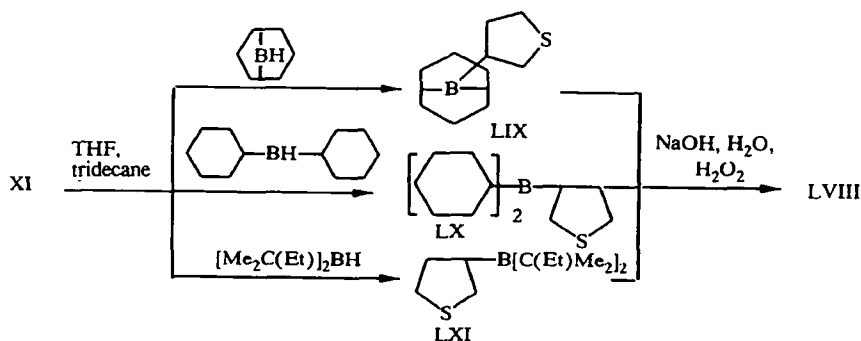


### 3.2.5. Addition of Organoboron Compounds

The complex of borane with dimethyl sulfide reacts with thiolene (XI) at room temperature with the formation of the addition product of  $\text{BH}_3$  to three molecules of dihydrothiophene (LVII). On treatment with sodium hydroxide and hydrogen peroxide, compound (LVII) is converted into 2-hydroxytetrahydrothiophene (LVIII) in practically quantitative yield [58].



A quantitative yield of alcohol (LVIII) was also achieved by treating adducts (LIX), (LX), or (LXI) with sodium hydroxide and 30% hydrogen peroxide. These adducts were formed by the addition of 9-bora-bicyclo[3.3.1]nonane, dicyclohexylborane, or  $[\text{Me}_2\text{C}(\text{Et})_2\text{BH}]$  to thiolene (XI) [58].

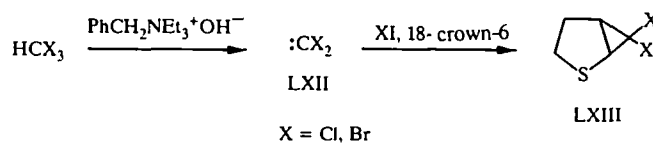


The individual isomers (R)-(LVIII) (80% yield) or (S)-(LVIII) (73% yield) were synthesized by reacting thiolene (XI) with (–)-diisocamphenylborane or (+)-diisocamphenylborane at 25°C for 12 h with subsequent treatment of the products formed with 3N aqueous sodium hydroxide and 30% hydrogen peroxide (25°C, 5 h) [59].

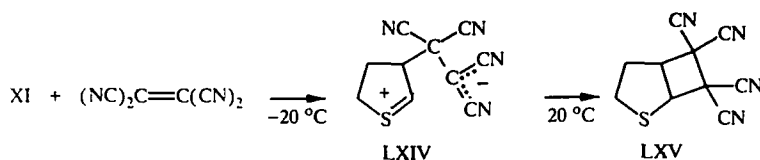
The rate of addition of 9-borabicyclo[3.3.1]nonane in THF at 25°C to various compounds containing a carbon–carbon double bond has been determined. The compounds and the relative rates of addition were: 1-hexene, 1.00; 2,3-dihydrofuran, 6.78; cyclopentene, 6.4; 2-methyl-2,5-dihydrofuran, 10.03; thiolene (XI),  $1.38 \cdot 10^{-3}$ . It was established that the reaction with thiolene (XI) goes strictly regioselectively with addition of the boron atom to the  $\beta$ -carbon atom (position 3) [60].

### 3.3. Cycloaddition Reactions

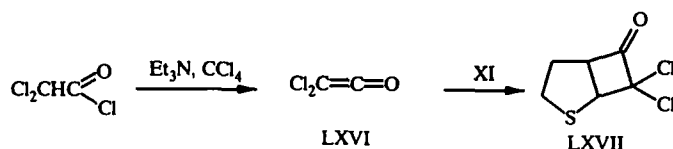
Carbenes (LXII) generated by the action of triethylbenzylammonium hydroxide on chloroform or bromoform react with thiolene (XI) at room temperature. 6,6-Dihalo-2-thiabicyclo[3.1.0]hexanes (LXIII) are formed in 25-30% yield by [2+1]-cycloaddition. The reaction was carried out under interphase catalysis conditions in the presence of 18-crown-6 or dibenzo-18-crown-6 (in the latter case more by-products are formed and the yield is lower) [61].



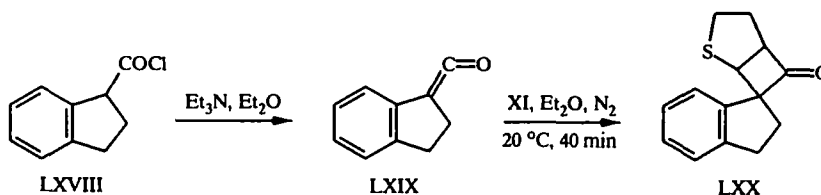
The bipolar ion (LXIV) formed by the reaction of thiolene (XI) with tetracyanoethylene at  $-20^\circ\text{C}$  is converted at  $20^\circ\text{C}$  into a [2+2]-cycloaddition product (LXV) in 85% yield [62].



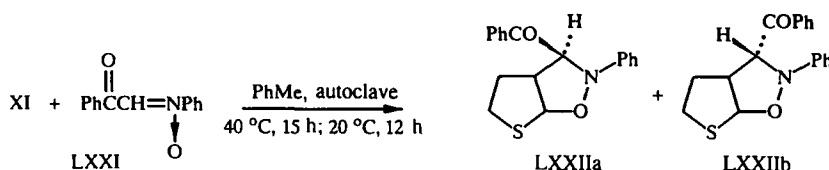
2,3-Dihydrothiophene (XI) reacts by a [2 + 2]-cycloaddition with the ketene (LXVI), formed on treatment of dichloroacetic acid chloride with triethylamine. This leads to 7,7-dichloro-2-thiabicyclo[3.2.0]heptan-6-one (LXVII) in 8-13% yield [19].



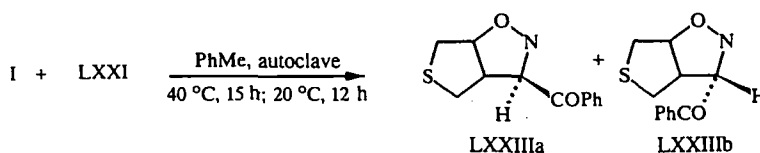
Ketene (LXIX) obtained by the action of triethylamine on indane-1-carboxylic acid chloride (LXVIII) reacts by a [2 + 2]-cycloaddition with thiolene (XI) to give spiro compound (LXX) in 81% yield [63].



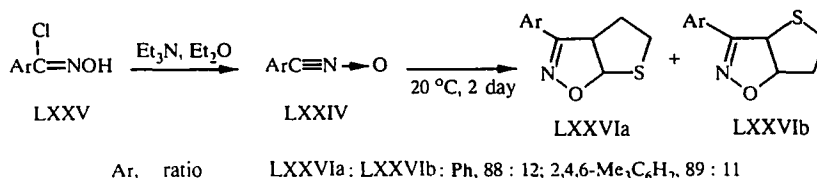
The [2 + 3]-cycloaddition product of thiolene (XI) with nitron (LXXI) was isolated as two diastereoisomers, the endo isomer (LXXIIa) and the exo isomer (LXXIIb) in a ratio of 76:24 [64].



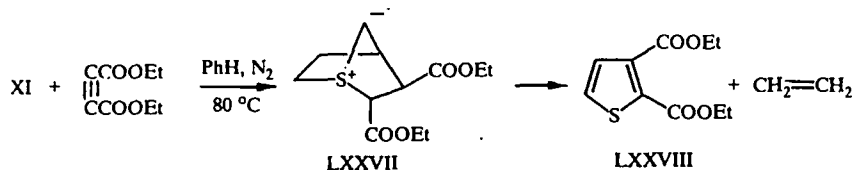
The reaction of thiolene (I) with nitron (LXXI) under the same conditions gave a mixture of exo and endo isomers of adducts (LXXIIIa) and (LXXIIIb), from which only the exo-(LXXIIIb) was isolated in a pure state (36.2% yield). The presence of endo-(LXXIIIa) was confirmed by PMR and it was thereby established that it was formed in lower amounts [64].



The nitrile N-oxides (LXXIV), obtained by the dehydrochlorination of the acid chlorides of the appropriate hydroxamic acid (LXXV) with triethylamine, react *in situ* by [2 + 3]-cycloaddition with thiolene (XI) at 20°C. A mixture of regioisomers (LXXVIa, b) was formed from which compound (LXXVIa) was isolated in 63 or 61% yield [65].



On heating thiolene (XI) with acetylenedicarboxylic acid diethyl ester in benzene, the bipolar ion (LXXVII) was formed. This [3 + 2]-cycloaddition product decomposed under the conditions of the reaction, being converted into thiophene-2,3-dicarboxylic acid diethyl ester (LXXVIII) (16% yield) and ethylene [66].



The authors of [67] determined the relative rates of the Diels-Alder reaction of 3,5-di(methoxycarbonyl)-1,2,4,5-tetrazine with 2,3-dihydrothiophene (XI) and certain other unsaturated five-membered cyclic compounds. Compounds and relative rates [ $10^5 \cdot k_2$  (liter/mole·sec)] were 2,3-dihydrofuran 136000, 2,3-dihydrothiophene 6310, cyclopentene 23500, 1,3-dithiole 35.5, 1,3-dioxole 13200, furan 4.86, cyclopentadiene 10400.

### 3.4. Polymerization and Copolymerization of 2,3-Dihydrothiophene

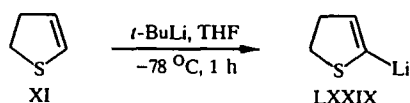
The polymerization and copolymerization of dihydrothiophene (XI) has been reported in only one publication [68]. It was shown that unlike acyclic sulfides  $\text{RSCH}=\text{CH}_2$  the cyclic sulfide (XI) was not capable of radical polymerization in the presence of aziso-butyrionitrile at  $60^\circ\text{C}$  or  $80^\circ\text{C}$  and the monomer remained quantitatively in an unchanged form. On the other hand, cationic polymerization of thiolene (XI) proceeded rapidly in the presence of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\text{SnCl}_4$ , or  $\text{TiCl}_4$  and was quantitative in the case of the latter two catalysts.

The copolymerization of thiolene (XI) with olefins at  $60^\circ\text{C}$  in benzene in the presence of azoisobutyronitrile has been studied. Olefin, reaction time (h), copolymer yield (%), and % thiolene in the copolymer were:  $\text{PhCH}=\text{CH}_2$ , 100, 48, 0;  $\text{CH}_2=\text{CHOCOMe}$ , 100, 10, 0;  $\text{CH}_2=\text{C}(\text{Me})\text{COOMe}$ , 40, 53, 17;  $\text{CH}_2=\text{CHCOOMe}$ , 50, 55, 42;  $\text{CH}_2=\text{CHCN}$ , 50, 90, 37; maleic anhydride, 12 (in  $\text{CHCl}_3$ ), 90, 45 [68].

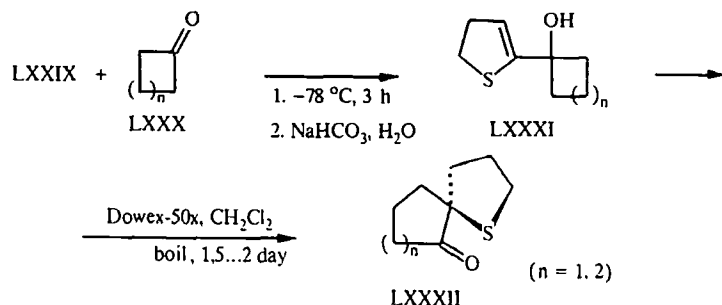
The comparative reactivity on copolymerization with methyl acrylate ( $60^\circ\text{C}$ ,  $\text{CHCl}_3$ ) has been determined for a series of vinyl sulfides and it was shown that they may be arranged in a series according to their rate of copolymerization as thiolene (XI) >  $\text{RSCH}=\text{CH}_2$  > 2,3-dihydrothiopyrane > 1,4-dithiine.

### 3.5. Reactions with Ketones

The lithium derivative (LXXIX) is formed by the action of tert-butyllithium on thiolene (XI).

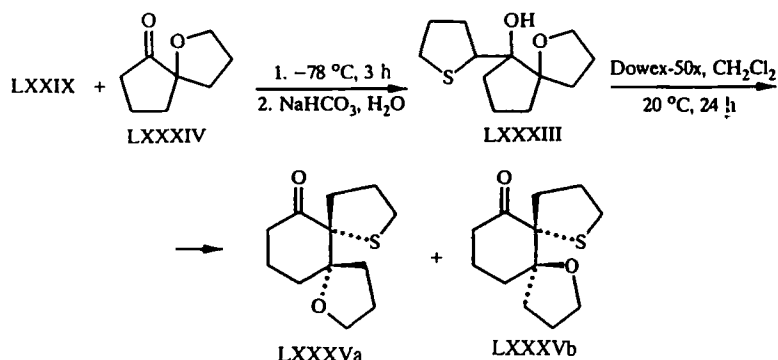


The tertiary allyl alcohols (LXXXI) were obtained from compound (LXXIX) and alicyclic ketones (LXXX). The allyl alcohols were converted, on heating with Dowex-50x ion exchange resin, into spiro compounds (LXXXII) by an acid-catalyzed rearrangement [69, 70].

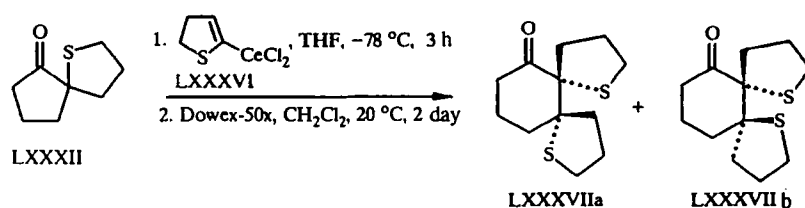


n, yield (%). LXXXI: 1, 65; 2, 75; 3, 72; 5, 52; 9, -

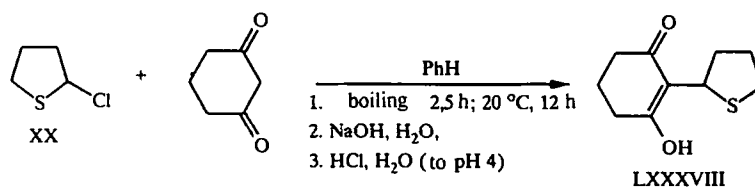
The reaction of lithium compound (LXXIX) with spiroketone (LXXXIV) gave the tertiary alcohol (LXXXIII), which was converted into bispiro compounds in the presence of Dowex-50x resin. These were isolated as two diastereoisomers, viz. (LXXXVa) in 11% yield and (LXXXVb) in 46% yield [69].



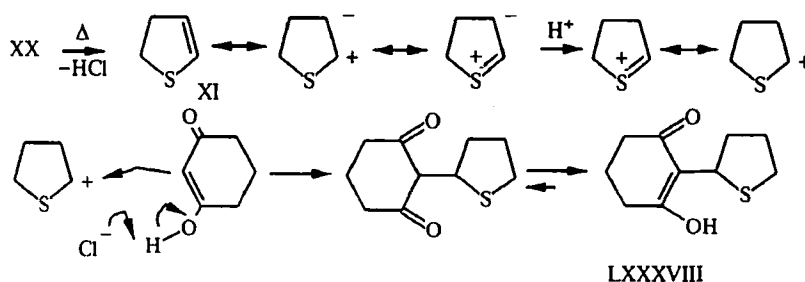
Reaction of spiroketone (LXXXII) ( $n = 1$ ) with the dihydrothiophene derivative (LXXXVI) and subsequent treatment of the condensation product with Dowex-50x ion exchange resin gave compound (LXXXVII) separated into two diastereoisomers (LXXXVIIa) (31% yield) and (LXXXVIIb) (37% yield) [69].



2-Chlorotetrahydrothiophene (XX) reacts with cyclohexane-1,3-dione on heating in benzene with the formation of compound (LXXXVIII) (25.4% yield) [71].

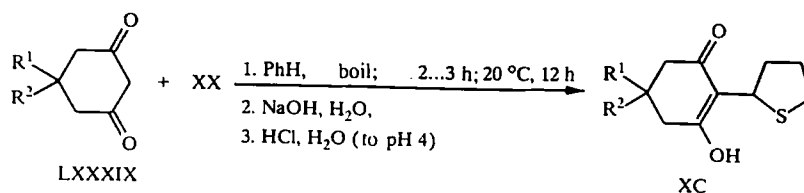


The authors of the cited work assumed that compound (LXXXVIII) is formed not as a result of the direct reaction of the chloro derivative (XX) with the diketone but through the intermediate formation of thiolene (XI) by the following scheme:



As is evident from the scheme, the eliminated hydrogen chloride plays an important role in this process.

Compound (XC) was synthesized analogously from 2-chlorothiophane (XX) and cyclic diketones (LXXXIX) [71].



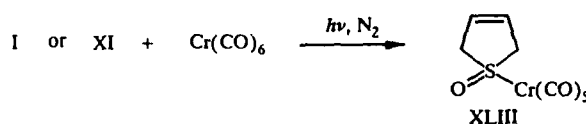
$\text{R}^1$ ,  $\text{R}^2$ , yield (%): H, Me, 33,4; H, Ph, 41,1; Me, Me, 44,7

Compound (XC) ( $R^1 = R^2 = \text{Me}$ ) was obtained in 53.1% yield on boiling diketone (LXXXIX) ( $R^1 = R^2 = \text{Me}$ ) with a mixture of dihydrothiophenes (I) and (XI) in benzene for 1.5 h [71].

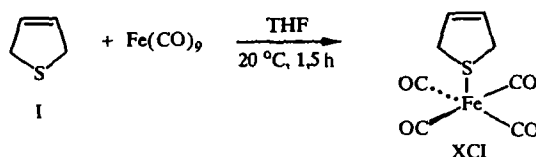
### 3.6. Complex Formation

Thiolenes (I) react with mercuric chloride in isopropyl alcohol forming the complex (I)· $\text{HgCl}_2$  with mp 217-220°C [33].

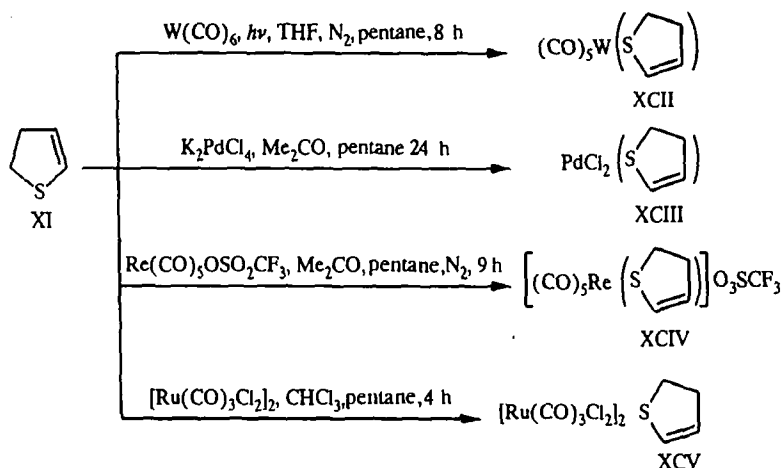
The same compound (XLIII) is formed when thiolenes (I) or (XI) react with hexacarbonylchromium in an inert atmosphere on irradiation with a quartz lamp [48].



The iron carbonyl  $\text{Fe(CO)}_5$  and dihydrothiophene (I) form the complex (XCI) at room temperature [72].



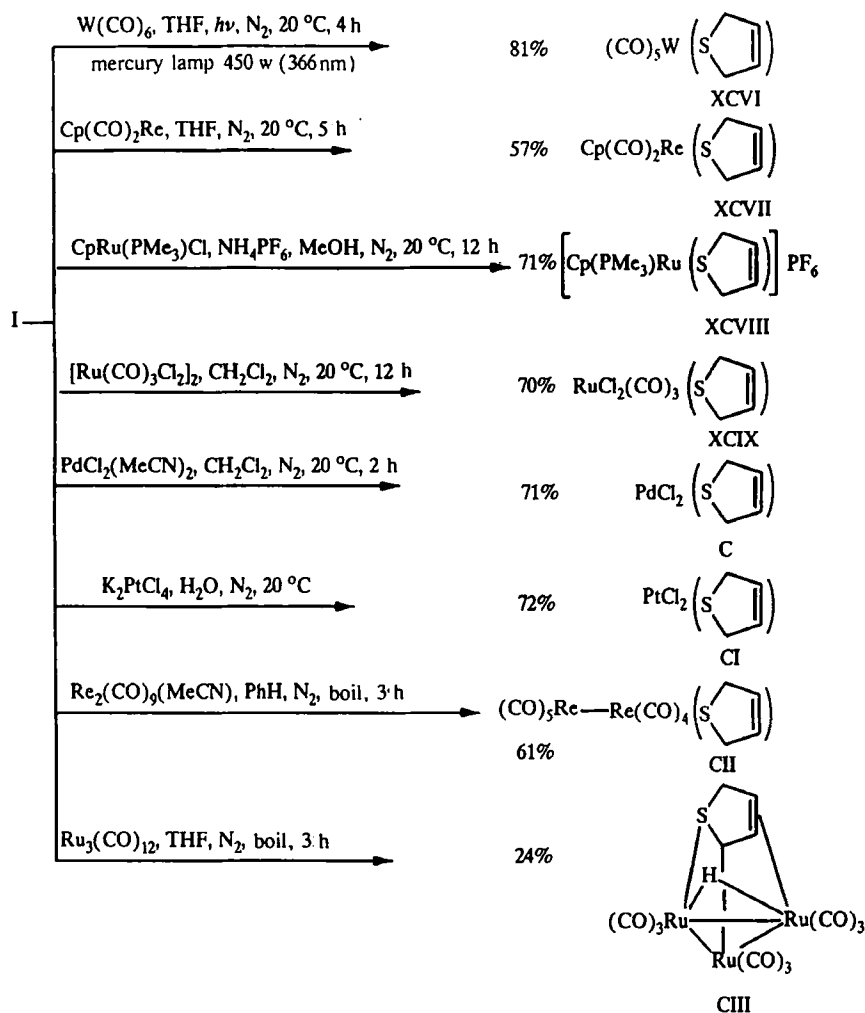
Reaction of thiolenes (XI) with  $\text{W(CO)}_6$  (on irradiation with a 450 W mercury lamp,  $\lambda = 366 \text{ nm}$ ),  $\text{K}_2\text{PdCl}_4$ ,  $\text{Re(CO)}_5\text{OSO}_2\text{CF}_3$  or  $[\text{Ru(CO)}_3\text{Cl}_2]_2$  gave the corresponding complexes (XCII)-(XCV) [73].



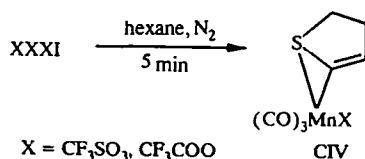
Dihydrothiophene (I) reacts with  $\text{W(CO)}_6$ ,  $\text{Cp(CO)}_2\text{Re}$ ,  $\text{CpRu(PMe}_3\text{)Cl}$ ,  $[\text{Ru(CO)}_3\text{Cl}_2]_2$ ,  $\text{PdCl}_2(\text{MeCN})_2$ , and  $\text{K}_2\text{PtCl}_4$  at room temperature to form the complexes (XCVI)-(CI). It was necessary to boil the reaction mixtures in benzene or tetrahydrofuran to obtain the complexes of thiolenes (I) with  $\text{Re}_2(\text{CO})_9(\text{MeCN})$  (CII) or  $\text{Ru}_3(\text{CO})_{12}$  (CIII) [74]. (See Scheme on the following page).

The sulfur atom and the double bond in complex (CIII) are coordinated with two different Ru atoms according to the data of x-ray structural analysis. The formation of this complex is accompanied by fission of the C – H bond in position 2 of the thiolenes and the formation of a C – Ru bond [74]. The reaction of cation  $[\text{HPt(Me}_2\text{CO)(PEt}_3)_2]^+$  with thiolenes (XI) occurs with displacement of the molecule of acetone and the formation of the complex  $\text{HPt(PEt}_3)_2(\text{thiolenes XI})^+$ . The latter slowly rearranges with addition of the Pt – H fragment to the double bond being converted into the complex  $(\text{PEt}_3)_2\text{Pt}(\overline{\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2})$  [75].





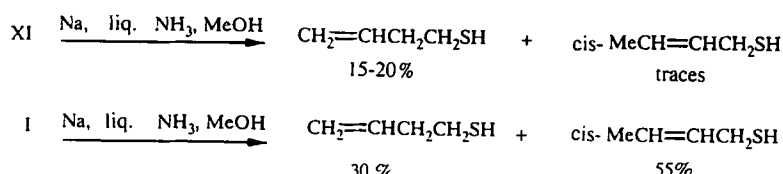
As was mentioned above, treatment of complex (XXXI) with gaseous hydrogen chloride causes conversion into complex (XXXII) [40]. If  $\text{CF}_3\text{SO}_3\text{H}$  or  $\text{CF}_3\text{COOH}$  is used in place of  $\text{HCl}$  then complexes (CIV) are obtained from compound (XXXI) [40].



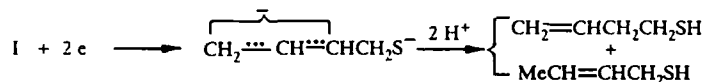
The reaction of complex  $[(\text{PPh}_3)_2\text{IrH}(\eta^4\text{-SC}_4\text{H}_5)]\text{PF}_6$  with thiolene (I) or thiolene (XI) at  $80\text{ }^\circ\text{C}$  in an atmosphere of hydrogen leads to complexes  $[(\text{PPh}_3)_2\text{Ir}(\text{H})_2(\eta^1\text{-2,3-SC}_4\text{H}_6)_2]\text{PF}_6$  or  $[(\text{PPh}_3)_2\text{Ir}(\text{H})_2(\eta^1\text{-SC}_4\text{H}_8)_2]\text{PF}_6$ . They are also formed by the reaction of compound  $[(\text{PPh}_3)_2\text{Ir}(\text{H})_2(\text{Me}_2\text{CO})_2]\text{PF}_6$  with the appropriate dihydrothiophene [41].

### 3.7. Decomposition of the Heterocyclic Nucleus

A mixture of 2-butenethiol and 3-butenethiol in various proportions is obtained on treating dihydrothiophenes (I) or (XI) with sodium and liquid ammonia in methanol [35].



The authors of this work proposed the following scheme for the formation of butenethiols on noncatalytic reduction of thiolene (I):

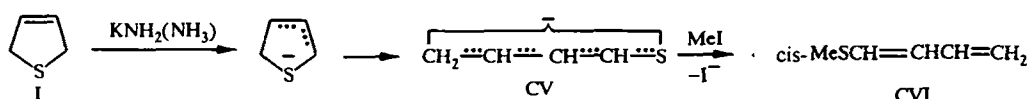


The hydrogenation of thiolene (XI) over  $G_1$  catalyst (sulfonated cobalt molybdate/ $Al_2O_3$ ) at various temperatures (270, 308, 372°C) leads to a mixture of butane and butenes of various composition [76].



For instance, 17.8% 1-butene, 44.0% trans-2-butene, and 38.2% cis-2-butene were present in the unsaturated products of the reaction at 308°C.

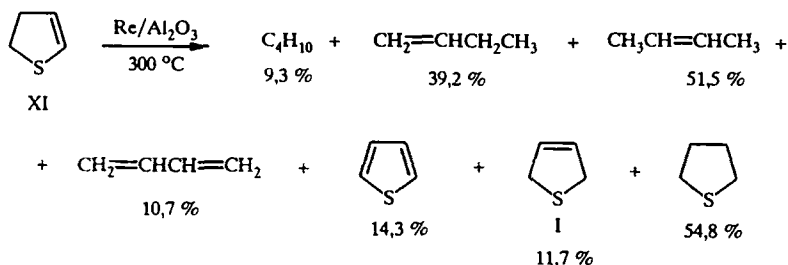
On reacting thiolene (I) with potassium amide in liquid ammonia (-60 to -40°C) an electrocyclic fission of the heterocyclic nucleus induced by base occurs with the formation of anion (CV) which forms sulfide (CVI) on reaction with methyl iodide [77].



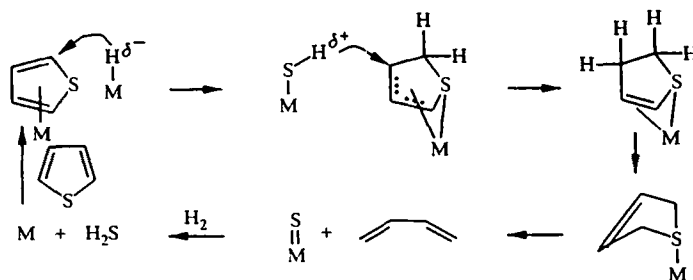
### 3.8. Desulfurization of Dihydrothiophenes

The considerable attention paid by investigators to the desulfurization of thioleues is explained by the fact that dihydrothiophenes are formed in processes used to remove sulfur-containing compounds (particularly thiophene) from products of oil refining.

A complex mixture of products is obtained on passing thiolene (XI) vapor over  $Re/Al_2O_3$  catalyst at 300°C. This consists of butanes, butenes, thiophene, thiophane, thiolene (I) and butadiene [72].



The authors of the cited work proposed a scheme for the desulfurization of thiophene passing through the stage of forming thiolene (XI), which is isomerized into thiolene (I), and both undergo desulfurization.



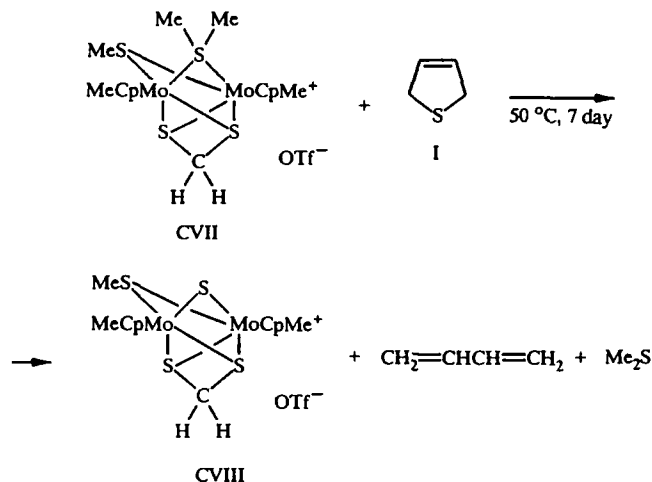
The desulfurization of thiolene (I) has been studied on  $Mo(110)-(4 \times 1)-S$  catalyst under high vacuum conditions ( $2 \cdot 10^{-10}$  mm) using temperature programming and photoelectron spectroscopy. It was established that the selectivity of eliminating butadiene was increased from 67% on a noncatalytic surface to 83% on  $Mo(110)-(4 \times 1)-S$  [78, 79].

Hydrodesulfurization [80] and deuterodesulfurization [81] of thiolene (I), thiolene (XI), thiophene, and thiophane have been carried out on Mo/Al<sub>2</sub>O<sub>3</sub> or Re/Al<sub>2</sub>O<sub>3</sub> catalysts at 300-400°C. It was discovered that the thioleues were significantly more actively desulfurized than thiophene or thiophane with the formation of butadiene [80]. Hydrodesulfurization of thioleues (I) or (XI) over Re/γ-Al<sub>2</sub>O<sub>3</sub> catalyst gave butadiene, butenes, butane, isomeric thioleues, thiophene, and thiophane, the proportions of which varied on changing the reaction temperature [80]. It was established that butadiene is split off directly on deuterodesulfurization of thiolene (I), while the formation of butadiene from thiolene (XI) included a few stages on the catalyst surface [81].

Undeuterated butadiene is formed on deuterodesulfurization of thiolene (I) over PbMo<sub>6</sub>S<sub>8</sub> catalyst at 400°C [82].

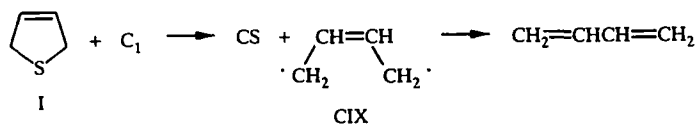
Complex (XCI), formed from thiolene (I) and Fe<sub>2</sub>(CO)<sub>9</sub>, is decomposed on heating to 120°C with the formation of butadiene and [(CO)<sub>4</sub>Fe=S] [72].

Butadiene (34%) and dimethyl sulfide (45%) were isolated on heating dihydrothiophene (I) with complex (CVII) in a sealed ampul in a dynamic vacuum, and the initial complex is converted into complex (CVIII) [83].



Keeping complexes (XCVI) and (XCVII) (see Section 3.6) in vacuum at 110°C leads to a mixture of thiolene (I) and butadiene in a ratio of 4:1. Thiolene (I) itself is not decomposed at 120°C for 3 days. Consequently S coordination of thiolene with metals promotes the elimination of butadiene (desulfurization of thiolene). Thiophene and thiolene (I) (ratio 1:1) and a little butadiene are formed on keeping complexes (XCIX) and (C) at 180°C in vacuum. The nature of the complex therefore determines the direction of decomposition [74].

Thiolene (I) reacts with singlet carbon (generated in vacuum between two carbon electrodes at 16 V) with the formation of carbon monosulfide and biradical (CIX), which is converted into butadiene (43% yield) [84].

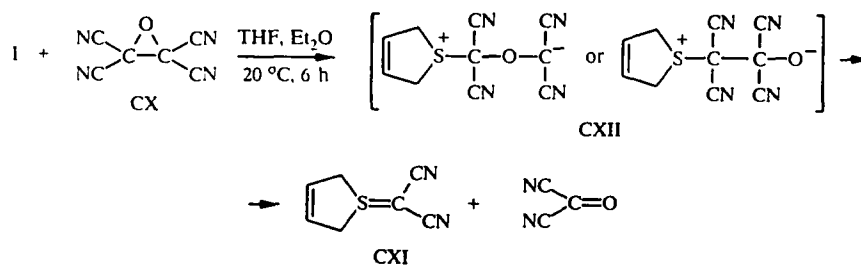


### 3.9. Interconversion of Thiolene (I) ⇌ Thiolene (XI)

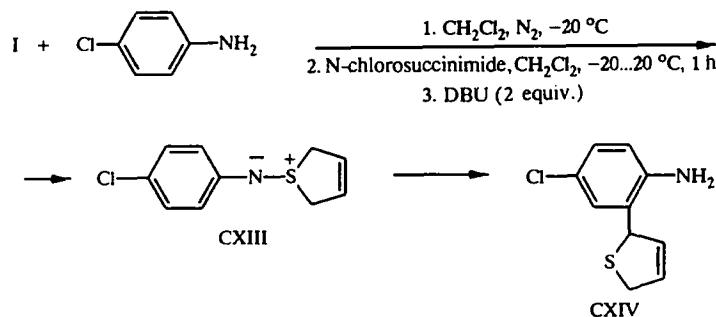
Thiolene (XI) is converted into thiolene (I) in the presence of Re/Al<sub>2</sub>O<sub>3</sub> catalyst at 300°C in yields of 6.9% [78] or 11.7% [72]. Under the same conditions thiolene (I) is isomerized into thiolene (XI) in 21.8% yield [78]. Isomerization of thiolene (XI) into thiolene (I) was also observed in the presence of the iron carbonyl Fe<sub>2</sub>(CO)<sub>9</sub> [81].

### 3.10. Individual Reactions

Compound (CXI) is obtained in 39% yield by the reaction of thiolene (I) with tetracyanoethylene oxide (CX) at room temperature. The process includes a step of forming the bipolar ion (CXII) [85].



The sulfilimine (CXIII), formed in 45% yield from thiolene (I) and 4-chloroaniline, is converted quantitatively on treatment with *N*-chlorosuccinimide and DBU at room temperature into 4-chloro-2-(2,5-dihydrothiophen-2-yl)aniline (CXIV) [86].



Thermolysis of thiolene (I) at 342–420 °C in a vacuum of 1–40 mm Hg leads to thiophene and hydrogen (ratio of 1:1). This process is a first order reaction [87].

Finally, it may be concluded that the study of the dihydrothiophenes, which are interesting and promising compounds, has not been paid sufficient attention. The addition to a double bond, cycloaddition reactions, and other chemical conversions of these compounds have been investigated in a totally inadequate manner. There are almost no literature data on the practical use of dihydrothiophenes. It has been reported only in patents that thiolenes (I) and (XI) may be used as odorants for domestic gas and additives for preventing corrosion of gas pipes [88], and also the fact that 1-methyl-4-(tetrahydrothiophen-2-yl)cyclohex-3-en-3-ol-5-one [the product of adding 5-methylcyclohexane-1,3-dione to thiolene (XI)] improves the stability of the latent image in light-sensitive emulsions based on AgBr or AgI [89].

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