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## Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

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### THERMAL TRANSFORMATIONS OF ORGANIC COMPOUNDS OF TETRA- AND HEXAVALENT SULFUR

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**To cite this Article** Voronkov, Mikhail and Deryagina, Eleonora(2002) 'THERMAL TRANSFORMATIONS OF ORGANIC COMPOUNDS OF TETRA- AND HEXAVALENT SULFUR', *Journal of Sulfur Chemistry*, 23: 3, 321 – 387

**To link to this Article:** DOI: 10.1080/01961770208050162

**URL:** <http://dx.doi.org/10.1080/01961770208050162>

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# THERMAL TRANSFORMATIONS OF ORGANIC COMPOUNDS OF TETRA- AND HEXAVALENT SULFUR

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*(Received 4 May 2001; accepted 20 February 2002)*

The literature on the thermal reactions of tetra- and hexavalent sulfur compounds are summarized and analyzed. The bibliography contains 305 references for the period 1950–2000.

*Keywords:* Thermal transformations, pyrolysis; Sulfoxides, sulfones; Sulfinic and sulfonic acids and their esters; Cyclic hydrocarbons; Heterocycles; Dienes; Acetylene compounds

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## 1. INTRODUCTION

Thermal transformations of organic compounds of bivalent sulfur have been under investigation since the nineteenth century. Thermolysis of these compounds can lead to new classes of organic compounds. The thermolysis of dialkyl sulfoxides is accompanied by sulfur dioxide elimination and the formation of olefines. Thermolysis of some dialkyl sulfoxides leads to the extrusion of sulfenic acid and the formation of heterocyclic compounds. Vinyl sulfoxides eliminate vinylsulfenic acid to give vinylalkyl ethers. The importance of the pyrolysis of sulfones is in the possibility of obtaining difficult to obtain unsaturated hydrocarbons, including functionally substituted ones. The pyrolysis of cyclic sulfones leads to cyclic hydrocarbons, heterocycles, dienes and acetylene compounds. The simplest method for the synthesis of macrocyclic hydrocarbons is based on a thermal elimination of  $\text{SO}_2$  from cyclic mono-, *bis*- and *tris*-sulfones. The data on the thermolysis of sulfinic and sulfonic acids and their ethers are given. The thermolysis of these compounds is of great preparative interest.

## 2. SULFOXIDES

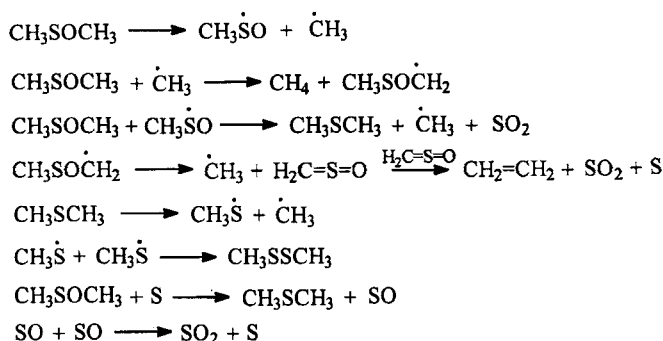
### 2.1. Dialkyl Sulfoxides

Thermal instability of dialkyl sulfoxides has been found as early as 1875 [1]. Dialkyl sulfoxides are usually decomposed under heating at  $100^\circ\text{C}$  with elimination of the corresponding olefin [2]. Secondary alkyl groups are cleaved easier than primary ones. Mixed *n*-alkyl, *sec*-alkyl sulfoxides are decomposed more rapidly than di(*n*-alkyl) sulfoxides [3]. The rate of the thermal decomposition reaction of sulfoxides is decreased with increasing steric hindrance of the  $\beta$ -carbon atom of the alkyl chain [4].

Thermal decomposition of dimethyl sulfoxide (DMSO) at  $180^\circ\text{C}$  under pressure in the presence of air or oxygen leads to the formation of dimethyl sulfide (42%), *bis*(methylthio)methane (31%) and dimethyl disulfide (8%). Under analogous conditions, but in the presence of nitrogen, DMSO is not decomposed. Addition of DMSO to a peroxide medium results in its decomposition [5].

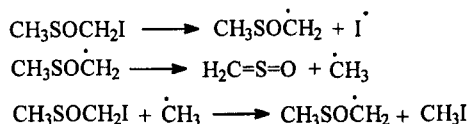
The thermolysis of DMSO in vacuum (10–400 mm) at  $297$ – $340^\circ\text{C}$  leads to the formation of methane, ethylene and sulfur dioxide [6]. A first-order reaction with respect to each product has been found  $E_{\text{act.}} = 48 \text{ Kcal/mol}$ ,  $A = 3.7 \times 10^{14} \text{ s}^{-1}$ . The formation of

dimethyl sulfide, dimethyl disulfide and sulfur dioxide is consistent with the following mechanistic scheme:



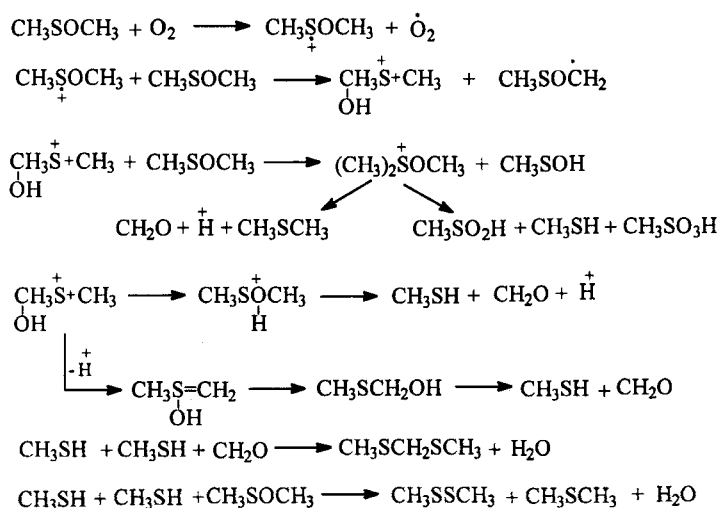
SCHEME 1

The formation of sulfine was detected by photoelectronic spectroscopy during the flash vacuum pyrolysis (FVP) of DMSO [7]. Sulfine is also generated during the FVP of methyl (iodomethyl) sulfoxide at 350°C [7].



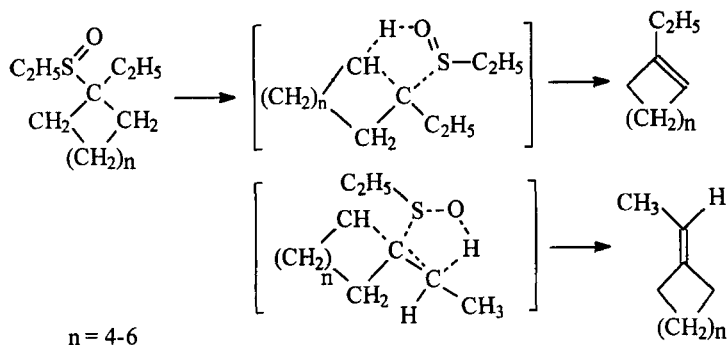
SCHEME 2

The FVP of DMSO (270–340°C) in the presence of oxygen involves the formation of methane, ethane, ethylene and dimethyl sulfide. Under higher concentrations of oxygen the yield of ethane and dimethyl sulfide is significantly increased [8]. The free radical mechanism of DMSO decomposition during initiation by oxygen is as follows [5].



SCHEME 3

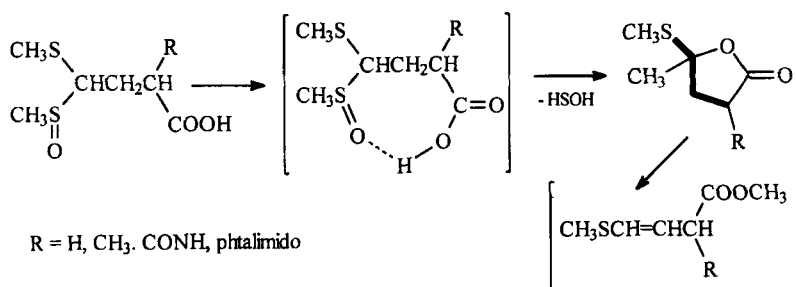




SCHEME 7

Total yield of olefins 79% ( $n=4$ ), 85% ( $n=5$ ), 80% ( $n=6$ ).

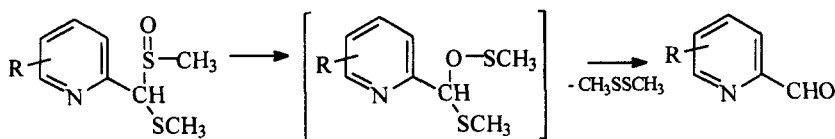
The pyrolysis of methylsulfinyl- $\gamma$ -methylthiobutyric acids involves the formation of the corresponding  $\gamma$ -methylthio- $\gamma$ -butyrolactones [19].



SCHEME 8

The reaction involves formation of an intermediate with a hydrogen bond between the sulfinyl and carboxyl groups.

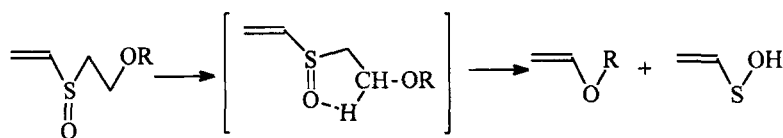
Methyl[methylthio(2-pyridyl)methyl] sulfoxide upon heating up to 150–240°C gives pyridine-2-carbaldehydes [20].



SCHEME 9

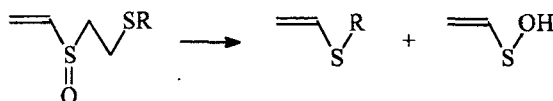
## 2.2. Alkylvinyl Sulfoxides

The pyrolysis of  $\beta$ -(alkoxy)ethyl vinyl sulfoxides under heating up to 280–290°C results in alkyl vinyl ethers in 65–71% yield. Concurrently vinylsulfenic acid is eliminated. The reaction proceeds via a cyclic intermediate [21,22].



SCHEME 10

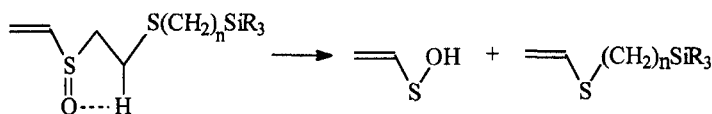
Similarly, vinylsulfenic acid is eliminated from  $\beta$ -(organylthio)ethyl vinyl sulfoxides at 220–320°C to give alkyl vinyl sulfides [23].



R = Me, Et, *i*-Pr, *t*-Bu, Ph

SCHEME 11

[[ $\beta$ -Triorganylsilylalkylthio]ethyl] vinyl sulfoxides are transformed into vinyl sulfides under heating up to 170–180°C [24].

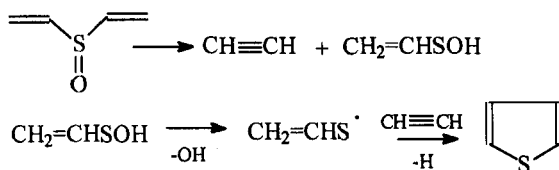


R = Me, Et, MeO; n = 1–3

SCHEME 12

### 2.3. Divinyl Sulfoxide

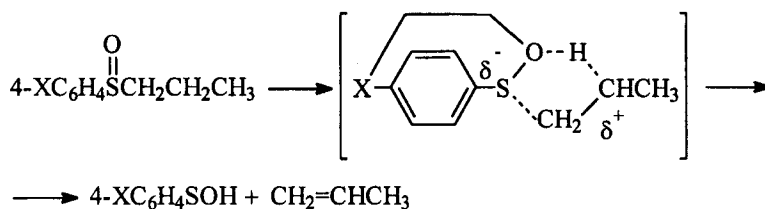
Gas-phase thermolysis (400°C) of divinyl sulfoxide results in the formation of thiophene in 60% yield. The mechanism of the reaction involves the decomposition of divinyl sulfoxide into acetylene and vinyl sulfenic acid. The latter generates  $\text{CH}_2=\text{CHS}^\cdot$  and  $\text{HO}^\cdot$  radicals. Then vinylthiyl radicals reacted with acetylene to give thiophene [25].



SCHEME 13

## 2.4. Alkyl Aryl Sulfoxides

The thermolysis of alkyl aryl sulfoxides involves the elimination of arylsulfenic acids and the formation of alkenes. The formation of propene during thermal destruction of aryl (*n*-propyl) sulfoxides in a solution of diphenyl ether is of first order and has low values of both activation energy and activation enthalpy (25–28 kcal/mol and –11.5–16 cal · unit<sup>-1</sup>, respectively) [17,26]. The presence of chlorine atoms as well as a nitro group in the aromatic ring accelerates the reaction and methyl- and methoxy group inhibits it. The constant of the reaction rate is correlated with the constants of Hammett derivatives in the aromatic ring. These data are indicative of high order of the intermediate product (may be cyclic one) in which positive charge is carried to propyl group and negative charge is carried to sulfur-containing fragment:

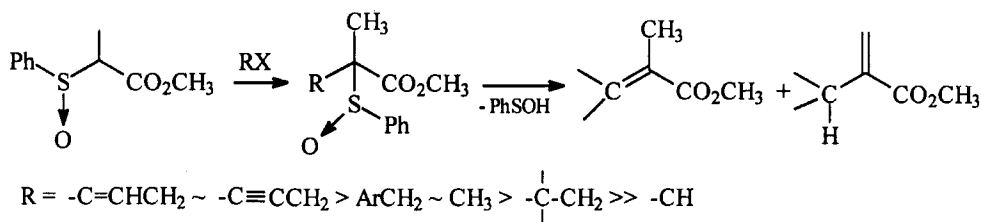


SCHEME 14

A kinetic isotopic effect  $k_H/k_D = 3.168$  (130°C),  $E_H - E_D = 1.15$  Kcal/mol,  $A_H/A_D = 0.76$  has been found during the thermolysis of deuterated heptyl phenyl sulfoxide in diglyme solution (190–230°C) [17].

An  $\alpha$ -acyl-derivative in the alkyl chain also accelerates the pyrolysis of aryl ethyl sulfoxides at 60–120°C. The  $\alpha$ -ethoxycarbonyl group [27] shows the best accelerating effect. A  $\beta$ -phenyl group and a  $\beta$ -cyano group accelerate the pyrolysis of aryl ethyl sulfoxides in anhydrous organic solvents at 100–140°C by 8 and 200 times, respectively [28].

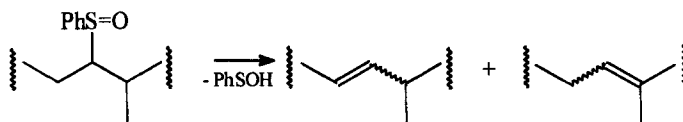
The following order of reactivity is observed during of the alkylative-elimination of 2-phenylsulfinylpropionate. In each case, abstraction of a methylene or methine hydrogen is contrast to that a methyl hydrogen [29].



SCHEME 15

The mixture of regioisomeric olefins is usually formed from sulfoxides having a non-symmetric structure.

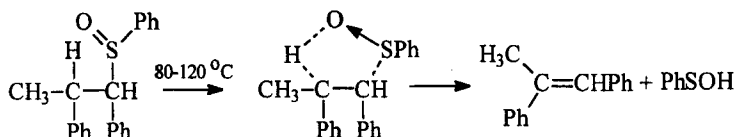




SCHEME 16

If a trimethylsilyl group is added to the  $\beta$ -carbon atom of such sulfoxides, the regioselectivity of the elimination of sulfenic acid is sharply increased [30].

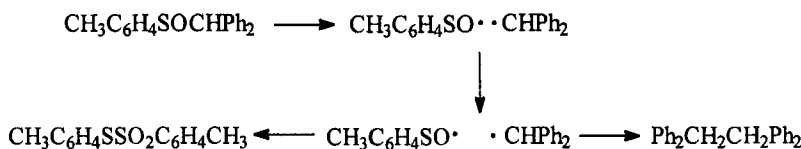
Thermal elimination of benzenesulfenic acid from diastereomeric 1,2-diphenyl 1-propyl phenyl sulfoxides proceeds stereospecifically. The reaction mechanism proposed involves the formation of a cyclic intermediate [31].



SCHEME 17

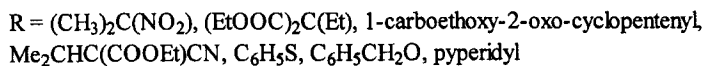
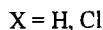
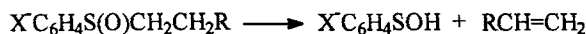
At temperatures above  $120^\circ\text{C}$  the stereospecificity of the reaction is broken resulting in both *cis*- and *trans*-elimination of sulfenic acid. In this case the reaction begins probably with homolytic cleavage of the C-S bond with the formation of radical pair. The formation of cyclic intermediate state follows the isomerization of a radical pair.

Thermal destruction of benzhydryl *para*-tolyl sulfoxide at  $100$ – $130^\circ\text{C}$  involves the formation of *para*-toluenesulfinyl and diphenylmethyl radicals due to the dissociation of the C-S bond. Thiosulfonate and tetraphenylethane are formed from the intermediate products [32].



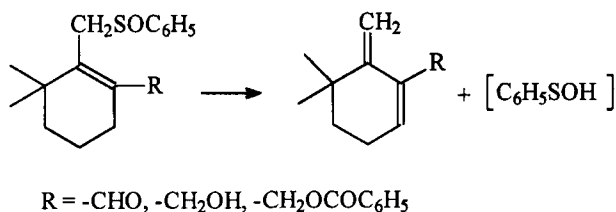
SCHEME 18

A series of aryl ( $\beta$ -organylethyl) sulfoxides are pyrolyzed in vacuum at  $180^\circ\text{C}$  with concurrent distillation of the corresponding ethylene derivatives [33].



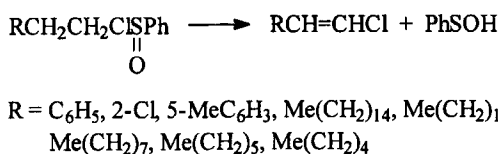
SCHEME 19

Gas-phase pyrolysis (350°C) of cyclooctyl phenyl sulfoxide leads to the formation of *cis*-cyclooctene (plus a small amount of the *trans*-isomer – 0.2%) [34]. The pyrolysis of cyclohexenylmethyl phenyl sulfoxides at the boiling toluene is used as a method for the preparation of the corresponding dienes in high yield (80–90%) [35].



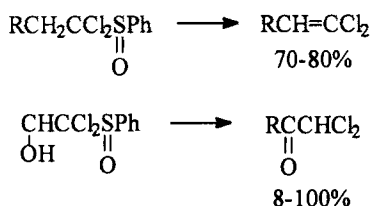
SCHEME 20

Liquid-phase pyrolysis of  $\alpha$ -chloroalkyl phenyl sulfoxides in xylene at 160°C leads to the formation of 1-chloroalkenes [36].



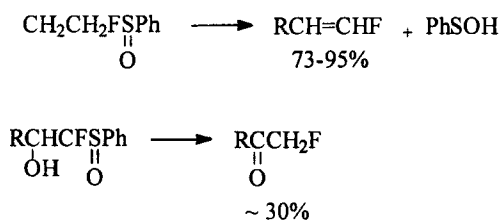
SCHEME 21

Under analogous conditions the corresponding 1,1-dichloroalkenes are formed from  $\alpha,\alpha$ -dichloromethyl phenyl sulfoxides, and dichloromethylketones are formed from  $\alpha,\alpha$ -dichloro-hydroxyalkyl- $\beta$ -alkyl phenyl sulfoxides [37].



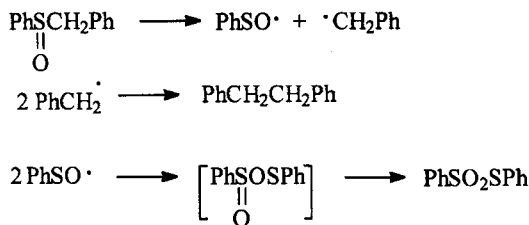
SCHEME 22

Under similar conditions  $\alpha$ -fluoroalkyl phenyl sulfoxides are transformed into vinylfluorides and  $\alpha$ -fluoro- $\beta$ -hydroxy-alkyl phenyl sulfoxides into  $\alpha$ -fluoro-methylketones [38].



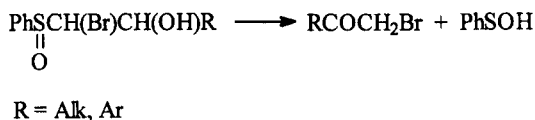
SCHEME 23

The flash vacuum pyrolysis of benzyl phenyl sulfoxide in vacuum at 500°C proceeds according to a radical mechanism due to the cleavage of the SO-C bond and involves the formation of 1,2-diphenylethane and phenylthiosulfinate [39].



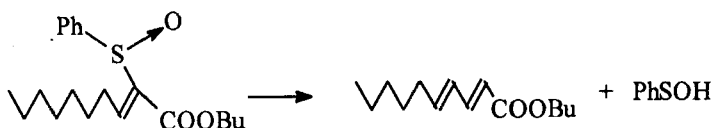
SCHEME 24

The thermolysis of  $\beta$ -hydroxy- $\alpha$ -bromoalkyl phenyl sulfoxides in boiling toluene or diglyme leads to the formation of the corresponding  $\alpha$ -bromomethylketones [40].



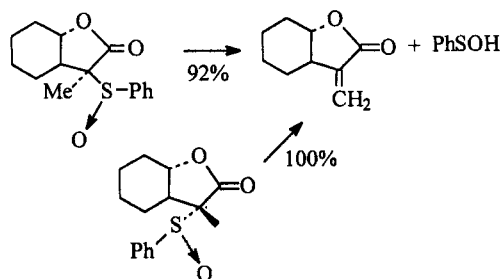
SCHEME 25

Boiling a xylene solution of butyl 2-(phenylsulfinyl)-*E*-deceonate results in a mixture of isomeric 2,4-dienoates [*E,E/Z,E* = 4 : 1] [41].



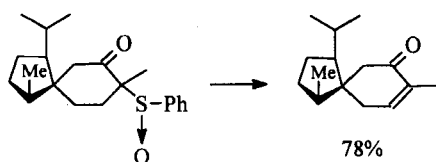
SCHEME 26

$\alpha$ -Phenylsulfinyl lactones under heating up to 115°C are pyrolyzed to give the corresponding  $\alpha$ -methylenebutyrolactones [42].



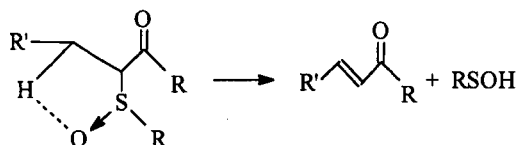
SCHEME 27

(±)Acorenone B has been prepared analogously but at 70°C in  $\text{CCl}_4$  [43].



SCHEME 28

The thermolysis of  $\alpha$ -sulfinyl ketones or ethers involves the formation of  $\alpha,\beta$ -unsaturated systems [44].

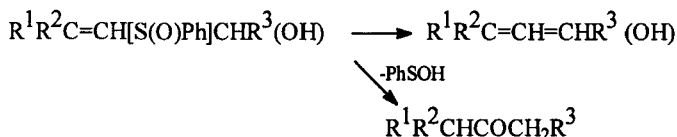


$R = \text{Ar}, 25\text{-}60^\circ\text{C}$

$R = \text{Alk}, 110\text{-}130^\circ\text{C}$

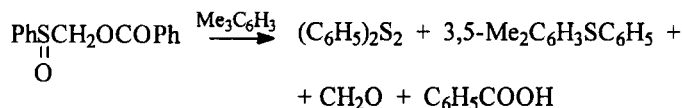
SCHEME 29

The pyrolysis of  $\beta$ -hydroxyalkyl phenyl sulfoxides at 130–180°C and under low pressure leads to the formation of allenic alcohols or unsaturated ketones [45]. Allenic alcohols are formed only in boiling xylene.



SCHEME 30

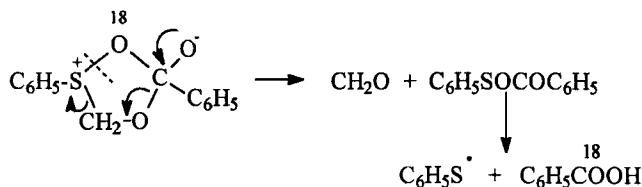
The thermolysis of benzoyloxymethyl phenyl sulfoxide in boiling mesitylene involves the elimination of both benzoic acid and formaldehyde. Due to this fact phenylthiyl radical is formed which can dimerize or substitute the methyl group in mesitylene [46].



SCHEME 31

This reaction involves the intermolecular attack of the oxygen atom of the sulfinyl group onto the CO group. This results in the formation of a cyclic di-polar ion intermediate that can eliminate formaldehyde. Support for this mechanism was

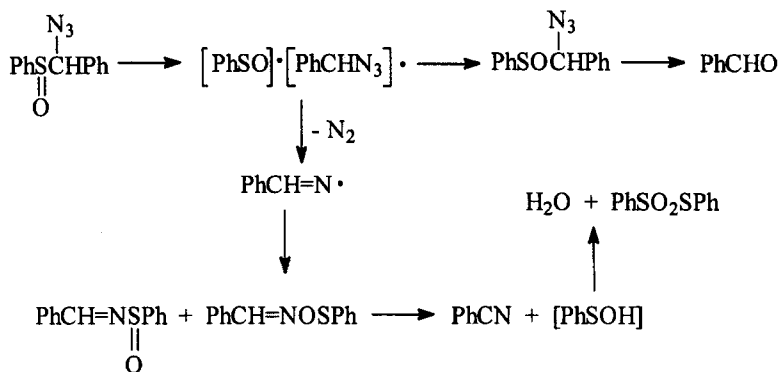
obtained by having the initial sulfoxide SO group, labeled with  $^{18}\text{O}$ . In this case the  $^{18}\text{O}$  label was completely incorporated into the  $\text{CO}_2$  group of benzoic acid.



SCHEME 32

Cyclohexanone phenyl sulfoxides are decomposed analogously but under heating in dioxane up to 60–130°C. Diphenyl disulfide and 2-cyclohexanone are formed from 2-oxocyclohexyl phenyl sulfoxide. Diphenyl disulfide as well as 6-methyl-2-cyclohexanone are formed from 2-oxo-3-methylcyclohexyl phenyl sulfoxides [47].

$\alpha$ -Azidobenzyl phenyl sulfoxide is decomposed at 70°C to give *N*-benzylidenebenzenesulfonamide, benzonitrile, benzaldehyde, diphenyl disulfide and diphenylthiosulfinate [48]. The reaction probably proceeds through the intermediate formation of radical pairs.



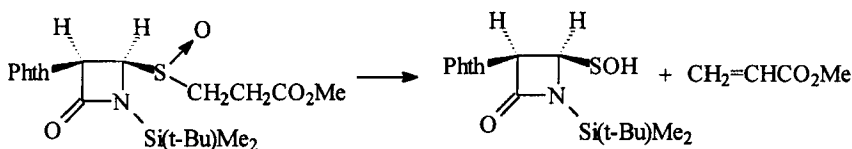
SCHEME 33

## 2.5. Diaryl Sulfoxides

Phenylthiosulfinate (40% yield) is the main product of impulse pyrolysis of diphenyl sulfoxide under vacuum at 700°C. The other products of the pyrolysis are diphenyl disulfide (12%), diphenyl (6%), diphenyl sulfide (12%) and phenol (traces) [39].

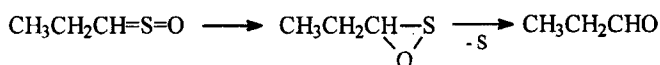
## 2.6. Other Sulfoxides

The stable 2-oxoazetidine-4-sulfenic acid (79% yield) has been obtained by heating of 2-oxoazetidine-4-alkyl sulfoxides in benzene up to 60°C. The product is stable over 6 months at 0°C or in boiling benzene for 24 h, but the acid decomposed in boiling xylene [49].



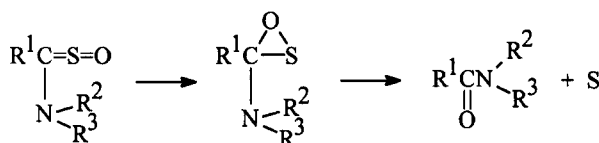
SCHEME 34

Thiopropenal-*S*-oxide is decomposed at room temperature after 1 h to give propanal and sulfur. The elimination of the latter is via the intermediate formation of a oxathiiranic intermediate [50].



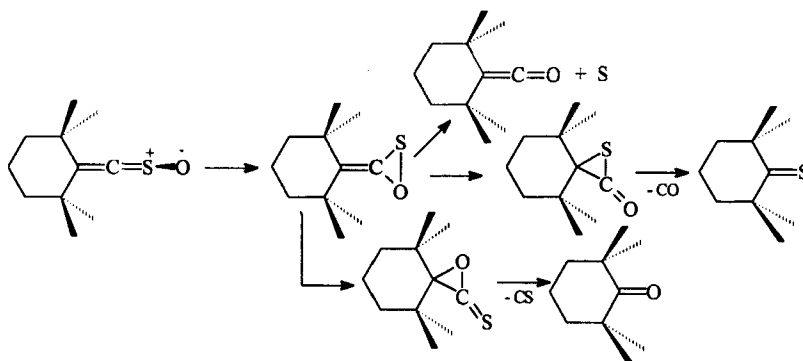
SCHEME 35

During the heating of *S*-oxides of carbonic acids thioamides sulfur atom is substituted for amide group, obviously, also through the formation of a oxathiiranic intermediate [51].



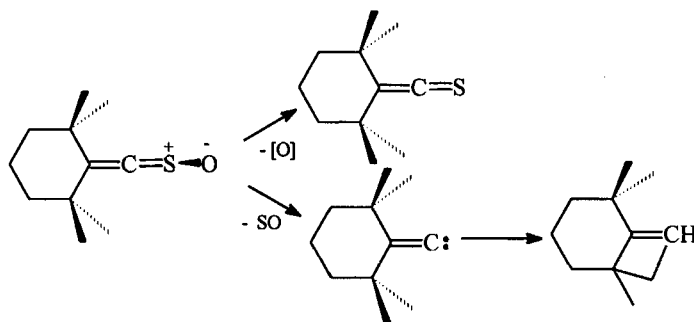
SCHEME 36

Gas-phase flash vacuum pyrolysis of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane-*S*-oxide involves the formation of the corresponding ketene, thioketene, ketone and thioketone. The ratio of the products depends upon the reaction temperature. The elimination of sulfur atom, CO or CS is followed by the electrocyclic opening of the oxathiiranic ring at 150°C [52,53].



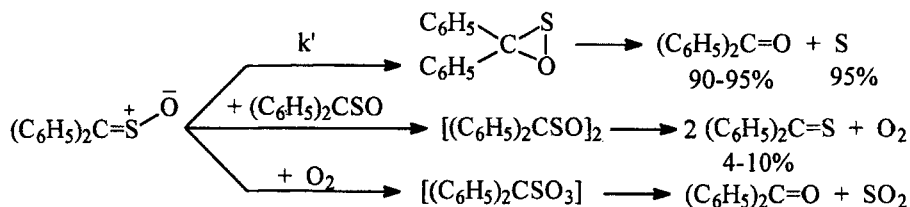
SCHEME 37

The extrusion of an oxygen atom at 610°C involves the formation of thioketene. The cleavage of the SO group leads to the formation of a carbene [52,53].



SCHEME 38

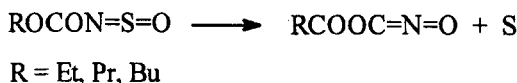
Thiobenzophenone-*S*-oxide is decomposed in diphenylamine solution at 130°C to give benzophenone, thiobenzophenone, elemental sulfur and sulfur dioxide. The decomposition proceeds by two competing routes of first and second order. Carbenes are not formed under the reaction conditions. Probably, thermally labile 3,3-diphenoxythiirane is the intermediate reaction product, which is monomerically decomposed into benzophenone and sulfur. The bimolecular reaction involves the formation of a dimer which is decomposed further [54].



SCHEME 39

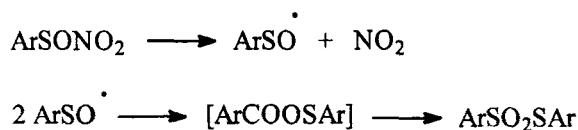
The rate of thiobenzophenone-*S*-oxide decomposition is sharply increased in the presence of oxygen. The basic products of the reaction are benzophenone (85% yield) and SO<sub>2</sub> (80%). The pyrolysis of thiobenzophenone-*S*-oxide in the gas phase at 230°C involves cleavage of the C-S bond and the formation of diphenylcarbene.

The heating of *N*-alkoxycarbonyl-substituted sulfoximides up to 150–210°C leads to the formation of alkoxy carbonylisocyanates [55]. The intermediate reaction products are probably (ROOCN=)<sub>2</sub> and ROCN.



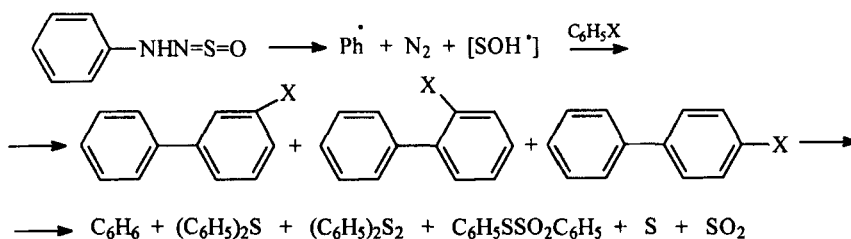
SCHEME 40

Sulfinylnitrates are easily rearranged into thiosulfonates in solutions of alcohol or  $\text{CCl}_4$  at room temperature [56].



SCHEME 41

The thermolysis of *N*-phenyl-*N'*-sulfinylhydrazine in solution of halobenzenes leads to the formation of a mixture of isomeric diphenyls as well as benzene (the main products). The following products are formed in a very low yield: diphenyl sulfide, diphenyl disulfide, diphenyl thiosulfone, sulfur and sulfur dioxide [48].

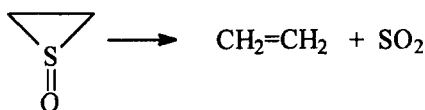


SCHEME 42

## 2.7. Cyclic Sulfoxides

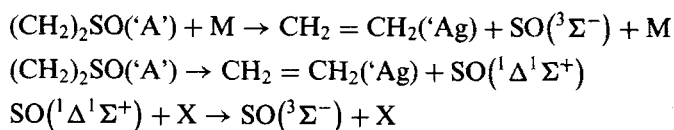
### 2.7.1. Thirane-Oxides

Ethylene episulfoxide (thiirane-oxide) is decomposed in vacuum (0.2 mm) at  $500^\circ\text{C}$  to give ethylene and  $\text{SO}_2$  [57–59].



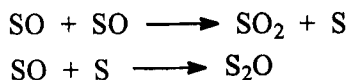
SCHEME 43

The reaction mechanism involves the biradical  $\bullet\text{CH}_2\text{-CH}_2\bullet$  and  $\text{SO}$ . Ethylene and  $\text{SO}$  are in basic electronic states:



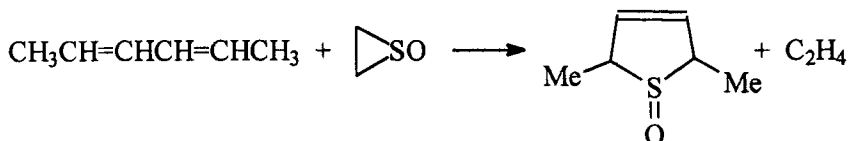


The basic reaction of thermolysis of ethylene episulfoxides involves the decomposition on the hot sides of the reaction tube (the first reaction). Sulfur oxide is unstable and is decomposed according to the following schemes:



SCHEME 44

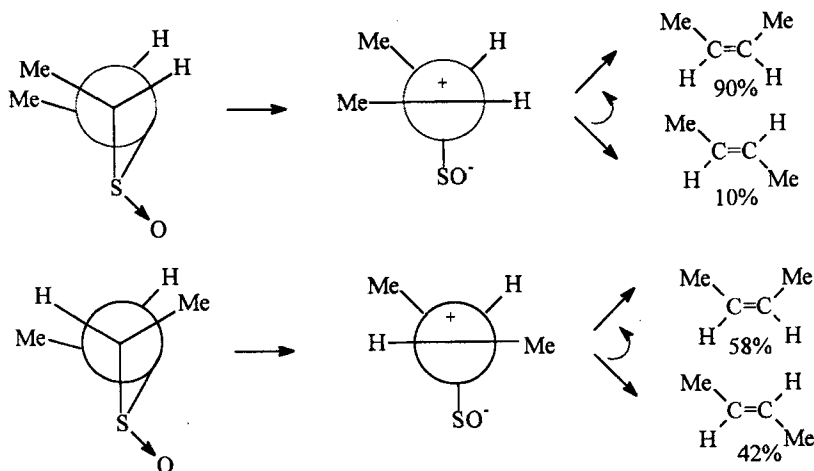
The thermolysis of thiirane oxide in a solution of 1,2-dichloroethane containing *trans-trans*-2,4-hexadiene at 115°C results in *trans,trans*- and *cis,trans*-2,5-dimethyl-3-thiolenes-*S*-oxides in a ratio of 88.2:11.8. In toluene the ratio is 89.5:10.5 [60].



SCHEME 45

The pyrolysis of *trans*-2,3-dideuterothiirane-1-oxide at 350°C leads to the formation of the mixture of *cis*- and *trans*-CHD=CHD in a 10:90 ratio. Under the same conditions the pyrolysis of *cis*-2,3-dideuterothiirane-*syn*- and *anti*-1-oxides results in the mixture of *cis*- and *trans*-CHD=CHD, but in a ratio of 95:5 [61]. The authors suppose that the addition of SO ( $^3\Sigma^-$ ) to the diene is followed by diene isomerization, thereafter the reaction proceeds stereoselectively.

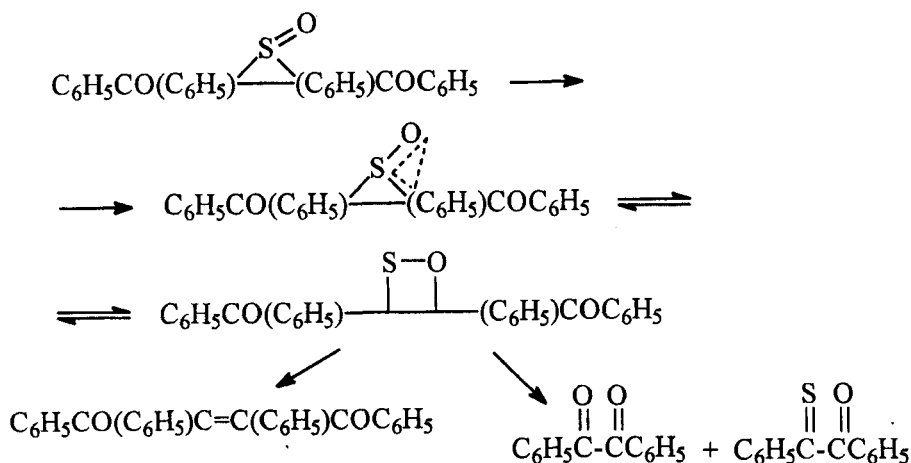
At 85–340°C *cis*-2-butane episulfoxide is transformed into *cis*-2-butene. Under analogous conditions the pyrolysis of *trans*-2-butane episulfoxide leads to a mixture of *cis*- and *trans*-2-butene (in almost equal ratio), and a two-stage reaction mechanism has been proposed. It involves the formation of an ion pair in the first stage (the cleavage of the C–S bond) followed by cleavage of the SO group [62,63]. The energy of activation for elimination of SO from the *cis* intermediate is comparable to that for bond rotation.



SCHEME 46

*Cis*- and *trans*-1,2-diphenylthiirane-*S*-oxide is pyrolyzed to give sulfur and SO<sub>2</sub>, and is transformed into stilbene. That *trans*-isomer gives *trans*-stilbene but *cis*-stilbene episulfoxide is transformed into a mixture of *cis*- and *trans*-stilbene [64]. It is suggested that a biradical intermediate is formed, which is isomerized into the more stable conformation before SO elimination.

The pyrolysis of a mixture of isomeric dibenzoylstilbene episulfoxides in vacuum at 200–210°C involves the formation of benzyl (51%), monothiobenzyl (11%), *cis*-dibenzoylstilbene (3%) and traces of *trans*-dibenzoylstilbene. The reaction proceeds via the formation of an intermediate thioxetane [65].

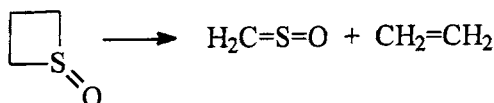


SCHEME 47

The pyrolysis of diarylsubstituted stilbene episulfoxides always leads to 1,2-oxetanes [63]. 2,3-Diphenylstilbene episulfoxide is stable at 130°C for 1 h and then is partly decomposed [66].

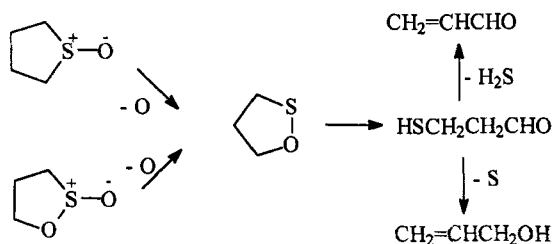
### 2.7.2. Thietane-, Thiolane-, Oxathiolane- and other *S*-oxides

The flash vacuum pyrolysis of thietane-*S*-oxides (600°C) results in sulfine and ethylene [7].



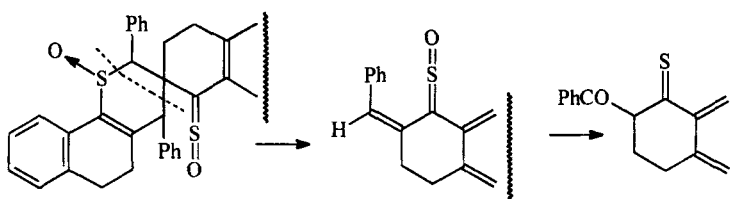
SCHEME 48

The cyclic sulfenate, 1,2-oxathiolane, is an intermediate product of flash vacuum pyrolysis (510–1130°C) of thiolane-*S*-oxide and 1,2-oxathiolane-*S*-oxide, leading to the formation of acrolein and allyl alcohol [67].



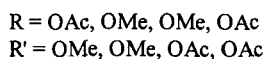
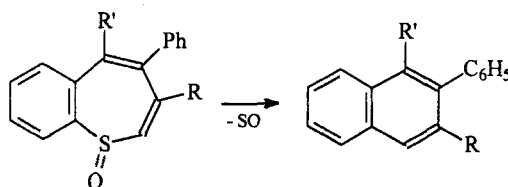
SCHEME 49

The thermolysis of a conjugated six-membered cyclic sulfoxide containing a sulfine group in the neighboring ring involves the formation of a keto-thione followed by formation of an  $\alpha,\beta$ -unsaturated sulfine [68].



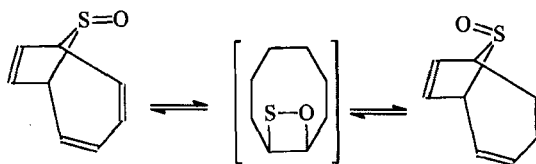
SCHEME 50

3,5-Disubstituted 4-phenyl-1-benzothiepine-1-oxides in boiling chloroform are transformed into 1,3-disubstituted 2-phenylnaphthalenes [69].



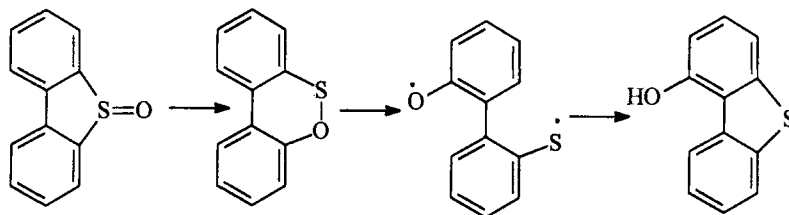
SCHEME 51

The heating of the bicyclic sulfoxide, 9-thiacyclo[4.2.1]-nona-2,4,7-trien-7-en-9-oxide, is accompanied by its inversion, via a suprafacial 1,3-migration of the SO bridged group [70].



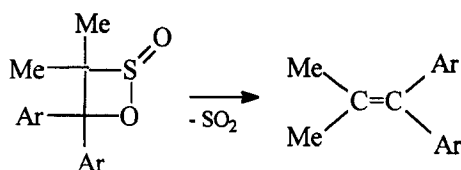
SCHEME 52

Dibenzothiophene-5-oxide is rearranged into 1-hydroxydibenzothiophene at 700–900°C probably via an intermediate cyclic sulfenate [39].



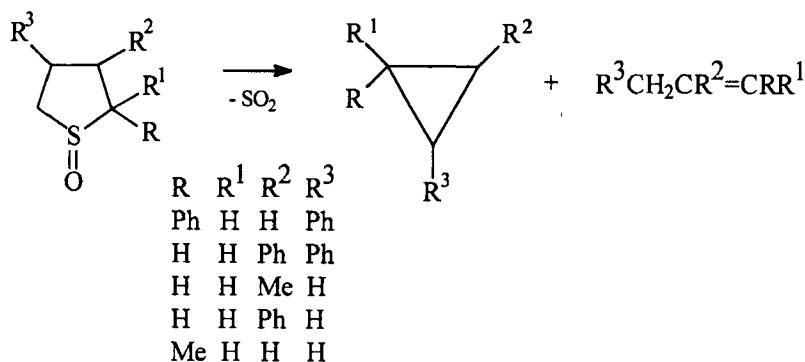
SCHEME 53

Some four-membered cyclic  $\beta$ -sultines are unstable. They are rapidly decomposed under heating up to 30°C to give the corresponding ethylenes [71].



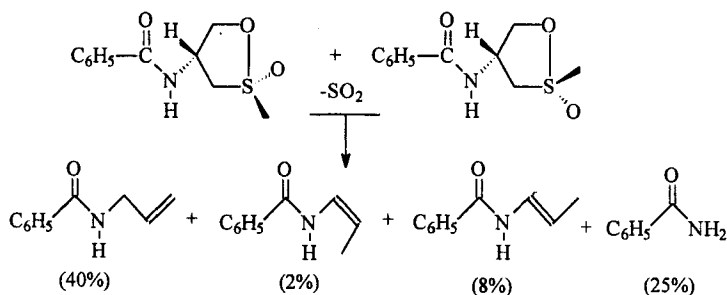
SCHEME 54

The flash vacuum pyrolysis of cyclic sultines at 550–950°C (0.07 mm) involves the formation of the corresponding cyclopropanes and alkenes (Scheme 55) [72]. The greatest amounts of cyclopropanes are formed from the first and second compounds at 750°C. Other reactions lead to the large amounts of olefins. Reactions at temperatures above 750°C lead to both alkylbenzenes and  $\alpha$ -methylstyrene.



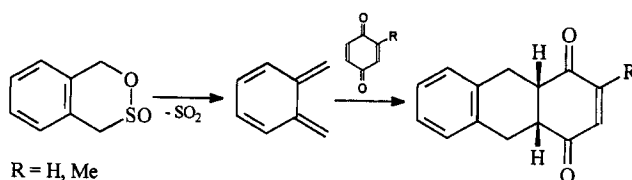
SCHEME 55

The flash vacuum pyrolysis of 4-benzamide- $\gamma$ -sultines results in a mixture of *N*-allyl-amide and enamides. The reaction involves the migration of the benzamide group [73].



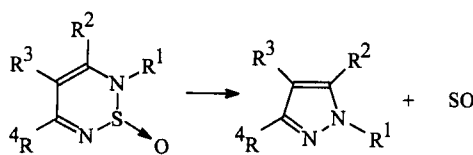
SCHEME 56

Durst–Charlton  $\text{SO}_2$  extrusion from 1,4-dihydro-2,3-benzooxathine 3-oxide generated *o*-quinodimethane, which was trapped *in situ* by *p*-benzoquinone and other *p*-quinones to afford tetrahydro-1,4-anthracenediones [74].



SCHEME 57

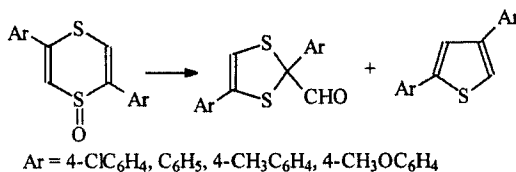
1,2,6-thiadiazine-*S*-oxides upon heating in toluene up to  $90^\circ\text{C}$  are transformed into the corresponding pyrazoles due to the extrusion of the SO group [75].



SCHEME 58

### 2.7.3. Di- and Trithiacyclanes Oxides

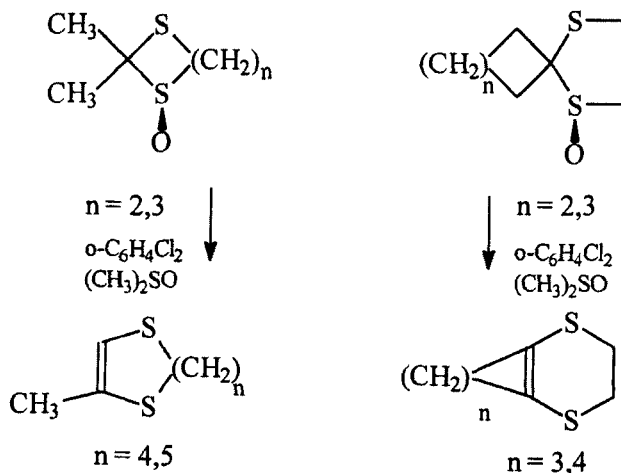
Heating of solutions of 2,5-diaryl-1,4-dithiine-1-oxides in acetonitrile up to  $75^\circ\text{C}$  leads to the corresponding 2-formyl-2,4-diaryl-1,3-dithioles and 2,4-diarylthiophenes [76].



SCHEME 59

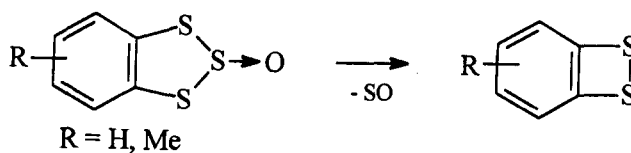
The use of  $\text{CCl}_4$  as the solvent leads to the formation of dithiols only. 2,4-Diarylthiophenes are exclusively formed in both benzene and 3,5-lutidine [77].

The heating of cyclic and spirocyclic sulfoxides in solution involves the  $\beta$ -*cis*-elimination of both sulfenic acid and olefin which enter into an electrophilic addition reaction to give new heterocyclic compounds [78].



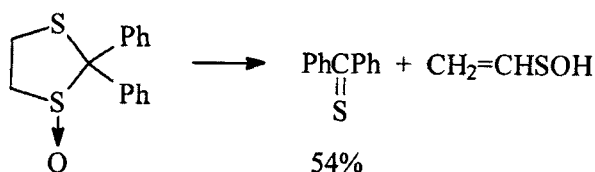
SCHEME 60

The flash vacuum pyrolysis of benzotrithiol-2-oxide ( $540\text{--}720^\circ\text{C}$ ) and its derivatives involves the elimination of sulfur and the formation of the corresponding benzo-dithietes [79].



SCHEME 61

The flash vacuum pyrolysis of 2,2-diphenyl-1,3-dithiolane-1-oxide in vacuum ( $0.01\text{ mm Hg}$ ) at  $400\text{--}650^\circ\text{C}$  involves the elimination of vinylsulfenic acid and the formation of thiobenzophenone [80].



SCHEME 62

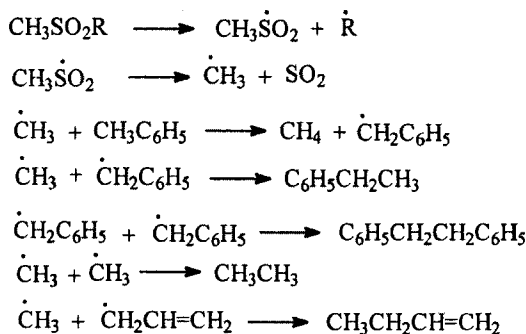
The pyrolysis of spiro-1,3,3-trimethylbicyclo[2,2,1]heptane-2,2,1-(1',3'-dithiolene-1'-oxide) under analogous conditions at 700–850°C leads to thiofenchone in 63% yield [80].

### 3. SULFONES

#### 3.1. Alkyl Sulfones

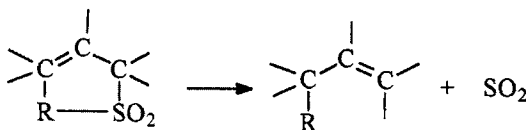
Thermal stability of sulfones depends upon the presence and number of  $\beta$ -hydrogen atoms. The absence of these or the presence of stabilizing groups leads to the stabilization of sulfones under heating (without solvent) up to 275°C during 1 h in vacuum. An  $\alpha$ -phenyl group acts as both an electron-acceptor and a stabilizer. Di(*tert*-butyl) sulfone is the least stable of the sulfones having 18  $\beta$ -hydrogen atoms. Dimethyl sulfone is the most stable compound of this series. The correspondence between thermal stability of sulfones and the stability of free radicals which were formed after the sulfones undergo homolysis has been found [81].

Dimethyl sulfone, benzyl methyl sulfone and allyl methyl sulfone are decomposed in a toluene jet at 360–640°C to give sulfur dioxide, methane, ethylbenzene, dibenzyl and the traces of ethane. The decomposition of allyl methyl sulfone also involves the formation of 1,5-hexadiene and 1-butene. Arrhenius values from the rate constants of sulfone decomposition have been determined. The mechanism of thermal decomposition of sulfones has been proposed [82].



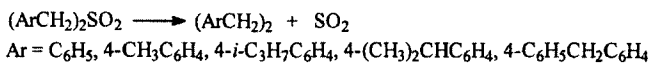
SCHEME 63

The thermal decomposition of allyl sulfones of various structures at 170–390°C involves the elimination of sulfur dioxide and the formation of the corresponding olefins. The mechanism of the reaction at low temperatures is via a cyclic intermediate, and at high temperatures via free radicals [83,84].



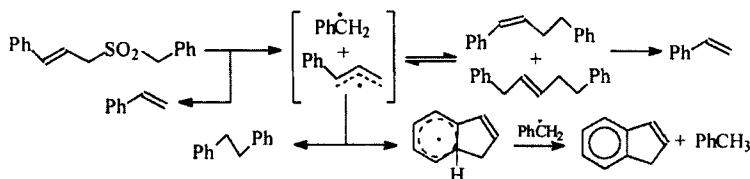
SCHEME 64

The flash vacuum pyrolysis of dibenzyl sulfones at 600–700°C leads to the corresponding dibenzyls [85–87]. Polymers (5–20%) are also formed concurrently.



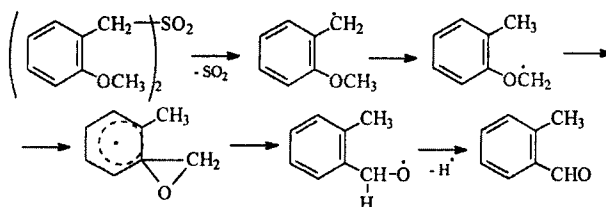
SCHEME 65

The flash vacuum pyrolysis of cinnamyl benzyl sulfone at 640°C results in indene, dibenzyl styrene and toluene. The decomposition involves cleavage of the C–S bond (not the extrusion of SO<sub>2</sub>) [88].



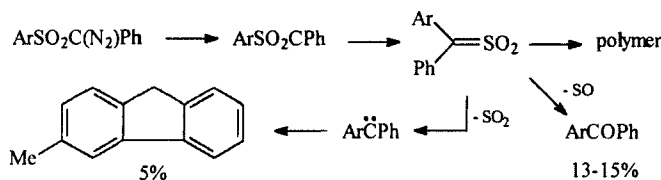
SCHEME 66

The flash vacuum pyrolysis (650°C) of dibenzyl sulfone with methoxy groups in the ortho-position of the benzene ring leads to ortho-toluenaldehyde. The reaction mechanism involves the isomerization of the 2-methoxybenzene radical [89].



SCHEME 67

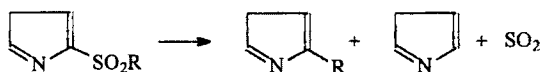
Phenyl(4-tolyl)ketone and 2-methylfluorene are the products of the pyrolysis of  $\alpha$ -(4-tolylsulfonyl)phenyldiazomethane at 350°C. The intermediate product of the reaction (sulfene) is generally polymerized [90].



SCHEME 68

2-Alkylsulfonylpyrazines upon heating up to 300–340°C are transformed into 2-alkylpyrazines, pyrazine and sulfur dioxide [91].





R = Me, Et, Pr, Bu, CH<sub>2</sub>Bu, *i*-Bu, *s*-Bu, *i*-Pr, CHMeCHMe<sub>2</sub>, *t*-Bu

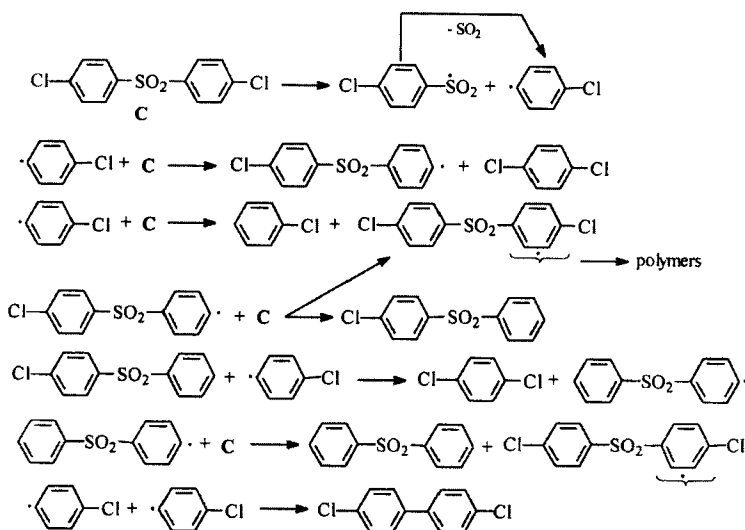
SCHEME 69

The ratio of the products depends upon the nature of the substituent *R*.

### 3.2. Aryl Sulfones

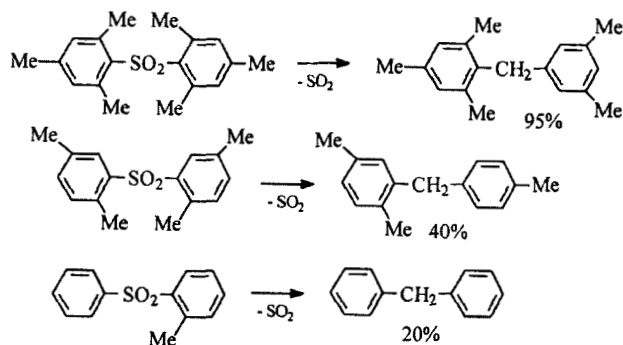
Diphenyl sulfone is not decomposed at 400°C over a long period of time [92]. The flash vacuum pyrolysis of diphenyl sulfone at 900°C leads to a small amount of diphenyl (10%) [39]. *Bis*(4-tolyl) sulfone can be distilled in vacuum at 405°C without decomposition. The long-time heating of *bis*(4-tolyl) sulfone at 400°C involves the formation of higher sulfones and hydrocarbons [93]. The heating of *bis*(4-tolyl) sulfone at 800–880°C over the catalyst (SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>) leads to 4-ditolyl and diphenyl [94].

The thermolysis of *bis*(4-chlorophenyl) sulfone at 360–400°C is accompanied by the formation of sulfur dioxide, chlorobenzene, 4-dichlorobenzene, diphenyl sulfide, 4,4'-diphenyl, 4-chlorodiphenyl sulfone and high-boiling poly-conjugated products [95]. The reaction scheme involves free radical transformations of the decomposition products followed by homolytic dissociation of the C–S bond.



SCHEME 70

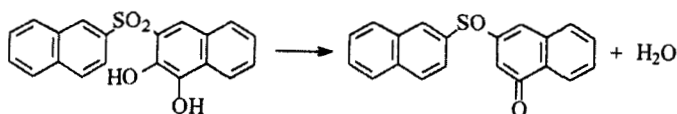
Diaryl sulfones containing a methyl group in the ortho-position of the benzene ring are decomposed at 370–400°C under pressure to give the corresponding diarylmethanes as shown in the following example [93].



SCHEME 71

The substitution of the  $\text{SO}_2$  group for a methylene bridge is probably formed synchronically through the formation of cyclic intermediate.

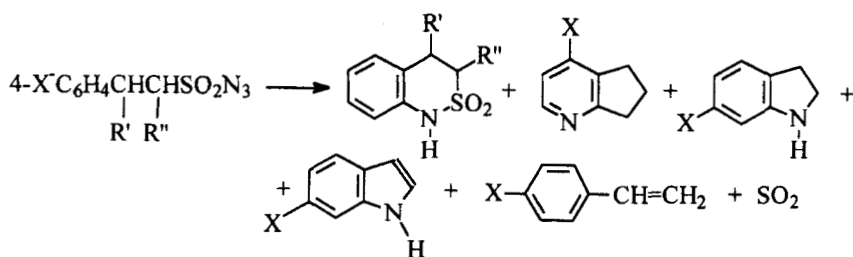
1-Naphthylsulfonyl-3,4-dioxynaphthalene is dehydrated at  $170\text{--}180^\circ\text{C}$  into  $\beta$ -naphthyl ( $\beta$ -benzoquinolyl-3) sulfoxide. The reaction involves the cleavage of an oxygen atom from  $\text{SO}_2$  group [96].



SCHEME 72

### 3.3. Sulfonylazides and Organylazo Sulfones

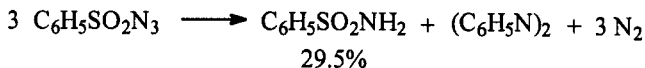
Flash vacuum pyrolysis of  $\beta$ -arylethylsulfonyl azides at  $250\text{--}300^\circ\text{C}$  gave some 3,4-dihydro-2,1-benzothiazine-2,2-dioxide, but the use of higher temperatures led to the formation of corresponding styrenes, indolines, indoles, sulfur dioxide and 4-substituted 6,7-dihydro-5H-1-pyridines, in good yields. The styrenes result from the elimination of  $\text{HN}_3$  and  $\text{SO}_2$  from azides, and indolines are formed in good yield by FVP of 3,4-dihydro-2,1-benzothiazine-2,2-dioxide at  $650^\circ\text{C}$  [97].



X, R', R'' = H, Me, Cl, OMe

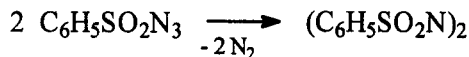
SCHEME 73

Thermal decomposition of benzenesulfonylazide and its derivatives in cyclohexane solution at 130–150°C involves the formation of benzenesulfonamide and azobenzene [98].



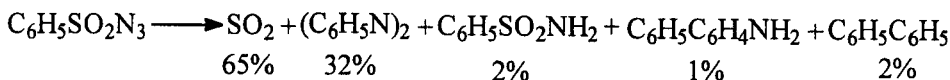
SCHEME 74

The products of dimerization of the solvent have also been found. Liquid-phase pyrolysis of benzenesulfonylazide and its derivatives in the absence of solvent leads to only azosulfonylbenzenes [98].



SCHEME 75

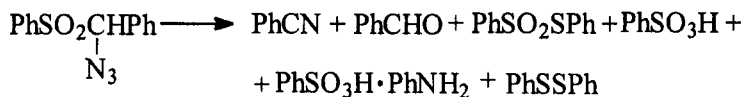
The flash vacuum pyrolysis of benzenesulfonylazide at 360°C proceeds more profoundly [99].



SCHEME 76

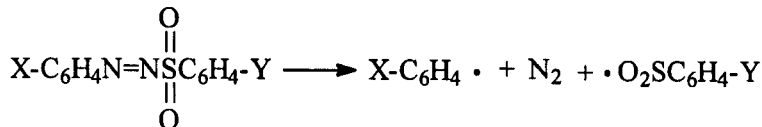
Benzylsultam (5%) and a resin (21%) were also isolated from 2-methylbenzenesulfonylazide.

Thermolysis of  $\alpha$ -azidobenzyl phenyl sulfone proceeds at temperatures above 150°C and gives a mixture of reaction products [100]. The reaction is catalyzed by the forming sulfonic acid.



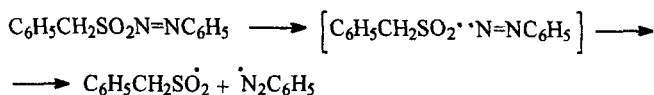
SCHEME 77

Aryl phenylazo sulfones are decomposed into free radicals upon heating in chlorobenzene solution at 80–180°C. The reaction proceeds according to first-order kinetics ( $E_A = 33\text{--}39$  Kcal/mol,  $S^\ddagger = 16\text{--}30$  entropy units). An isokinetic relationship was found to hold between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  ( $B = 101.0^\circ\text{C}$ ). The substituents on the benzosulfonyl group influenced the rates very little, whereas the substituents on the phenylazo group decreased rates (especially the electron-releasing substituents) [101].



SCHEME 78

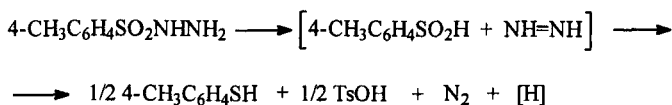
Benzylazo sulfone under heating in toluene, anisole, chlorobenzene or nitrobenzene is decomposed into diazobenzene and benzylsulfonyl radicals (trapped by a stable radical). The intermediate product is the radical pair, which is solvated in the polar media [102].



SCHEME 79

### 3.4. Sulfonylamines, Sulfonamides, -diimides and -imines

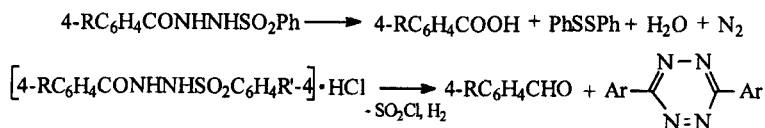
4-Tosylhydrazine is decomposed at 140°C to give a mixture of reaction products [103].



SCHEME 80

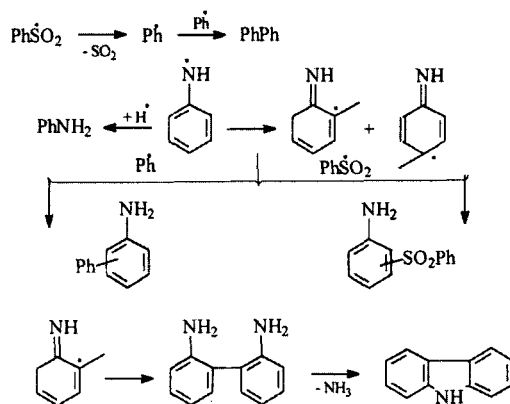
The first stage of the reaction is thought to be the decomposition of the initial product into  $\text{N}_2\text{H}_2$  and 4- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}$ . The further disproportionation of the acids involves the formation of 4-thiocresol and TsOH.

The corresponding benzoic acids and diphenyl sulfide have been found in the products of the pyrolysis of 1-aryl-2-phenylsulfonylhydrazines. The pyrolysis of *N*-arylsulfonylarylhyaazidoyl chlorides under analogous conditions leads to substituted benzaldehyde and 3,6-diaryl symmetric tetrazines [104].



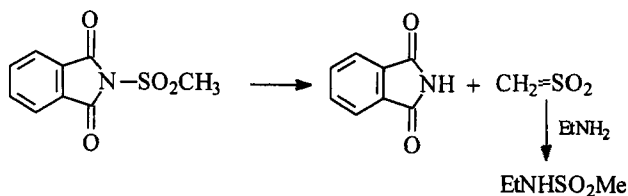
SCHEME 81

The heating of *N*-phenylbenzenesulfonamide up to 300°C leads to aniline, diphenyl, carbazole, a mixture of isomeric aminodiphenyls and sulfur dioxide [105].



SCHEME 82

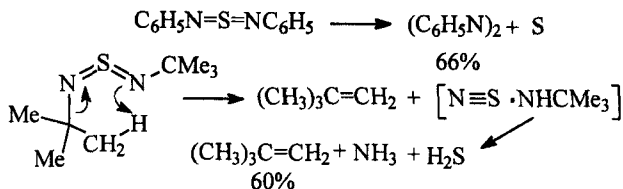
The flash vacuum pyrolysis of *N*-methylsulfonylphthalimide (0.1 mm) at 600°C involves the formation of sulfene and phthalimide [106].



SCHEME 83

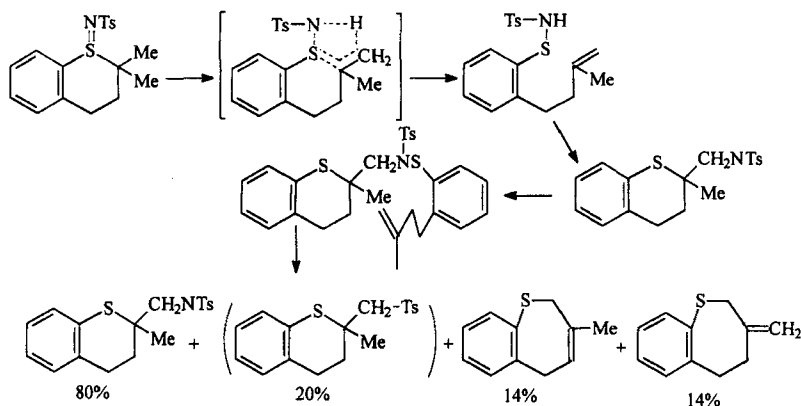
The pyrolysis of *N*-benzylsulfonylphthalimide under analogous conditions results in only benzaldehyde in quantitative yield.

The heating of diphenylsulfodiimide up to 265°C leads to sulfur and azobenzene. The pyrolysis of di(*tert*-butyl)sulfodiimide at 200°C involves elimination of ammonia and hydrogen sulfide and the formation of 2-methylpropene [107].



SCHEME 84

The boiling of 2,2-dimethyl-1-(4-toluenesulfonylimino)thiochromane in benzene solution for 1 h leads to *N*[2-(3-methyl-3-butenyl)-phenylthio]-*N*-(2'-methylthiochroman-2'-ylmethyl)-4-toluenesulfamide in quantitative yield. The latter is decomposed in boiling xylene, to give several products [108].

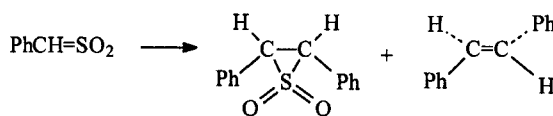


SCHEME 85

### 3.5. Cyclic sulfones

#### 3.5.1. Three-membered Heterocycles

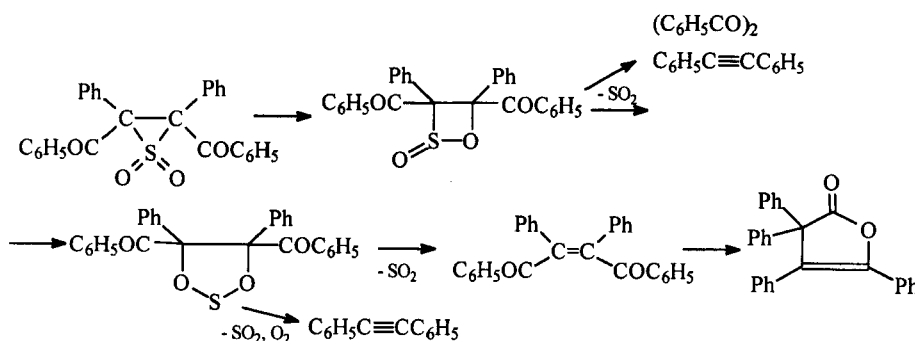
Episulfone is thermally unstable. Its various derivatives show higher stability. The heating of episulfone derivatives at temperatures above 60–100°C involves the quantitative elimination of SO<sub>2</sub>, and the formation of the corresponding olefins [109]. The reaction is strongly stereospecific. The thermolysis of *cis*-epithio-2-butenedioide [110], chloroepisulfones [111,112], 2-methyl- and 2-bromo-episulfone [113], asymmetric alkyl-, phenyl-, benzene-episulfones [114] have been studied. The pyrolysis of 2,3-diaryl-2,3-diethyl- and 2,2-diaryl-3,3-diethyl-thiirane-dioxides at 100°C involves the elimination of SO<sub>2</sub> and formation of the corresponding substituted ethylenes (*trans*-isomers) [115,116]. *Trans*-stilbene episulfone is less stable than its *cis*-isomer [117,118]. The moderate heating of phenylsulfene leads to both *cis*-stilbene episulfone and *trans*-stilbene (instead of a mixture of *cis*- and *trans*-stilbene episulfones).



SCHEME 86

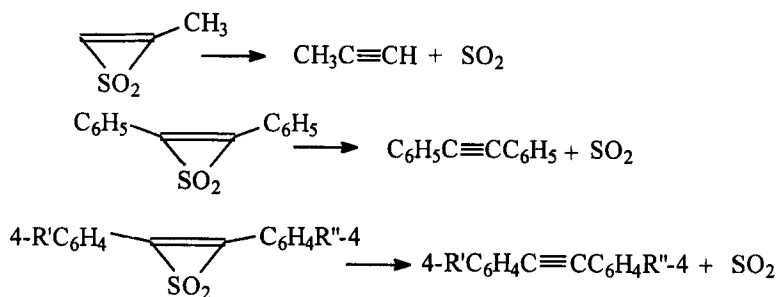
The pyrolysis of *cis*-stilbene episulfone at 90°C involves the elimination of SO<sub>2</sub> and formation of *cis*-stilbene. The heating of tetraphenylethylene sulfone in vacuum up to 50–160°C leads to the elimination of SO<sub>2</sub> as well as formation of tetraphenylethylene.

The heating of *cis*-dibenzene stilbene episulfone in vacuum up to 300°C results in SO<sub>2</sub>, dibenzene, diphenylacetylene and 2,2,3,4-tetraphenyl-2(3H)-furanone [119]. The reaction mechanism involves the transformation of the 3-membered ring episulfonic into the 5-membered 1,2,3-dioxathiolane followed by the transformation into less strained 4-membered ring cyclic sulfinate.



SCHEME 87

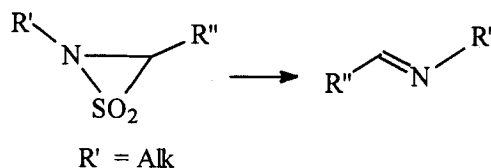
Thiirene-1,1-dioxides are more stable than their saturated analogs (episulfones). The pyrolysis of thiirene-1,1-dioxides at 120–130°C involves the elimination of SO<sub>2</sub>, and formation of the corresponding acetylenic hydrocarbons [120,121].



SCHEME 88

The rate constants for  $\text{SO}_2$  extrusion of the substituted thiirene-1,1-dioxides are best correlated with  $\sigma^+$  constants. This is indicative of a stepwise mechanism of  $\text{SO}_2$  group cleavage [122]. The experimental values of the rate constants coincide with those calculated for the stepwise mechanism but differ from those calculated for the mechanism of  $\text{SO}_2$  extrusion. Thiirenes show the following order of stability: thiirenes < thiirene-1,1-dioxides < thiirene-1-oxides. Thiirene-1-oxides are the most thermally stable in this series due to the strong conjugation effect in its molecule ( $p$ - $\pi$ -conjugation due to free pair of electrons of sulfur atom). But the low thermal stability of sulfones could be explained by the fact that  $\text{SO}_2$  is cleaved easier than  $\text{SO}$ .

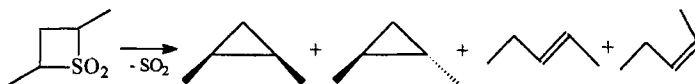
Thiaziridine-1,1-dioxides are decomposed at 40–70°C to give the corresponding aldimines [123].



SCHEME 89

### 3.5.2. Four-membered Heterocycles

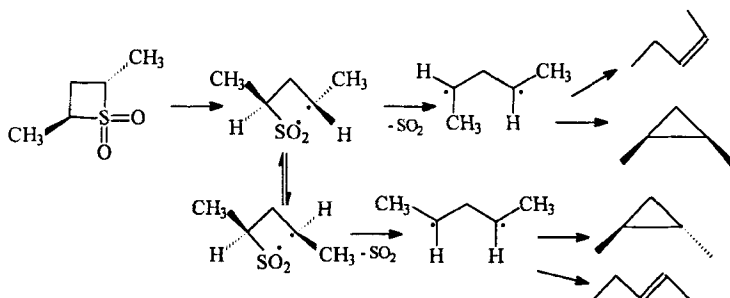
The pyrolysis of both *cis*- and *trans*-2,4-dimethyl-thietane-1,1-dioxide at 350°C leads to *cis*- and *trans*-1,2-dimethylcyclopropane (50%) as well as *cis*- and *trans*-2-pentene (16%) [124].



SCHEME 90

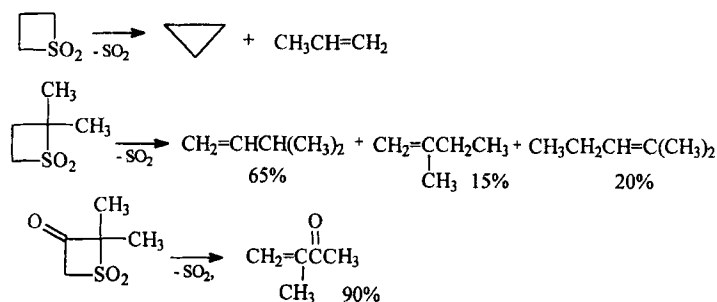
An increase of the reaction temperature results in an increasing yield of pentenes as well as decreasing the reaction stereospecificity. The reaction mechanism involves

biradical formation (via cleavage of C-S bond), SO<sub>2</sub> extrusion and the transformation of a biradical into cyclopanes or 2-pentenes.



SCHEME 91

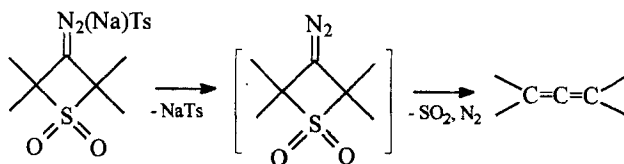
The flash vacuum pyrolysis of thietanes and 3-oxo-thiethane-1,1-dioxide at 930–960°C involves the elimination of SO<sub>2</sub> and the formation of the corresponding unsaturated product [125,126].



SCHEME 92

The pyrolysis of 3-thiethanol-1,1-dioxide at 935°C leads to acetaldehyde, formaldehyde, acetone, acrolein, dimethylacetal, ethane, ethylene and SO<sub>2</sub>.

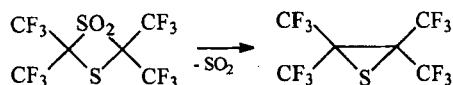
The dried sodium salt of 2,2,4,4-tetramethyl-3-oxo-thiethane-1,1-dioxide tosylhydrazone is decomposed in vacuum at 110–160°C to give tetramethylallene and sodium 4-tolylsulfinate [127].



SCHEME 93

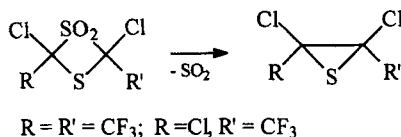
Tetra(trifluoromethyl)-1,3-dithietane-1,1-dioxide is transformed at 550°C into tetra (fluoromethyl)thiirane [128].





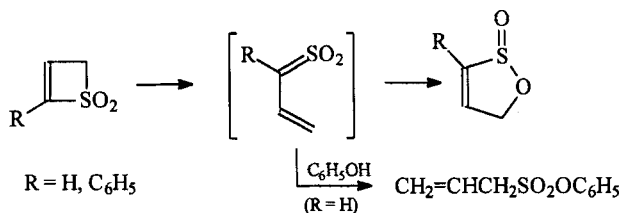
SCHEME 94

Dichloro-2,3-*bis*(trifluoromethyl)thiirane and 2,2,3-trichloro-3-fluoromethylthiirane were isolated by thermolysis (FVP) of the two 1,3-dithietane-1,1-dioxides under  $\text{SO}_2$  extrusion [129].



SCHEME 95

Thiete-1,1-dioxide in the liquid or gas phase is thermally rearranged into sultine probably through the intermediate formation of a vinylsulfene [125].

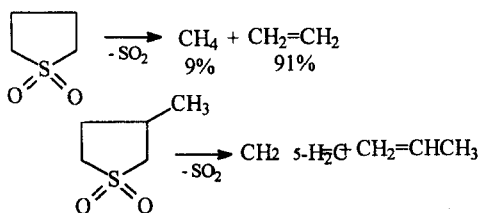


SCHEME 96

In the presence of phenol, vinylsulfene gives phenyl 2-propene-1-sulfonate.

### 3.5.3. Five-membered Heterocycles

Sulfolane and its derivatives are decomposed at 365–405°C to give  $\text{SO}_2$  as well as both saturated and unsaturated hydrocarbons, as shown in the following example [126,130].

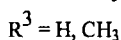
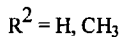
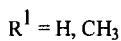
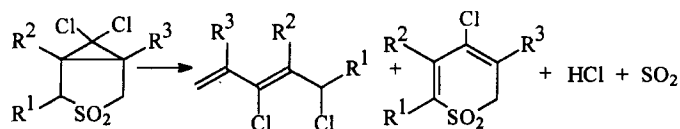


SCHEME 97

The Arrhenius constant for the pyrolysis rate of 3-methylsulfolane has been determined. The reaction mechanism involves C–S bond cleavage (the main stage), then C–C bond cleavage and  $\text{SO}_2$  elimination. An alternative mechanism with formation

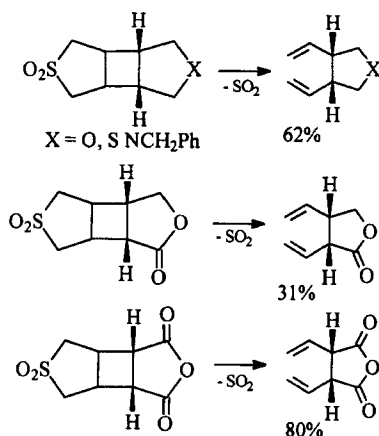
of a C<sub>4</sub> biradical with SO<sub>2</sub> extrusion is highly improbable [126]. The mechanisms of the thermal reactions of sulfolanes have been discussed in a review [131].

Thermal decomposition of the dichlorocarbene adduct of sulfolenes at 140–160°C leads to the corresponding dichlorodienes and chlorothiopyranedioxides [132].



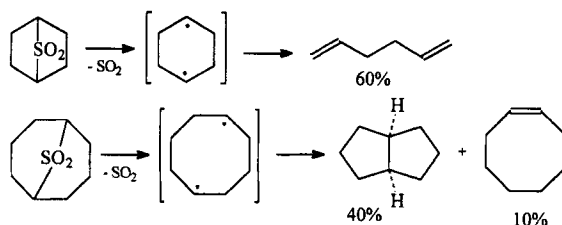
SCHEME 98

The flash vacuum pyrolysis of thieno-cyclobuta[1,2-*c*]furan *S,S*-dioxide ( $X = \text{O}$ ) and its analogues at 625°C results in *cis*-1,2-divinyl heterocycles [133].



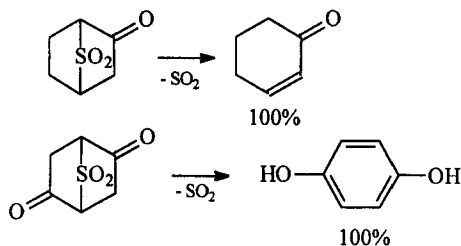
SCHEME 99

The sublimation of 7-thiabicyclo[2.2.1]heptane-7,7-dioxide at 0.04 mm in a quartz tube at 520°C leads to 1,5-hexadiene. The pyrolysis of 9-thiabicyclo[3.3.1]nonane-9,9-dioxide at 710°C (0.1 mm) results in *cis*-bicyclo[3.3.1]octane and cyclooctene [134].



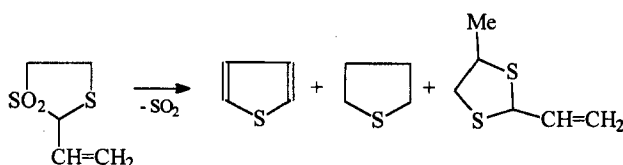
SCHEME 100

The heating of 7-thiabicyclo[2.2.1]heptanone and -heptadione at 160–220°C involves the elimination of SO<sub>2</sub> and the formation of 2-cyclohexenone and hydroquinone [135].



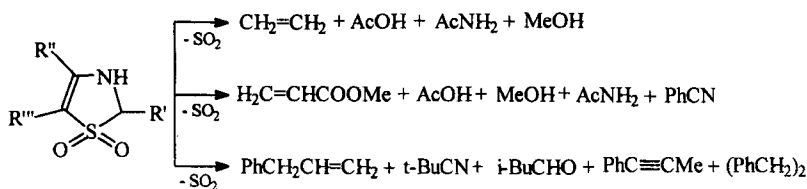
SCHEME 101

The flash vacuum pyrolysis of 2-vinyl-1,3-dithiolane-1,1-dioxides at 430–600°C leads to thiophene, dihydrothiophene and 2-propenethials [136].



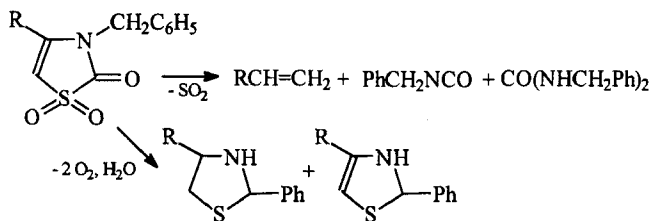
SCHEME 102

The flash vacuum pyrolysis of thiazolidine-1,1-dioxides proceeds in three directions depending upon the compound's structure [137].



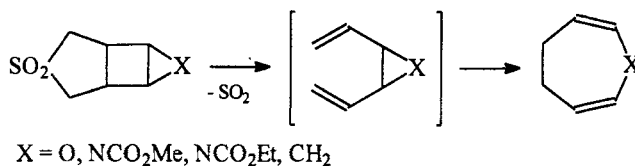
SCHEME 103

4-Substituted 3-benzyl thiazolidine-1,1-dioxides at 600–655°C are transformed into a mixture of five products [138].



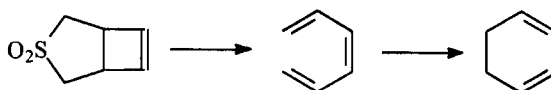
SCHEME 104

The flash vacuum pyrolysis of tricyclic sulfolane derivatives at 550–580°C leads to *cis*-1,2-divinyl compounds which undergo Cope rearrangement [139,140].



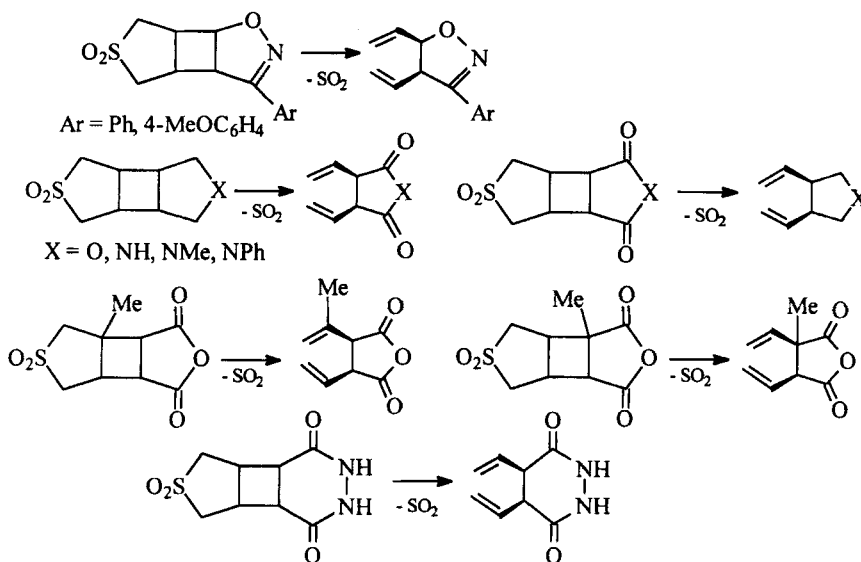
SCHEME 105

The flash vacuum pyrolysis of 3-thiabicyclo[3.2.0]hept-6-ene at 500°C results in stereospecific extrusion of SO<sub>2</sub> to give *Z*-hexa-1,3,5-triene which undergoes electrocycloisatation to give cyclohexa-1,3-diene [139,140].



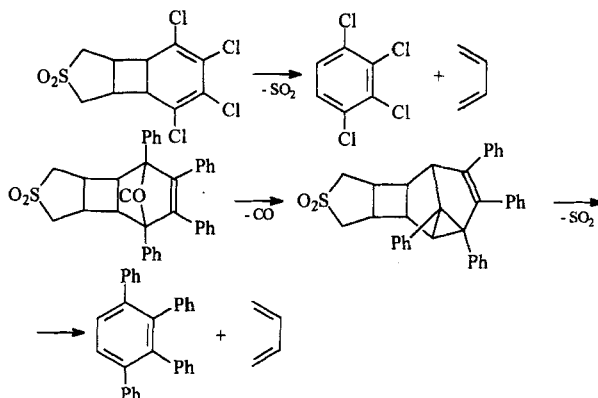
SCHEME 106

Upon FVP, the tricyclo[5.3.0.0]skeleton loses SO<sub>2</sub> to give stable *cis*-1,2-divinyl compounds [139–141].



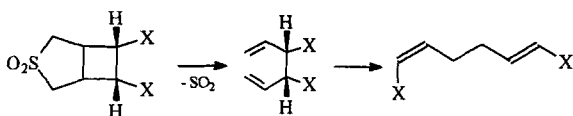
SCHEME 107

The tricyclic Diels-Alder adducts upon FVP lose SO<sub>2</sub> and butadiene to give tetrasubstituted benzenes [139,140].



SCHEME 108

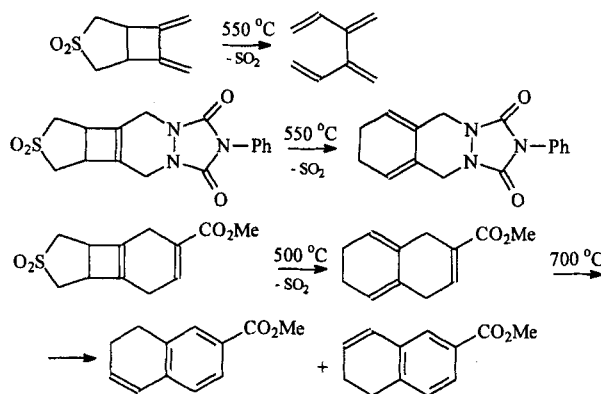
The flash vacuum pyrolysis of tricyclic systems containing 3-thiabicyclo[3.2-*b*]-3,3-dioxide at 550–620°C involves the formation of *cis*-divinyl-substituted systems, [133(131)] which are transformed further into *E,Z*-dienes [142].



X = CO<sub>2</sub>H (34%), CH<sub>2</sub>OAc(30%), CH<sub>2</sub>OH(39%), CH<sub>2</sub>OMe(47%), CO<sub>2</sub>Me(87%)

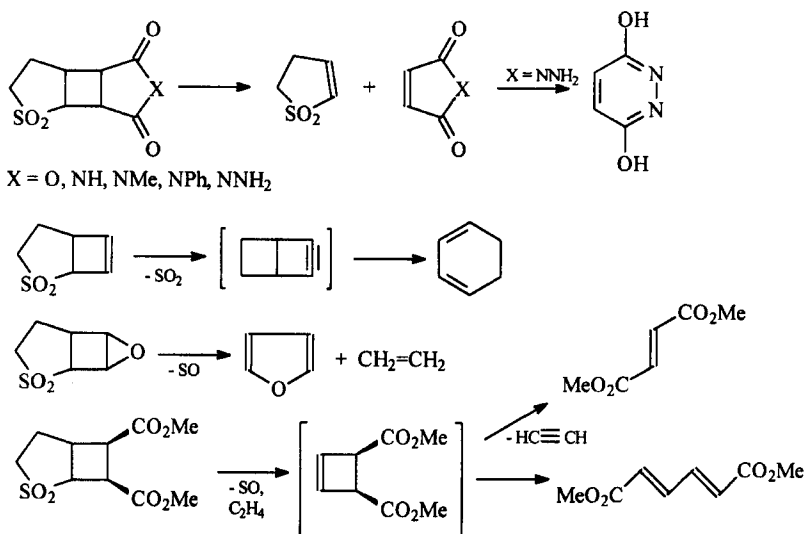
SCHEME 109

Previous limitations of highly reactive [4]dendralene (3,4-dimethylenehexa-1,5-diene) as a tandem annulating reagent in Diels–Alder reactions are overcome by the use of its masked form 6,7-dimethylene-3-thiabicyclo[3.2.0]-heptane-3,3-dioxide, and subsequent extrusion of SO<sub>2</sub> under flash pyrolytic conditions. Similar pyrolyses of other cycloadducts obtained from the diene and a variety of dienophiles generated tetra- and hexahydronaphthalene derivatives in good-to-excellent yields [143].



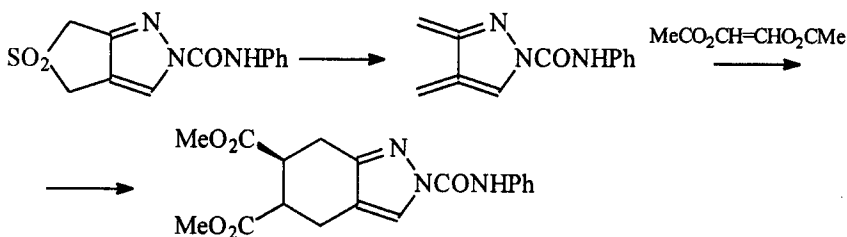
SCHEME 110

The flash vacuum pyrolysis of new bi- and tri-cyclic sulfones and containing the novel 2-thiabicyclo[3.2.0]heptane 2,2-dioxide ring system (450–775°C) results in either cycloreversion with elimination of 2-sulfolene or, in one case extrusion of ethane and SO to give the 1,3-diene. Pyrolysis of bicyclic alkene results in loss of only SO<sub>2</sub> to give cyclohexa-1,3-diene, but its epoxide loses SO<sub>2</sub> and ethene to afford furan [144].



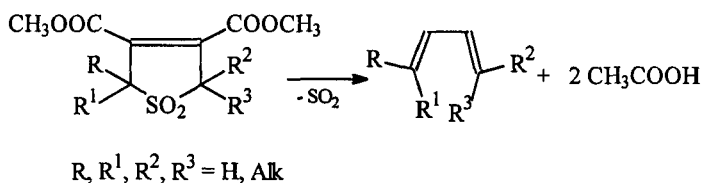
SCHEME 111

Extrusion of SO<sub>2</sub> from *N*-anilincarbonylpyrazolo-3 sulfolenes was achieved at 180–190°C and the transient intermediate, the pyrazolo-*o*-quinodimethane, could be trapped with dienophiles to give annulated pyrazoles [145].



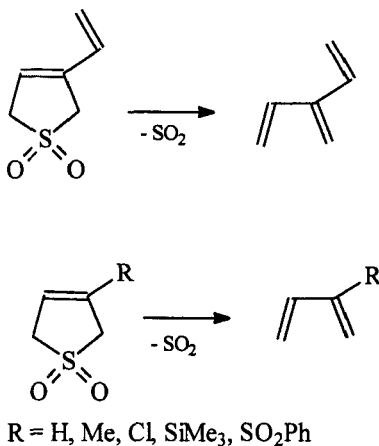
SCHEME 112

Thermal reactions of sulfolene and its derivatives proceed through an intermediate product with synchronic formation (or cleavage) of C–S bonds. The reaction is strictly stereospecific. In some cases the reaction mechanism can be two-staged and involves the cleavage of the S–C bond as well as the formation of a biradical in the first stage. As a result a mixture of isomeric dienes is formed [146–149].



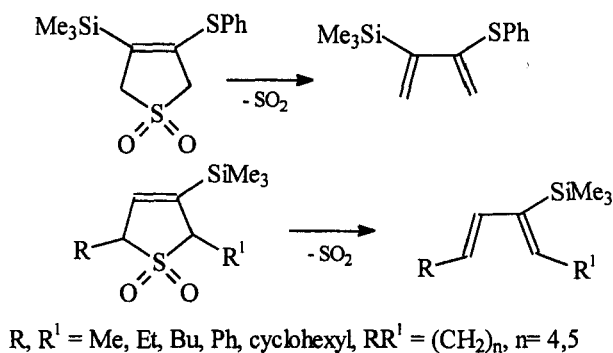
SCHEME 113

Cheletropic extrusion of  $\text{SO}_2$  from 3-vinyl-2,5-dihydrothiophene-1,1-dioxide provides a clean and efficient route to [3] dendralene (3-methylenepenta-1,4-diene) under flash vacuum pyrolytic conditions ( $550^\circ\text{C}$ , 0.001 mm Hg), the simplest member of the diene-transmissive polyenes [150].



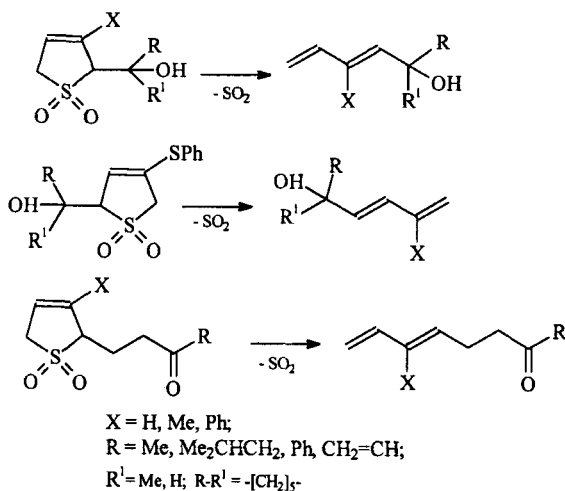
SCHEME 114

Thermolysis of other sulfones gave substituted butadienes [151–153].



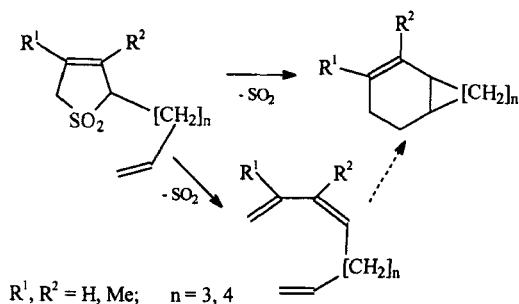
SCHEME 115

A stereoselective synthesis of (*E*)- $\alpha$ -hydroxy-1,3-dienes, by thermal ( $125^\circ\text{C}$ ,  $\text{NaHCO}_3$ ) extrusion of  $\text{SO}_2$  from sulfones is presented [154,155].



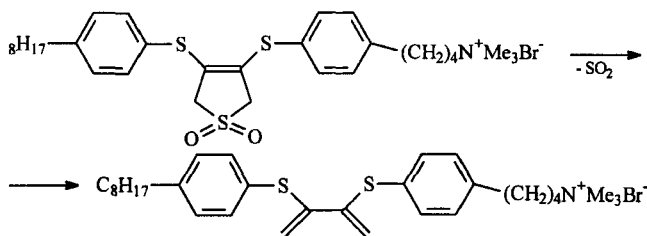
SCHEME 116

Thermolysis of several new 2-( $\omega$ -alkenyl)-3-sulfolenes through a tube in a furnace under  $\text{N}_2$  at  $580^\circ\text{C}$  led to cheletropic extrusion of  $\text{SO}_2$  followed by intramolecular Diels–Alder reaction to yield the corresponding hydroindanes and hydronaphthalenes [156].



SCHEME 117

The ability of aqueous surfactant aggregates to control the regiochemistry of Diels–Alder reactions was investigated with surfactant 1,3-diene. Diene was derived *in situ* from surfactant sulfone by thermal extrusion ( $130^\circ\text{C}$ ) of  $\text{SO}_2$  as illustrated [157].

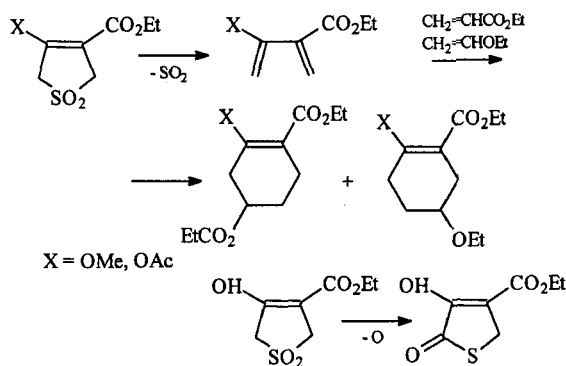


SCHEME 118

The thermal extrusion of  $\text{SO}_2$  from disubstituted 3-sulfolenes leads to 2,3-donor–acceptor-substituted 1,3-butadienes. These dienes react with acrylic acid ester and

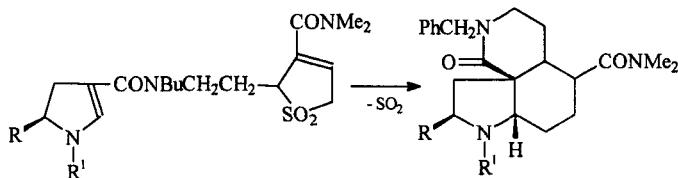


ethyl vinyl ether to give the corresponding Diels–Alder adducts. The pyrolysis of 3-sulfolene ( $X=OH$ ) afforded the thiolactone [158].



SCHEME 119

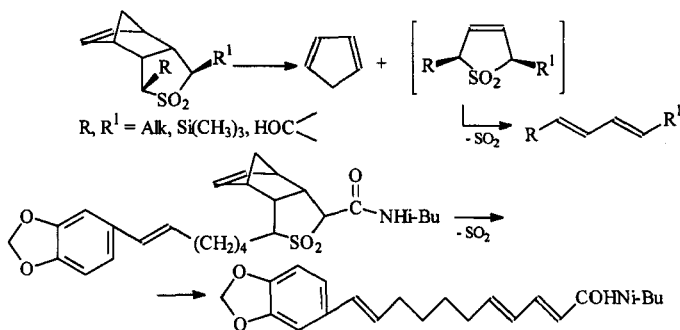
A tandem sulfolene  $SO_2$  extrusion – intramolecular Diels–Alder cyclization of sulfolene derivatives gave the C-5 epimers of the manzamine tricyclic ABC ring system via a C-5 to C-8 diene bearing a C-5/C-6 Z-alkene [159].



SCHEME 120

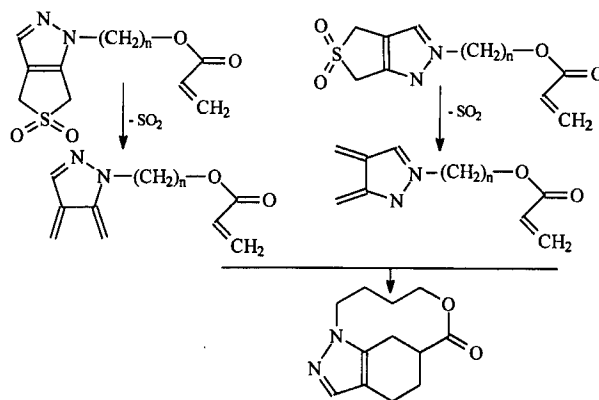
Flash vacuum pyrolysis of the  $\eta^5$ -(cyclopentadienyl)cobalt  $\eta^4$ -thiophene 1,1-dioxides gave the Co cyclobutadiene complexes with  $SO_2$  extrusion [160,161].

The retro Diels–Alder reaction involving the elimination of  $SO_2$  gave *cis*-2,5-disubstituted-2,5-dihydrothiophene-1,1-dioxides which were transformed into the corresponding (*E,E*)-conjugate dienes [162–166].



SCHEME 121

Thermolysis of two isomeric series of homologous *N*-(acryloyloxy)alkylated pyrazolo-3-sulfolenes provides the corresponding *o*-quinodimethanes which underwent "type-two" intramolecular Diels–Alder reactions to form two- and three-atom-bridged tricyclic pyrazoles [167].

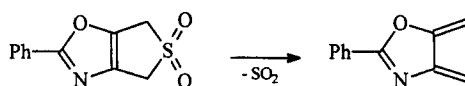


SCHEME 122

When heated in the presence of electron-poor dienophiles and [60] fullerene, sultines underwent extrusion of  $\text{SO}_2$ , and the resulting heterocyclic *o*-quinodimethanes were intercepted as the 1:1 adducts in good to excellent yield [168].

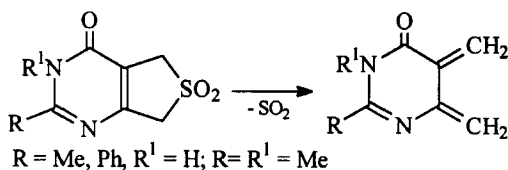
*N*-(Acetyl), 2-alkyl- or 2-aryl pyrazolo-3-sulfolenes readily undergo  $\text{SO}_2$  extrusion upon heating and, in the presence of dienophiles, such as *N*-phenylmaleimide and fumarate, give the corresponding [4 + 2] cycloadducts in good yields [169].

2-Phenyloxazolo-3-sulfolene undergoes a  $\text{SO}_2$  extrusion reaction to afford a reactive 2-phenyloxazolo-*o*-quinodimethane at room temperature. To explain the exceptional thermal reactivity of 2-phenyloxazolo-3-sulfolene, oxazolo- and other 5-membered heteroaromatic-fused 3-sulfolenes were studied theoretically [170].



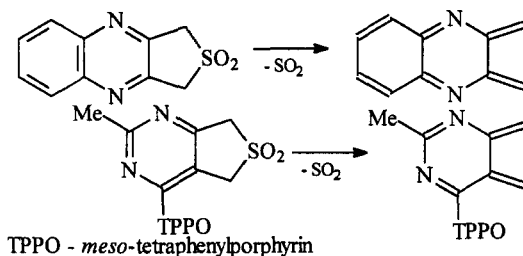
SCHEME 123

2-Methyl-5,6-dimethylenepyrimidin-4-one is generated by thermal extrusion of  $\text{SO}_2$  from fused 3-sulfolene and can be trapped with dienophiles and nucleophiles [171,172].



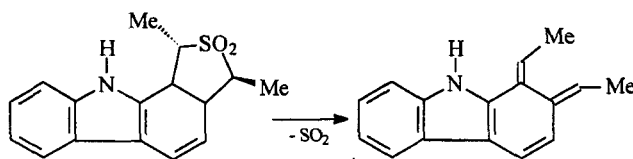
SCHEME 124

The generation of *o*-quinodimethane from unsubstituted quinoxaline-3-sulfolene was achieved at temperatures higher than 290°C [173–175].



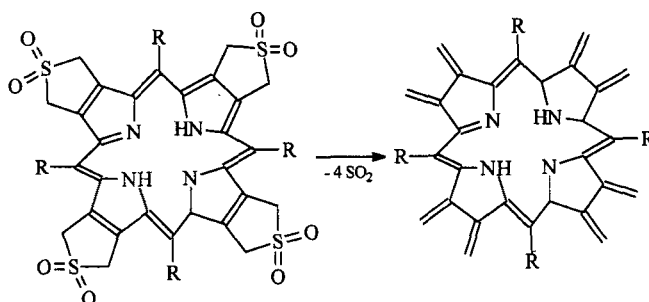
SCHEME 125

Carbazole-1,2-quinodimethane was generated by thermal extrusion of SO<sub>2</sub> from an appropriate dihydrothieno[3,4-*a*]carbazole-*S,S*-dioxide. This novel ortho-quinodimethane was trapped *in situ* by Diels–Alder reactions with *N*-phenylmaleimide, 1,4-naphthoquinone, or fumarate to give the corresponding carbazole [176].



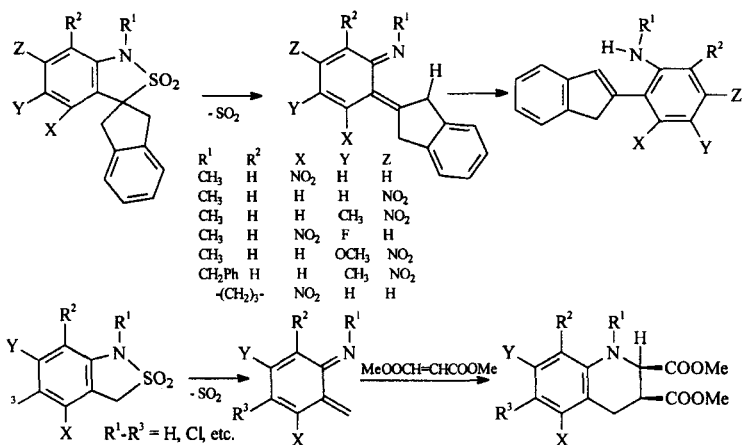
SCHEME 126

Thermolysis of symmetrical tetrasulfolenoporphyrins provides the corresponding *o*-quinodimethanes [177].



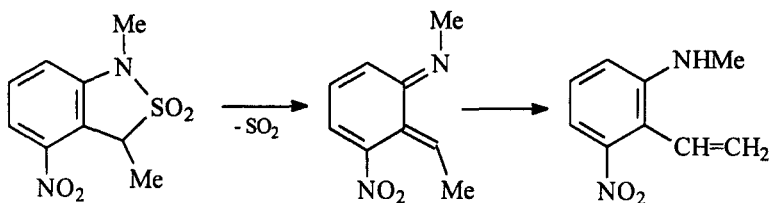
SCHEME 127

Aza-*o*-xylylenes generated via thermal extrusion (215°C) of SO<sub>2</sub> from 1,3-dihydro-2,1-benzisothiazolo-3-spiro-2'-indan 2,2-dioxides undergo a [1,5] hydrogen shift to give 2-phenylindene derivatives in good yield [178,179].



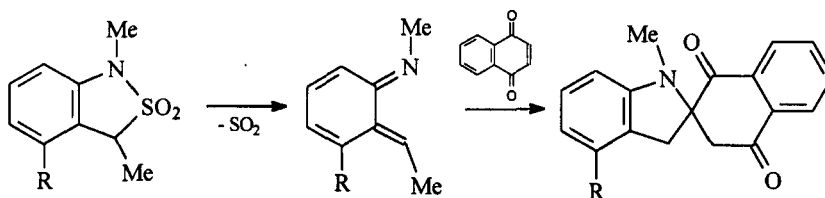
SCHEME 128

Aza-*ortho*-xylylenes generated by the thermal extrusion (215°C) of SO<sub>2</sub> from 3-alkyl-2,1-benzisothiazoline 2,2-dioxides, undergo [1,5] hydrogen shift leading to 2-amino-1-styrene derivatives [180–183]



SCHEME 129

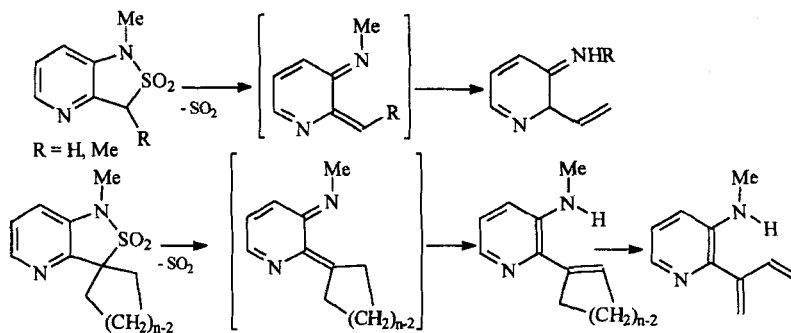
Reactions of 1,4-naphthoquinone with aza-*o*-xylylenes generated via thermal extrusion of SO<sub>2</sub> from 2,1-benzisothiazoline 2,2-dioxides, leads to tetrahydronaphthalene-2-spiro-2'-dihydroindole derivatives [184].



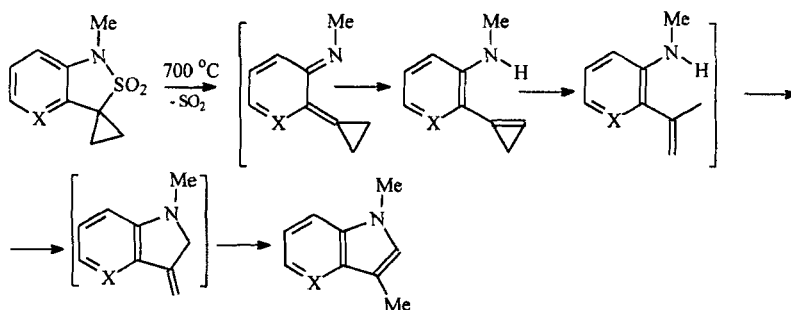
SCHEME 130

2,3-Dihydro-3-imino-2-methylenepyridines, generated by thermal extrusion (215°C) of SO<sub>2</sub> from 1,3-dialkyl-1,3-dihydroisothiazolo[4,3-*b*]pyridine 2,2-dioxides, underwent [1,5] hydrogen shifts, which led to 3-alkylamino-2-vinylpyridine derivatives. Cycloalkanespiro-3-pyridinosultams gave 3-alkylamino-2-cycloalkenylpyridine derivatives. Cyclobutanespiro-3-pyridinosultam, after thermal extrusion of SO<sub>2</sub>, formed

a cyclobutenyl derivative, which underwent a ring-opening reaction to form a butadiene derivative [185].

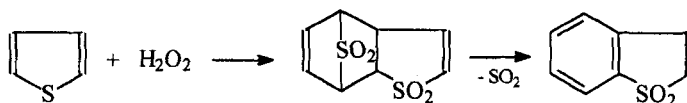


SCHEME 131



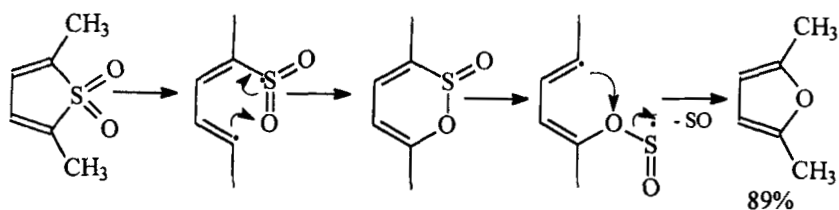
SCHEME 132

Thiopheneoxide and thiophenedioxide are unstable dienes possessing high reaction ability. They have been prepared by multi-stage synthesis but were not obtained as pure products. Due to their instability they exist only in solutions [186,187]. The oxidation of thiophene by hydrogen peroxide leads to 4,7,8,9-tetrahydro-4,7-sulfonylthianaphthene-1,1-dioxide. The latter under heating up to 180°C is transformed into benzo[*b*]thiophene-1,1-dioxide [188].



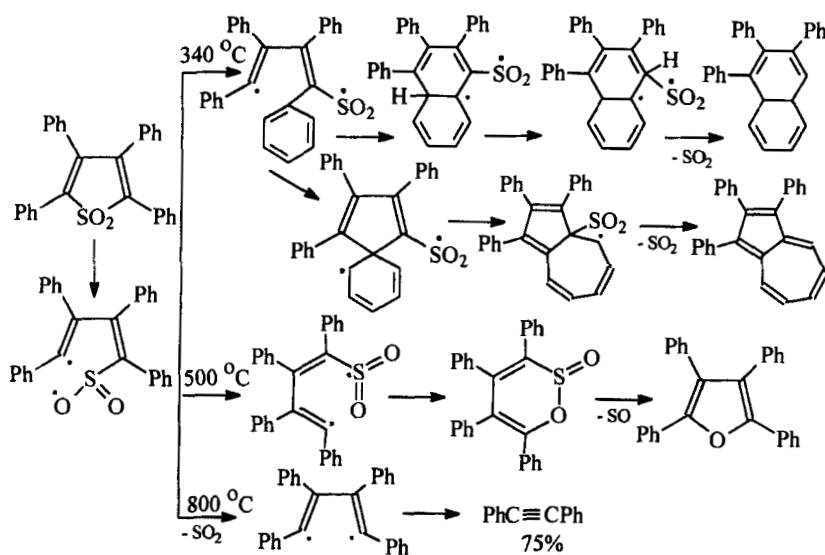
SCHEME 133

2,5-Disubstituted-thiophenedioxides are thermally stable compounds. The impulse pyrolysis of 2,5-dimethylthiophene-1,1-dioxide at 880°C leads to 2,5-dimethylfuran [189].



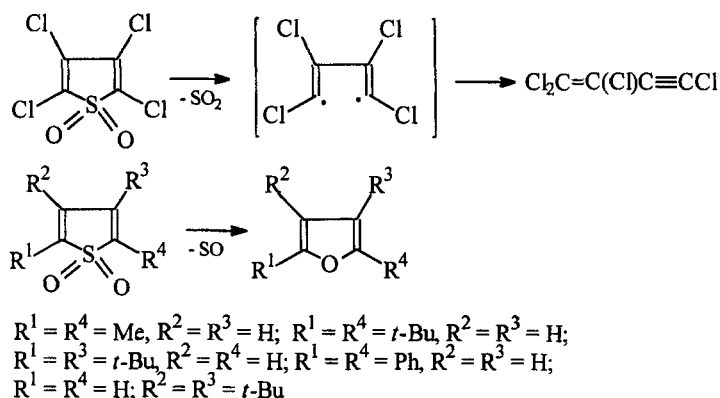
SCHEME 134

Tetraphenylthiophene-dioxide at 340°C is transformed into both 1,2,3-triphenyl-naphthalene and 1,2,3-triphenylazulen. The gas-phase pyrolysis of tetraphenylthiophene-dioxide at 500–550°C leads to tetraphenylfuran and tetraphenylthiophene. The impulse pyrolysis of tetraphenylthiophene-dioxide in vacuum (880°C) results in diphenylacetylene [189,190]. The first stage of tetraphenylthiophene-dioxide pyrolysis involves C–S bond cleavage. The radical formed at 340°C is isomerized into a vinyl radical, which is intramolecularly cyclized with SO<sub>2</sub> extrusion. The reactions of opening–closing of the thiophene ring in the gas phase at 500°C involves the elimination of atoms of sulfur or oxygen. The extrusion of SO<sub>2</sub> as well as the formation of hydrocarbon biradical is observed at 880°C.



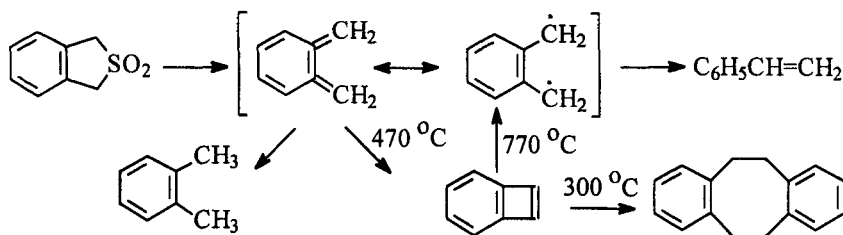
SCHEME 135

The flash vacuum pyrolysis of tetrachlorothiophene-dioxide leads to perchlorovinyl-acetylene. The vacuum pyrolysis of 2,5-, 2,4- or 3,4-dialkyl(diphenyl)thiophene-1,1-dioxides results in the corresponding 2,5-, 2,4- or 3,4-dialkyl(diphenyl)furans [189,191,192].



SCHEME 136

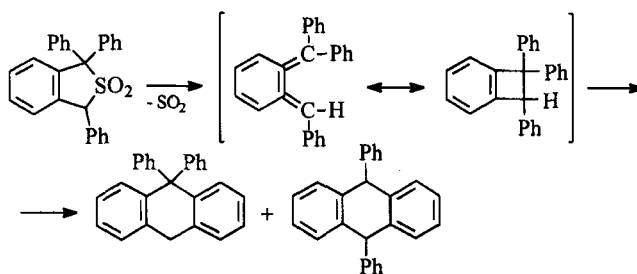
The pyrolysis of 1,3-dihydrobenzo[*c*]thiophene-2,2-dioxide in the melt at 380–300°C involves the formation of SO<sub>2</sub>, *ortho*-xylene, as well as benzocyclobutene and its dimer. The pyrolysis in gas phase at 460–470°C leads to only benzocyclobutene in high yield [193,194].



SCHEME 137

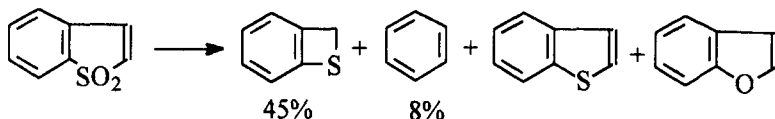
*Ortho*-quinodimethane is the initial product of the reaction. Substituted benzocyclobutanes are formed analogously. Substituted 1,3-dihydro[*c*]thiophene-2,2-dioxides are transformed into the corresponding stilbenes at 600–700°C [195].

The thermolysis of 1,1,3-triphenyl-1,3-dihydroisothionaphthene-2,2-dioxide proceeds at 150°C to give 9,10-dihydroanthracene derivatives [196].



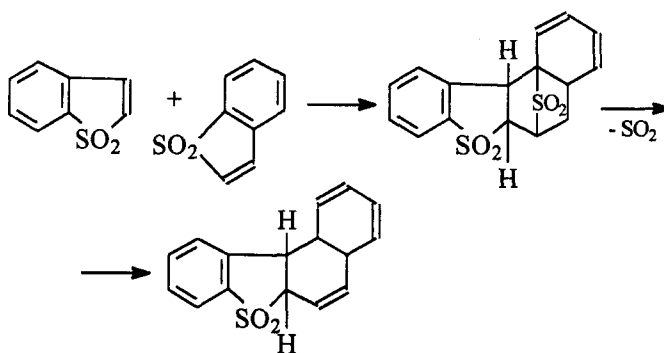
SCHEME 138

Gas-phase pyrolysis of benzothiophene-1,1-dioxide (1000°C) leads to benzothiete (45%), benzene (8%) as well as benzothiophene and benzofuran [188,197].



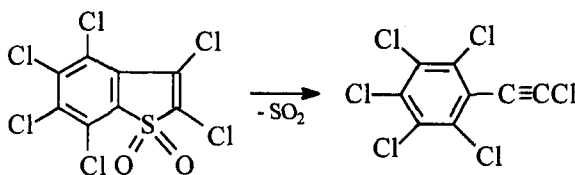
SCHEME 139

Liquid-phase pyrolysis of benzothiophene-1,1-dioxide, both in the presence and absence of solvent, leads to dimerization of the Diels-Alder type. The reaction involves the elimination of  $\text{SO}_2$  and the formation of 6-*a*,11-*b*-dihydronaphtho[2,1-*b*]-benzo[*d*]thiophene-7,7-dioxide [198].



SCHEME 140

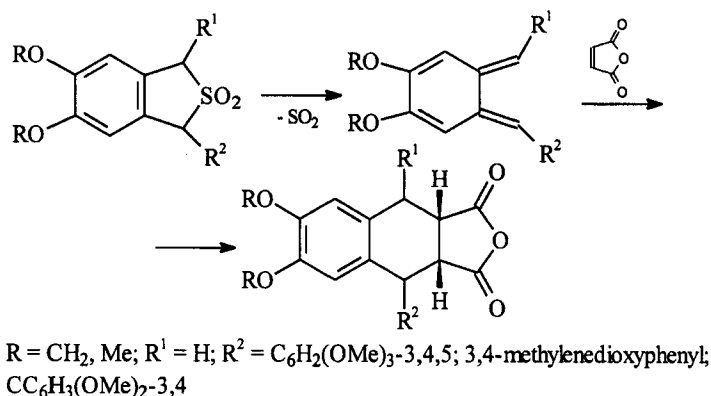
The flash vacuum pyrolysis of hexachlorobenzo[*b*]thiophene-1,1-dioxide (840°C, 0.01 mm Hg) leads to hexachlorophenylacetylene [199].



SCHEME 141

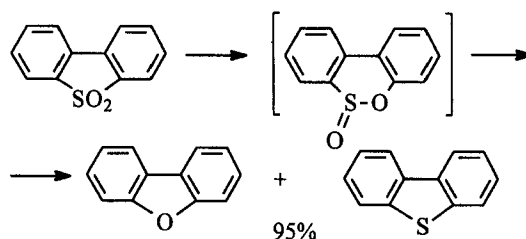
Quinodimethanes, obtained by thermal extrusion of  $\text{SO}_2$  from benzothiophene dioxides, reacted with dienophiles to give analogs of the aryltetralin and aryl-naphthalene lignans [200].





SCHEME 142

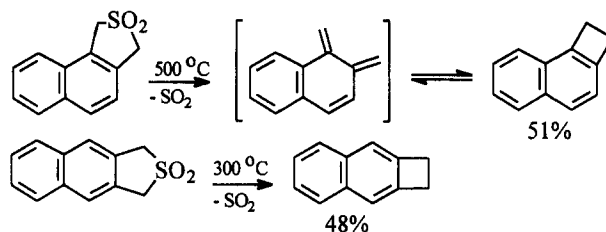
Gas-phase pyrolysis of dibenzothiophene-5,5-dioxide (650–1000°C) results in dibenzothiophene and dibenzofuran [188,201]. Dibenzo[*c,c*][1,2]oxathine-6-oxide is the intermediate product of the reaction. It is further transformed (690–900°C) into dibenzothiophene and dibenzofuran in a similar ratio [188,201–204].



SCHEME 143

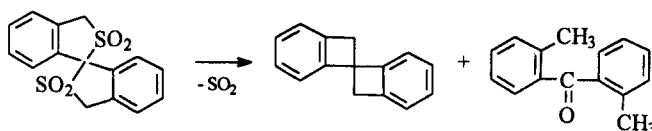
The pyrolysis of dibenzothiophene-5,5-dioxide in the glow discharge plasma (240°C/1 mm Hg) leads to diphenylene. Dibenzofuran, naphthalene and dibenzothiophene are the other products of the reaction [205].

The flash vacuum pyrolysis of naphthothiophene-dioxides involves the formation of the corresponding cyclobutene aromatic hydrocarbons [206,207].



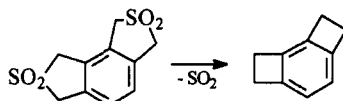
SCHEME 144

The flash vacuum pyrolysis of the corresponding spirodisulfone at 700°C (10 mm Hg) leads to 1,1'-spirodibenzocyclobutene and 2,2'-dimethylbenzophenone [208].



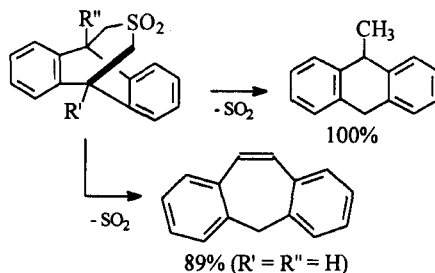
SCHEME 145

The pyrolysis of 1,3,6,8-tetrahydrothiophene[1,2-*c*-3,4-*c'*]benzene-2,2,7,7-tetroxide in vacuum proceeds at 280°C and leads to dicyclobutenebenzene [209].



SCHEME 146

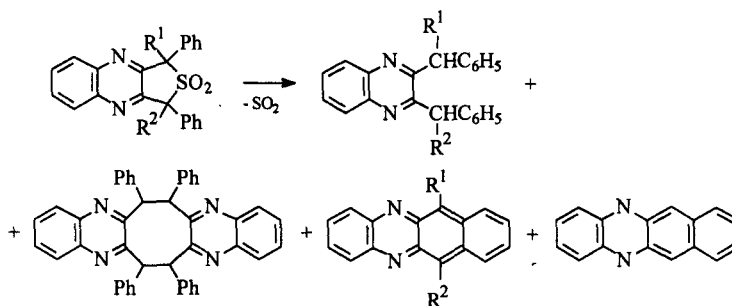
The pyrolysis of 9,10-dihydro-11-thia-9,10-ethanoanthracen-11,11-dioxide (or its substituted derivative) in vacuum at 300°C results in 9-methyldihydroanthracene. The pyrolysis of the same compound at 500°C involves the formation of 5H-dibenzo[*a,d*]cycloheptene [210].



$R' = \text{Me}, R'' = \text{H}; R' = R'' = \text{Me}$

SCHEME 147

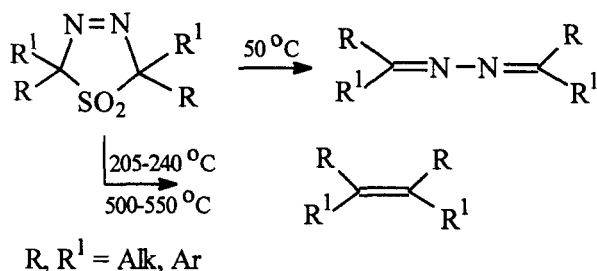
The pyrolysis of the mixture of *cis*- and *trans*-1,3-diphenyl-1,3-dihydrothieno[3,4-*b*]quinoxaline-2,2-dioxide (180–550°C) leads to 2,3-dibenzylquinoxaline and some of its derivatives [211].



$R^1 = R^2 = \text{H, Alk, Ph}$

SCHEME 148

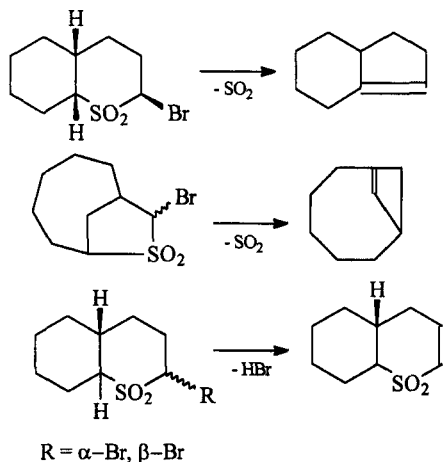
Substituted 2,5-dihydro-1,3,4-thiadiazole-1,1-dioxide eliminates  $\text{SO}_2$  at  $50^\circ\text{C}$ . The reaction also involves the formation of the corresponding ketazine derivatives [212,213]. Rapid heating up to  $205\text{--}240^\circ\text{C}$  as well as gas-phase pyrolysis of the substituted 2,5-dihydro-1,3,4-thiadiazole-1,1-dioxide at  $500\text{--}550^\circ\text{C}$  leads to ethylene derivatives [214,215].



SCHEME 149

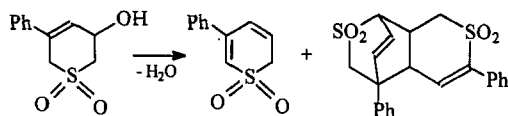
### 3.5.4. Six-membered Heterocycles

The intramolecular Ramberg–Becklund reaction (the 1,3-elimination of  $\text{HBr}$  followed by  $\text{SO}_2$  extrusion from  $\alpha$ -bromosulfones) was examined in the 1-thiadecalin system. A convenient method for the synthesis of strained bridgehead olefins was offered [216].



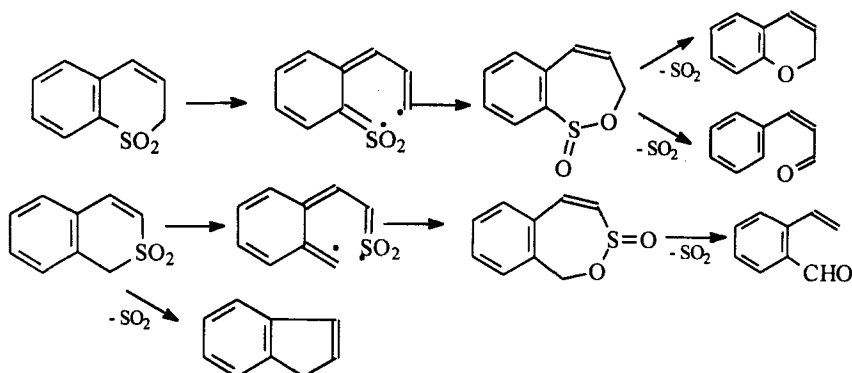
SCHEME 150

The thermolysis of 3-phenyl-5-oxy-2H-thiopyrane-1,1-dioxide does not involve extrusion of  $\text{SO}_2$  and leads to 5-phenyl-2H-thiopyrane-1,1-dioxide and its dimer [217].



SCHEME 151

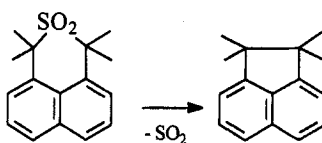
The flash vacuum pyrolysis of 2H-1-benzothiopyrane-2,2-dioxide at 650–775°C leads to cinnamyl aldehyde and 2H-1-benzopyrane. The pyrolysis of 1H-2-benzothiopyrane-2,2-dioxide under analogous conditions results in *ortho*-vinylbenzaldehyde and indene [218].



SCHEME 152

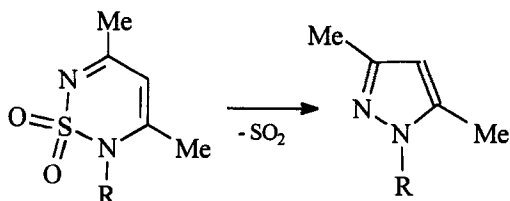
The breaking of the S–O ring bond as well as SO group cleavage leads to the formation of a biradical which is either closed into a pyrane ring, or is isomerized. Indene is the product of SO<sub>2</sub> extrusion from the initial 1H-2-benzothiopyrane-2,2-dioxide.

The heating of 1,1,3,3-tetramethylnaphtho[1,8-*c,d*]-thiopyrane-2,2-dioxide under an argon atmosphere at its boiling (~400°C) involves the elimination of SO<sub>2</sub> and the formation of 1,1,2,2-tetramethylacenaphthene [219].



SCHEME 153

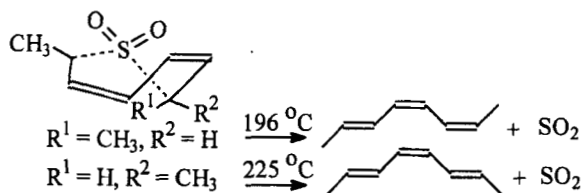
A novel synthesis of the pyrazole ring involving SO<sub>2</sub> extrusion by flow vacuum pyrolysis of a 1,2,6-thiadiazine 1,1-dioxide has been described. The reaction has potential industrial significance for routes to pyrazoles or functionalized pyrazoles that do not involve hydrazines [220].



SCHEME 154

### 3.5.5. Seven-membered Heterocycles

The ring of 2,7-dimethyl-2,7-dihydrothiepine-1,1-dioxide is opened under heating. The reaction involves the elimination of  $\text{SO}_2$  and formation of 2,4,6-octatriene [221].



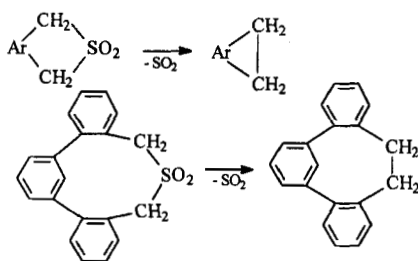
SCHEME 155

### 3.5.6. Macrocyclic Sulfide Dioxides

The method for the synthesis of macrocyclic hydrocarbons based on  $\text{SO}_2$  elimination from cyclic mono-, bis- and tris-sulfones during their vacuum pyrolysis has found wide application. The pyrolysis of sulfones as a synthetic method for the simple one-stage preparation of various cyclophane systems has been fully considered in articles and reviews [222–224]. The literature on the technology of impulse vacuum pyrolysis has also been summarized.

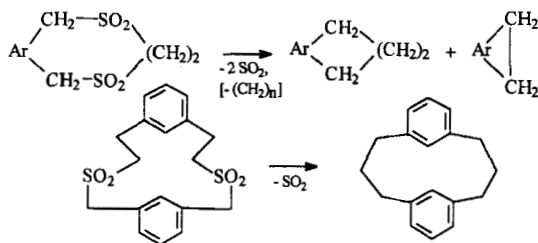
Three routes of the pyrolysis of cyclic sulfones have been shown [222].

1. The pyrolysis of double benzyl sulfones is shown below [225–251].



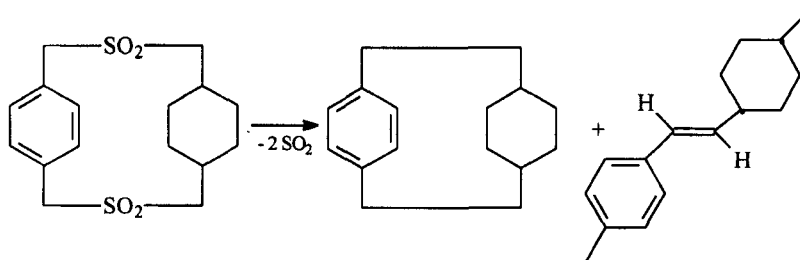
SCHEME 156

2. The pyrolysis of semi-benzyl sulfones is shown below [225,252–264].



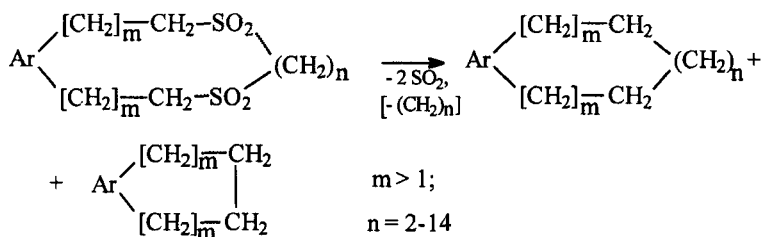
SCHEME 157

Extrusion of  $\text{SO}_2$  (400–500°C) from 2,11-dithia-4,5,6,7,8,9-hexahydro[3,3]paracyclophane 2,2,11,11-tetraoxide gave hexahydro[2,2]paracyclophane. It is the first cyclophane to contain both a benzene ring and a cyclohexane ring [265].



SCHEME 158

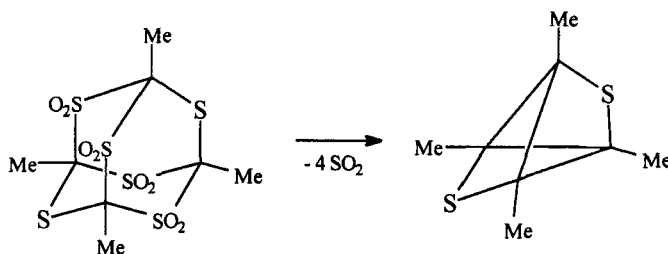
3. The pyrolysis of non-benzyl sulfones is shown below [222,263,266].



SCHEME 159

In the last two cases the elimination of  $\text{SO}_2$  can be accompanied by the elimination of a part of the hydrocarbon chain.

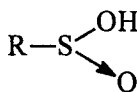
Thermal decomposition of the tricyclic tetrasulfone, derived from tetramethylhexathiaadamantane occurs in three distinct and increasingly significant steps centered at 175 (~12% weight loss), 260 (~20% weight loss) and 305°C (~58% weight loss). Gas phase FT-IR detection of the evolved gases revealed  $\text{SO}_2$  liberation during the latter two weight loss steps [267].



SCHEME 160

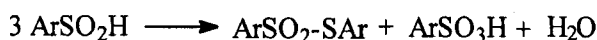
#### 4. SULFINIC ACIDS AND THEIR ESTERS

Sulfinic acids are easily formed during the reduction of sulfonyl chlorides. Usually the acids have the following structure:



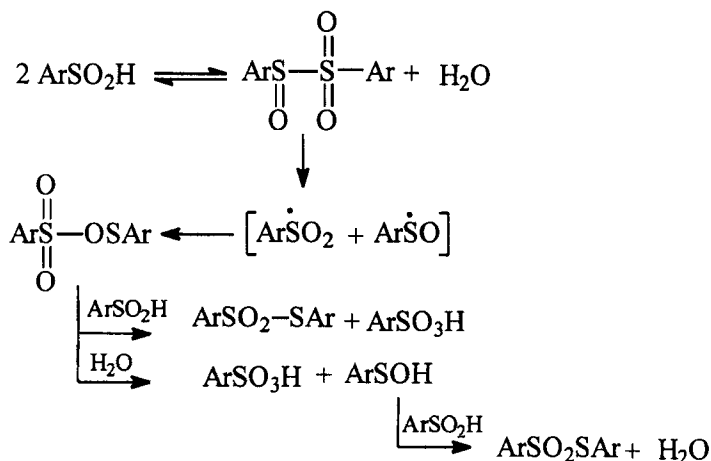
SCHEME 161

Sulfinic acids are very unstable and undergo disproportionation and decomposition easily. Aromatic sulfinic acids are more stable than aliphatic ones. Their disproportionation proceeds at 25–110°C and involves the formation of thiosulfonates and sulfonic acids [268].



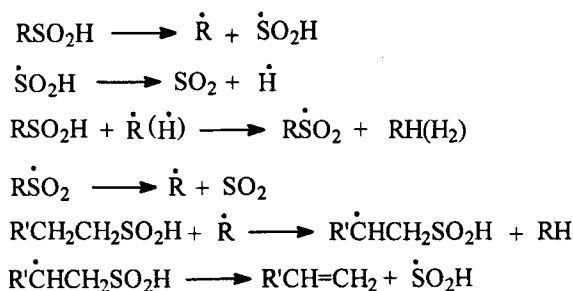
SCHEME 162

Electron-donor substituents in the aromatic ring accelerate the reaction rate while electron-acceptor substituents inhibit the reaction [269]. The first rapid stage of the reaction leads to the formation of a sulfinyl sulfone, which is slowly isomerized into a sulfonylsulfonate. The latter reacts with the initial sulfinic acid to give thiosulfonate and sulfonic acid [270–272].



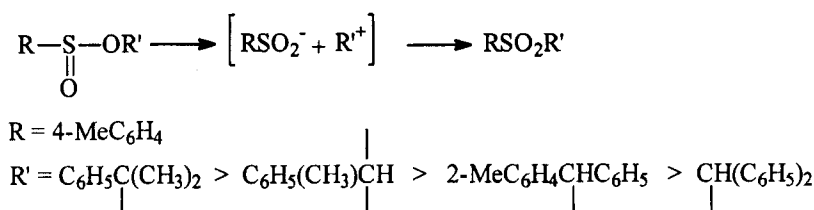
SCHEME 163

Sulfinic acids are decomposed in vacuum at 275°C to give SO<sub>2</sub>, olefins, saturated hydrocarbons and hydrogen [273]. According to the scheme the reactions mechanism involves free radicals.



SCHEME 164

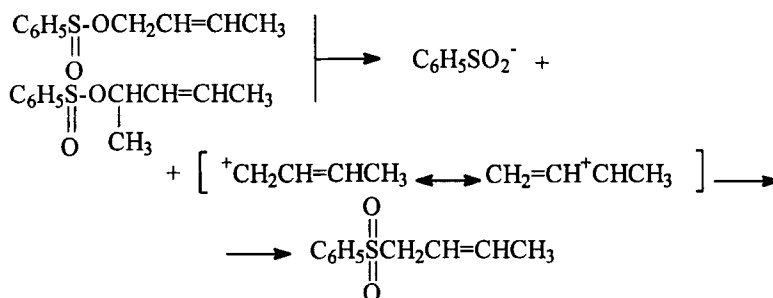
Some esters of sulfinic acids are isomerized upon heating into their corresponding sulfones [274,275].



SCHEME 165

The rearrangement is performed due to the presence of methyl or phenyl substituent in  $\alpha$ -carbon atom of the sulfinate molecule. The reaction is accelerated if  $R$  and  $R'$  are the electron-donors and the reaction medium is polar [276]. The isomerization of sulfonates into sulfones proceeds through the intermediate generation of carbonium ions [275,276,230,231].

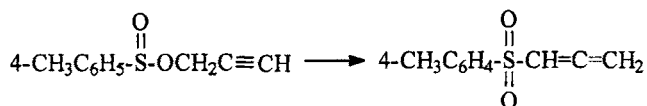
Crotyl- and  $\alpha$ -methylallylphenylsulfinate are isomerized only to crotyl phenyl sulfone [274].



SCHEME 166

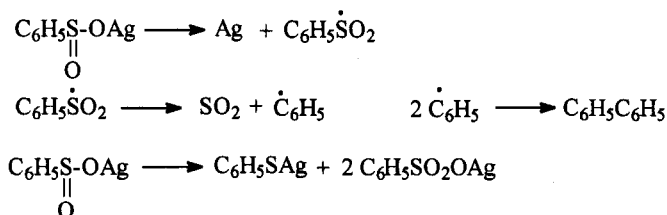
The boiling of a sulfinate having a  $\beta$ -acetylenic group in chlorobenzene solution leads to the sulfone of an allenyl sulfone [277].





SCHEME 167

The pyrolysis (250–350°C) of silver arylsulfonates involves two parallel reactions, first cleavage of the O–Ag bond and then disproportionation [278].

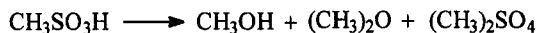


SCHEME 168

The first reaction leads to di- and terphenyl while the second results in diaryl sulfides, diaryl sulfones, etc. The addition of a chlorine atom to the *ortho*-position of the aromatic ring promotes the cleavage of SO<sub>2</sub> from the ArSO<sub>2</sub> radical.

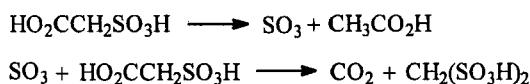
## 5. SULFONIC ACIDS AND THEIR ESTERS

The pyrolysis of many sulfonic acids has been investigated only in the last century. Methanesulfonic acid is decomposed on heating at a temperature above 130°C. The distillation of methanesulfonic acid in vacuum (10 mm) at 167°C involves no decomposition. The destruction of this acid in the gas phase at 225–500°C in the presence of metals (Al, Bi, Hg) leads to methanol, dimethyl ether and dimethylsulfate [279].



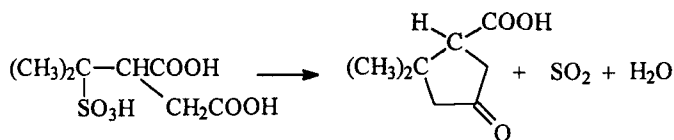
SCHEME 169

Sulfoacetic acid undergoes disproportionation upon heating to 190–210°C to give SO<sub>3</sub> and CO<sub>2</sub> [280,281].



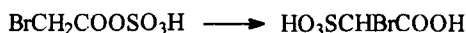
SCHEME 170

Sulfoisopropyl-succinic acid at 160–170°C is transformed into terebinic acid [282].



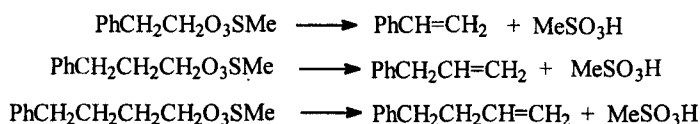
SCHEME 171

The heating of bromoacetylsulfuric acid leads to bromosulfoacetic acid [283].



SCHEME 172

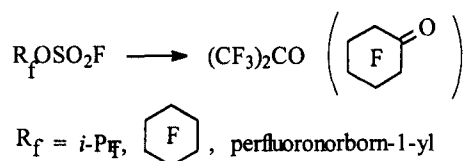
The pyrolysis of  $\omega$ -phenylalkylmethanesulfonates proceeds at 280–340°C via elimination of methanesulfonic acid [284].



SCHEME 173

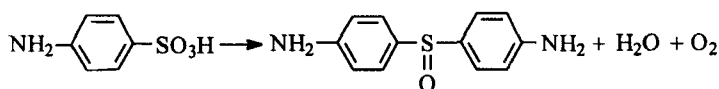
Perfluorosulfonic acids  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{C}_2\text{F}_5\text{SO}_3\text{H}$  and their anhydrides are thermally stable up to a temperature of 180°C. In solutions these acids or their anhydrides form perfluorosulfonic esters at room temperature [285].

2H-Heptafluoropropylfluorosulfates in the presence of cesium fluoride are transformed into perfluoro ketones (125°C) [286].



SCHEME 174

The distillation of arylsulfonic acid leads to the corresponding hydrocarbons and sulfones. The heating of 4-sulfanylic acid results in 4,4'-diaminodiphenyl sulfoxide [287].



SCHEME 175

Benzosulfonates of alkaline metals in an inert atmosphere or in air at 510–570°C are transformed into phenol, thiophenol, diphenyl sulfide, thiantrene, diphenyl ether, SO<sub>2</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S, C<sub>2</sub>H<sub>4</sub> and water [288].

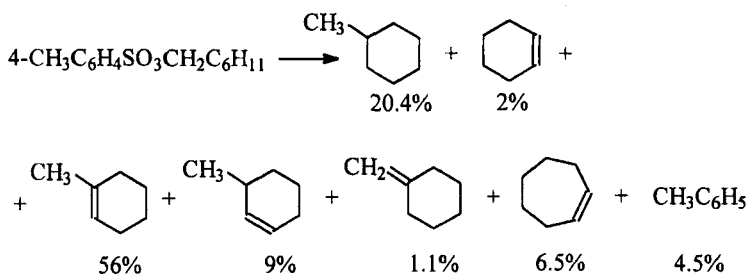
Aromatic sulfonic acids alkyl esters are decomposed on heating to give arylsulfonic acids and alkenes [289,290].



SCHEME 176

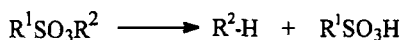
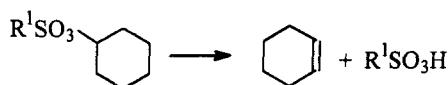
The pyrolysis of benzyl benzenesulfonate at 125°C involves the formation of benzenesulfonic acid and a polymer of phenylmethylene. The heating of phenyl( $\beta$ -chloroethyl) sulfate leads to the elimination of both vinyl chloride and benzenesulfonic acid [289].

The pyrolysis of cyclohexylmethyl 4-toluenesulfonate is accompanied by the formation of methylcyclohexane, cyclohexene, 1-methylcyclohexene, 3-methylcyclohexene, methylenecyclohexane, cycloheptene and toluene [291,292].



SCHEME 177

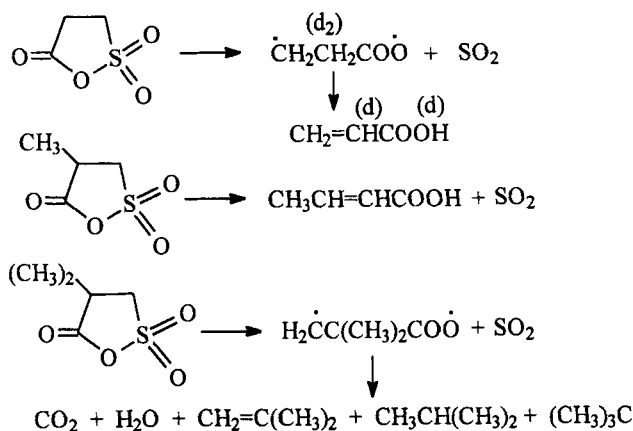
The thermolysis (90–150°C) of 2-pyridinesulfonic acid cyclohexyl ester leads to cyclohexene. Other sulfonates are decomposed analogously [293].



R<sup>1</sup> = 8-quinolyl, 2-pyridyl; R<sup>2</sup> = cyclohexyl;  
 R<sup>1</sup> = *trans*-4-*t*-butylcyclohexyl,  
 R<sup>2</sup> = *exo*-norbornyl, 1-methyl, d,l-neomentyl, oct-2-yl,  
*trans*-4-butylcyclohexyl and other

SCHEME 178

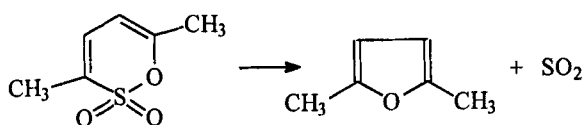
Thermal decomposition of  $\beta$ -sulfopropionic acid cyclic anhydride at 180°C involves the formation of acrylic acid [294].



SCHEME 179

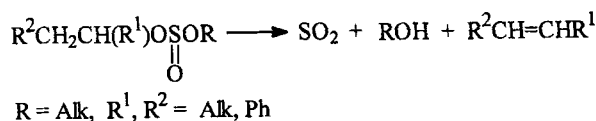
The  $\alpha$ -hydrogen atom is shifted to the carbonyl group of the intermediate radical. Analogously  $\beta$ -sulfoisobutyric acid cyclic anhydride is transformed into methacrylic acid at 220°C. If the cyclic anhydride does not contain an  $\alpha$ -hydrogen atom the thermolysis of the anhydride proceeds in another way. For example, the decomposition of  $\beta$ -sulfotrimethylenesulfonic acid at 230°C leads to a complex mixture of the products. The intermediate biradical either loses  $\text{CO}_2$  to give hydrocarbon mixtures or adds two hydrogen atoms to give trimethylacetic acid [295].

The thermolysis of  $\delta$ -sulfones containing double bonds at 230–250°C leads to furan derivatives [296,297].



SCHEME 180

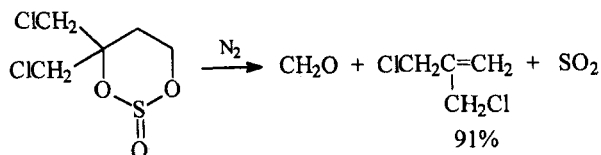
The main products from thermolysis at 150–350°C of sulfites are the corresponding alcohol and olefin [298–300].



SCHEME 181

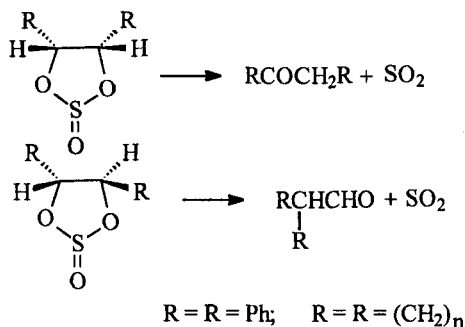
Olefins are formed from methyl-*S*-alkylsulfites (90% yield) as well as from methyl-primary alkylsulfites (in lower yield).

Gas-phase pyrolysis of the cyclic sulfite, 2-oxo-5,5-bis(chloromethyl)-1,3,2-dioxathiane at 500°C results in formaldehyde, sulfur dioxide and 3-chloro-2-chloromethyl-1-propene [300].



SCHEME 182

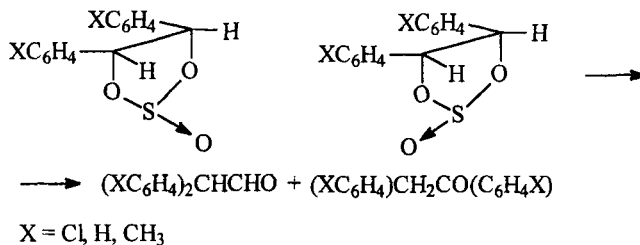
The pyrolysis (240–350°C) of the *cis*-isomer of the cyclic sulfite of hydrobenzoin leads to desoxybenzoin. The pyrolysis of the *trans*-isomer results in diphenylacetaldehyde. Analogously, cyclohexanone is the product of the pyrolysis of the *cis*-isomer of the cyclic sulfite of cyclohexanediol. Cyclopentanealdehyde is the product of the pyrolysis of the corresponding *trans*-isomer [300].



SCHEME 183

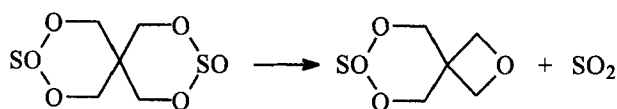
This effect can be explained by the differences of the intermediate zwitterions, which are formed due to the cleavage of the C–O bond in the sulfites. In the second case the migration of a  $\beta$ -proton through a quasi-six-membered cycle is preferable.

The pyrolysis of *S*-epimeric cyclic sulfites leads to a mixture of the corresponding aldehydes and ketones [301,302]. The difference in ratio of ketone to aldehyde between the *cis* and *trans*-sulfite starting material has been explained by the possibility of  $\alpha$ -proton capture by the oxygen atom of the sulfite group in a *cis*-position. This leads to the formation of ketone according to an enol mechanism.



SCHEME 184

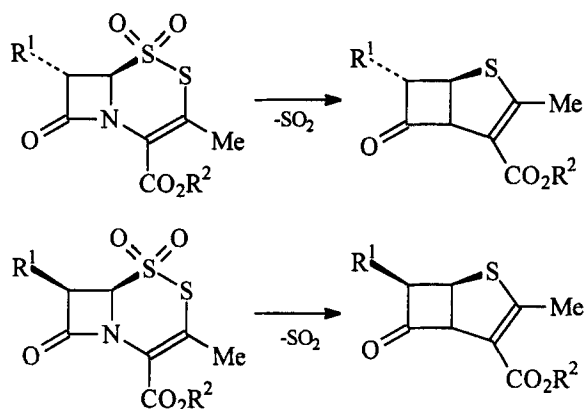
The pyrolysis of pentaerithrol cyclic disulfite at 260–270°C involves the elimination of sulfur dioxide and closing of one cycle [303].



SCHEME 185

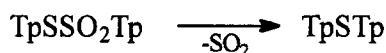
2,2-Dimethylpropanediol sulfite is stable at 500°C. The pyrolysis of propanediol-1,3-sulfite at 300°C leads to a polymer of formaldehyde.

Stereospecific extrusion of SO<sub>2</sub> occurred from cyclic thiosulfonates upon storage or mild heating; (5*R*)-penems were obtained even in cases where the biologically inactive 5*S* epimers had been anticipated as a consequence of the *trans*-directing effect of the C7 substituent [304].



SCHEME 186

*Bis*(9-trypticyl) sulfides were prepared by pyrolytic extrusion of SO<sub>2</sub> (250–300°C) from the corresponding thiosulfonates [305].



a: Tp = 9-trypticyl;

b: Tp = 2-chloro-9-trypticyl

SCHEME 187

## 6. CONCLUSION

It is hoped that this review of the thermal reactions of the compounds of tetra- and hexavalent sulfur will be of great interest to chemists who are developing new methods for the synthesis of organic compounds. Besides, the review may be useful for the technologists, and the manufacturers of monomers and polymers.

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