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Sulfides in organic synthesis. Applications of sulfides

I V Koval'

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Abstract. The results of studies on the use of sulfides as synthons in organic synthesis are treated systematically and surveyed. The practical applications of sulfides are examined. The bibliography includes 187 references.

I. Introduction

The application of sulfides as synthons in fine organic synthesis is based on the characteristics of their reactivity manifested in the polarisation and low strength of the C–S bond, as a result of which it is relatively easily cleaved by both nucleophiles and electrophiles. The high lability of this bond makes it possible to eliminate, when required, the sulfide functional group, which thus fulfills its purpose. The use of sulfides for the protection of various functional groups and also as synthons for alkyl halides, acid chlorides, etc. is based on this fact. For example, methyl methylthiomethyl sulfide is a synthon for the non-existent formyl nucleophile,[1] because the conversion of RX into RCHO can be achieved with its aid.

$$(MeS)_2CH_2 \xrightarrow{BuLi} (MeS)_2CHLi \xrightarrow{RX} (MeS)_2CHR \xrightarrow{HgCl_2(H_2O)} RCHO$$

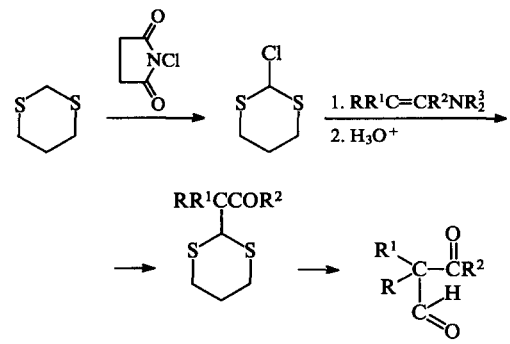
Bearing in mind the final results of the use of 2-chloro-1,3-dithiane in the synthesis (Scheme 1), it can be regarded as a synthon for the formyl cation.[2]

It is noteworthy that the strength of the C–S bond in sulfides is greatly influenced by the presence in the α-position of other heteroatoms (Cl, Br, N, O) and functional groups (C=O, C=C, C≡C, OH, SR, SO_2R, etc.). Therefore the introduction of heteroatoms and groups in the α-position relative to the sulfur atom makes it possible to regulate the lability of the C–S bond in sulfides.

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Scheme 1



Yet another feature of sulfides used in organic synthesis is the high susceptibility of the sulfur atom to attack by nucleophiles with formation of relatively stable and at the same time highly reactive intermediates (sulfonium salts, ylides, carbenes, etc.) participating in the transfer of alkylidene and other groups and also in a wide variety of rearrangements with formation of various products.

The ability of the sulfur atom in sulfides to pass fairly readily from one valence state to another and also to stabilise the α-carbanionic centre is frequently used in organic synthesis, for example, for the formation of saturated and unsaturated carbon–carbon bonds.

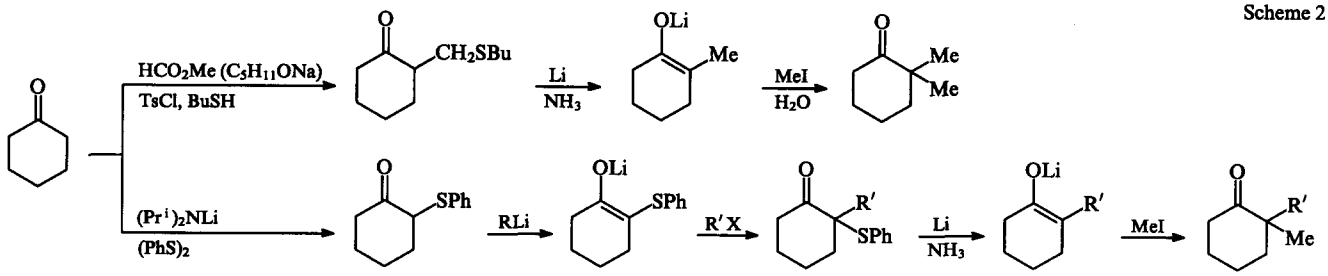
The primary products of the reactions of sulfides such as sulfoxides, sulfonium salts, sulfur ylides, sulfilimines, etc. have found extensive application in organic synthesis. Therefore a whole series of syntheses based on sulfides involve the conversion of the sulfide group into these products with subsequent transformation of the latter without their isolation from the reaction mixture.

Apart from fine organic synthesis, sulfides are widely used in agriculture, in the industrial manufacture of polymers, in the pharmaceutical industry, and in other fields of human activity. This is also reflected in the present review.

II. Cleavage of the C–S bond

The application of sulfides in organic synthesis, based on the cleavage of the C–S bond, has been known for a relatively long time.[1] For example, chlorolysis of the C–S bond in sulfides serves as a basis of a series of preparative methods of synthesis of sulfenyl chlorides. The reductive cleavage of the C–S bond is

Scheme 2

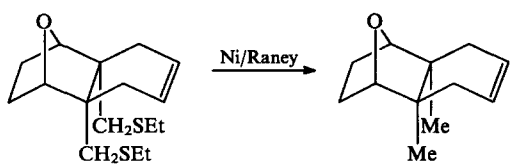


used in the synthesis of certain thiols and, in particular, toluenethiol and 2-propene-1-thiol. The thermal disproportionation of dialkyl sulfides and carboxylic acid esters is a useful alternative esterification procedure. By virtue of the high lability of the C–S bond, benzyl methyl sulfide $PhCH_2SMe$ is used as a source of the benzylcarbonium ion $PhCH_2^+$, the interaction of which with activated arenes in the presence of $ZnCl_2$ or $CuCl_2$ results in the formation of *ortho*- and *para*-substituted derivatives. The use of sulfides for the interconversion of functional groups in complex multistage organic syntheses began to be used only in the last 10–15 years, which can be explained by the lack of effective methods for the generation and removal of the sulfide functional group. Some of these reactions can be achieved also by other procedures, but the reactions using sulfides are as a rule distinguished by a higher selectivity.[1] A series of effective methods based on the use of thiols,[1,3] sulfenyl chlorides,[4–10] α-chlorosulfides,[1,11–13] unsaturated sulfides,[14,15] α-chlorocarbonyl sulfides,[16] α-chloroimide sulfides,[17] and organometallic compounds[18] have been developed in recent years for the introduction of the sulfide functional group into the molecules of organic substances. Depending on the nature of the reaction, a whole series of chemical, electrochemical, thermal, photolytic, and other methods have been developed for the removal or transformation of the sulfide functional group.

1. Hydrogenolysis of the C–S bond

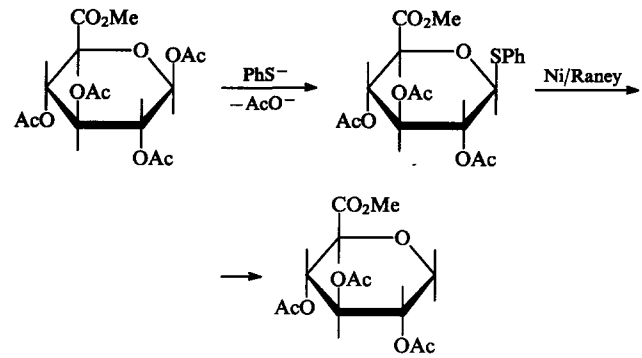
The hydrogenolysis and reductive cleavage of the C–S bond take place in the presence of reagents such as lithium in ethylamine, sodium in liquid ammonia, lithium tetrahydroaluminate, Raney nickel in boiling ethanol, and sodium tetrahydroborate in isopropyl alcohol. The electrochemical reductive cleavage of the C–S bond has come to be used increasingly in recent years.[1]

One of the first examples which demonstrated the advantage of the generation of the sulfide functional group with its subsequent removal by reductive cleavage has been Stork's synthesis of cantharidin, in the last stages of which the reductive cleavage of the C–S bond with the aid of Raney nickel was used to convert the ethylthiomethyl group into the methyl group.

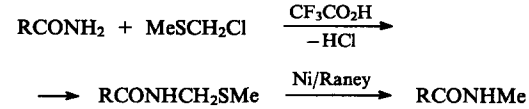


The replacement of the acetoxy-group by the phenylthio-group with subsequent reductive cleavage of the C–S bond is used for the selective elimination of the acetoxy-group and the conversion of a D-glucuronic acid derivative into the deoxy-analogue.[19]

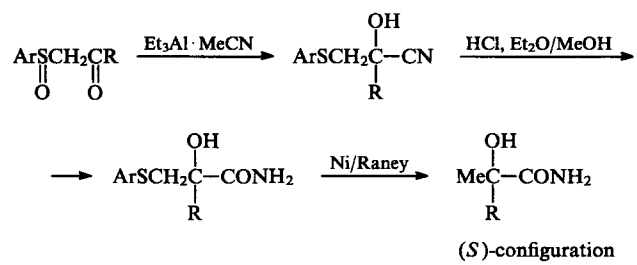
The introduction of the sulfide functional group with subsequent hydrogenolysis of the C–S bond (Scheme 2) has found extensive applications for the synthesis of alkyl-substituted cyclic ketones.[1]



The application of chloromethyl methyl sulfide in the synthesis of *N*-methyl-substituted carboxylic acid amides has been described.[20] The reductive cleavage of the C–S bond is used to eliminate the methylthio-group in the last stage of this synthesis.



The hydrogenolysis of the C–S bond has been used increasingly in recent years in stereospecific syntheses.[21–23] For example, the asymmetric synthesis of α-hydroxyacid amides from chiral β-oxosulfoxides[23] includes stages involving the reduction of the sulfoxide group to the sulfide group and the hydrogenolysis of the C–S bond with the aid of Raney nickel.



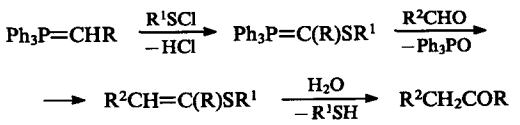
(*S*)-configuration

2. Hydrolysis of the C–S bond

Aqueous solutions of mercury acetate and inorganic acids, hydrogen chloride and bromide in acetic acid, divalent mercury salts in an acid medium, etc. are used for the hydrolytic cleavage of the C–S bond.[1]

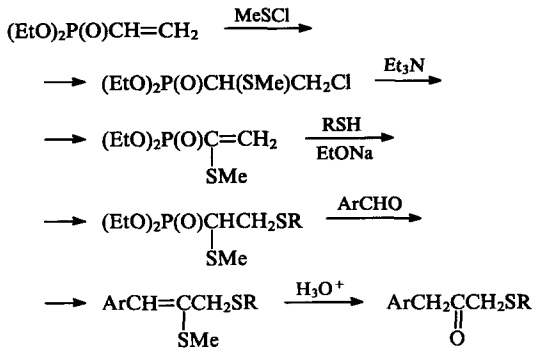
In contrast to unsaturated sulfides, the hydrolysis of which proceeds under severe conditions, unsaturated sulfides are relatively easily hydrolysed with formation of unsaturated alcohols which rearrange to carbonyl compounds. This is frequently used to synthesise aldehydes and ketones. For example,

the conversion of phosphorus ylides into ketones[24,25] includes stages where the sulfide functional group is introduced and the C–S bond is subjected to hydrolytic cleavage.

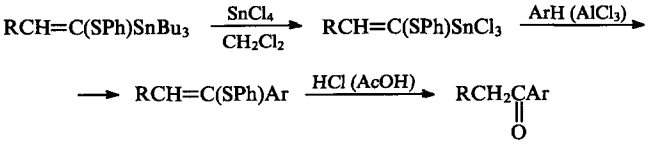


R = H, Me, COOEt, CN, COPh, 2-$NO_2C_6H_4$;
$R^1 = R^2$ = Alk, Ar.

A similar synthetic procedure has been used in the preparative synthesis of α-alkylthioketones.[26]

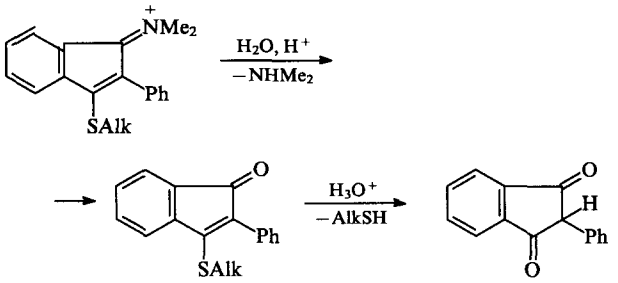


A new method of synthesis of ketones from organotin compounds[27] also includes a stage involving the hydrolytic cleavage of the C–S bond.

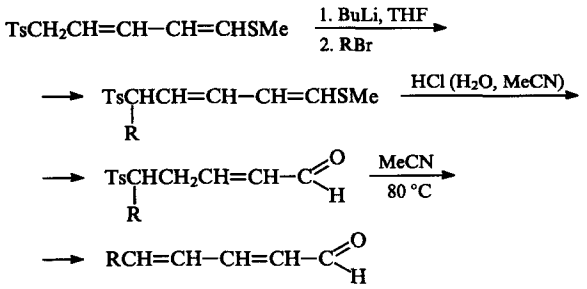


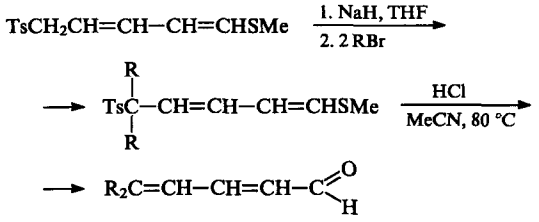
R = Pr, Pr^i, Bu^i; Ar = Ph, *p*-MeC_6H_4.

In the synthesis of cyclic 1,3-diketones from 3-alkylthio-2-phenyl-1-indenyl-*N,N*-dimethyliminium salts,[28] one of the keto-groups is formed as a result of the hydrolytic cleavage of the C–S bond.

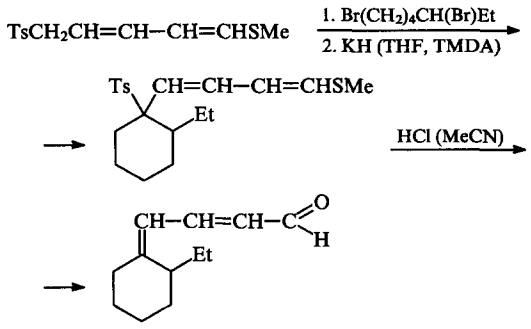


A new method of synthesis of conjugated dienals, consisting of the stepwise introduction of the aldehyde group as a result of hydrolytic cleavage of the C–S bond and the introduction of a double bond as a result of the elimination of the tosyl group, has been described.[29]





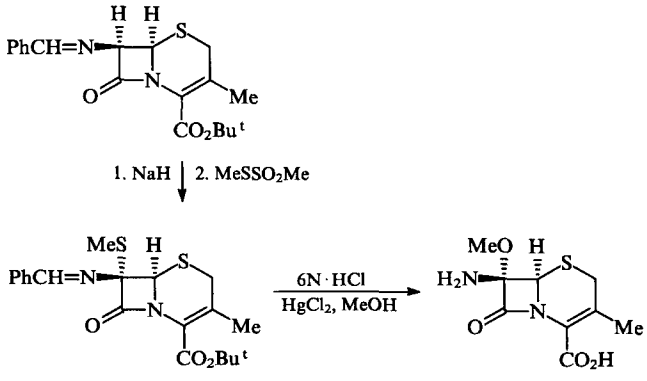
R = $PhCH_2$.



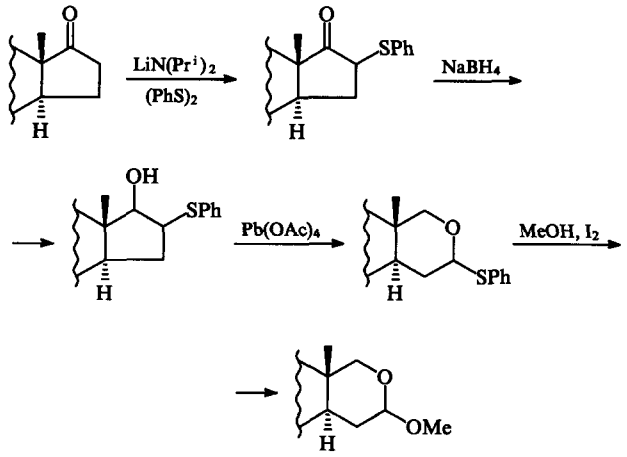
TMDA = tetramethylenediamine.

3. Alcoholysis of the C–S bond

The reaction involving the substitution of the sulfide group by an alkoxy group is used in rare instances, which is evidently due to the lack of effective methods for carrying out this process. As a rule, the alcoholysis of the C–S bond proceeds on treatment with alcohols in the presence of mercury dichloride, iodine, and other inorganic reagents. For example, methanol in the presence of mercury dichloride is used to substitute the methylthio-group by the methoxy-group in the synthesis of a derivative of cephalosporin.[1]

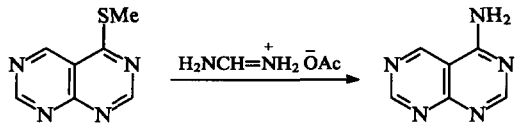


In the synthesis of acetals from cyclic ketones,[30] methanol in the presence of iodine is used to substitute the phenylthio-group by the methoxy-group.

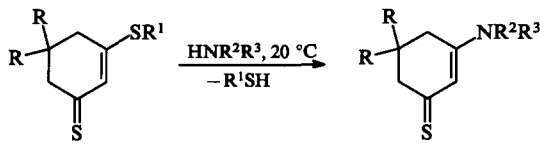


4. Aminolysis of the C–S bond

The replacement of an alkylthio-group with a saturated carbon atom by the amino-group or a substituted amino-group takes place when sulfides are treated with ammonia, amines, amidines, and other nitrogen-containing compounds. For example, azaheterocyclic sulfides undergo aminolysis fairly readily on treatment with formamidine [formamidinium? (Translator)] acetate—a process which is used in subsequent reactions of these heterocyclic compounds. [1]

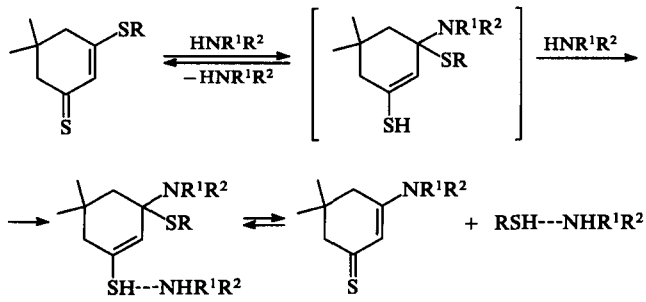


As a synthetic procedure, the aminolysis of the C–S bond has been used in recent years to modify groups such as $RSC=CR^1-CR^2=S$ and $RSC=CH-CH=NR^1$ in thiones and enamines. It has been noted, [31] for example, that 3-alkylthiocyclohex-2-ene-1-thiones react readily with ammonia and primary and secondary amines at 20 °C in benzene, chloroform, and alcohols, and dimethylformamide (DMF), affording 3-aminocyclohex-2-ene-1-thiones:

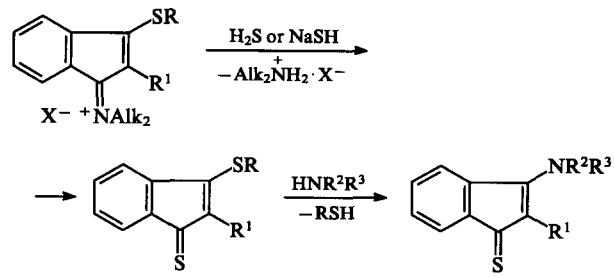


R = Me; R^1 = Me, Et; R^2 = Me; R^3 = Alk.

Detailed study of this reaction showed [32] that the aminolysis proceeds via a stage involving the formation of a stable intermediate in mobile equilibrium with the final product and that the aminolysis process itself can be described as 1,4-addition–elimination.

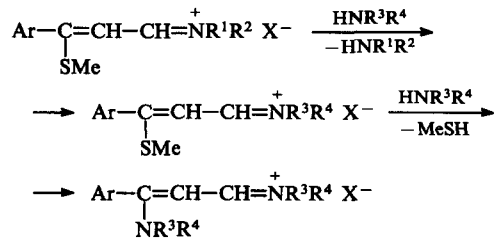


N,N-Disubstituted indenyliminium salts are converted into 3-amino-2-arylindene-1-thiones via a stage in which the intermediate 3-alkylthio-2-arylindene-1-thiones are subjected to aminolysis. [32]



R = Me, Et; R^1 = Ph; R^2 = Ph, Me; R^3 = Me; X = BF_4, I.

It has been noted [33] that, in the reaction of 3-alkylthiopropenyliminium salts with alkyl- and aryl-amines, transamination is accompanied by the aminolysis of the C–S bond, which results in the formation of salts of enaminoimines containing identical substituents at the nitrogen atom.

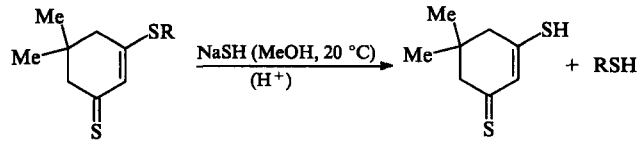


Ar = Ph, 4-$MeOC_6H_4$;
R^1 = R^2 = Alk; R^3 = Alk, H; R^4 = Alk, Ar;
X = ClO_4, I.

The exchange of the alkylthio-group for the amino-group proceeds in an acid medium. In the case of X = ClO_4, the yield of the final product is 80%, while for X = I it is only 38%.

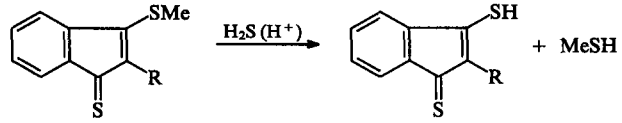
5. Hydrothiolysis of the C–S bond

The replacement of the alkylthio-group by the mercapto-group at an unsaturated carbon atom takes place in the reaction of unsaturated sulfides with sodium hydrogen sulfide in methanol, which is used in the synthesis of 5,5-dialkyl-3-mercaptocyclohex-2-ene-1-thiones. [34]



R = Me, Et.

A similar replacement occurs in the reaction of unsaturated sulfides with hydrogen sulfide in an acid medium. This property is used in the synthesis of 3-mercaptoindene-1-thiones. [32,36]

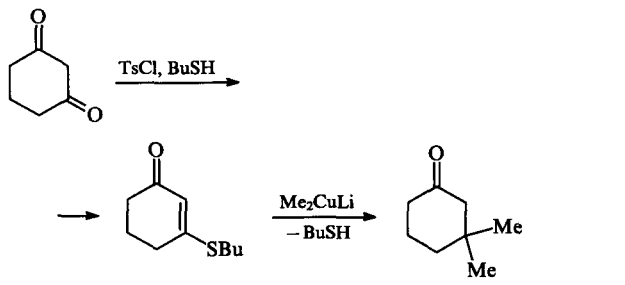


R = H, Et, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4.

6. Cleavage of the C–S bond by organometallic compounds

When sulfides are acted upon by organometallic compounds, the sulfide group may be replaced by an alkyl group. The presence in the α-position in sulfides of groups such as C=O, C=C, C≡C, etc. promotes this reaction. For example, ketones are formed in high yields in the reactions of α-oxoalkyl sulfides with R_2CuLi; the formation of tertiary alcohols due to the competing attack on the carbonyl group is not observed under these conditions.[1,36] One of the stages of the synthesis of the pheromone of the German cockroach [3,11-dimethyl-2-nonacosanone (Translator)] involves the cleavage of the C–S bond by treat-ment with similar reagents.[37]

The replacement of the sulfide group by alkyl groups with the aid of organometallic compounds is used also in the synthesis of cyclic ketones[38,39] and acetylenes.[40]



$$MeSC{\equiv}C{-}C{\equiv}CEt + PrLi \xrightarrow[-MeSLi]{} PrC{\equiv}C{-}C{\equiv}CEt$$

7. Desulfurisation of sulfides

Sulfides containing other heteroatoms and functional groups in the α-position tend as a rule to undergo sulfur displacement reactions. The desulfurisation of such sulfides proceeds in the presence of alkali metal hydrides or trivalent phosphorus compounds. Thiirans are then formed at an intermediate stage.[1]

$$ArCH_2SCH(Cl)Ar \xrightarrow{Ph_3P,\ Bu^tOK} \left[\begin{array}{c} ArCH-CHAr \\ \quad\ \backslash / \\ \quad\ S \end{array}\right] \xrightarrow[-H_2S]{} ArCH{=}CHAr$$

The desulfurisation of sulfides is used as a synthetic procedure in the synthesis of sterically hindered alkenes[41] and also in the synthesis of corrins in order to form a C=C bond.[1]

$$RN{=}CR^1SCH_2COAr \xrightarrow{(EtO)_3P} RNHC(R^1){=}CHCOAr$$

8. Thermolysis of the C–S bond

The cleavage of the C–S bond in sulfides at high temperatures leads to the formation of thiyl and alkyl (or aryl) radicals.[42–45] The radicals undergo further reactions under the thermolysis conditions with formation of the final products, the composition of which is determined both by the structure of the initial sulfide and by the thermolysis conditions. For example, the thermolysis of diethyl sulfide results in the formation in the gas phase of a mixture, the main components of which are hydrogen sulfide and ethylene.[42,45]

$$(C_2H_5)_2S \xrightarrow{\Delta} C_2H_5\dot{S} + \dot{C}_2H_5 \longrightarrow C_2H_5SH + CH_2{=}CH_2$$

$$C_2H_5SH \longrightarrow C_2\dot{H}_5 + S\dot{H}$$

$$C_2H_5SH + \dot{S}H \longrightarrow Me\dot{C}HSH + H_2S$$

$$C_2H_5SH + \dot{C}_2H_5 \longrightarrow Me\dot{C}HSH + C_2H_5H$$

The thermolysis of dimethyl sulfide at 600–650 °C leads to the formation of thiophene.[46,47]

$$Me_2S \xrightarrow[-H_2]{600-650\ ^\circ C} \left[\begin{array}{c} CH_2-CH_2 \\ \quad\ \backslash / \\ \quad\ S \end{array}\right] \longrightarrow \left[CH_2{=}CHSH\right] \longrightarrow \text{thiophene}$$

At 450–500 °C in the presence of phenylacetylene, the same sulfide gives rise to 3-phenylthiophene and benzo[*b*]thiophene.[48]

$$Me_2S \xrightarrow{450-500\ ^\circ C} \left[CH_2{=}CH\dot{S}\right] \xrightarrow{PhC{\equiv}CH} \left[\begin{array}{c} C{=}C\dot{H} \\ \quad\ | \\ \quad\ S \\ \quad\ | \\ H_2C{=}CH \end{array}\right] \xrightarrow[-[\dot{H}]]{-[CH_2{=}\dot{C}H]} \text{benzo[}b\text{]thiophene},\ \text{3-phenylthiophene}$$

The thermolysis of certain disulfides results in the formation of extremely rare and synthetically valuable intermediates. For example, the vacuum thermolysis of dipropargyl sulfide has been used as a selective path to the synthesis of the unstable thiopropynal.[49]

$$(CH{\equiv}CCH_2)_2S \xrightarrow[-MeC{\equiv}CH]{750-850\ ^\circ C,\ 10^{-3}\ Torr} \left[CH{\equiv}C{-}CH{=}S\right]$$

The flash thermolysis of diallyl sulfide and allyl benzyl sulfide leads to the formation of thioacrolein and thiobenzaldehyde respectively.[50–53]

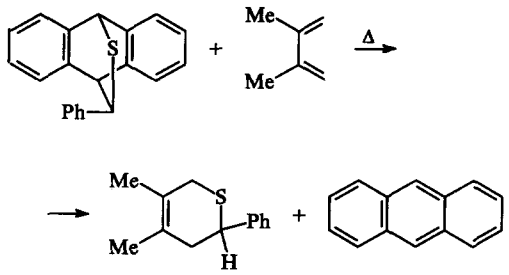
$$(H_2C{=}CH{-}CH_2)_2S \xrightarrow[-MeCH{=}CH_2]{550\ ^\circ C,\ 10-50\ Torr} \left[CH_2{=}CH{-}CH{=}S\right]$$

$$PhCH_2SCH_2CH{=}CH_2 \xrightarrow[-MeCH{=}CH_2]{500-600\ ^\circ C,\ 10-50\ Torr} \left[PhCH{=}S\right]$$

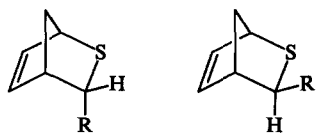
The thermolysis of these sulfides is usually carried out in the presence of dienes or anthracene, which serve as 'trapping agents' for the thioaldehyde formed. For example, anthracene reacts with thiobenzaldehyde to form an adduct which is itself a source of thiobenzaldehyde.[54,55]

$$\left[PhCH{=}S\right] + \text{anthracene} \longrightarrow \text{adduct}$$

When this adduct is heated with 2,3-dimethylbutadiene in a sealed tube, the corresponding 2*H*-dihydrothiane and anthracene are formed.

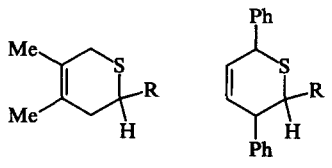


The α-sulfonyldisulfides $RCH_2SSCH(Ts)R$ (R = EtOCO) are excellent substrates for the synthesis of alkoxycarbonylthioformaldehydes.[56] The interaction of these disulfides with triethylamine in the presence of cyclopentadiene affords a mixture of *endo*- and *exo*-adducts, which are extremely valuable for preparative purposes.



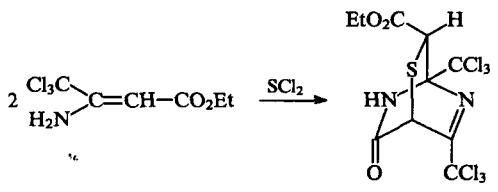
R = EtOCO.

Ethoxycarbonylthioformaldehyde may be generated from these adducts and made to react with other conjugated dienes. For example, when it is heated with 2,3-dimethylbuta-1,3-diene and 1,4-diphenylbuta-1,3-diene, the following adducts are formed:

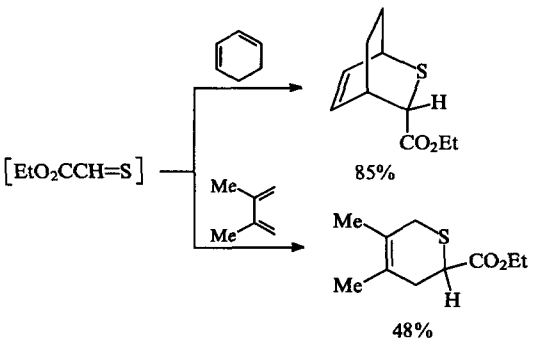


R = EtOCO.

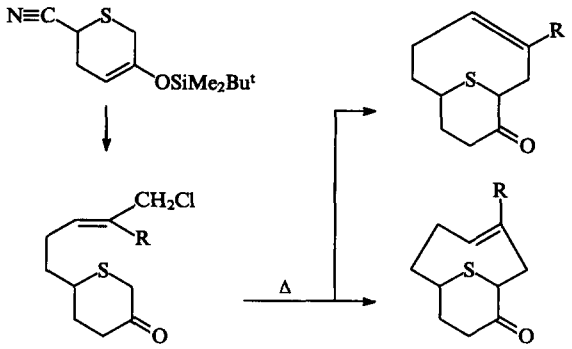
It has been suggested also that a derivative of diazathiabicyclooctane, formed in 34% yield in the reaction of ethyl 3-amino-4,4,4-trichlorocrotonate with sulfur dichloride, be used as a source of alkoxycarbonylthioformaldehydes.[57]



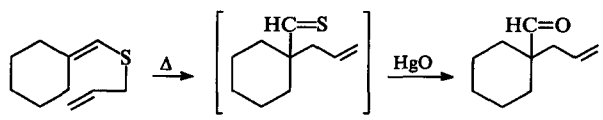
Heating of a solution of this compound in chlorobenzene at 80 °C induces the Diels-Alder retro-reaction and the formation, together with other products, of ethoxycarbonylthioformaldehyde, which reacts with cyclohexa-1,3-diene and also with 2,3-dimethylbuta-1,3-diene.[58]



The synthesis of 11-thiabicyclo[5.3.1]undecenes, which are otherwise difficult to obtain, from the adduct of cyanothioformaldehyde with 2-(*tert*-butyldimethylsiloxy)-buta-1,3-diene has been developed.[59,60]

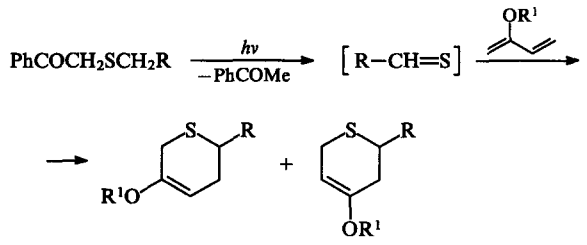


The thermolysis of certain sulfides in the presence of oxidants is of interest for preparative synthesis. For example, whereas the thermolysis of a cyclic sulfide at 160–180 °C leads to polymeric products, in the presence of mercury(II) oxide an aldehyde is formed in 82% yield.[58]



9. Photolysis of the C–S bond

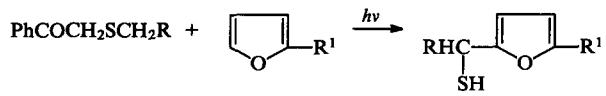
There are so far few examples of the photolytic cleavage of the C–S bond in sulfides and it has not found extensive application as a synthetic procedure for the transformation of the sulfide group. A simple method for the generation of dienophile thioaldehydes by the irradiation of a mixture of organyl phenacyl sulfides with a diene at 0 °C has been described.[58,61]



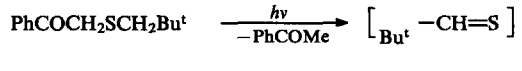
R = H, Ph, MeCO, PhCO, CN, AlkOCO, Ph_2PO, $PhSO_2$;
R^1 = $SiMe_2Bu^t$.

The use of the most reactive dienes in this process makes it possible to 'trap' even thioformyl sulfone $PhSO_2CH{=}S$ and thioformylphosphine oxide $Ph_2P(O)CH{=}S$, the oxygen analogues of which are unknown.

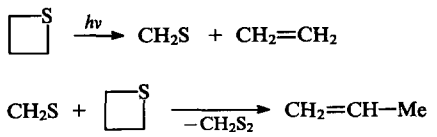
The photolysis of organyl phenacyl sulfides in the presence of furan proved to be a convenient and effective method of synthesis of mercaptoalkylfurans.[62]



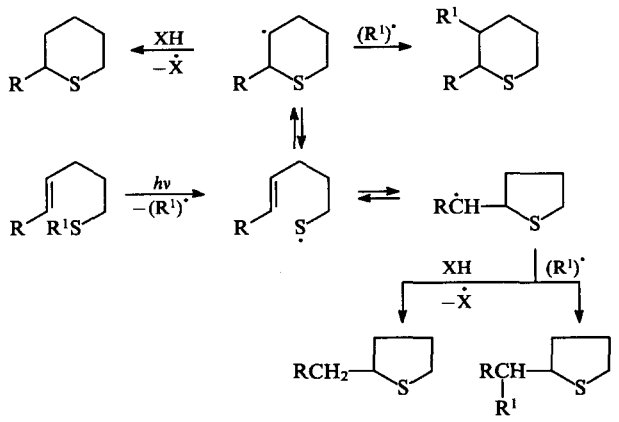
The photochemical decomposition of neopentyl phenacylsulfide is one of the most important methods of synthesis of the relatively stable 2,2-dimethylpropanethial.[63]



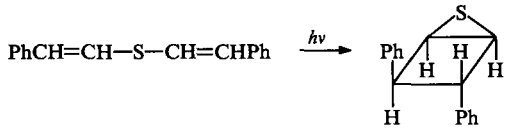
When thietane is irradiated with UV light at wavelengths of 254 and 313 nm in the temperature range 20–200 °C, ethylene and thioformaldehyde are formed. The latter reacts with a molecule of thietane to form an intermediate biradical, the subsequent decomposition of which leads to propene. [64]



The primary stage of the photolysis of alkenyl sulfides is again the cleavage of the C–S bond. The thiyl radicals produced in this process undergo subsequent intramolecular cyclisation with formation of cyclic products. [64]



UV irradiation of bis(2-phenylvinyl) sulfide leads to *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane. [64]

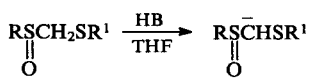


III. Generation of α-sulfenylcarbanions

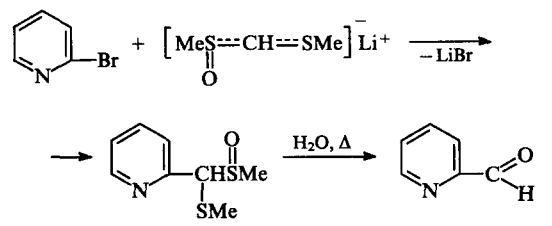
The stabilisation of the α-carbanionic centre by a divalent sulfur atom is used to generate α-sulfenylcarbanions, which are widely used in organic synthesis to produce both single and double carbon–carbon bonds. Together with alkyl(aryl)thio-groups, other functional groups such as C=O, [6,66] CN, [7,66] EtOCO, [8,66] RSO, [67] NO_2, [68,69] $SiMe_3$, [70,71] RSO_2, [72] etc. can participate in the stabilisation of the carbanionic centre. Carbon–carbon bonds are formed as a result of the alkylation or acylation of α-sulfenylcarbanions and also as a result of the addition of the carbanionic centre to the sp^2-hybridised carbon atom in the C=O and C=C bonds. These synthetic procedures are widely used in the preparation of various compounds together with the elimination of the sulfide group.

1. Synthesis of carbonyl compounds

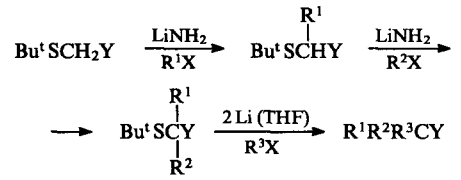
Carbanions containing functional groups other than the alkylthio- or arylthio-groups are frequently employed in the syntheses of carbonyl compounds. For example, the carbanions generated from ethyl methylthiomethyl or ethylthiomethyl methyl sulfoxide by treatment with NaH, BuLi, or Pr^i_2NLi in tetrahydrofuran are used successfully as synthons for acyl anions.



In the form of sodium or lithium salts, these carbanions react readily with primary alkyl halides or tosylates, affording aldehydes after hydrolysis. The interaction of the carbanion $MeS(O)\bar{C}HSMe$ with 2-bromopyridine leads to an intermediate, which affords pyridine-2-aldehyde on distillation. [67]



α-(*tert*-Butyl)thio-derivatives of carboxylic acid esters, nitriles, and ketones undergo stepwise alkylation via α-carbanions. The subsequent removal of the *tert*-butylthio-group by lithium in tetrahydrofuran with added naphthalene or trimesitylborane at 20 °C leads to alkyl-substituted carbonyl compounds. [64]

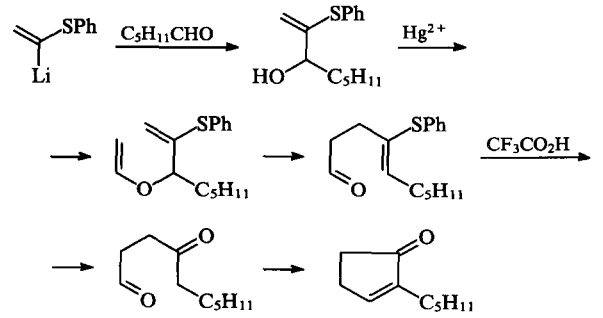


Y = CO_2Me, CO_2Bu^t, CN, COMe.

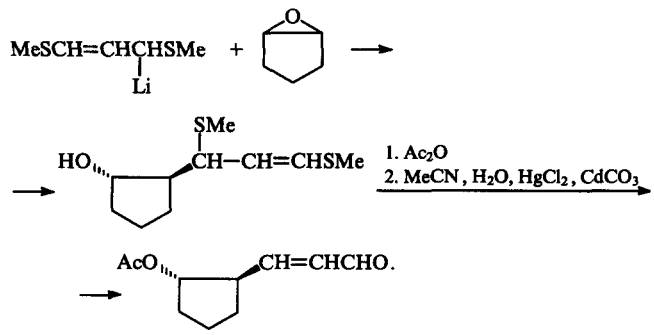
Phenylthiotrimethylsilylcarbanions are used to convert alkyl halides into aldehydes via alkylation, oxidation of the alkylation products to the sulfoxide, and rearrangement of the sulfoxide to α-trimethylsiloxysulfide, the hydrolysis of which leads to an aldehyde. [73]



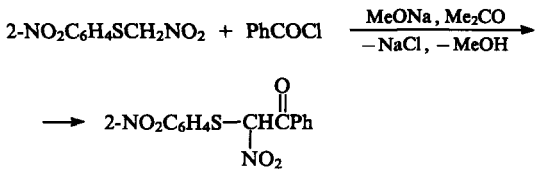
The α-carbanions obtained from vinyl sulfides can be regarded as acyl-anionic synthons, since they are capable of hydrolysing with formation of a carbonyl group, which in fact determines their use in organic synthesis. The synthesis of an unsaturated cyclic ketone by the addition of the carbanion of phenyl vinyl sulfide to hexanal has been described. [64] The alcohol formed is converted by transacetalisation with vinyl ether in the presence of divalent mercury salts into [a substituted?, Translator] vinyl ether, which is converted at 120 °C into an aldehyde. The hydrolysis of the aldehyde in the presence of trifluoroacetic acid leads to a ketoaldehyde, which cyclises to 2-pentylcyclo-penten-2-one.



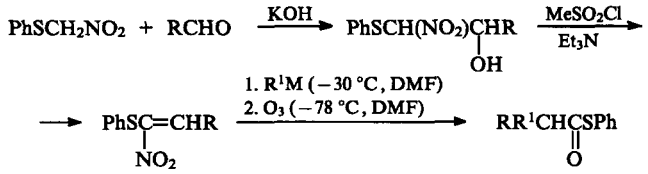
1,3-Bis(methylthio)allyllithium, which is a synthetic equivalent of the anion $\bar{C}H=CH-CH=O$, has found extensive application in the synthesis of *trans*-α,β-unsaturated aldehydes. One of the examples of such synthesis is presented in the scheme below: [64]



It has been shown in relation to the carbanion of 2-nitrophenylthionitromethane [68,69] that α-sulfenylcarbanions are relatively easily acylated by carboxylic acid chlorides with formation of α-arylthioketones.



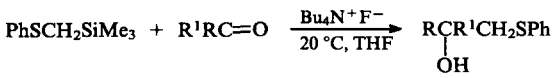
In view of the possibility of the subsequent removal of the sulfide group, one can regard this method as one of the alternative procedures for the synthesis of ketones.



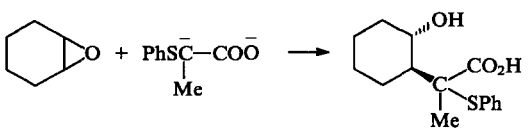
The addition of the anion of phenylthionitromethane to the carbonyl group of aldehydes with subsequent dehydration and ozonisation is used in the synthesis of thioloesters of carboxylic acids. [74]

2. Synthesis of alcohols

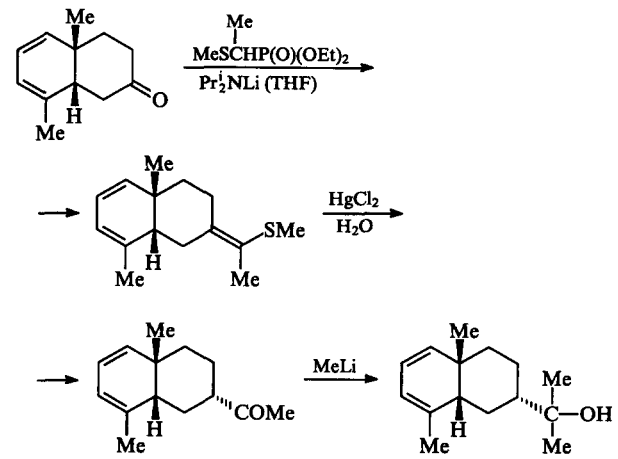
A hydroxy-group may be formed either as a result of the addition of α-sulfenylcarbanions to the sp^2-hybridised carbon atom of the carbonyl group or as a result of the opening of the oxirane ring. For example, the synthesis of secondary alcohols containing the phenylthio-group in the α-position from phenylthio(trimethylsilyl)methane and ketones with subsequent elimination of the trimethylsilyl group has been described. [75]



The opening of the oxirane ring by treatment with the dianion of 1-carboxyethyl phenyl sulfide is used in the synthesis of α-derivatives of cyclohexanol. [65]

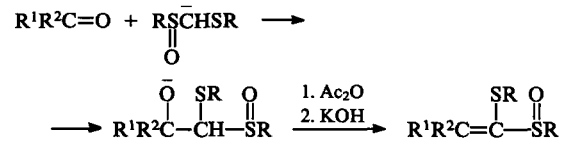


A multistage synthesis of tertiary alcohols has been described in the literature. [76] It is based on the addition of methyl α-diethoxyphosphonoethyl sulfide to the carbonyl group of a cyclic ketone, the subsequent stepwise elimination of the diethyl phosphonate and of the methylthio-group, and the addition of methyllithium to the carbonyl group.

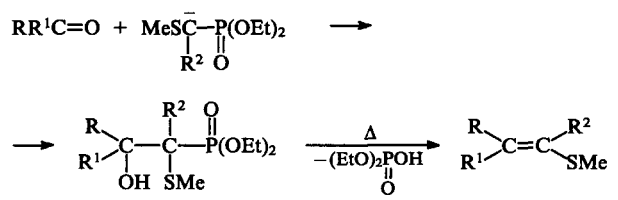


3. Synthesis of unsaturated compounds

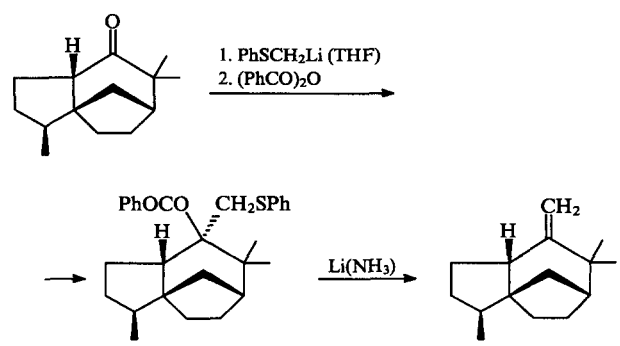
The use of α-sulfenylcarbanions for the formation of new C=C bonds under mild conditions is very important. The addition of α-sulfenylcarbanions to the carbonyl group of ketones leads to β-hydroxysulfides, which are converted into unsaturated sulfides after the elimination of the hydroxy-group. [1]



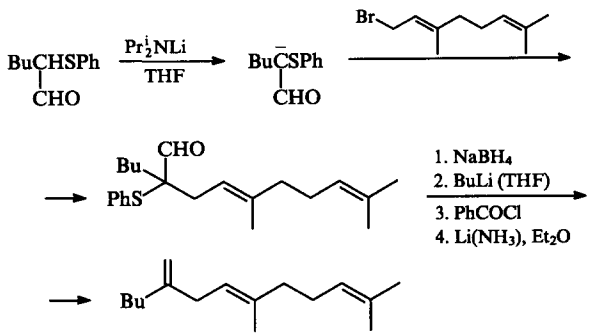
R = Me, Et; $R^1 = R^2 = Me$.



Several methods for the methylenation of ketones involving the use of α-sulfenylcarbanions have been developed. [64] One of them consists in the addition of α-sulfenylcarbanions to ketones with formation of β-hydroxysulfides, which are converted into methylene derivatives after acylation and reductive elimination of the phenylthio-group. The sesquiterpene zizaene has been obtained in this way.

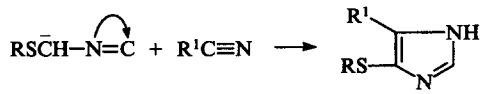


Alkylation of the carbanion $Bu\bar{C}(CHO)-SPh$ followed by the reductive cleavage of the C–S bond is used in the synthesis of 2-butyl-5,9-dimethyldeca-1,4,8-triene. [1]

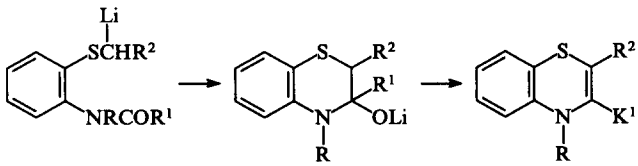


4. Synthesis of heterocyclic compounds

α-Sulfenylcarbanions with functional group substituents are frequently used in the synthesis of heterocyclic compounds. For example, the interaction of the α-isocyano-α-sulfenylcarbanion with nitriles leads to the formation of imidazoles. [64]

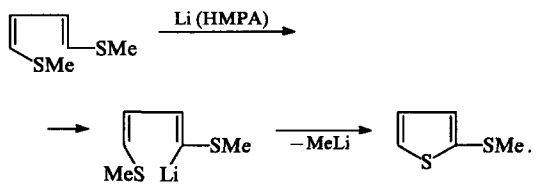


The synthesis of 4*H*-1,4-benzothiazines in accordance with the scheme

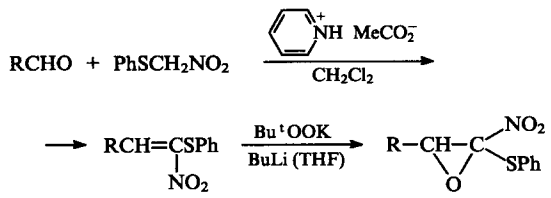


has also been described. [71]

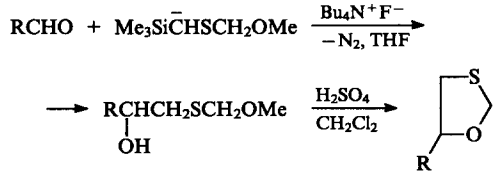
It has been noted [64] that the metallation of a 1,4-bis(alkylthio)alkadiene with lithium in the presence of hexamethylphosphoramide (HMPA) is accompanied by cyclisation with formation of alkylthio-derivatives of thiophene, for example:



The addition of the phenylthionitromethane anion to the carbonyl group in aldehydes with subsequent dehydration and selective oxidation of the ethylene bond constitutes the basis of the synthesis of oxiranes containing the phenylthio-group. [78, 79]



Functionalised β-hydroxysulfides, formed as a result of the addition of α-sulfenylcarbanions to the carbonyl group of aldehydes, can cyclise with participation of the hydroxy-group and other functional groups, which is used in the synthesis of 1,3-oxathiolanes. [80]



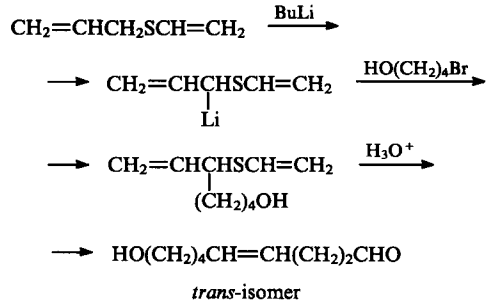
R = Ph, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$.

The synthesis of thiiranes [80] and other heterocyclic compounds [81] from α-sulfenylcarbanions has also been described.

5. Synthesis of natural products

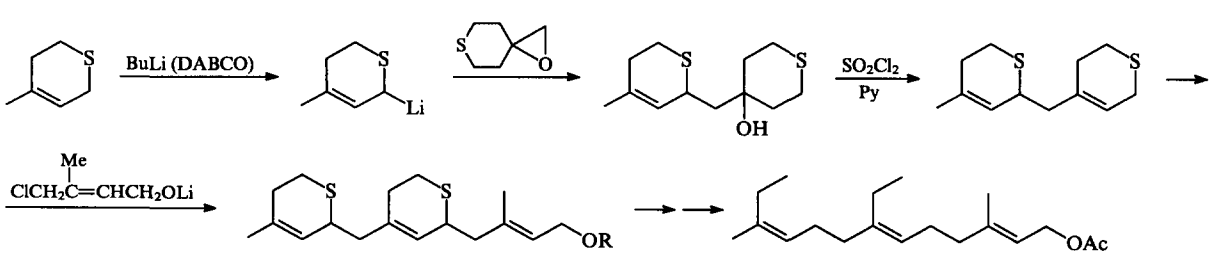
Apart from the synthesis of the sesquiterpene zizaene described above, α-sulfenyl carbanions with functional group substituents have found extensive application also in the syntheses of other natural products. For example, allyl carbanions are most important intermediates in the synthesis of juvenile hormones — cembranolides (Scheme 3). [64]

The hydroxyaldehyde which is a key compound in the synthesis of the pheromone propylure has been obtained by metallating allyl vinyl sulfide and subsequent alkylation and thio-Claisen rearrangement. [64]

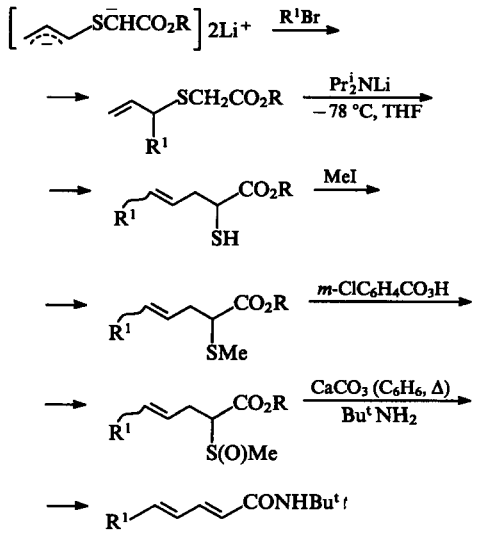


The dianion of allylthioacetic ester is a convenient reagent for the stereoselective synthesis of derivatives of (2*E*,4*E*)-dienoic acids, for example the precursor of the insecticide pellitorine. [82, 83]

Scheme 3

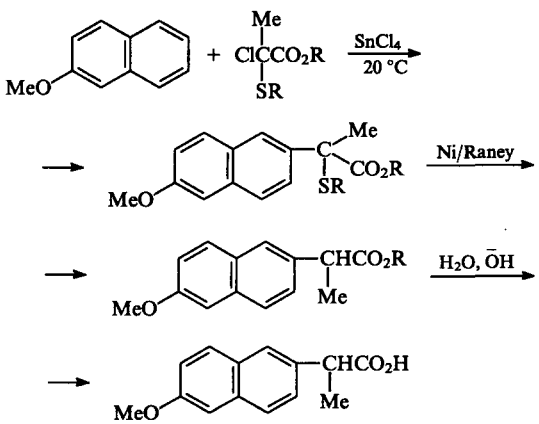


DABCO = diazabicyclo[2.2.2]octane

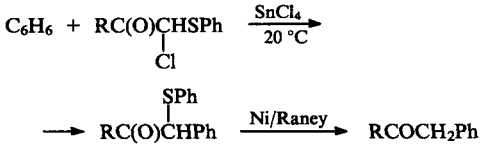


IV. Generation of α-sulfenylcarbonium ions

The sources of α-sulfenylcarbonium ions are as a rule α-chlorosulfides, on the basis of which a series of methods have been developed for the introduction of the sulfide group into aromatic compounds. This synthetic procedure is used in multistage organic syntheses, in particular in the syntheses of various carbonyl compounds. For example, the synthesis of α-(6-methoxy-2-naphthyl) propionic acid includes stages in which β-methoxynaphthalene is alkylated by the α-alkylthio-α-chloropropionic acid ester with subsequent elimination of the alkyl group and hydrolysis of the ester group.[84]

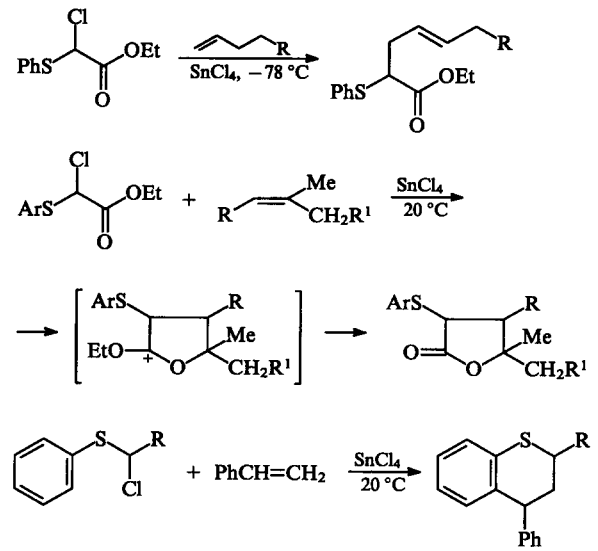


A series of alkyl(aryl) benzyl ketones have been obtained by alkylating benzene with acylchloromethyl phenyl sulfide in the presence of tin tetrachloride and subsequent reductive elimination of the phenylthio-group.[85]



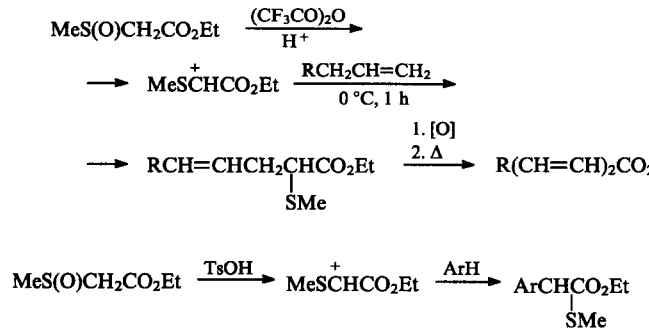
R = Me, Ph, CH_2Ph, $(CH_2)_2Ph$.

Another aspect of the use of α-sulfenylcarbonium ions in multistage organic syntheses involves their ene-type interaction with terminal alkenes,[86] which is sometimes used to obtain certain heterocyclic compounds.



R = CO_2Et, $CONMe_2$; R^1 = Alk.

Certain sulfoxides are also used as sources of α-sulfenylcarbonium ions. They generate α-sulfenylcarbonium ions under the conditions of the Pummerer rearrangement. For example, it has been noted[64] that the carbonium ion $MeS\overset{+}{C}HCO_2Et$, obtained by the Pummerer rearrangement from the sulfoxide $MeS(O)CH2CO_2Et$, reacts with terminal alkenes via the ene pathway (it is used in the synthesis of dienoic acids) and also enters into alkylation reactions of aromatic hydrocarbons.[87]

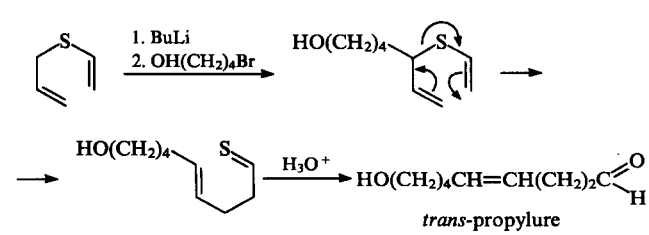


Ar = Ph, C_6H_4Me, C_6H_4Cl.

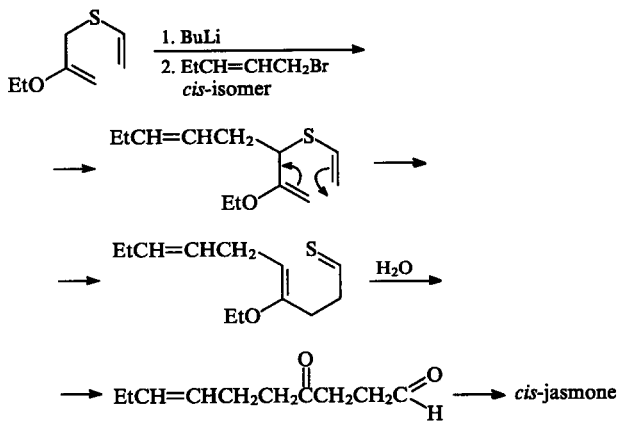
V. Reactions involving the rearrangement of sulfides

Among the known rearrangements of sulfides, the thio-Claisen rearrangement and also various sigmatropic migrations of alkylthio- and arylthio-groups have found most extensive application. Rearrangements involving the migration of other functional groups and hydrogen atoms are also used.

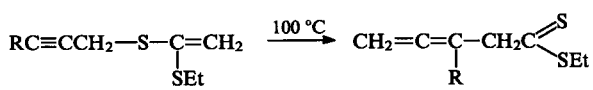
The thio-Claisen rearrangement of carbanions derived from allyl sulfides with subsequent alkylation and cleavage of the $C_{All}-S$ bond (or its hydrolysis) constitutes a convenient method of synthesis of certain aliphatic natural products.[1]



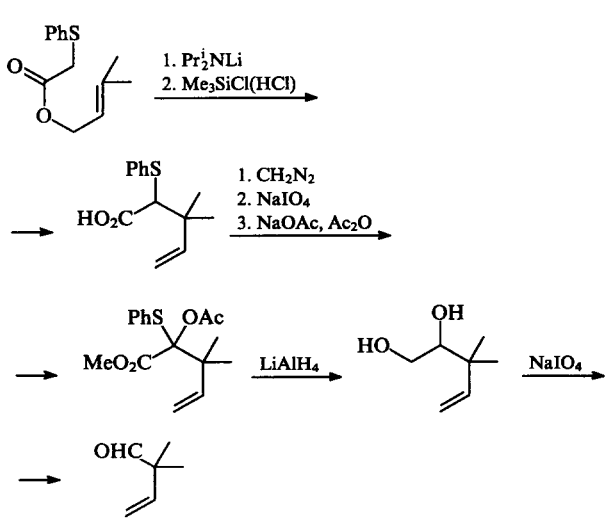
trans-propylure



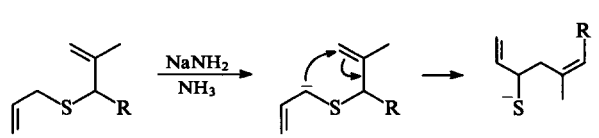
The thio-Claisen rearrangement of 1-alkylthio-1-propargylthioalkenes[1] to the alkyl esters of dienedithiocarboxylic acids, which are otherwise difficult to obtain and for which other methods of synthesis have not yet been developed, is of special interest.



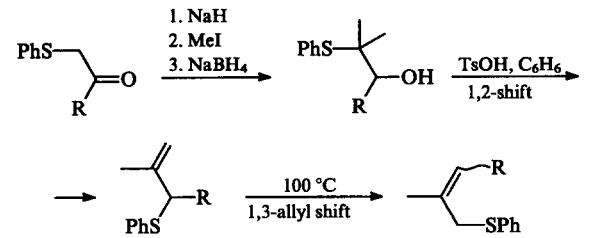
The Claisen rearrangement of allyl α-phenylthioacetates leads to α-phenyl-substituted thiocarboxylic acids, which can be converted further into β,γ-unsaturated aldehydes and the relatively difficult to obtain (*Z*)-diene-2-carboxylic acids.[88]



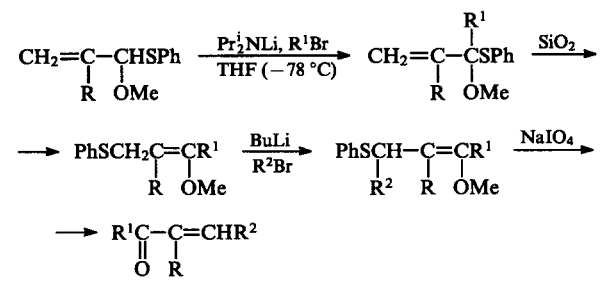
In the synthesis of unsaturated thiolates from allyl sulfides, the [2,3]-sigmatropic rearrangement of the carbanion derived from the allyl sulfide takes place.[89]



A large number of the rearrangements of sulfides involve the migration of the alkylthio- or arylthio-groups.[90–95] For example, the synthesis of unsaturated sulfides from β-oxoalkyl sulfides includes rearrangements involving 1,2- and 1,3-shifts, which make it possible to move the phenylthio-group by one carbon atom along the chain.[90]

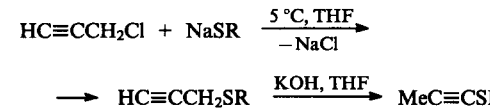


The synthesis of unsaturated ketones from β-methoxysulfides[91] includes a stage involving a rearrangement with migration of the phenylthio-group of the 1,3-shift type.



R = H, Me; $R^1 = R^2$ = Me, Et.

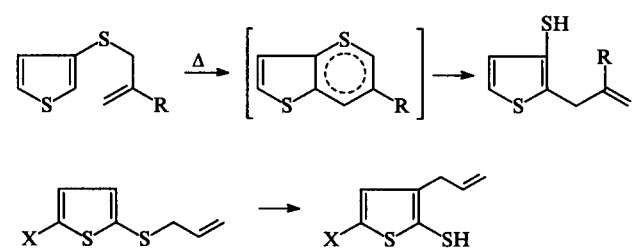
The rearrangement of alkyl propargyl sulfides with the 1,3-shift of the alkylthio-group constitutes the basis of the synthesis of alkylthiopropynes, which are used to obtain polymers.[93]



R = Me, Et, Bu, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$.

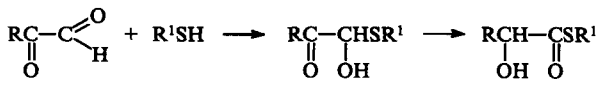
The migration of the alkylthio-group in indole from the 3-position to the 2-position, occurring under the influence of trifluoroacetic acid,[95] is extremely important for the synthesis of alkyl 2-indolyl sulfides, since the sulfenylation of indole by sulfenyl chlorides takes place as a rule in the 3-position.[96,97]

The [3,3]-sigmatropic rearrangement of allyl 2-thienyl and allyl 3-thienyl sulfides, which proceeds via a six-membered transition state, is very important from the standpoint of the synthesis of 2- and 3-allylthiophenethiols.[89]



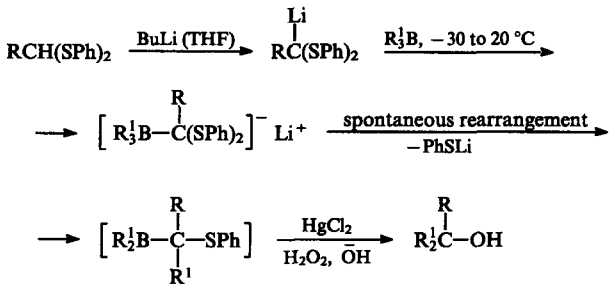
X = H, Me, MeO, MeS, Cl, Br.

Together with the syntheses presented above, a whole series of syntheses based on rearrangements involving the migration of hydrogen atoms and alkyl, arenesulfonyl, and other functional groups have been developed. For example, the synthesis of α-hydroxy-substituted thiocarboxylic acids from α-oxoaldehydes and thiols is based on the rearrangement of the intemediate α-hydroxy-β-oxoalkyl sulfides, which proceeds with migration of a hydrogen atom.

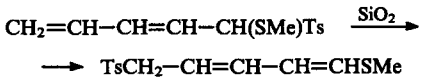


R = Me, Et, Pr; R^1 = Et, Bu.

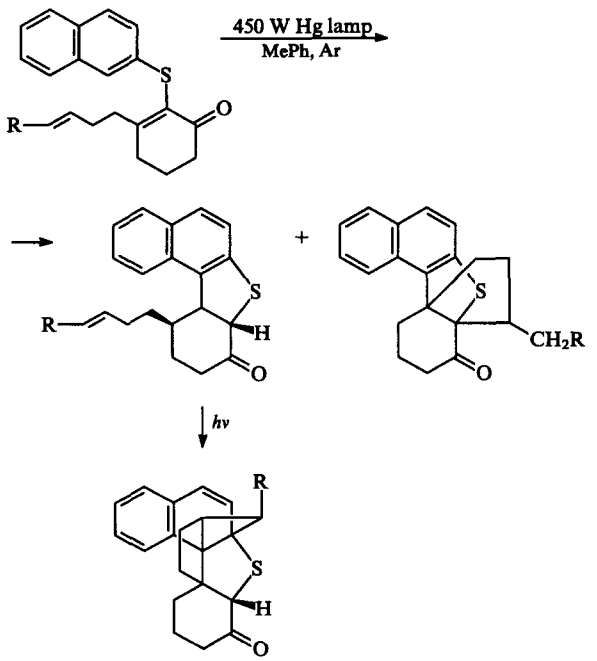
The migration of an alkyl group is especially characteristic of sulfides containing boralkyl groups, which are used in the synthesis of tertiary alcohols from thioacetals. [98]



The rearrangement with migration of the arenesulfonyl group is characteristic of sulfides containing arenesulfonyl and alkyl(aryl)thio-groups at the allylic carbon atom. [99,100] For example, the synthesis of 1-methylthio-5-tosylpenta-1,3-diene is based on the rearrangement of 1-methylthio-1-tosylpenta-2,4-diene.



The synthesis of cyclic sulfides based on the photoinduced intramolecular cycloaddition reactions of arylthiocyclohexenones [101] and phenylthiocyclohexanones has been described. [102]

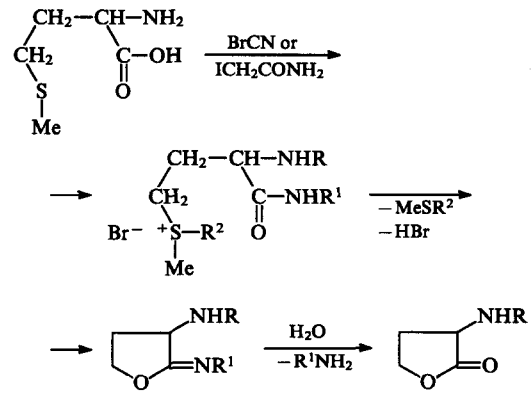


VI. Syntheses based on the primary products of the reactions of sulfides

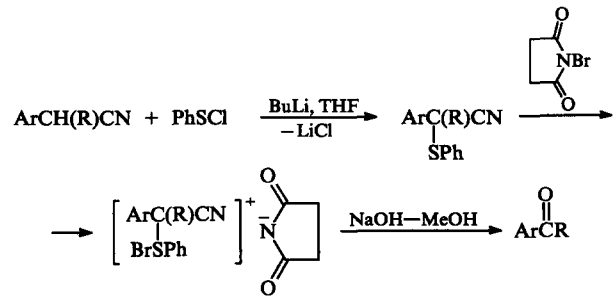
The conversion of the sulfide group into the sulfonium, ylide, sulfoxide, sulfilimine, and other groups with their subsequent transformation is widely used in multistage organic syntheses. The products of the primary reactions of sulfides are then formed as a rule in high yields and are frequently employed without isolation from the reaction mixture.

1. Syntheses via sulfonium salts

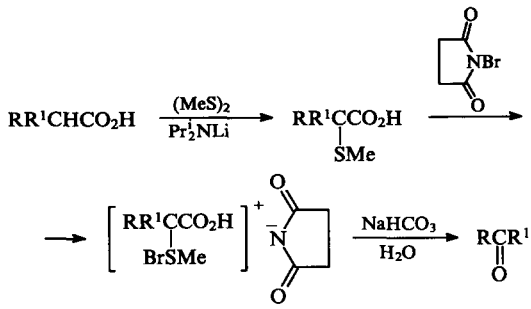
The conversion of the sulfide group into the sulfonium group is one of the most important synthetic procedures widely used in multistage organic syntheses. For example, the protection of the carboxy-group by means of the formation of alkylthiomethyl esters $RCO_2CH_2SR^1$ affords derivatives resistant to the action of alkalis and reductants, which has found applications in the peptide and phosphatide syntheses. [1] In order to remove the alkylthiomethyl group by treatment with methyl iodide, the former is converted into the sulfonium group, which is then cleaved by a solution of alkali, i. e. the conversion of the sulfide group into the sulfonium group with subsequent cleavage is one of the methods for the elimination of the former. A method for the specific cleavage of peptides at the methionine linkages with intramolecular substitution of the oxygen atom of a neighbouring amide group has been developed on the basis of the formation reaction of sulfonium salts. [1]



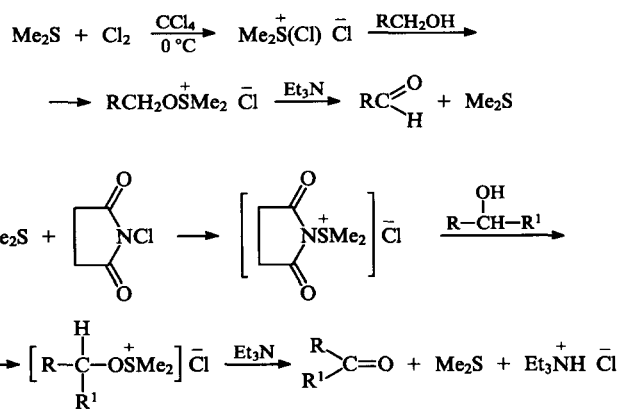
The synthesis of ketones from nitriles ArCHRCN (R = alkyl, aryl) consists in the phenylsulfenylation of the nitrile, the conversion of the sulfide group into the sulfonium group, and the cleavage of the latter with the aqueous NaOH solution – MeCN system.



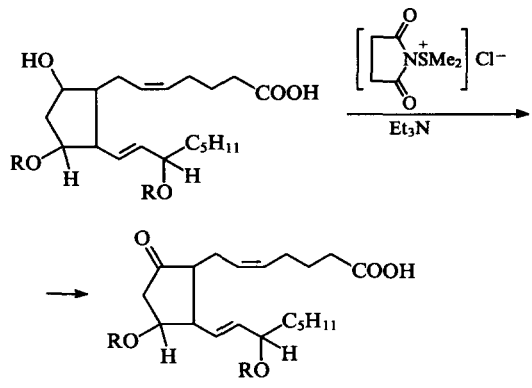
A similar synthetic procedure has been used in the oxidative decarboxylation of carboxylic acids, where *N*-bromosuccinimide served as the oxidant. [1]



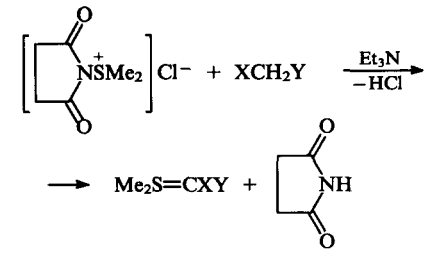
The complexes of dimethyl sulfide with chlorine and *N*-chlorosuccinimide (the Corey–Kim reagent) are widely used in the oxidation of primary and secondary alcohols to carbonyl compounds in synthetic organic chemistry. The carbonyl compound is formed in this case as a result of the cleavage of the intermediate alkoxysulfonium salt. [103]



In the improved synthesis of prostaglandins described by Fieser and Fieser,[103] the Corey–Kim reagent is used to convert the hydroxy-group into the keto-group.

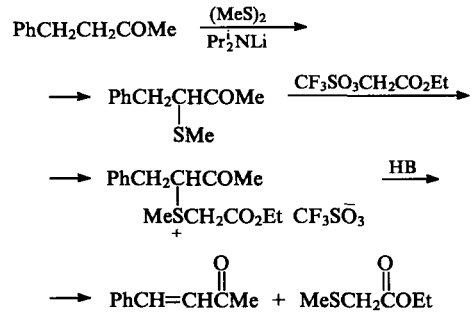


It has been shown [104] that the interaction of the above reagent with CH acids in the presence of triethylamine leads to the formation of sulfur ylides.



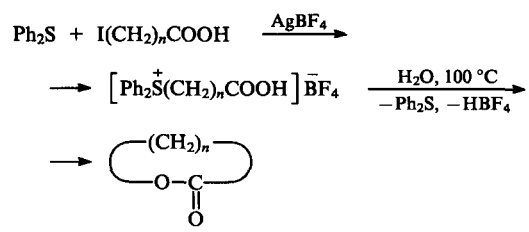
X = Br, Ac, CN; Y = Br, Ac, CO_2Et, CO_2Me, Ph.

The sulfonium centre attacks the β-hydrogen atoms, while the eliminated sulfonium group can function as the leaving nucleophile in E_2 reactions. The conversion of the sulfide group into a sulfonium group with subsequent removal of the latter is used as a method for the introduction of a carbon–carbon double bond, for example in the synthesis of unsaturated ketones from saturated ones. [105]



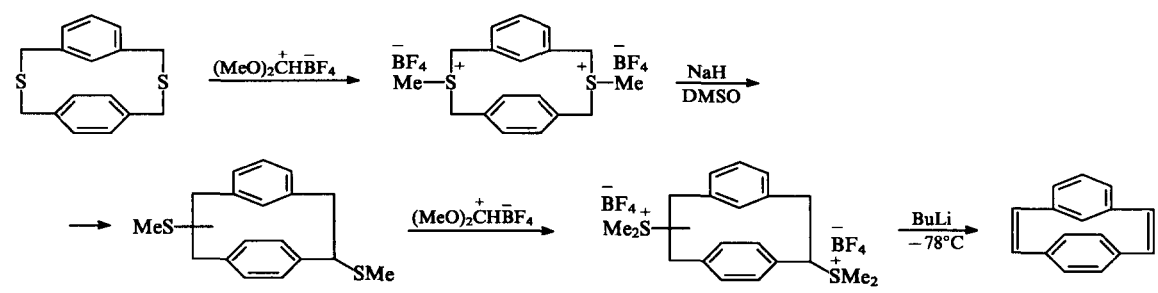
A similar synthetic procedure has been used to convert macrocyclic sulfides into unsaturated hydrocarbons. [103] For example, the key stage in the synthesis of *m,p*-[2,2]cyclophane-1,9-diene is the replacement of the sulfide group by a carbon–carbon double bond, which is achieved as a result of the Stevens rearrangement of the intermediate ylide with subsequent elimination of the sulfonium group (Scheme 4).

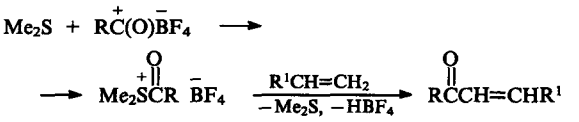
The high lability of the C–S bond in sulfonium salts makes it possible to employ them as alkyl and acyl group transferring agents, which has found applications in biological methylation reactions [106] and also in the syntheses of alkanecarboxylic acid lactones [107] and unsaturated ketones. [108, 109]



n = 3–7

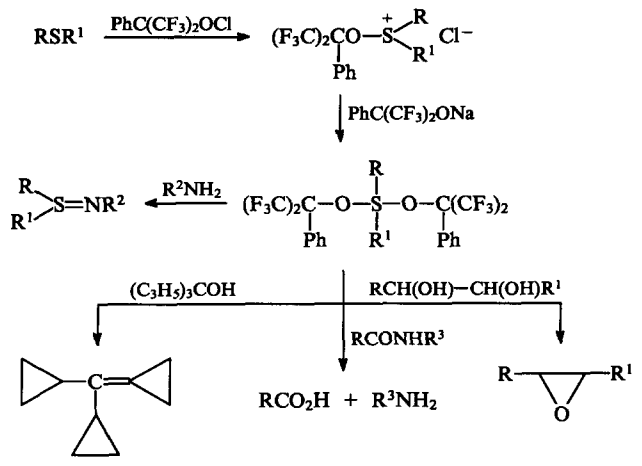
Scheme 4





R = Me, Bu^t; R^1 = Ph.

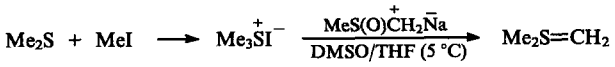
Alkyl sulfonium salts, formed in the reactions of sulfides with alkyl hypochlorites, are readily converted in the presence of alkoxides into highly reactive and relatively stable dialkoxysulfuranes, on the basis of which a whole series of syntheses of sulfilimines, oxiranes, carboxylic acids, and unsaturated hydrocarbons have been developed. [110]



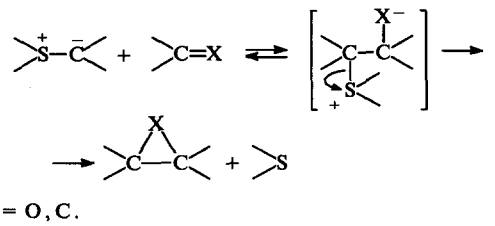
2. Formation of sulfur ylides

a. Transfer of alkylidene groups

The conversion of sulfides into sulfur ylides in multistage organic syntheses is determined primarily by the fact that the latter, being nucleophiles, can participate in the transfer of alkylidene groups to the electrophilic double bond with formation of a three-membered ring, which is frequently used in the syntheses of cyclopropanes, oxiranes, and other cyclic compounds. In view of the ready availability of aldehydes and ketones, the conversion of sulfides into sulfur ylides followed by their condensation with aldehydes and ketones is an important synthetic method for the preparation of oxiranes with a wide variety of structures. [1,103,111,112] Dimethylsulfonium methylide, formed as a result of the reaction of dimethyl sulfide with methyl iodide and subsequent dehydrogenation of the resulting sulfonium salt, is widely used in preparative organic chemistry as a methylene group transferring agent. [1,66]

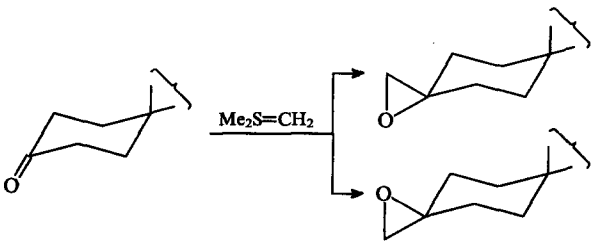


The overall mechanism of the transfer of the alkylidene group with the aid of ylides is presented below. [1] The inter-mediate betaine cyclises via direct substitution at a carbon atom.



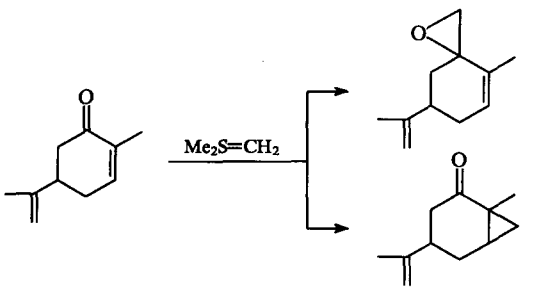
X = O, C.

Depending on the structure of the ylide and the substrate, their addition to one another can lead to the formation of diastereoisomeric or structurally isomeric betaines. The decomposition of such betaines affords various products. For example, the addition of dimethylsulfonium methylide to cholestan-3-one leads to the formation of two structurally isomeric products with oxirane rings.

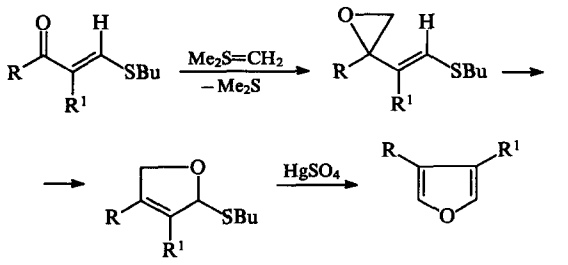


main product

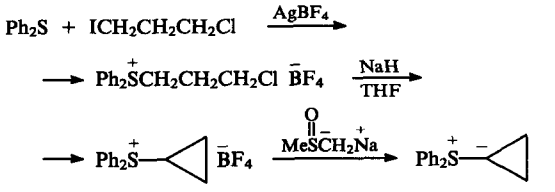
The addition of the same ylide to carvone leads to two different products containing the oxirane and cyclopropane rings with the former predominating.



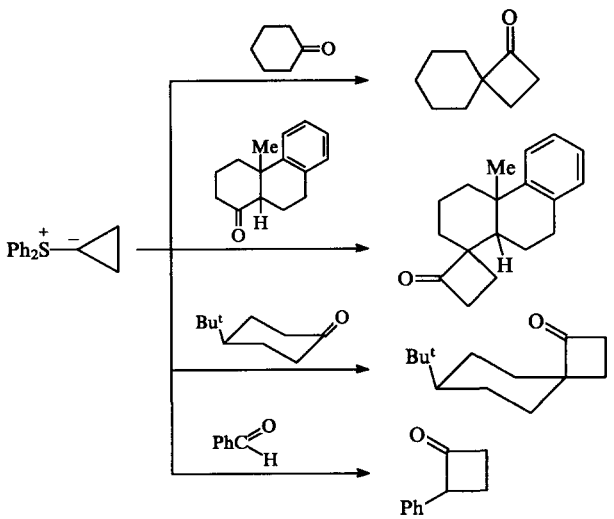
When the substrate molecule contains a mobile hydrogen atom, the oxirane ring formed may be opened with subsequent formation of a five-membered ring, which is used in the synthesis of furans from dimethylsulfonium methylide and unsaturated ketones. [103]



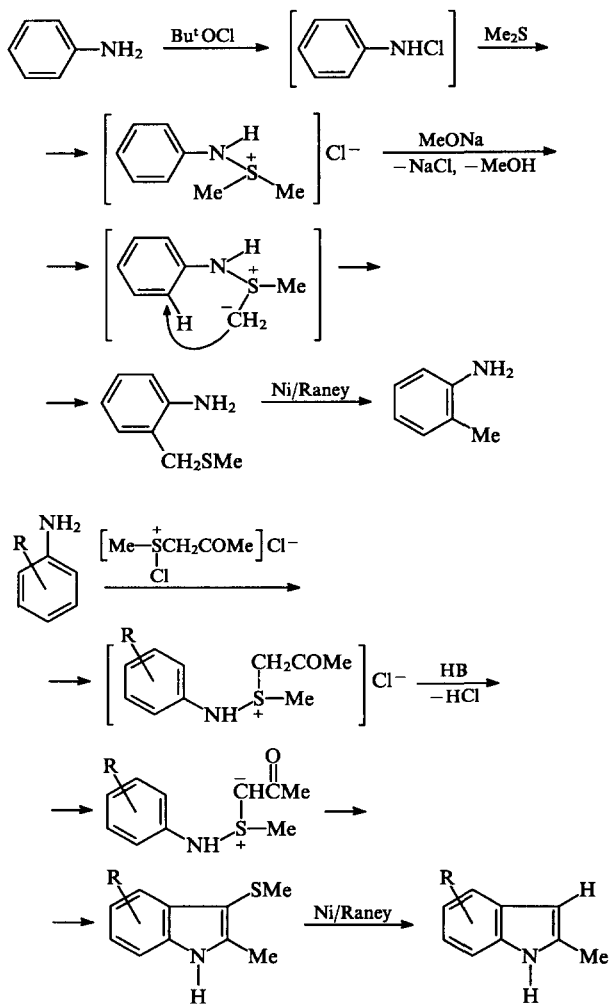
Diphenylsulfonium cyclopropylide, formed in the reaction of diphenyl sulfide with 3-chloro-1-iodopropane in the presence of silver tetrafluoroborate, is used in preparative organic chemistry for the transfer of the trimethylene fragment. [103]



The transfer of the trimethylene fragment to the electrophilic double bond with the aid of diphenylsulfonium cyclopropylide is one of the alternative methods of synthesis of spirocycloalkanones and cyclic ketones. [103]

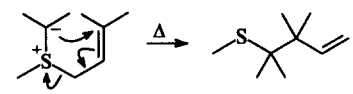


The intramolecular transfer of alkylthiomethylene groups in sulfur ylides is used for the *ortho*-methylation of anilines [113] and in the synthesis of indoles. [114]

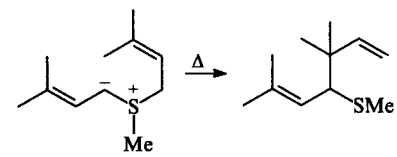


b. Rearrangements of ylides

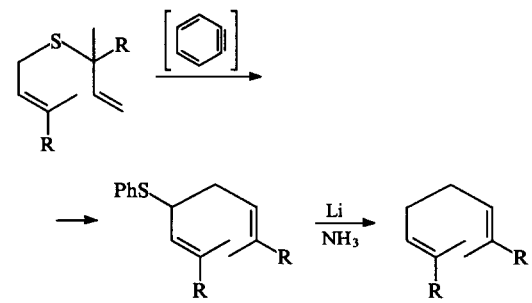
A second aspect of the use of sulfur ylides in organic synthesis is the formation of products as a result of their rearrangement. These rearrangements usually occur fairly readily with formation of a new carbon–carbon bond. For example, the [2,3]-sigmatropic rearrangement of allylsulfonium alkylides leads to but-3-enyl sulfides. [1]



As a rule, this rearrangement takes place with inversion of the allyl group and can be used for the transfer of chirality from the sulfur to a carbon atom. [115]

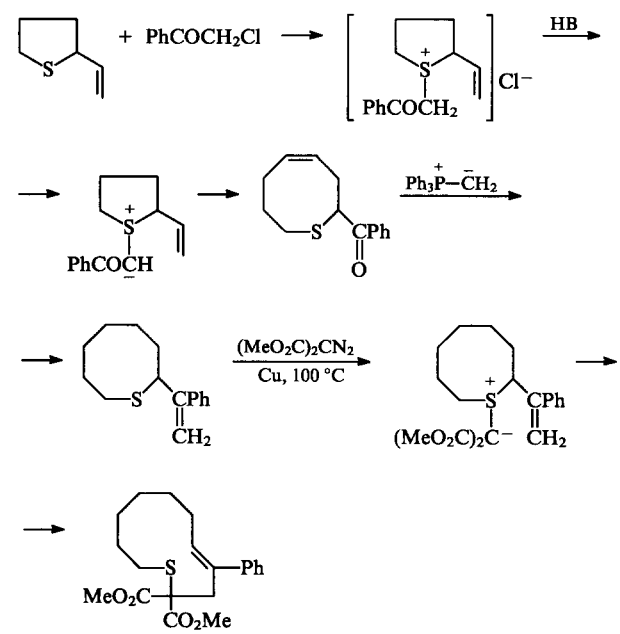


The [2,3]-sigmatropic rearrangement of allylsulfonium alkylides has been used in the synthesis of squalene. [116]

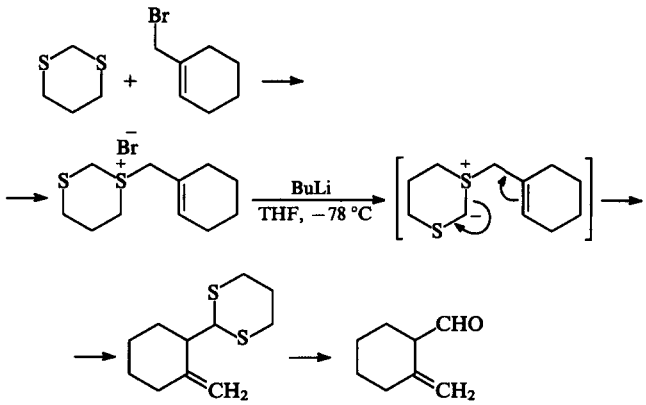


R = $Me_2C{=}CH(CH_2)_2C(Me){=}CH(CH_2)_2$.

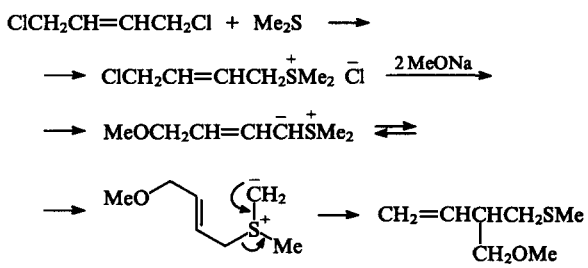
A similar rearrangement is used in the method involving successive ring expansion in cyclic sulfides described by Vedejs and Hagen. [117].

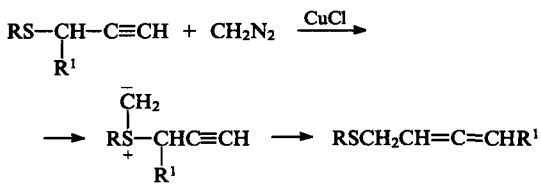


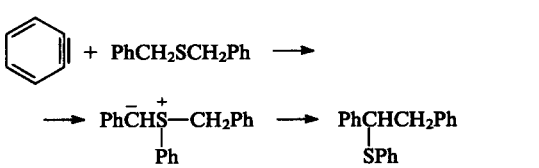
One of the stages in the synthesis of β,γ-unsaturated aldehydes from 1,3-dithiane [103] involves the [2,3]-sigmatropic rearrangement of an intermediate ylide.



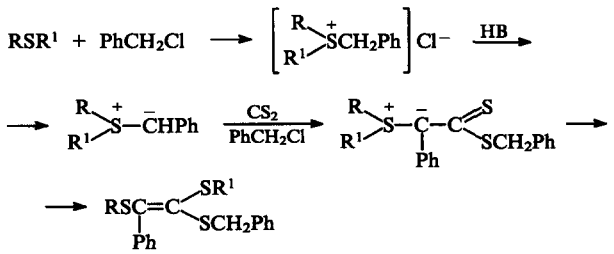
A series of methods of synthesis of polyfunctional sulfides have been developed on the basis of the rearrangement of the corresponding sulfur ylides via a 1,2-shift.[1,118]





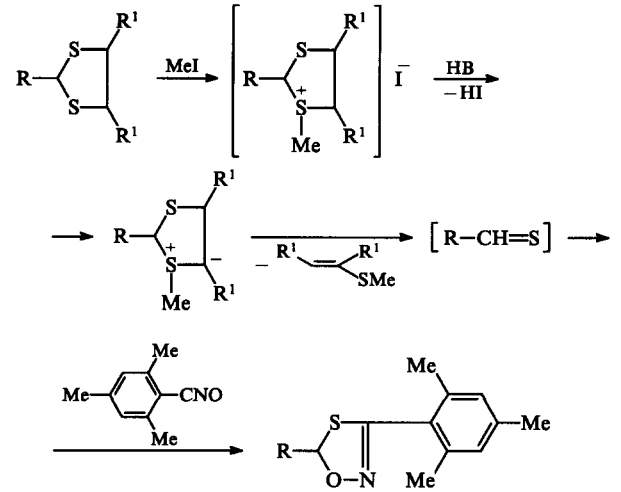


Examples of the use of other rearrangements of sulfur ylides in syntheses of sulfides have been described. For example, the synthesis of 1,1,2-tris(alkylthio)alkenes from dialkyl sulfides includes the rearrangement of ylides stabilised by the introduction of the thiocarbonyl group.[118]



c. Fragmentation of sulfur ylides

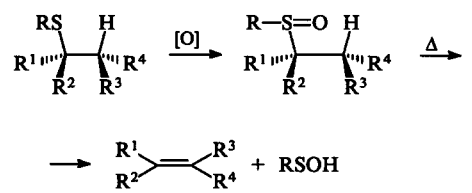
The conversion of 1,3-dithiolanes into thioaldehydes is based on the fragmentation of the intermediate ylide.[119] Mesitonitrile *N*-oxide is used to trap the thioaldehyde. It reacts with the thioaldehyde to form stable 1,4,2-oxathiazoles. In the absence of a 'trapping agent', polymers or trimers are formed.



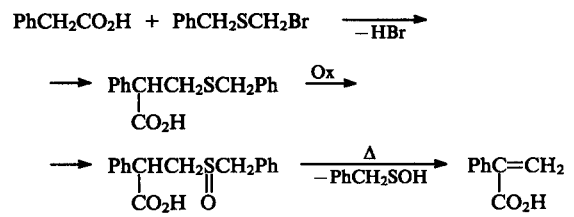
By virtue of the fragmentation reaction of sulfur ylides, 1,3-dithiolanes are convenient reagents for the synthesis of various thioaldehydes.

3. Syntheses of sulfoxides

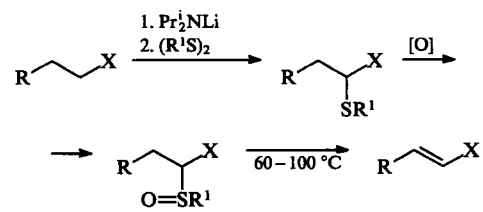
Another approach to the problem of the cleavage of the C–S bond in sulfides is based on the tendency of sulfoxides to undergo thermal *cis*-elimination, which results in the formation of a carbon–carbon double bond.[1]



An important factor for this reaction is the availability of effective selective methods for the oxidation of sulfides, the search for which has been prosecuted vigorously in recent years.[120–126] The presence of powerful electron-accepting groups in the sulfoxide molecule promotes the thermal *cis*-elimination. A clear example of this is provided by the synthesis of α-phenylacrylic acid.[127]

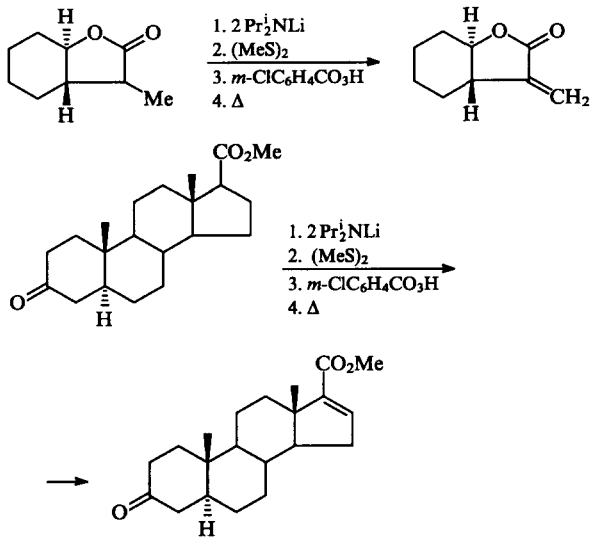


The method for the introduction of a carbon–carbon double bond with the (*E*)-configuration has been investigated in greater detail by Trost et al.[128] The essential feature of the method is the introduction of the phenylthio- or methylthio-group into the α-position relative to the electron-accepting group, the oxidation of the sulfide group to the sulfoxide group, and thermal elimination of the latter.

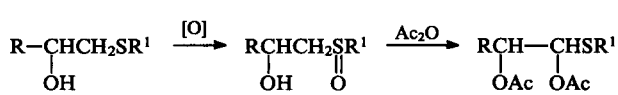


X = COR, CO_2R, CN; R = Alk, Ar; R^1 = Ph, Me.

The elimination of benzenesulfenic acid takes place very readily on refluxing in benzene or carbon tetrachloride, whereas heating in toluene is necessary to split off methanesulfenic acid. A similar chain of reactions is used in the synthesis of α-methylene-3-lactones and also for the selective introduction of a double bond in the α,β-position relative to the ester group in steroids. [129]



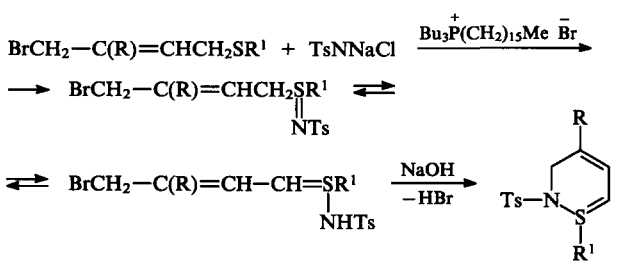
Another aspect of the use of sulfoxides in organic synthesis is their rearrangement in the presence of acetic anhydride (the Pummerer rearrangement). This rearrangement is used widely to convert one sulfide into another. [1, 130]



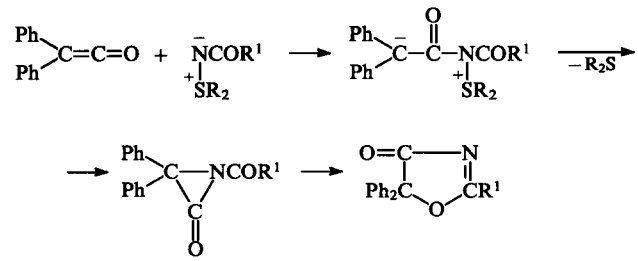
4. Reactions accompanied by the formation of sulfilimines

a. Cyclisation and cycloaddition reactions

The conversion of sulfides into sulfilimines with their subsequent cyclisation or cycloaddition to compounds containing double or triple bonds is used in syntheses of heterocyclic compounds. For example, the preparation of nitrogen-containing heterocyclic compounds from alkyl allyl sulfides, involving a stage with oxidative imination of the sulfide by the sodium salt of the chloramide of toluene-*p*-sulfonic acid and subsequent cyclisation of the resulting sulfilimine, has been described. [131]

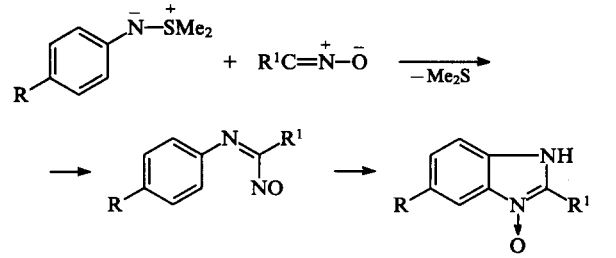


N-Acylsulfilimines, formed as a result of the reaction of sulfides with the *N*-chloramides of carboxylic acids, enter relatively readily into a cycloaddition reaction with diphenylketene, which is used in the synthesis of 1,3-oxazol-4-ones. [132]

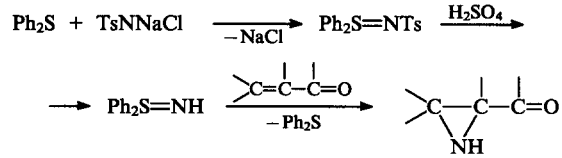


In essence, the reaction represents the transfer of the acylamino-group to the electrophilic double bond.

The cycloaddition of *N*-arylsulfilimines to nitrile oxides is used to obtain benzimidazole *N*-oxides. [133]

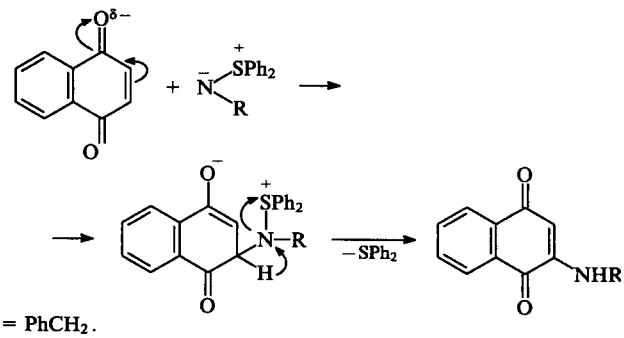


The synthesis of aziridines from sulfides is based on the cycloaddition of diphenylsulfilimines to the double bond in α,β-unsaturated ketones. [134, 135]

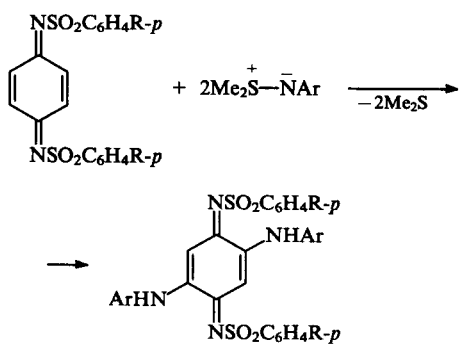


b. Transfer of arylamino-groups

Apart from the cycloaddition reactions, the transfer of the imine fragment of sulfilimines to the electrophilic double bond is used also to introduce arylamino-groups into the quinonoid rings of quinones [136] and quinone imines. [137]



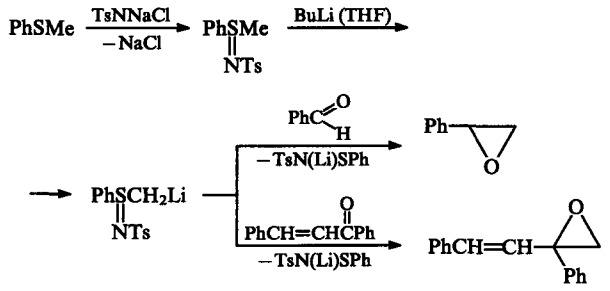
R = PhCH$_2$.



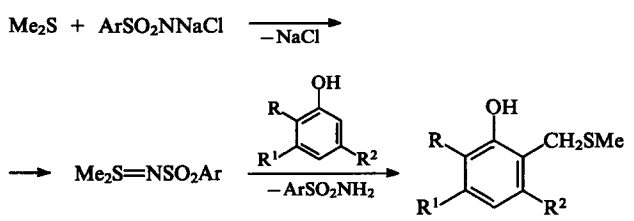
R = H, Me; Ar = Ph, *p*-MeC$_6$H$_4$, *p*-ClC$_6$H$_4$, *p*-NO$_2$C$_6$H$_4$.

c. Transfer of alkylidene groups

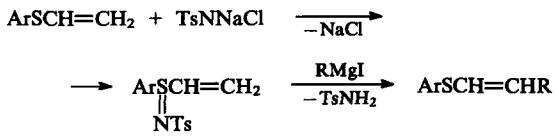
The strong electron-accepting influence of the arenesulfonylimino-group in *N*-arenesulfonylsulfilimines increases the acidity of the α-hydrogen atoms in the *S*-alkyl groups, which promotes their substitution by an alkali metal atom. Such organo-metallic compounds are used as nucleophiles which transfer alkylidene groups to an electrophilic double bond (for example, C=O) with formation of a three-membered ring.[138,139] The stable anion of *N*-arenesulfonylsulfenamide is the leaving group, the elimination of which leads to the formation of a three-membered ring, which also promotes the occurrence of this process.



The introduction of the methylthiomethyl group into the ring of phenols with the aid of *N*-arenesulfonyl-*S*,*S*-dimethylsulfilimines is used in the synthesis of benzylmethyl sulfides.[139,140]

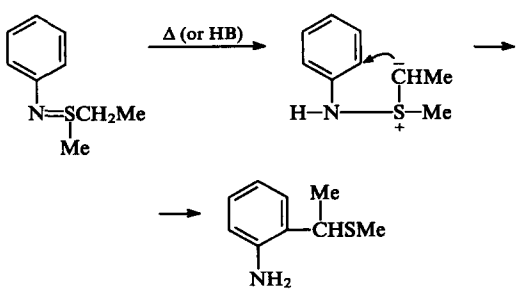


The conversion of the vinyl sulfide $ArSCH=CH_2$ into $ArSCH=CHR$ via the corresponding sulfilimine by means of a Michael type reaction using organomagnesium compounds has been described.[141]

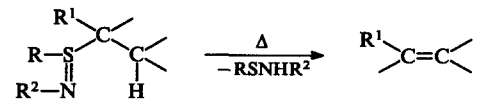


d. Rearrangements of sulfilimines

On heating and also on treatment with bases, certain *N*-arylsulfilimines undergo a Sommelet type rearrangement, which is used to introduce alkylthiomethyl groups into the *ortho*-position in anilines.[139]

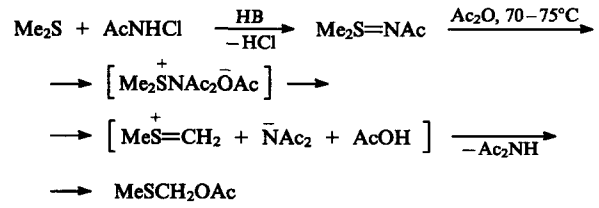


S-Alkylsulfilimines containing β-hydrogen atoms undergo on heating a rearrangement with formation of alkenes,[142] which can serve as one of the methods for the elimination of the sulfide group.



R^1 = H, Me; R^2 = Ar, MeCO.

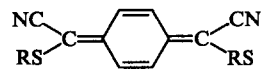
The Pummerer rearrangement of *N*-acylsulfilimines is used to convert dimethyl sulfide into acetoxymethyl methyl sulfide.[1]



VII. Practical applications of sulfides

1. Sulfides in macromolecular chemistry

Sulfides are used in macromolecular chemistry in several ways. One of these involves the employment of sulfides as monomers. As a rule, in this case sulfides contain, apart from the sulfide group, unsaturated bonds or other functional groups which participate directly in the formation of the polymer chain as a result of polymerisation or polycondensation reactions.[143] Thus a series of homopolymers and copolymers containing sulfur atoms in the main chain have been obtained from divinyl sulfide.[144] The synthesis of 7,8-bis[alkyl(aryl)thio]-7,8-dicyanoquinodimethanes having the general formula



R = Et, Bu^t, Ph,

has been described and their reactions have been investigated.[145] For R = Et, the polymerisation proceeds via radical, anionic, and cationic mechanisms with formation of a polymer having an ethylthio-group in the side chain, for R = Ph it proceeds via radical and anionic mechanisms, and for R = Bu^t the monomer does not polymerise, which the authors believe[145] to be due to a steric effect.

The synthesis of poly(phenylene sulfide) via the polycondensation of *o*- and *m*-di(chlorophenyl) sulfides with sodium sulfide in an organic solvent has been described in the patent literature.[146,147] Aromatic polythioesteramideimides with effective mechanical properties, a high heat resistance, and a high plasticity have been obtained by the polycondensation of the disulfide $NH_2C_6H_4SC_6H_4SC_6H_4NH_2$ with the monochloride of trimellitic acid and subsequent cyclisation of the polyamido-acid.[148] The synthesis of aromatic polyketones containing sulfur atoms in the main chain is based on the polycondensation of diphenyl sulfide and phosgene.[149] A new type of sulfide-formaldehyde polymer, capable of being cross-linked, has been obtained by the polycondensation of di(2-hydroxyphenyl) sulfide and formaldehyde.[150]

A second application of sulfides in macromolecular chemistry involves their participation in the regulation of polymer formation processes. It has been noted,[151] for example, that the sulfides $PhCH_2SR$ and $C_6H_4(CH_2SR)_2$ are inifers of the radical polymerisation of styrene. The principle of the action of such

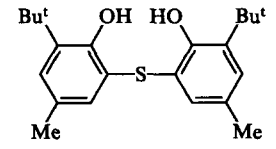
inifers consists in the initiation of the radical polymerisation and transfer of the polymer chain in the concluding stage of the polymerisation reaction, which leads ultimately to a linear dependence of the number-average molecular weight of the polymer on the polymerisation time. The influence of sulfides on the cationic polymerisation of vinyl ethers initiated by UV light and sulfonium salts,[152] the rate of which diminishes with increase in the nucleophilicity of the sulfide, has also been noted.

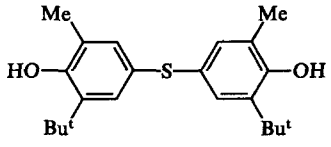
2-Benzothiazolyl 2,4-dinitrophenyl sulfide has found extensive application in the manufacture of white and light-coloured rubbers as a vulcanisation accelerator which does not induce additional vulcanisation.[153]

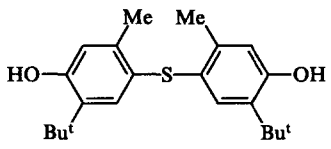
The third application of sulfides in macromolecular chemistry is the stabilisation and protection of polymeric materials against the negative influence of various factors (light, heat, oxygen, etc.) For example, dialkyl sulfides decompose the peroxides formed in the oxidative degradation of polymers without the formation of free radicals, which is very important for the arrest of oxidative degradation.[154,155] These compounds are very effective in mixtures with other stabilisers, in particular stabilisers of the phenolic or amine types.

The mutual intensification of the protecting effect can be explained by the fact that one of the stabilisers terminates the degradation process, giving up hydrogen to the peroxyl radicals, while the other decomposes hydroperoxides. Dialkyl and diaryl sulfides mixed with other substances are effective stabilisers of vinyl polymers, polyolefins, and poly(vinyl acetals).

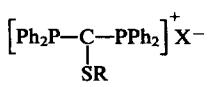
Diaryl sulfides containing hydroxy- and alkyl groups in the aromatic rings have found an application as stabilisers of rubber, protecting it against the effects of oxygen and heat.[156]







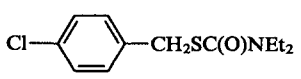
Phosphorus-containing sulfides are effective antipyrenes, which protect polymeric materials against combustion.[25]



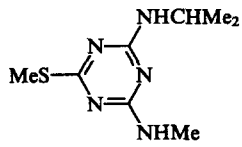
X = SO_4, BF_4, $AlCl_4$.

2. Biological activity of sulfides

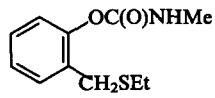
A whole series of compounds containing the sulfide group are used in agriculture as effective pesticidal preparations.[157] For example, 2-chlorobenzyl-2-chlorophenyl sulfide, known under the commercial name chlorbenzid or chlorocid, is used as an effective acaricidal preparation against plant ticks on fruit. Benthiocarb



and desmetryn



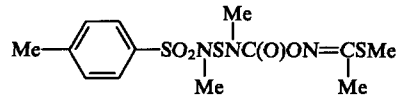
are used as herbicidal preparations to combat oat-like weeds. Ethiofencarb



is used as an insecticide against aphids. 2-Benzothiazolyl butyl sulfide is employed as a defoliant of the thin-fibre cotton plant.

Studies on the biological activity of sulfides have been directed in recent years both to the search for new and the modification of already known pesticides in order to reduce their toxicity to warm-blooded animals. For example, methomyl MeNHCOON=C(Me)–SMe and aldicarb MeNHCOON=CH–$(CH_2)_2$–SMe possess outstanding insecticidal and acaricidal properties, but are toxic to warm-blooded animals.[158]

It has been established for carbamates[159] that the substitution of a hydrogen atom at the nitrogen atom by an amino- or amidosulfenyl group lowers sharply their toxicity to warm-blooded animals whilst retaining and in certain cases actually intensifying their pesticidal activity. Several groups of investigators therefore undertook studies on the synthesis of aminosulfenylated derivatives of methomyl, aldicarb, and ethiofencarb.[159–167] Apart from *N*-amino(amido)sulfenylated derivatives of methomyl,[168–173] aldicarb,[174] ethiofencarb,[25] and their analogues, these studies led to the synthesis also of a whole series of *N*,*N*′-dicarbamoyl sulfides[175–178] and *N*-sulfenylated 2-(alkylthiomethyl)phenyl-*N*-alkylcarbamates[179] with insecticidal activity. The above studies also made it possible to obtain an insectoacaricidal preparation with systemic activity, a better phytotoxicity than methomyl, and an effectively long duration of activity.[180]



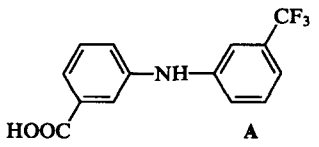
A series of biologically active sulfides which are potential pesticides have been synthesised in recent years. For example, it has been noted[69] that the sulfides 2-$NO_2C_6H_4SCH_2NO_2$ and (2-$NO_2C_6H_4S)_2CHNO_2$ exhibit a relatively high nematocidal activity and an insectoacaricidal activity against the beetroot aphid. The sulfides 4-$NO_2C_6H_4SCH(CN)_2$, 2,4-$(NO_2)_2C_6H_3SCH(CN)_2$, and 2-$NO_2C_6H_4SCH(COMe)_2$ possess a relatively high insectoacaricidal activity in relation to the rice snout-beetle and the arachnoid tick.[68]

3. Sulfides as pharmaceutical preparations

One of the important properties of medicinal preparations is solubility in lipids, its increase enhancing their effectiveness (by facilitating their transport in the organism and their permeation through membranes and by increasing their concentration in lipid regions).[181,182] The solubility of medicinal preparations can be increased by introducing into their molecules lipophilic groups, the relative lipophilicity of which is characterised by Hantzch's π constants. According to literature data,[183,184] these constants for certain groups have the following values: 1.44 (SCF_3), 1.28 (SCF_2Br), 1.23 (C_2F_5), 1.04 (OCF_3), 1.01 (OCF_2Br), 0.88 (CF_3), 0.68 (SCF_2H), 0.61 (SMe), 0.58 (OCF_2H), 0.56 (Me), 0.55 (SO_2CF_3).

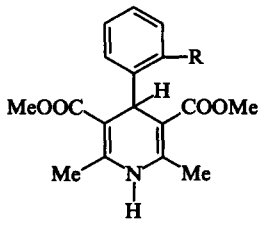
As can be seen from these data, the trifluoromethylthio-group exhibits a fairly high lipophilicity and its introduction into the molecules of medicinal preparations should evidently increase their effectiveness.

This hypothesis has been to some extent confirmed by the introduction of the trifluoromethylthio-group and other lipophilic groups in various positions in the benzene ring A of flufenamic acid.[182]



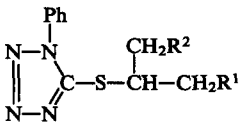
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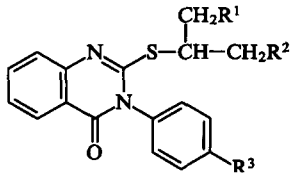
It was found that the sulfide formed as a result of the introduction of the trifluoromethylthio-group has a lower anti-inflammatory activity than flufenamic acid, but is superior to the latter in its antiproteinase activity. The antiproteinase activity of derivatives of flufenamic acid increases in the following sequence of substituents $HF_2CO < CHF_2SO_2 < CF_3 < SCF_3$, which corresponds approximately to the increase in their lipophilicity. Especially interesting results have been obtained following the introduction of the above substituents in the *ortho*-position in the benzene ring of 4-phenyl-1,4-dihydropyridine.



Such preparations exert a powerful effect on the cardiovascular system and are antagonists of calcium ions.[182]

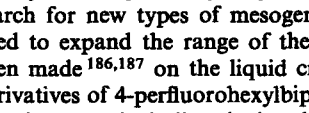
Certain sulfides, in particular those containing the tetrazole and pyrimidine rings, have radioprotecting properties.[185]





4. The liquid crystal properties of sulfides

Organic compounds forming liquid crystals have found extensive applications in the reproduction and recording of information in various branches of science and engineering. Such compounds have the ability to generate, on heating and cooling in the range between the liquid crystal state and the isotropic liquid melt, intermediate smectic and nematic mesophases which differ in the degree of molecular order.[182] Derivatives of various classes of organic compounds, the molecules of which have a linear shape and have largely a structure of the same type, possess the properties of liquid crystals. These compounds (mesogens) contain a central rigid fragment, consisting of a conjugated aromatic or bridged system, and also end groups of different nature (alkyl, alkoxy-, alkoxycarbonyl, cyano-, nitro-groups, etc.). In the search for new types of mesogens and in connection with the need to expand the range of their characteristics, studies have been made[186,187] on the liquid crystal properties of a series of derivatives of 4-perfluorohexylbiphenyl containing various functional groups, including the butylthio-group in the *para*-position in the second benzene ring.



X = H, CN, NHBu, SBu.

It has been established that the introduction of the strong electron-donating butylamino-group ($\sigma_n = -0.60$) leads to the appearance of a liquid crystal phase of the more ordered smectic type with an increased thermal stability. When the butylamino-group is replaced by the less electron-donating butoxy-group ($\sigma_n = -0.32$), the formation of a liquid crystal phase of the smectic type is nevertheless still ensured. On further weakening of the electron-donating properties of the substituents and, in particular, following the introduction of the butyl group ($\sigma_n = -0.16$) and the butylthio-group ($\sigma_n = 0.03$), the mesogenic property vanishes.

* * *

It is seen from the present review that the use of sulfides as synthons in fine organic synthesis has undergone in recent years considerable expansion based on the characteristic features of the reactivity of sulfides—the high lability of the C–S bond. The sulfide group can be replaced by a hydrogen atom and hydroxy-, alkyl, alkoxy-, thiyl, and other functional groups. The thermal and photolytic cleavage of the C–S bond leads to the formation of highly reactive intermediates, which are used in the synthesis of various cyclic adducts. A characteristic feature of the reactivity of sulfides, which is of great synthetic importance, is their tendency to form α-sulfenylcarbanions, which are used widely in multistage organic syntheses for the formation of carbon–carbon bonds. The ease of the conversion of sulfides into sulfonium, ylide, sulfoxide, and sulfilimine intermediates is also used widely in multistage organic syntheses for the transfer of various groups to an electrophilic double bond, for the formation of a carbon–carbon double bond, and for other transformations.

The practical applications of sulfides in macromolecular chemistry, in agriculture, in pharmaceutical industry, and in other fields of human activity are no less important and this too has been reflected in the present review.

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