# Key reactions of Organosulfur Compounds

(Students references)

Organosulfur compounds and reactions

Sulfur has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^4$. Sulfur exists in acyclic and cyclic S_n species or allotropic form owing to have a marked tendency to react with itself (catenation). The sulfur-sulfur bond in elemental sulfur is probably a resonance hybrid for which S_8 ring exists in the energetically favoured crown shape. All the chain and ring forms of sulfur are thermodynamically less stable than cyclooctasulfur (S_8) at 25°C.

Saturated hydrocarbons can be dehydrogenated by heating with sulfur. For example, cyclohexane is converted to benzene.
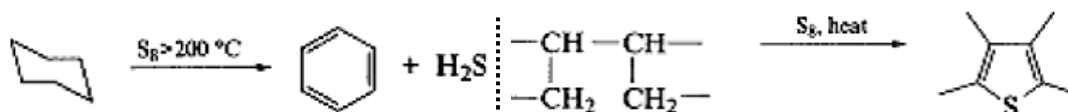

Sulfur, like most elements in the second and higher rows of the periodic table, is reluctant to form normal π-double bonds; thus, thiocarbonyl (C=S) compounds are comparatively rare and are usually unstable with a tendency to polymerise. This is a result of the relatively low effectiveness of pπ-dπ bonding involving lateral overlap of the 3p-orbitals and arising from the larger size of the sulfur atom as compared with carbon.

The sulfur atom (atomic radius 1.02Å; 1 Å = 0.1 nm) is larger than oxygen (atomic radius 0.73 Å). Sulfur is consequently more polarisable than oxygen; the sulfur lone pairs of electrons are better nucleophiles but weaker bases in reactions with acids. The outer electronic shell in sulfur contains not only s-electrons and p-electrons but also vacant 3d-orbitals which can be utilised in bonding.

The 3p orbitals of sulfur are too large to overlap effectively with 2p orbitals on oxygen or carbon. There is little pi character in the S-O bonds of dimethylsulfoxide and dimethylsulfone indicating mostly a single bond character in S-O bond. A sulfoxide can be viewed like a carbocation. The LUMO resembles σ_{sc}^*.
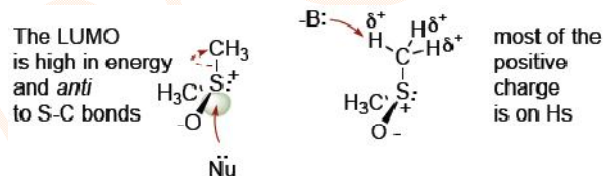

The little pi character in the S-O bonds of sulfoxides and sulfones suggests that both sulfoxides and sulfones have fewer propensities to be in conjugation with double bond than that of enones, ethers and thioethers.
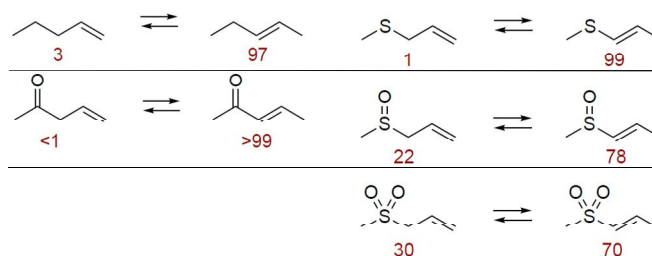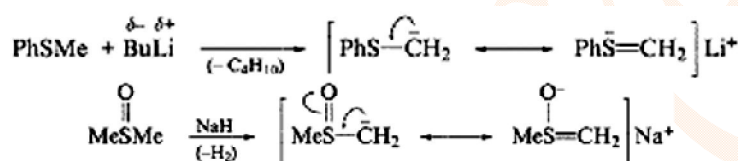
# Organosulfur compounds and reactions

The little pi character in the S-O bonds of sulfoxides can also explain the acidity difference between ketone and dimethyl sulfoxide. The stability of conjugate base derived from ketone is much stable than that of sulfoxide.


| | pKa | 20 | 35 | | pKa' | 45 | 35 | 31 |
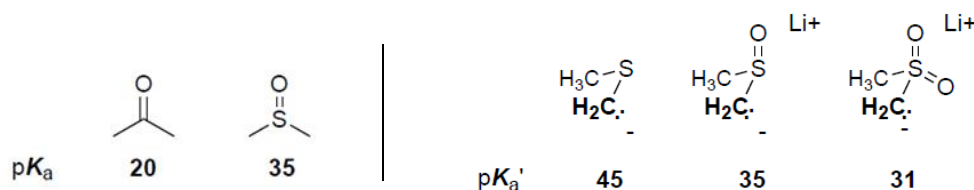
The carbanions are generated using following reactions

Similarly, the S=O of sulfoxide is 10^5 times more basic than a C=O of ketone. The conjugate acid of former is more stable than that of a ketone.

pKa   -7.2   -6.5   -1.8
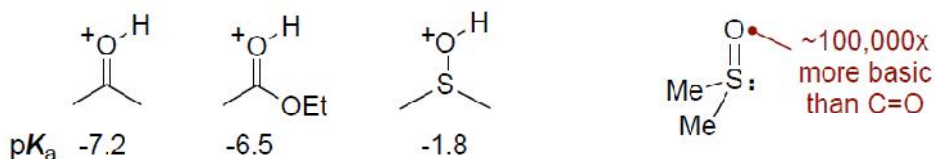
The lone pairs of sulfur on thioethers (RSR) are more nucleophilic than that on sulfoxides (RSOR). That means it can be stopped the oxidation of sulfides at sulfoxides without over-oxidizing to sulfones.
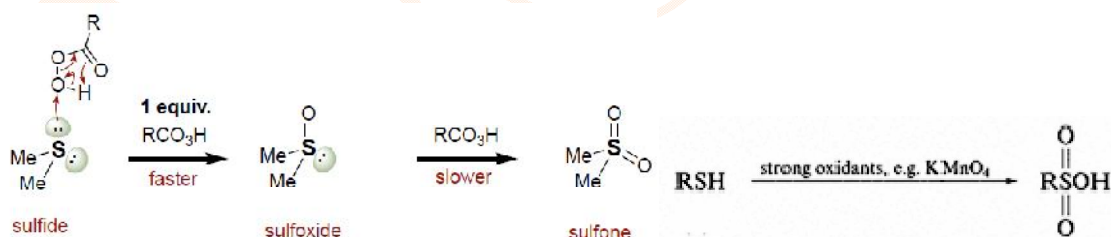
Sulfoxides possess a non-planar pyramidal configuration. Chiral sulfoxides can exist as optical enantiomers. For example, the structures of ethyl methyl sulfoxide are illustrated below. The presence of chiral centre in organosulfur compounds can be resolved into optically active forms.
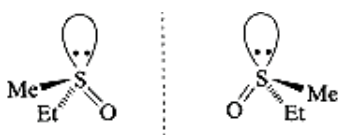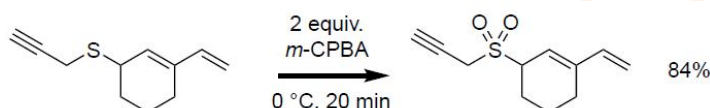
Organosulfur compounds and reactions

The oxidation of 4-ter/-butylthiane has been attributed to thermodynamic or kinetic control forming geometric isomers.
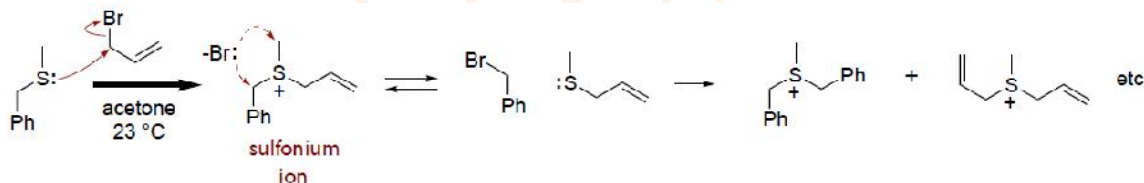

Thioether oxidation is faster than epoxidation. This indicates that the second oxidation from sulfoxide to sulfone is also faster than epoxidation of alkene.


However, sulfoxide lone pairs aren't much nucleophilic as the higher temperature is required for converting sulfoxonium ion.


The sulfonium ions are formed by following way.

The C=S bond isn't highly polarized and sulfur atom acts as electrophilic centre in C=S bond. With two phenyl substituents on the thioketone, the nucleophile adds to sulfur, not carbon, to generate a carbanion.
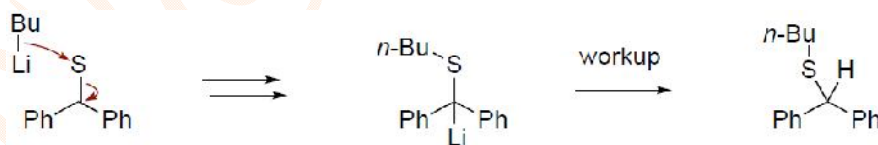

The oxygen contains lot of negative charge and becomes a hard nucleophile. It reacts more rapidly than sulfur with "hard" electropositive electrophiles. The HOMO is larger on sulfur. "Soft" electrophiles with low-lying LUMOs and little positive charge react fastest on sulfur.
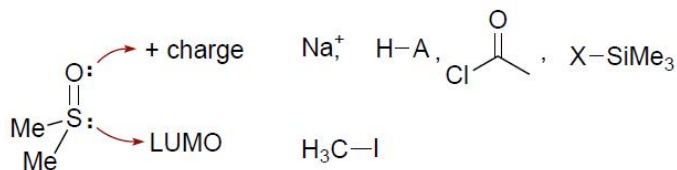
Organosulfur compounds and reactions

Sulfur compounds may also act as nucleophiles; they are better nucleophiles than their oxygen analogues and generally react faster. The formation of 2-ethylthioethanol involves selective nucleophilic attack by the mercapto (SH) moiety while the hydroxy group remains intact, showing that the former is a more powerful nucleophile.

$$Et-Br + H\overset{..}{S}CH_2CH_2OH \xrightarrow[\text{(-HBr)}]{NEt_3,\ DMSO} EtSCH_2CH_2OH$$
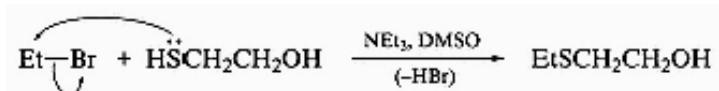
The carbon–sulfur bond formations represent a class of reactions in biological processes such as

i) an initial C–S bond formation between bisulfite and phosphoenolpyruvate to synthesize coenzyme M in methanogenic bacteria.
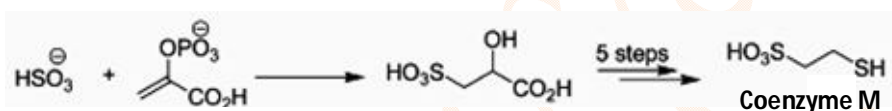

ii) the metabolism of toxic acrylamide in heated food by the **sulfa-Michael addition** (SMA) of glutathione to 1,4 addition of acrylamide double bond.
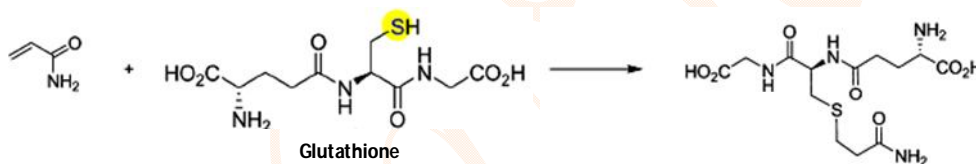
Sulfonation of aryl group using concentrated sulfuric acid results in the formation of synthetic detergents with n= 9-15 which has the advantage over ordinary soap sodium stearate, $C_{17}H_{35}CO_2Na$, that they do not produce scums when used in hard water because the calcium and magnesium sulfonates are more soluble.
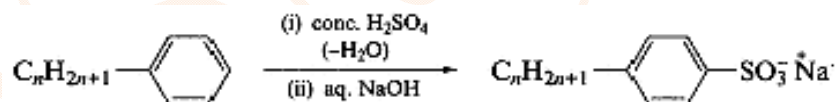

Many commercial dyes including congo red contain one or more sulfonic acid groups to confer water solubility to the dye and assist in binding the dye to the polar fibres in the textile (cotton, nylon, silk, wool, etc.).
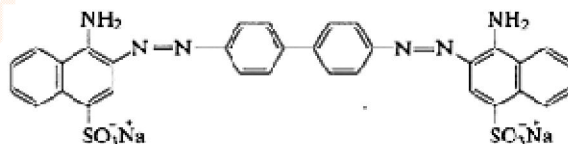
Organosulfur compounds and reactions
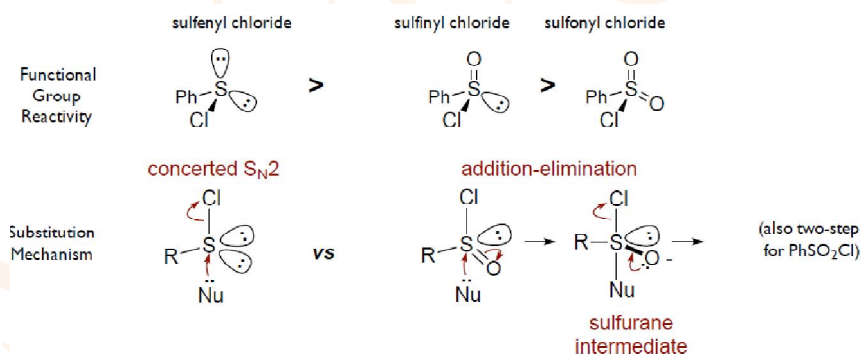
Protection of –OH group

There is a contrast in mechanisms for sulfonylation under the two most typical conditions: TsCl/pyridine vs. MsCl/Et$_3$N.
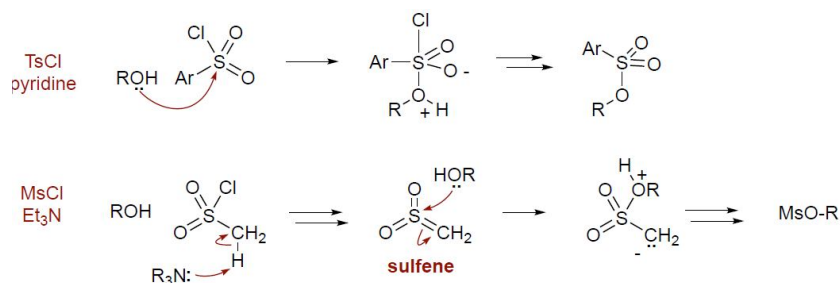

Sulfenylating reagents lead to episulfonium ion intermediates. Heat reverses the reaction. RSOCl and RSO$_2$Cl don't react with alkenes.

Contrast the electrophilicity and mechanisms for substitution

The *slow attack at RSO$_2$X sulfur* otherwise indicates why tosylate and mesylate are good leaving group for S$_N^2$. There is also peculiar reactivity of sulfuryl chloride (SO$_2$Cl$_2$) which is not at all like thionyl chloride (SOCl$_2$).
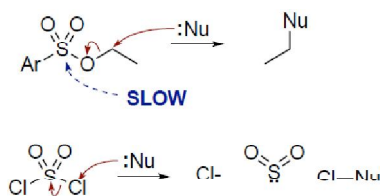
# Organosulfur compounds and reactions

Pummerer reaction

The classical Pummerer reaction involves the reaction between chiral sulfoxide (geometry with one lone pair) and acetic anhydride in presence of a base. A sulfoxide containing at least one α-hydrogen atom is reduced to a sulfide with concomitant oxidation at the α-carbon atom. The Pummerer rearrangement is generally effected by treatment of the sulfoxide with acetic anhydride to yield the corresponding α-acetoxy sulfide. The reaction pathway is shown below. The elimination step is often depicted as a concerted E_2 process.

Pathway:
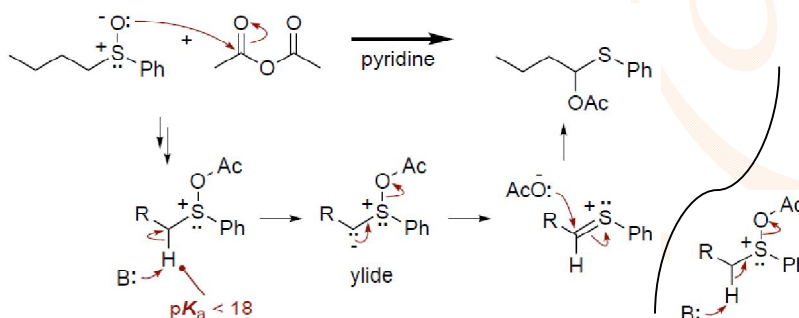
In the classical Pummerer reaction, a proton α- to the sulfur of sulfonium species 1 is abstracted and nucleophilic attack leads to α-substituted sulfides. As the nucleophile attacks a position which was previously nucleophilic in the sulfoxide starting material, this can also be considered an Umpolung process.
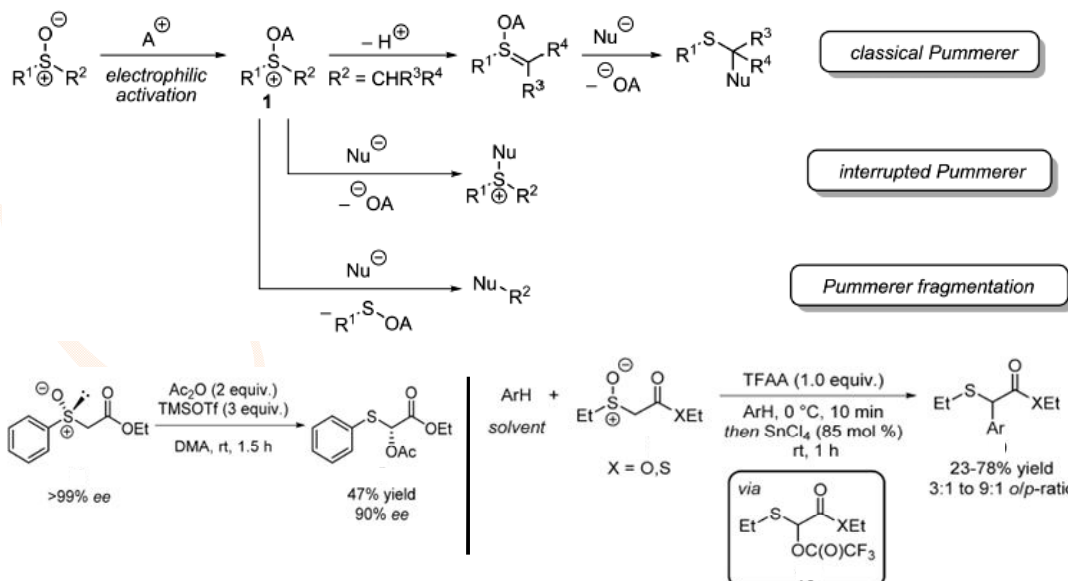

In the aromatic Pummerer reaction, if an acidic hydrogen on a substituent (-OH, NH, CH group) is at *ortho* or *para* position, the nucleophilic attack will occur in *meta*-position to the sulfoxide, otherwise *ortho*- or *para*-substitution is observed.

Organosulfur compounds and reactions
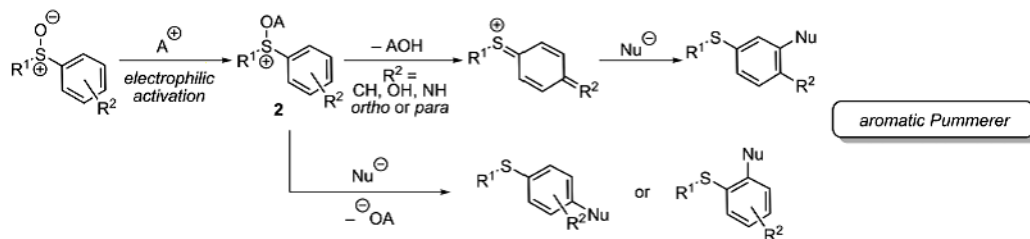
In vinylogous Pummerer reaction, an activated vinyl sulfoxides tender deprotonation of the γ-position followed by nucleophilic addition to the same carbon. Direct nucleophilic attack on the double bond leads to extended Pummerer reaction and further nucleophilic attack to the α-position of this intermediate results additive Pummerer reaction.
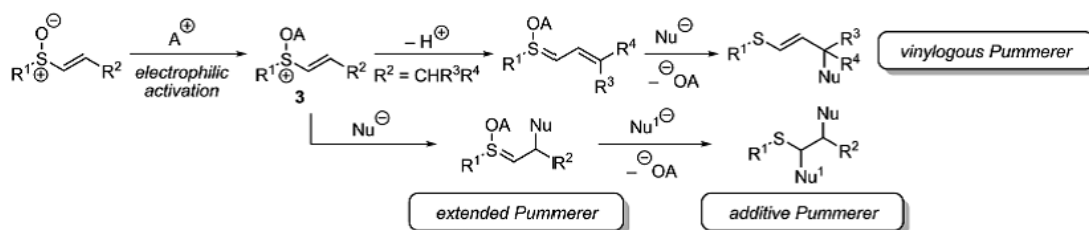

The intermediate acylsulfonium ylide which rapidly decomposes to sulfur-stabilised carbocation is trapped suitably placed electron-rich centre.
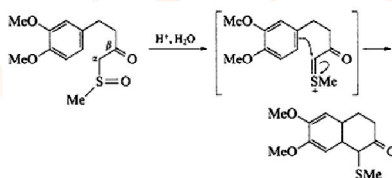

Julia Olefination (Julia-Lythgoe Olefination)

It is a conversion of sulfone to olefin. The sulfone containing α−H undergoes reaction with carbonyl groups to form an adduct in the presence of base (usually alkyl lithium). The adduct is treated with acetic anhydride to afford acetyl derivative that proceeds reductive elimination in the presence of sodium amalgam to form alkene. The reaction affords high stereoselectivity (E)-alkenes.
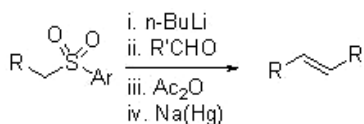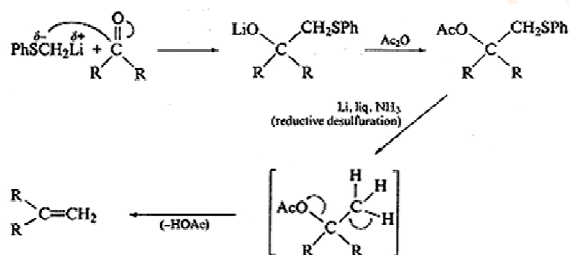
# Organosulfur compounds and reactions
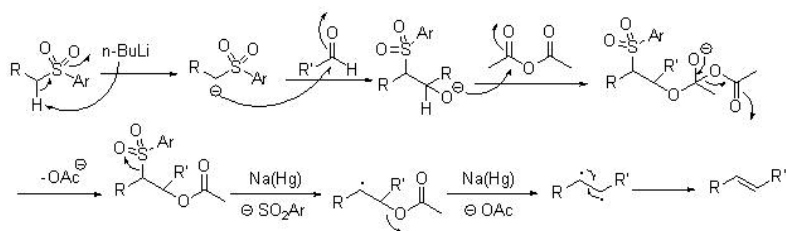
Analogous method: Carbonyl ⟶ Alkene

Use of sulfenyl carbanions in the formation of new carbon-carbon bonds under mild conditions is achieved by reaction of the carbanion with a ketone and reductive desulfuration of the intermediate acetoxy sulfide to produce the alkene.
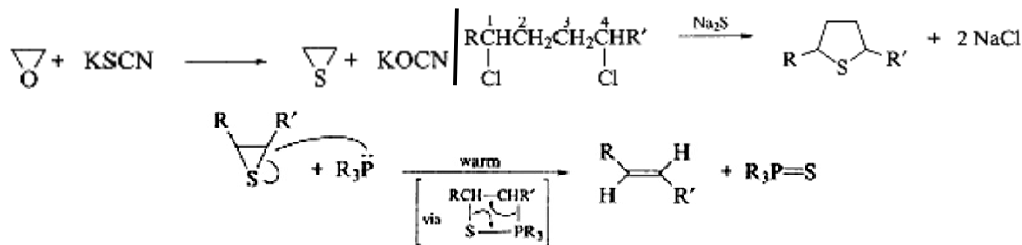

Alkene formation

Treating with moist silver oxide (AgOH), sulfonium salts are converted into the corresponding sulfonium hydroxide which on heating undergoes a bimolecular (E_2) elimination reaction obeying the Hofmann rule.
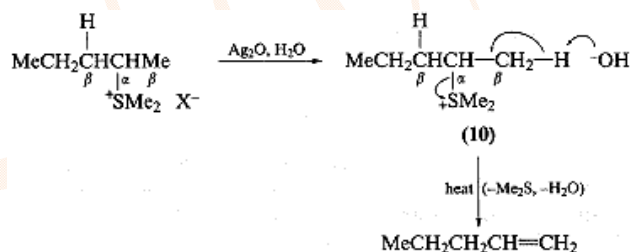

Episulfide ⟶ Alkene

Cyclic sulfide (or Episulfides) is converted to alkenes by treatment with phosphorus (III) compounds, like triphenylphosphine. The reaction occurs via a four-centre T.S analogous to that involved in the Wittig reaction.
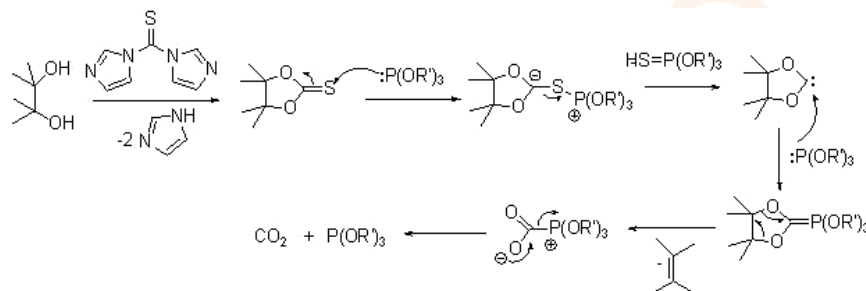
Organosulfur compounds and reactions

Corey-Winter Olefination

This method is an effective route for the transformation of 1,2-diol to alkenes. The reaction includes a cyclic thiocarbonate intermediate followed by a reaction with phosphorus reagent via a syn elimination to afford alkene.
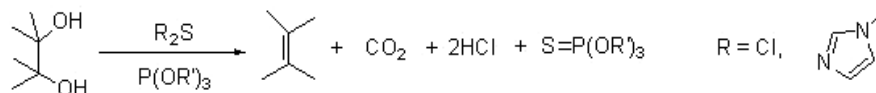

Mechanism

Reaction of sulfur Ylide: Corey-Chaykovsky Reaction

Mainly two types of sulfur ylides are extensively used in organic synthesis: i) diemthylsulfonium methylide which is unstabilized ylide and ii) dimethyloxosulfonium methylide which is stabilized ylide. These reagents are called *Corey-Chaykovsky reagents*.


Unstabilized sulfonium ylide

stabilized sulfonium ylide
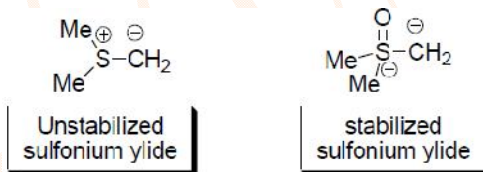
A condensation reaction of diemthylsulfonium methylide with aldehydes or a ketone occurs through nucleophilic addition which subsequently proceeds via an intramolecular nucleophilic substitution to give an **epoxide**. In case of α, β -unsaturated compounds, diemthylsulfonium methylide gives **epoxide** whereas stabilized dimethyloxosulfonium methylide provides **cyclopropane**. Dialkylsulfoxonium ylides are less reactive than dialkylsulfonium ylides.
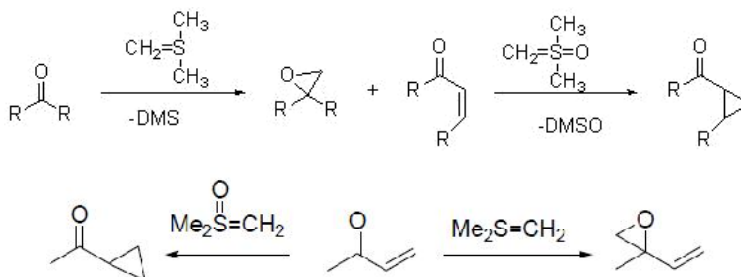
Organosulfur compounds and reactions

Unlike in Wittig ylides to form P=O double bond as the driving force of Wittig reaction, the sulfur ylides govern the leaving aptitude of the leaving group (Me₂S or DMSO) owing to lower stability of the sulfur-oxygen double bond.
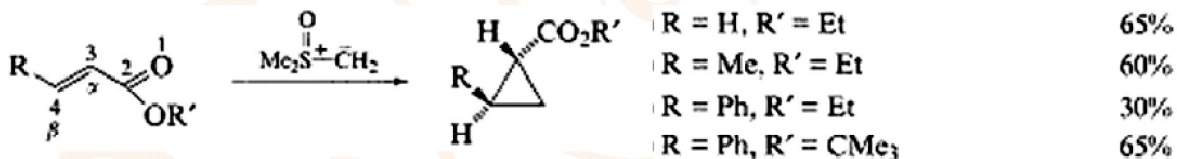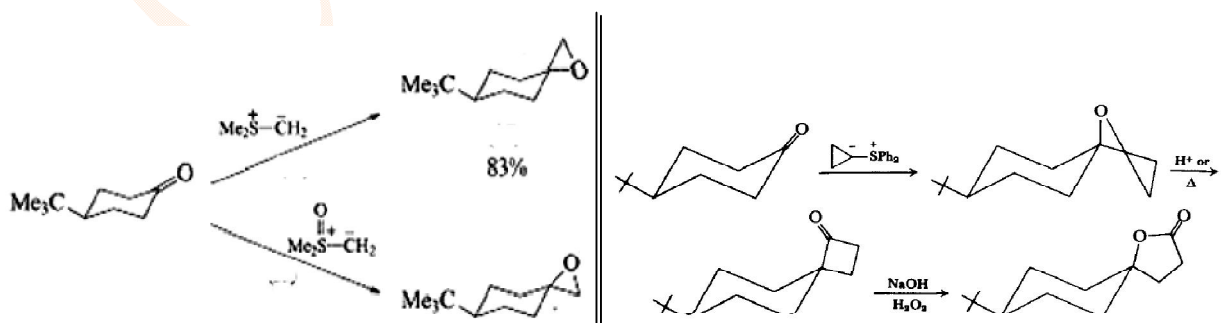
Mechanism
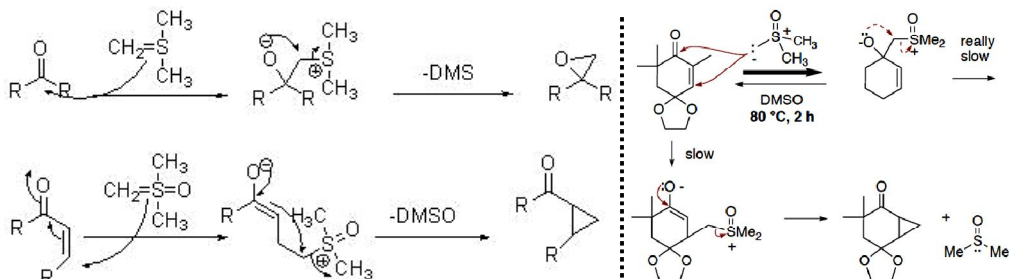
Sulfoxonium ylides are less basic and it also produces epoxide by the reaction with aldehyde or ketone.
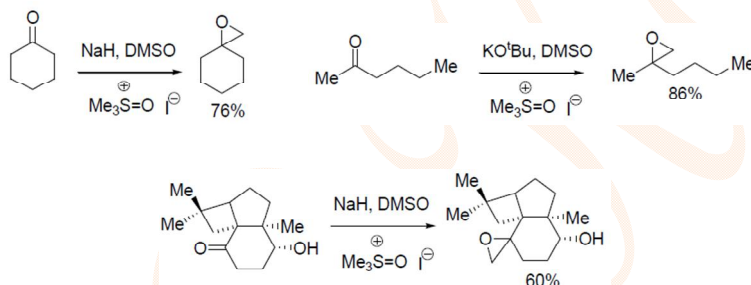
Small R groups on the β-carbon atom permit facile conjugate addition leading to good yields (60–65%) of the corresponding cyclopropane derivatives.


|	
R = H, R' = Et	65%
R = Me, R' = Et	60%
R = Ph, R' = Et	30%
R = Ph, R' = CMe₃	65%

More reactive and smaller size of sulfonium ylides reacts with rigid 4-t-butylcyclohexanone very quickly by axial attack to form mainly the kinetically controlled epoxide whereas large size of sulfoxonium ylide reacts at slow rate from equiatorial side to yield thermodynamically controlled epoxide.
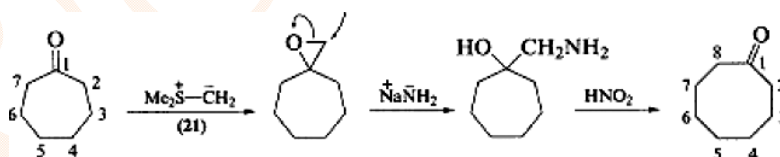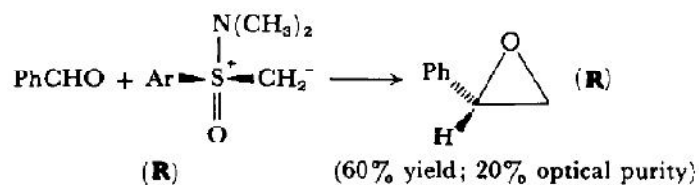
Organosulfur compounds and reactions

S-ylide	Ratio
$(CH_3)_2\overset{+}{S}(O)\overset{-}{C}H_2$	2.3:1
$(CH_3)_2\overset{+}{S}\overset{-}{C}H_2$	1:15.7
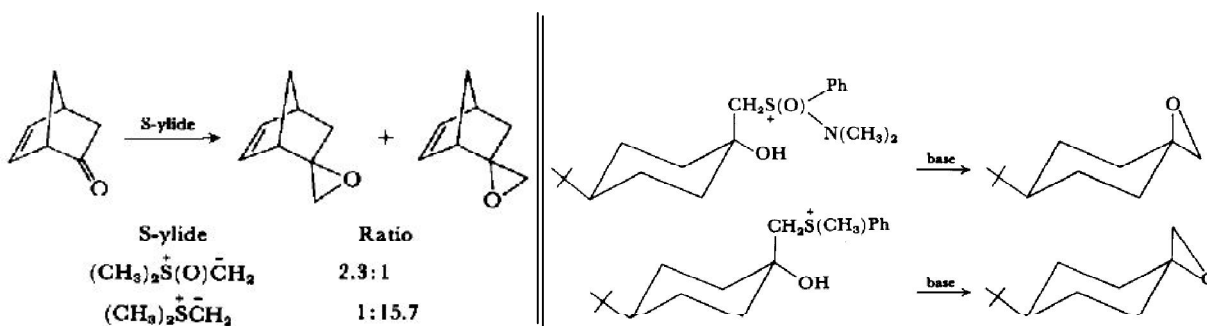
The cyclopropanation reaction is greatly facilitated by electron withdrawal from the alkenic double bond.

Cyclohexenone	Ylide	Product	Cyclohexenone	Ylide	Product
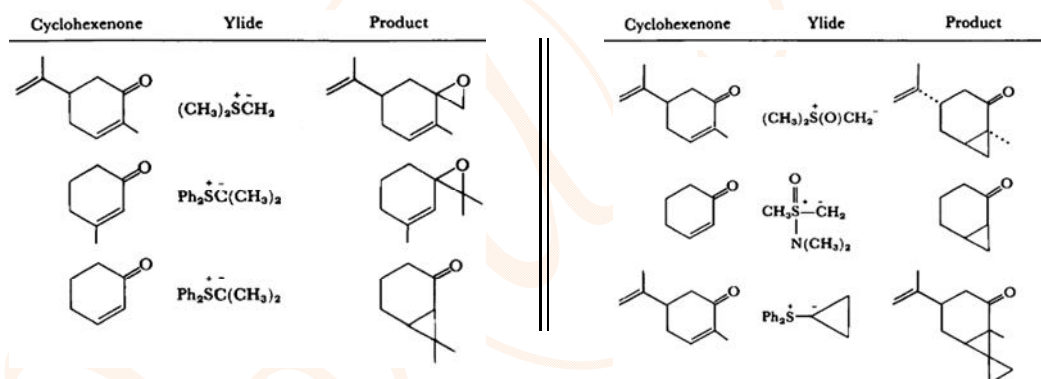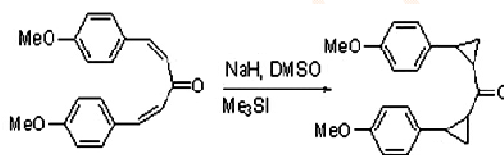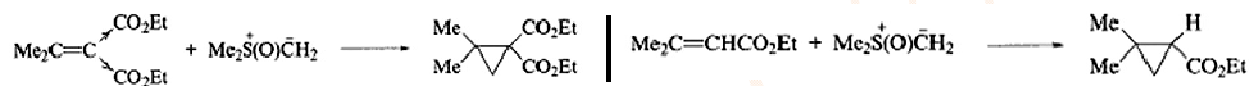
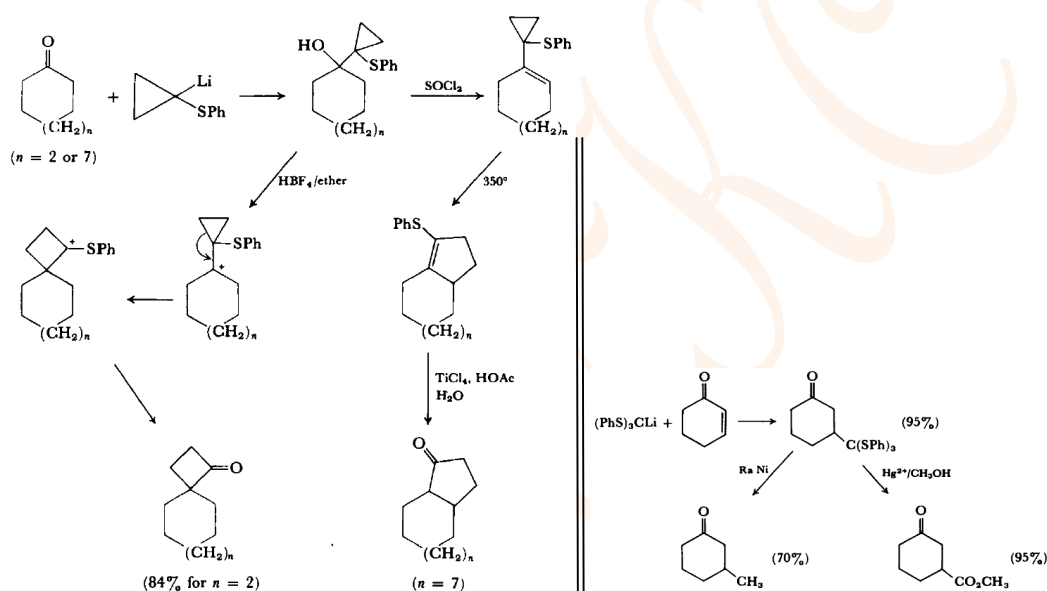**Ring expansion**

Stereochemistry
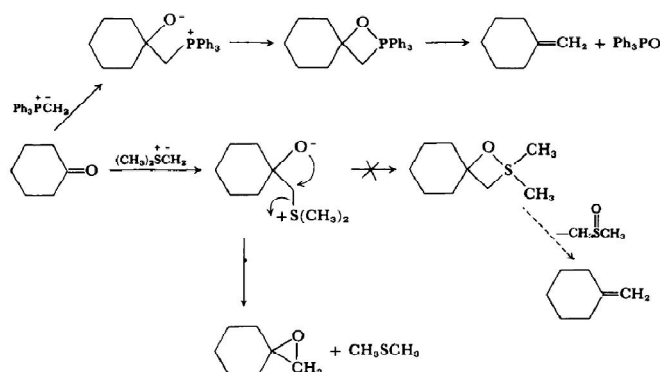

(60% yield; 20% optical purity)

Organosulfur compounds and reactions

## Reaction of sulfur containing carbanion to carbonyl

---

Reaction with Dimsyl anion

DMSO is a weak acid and with strong bases (NaH, Ph₃C) yields dimsyl anion or dimsylsodium. Dimsyl anion is very reactive nucleophile and the sulfoxide adduct can be removed by reduction or thermally. It reacts with or ketone to give epoxide. However, with ester it yields β-ketosulfoxides.
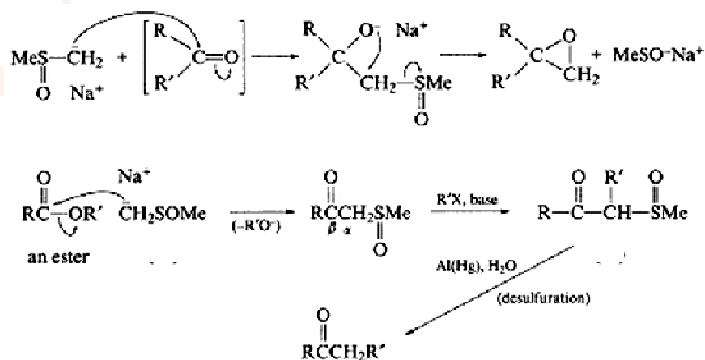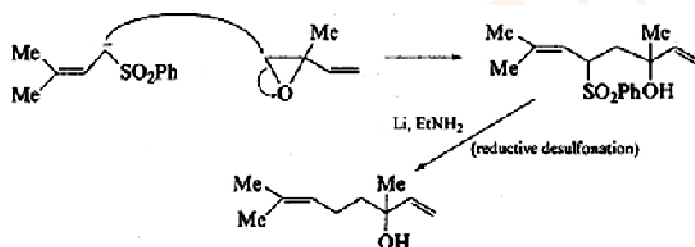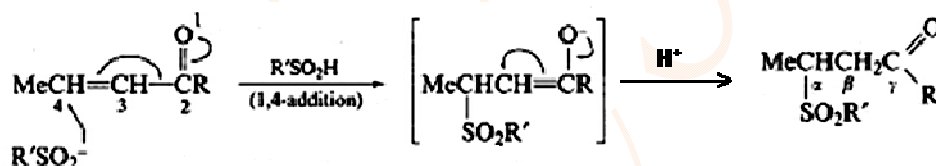
Organosulfur compounds and reactions
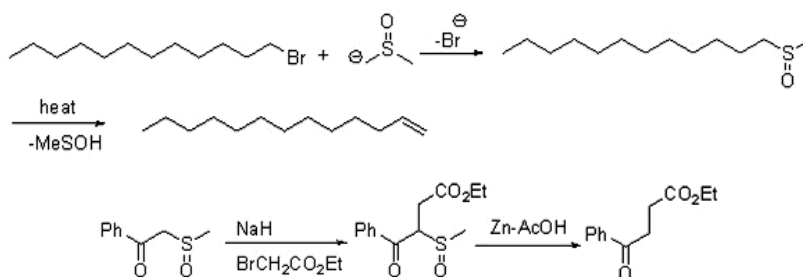
Reaction with Sulfonyl carbanions

Sulfonyl carbanions are more stable than sulfinyl carbanions. They can be alkylated and acylated at the α-carbon atom using organolithium bases.


1,4 addition of sulfones to α,β-unsaturated carbonyl compounds forms γ-ketosulfones.

Smiles rearrangement

Sulfonyl carbanion undergoes an intramolecular rearrangement in which ArO⁻ group acts as the nucleophile and the SO₂Ar is the leaving group provided the *ortho*-position being activated by the electron-withdrawing nitro group. A specific example is cited for the conversion of 2-hydroxy2'-nitrodiphenyl sulfone to diphenyl ether sulfinate.

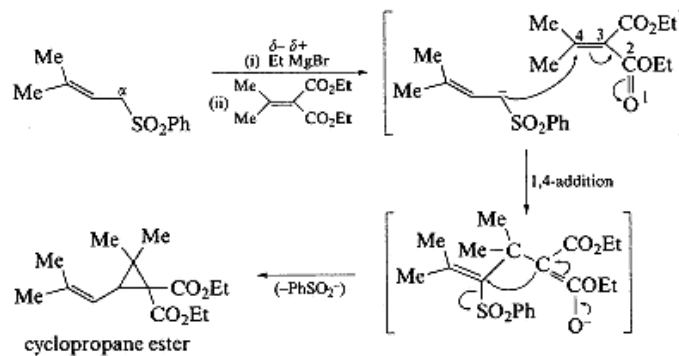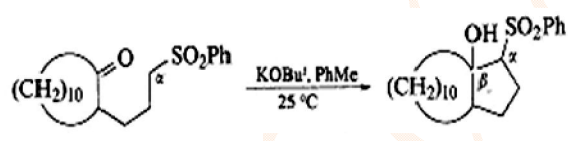**Example**
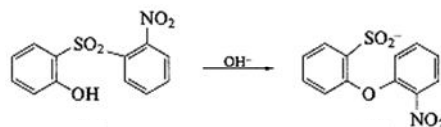
Cyclopropyl ester

Sulfonyl carbanions undergoes Michael addition with α,β-unsaturated esters followed by intramolecular elimination of the benzenesulfinate anion providing a useful preparation of cyclopropane esters.
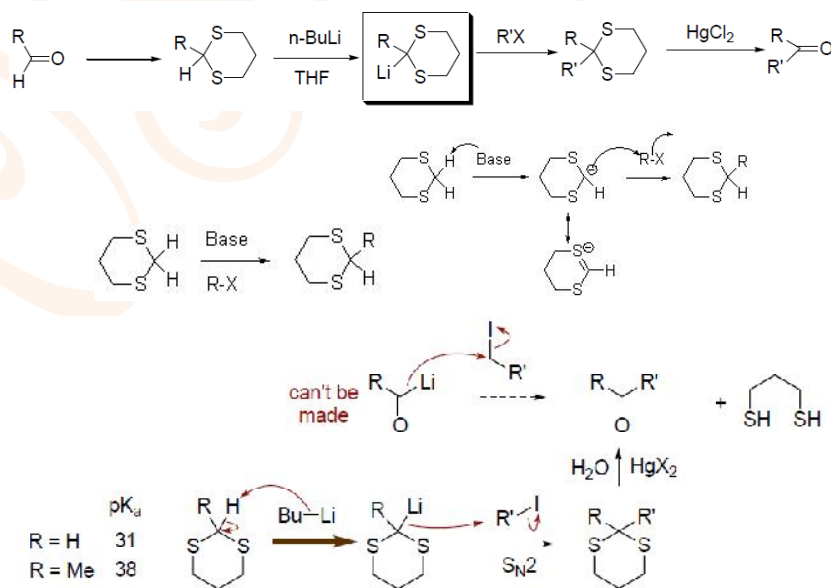
Organosulfur compounds and reactions


Intramolecular cyclization

Corey-Seebach Reaction

Corey-Seebach reaction provides an effective route for the transformation of aldehydes to substituted ketones. The reaction is called as ***Umpolung reactivity***. The aldehydes readily reacts with 1,3 dithaian using acid catalysis to afford dithioacetal in which the acidic hydrogen of the acetal is removed by base such n-BuLi to generate the carbonanion which further reacts to alkyl, acyl, epoxide etc. groups resulting a ketone after hydrolysis with mercury(II) salt. The intermediate carbanion is stabilized by vacant d orbital of sulfur atom.

The corresponding 5-membered dithiolane anions can't be made efficiently due to fragmentation.
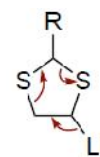
Organosulfur compounds and reactions

Examples:
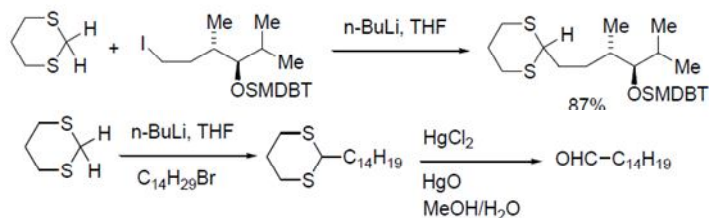
The addition of alkyl group to lithio dithiane occurs at equatorial position probably through the initial complex formation.

`

Corey-Nicolaou Macrocyclization

It is a macrolactonizations consisting the thioester formation from the carboxylic group and 2,2'-dipyridyl disulfide at room temperature which on reflux undergoes lactonization.

Mechanism

Organosulfur compounds and reactions

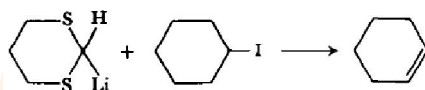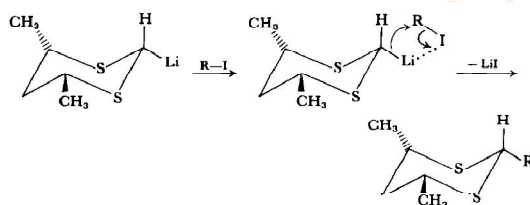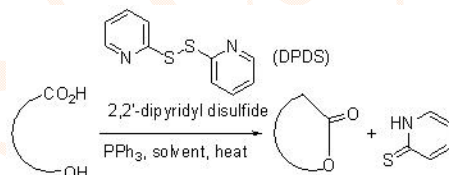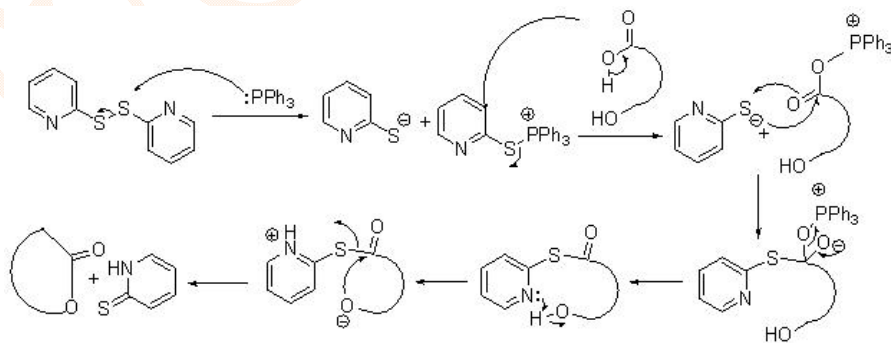## Sulfoxide Elimination

The carbonyl containing activated C−H bond or α−H reacts with diphenyl or dimethyl disulfide in the presence of a base to yield substituted sulfide that readily oxidizes to sulfoxide. The sulfoxide derivatives readily undergoes elimination on heating to give α, β - unsaturated carbonyl compound.
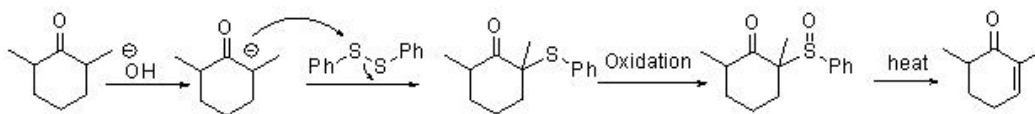
Corey-Kim oxidation

N-Chlorosuccinimide-dimethyl sulfide, prepared *in situ* from NCS and DMS, is used as mild oxidizing reagent and the reagent is called Corey-Kim reagent.
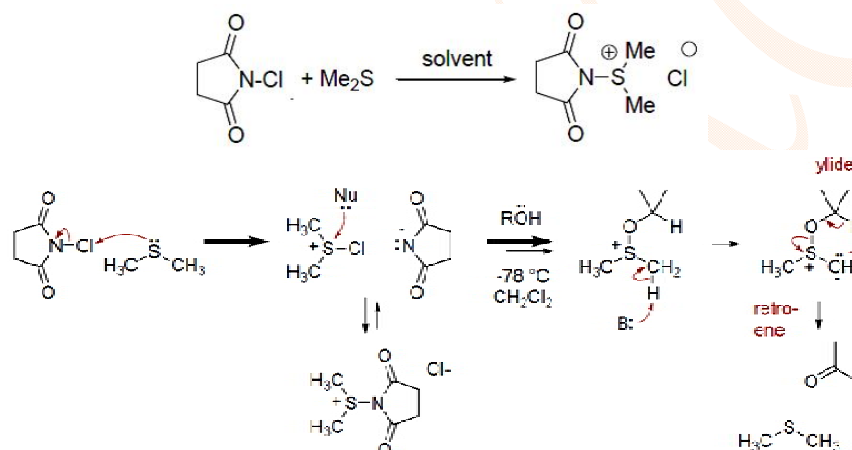
Examples:

Oxidation reaction

$$ArCOCH(OH)Ar \xrightarrow[\substack{\text{(a) } Ac_2O, 25° \\ \text{(b) } Ms_2O, -20°}]{DMSO} ArCOCOAr$$

(a) Ar = pCH$_3$OC$_6$H$_4$, 89%
(b) Ar = Ph, 99%

$$PhCH(OH)C(CH_3)_3 \xrightarrow[Ac_2O]{DMSO} PhCOC(CH_3)_3$$
$$(98\%)$$
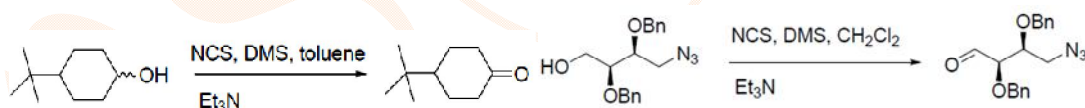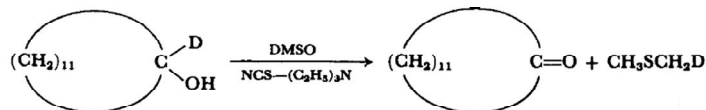
Organosulfur compounds and reactions

Reaction with thiocarbonyl

Thioketones are synthesized by the acid-catalysed reaction of ketones with hydrogen sulfide. The reaction is reliant on the temperature, nature of the solvent, concentration of the ketone and stability of the thioketone. Aromatic thioketones are rather synthesized by heating the corresponding ketones with phosphorus pentasulfide in boiling toluene, pyridine or xylene.

The pathway of the P_2S_5 mediate thiocarbonylation is depicted as follow:

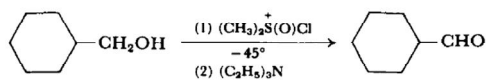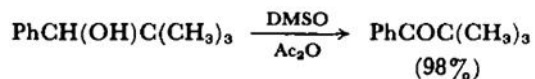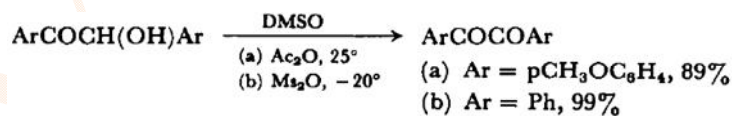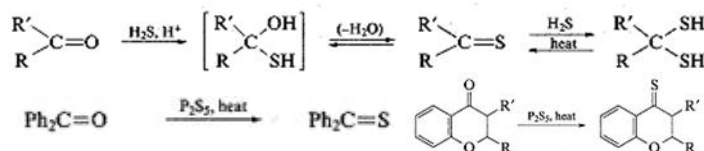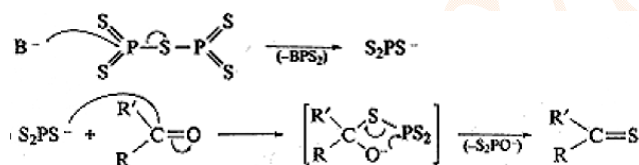Lawesson's reagent is prepared by heating anisole and phosphorus pentasulfide together in a 10:1 molar ratio. The ketone is heated with Lawesson's reagent in either boiling benzene or toluene to form thioketones. The completion of the reaction is understood until the evolution of hydrogen sulfide gas has ceased.

anisole · Lawesson's reagent
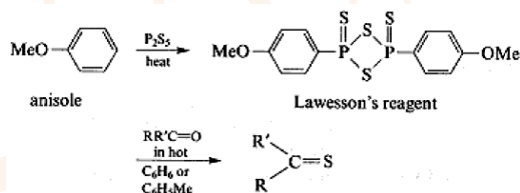
Some common reactions of thiocarbonyl are depicted below.
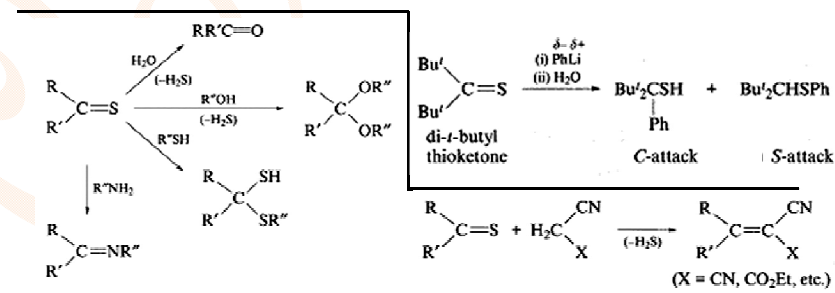
Aliphatic thioketones readily condense with active methylene compounds in a Knoevenagel-type reaction. Enolisable thioketones e.g thiocyclohexanone are easily methylated by treatment with diazomethane. Reaction of thiocarbonyl with diazomethabe yield episulfides.

Aliphatic thioketones such as di-t-butyl thioketone, the nucleophile attacks both the carbon and sulfur atoms, yielding a mixture of the products. It is contrast to carbonyl addition where C-Nu bond is formed.

Organosulfur compounds and reactions

Swern oxidation

In a mixture of dimethyl sulfoxide and oxalyl chloride, a primary alcohol is reacted at basic condition at -78 °C gives an aldehyde following simultaneous decarbonylation and decarboxylation.

Mechanism
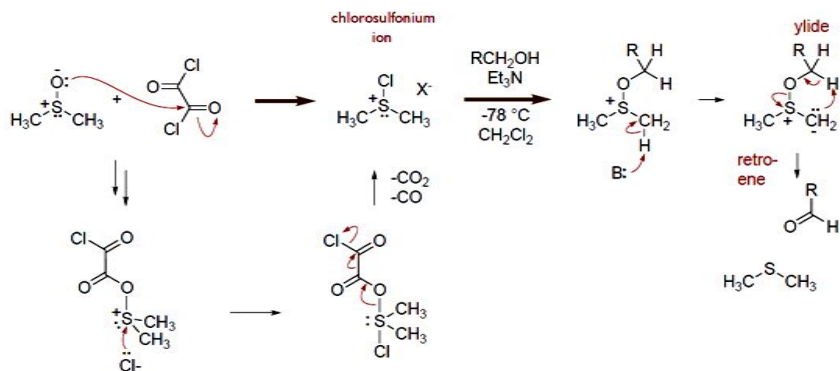
Kornblum Oxidation

The conversion of alkyl halide to carbonyl group in presence of DMSO and a base is known as Kornblum oxidation. The oxidation of α-haloketone mediated by the combination of DMSO and α-haloketone is also Kornblum oxidation.
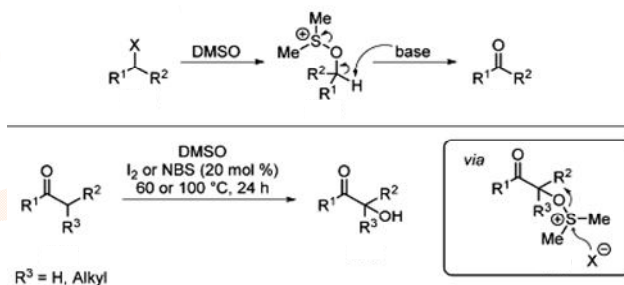
Pericyclic reactions of organosulfur compounds

Chelotropic reaction

Sulfur dioxide will participate in a typical concerted Chelotropic transformation ($\pi^4_s + \omega^2_s$) with 1,3-butadienes to yield cyclic sulfones. The "sulfolene reaction" is fully reversible so that sulfolenes are useful intermediates for the modification, purification, and storage of dienes.
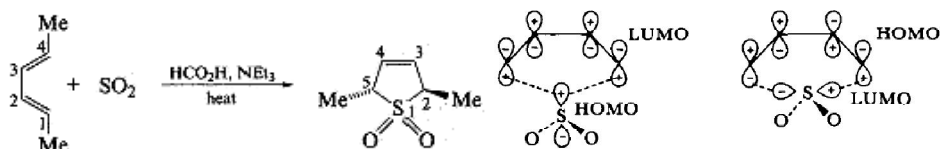
Organosulfur compounds and reactions

However, the stereochemistry of sulfur dioxide elimination from sulfolenes is disrotatory under thermal conditions. The corresponding photochemical process is not completely stereospecific but does favour the conrotatory path.

Episulfone decomposition is stereospecific and suprafacial with respect to olefin. The fastest rate of decomposition of 3-membered sulfones is due to ring strain. The relative rate of concerted fragmentation decreases as the size of the sulfone ring increases. The fragmentation of 7-membered sulfone proceeds predominantly (97%) antaraf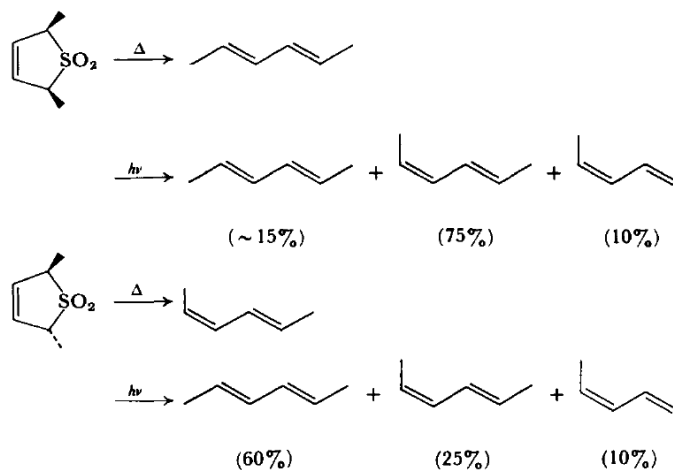acial manner with respect to the triene, i.e., conrotatory rotation via a $(\pi^6a + \omega^2_s)$ linear chelotropic process. The nonlinear $(\pi^6_s + \omega^2_a)$ cheletropic process for 10-membered sulfone is the relatively slow of sulfur dioxide elimination. The geometry of this compound permits only suprafacial elimination with respect to the triene. The last compound decomposes 60,000 times more slowly than its isomerie structure for which a $(\pi^4_s + \pi^2_a)$ fragmentation is possible.

| Sulfone	k_{rel} fragmentation (125°)
$\triangleright$SO$_2$	15.0
SO$_2$	1.0
SO$_2$	1.2
SO$_2$	5.9
SO$_2$	0.0001

Few transformations
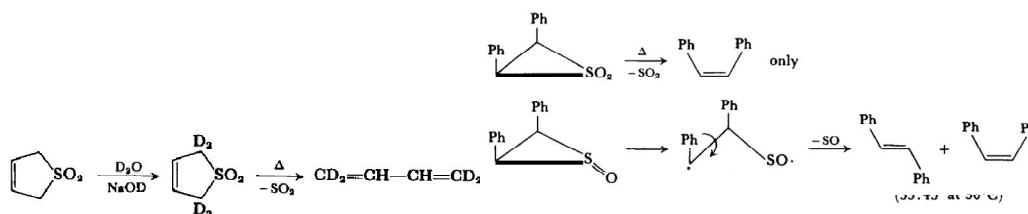
Organosulfur compounds and reactions

[1,2] Sigmatropic rearrangement

[1,2] shifts with sulfur containing compounds are basically anionic [1,2] sigmatropic rearrangement. Stevens and Witting rearrangements are the typical examples. It is assumed that radical pair mechanism operate for these reactions together with, or to the exclusion of, concerted mechanisms. However, both reactions are kinetically and thermodynamically favourable.

Stevens rearrangement
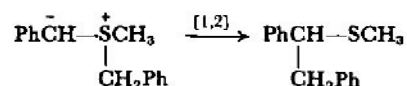
Wittig rearrangement
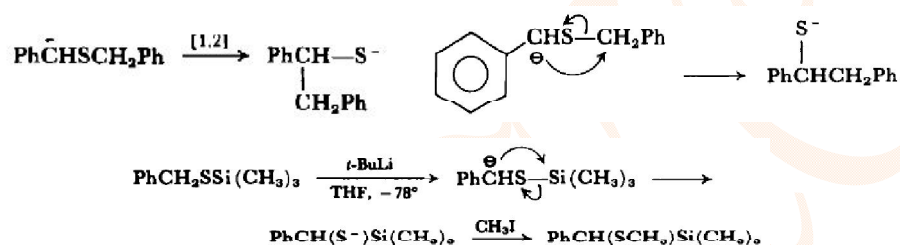
[1,3] Sigmatropic rearrangement

Neutral [1,3] sigmatropic shit are orbital symmetry forbidden. It does not obey suprafacial migration with respect to the migrating center. The transition state (T.S) geometry for the allowed antarafacial process at sulfur is essentially unfavorable. There is evidence that 1,3-thioallylic rearrangement of allyl aryl sulfides involves a dipolar intermediate while the analogous 1,3-migration on the basis of the activation parameters is thought to involve diradicals.

$$\Delta H^{\ddagger} = 27.8 \text{ kcal/mole}$$
$$\Delta S^{\ddagger} = -4 \text{ e.u.}$$
$$\Delta G^{\ddagger} = 29.5 \text{ kcal/mole at } 110.7°$$
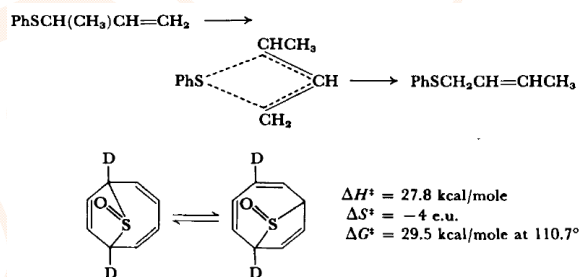
[1,4] Sigmatropic rearrangement
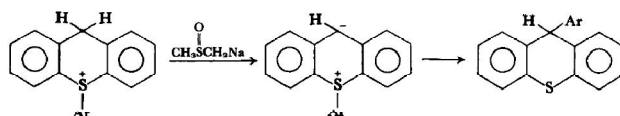
Organosulfur compounds and reactions

[2,3] Sigmatropic rearrangement on activated sulfoxide

A general representation of [2,3] sigmatropic rearrangement is given below:

Sommelet–Hauser rearrangement

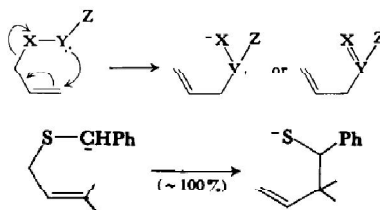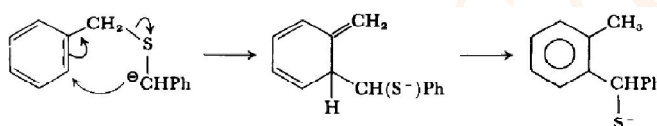The reaction proceeds readily despite the fact that it requires sacrifice of benzene resonance at the critical stage.

Mislow–Braverman–Evans rearrangement

Mislow–Braverman–Evans (or Mislow–Evans) rearrangement is the archetypical example of [2,3]-sigmatropic rearrangements using sulfoxides. It involves a thermal reorganization of allylic sulfoxides to allylic sulfenates.

Mislow-Braverman-Evans rearrangement
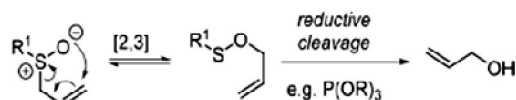
The following stereoretentive [2,3]-sigmatropic rearrangements is the construction of allylic stereocenters following conjugate addition to enantiopure vinyl sulfoxide derivatives.
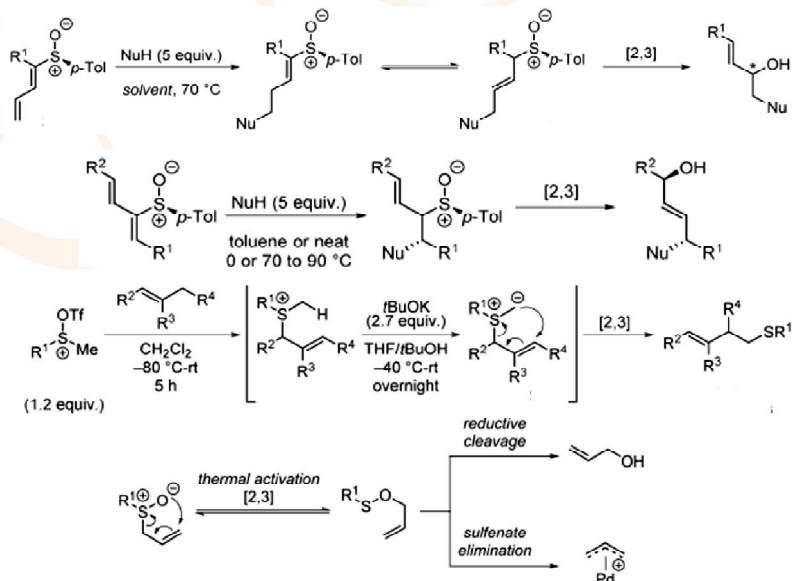
Organosulfur compounds and reactions

[3,3] Sigmatropic rearrangement on activated sulfoxide

Among hetero Cope reaction, [3,3] sigmatropic process involving sulfur is termed as a thio-Claisen reaction.

The driving force of the following thio-Claisen rearrangement derives from electron displacement in the direction of the heteroatom producing trigonal hybridization of the 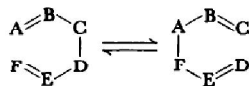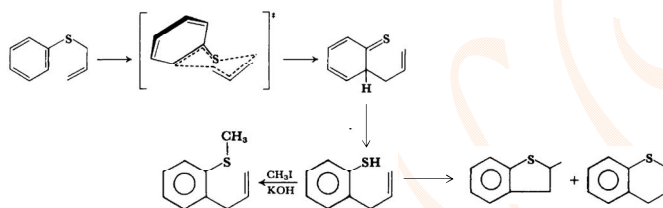allylic carbon. In contrast to the oxy-Claisen reaction where electrophilic catalysis is observed, an unusual feature of thio Claisen reaction remains in its susceptibility to catalysis by nucleophiles.

A sequential [3,3]-sigmatropic rearrangement, rearomatization, and triflate elimination occur following a mechanistically elegant transformation involving base-promoted isomerization of an intermediate enol trilate to afford sulfur-ylide and rearrangement to form the desired propargyl arene products.
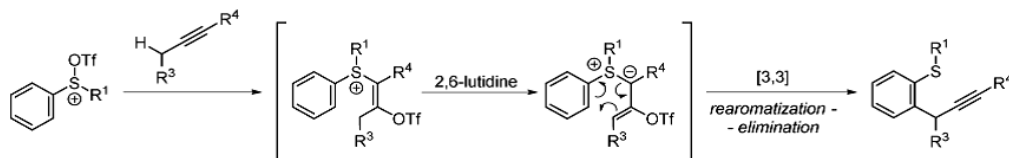
Rearrangement of sulfurylids

Sulfur ylides undergoes intramolecular rearrangement by following way:
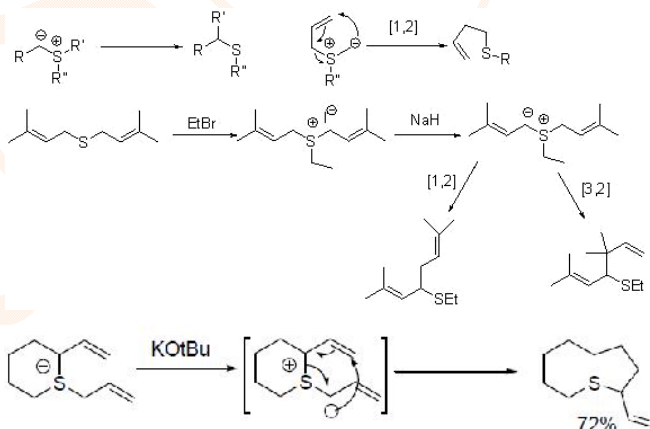
Oxidative Allylic and Benzylic Functionalization

An addition to allylic functionalization using activated DMSO providing a direct path to allylic chlorides. This transformation is based on an ene-type allylic chlorination of electron-rich alkenes, critically attacking the chlorosulfonium ion at chlorine rather than sulfur.

Organosulfur compounds and reactions

Interestingly, the converse unusual attack of a benzylic enolate on the sulfur atom of DMSO enables a base-mediated benzyl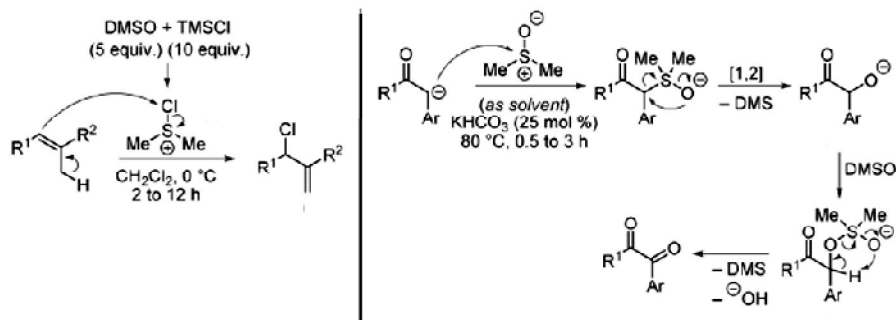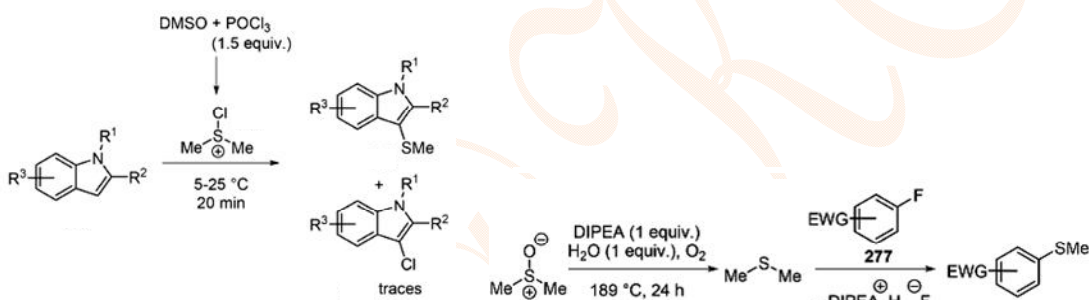ic oxidation. The intermediate, formed after this initial attack, undergoes [1,2]-sigmatropic rearrangement to afford an alkoxide which is further oxidized following a second attack on DMSO and E1cb-elimination.

Methylthiolations of Arenes with DMSO

DMSO and $POCl_3$ form chlorodimethylsulfonium ion which accounts for methylthiolation in indole moiety and trace of 3-substitued chlorinated product is isolated. Methylthiolation of aryl moiety by repalcing electron-deficient fluorine group is carried out with *in situ* formation of dimethyl sulfide obtained from DMSO via S_NAr.

Halogenenation of arene

The following procedure reflects the kilogram-scale halogenation of arenes enabled through DMSO-mediated slow release of X_2.

49-99% yield
up to 1.58 kg scale

Dibromination and bromohydrin formation

The combination of DMSO and hydrogen bromide produces bromodimethylsulfonium ion as the active reagent, leading to intermediate bromonium ion formation, followed by ring opening with a further equivalent of bromide. This process can be recognized as Br_2-free dibromination of olefins.

Organosulfur compounds and reactions
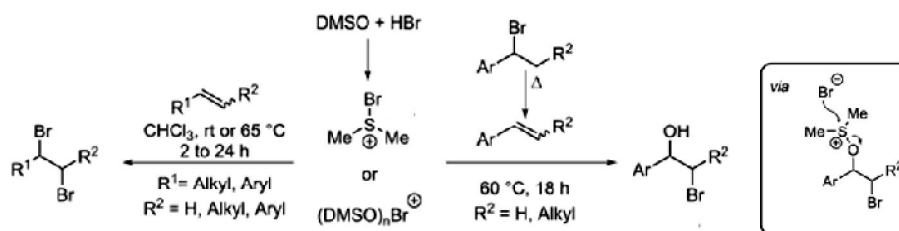
Umpolung Halogenation/Halolactonization of Alkenes

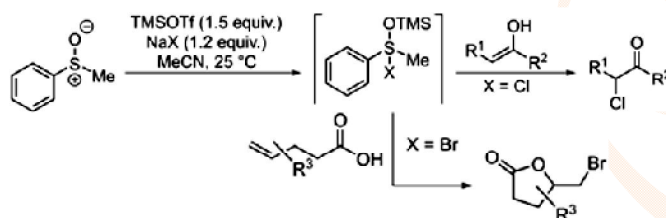Lewis acid activation of a sulfoxide enables the addition of a halide, forming tetrahedral intermediate. This electrophilic species undergoes attack by the alkene in a halonium-type fashion.

Episulfide

Cyclic sulfides (episulfides) are known and may be prepared by reaction of an epoxide with potassium thiocyanate to give the episulfide, or by reaction of sodium sulfide with 1,4-or 1,5-dihalides.
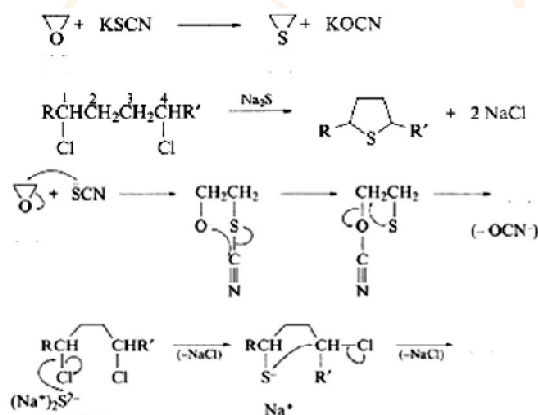
Radical reaction

Dithioacetals react with tri-n-butyltin hydride to replace successive alkylthio groups with a hydrogen atom. The first thioacetal group is replaced more rapidly than the second. The greater reactivity of the first ethylthio group is due to formation of an intermediate, carbon-centered radical that is stabilized by the sulfur atom in the remaining ethylthio group.

Organosulfur compounds and reactions
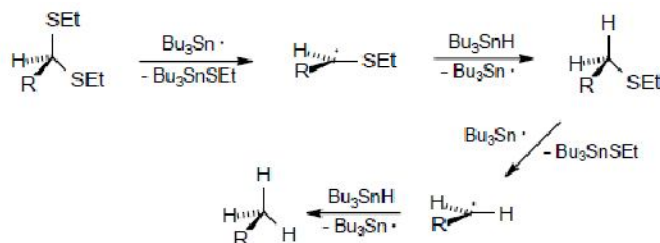
Behaviour of tosylhydrazone

Unlike keto-tosylhydrazones that produce C, N dianions with organolithiums, aldehyde tosylhydrazones rather form N, N dianions with organolithiums following the incorporation of reagent to the carbon-nitrogen double bond. Aqueous work-up affords the alkane and alkene from aldehyde and keto-tosylhydrazones respectively.

Aldehyde-tosyl hydrazone   **Keto-tosyl hydrazone**
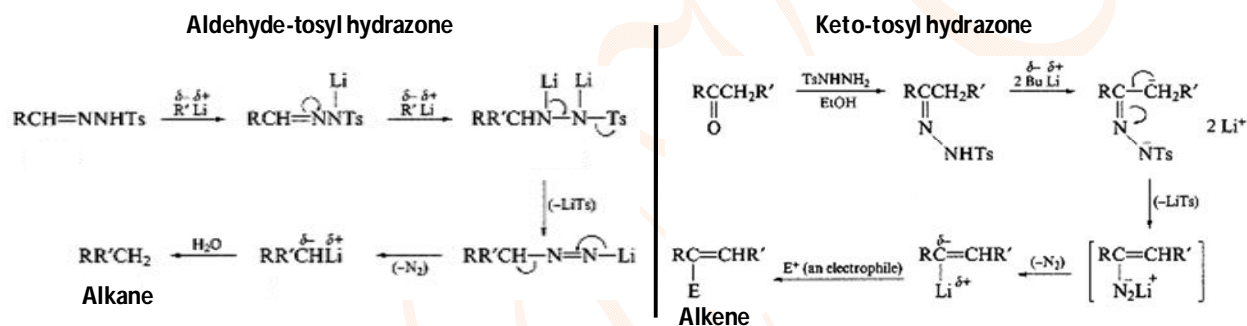
Bamford-Stevens reaction uses bases like lithium hydride, sodium hydride, sodium amide or sodium in ethylene glycol; with sodium in ethylene glycol.

Organosulfur compounds and reactions

References

1. Carey, F., Sundberg, R. Advanced Organic Chemistry, Part B: Reactions and Synthesis 5th Ed, Springer, USA, 2007.

2. B. M. Trost and L. S. Melvin, Jr., Sulfur Ylides, Academic Press, New York, USA 1975.

3. Cremlyn, R. J. An Introduction to Organosulfur Chemistry, John Wiley & Sons Ltd. UK, 1996.

4. Block, E. Reactions of Organosulfur Compounds, Academic Press, New York, USA, 1978.

5. Encyclopedia of Reagents for Organic Synthesis, John Wiley and Sons, Inc., L. A. Paquette, Ed., New York, 1995.

6. Kaiser, D., Klose, I., Oost, R., Neuhaus, J., Maulide, N. Bond-Forming and -Breaking Reactions at Sulfur(IV): Sulfoxides, Sulfonium Salts, Sulfur Ylides, and Sulfinate Salts, Chem. Rev. 2019, 119, 8701.

7. Oae, S. Organic Chemistry of Sulfur, Plenum Press, New York, USA, 1977.

8. Pizey, J. S. Reactions of Sulfur with Organic Compounds, Consultants Bureau, USA, 1987

9. E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 87, 1353 (1965).

10. Kharasch, N. Organic Sulfur compounds, Pergamon Press, USA, 1961.