# ORGANOSULPHUR COMPOUNDS

## CONTENTS



## *3.1 OBJECTIVES*

In this unit learner will be able to:

- Know about Organo Sulphur compounds
- Understand and discuss the preparations and Properties of various Organo sulphur compounds.
- Understand the important physical and chemical properties of Organo sulphur compounds.

## *3.2 INTRODUCTION*

**Organosulfur compounds** are organic compounds that contain sulfur. They are often associated with foul odors, but many of the sweetest compounds known are organosulfur derivatives, e.g., saccharin. Nature abounds with organosulfur compounds—sulfur is essential for life. Of the 20 common amino acids, two (cysteine and methionine) are organosulfur compounds, and the

antibiotics penicillin and sulfa drugs both contain sulfur. While sulfur-containing antibiotics save many lives, sulfur mustard is a deadly chemical warfare agent. Fossil fuels, coal, petroleum, and natural gas, which are derived from ancient organisms, necessarily contain organosulfur compounds, the removal of which is a major focus of oil refineries.

Organo Sulphur compounds are derivatives to organic compounds containing oxygen with the difference that oxygen has been replaced by sulphur. These compounds give the reactionssimilar to other oxygen containing compounds. The some of the common examples of the sulphur containing Organic compounds are given as:

R-S-H = Thiols

-S-H = Thiol group

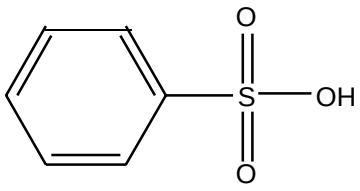
R-S-H = Thioethers

-S- = Thioether group

There are many Organosulphur compounds containing sulphur- oxygen bonds with double bondcharacter; for example, sulphoxides such as dimethylsulphoxide and sulphonic acids.

$(CH_3)_2$ SO

(Dimethyl sulphoxide)




benzene sulphonic acid

## *3.3 NOMENCLATURE*

**Nomenclature of Mercaptans:** Mercaptans can be named by naming the parent compound immediately followed by the word thiol. The -SH group can also be named as a substituent using the group name, sulfhydryl. Mercaptans can also be named by naming the carbon group as a separate word followed by the word mercaptan. For example the names of $CH_3$-SH are methanethiol, sulfhydryl methane and methyl mercaptan.

**Nomenclature of Sulfides:** Sulfides can be named most readily by naming each of the two carbon groups as a separate word followed by a space and the word sulfide.

$CH_3$-$CH_2$-S-$CH_3$ (ethyl methyl sulfide)

**Nomenclature of Disulfides:** Disulfides can be named most readily by naming each of the two carbon groups as a separate word followed by a space and the word disulfide.

$CH_3CH_2$-S-S-$CH_2CH_2CH_3$ (ethyl 1-propyl disulfide)

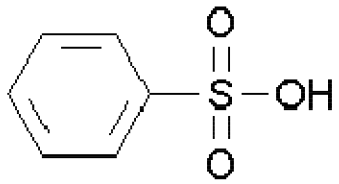
### Nomenclature of Sulfoxides:

Sulfoxides can be named most readily by naming each of the two carbon groups as a separate word followed by a space and the word sulfoxide.

$CH_3CH_2SOCH_3$ (ethyl methyl sulfoxide)

### Nomenclature of Sulfonic Acids:

Sulfonic acids can be named most readily by naming the carbon group as a separate word followed by the word's sulfonic acid.



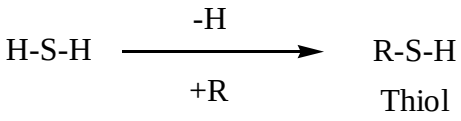

*Phenyl sulfonic acid*

## *3.4 ORGANO SULPHUR COMPOUNDS; THIOLS, THIOETHERS, SULPHURIC ACID, SULPHONAMIDES AND SULPHGUANIDINE*

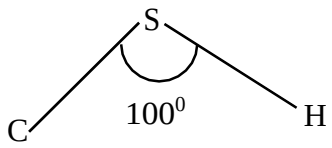
### A. THIOLS:

Thiol is Sulphur derivatives of alcohols in which the oxygen has been replaced by sulphur atom.The functional group of thiols is –SH. It is also known as mercapto group. It is weak acid like $H_2S$

and they react with mercuric acid to form insoluble salt. Therefore, they were given the name mercaptans.

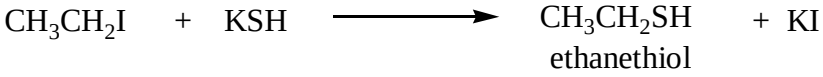



**Structure:** The structure of thiol is similar to alcohol. The properties of S-H bond are lower as compared to that of O-H bond is alcohols. This is due to low electronegativity of sulphur in compare to oxygen. The shape of thiol is bent like structure and the bond angle is $100^0$.

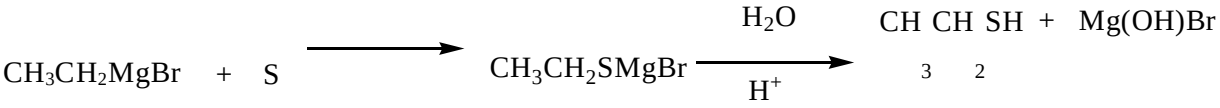



## Methods of Preparation:

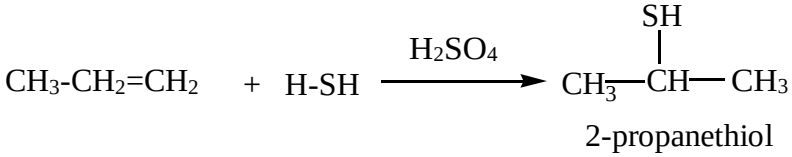
1. **By the reaction of alkyl halides with potassium hydrosulphide (KSH) solution:** When ethyl iodide reacts with potassium hydrosulphide (KSH) in the presence of heat, then it gives ethane thiol.




2. **By the reaction of Grignard reagent with sulphur:** In this reaction Grignard reagents initially react with sulphur atom gives an addition product, which on further acidic hydrolysis to form ethanethiol.



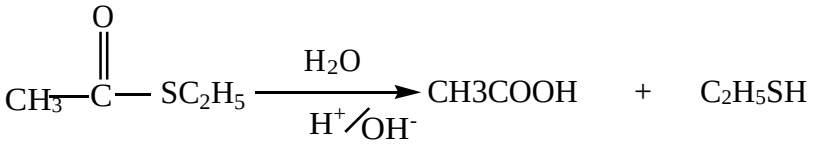

3. **By the addition of hydrogen sulphide to alkene in the presence of sulphuric acid:** When alkenes react with hydrogen sulphide in the presence of sulphuric acid to form thiol.



4. **By the reaction of alcohol with phosphorus pentasulphide:** When any alcohols react with phosphorus pentasulphide to give thiol.

$$5C_2H_5OH + P_2S_5 \longrightarrow 5C_2H_5SH + P_2O_5$$

5. **By hydrolysis of thioester:** Thioester when react with dilute acid or alkali to form thiol.




**Chemical properties of thiol:**

1. **Acidic Nature:** Thiols are weaker acid but more acidic than alcohols because sulphur has lower electronegative than oxygen. This could be due to following reasons:

   (1) The S-H bond is weaker than O-H bond due to which S-H easily donate $H^+$ ion than alcohol

   (2) The $RS^-$ anion obtained after the release the proton is more stable than $RO^-$ ion obtained from alcohols, due to which negative charge accommodate the negative charge more easily than $RO^-$ ion because of larger size of sulphur atom.

2. **Reactive with alkali and alkaline earth metals:** Thiol reacts with active metals like Na, K, Ca etc. releasing hydrogen gas.

$$CH_3CH_2SH + Na \longrightarrow 2CH_3CH_2S^-Na^+$$

3. **Reaction with acids and acid chloride:** Thiol reacts with acids and acid chlorides to form thioester.

$$CH_3CO\boxed{OH + H}SC_2H_5 \longrightarrow CH_3COSC_2H_5 + H_2O$$

Ethyl thioacetate

4. **Reaction with alkyl halides:** Sodium salt of thiols when react with alkyl halides to form diethyl thioether.

$$C_2H_5S\boxed{Na + Br}C_2H_5 \longrightarrow C_2H_5SC_2H_5 + HBr$$

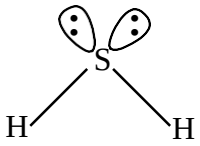
## B. THIOETHERS:

Thioether is a functional group in organosulfur compounds with the connectivity C–S–C. A thioether is similar to an ether except that it contains a sulfur atom in place of the oxygen. The grouping of oxygen and sulfur in the periodic table suggests that the chemical properties of ethers and thioethers are somewhat similar.

$$H\text{-}S\text{-}H \xrightarrow[+2R]{-2H} R\text{-}S\text{-}R$$

**Structure of Thioethers:**

Thioethers have tetrahedral structure with two positions occupied by loan pair of electrons as given below.




**Methods of preparation:** Some of the commen methods used for the preparation of thioethers, which are given below.

1. **Reaction of alkyl halide with sodium or potessiom merceptide:** In this reaction sodium of potassium merceptide react with alkyl bromide than it forms corresponding thioether.

   $C_2H_5S\boxed{Na + Br}\ CH_3 \longrightarrow C_2H_5\text{-}S\text{-}CH_3 + NaBr$

2. **From alkenes:** Addition of thiols to alkenes in the presence of peroxide gives thioethers.

   $$R\text{-}CH{=}CH_2 + R'SH \xrightarrow{\text{Peroxide}} R\text{-}CH_2\text{-}CH_2\text{-}S\text{-}R'$$

3. **From ethers:** Ehters when heated with phosphorus penta sulphide to form thioether.

   $5C_2H_5\text{-}O\text{-}C_2H_5 + P_2S_5 \longrightarrow 5C_2H_5\text{-}S\text{-}C_2H_5 + P_2H_5$

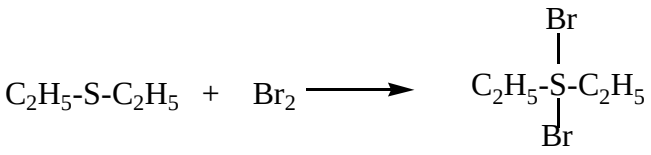
4. **From thiols:** Vapours of thiol when passed through a mixture of aluminium tri oxides and zinc sulphide at 575K temperature to form thioether.

   $$2C_2H_5SH \xrightarrow[575K]{Al_2O_3,ZnS} 5C_2H_5\text{-}S\text{-}C_2H_5 + H_2S$$

**Chemical reactions of Thioethers:**

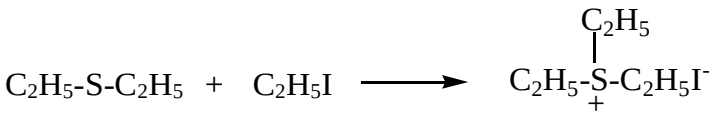
Some of the important chemical reactions of thioethers are given below:

1. **Reaction with halogens:** Thioethers when react with halogen like Cl, Br and I to form dihalide.



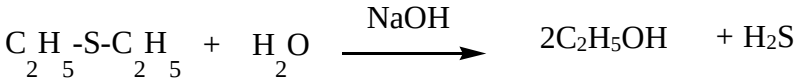
Diethyl sulphide dibromide

2. **Reaction with alkyl halide:** Thioethers when react with alkyl halide to form sulphoniumsalts.

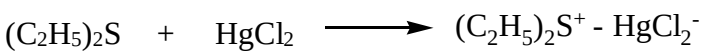


Triethyl sulphonium iodide

3. **Hydrolysis reaction:** Thioether on hydrolyzed with aqueous NaOH to form alcohols and $H_2S$ gas.



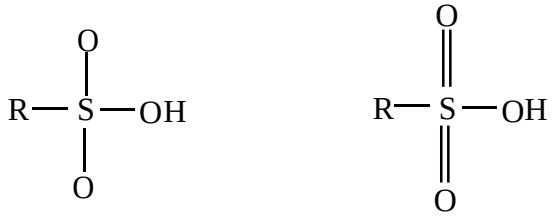
4. **Reaction with metallic salts:** Thioethers react with metallic salt like $HgCl_2$ and $SnCl_4$ to form metallic salt.



## C. SULPHONIC ACID:

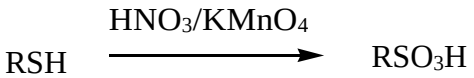
A sulfonic acid (or sulphonic acid) is a member of the class of organosulfur compounds with the general formula $R{-}S(=O)_2{-}OH$, where R is an alkyl or aryl group and the $S(=O)_2(OH)$ group a sulfonyl hydroxide.

**Structure:** There are two main types of the representations of sulphonic acid are given below:



**Methods of preparation:**

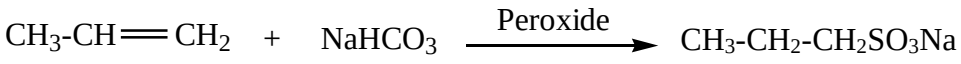
1. **By oxidation of thiols:** Oxidation of thiol with strong oxidizing agents such as $HNO_3$ and $KMnO_4$ to form alkane sulphonic acid.



$$RSH \xrightarrow{HNO_3/KMnO_4} RSO_3H$$

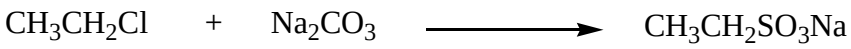
Where R = Alkyl groups

2. **By the addition of sodium sulphate with alkenes:** Addition of sodium bisulphate toalkenes in the presence of peroxide gives sodium salt of alkyl sulphonate.



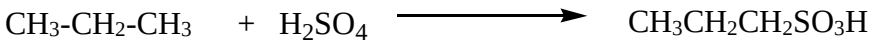
$$CH_3\text{-}CH{=}CH_2 + NaHCO_3 \xrightarrow{Peroxide} CH_3\text{-}CH_2\text{-}CH_2SO_3Na$$

3. **By the reaction of sodium sulphate with alkyl halide:** When the mixture of sodium sulphate and alkyl halide is heated, sodium salt of alkane sulphonic acid is obtained.



$$CH_3CH_2Cl + Na_2CO_3 \longrightarrow CH_3CH_2SO_3Na$$

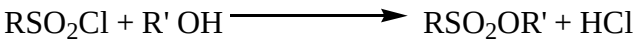
4. **From sulphonation of alkane:** When any alkanes react with sulphuric acid than it gives alkyl sulphonic acid.



$$CH_3\text{-}CH_2\text{-}CH_3 + H_2SO_4 \longrightarrow CH_3CH_2CH_2SO_3H$$

**Chemical properties of sulphonic acid:**

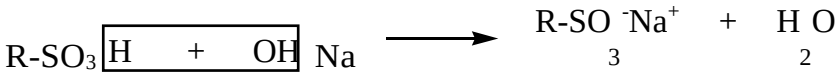
1. **Esterification**: Alkyl or aryl sulphonyl chloride when react with alcohol to form corresponding ester. This reaction is known as esterification reaction.



$$RSO_2Cl + R'OH \longrightarrow RSO_2OR' + HCl$$

Where R= Alkyl or aryl groups

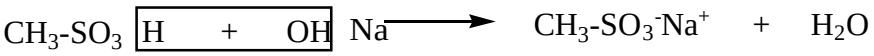
2. **Salt formation:** Sulphonic acid are strongly acidic, they form salt with hydroxide, carbonate and bicarbonates.

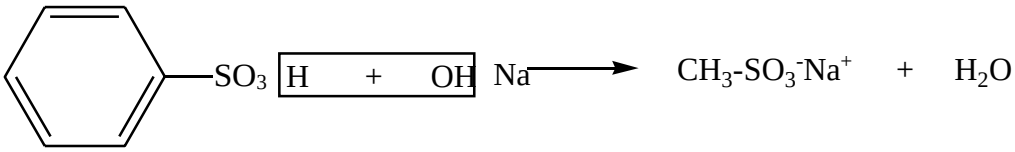


$$R\text{-}SO_3\boxed{H + OH}Na \longrightarrow R\text{-}SO_3^-Na^+ + H_2O$$

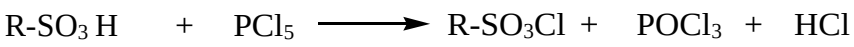
Where R = alkyl or aryl groups

**Example:**

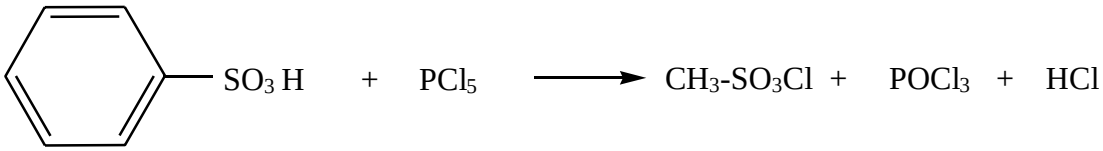




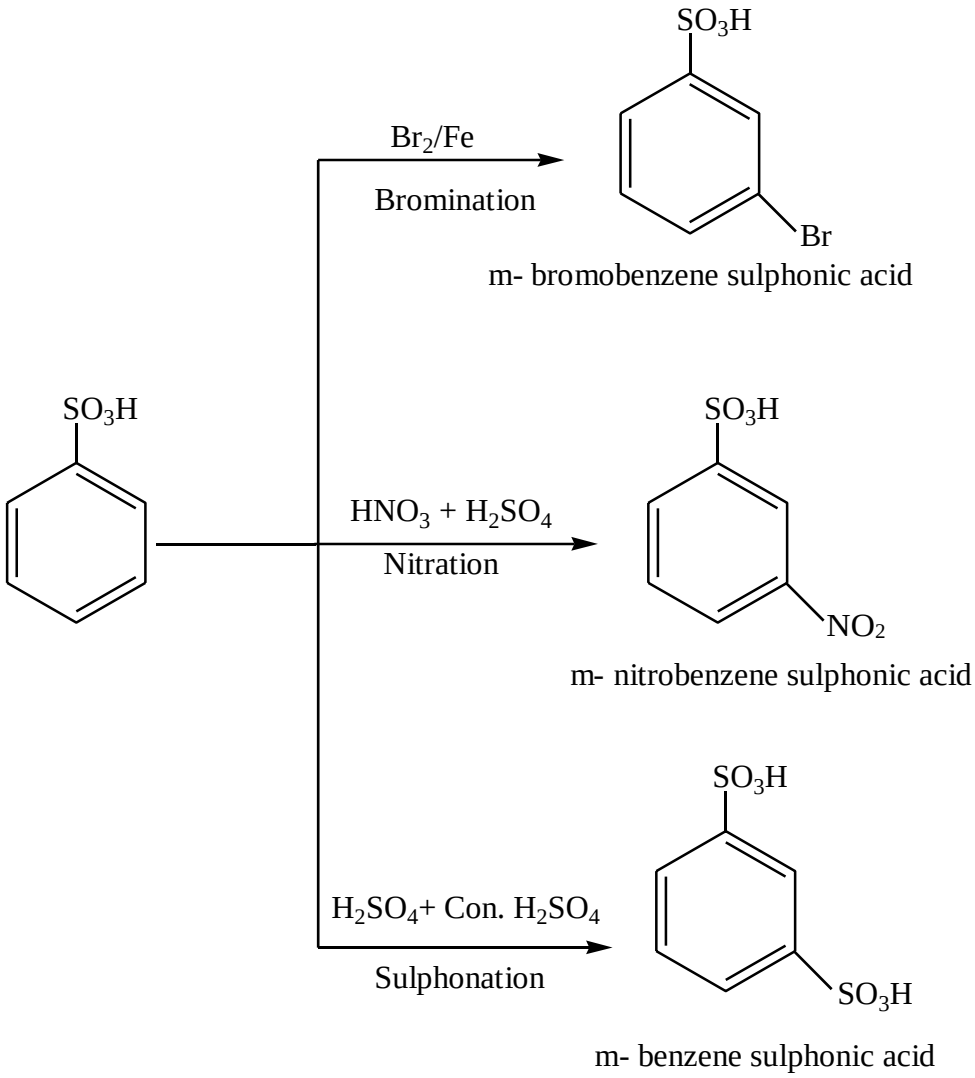
3. **Formation of sulphonyl chloride:** Sulphonic acid forms sulphonyl chloride when rect with phosphorus chloride or thionyl chloride.



**Example:**

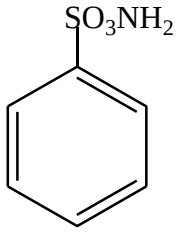


4. Electrophilic substitution reaction: Aromatic sulphonic acid undergoes electrophilic substitution reactions gives different types of substituted products. Some common electrophilic substitution reactions are given below.




## SULPHONAMIDES (Benzene sulphonamides):

Sulphonamide is a functional group that is the main component of various groups of drugs, which are called sulphonamides, sulpha drugs.

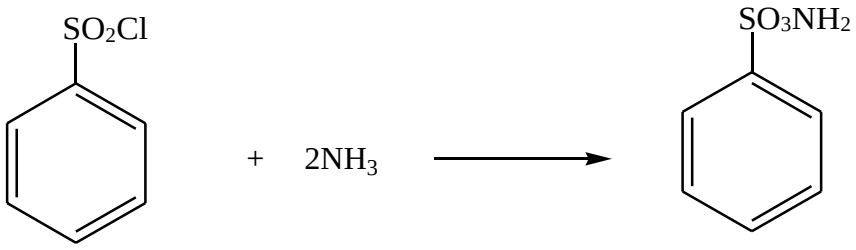



Benzene sulphonamide

**Method of Preparation:**

1. **From benzene sulphonyl chloride:** Benzene sulphonamide is prepared by the reaction

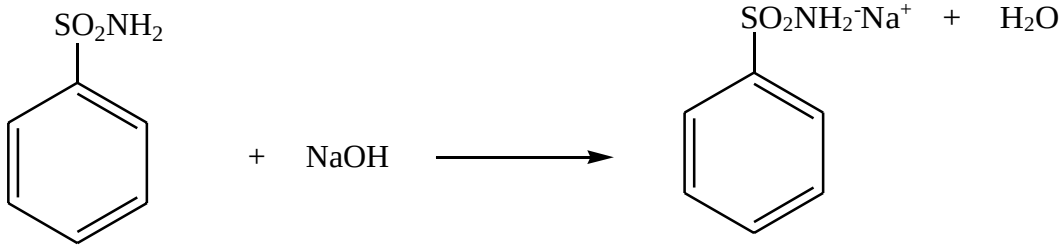
of ammonia with benzene sulphonyl chloride.




Benzene sulphonamide

**Chemical properties:**

1. **Acidic in nature:** It is weakly acidic in nature and hence react with strong base like NaOH or KOH gives corresponding salt.




sodium salt of Benzene sulphonamide

2. **Hydrolysis reaction:**