Class-1

Organosulphur Compound

Organosulphur compounds are those compounds where carbon is covalently bonded with sulphur atom.

C — S covalent bond.

Sulphur is slightly more electronegative than carbon so C—S bond has not much Polarity ($C^{\delta+}-S^{\delta-}$) unlike ($C^{\delta+}-O^{\delta-}$) where electronegativity difference is much high. So reactivity of C–S bond is less than C–O bond.

Organosulphur compounds are analogous to organic compounds containing oxygen atom.

Examples of organosulphur compounds :

R—S—H (Thiol) ⟶ oxygen analogue (R—OH) Alcohol

R—S—R (Thioether) ⟶ " " R—O—R (Ether)

R—S(=O)(=O)—O—H (Alkyl sulphonic acid).

R—S(=O)(=O)—NH$_2$ (Sulphonamide)

SH - Group is called mercapto group if OH is called hydroxy group.

{ OH ⟶ alcohol.
SH ⟶ Thiol }

Thiols - R–SH

Synthesis :- ① $R-I + KSH \xrightarrow{\Delta} R-SH + KI$

② $R-MgBr + S \xrightarrow{\text{oxidative addition}} R-S-MgBr \xrightarrow[H^+]{H_2O} R-SH + Mg(Br)(OH)$

③ $R-CH=CH_2 + H-SH \xrightarrow{H_2SO_4} R-\underset{\underset{SH}{|}}{CH}-CH_3$
(Markovnikov addition)

④ $H_3C-CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-Na^+ + NaHS \longrightarrow H_3C-CH_2-SH + Na_2SO_4$

⑤ $H_3C-\overset{\overset{O}{\|}}{C}-SC_2H_5 + H_2O \xrightarrow{H^+ \text{ or } OH^-} H_3C-\overset{\overset{O}{\|}}{C}-OH + C_2H_5SH$
Ethanethiol.

Mind it ⇒ The smell coming out of the leakage of LPG cylinders is because of the Presence of following two Sulphur Compounds

H_3C-SH or C_2H_5SH
methane thiol ethanethiol.

HW → • Between R—OH and RSH which one is more acidic and why?

* n-Propyl alcohol is more soluble in water than 1-Propanethiol

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Reaction of thiol :-

1. $2\,R-SH + Na \longrightarrow 2\,RS^{-}Na^{+} + H_2\uparrow$

2. $2\,RSH + R'-CHO \xrightarrow{\text{dry HCl}} R'-\underset{\underset{SR}{|}}{\overset{\overset{SR}{|}}{C}}-H$ Thioacetal

3. $2\,RSH + R'-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{\text{dry HCl}} R'-\underset{\underset{SR}{|}}{\overset{\overset{SR}{|}}{C}}-R'$ Thioketal.

(Try to draw the mechanism, very common, like rexn with alcohol)

4. $H_3C-\underset{\underset{SC_2H_5}{|}}{\overset{\overset{SC_2H_5}{|}}{C}}-CH_3 + 4[O] \xrightarrow{KMnO_4} H_3C-\underset{\underset{O=S=O}{|}}{\overset{\overset{O=S=O}{|}}{C}}-CH_3$

Sulphonal.

5. Synthesis of ethyl thioacetate

$$H_3C-\underset{\underset{O}{\|}}{C}-OH + H-S-C_2H_5 \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} H_3C-\overset{\overset{O}{\|}}{C}-S-C_2H_5$$

$$H_3C-\underset{\underset{O}{\|}}{C}-Cl + H-S-C_2H_5 \xrightarrow[-HCl]{\ominus OH} H_3C-\overset{\overset{O}{\|}}{C}-S-C_2H_5$$

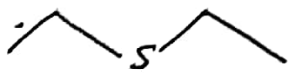
6. **Oxidation of thiol:**

$$2\,RSH + I_2 \longrightarrow R-S-S-R + I_2$$

$$2\,RSH + H_2O_2 \longrightarrow R-S-S-R + 2H_2O$$

$C_2H_5SH \xrightarrow[\text{or Conc. } HNO_3]{KMnO_4} C_2H_5SO_3H$.
Ethanesulphonic acid.

Synthesis of thioether :

$C_2H_5SNa + C_2H_5Br \xrightarrow{SN2}$ 
Diethyl thioether.

Distinguish chemically between ethanethiol and ethyl alcohol :

$HgCl_2$ Test :-

Thiol reacts with Mercuric chloride solution to form a Precipitate of dialkyl or diethyl mercaptide.

$C_2H_5SH + HgCl_2 \longrightarrow (C_2H_5S)_2Hg\downarrow + 2HCl$.

Ethyl alcohol does not give this reaction.

Convert ethanethiol to ethane : (desulphurization)

$C_2H_5SH \xrightarrow[\Delta]{Ni} C_2H_6 + NiS$.

HW. $H_3C-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} ? \xrightarrow{NaSH} ?$

HW $EtBr + S=C(NH_2)(NH_2) \longrightarrow ? \xrightarrow{NaOH} ?$

HW.