

# \* Unit Process \*

of Unit Process :- [subjected as a step in manufacture]

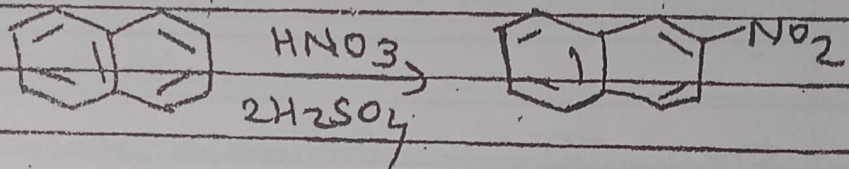
Useful chemical changes with or without physical changes occur in chemical process. Industries is called Unit Process. (Chemical change to which material is

Example - Nitration, Chlorination, Bromination, Alkylation, Sulphonation etc.

## ④ Nitration of Hydrocarbons

Nitration is an electrophilic substitution reaction in which one or more hydrogen atoms in the aromatic ring which are substituted by Nitro ( $\text{NO}_2$ ) group.

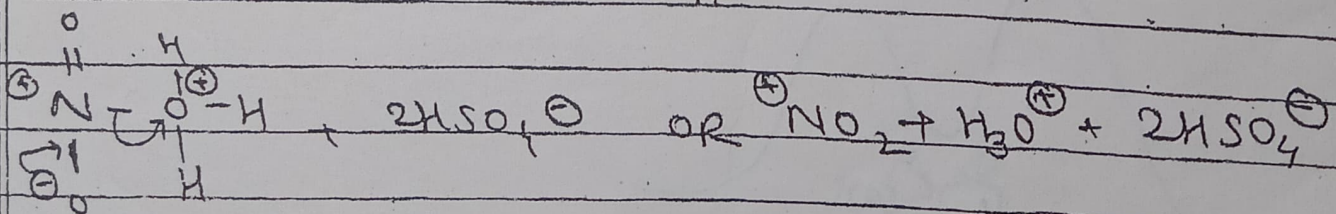
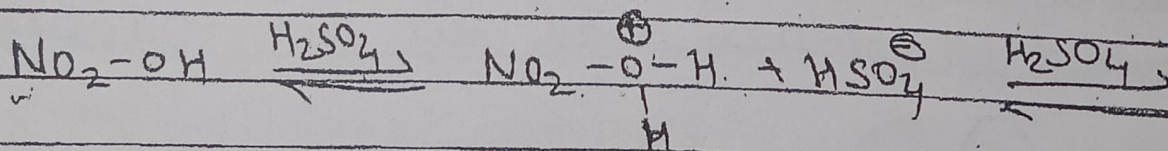
General Reaction



Mechanism:

### Step I :- Formation of Nitronium Ion

The reaction is simply an acid base equilibrium in which sulphuric acid acts as an acid and nitric acid acts as base. Actually sulphuric acid causes nitric acid to ionise into  $\text{OH}^+$ ,  $\text{NO}_2^+$  species gives nitronium ion.

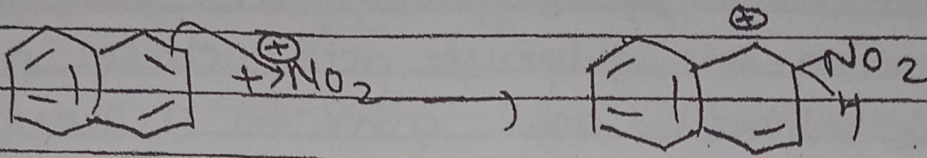




# PRAPHOL UTIAMI RAMBLE

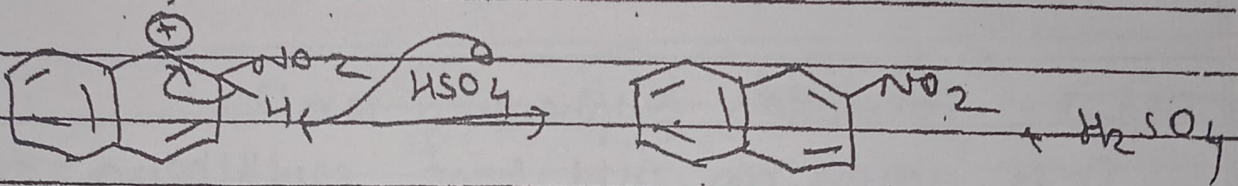
## Step II: formation of sigma complex

The electrophile deficient nitronium ion get complexed with  $\pi e^-$  cloud to form a  $\pi$  complex which is slowly changes to sigma complex, where the nitrogen form sigma bond with one of the carbon atom of the ring.



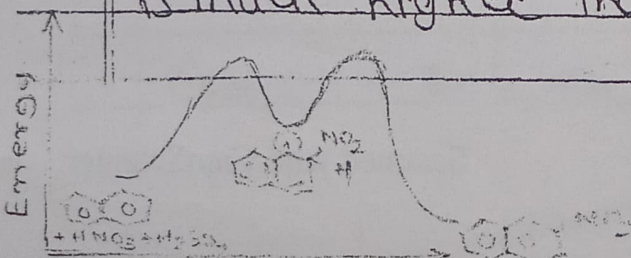
## Step III: Abstraction of proton

The basic ion  $HSO_4^-$  abstracts the proton from from intermediate carbocation to form (yield) the substituted product aromatisation of the ring



## (\*) Energy profile diagram -

- ① Attack of electrophile into  $\sigma$  complex the T.S. for this state is  $TS_1$ .
- ② Each represents energy of activation for formation of sigma complex.
- ③ When the  $\sigma$  complex changes to the product the T.S. is represented by  $TS_2$  & energy of activation is  $E_{act}$ .
- ④ First step is slow & 2<sup>nd</sup> step is fast hence  $E_{act}$  is much higher than  $E_{act}$ .

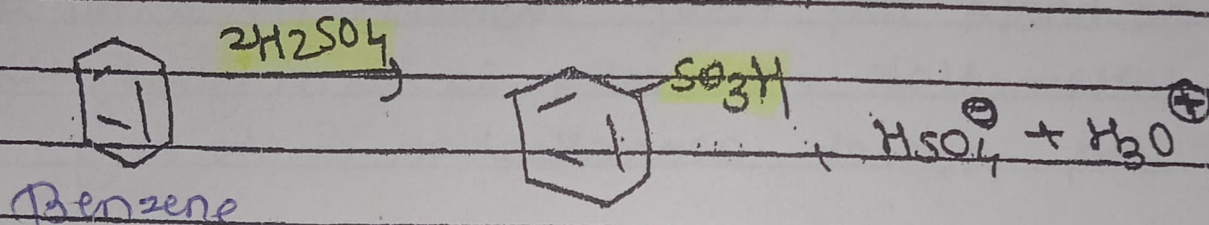




## Sulphonation of aromatic compounds -

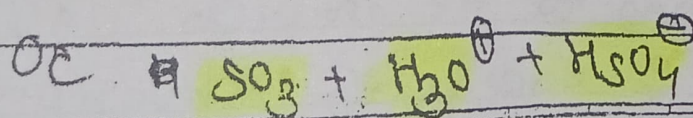
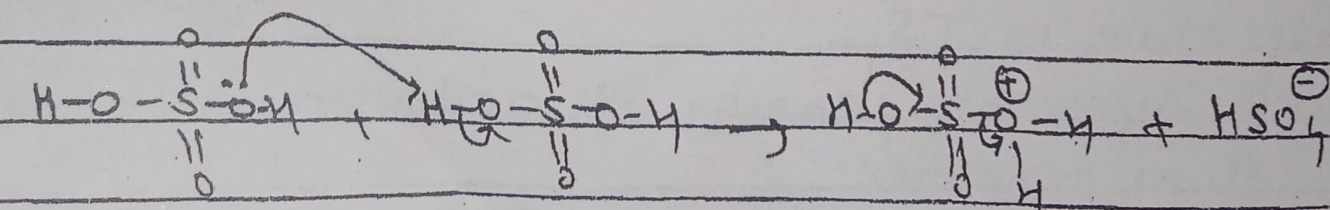
Sulphonation is an electrophilic substitution reaction in which one or more H atoms of aromatic ring is substituted by sulphonyl acid ( $\text{SO}_3\text{H}$ ) group. In this reaction one sulphuric acid acts as acid and another sulphuric acid acts as a base.

### General reaction



### Step-I - formation sulphonium ion.

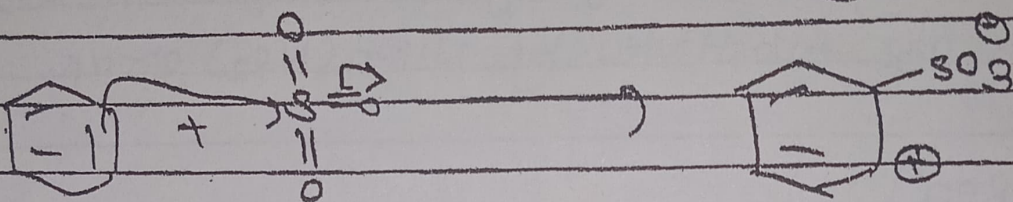
It is simply an acid base equilibrium, in which one sulphuric acid acts as a acid and another sulphuric acid acts as base.



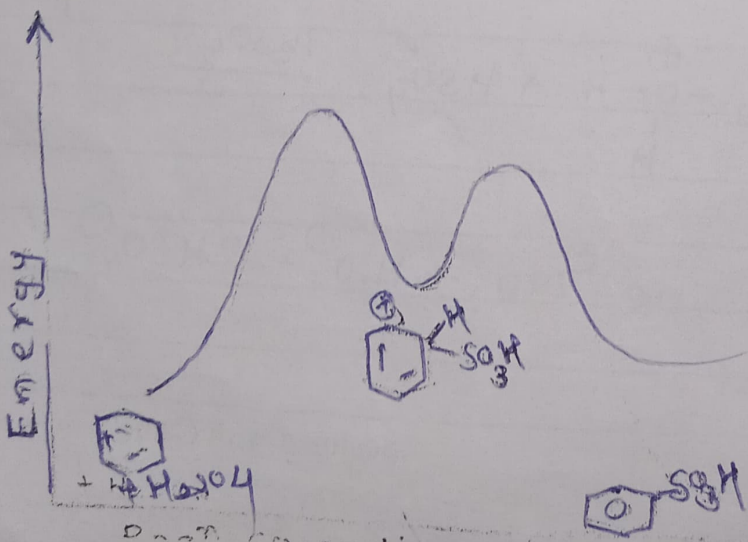
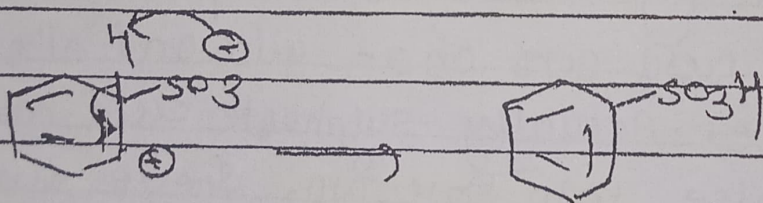


Step II :- formation of sigma complex

Sulphonium ion get complexed with  $\pi$  cloud form a  $\pi$  complex which slowly changes to  $\sigma$  complex where sulphur form sigma bond with one of the carbon atom of the ring.



Step III :- Aromatization. Abstraction of proton. The  $SO_3^-$  ion abstracts the H atom from the intermediate carbocation to yield the substituted product aromatization of the ring.





## Halogenation

### \* Introduction -

It is a process where by one or more halogen atoms are introduced into the organic compound.

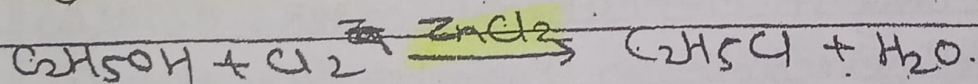
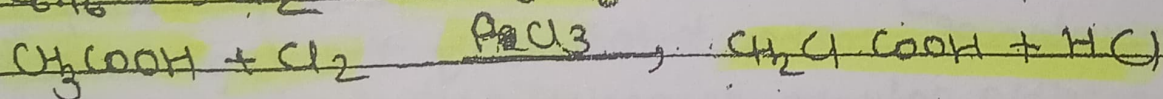
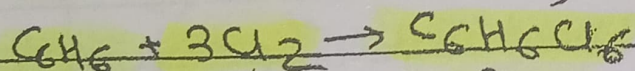
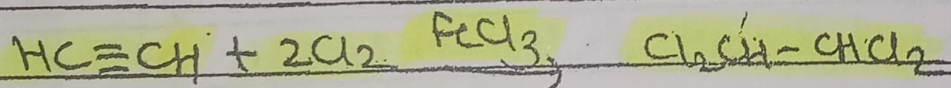
The preparation of organic compounds containing F, Cl, Br & I can be done by variety of methods

Halogenation may involve reactions of

1) Addition

2) Substitution i.e. of H.

3) Replacement i.e. of groups e.g. the hydroxy) or sulphonic acid group.



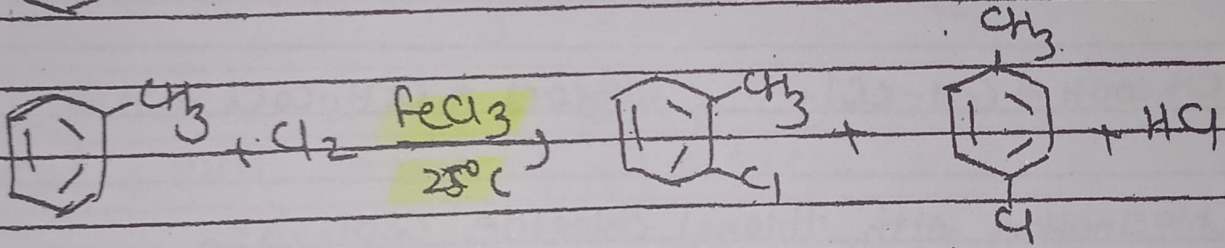
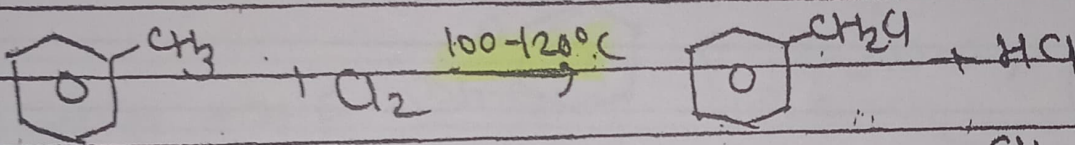
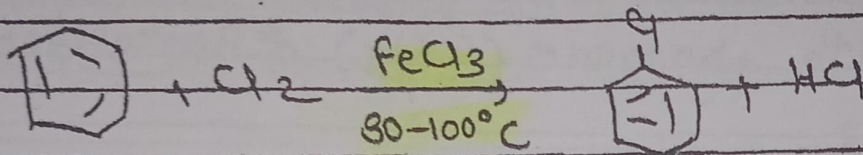
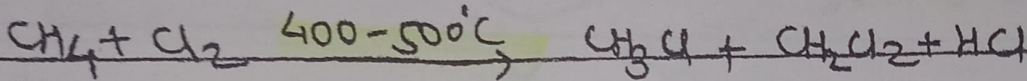
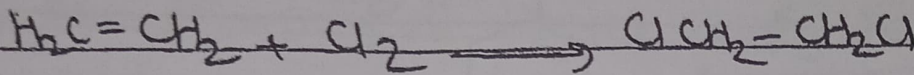
many of the catalysts are halogen carriers Iron, antimony & phosphorous, which are able to exist in two valences as halogen compounds, are used as they are less stable at higher valence



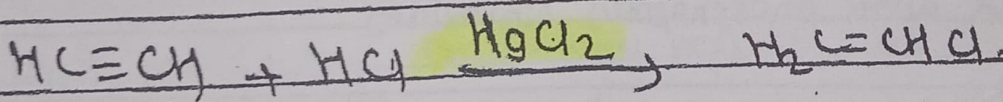
## ① Chlorination

Imp. methods for preparing chlorine comp.

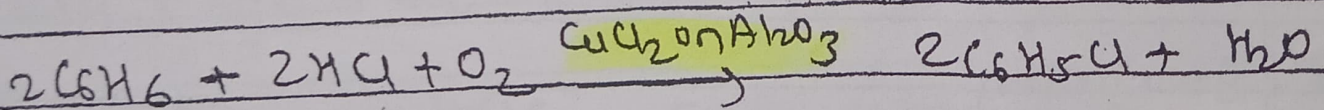
1) Direct action of chlorine gas.



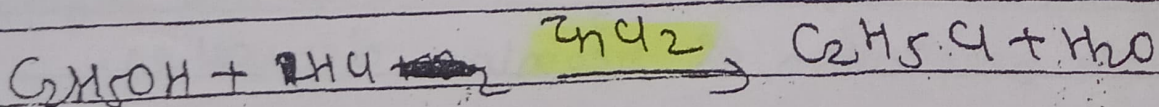
ii) HCl acts as the chlorinating agent.  
Addition rxn, direct action.



substitution rxn, indirect action.

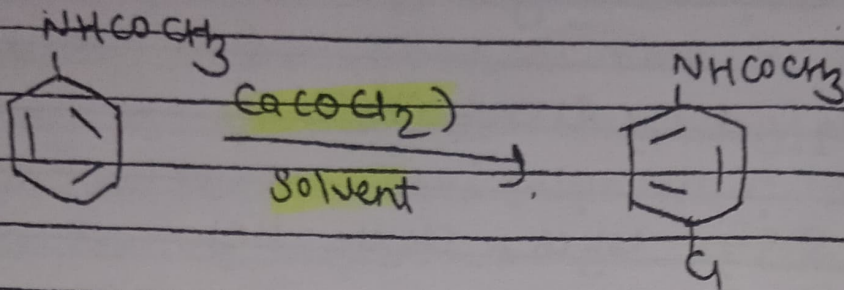
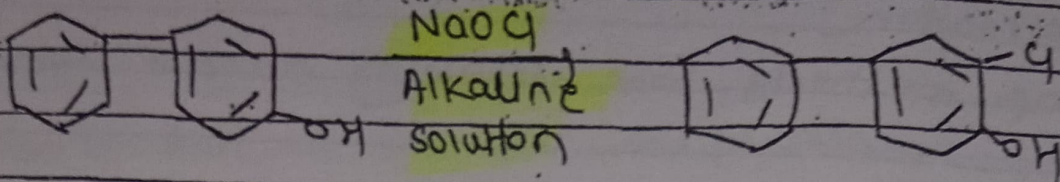


replacement reaction

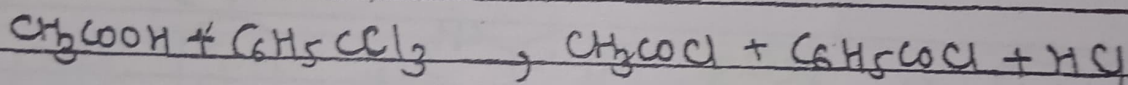
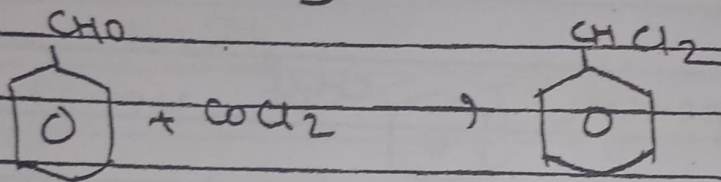




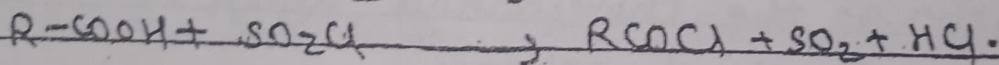
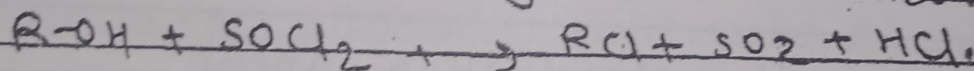
### 3) Sodium Hypochloride as chlorinating agent



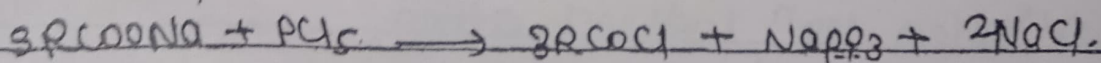
### 4) Chlorination with phosgene (COCl<sub>2</sub>) & Benzotrichloride (C<sub>6</sub>H<sub>5</sub>CCl<sub>3</sub>)



### 5) Chlorination with thionyl chloride (SOCl<sub>2</sub>)



### 6) Chlorination with phosphorus chlorides

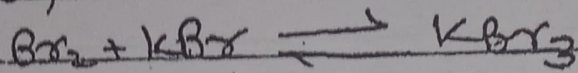


### ⊛ Bromination

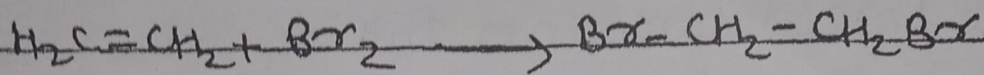
In many instances, bromination may be carried out in a manner similar to that employed for the preparation of bromine derivatives.



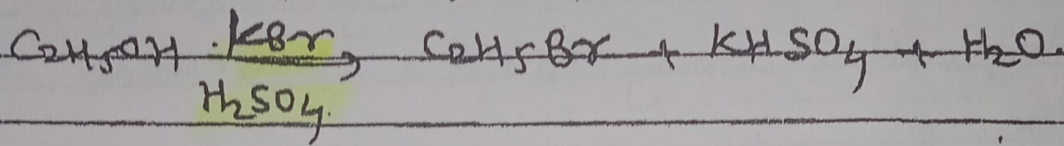
Reactions involving addition & substitution are common. Bromine dissolving in water are frequently employed. Particularly in the bromination of phenols. Potassium bromide is generally added to aq. bromine solution to increase the concentration of soluble molecular halogen.



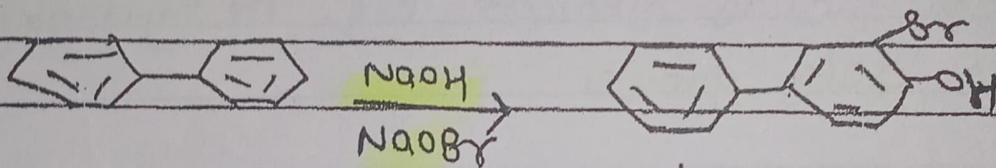
Addition reactions



Replacement reactions

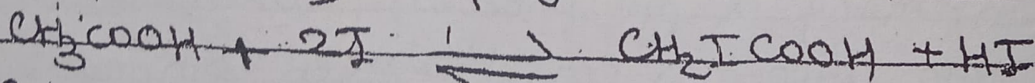


Substitution reaction -

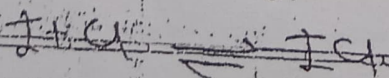


⊗ Iodination -

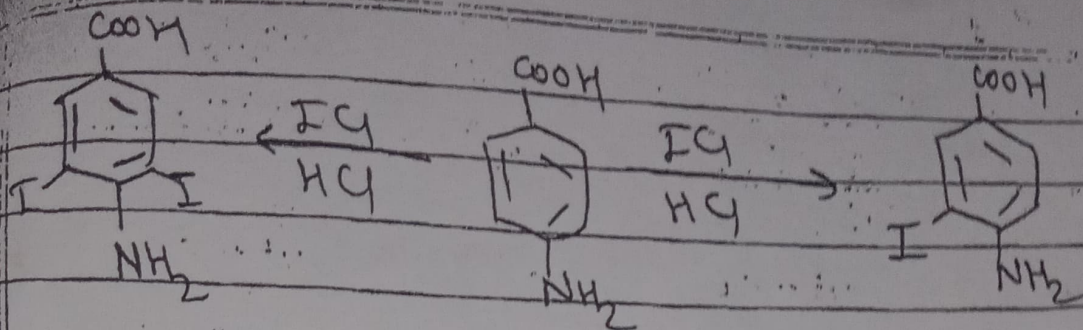
The relatively weak C-I bond makes permanent direct union of carbon to iodine by the replacement of H possible only in exceptional cases. Such iodination are reversible as character for instance the iodination of acetic acid & are governed largely by the conditions employed.



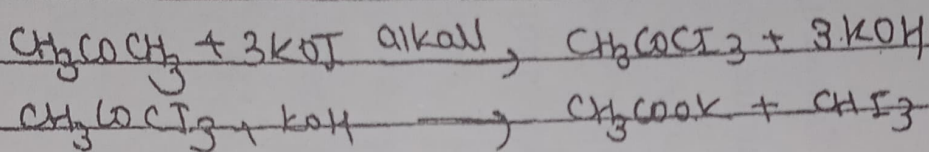
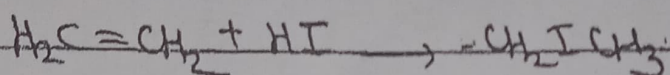
Catalysts are only infrequently employed in iodination, phosphorus being the principle accelerators. Iodine monochloride because of its activity under mild operating is the useful catalysis for the iodination of amino compounds.







Hydroiodic acid and alkali hypoiodites like the corresponding chlorine & Br compds find employment in iodination.

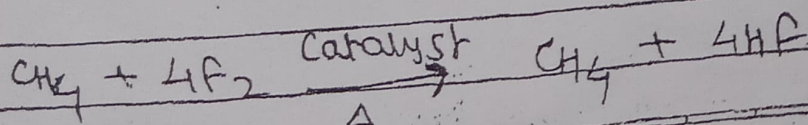


### Fluorination:

Fluorine acts directly on hydrocarbons to produce fluorides, but the reaction is violent and constitutes an explosion hazard. Some reactions can be carried out by careful control of temp & fluorine concentration but even these may be a cleavage of C-C bonds.

### Direct fluorination:

Direct vapour phase fluorination using elemental fluorine is done by using large volumes of an inert gaseous ~~for~~ fluorine & hydrocarbon carrier such as nitrogen a mixing system that rapidly & intimately brings the two reactants into contact & a reactor design that effectively removes the heat of reaction. Hydrocarbons can be fluorinated to their corresponding fluoalkanes.



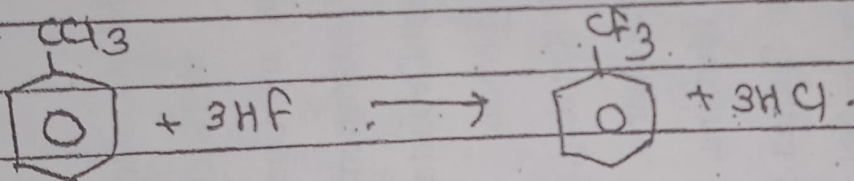
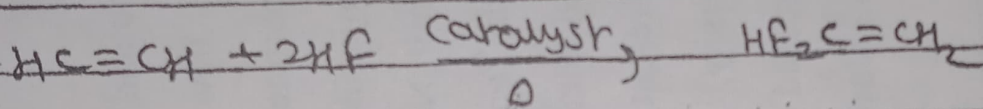
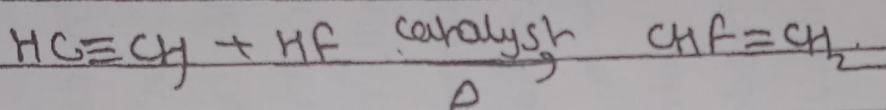


Dilute Fluorine reacts with metal carbides such as  $UC_2$ ,  $ThC_2$  &  $CaC_2$  producing fluoro-carbons & metal fluorides.

All these direct fluorination reactions are accompanied with high energy type of condensation reaction where fluoro-carbons of higher carbon chain length are formed.

HF as fluorinating agent:-

Hydrogen fluoride adds in the vapour phase by means of catalysts of acetylene.



\* Fluorination with metal fluorides:-

The majority of organic fluorides produced today are still made by antimony halide process starting with hydrogen fluoride & antimony pentachloride

