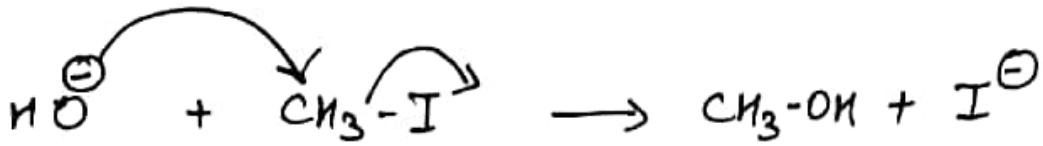
I. Substitution Reaction

1. Nucleophilic Substitution reaction



$$HO^{\ominus} + CH_3\text{-}I \longrightarrow CH_3\text{-}OH + I^{\ominus}$$

Nucleophile — Methyl iodide — Methanol — Iodide ion

2. Free radical Substitution reaction

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

Mechanism -

Chain initiation

$$Cl_2 \xrightarrow{h\nu} 2\dot{Cl}$$

(free radicals)

Chain propagation

$$CH_4 + \dot{Cl} \longrightarrow \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \dot{Cl}$$

Chain termination

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$$

$$\dot{Cl} + \dot{C}H_3 \longrightarrow CH_3Cl$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6$$

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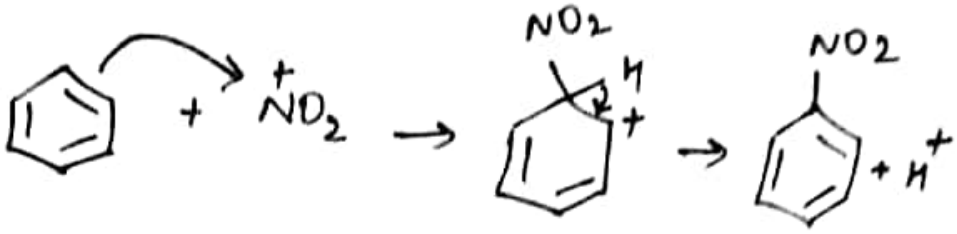
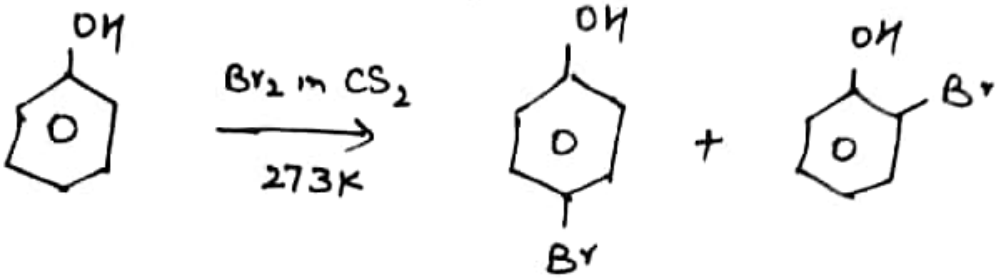
3. Electrophilic Substitution reaction

Eg-1

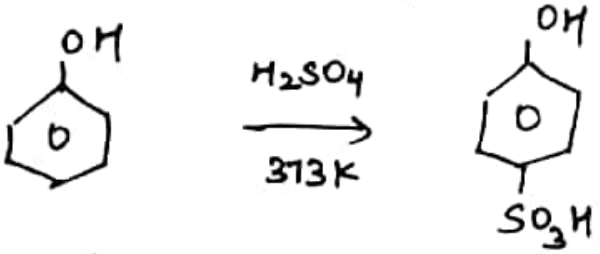


Eg-2 Halogenation of phenol

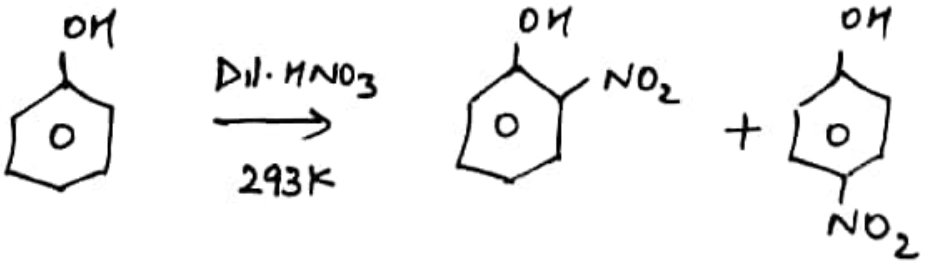


(major) (minor)

Eg-3 Sulphonation of phenol



Eg-4 Nitration of phenol



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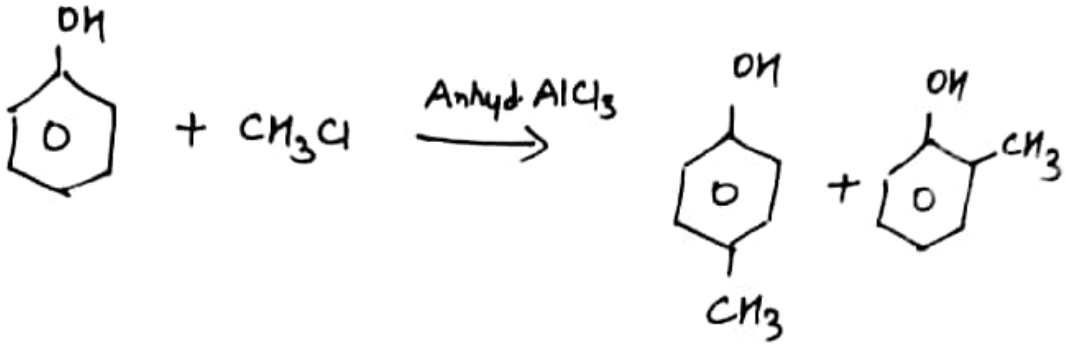
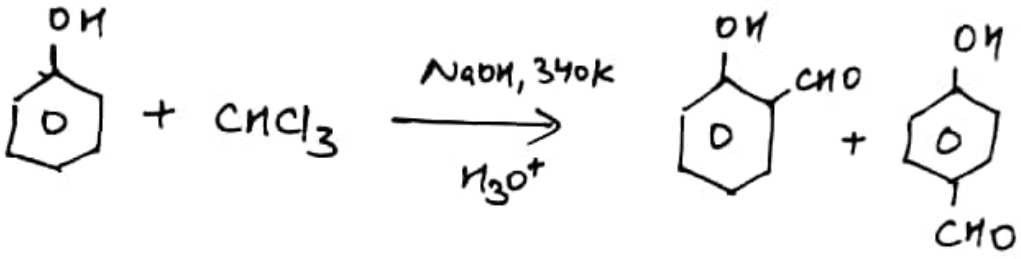
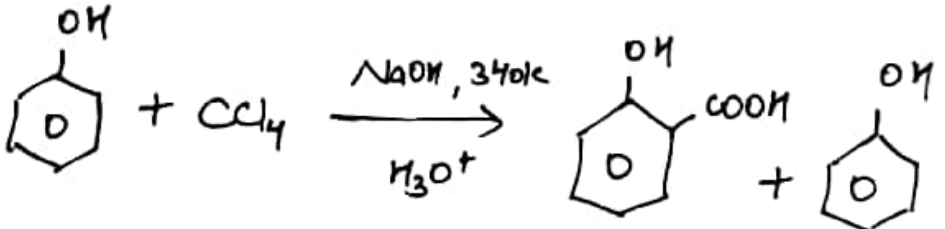
Eg-5 Friedal Craft Alkylation reaction



Eg-6 Reimer-Tiemann reaction



Eg-7



Salicylic acid (major)

(minor)

(Involve dichlorocarbene as an reactive intermediate in mechanism of reaction)

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S_N1 Mechanism

1. It follows first order kinetics.
2. Two step reaction.
3. Carbocations are rxn intermediates
4. Rearrangements are generally observed.
5. Elimination is an imp. side reaction.
6. Order of reactivity follows $3^\circ > 2^\circ > 1^\circ >$ methyl halides
7. Weak nucleophiles such as water, alcohols etc favours these reactions.
8. Low concentration of nucleophiles generally favour them.

S_N2 Mechanism

1. It follows second order kinetics.
2. One step reaction.
3. Reaction involves transition state
4. Rearrangements are not observed.
5. Elimination is not an imp. side reaction.
6. Order of reactivity follows Methyl $> 1^\circ > 2^\circ > 3^\circ$
7. Strong nucleophiles such as alkoxide ions follows these reactions.
8. High concentration of nucleophiles favour them.

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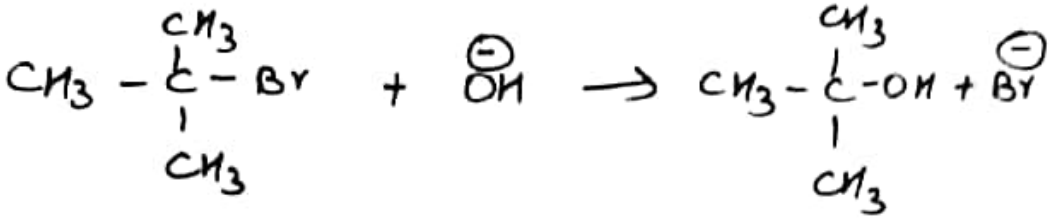
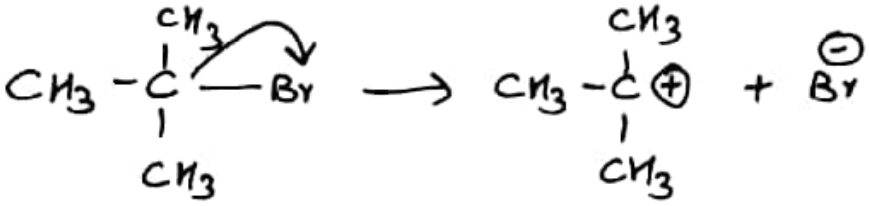
Mechanism of Unimolecular Nucleophilic Substitution Reaction

Eg-

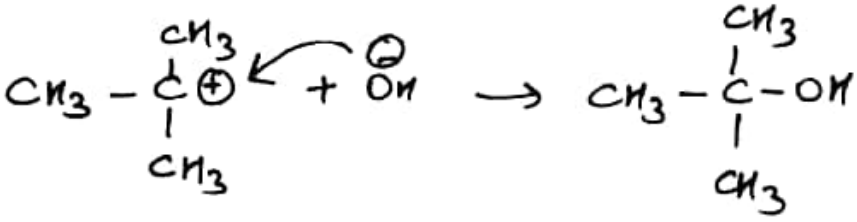


Rate of rxn $\propto [(CH_3)_3CBr]$

Step-1

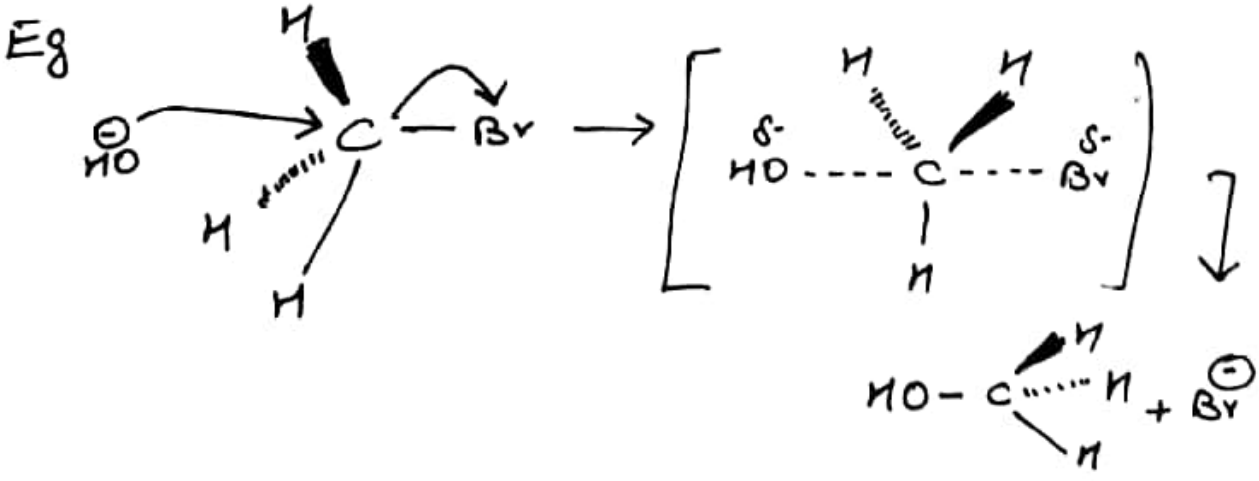


Step-2



Mechanism of Bimolecular Nucleophilic Substitution Reaction

Eg



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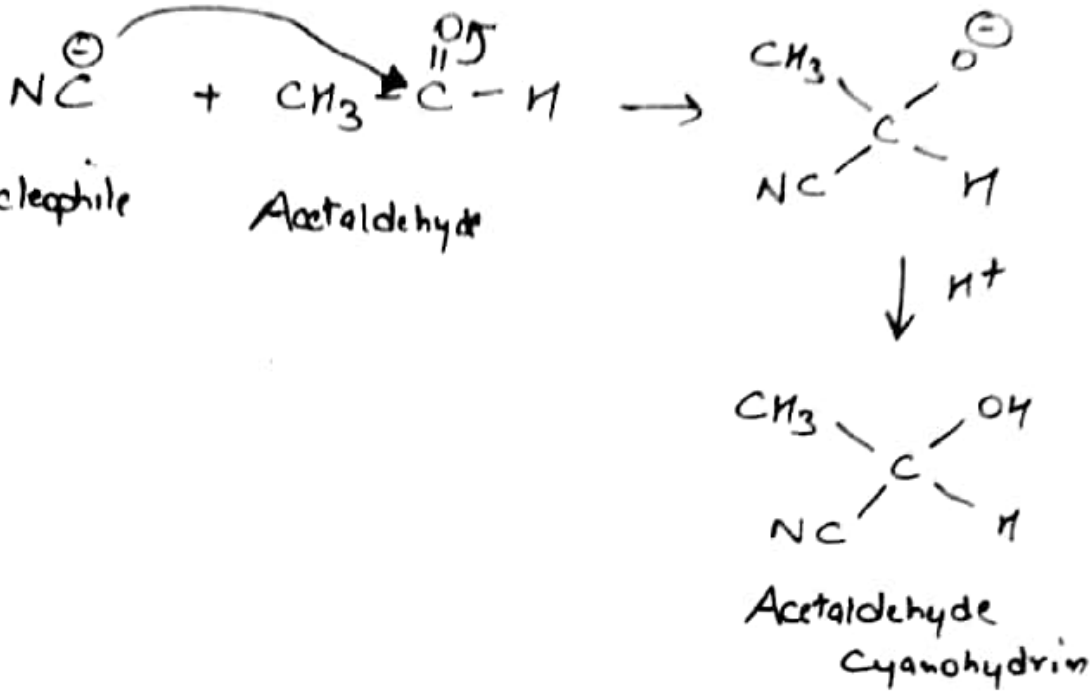
II Addition Reaction

1. Nucleophilic addition reaction



Acetaldehyde Cyanohydrin

2. Free radical addition reaction

$$CH_3-CH=CH_2 + HBr \xrightarrow[\text{peroxide}]{\text{Benzoyl}} CH_3CH_2CH_2Br$$

Mechanism involves chain initiation, propagation and termination step involving Benzoyl free radical and 2° free radical formation. It follows Anti-Markovnikov's Rule and such effect is known as Peroxide / Kharasch effect.

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Chain initiation step -

a) $C_6H_5CO-O-O-COC_6H_5 \xrightarrow{\Delta} 2\,C_6H_5CO-\dot{O}$

b) $C_6H_5CO-\dot{O} + HBr \longrightarrow C_6H_5COOH + \dot{B}r$

Chain propagation step -

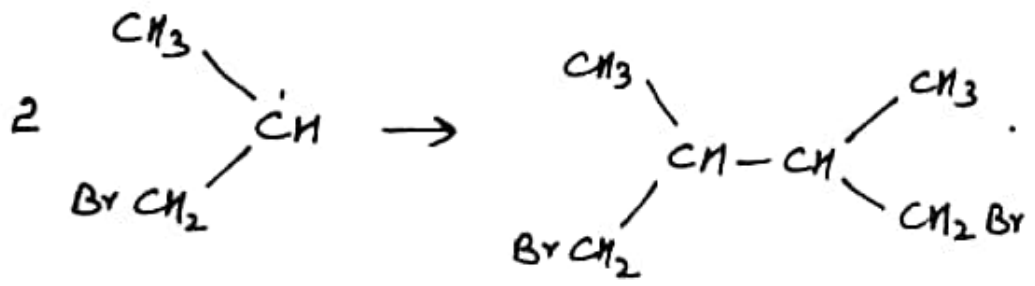
a) $CH_3CH=CH_2 + \dot{B}r \longrightarrow CH_3\dot{C}H-CH_2Br$

b) $CH_3\dot{C}H-CH_2Br + HBr \longrightarrow CH_3-CH_2-CH_2-Br + \dot{B}r$

Chain termination step -

a) $2\dot{B}r \longrightarrow Br_2$

b) $CH_3-\dot{C}H-CH_2Br + \dot{B}r \longrightarrow CH_3-CHBr-CH_2Br$

c) 

(1,4-dibromo-2,3-dimethyl butane)

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3. Electrophilic addition reaction

$$CH_3CH=CH_2 + HCl \longrightarrow CH_3\overset{+}{C}H-CH_3 + \bar{C}l$$

$$\downarrow$$

$$CH_3 - CHCl - CH_3$$

Mechanism of this reaction involves carbocation formation and it follows Markovnikov's Rule as addition of un-symmetrical reagent to unsymmetrical alkenes occurs in such a way that negative part of addendum goes to that carbon atom of double bond which carries lesser number of hydrogen atoms.

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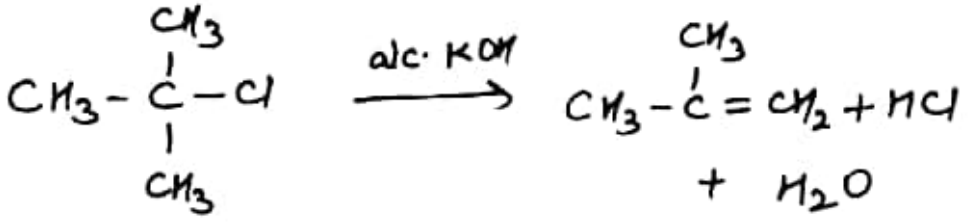
III Elimination reactions

1. Unimolecular (E_1) reaction

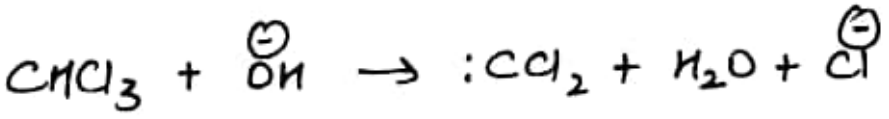
Eg-



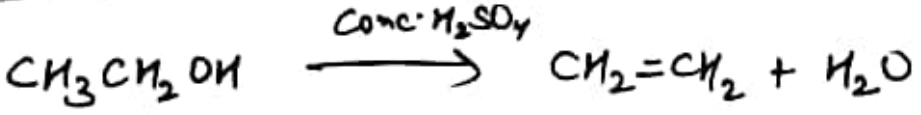
Rate determining step involves only one molecule

2. Bimolecular (E_2) reaction - in which rate determining step involves two molecules

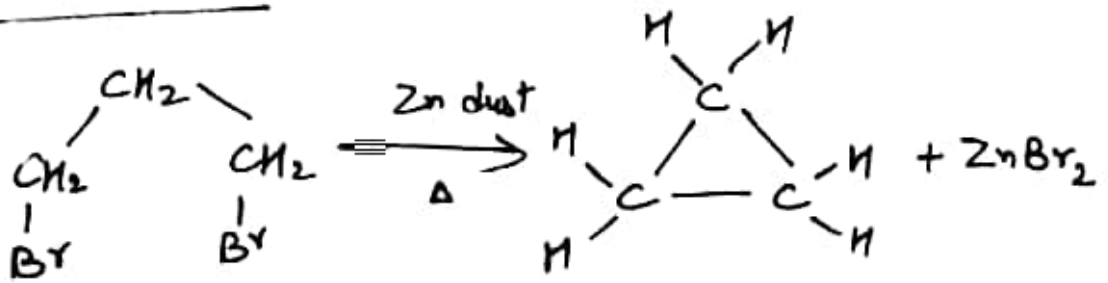
α- elimination



β - elimination



γ- elimination



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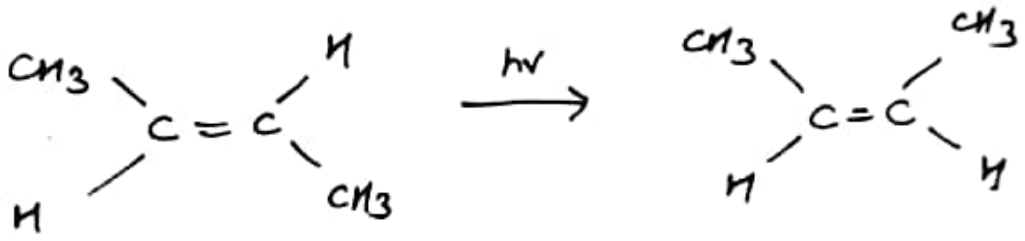
IV Rearrangement reactions

a) $CH_3CH_2CH_2CH_2Br \xrightarrow[575K]{AlCl_3} CH_3CH_2CHBr-CH_3$

b) $NH_4CNO \xrightarrow{\Delta} NH_2CONH_2$

V Isomerisation reactions



trans but-2-ene cis but-2-ene

VI Condensation reactions

$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO$$

(2-hydroxybutanal)

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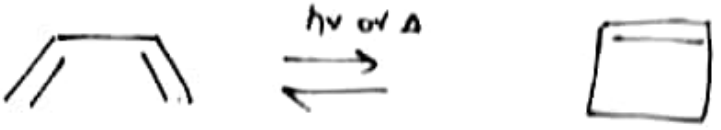
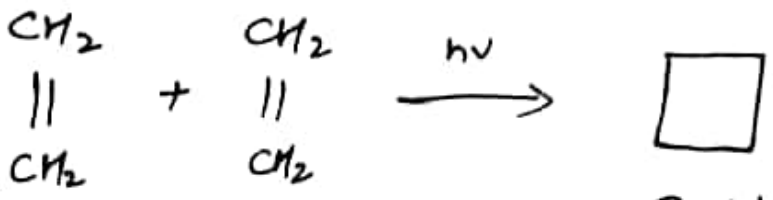
VII Electrocyclic reactions



Buta-1,3-diene Cyclobutene

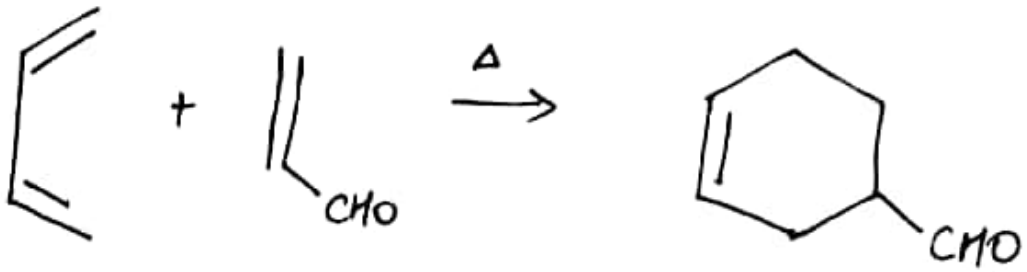
VIII Cycloaddition reactions

Eg-



Cyclobutane

Eg-



Buta-1,3-diene Acrolein Cyclohex-3-ene-1-carbaldehyde

Diels Alder reaction

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IX Reduction Reactions

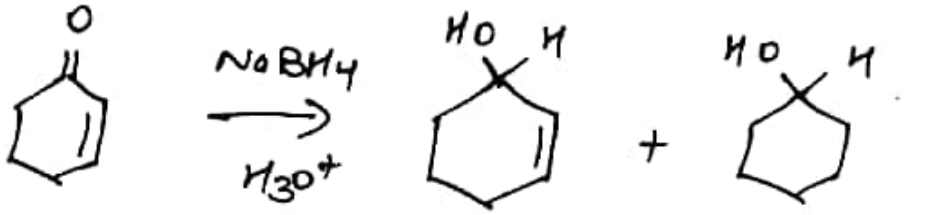
I Catalytic Hydrogenation by Ni, Pt, Pd / H_2

Eg - $CH_3CH_2CHO \xrightarrow{H_2/Ni,Pt,Pd} CH_3CH_2CH_2OH$

II Reduction by $NaBH_4$

Eg - $CH_3CH_2CH_2CHO \xrightarrow[H_3O^+]{NaBH_4} CH_3CH_2CH_2CH_2OH$

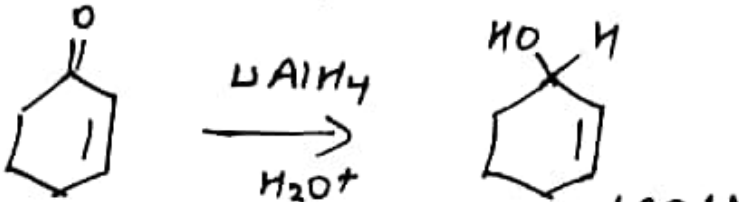
Eg - $CH_3-CH=CH-CHO \xrightarrow[H_3O^+]{NaBH_4} CH_3-CH=CH-CH_2OH$ (85%.)

Eg - 

(59%.) (41%.)

III Reduction by $LiAlH_4$

Eg - $CH_3CHO \xrightarrow[H_3O^+]{LiAlH_4} CH_3CH_2OH$

Eg - 

(98%.)

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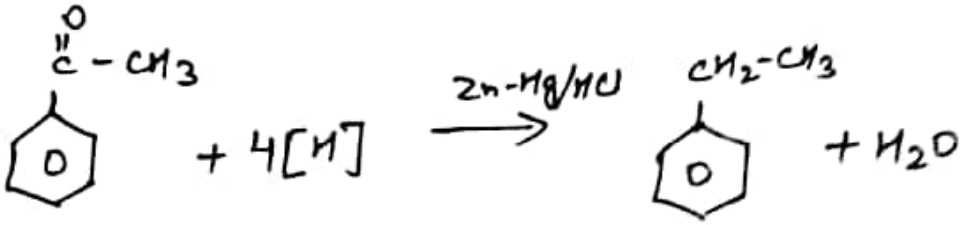
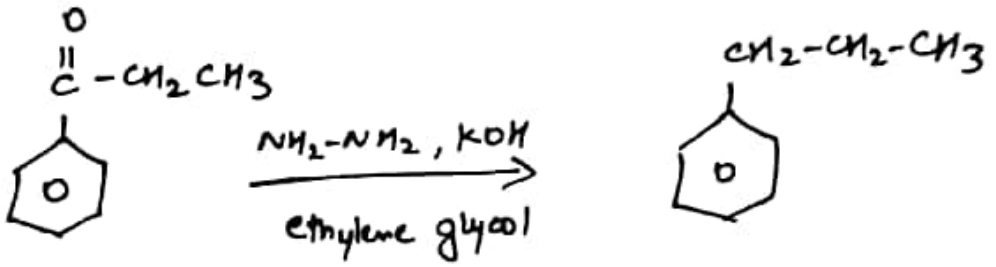
IV Rosenmund reduction (Pd, $BaSO_4$, S, Xylene)

Eg- $CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[\text{Xylene}]{Pd, BaSO_4, S} CH_3-\overset{O}{\overset{\|}{C}}-H + HCl$

V Clemmensen reduction (Zn-Hg / HCl)

Eg- 

VI Wolff - Kishner reduction (NH_2-NH_2, KOH, ethylene glycol)

Eg- 

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Z. Oxidation Reactions

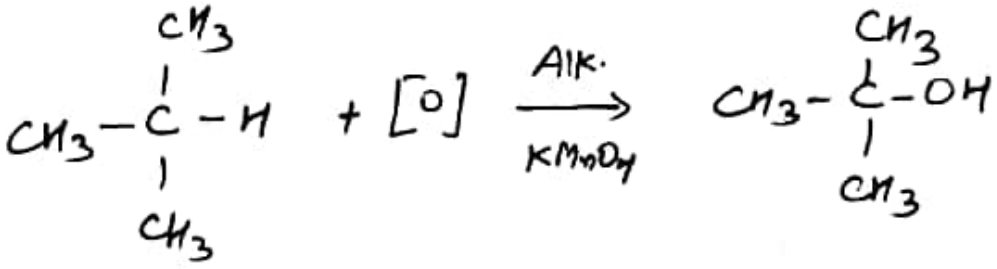
1. Oxidation by O_2

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

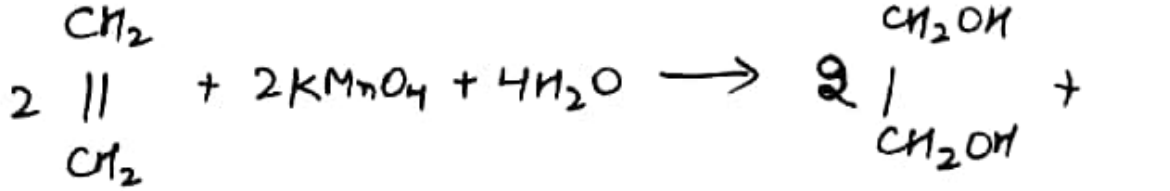
2. Oxidation by $KMnO_4$

a) $CH_3CH_2OH + [O] \xrightarrow{KMnO_4} CH_3CHO \xrightarrow{[O]} CH_3COOH$

b)



c)



$$2MnO_4 + 2KOH$$

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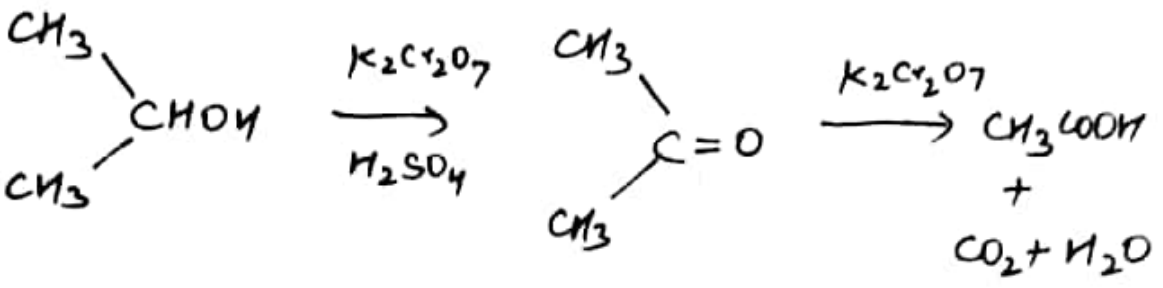
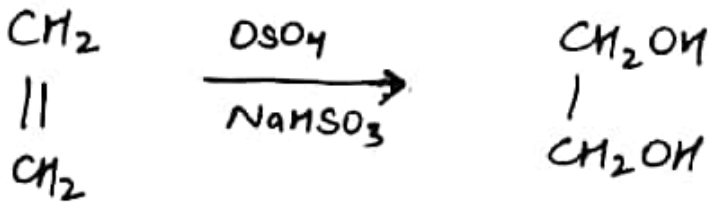
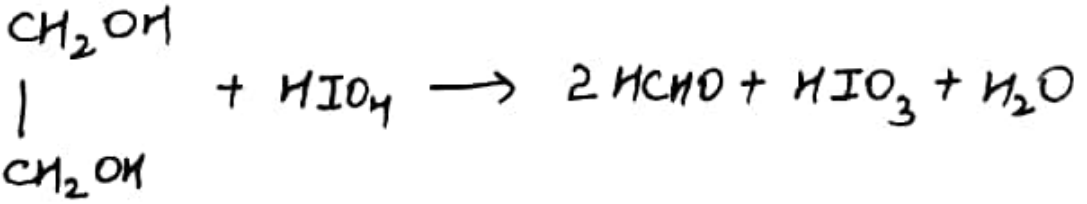
3 Oxidation by $K_2Cr_2O_7$



4 Oxidation by OsO_4 (Osmium tetraoxide)



5. Oxidation by HIO_4 (Periodic acid)



6. Oxidation by O_3 (Ozone)

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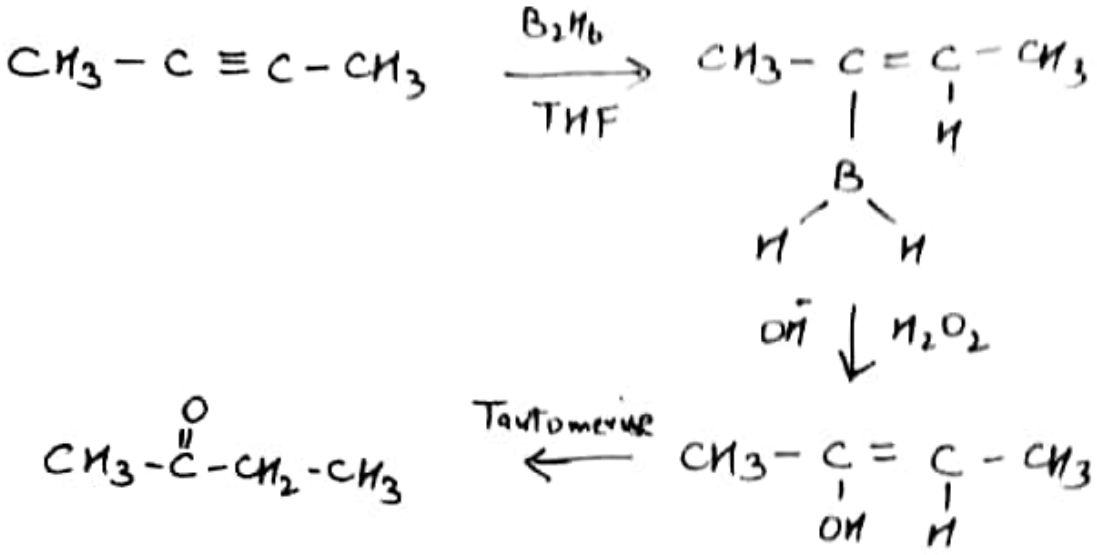
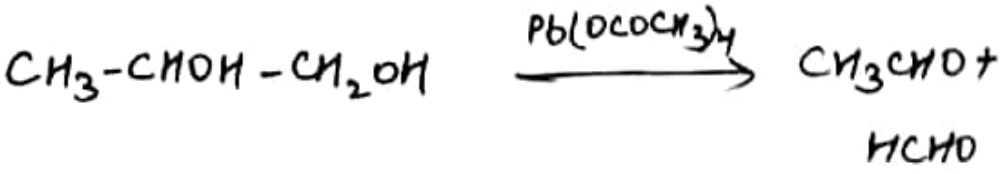
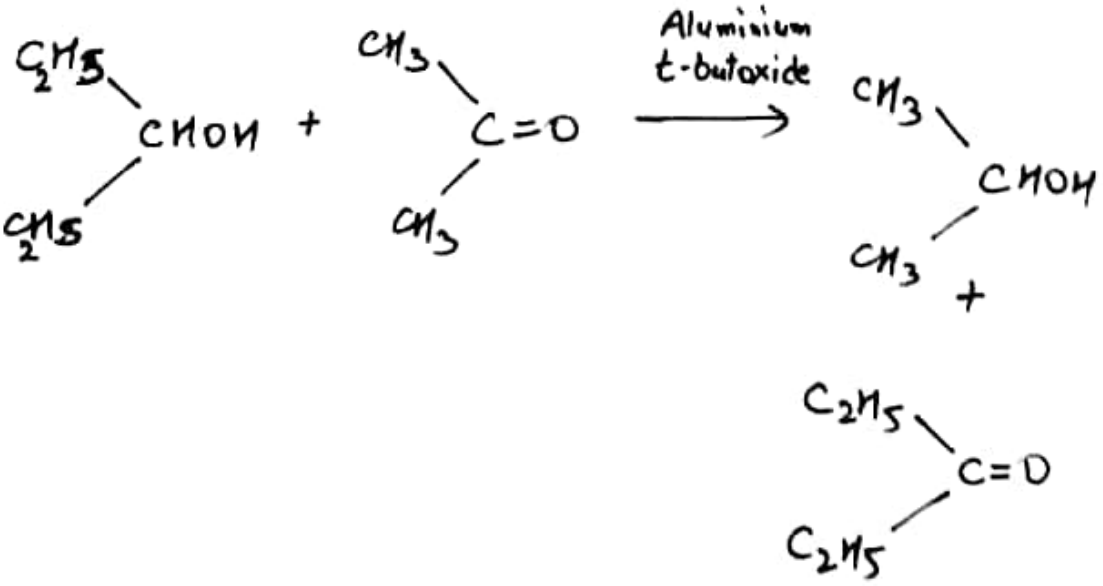
7. Oxidation by H_2O_2



8. Oxidation by $Pb(OCOCH_3)_4$



9. Oppenauer oxidation



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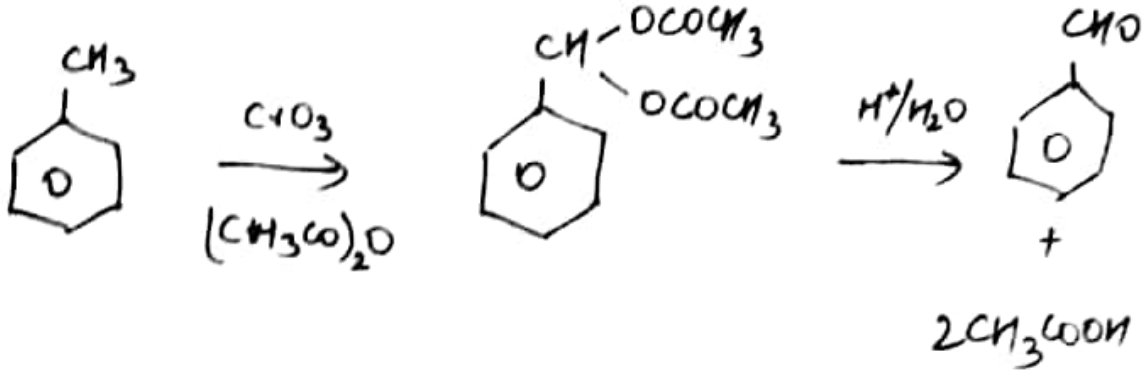
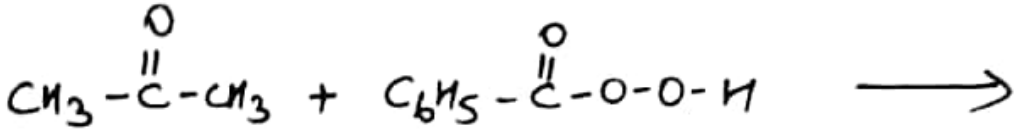
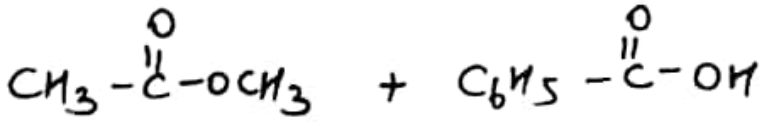
10. Oxidation by CrO_3



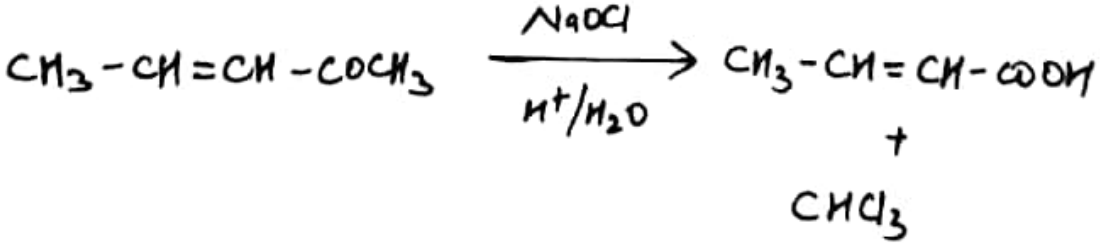
11. Baeyer - Villiger Oxidation





12. Oxidation with Tollen's reagents

13. Oxidation with sodium hypohalite



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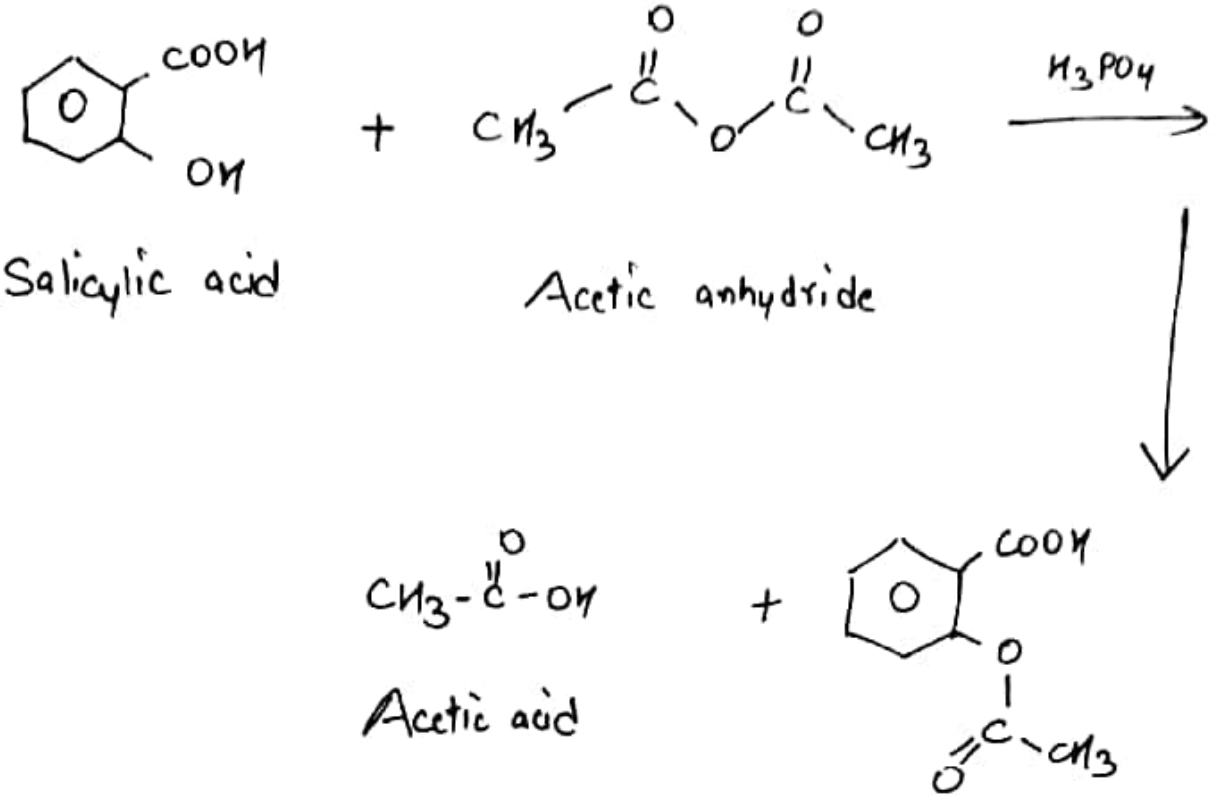
XI Synthesis of ASPIRIN



Salicylic acid

Acetic anhydride

Acetic acid

Acetylsalicylic acid
(ASPIRIN)

Salicylic acid used in this reaction can be prepared by Reimer-Tiemann reaction. Acetic anhydride can be prepared by treatment of Acid chloride with sodium acetate.

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