Unit III

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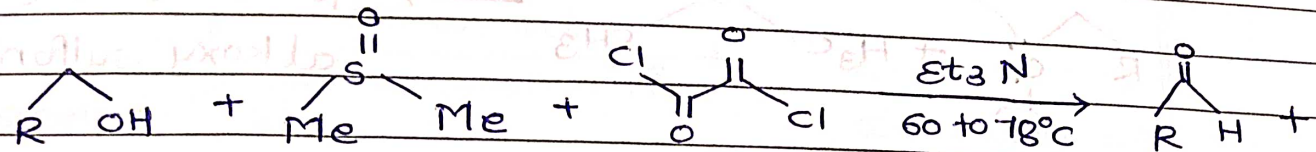
Date

Swern oxidation :-

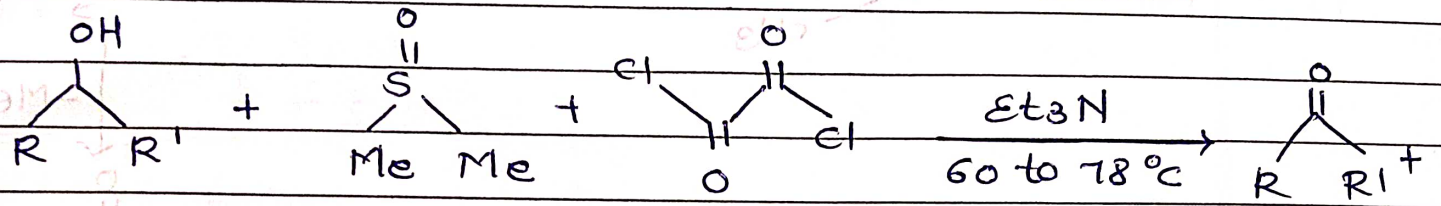
G.R :-



1° alc. DMSO (Sulfoxide) oxalic chloride $(CH_3)_2S + CO\uparrow + CO_2\uparrow$

DMS

Hazardous

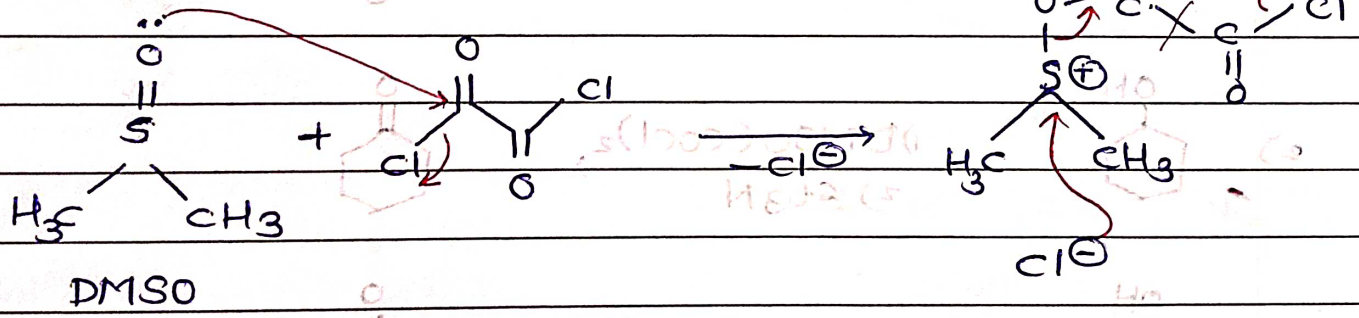


2° alc.

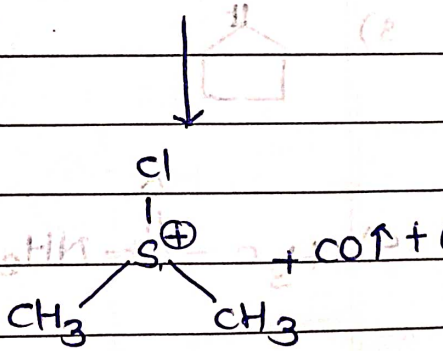
$(CH_3)_2S + CO\uparrow + CO_2\uparrow$

Mechanism :-

Step I :- preparation of dimethyl chlorosulphonium ion.

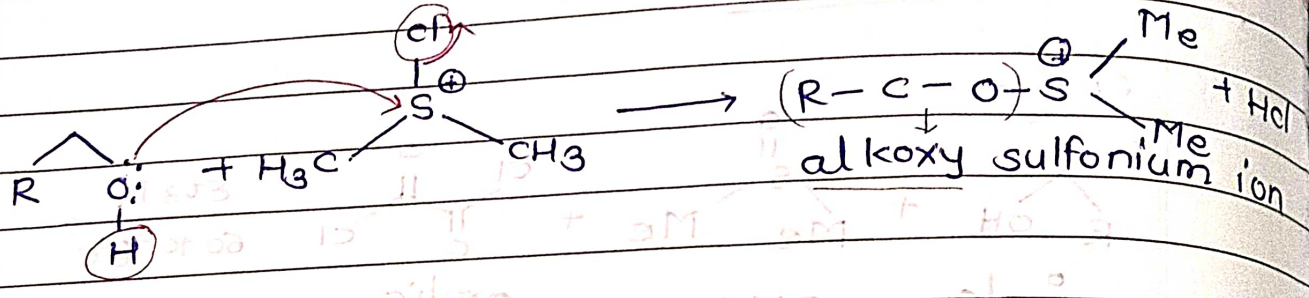


DMSO

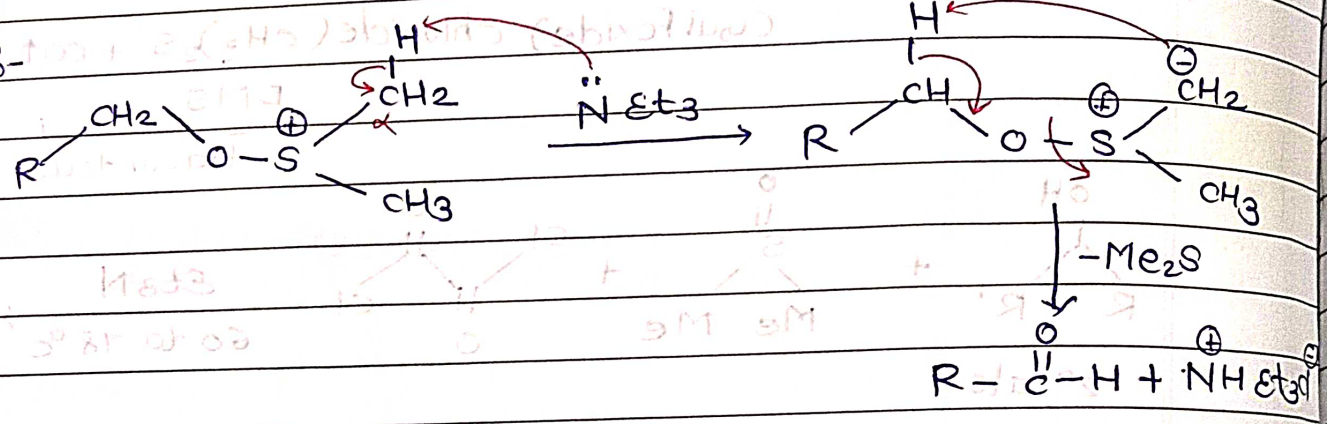


dimethyl chlorosulfonium

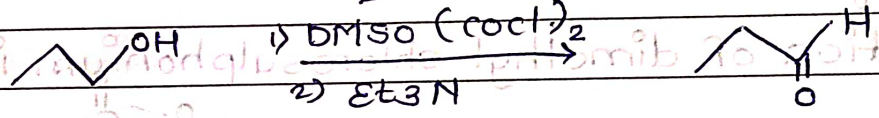
Step II :-

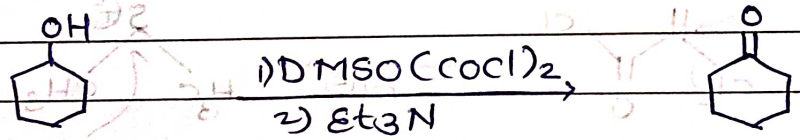


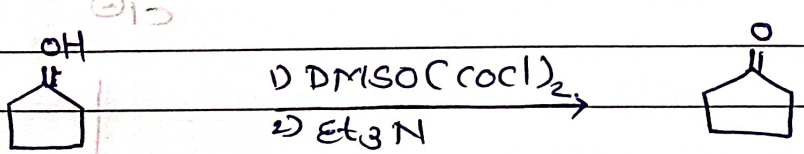
Step III :-



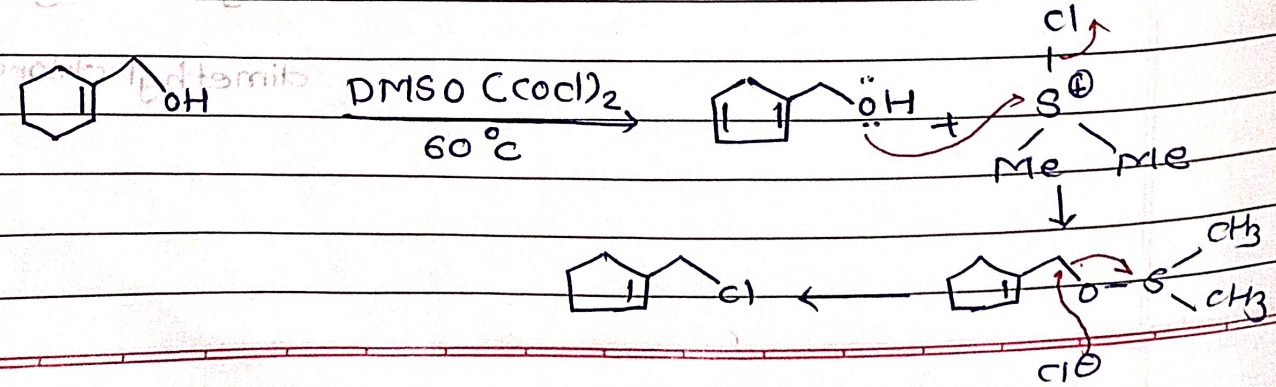
Application :- active $Nu^{\ominus}$

1) 

2) 

3) 

4) $H_3C-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{Oxd}^n]{\text{Swern}} H_3C-C\equiv N$

5) 

unit III

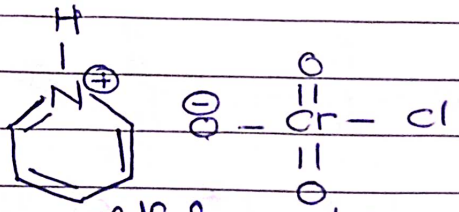
Imp *

PCC [corey's reagent] → oxidizing agent

[pyridinium chloro chromate]

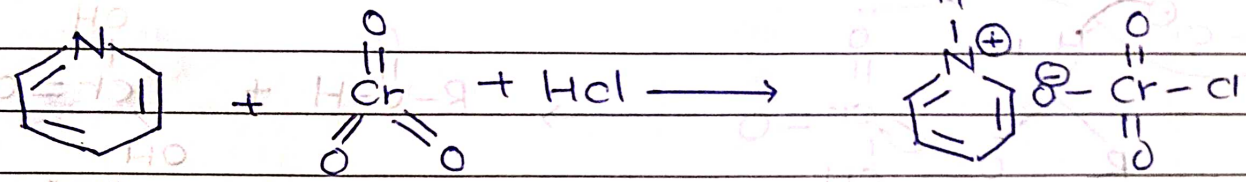
[corey - sugas reagent]

structure :-

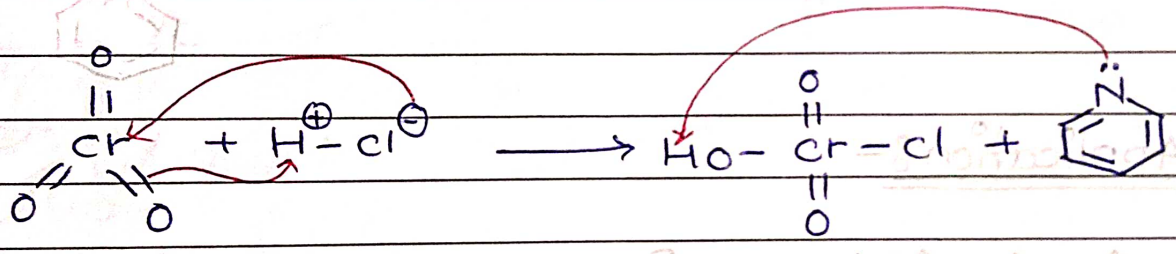


pyridinium chloro chromate

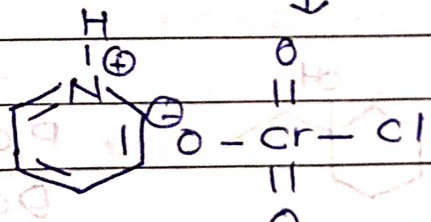
synthesis :-



pyridine

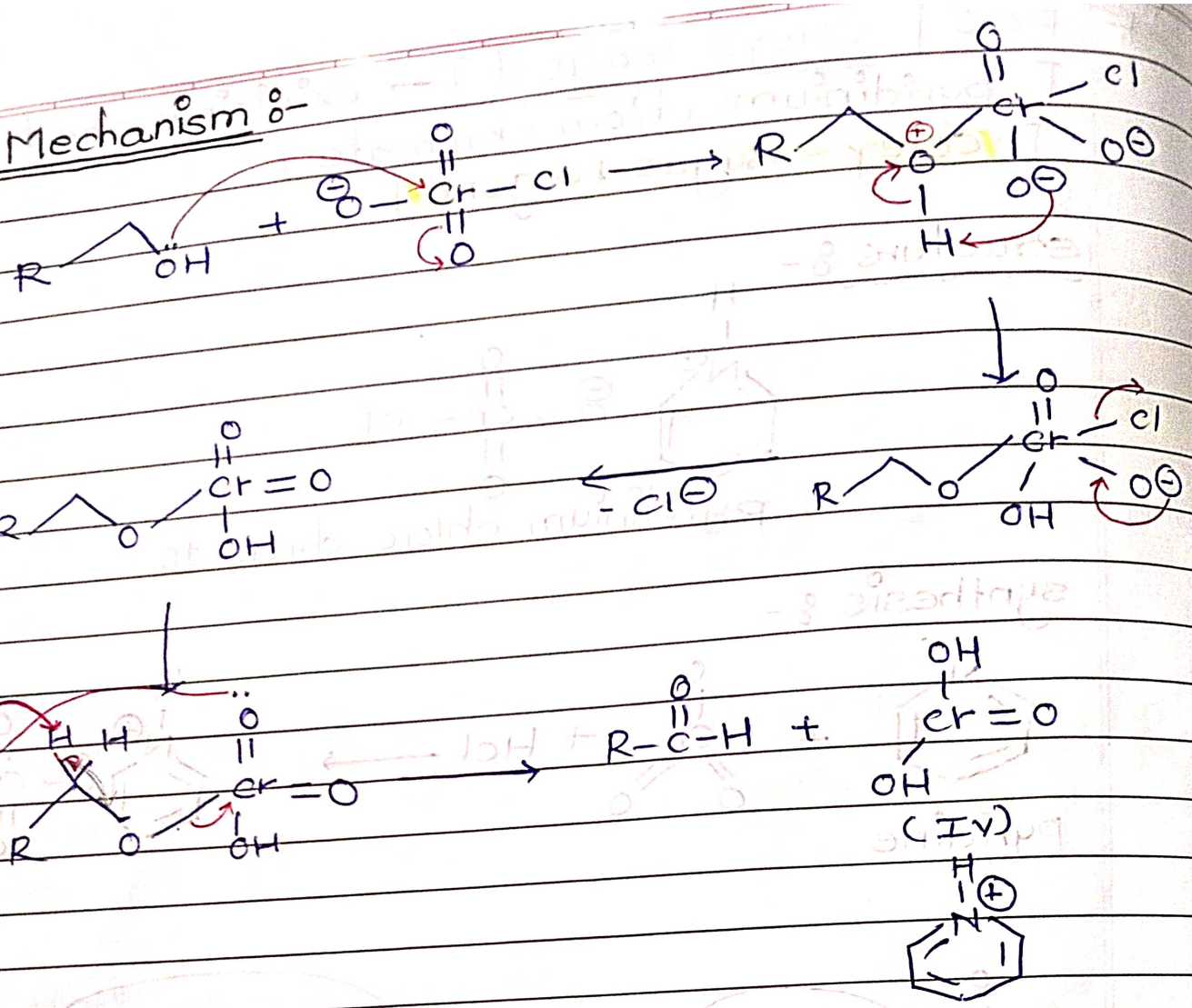


chloro chromic acid

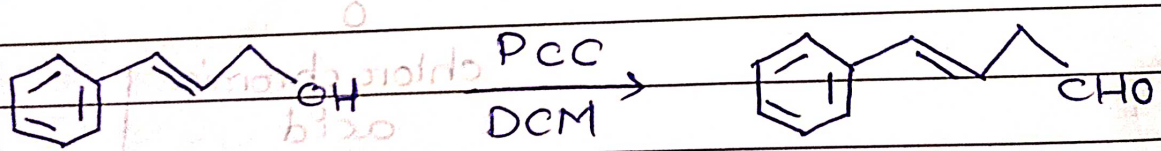


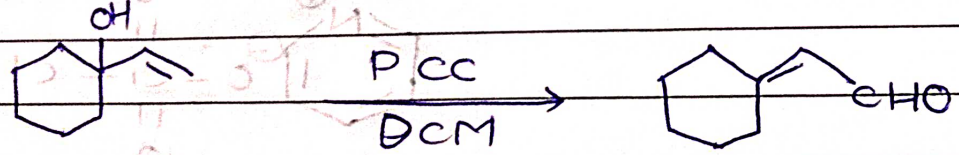
pyridinium chloro chromate

Mechanism :-



Application :-

① 

② 

unit -III

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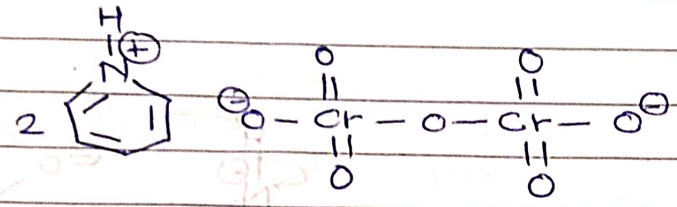
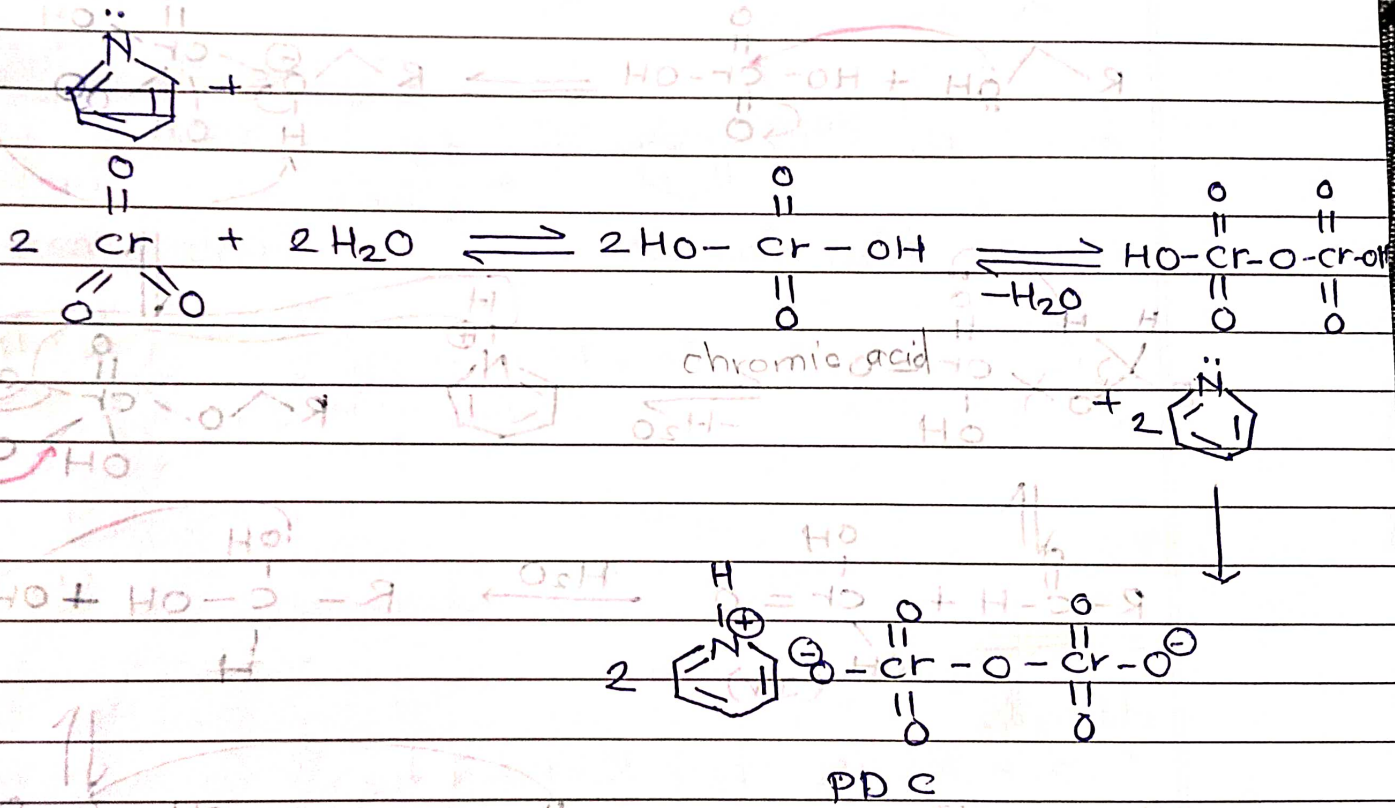
PDC [pyridium dichromate]
↑ oxidizing agent
[corn forth reagent] [corey-schmidt reagent]

structure :-

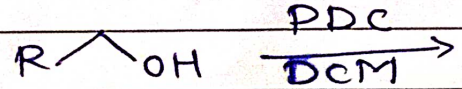


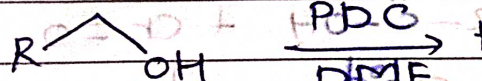
pyridinium dichromate

synthesis :-

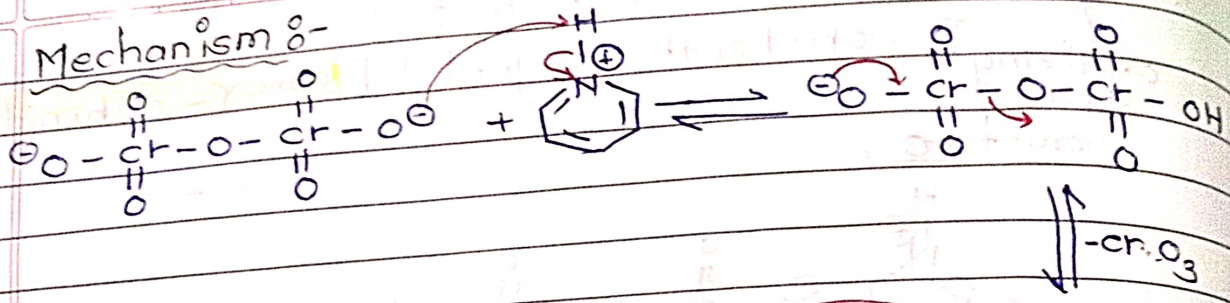


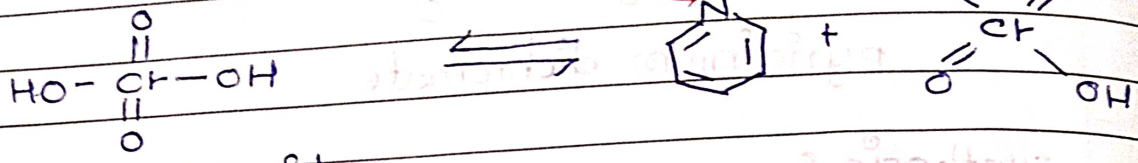
PDC in DCM/DMF → corey-schmidt reagent
↳ Dimethyl Formamide



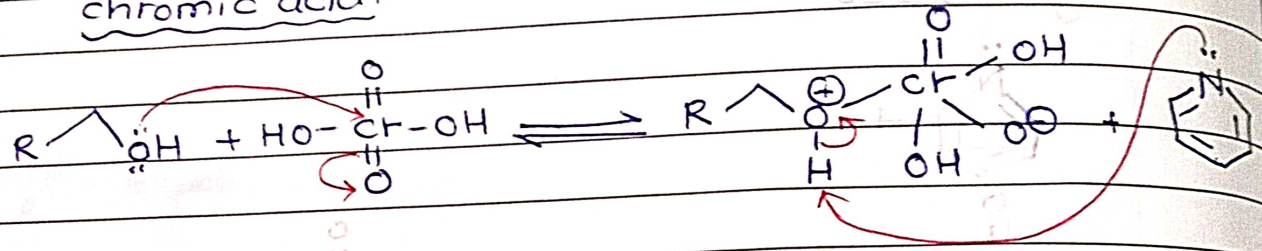


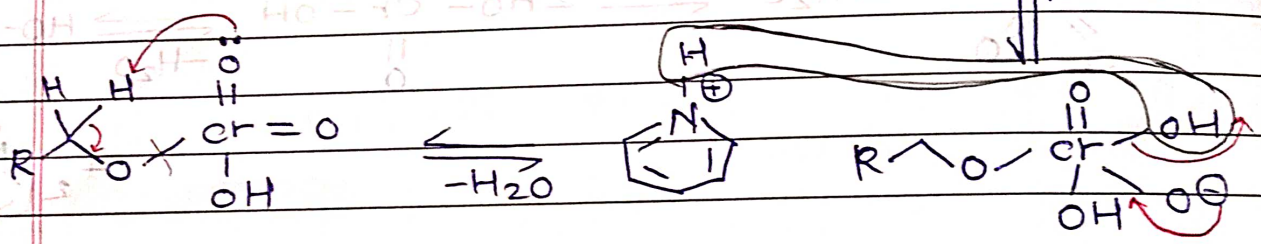
Mechanism :-

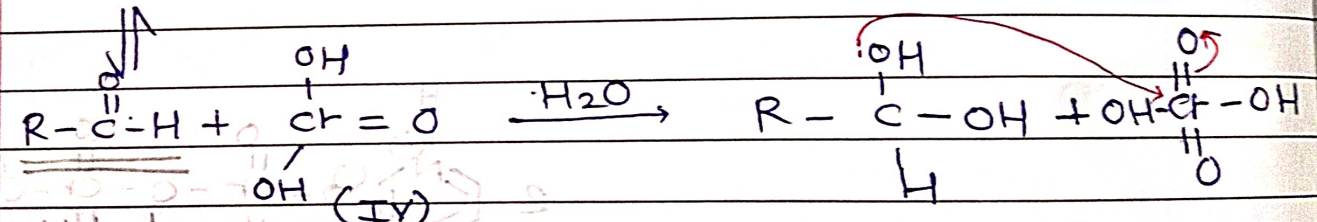




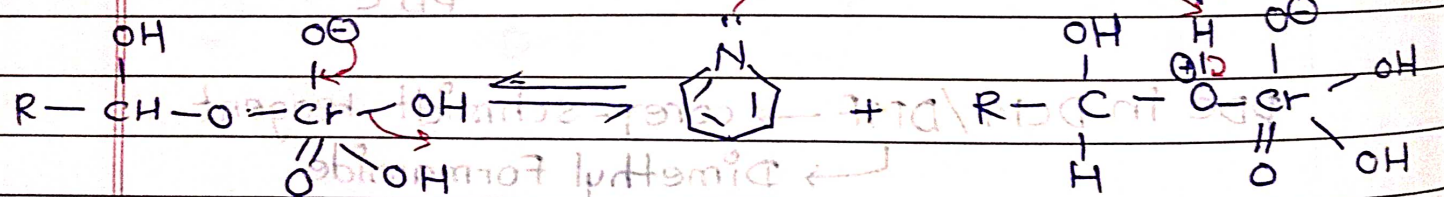
chromic acid.

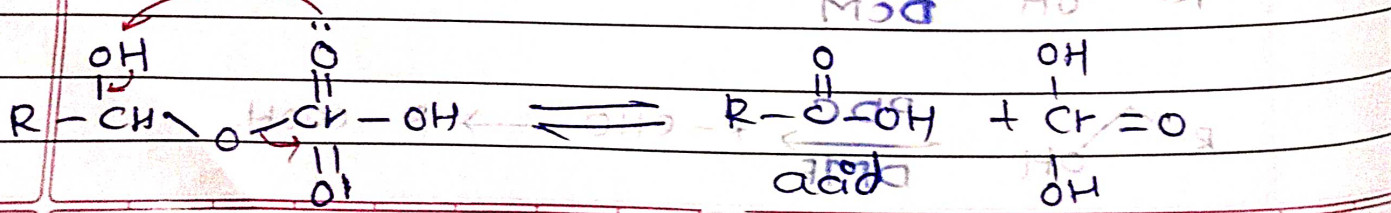






aldehyde





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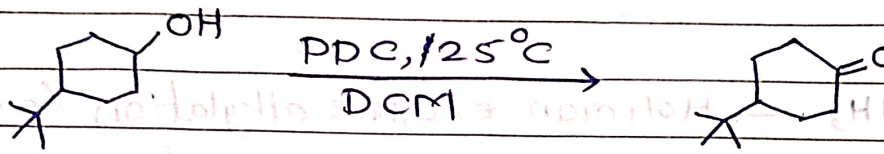
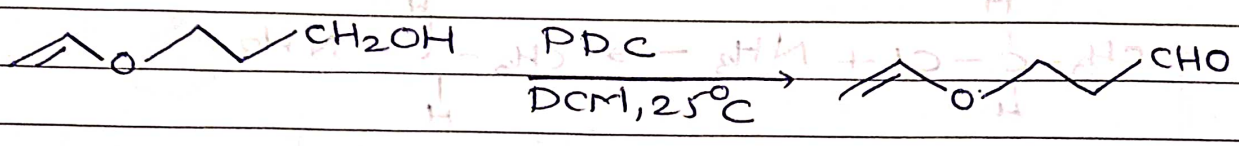
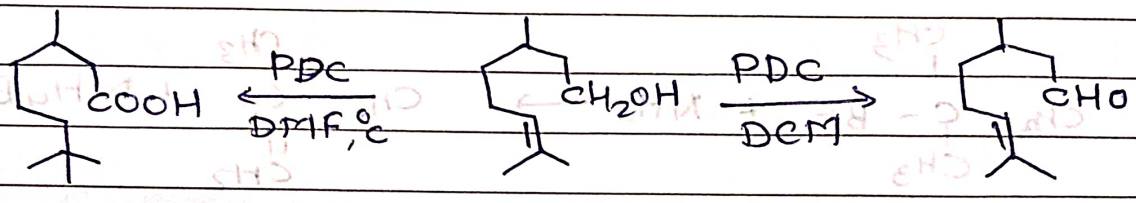
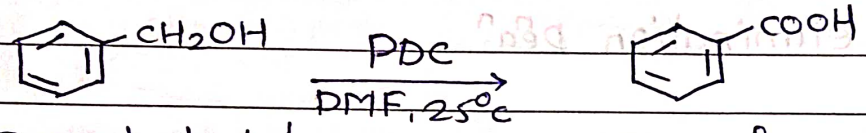
Application :

1) 

2) 

3) 

4) 

Benzyl alcohol — Benzoic acid.

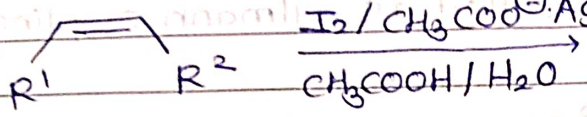
NGP – anchimeric assistance

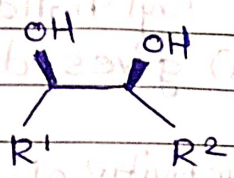
Date

woodward - prevost hydroxylation. S_N2 mech | NGP | back side attack

Imp

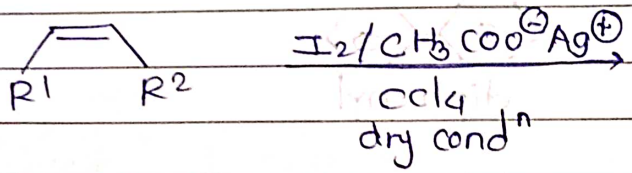
Woodward → cis-hydroxyln

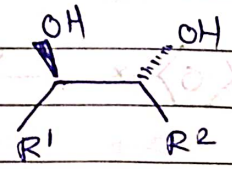




cis-diol.

prevost → trans hydroxyl





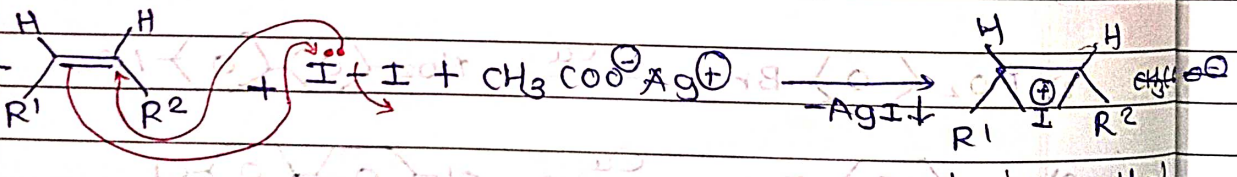
trans diol

woodward Reagent :-
soln of equimolar mixture of I_2 & $CH_3COOAg^{\oplus}$ 1:1
CH_3COOH / H_2O

Prevast Reagent :-
I_2 & $CH_3COOAg^{\oplus}$ 1:2
/ CCl_4

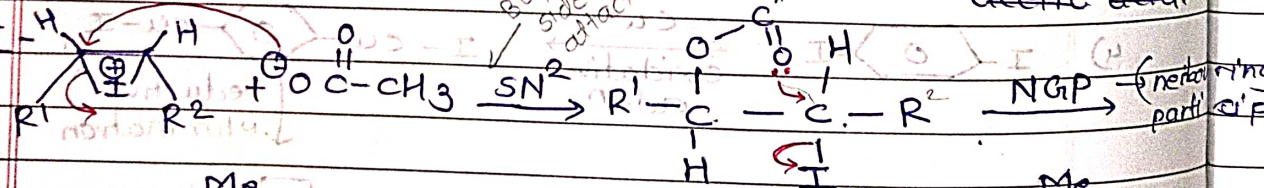
Mechanism :-

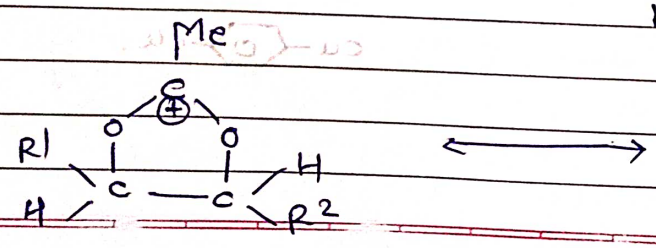
step I -

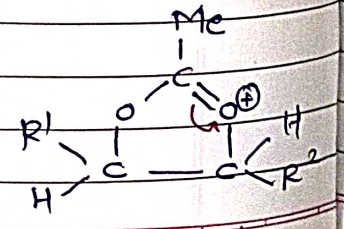


Iodonium salt of acetic acid.

step II -







oxonium ion

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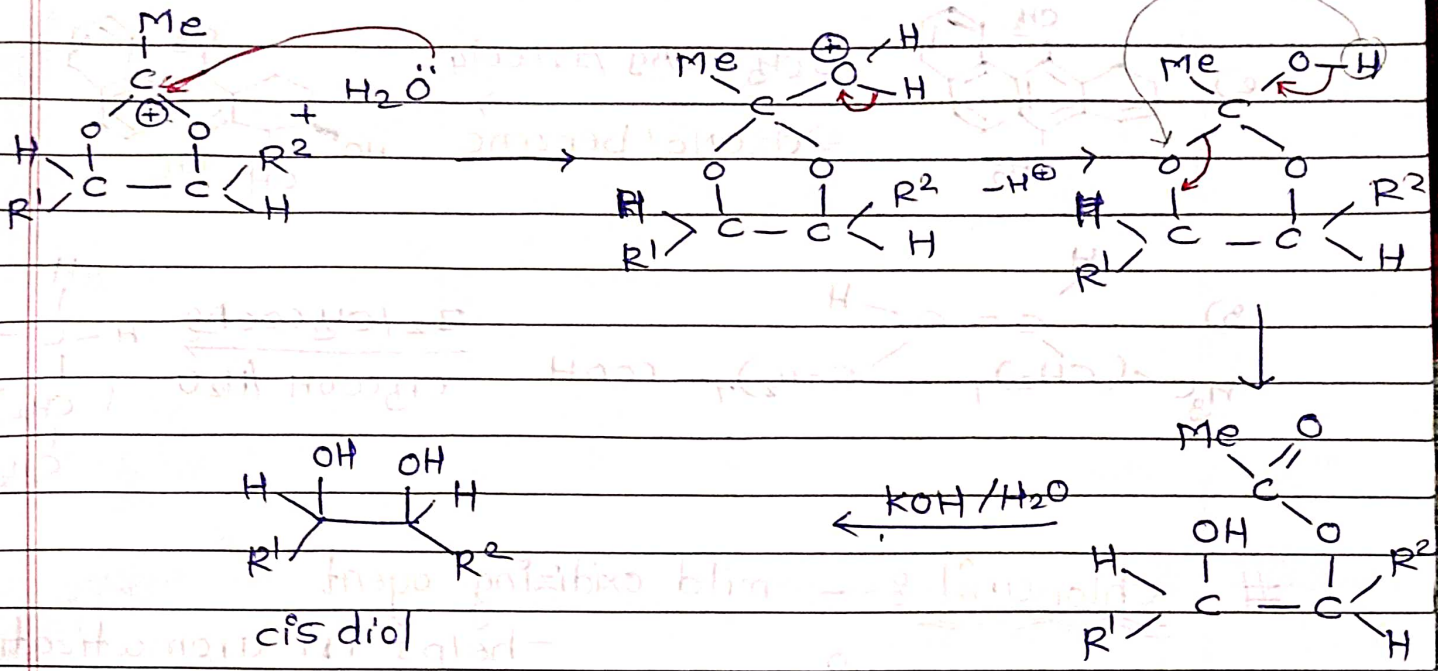
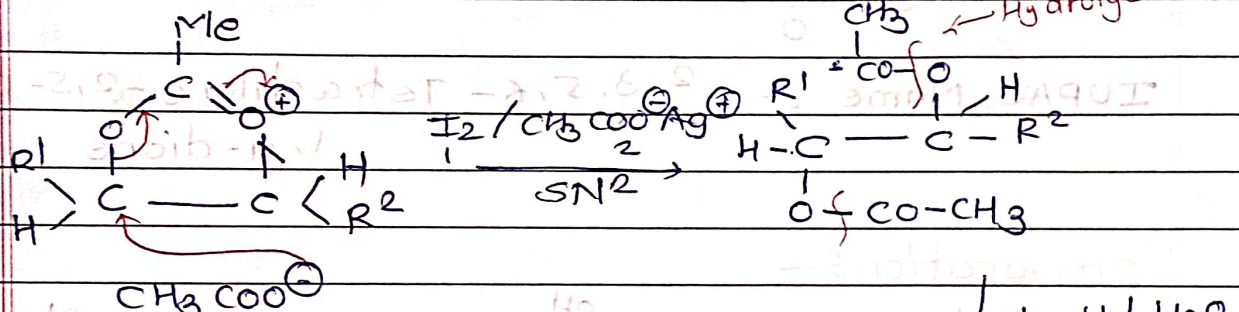
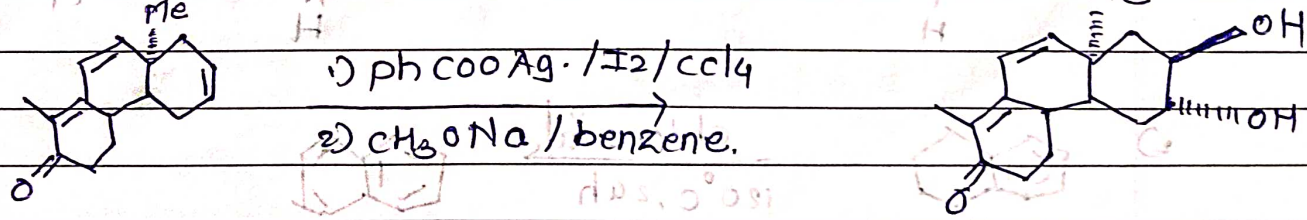
woodward ↓

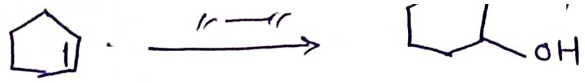


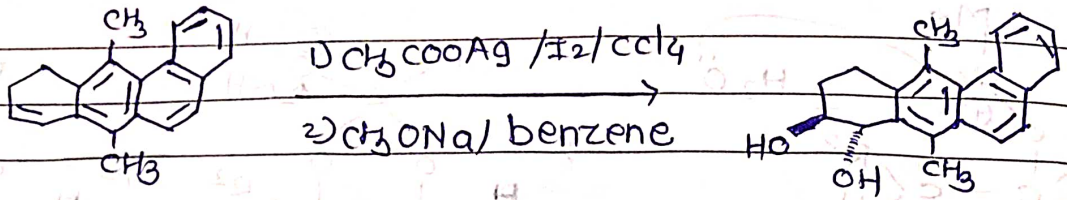
Prevost :—

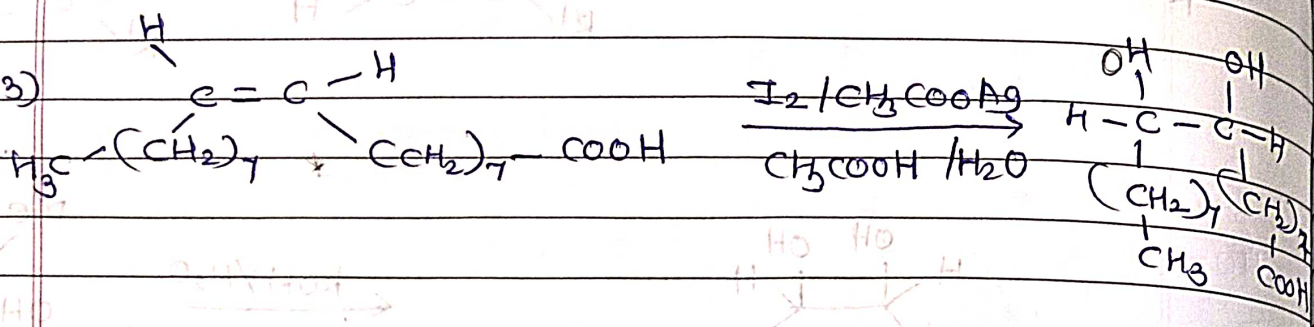


Application :—

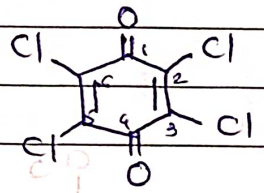


4) 

2) 

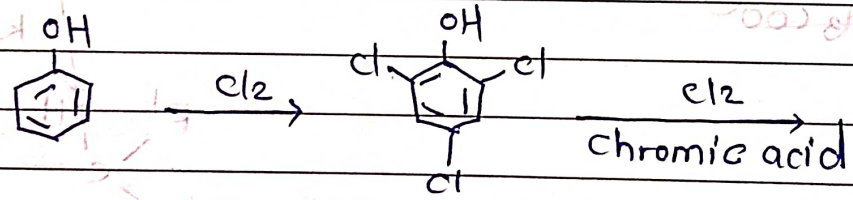
3) 

Chloranil :- mild oxidizing agent
- helps in aromatization.
- act as Hydrogen acceptor.

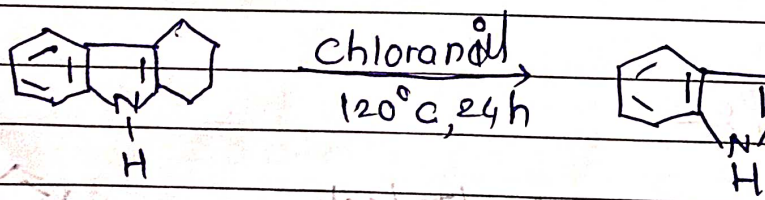


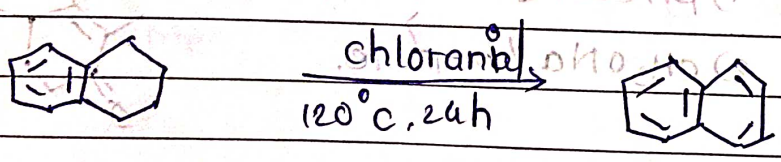
IUPAC Name :- 2,3,5,6- Tetrachloro-2,5-diene-1,4-dione.

preparation :-

1) 

Application :-

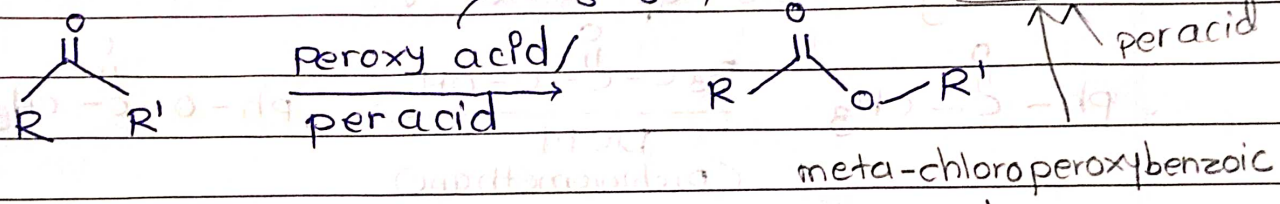
1) 

2) 

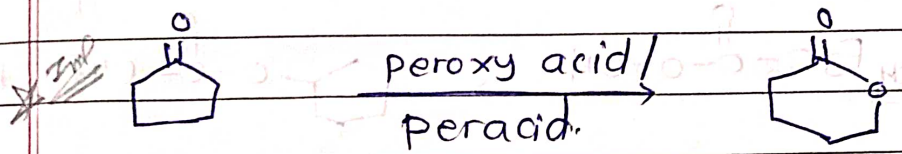
Imp #

Baeyer villiger oxidation :-

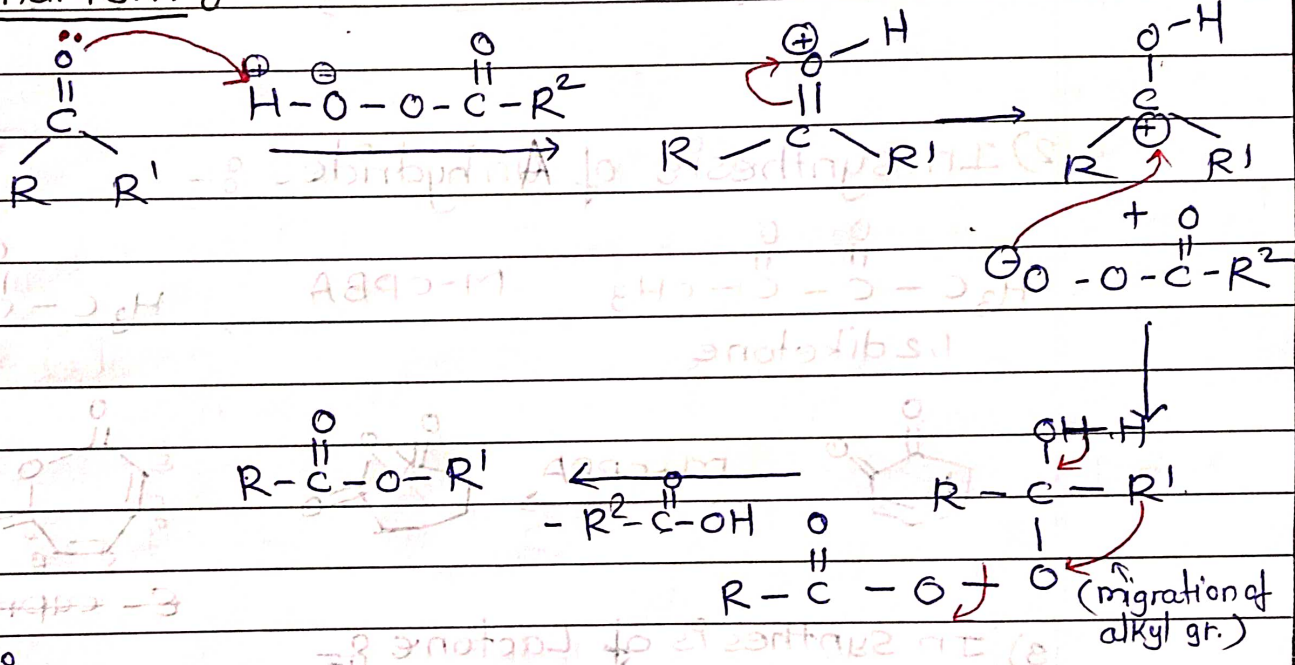
GR



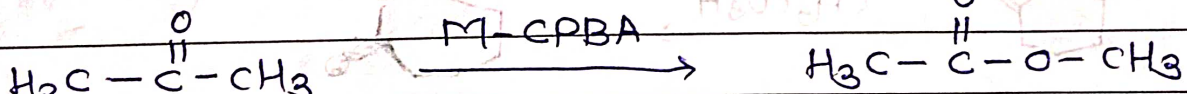
Imp



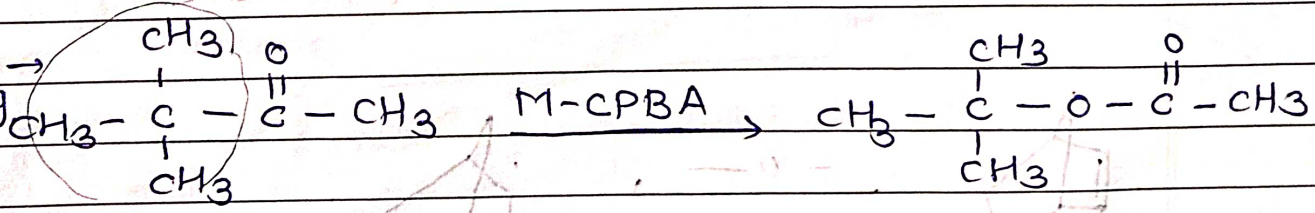
Mechanism :-



e.g :-



releasing gr.

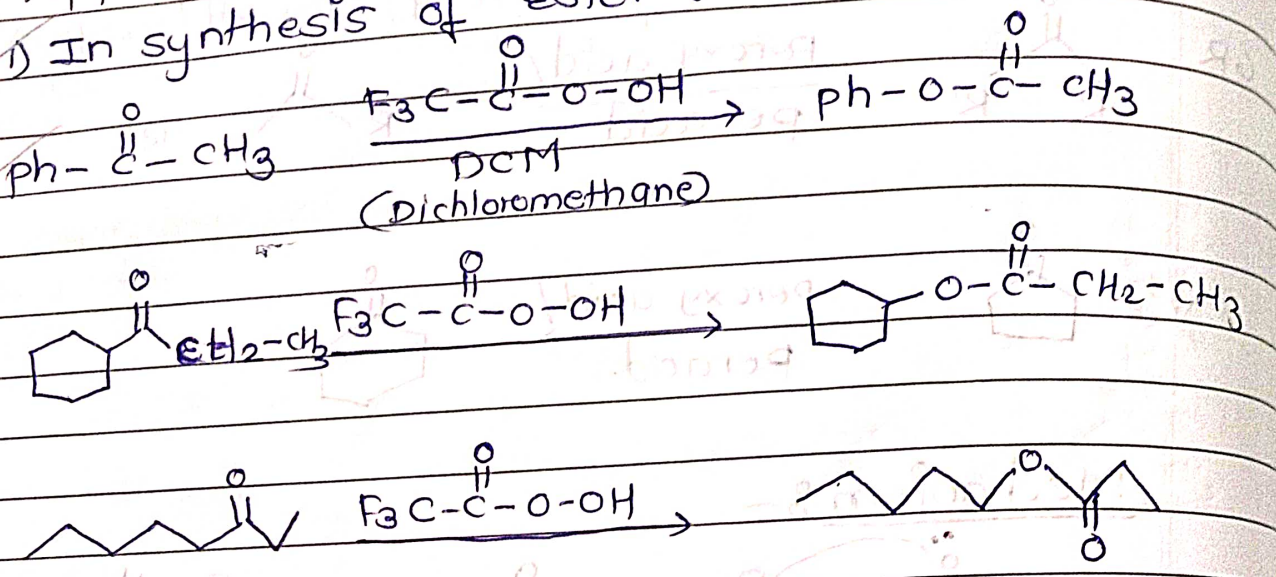


Migratory aptitude — $3^\circ > 2^\circ > 1^\circ > CH_3$

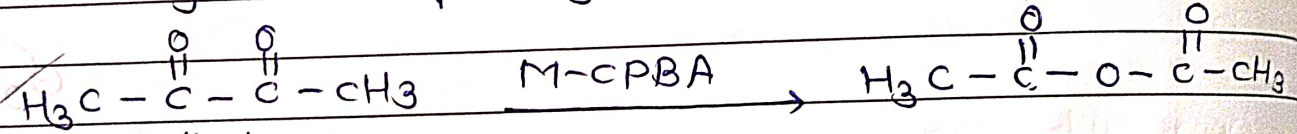
EWG – COOH
ERG – COOH → weak acid

Application :-

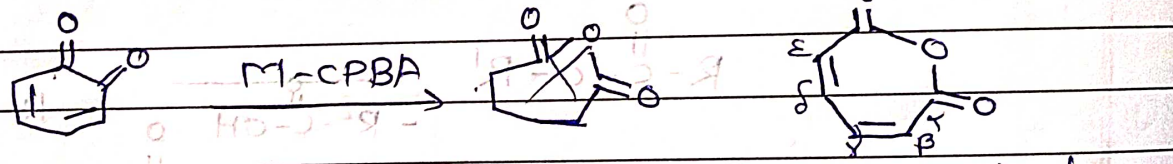
1) In synthesis of ester :-



2) In synthesis of Anhydrides :-

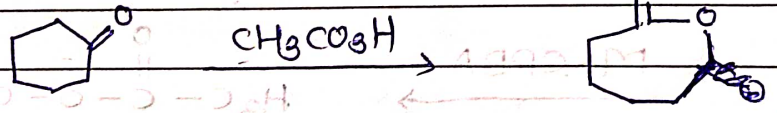


1,2 diketone

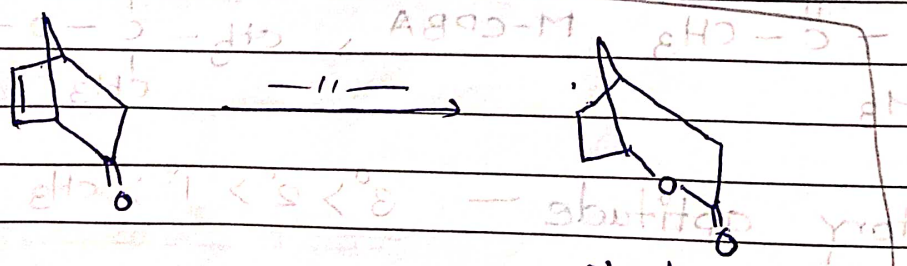


ε- caprolactone

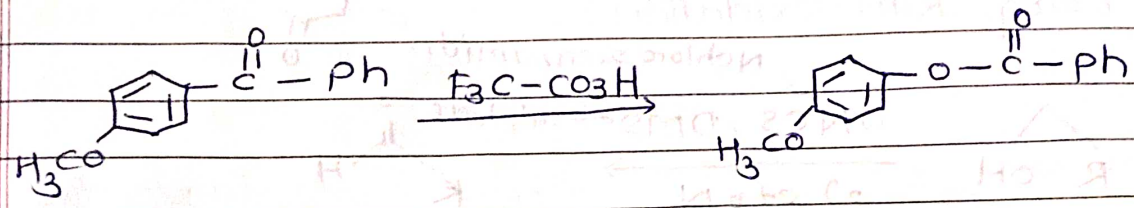
3) In synthesis of Lactone :-

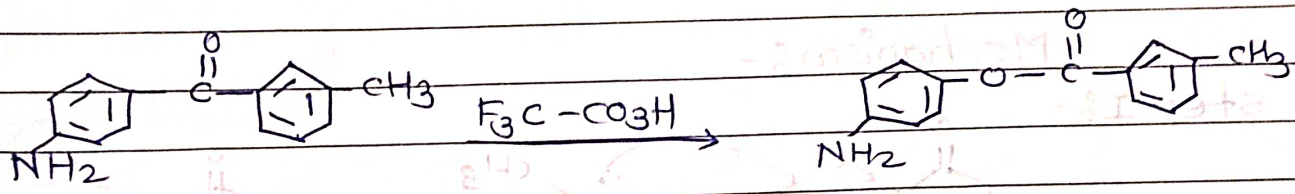


ε- Caprolactone

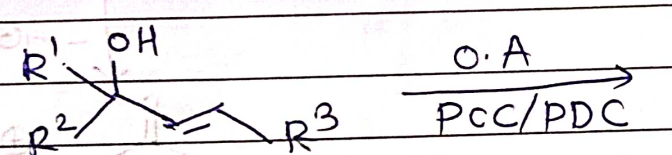


Norbornenone

1) 

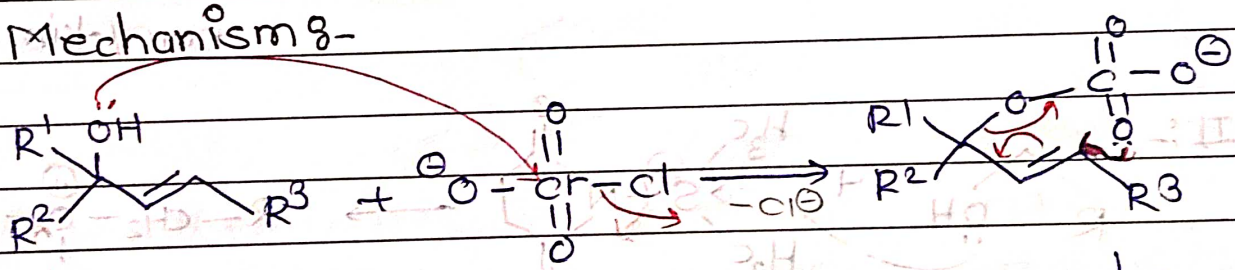
2) 

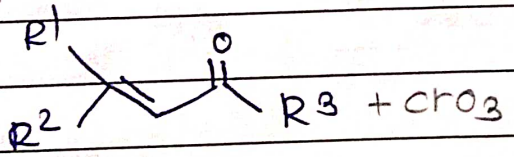
Babler oxidation :-



[3,3] sigmatropic rearrangement

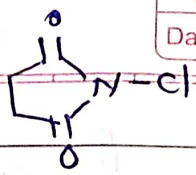
Mechanism :-



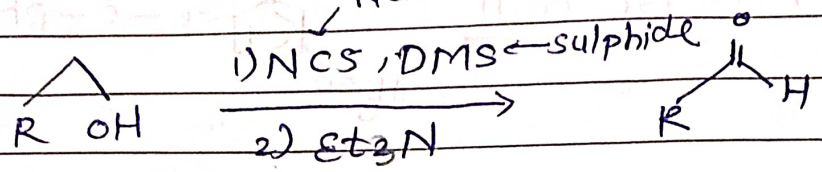


enone

corey kim oxidation :-

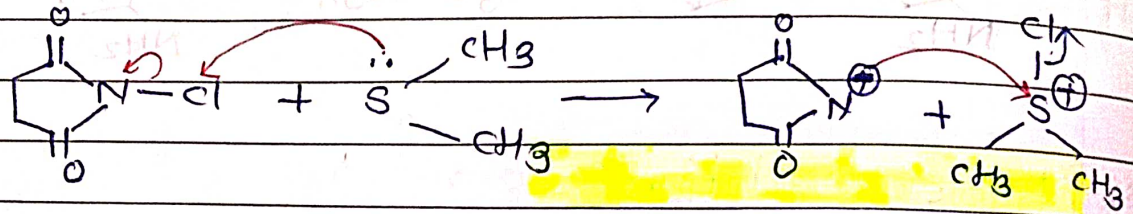


N chlorosuccinamide

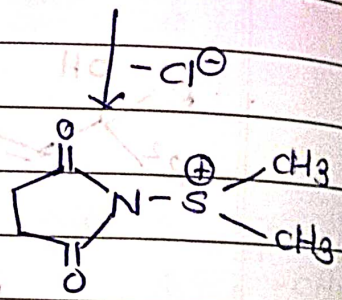


Mechanism :-

step I :-

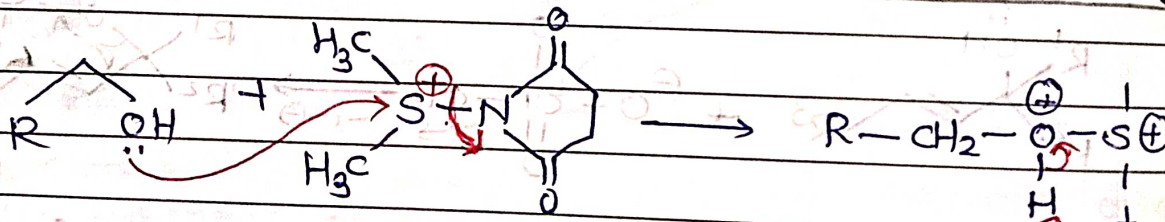


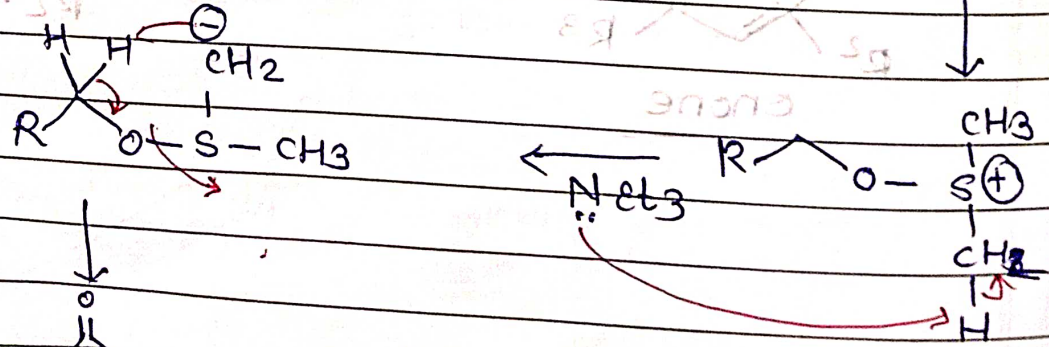
NCS
(N-chlorosuccinamide)



corey-kim reagent

step II :-





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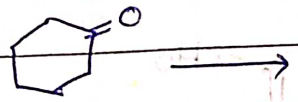
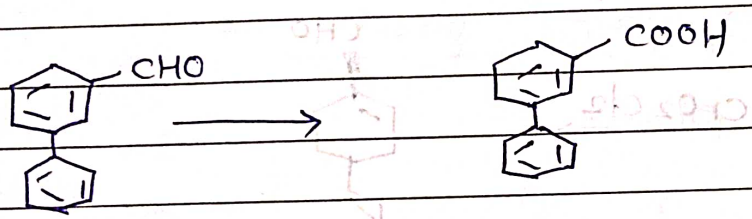
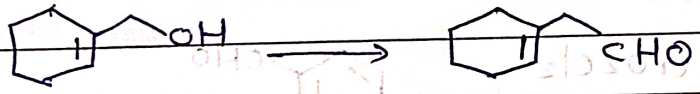
Advantage:-
- carry out in room temp.

Disadvantage -
1) NCS shows chlorination

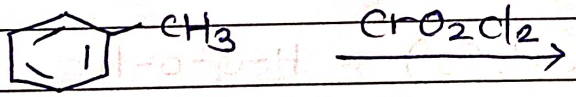
Application →



2) 

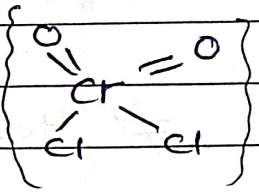
3) 

Etard Reaction :- [2,3 sigmatrophic rearrangement]
Direct oxidation of aromatic ~~ring~~ or heterocyclic bound methyl group to aldehyde



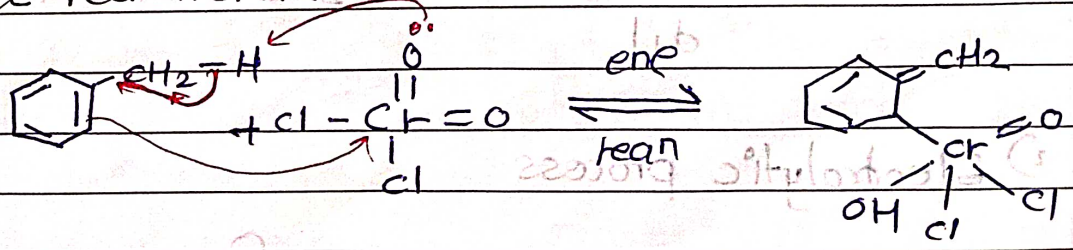
Toulene

Benzaldehyde

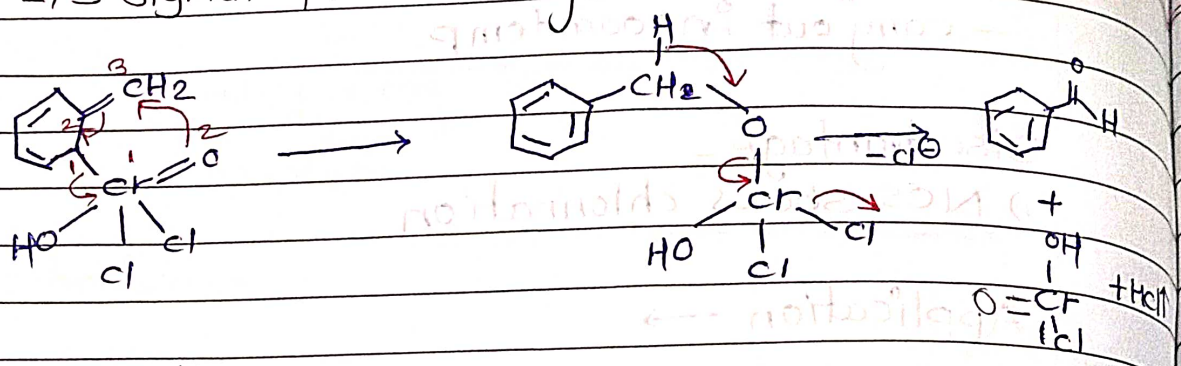


Mechanism :-

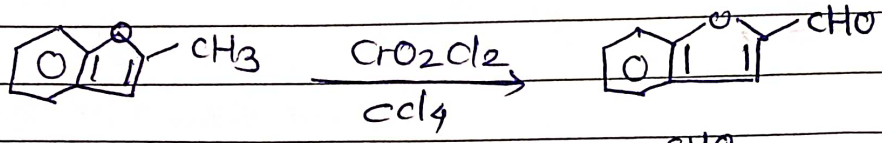
1) Ene reaction :-

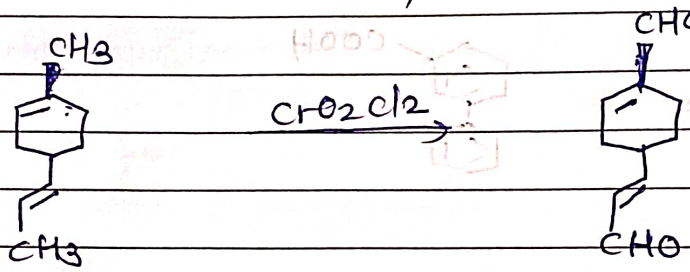


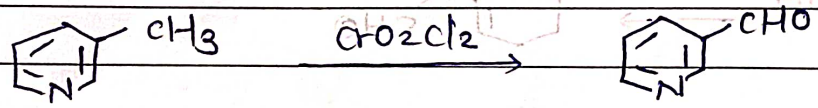
2] 2,3 sigmatropic rearrengment :-

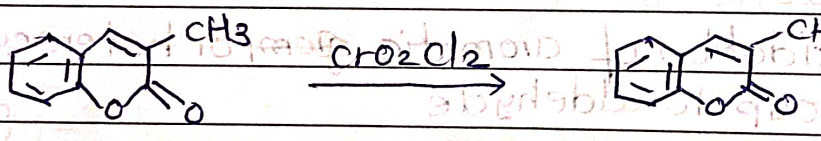


Application :-

1) 

2) 

3) 

4) 

Hydrogen peroxide (H_2O_2) — H-O-O-H

1) Barium peroxide

$$BaO_2 + \underset{dil}{H_2SO_4} \longrightarrow H_2O_2 + BaSO_4\downarrow$$

2) Electrolytic process

$$2H_2SO_4 \rightleftharpoons 2H^+ + 2HSO_4^{\ominus}$$

$$2e^{\ominus} + 2H^{\oplus} \longrightarrow H_2$$

caro's acid → H_2SO_5

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$2HSO_4^{\ominus} \longrightarrow H_2S_2O_8 + 2e^{\ominus}$

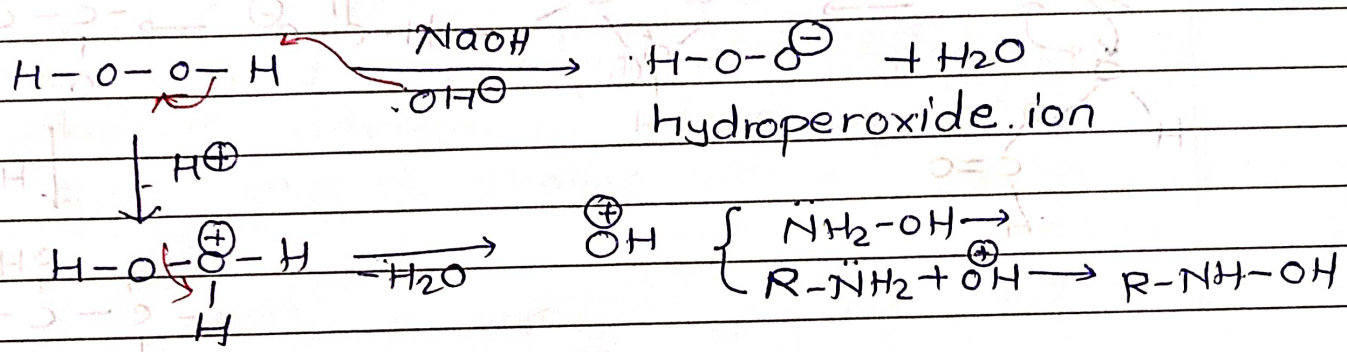
Perdisulphuric acid.

$H_2S_2O_8 \xrightarrow{H_2O} H_2SO_5 + H_2SO_4$

caro's acid.

persulphuric acid.

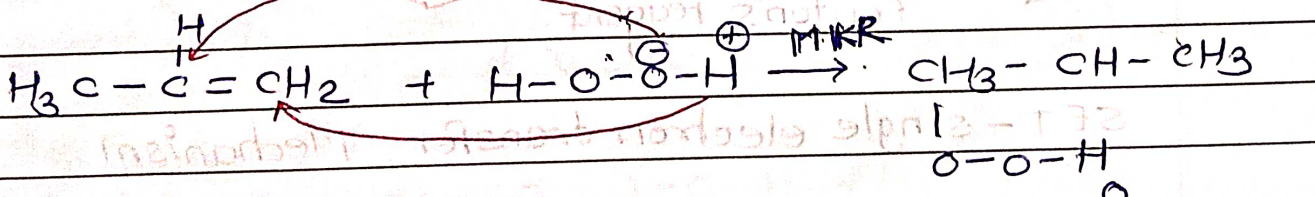
$H_2SO_5 \xrightarrow{H_2O} H_2O_2 + H_2SO_4$



Imp Application :-

1) preparation of alkyl peroxides (R-O-O-H)

$R-X + H-O-O-H \xrightarrow{NaOH} R-O-O-H + NaX + H_2O$



2) preparation of acyl peroxides ($R-\overset{O}{\overset{\|}{C}}-O-O-H$)

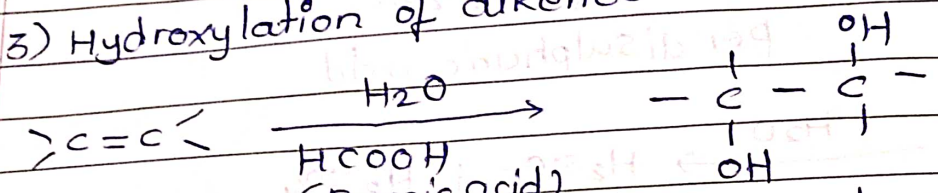
$CH_3-COOH \xrightarrow{H_2O_2} CH_3-\overset{O}{\overset{\|}{C}}-O-O-H + H_2O$

per acetic acid.

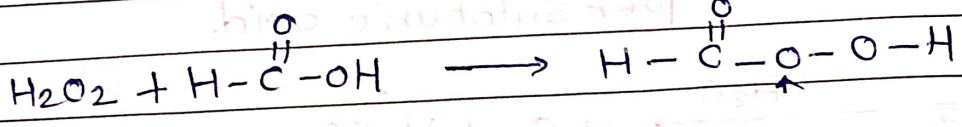
Fenton's reagent → H_2O_2 + FeSO4

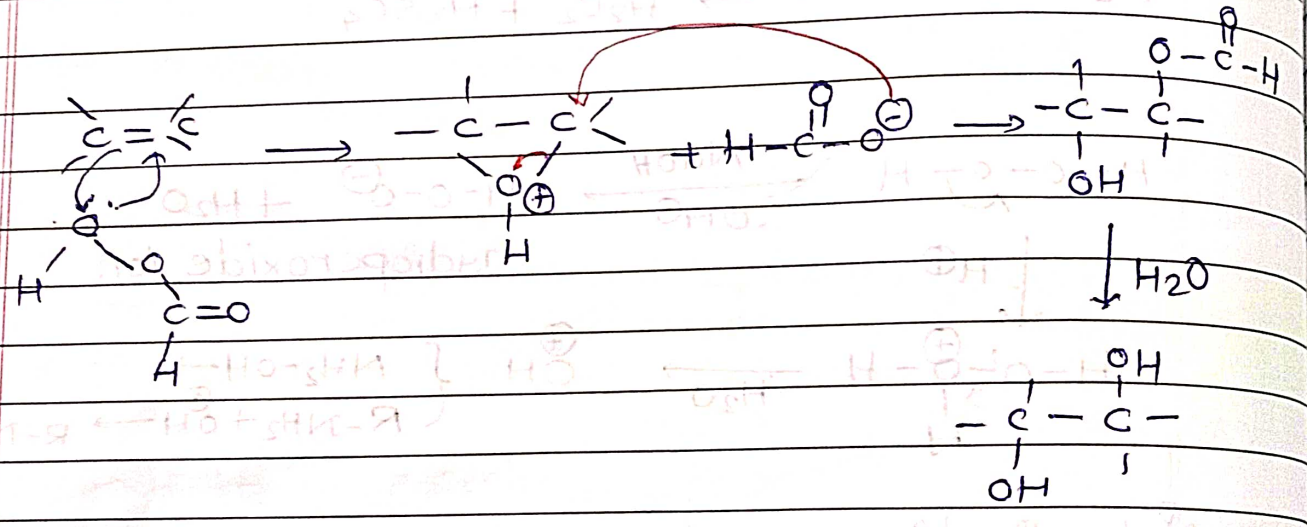
Date

3) Hydroxylation of alkenes

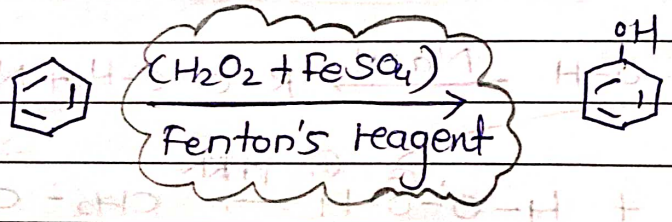


trans hydroxylation



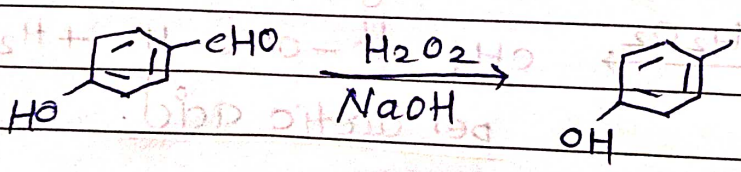


4) Hydroxylation of aromatic hydrocarbons.



SET - single electron transfer. Mechanism

5) substitution of aldehyde group by -OH (Dakin reaction)



1,4 Benzene diol

ot-ethyl

e) oxidation of nitriles

$$R-C\equiv N \xrightarrow[NaOH]{H_2O_2} R-\overset{O}{\overset{\|}{C}}-NH_2$$

7) oxidation of amines

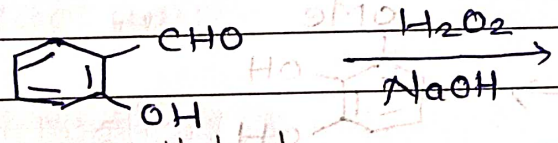
1° → $C_2H_5-NH_2$ $\xrightarrow[OH^\ominus]{H_2O\ H^\oplus}$ $C_2H_5-NH-OH$

2° → $(C_2H_5)_2-NH$ $\longrightarrow$ $(C_2H_5)_2N-OH$

3° → $(Et)_3N$ $\longrightarrow$ $(Et)_3\overset{\oplus}{N}-\overset{\ominus}{O}$

Dakin oxidation :-

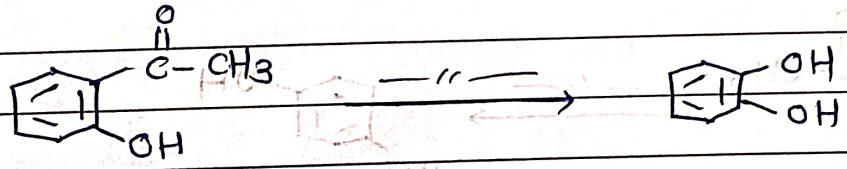
replacement of aldehyde or acetyl group of phenolic aldehyde or ketone by OH in presence of alkaline NaOH or H_2O_2



salisylaldehyde

catechol

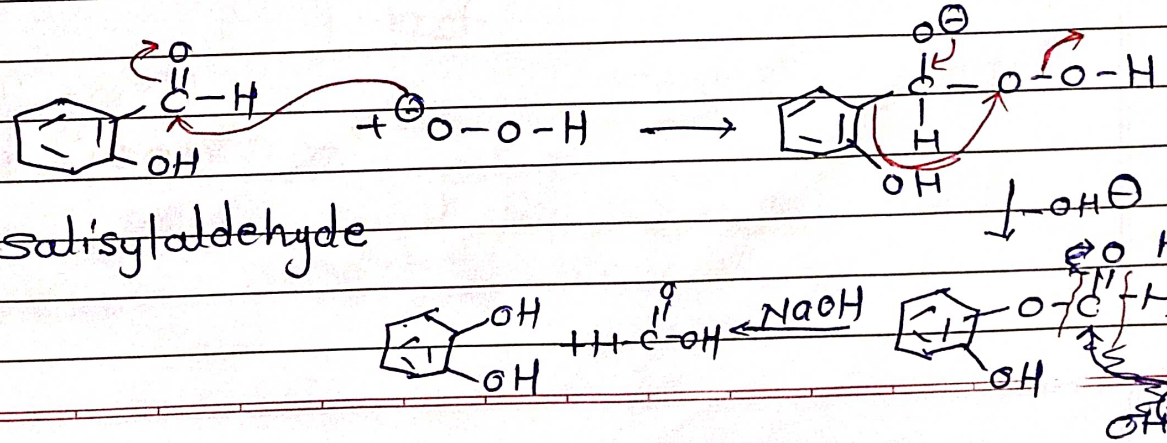
or



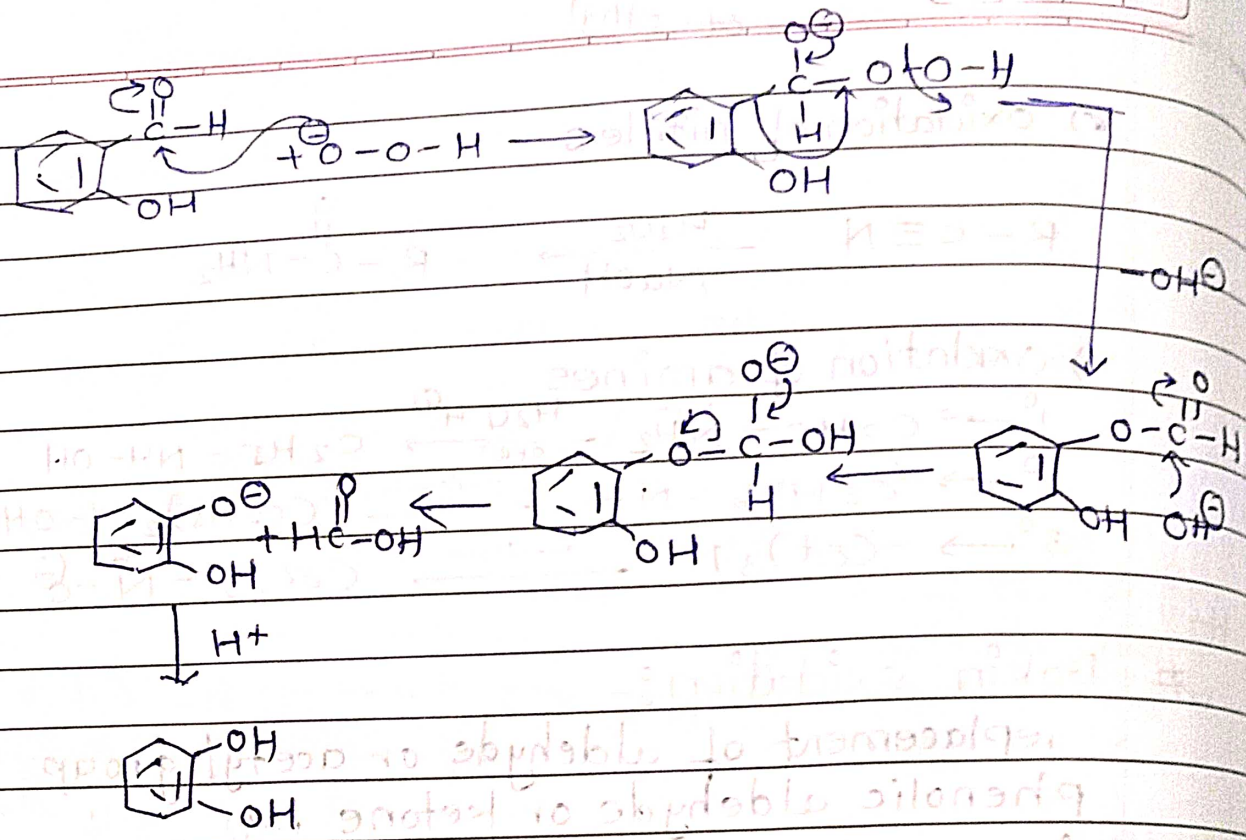
Mechanism :-

1) $H_2O_2 + NaOH \rightleftharpoons \overset{\ominus}{O}-O-H + H_2O + Na^\oplus$

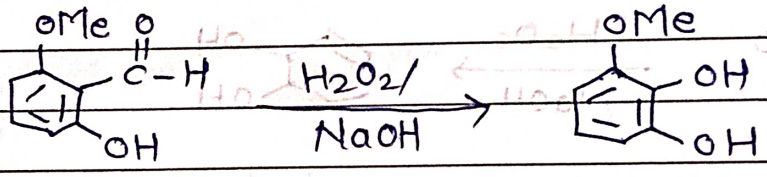
hydroperoxide ion

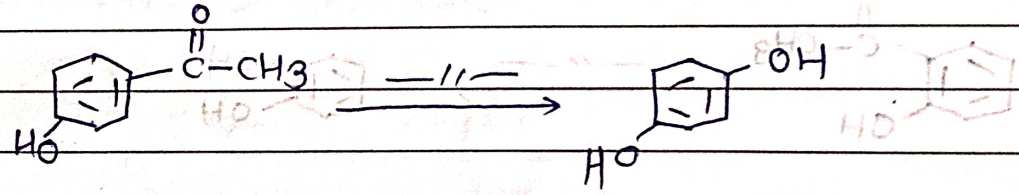


salisylaldehyde



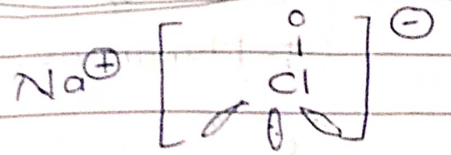
Application :-

1) 

2) 

Sodium hypochlorite (NaOCl) — $Na^{\oplus}\ ^{\ominus}OCl$

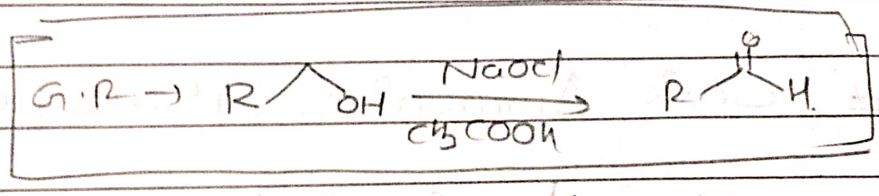
unstable at room temp.



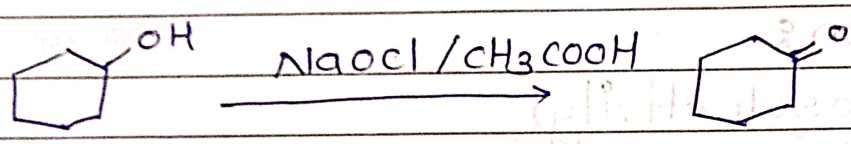
It is also known as household bleach → 5-9% Cl — active Cl

$Ca(OCl)_2$ ⟶ 60-70% Cl

preparation :-

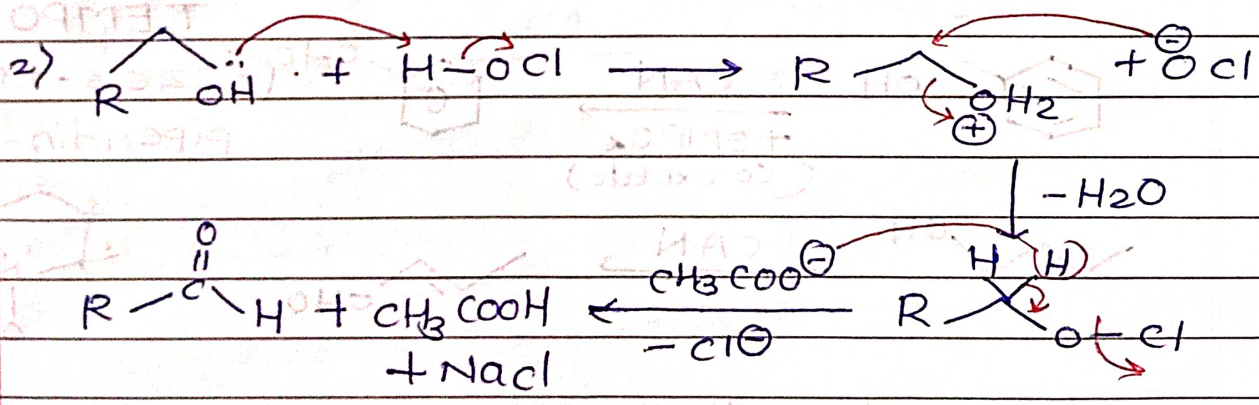


$$2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

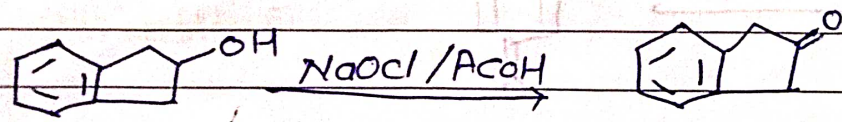


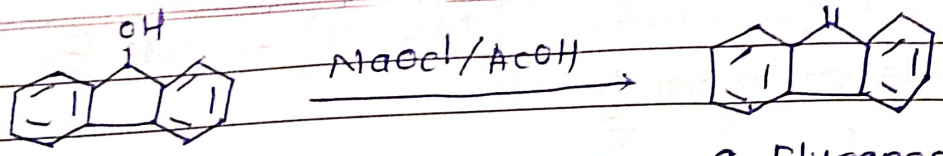
Mechanism :-

1) $NaOCl + CH_3COOH \longrightarrow \underset{\text{hypochlorous acid.}}{HOCl} + CH_3COONa$

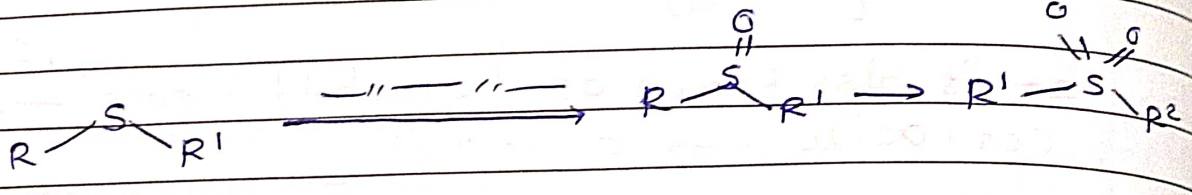


Application :-



2) 

9-fluorenol — 9-fluranone. 95% yield

3) 

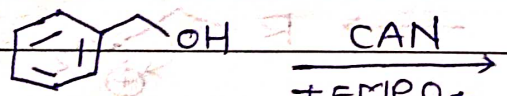
Ceric Ammonium Nitrate [CAN] :- orange red water soluble

$(NH_4)_2[Ce(NO_3)_6]$

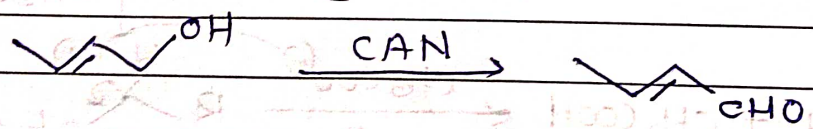
Application :-

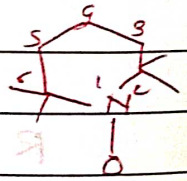
1] chemoselectivity
- oxidises 2° alcohol

2] · Allylic / Benzylic alcohols :.

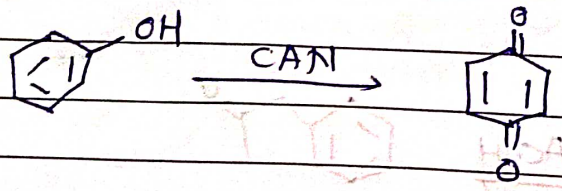


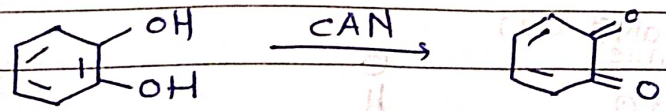
TEMPO- (2,2,6,6-tetramethylpiperidin-1-yl)oxyl

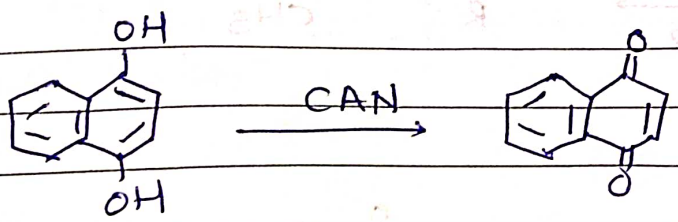




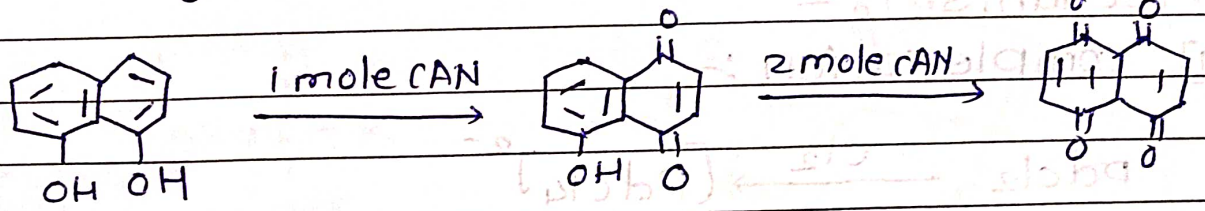
3] Phenol derivatives



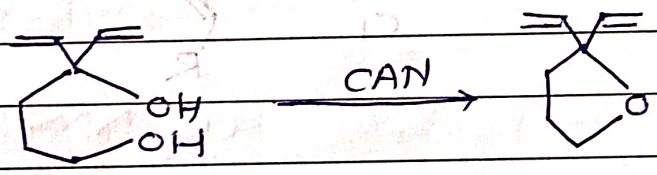


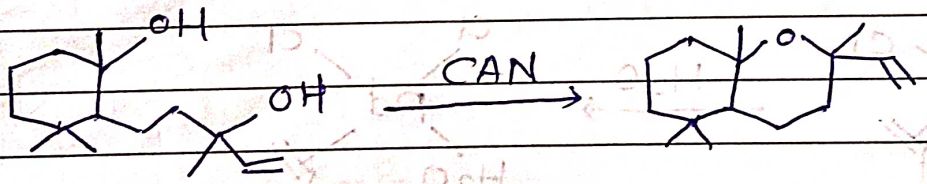


~~4) Tertiary alcohols :-~~

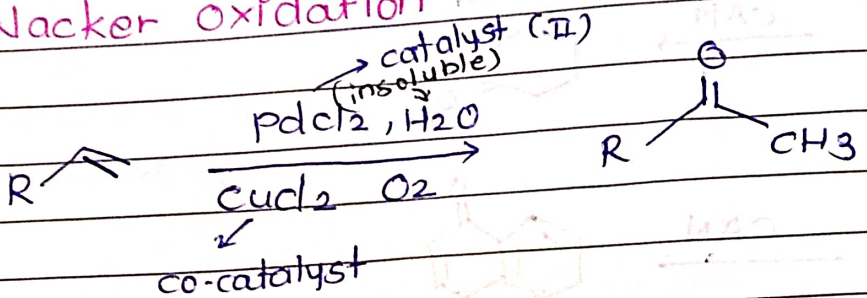


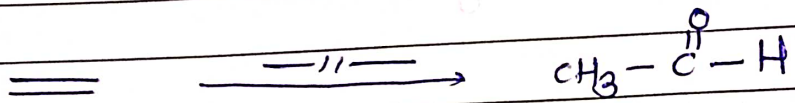
4) Tertiary alcohols :-





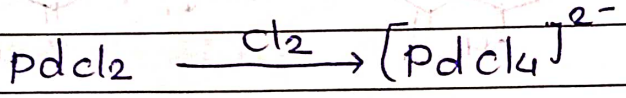
Wacker oxidation :-

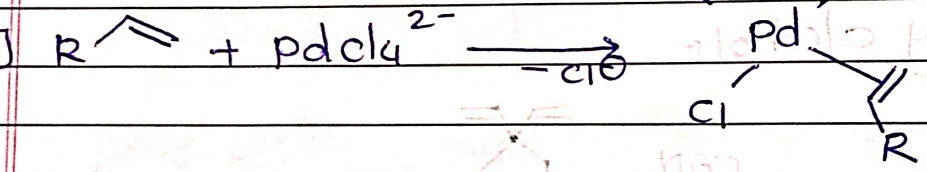




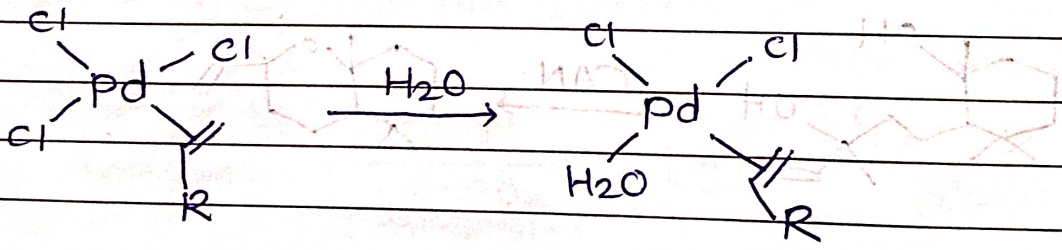
Mechanism :-

1] complexation :-

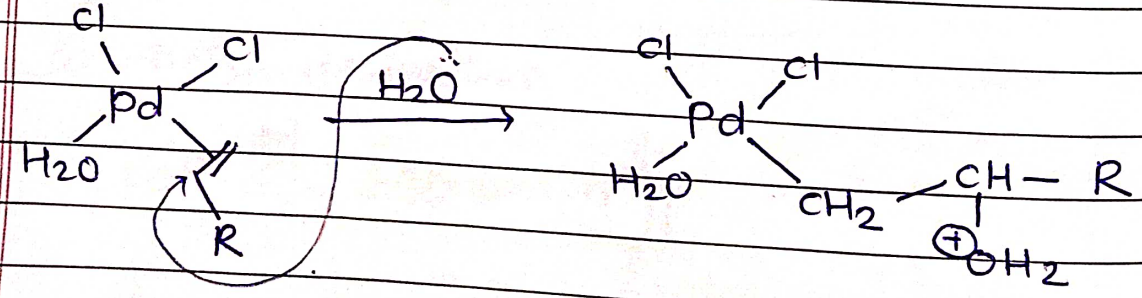


2] 

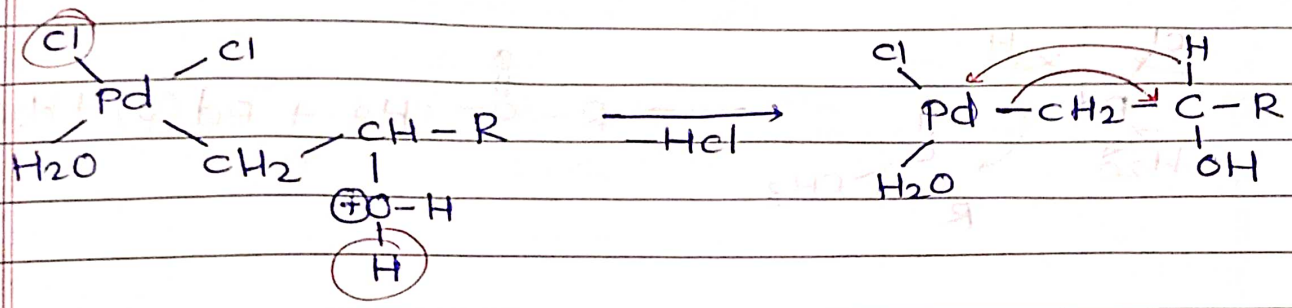
3] Ligand exchange



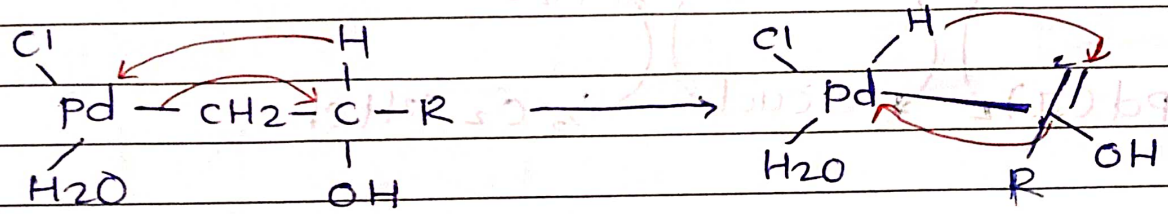
4] Nucleophilic attack



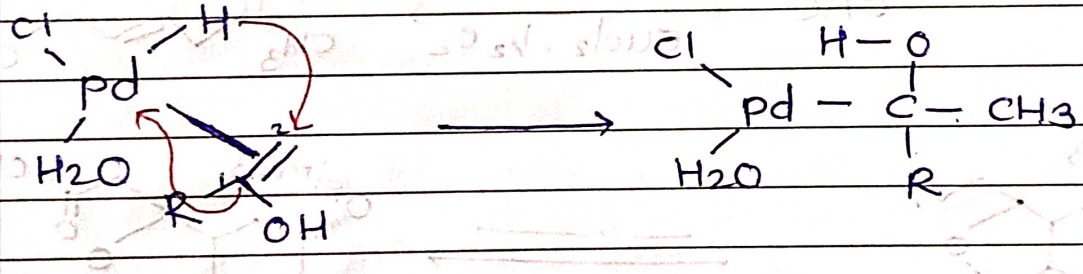
5] Rate determining step



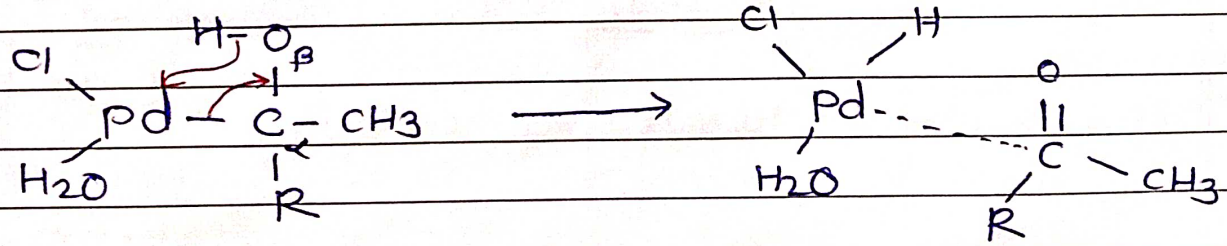
6] β-hydride elimination.



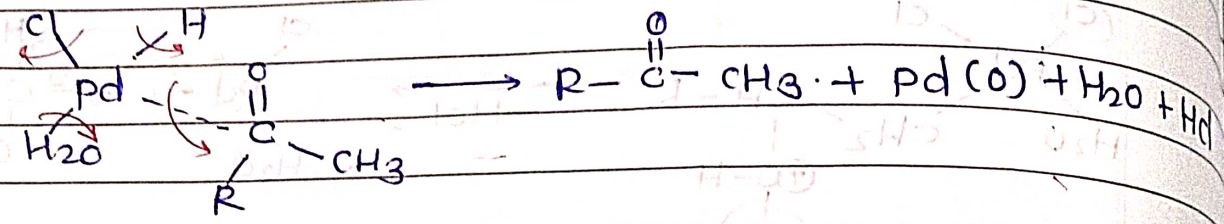
7] 1,2- insertion.



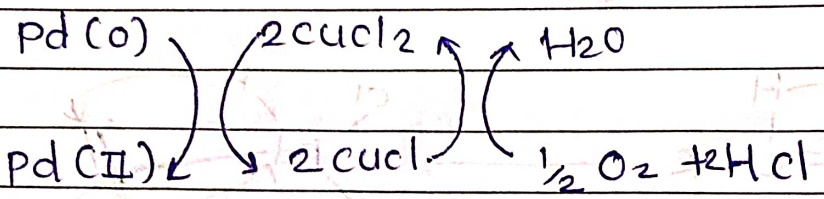
8] β-hydride elimination



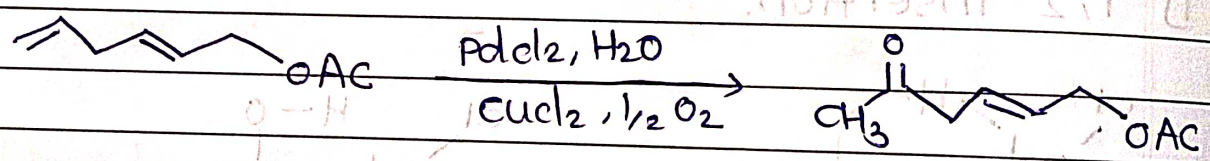
9] Reductive elimination.



10]



Application:-

1) 

2)