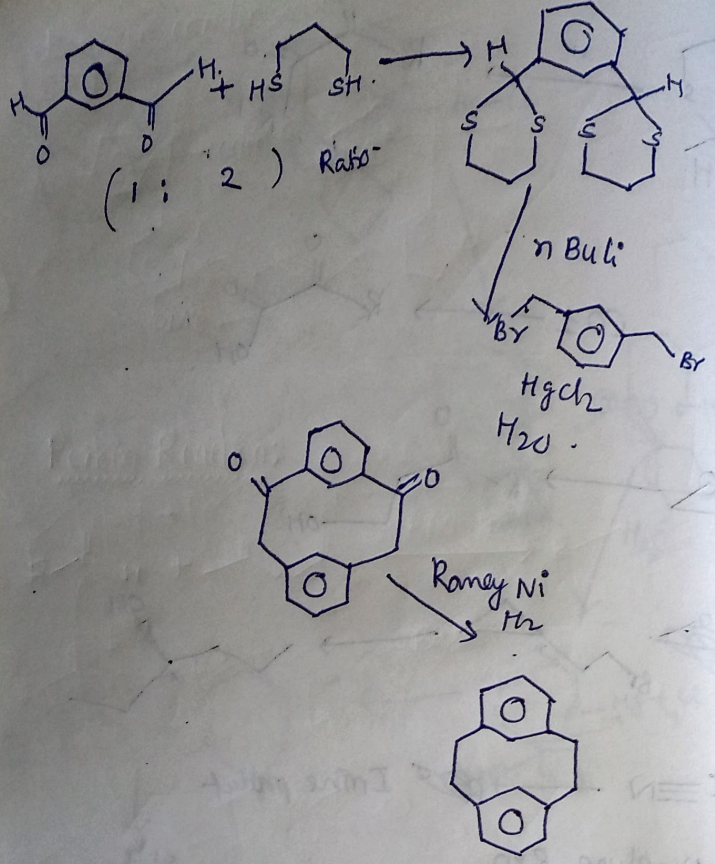
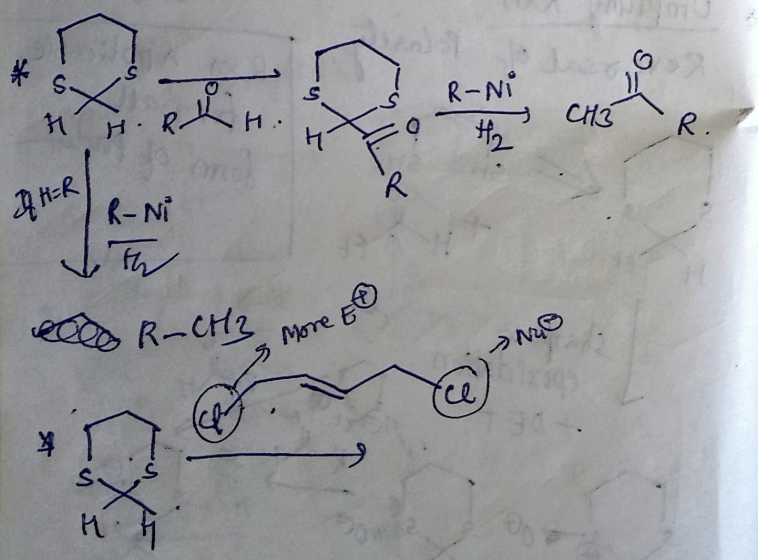
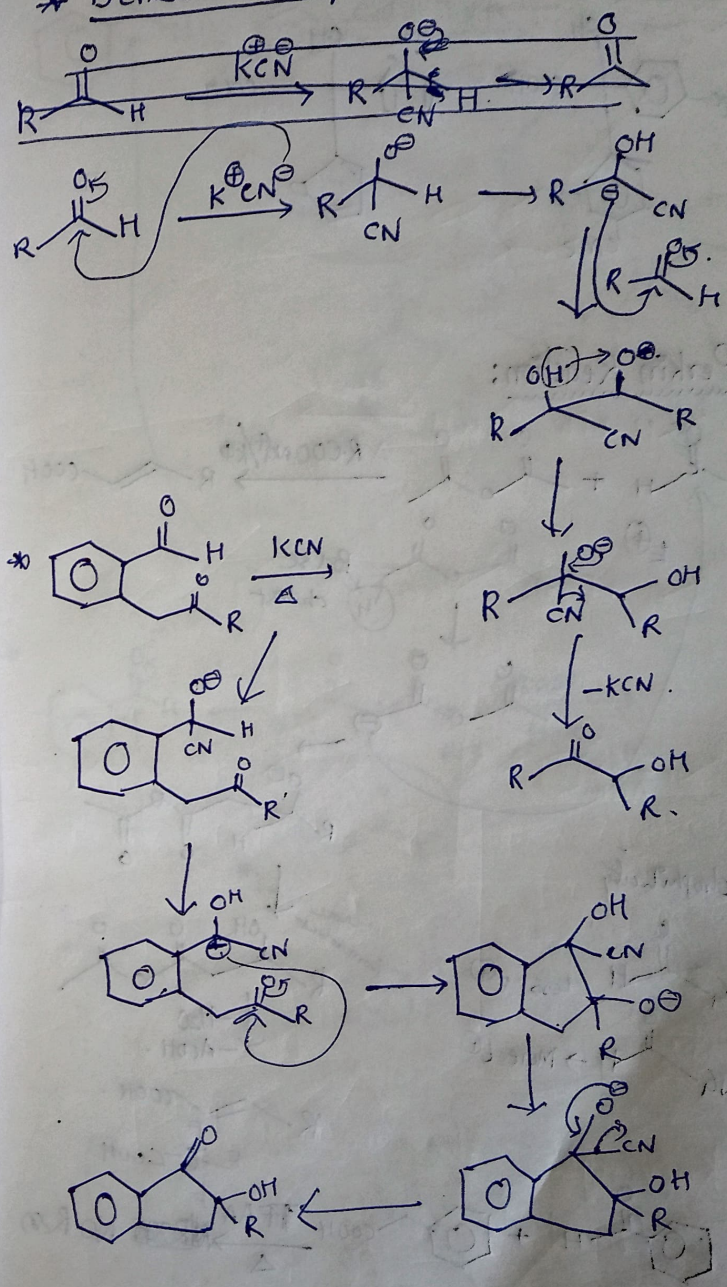
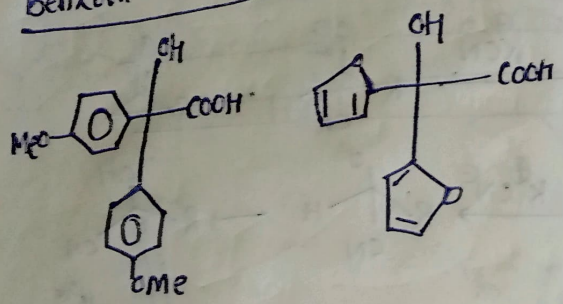




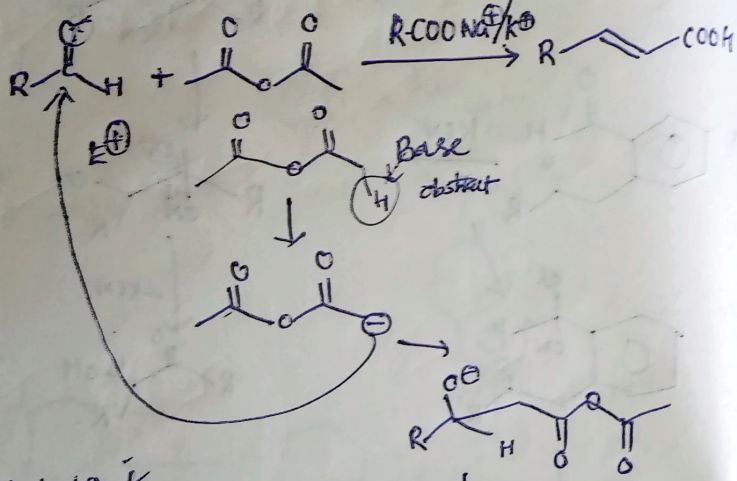
* Benzoin Rxn / condensation



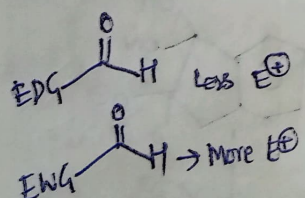
Benzoin condensation

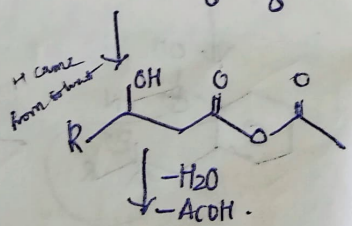


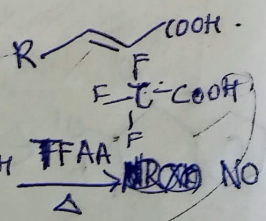
Perkin Reaction:

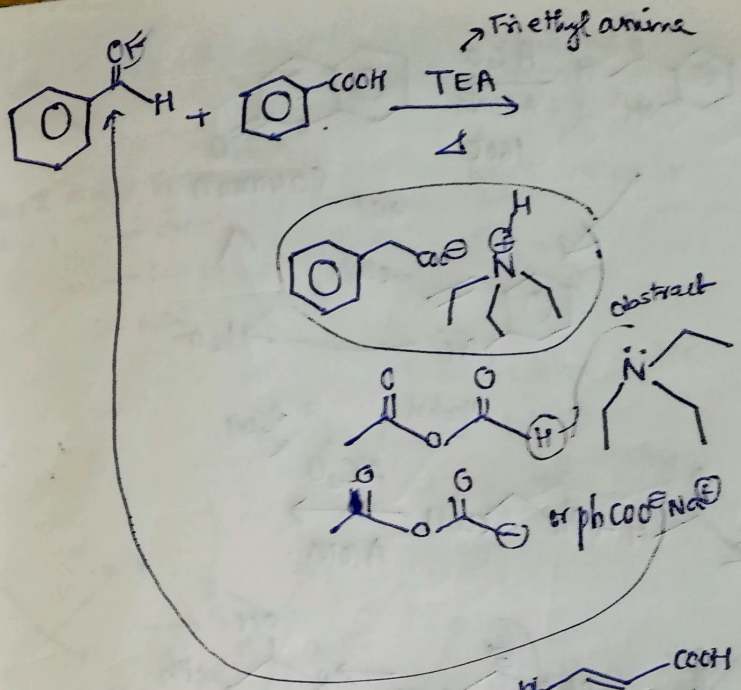


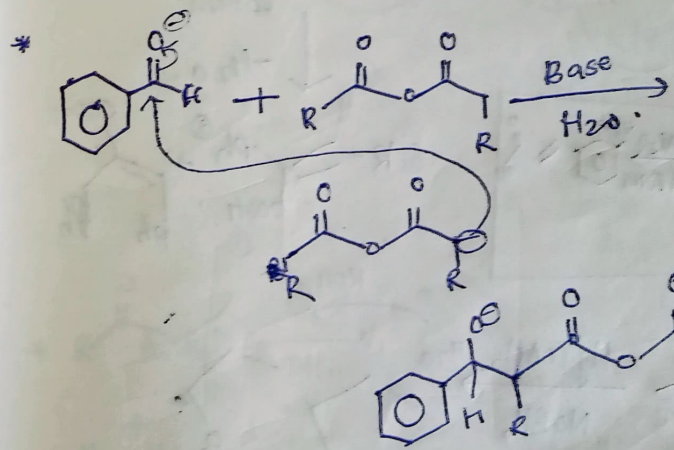
Electrophilicity

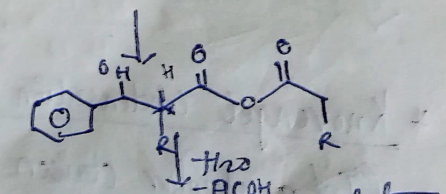


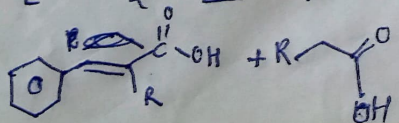


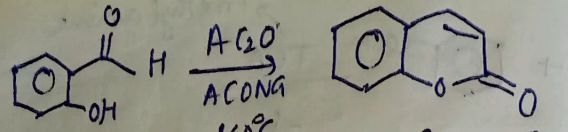


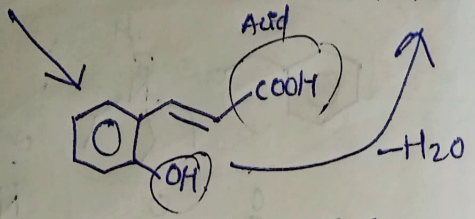


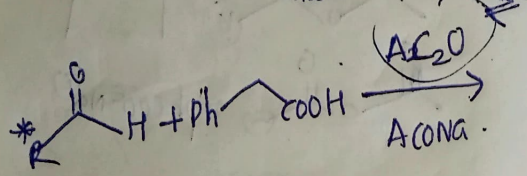


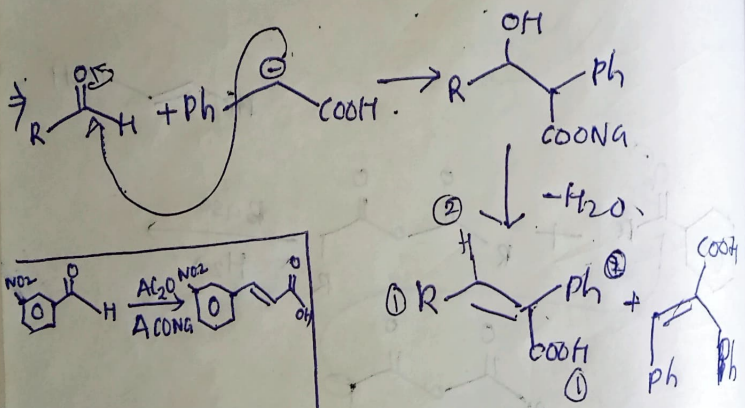


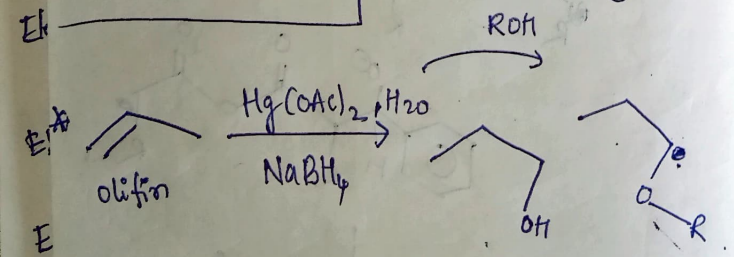






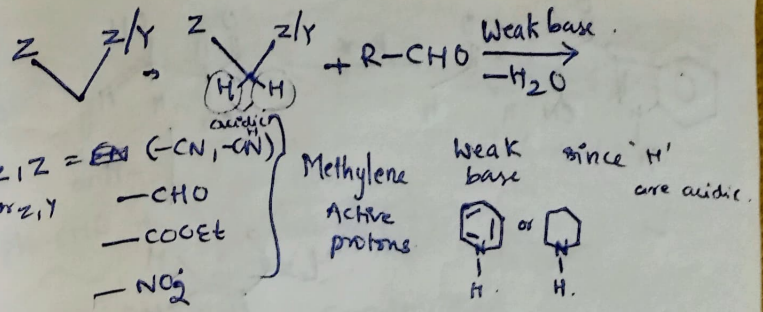




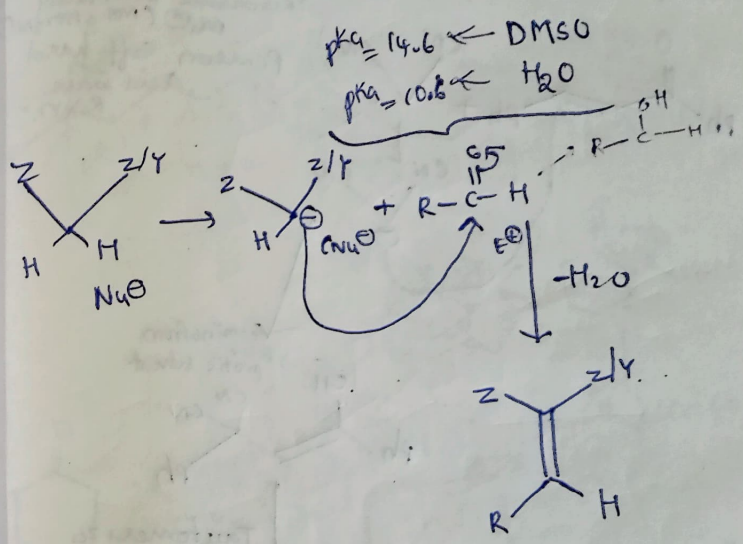


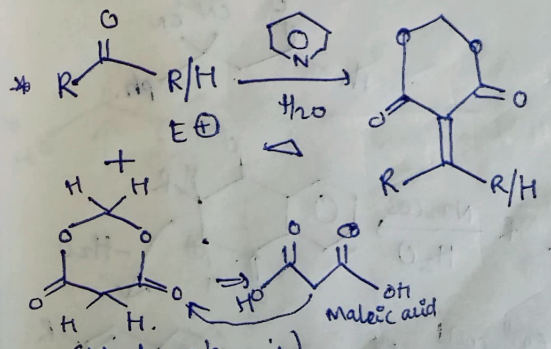
* Knovengel Condensation Rxn:

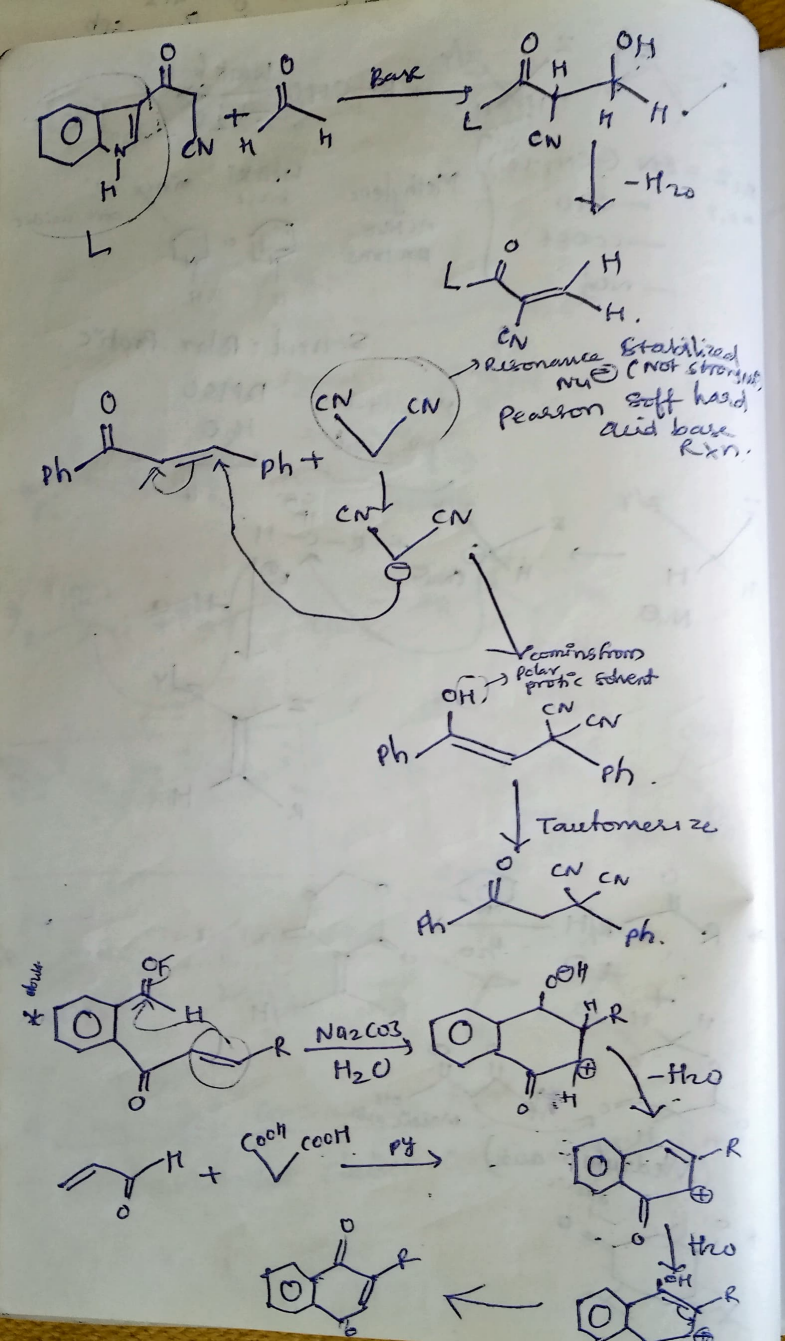
(Intramolecular claisen Condensation Rxn)

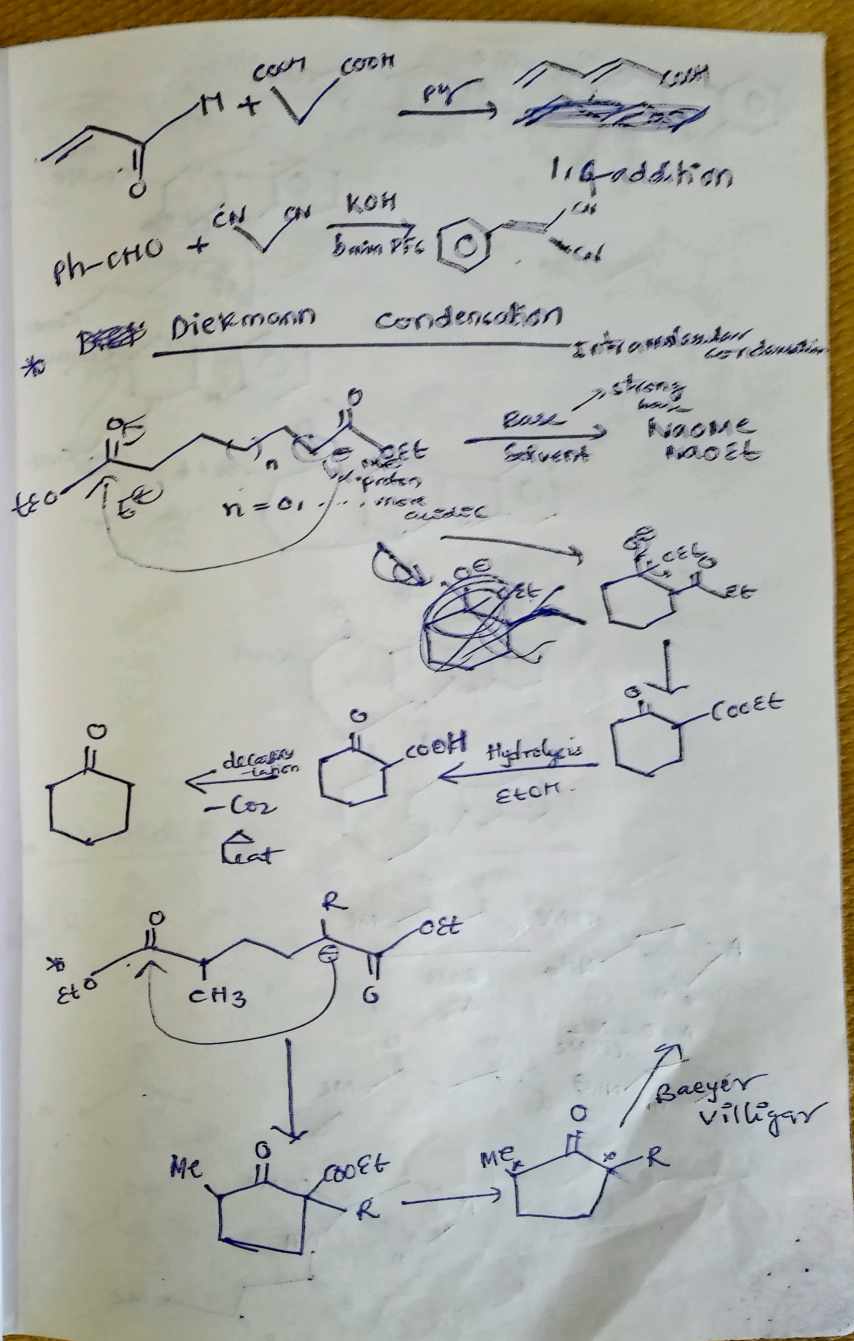


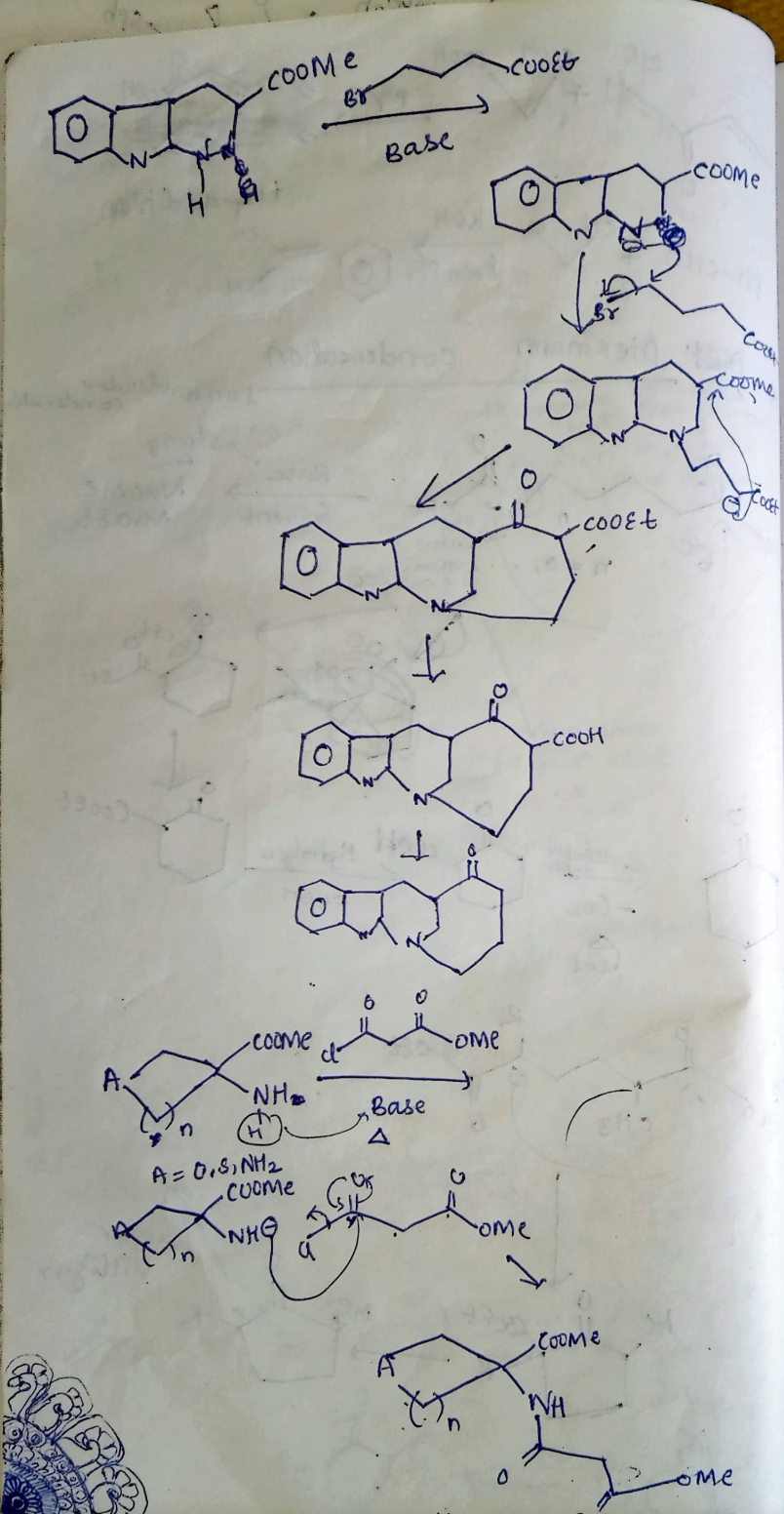
Solvent: Polar Protic.

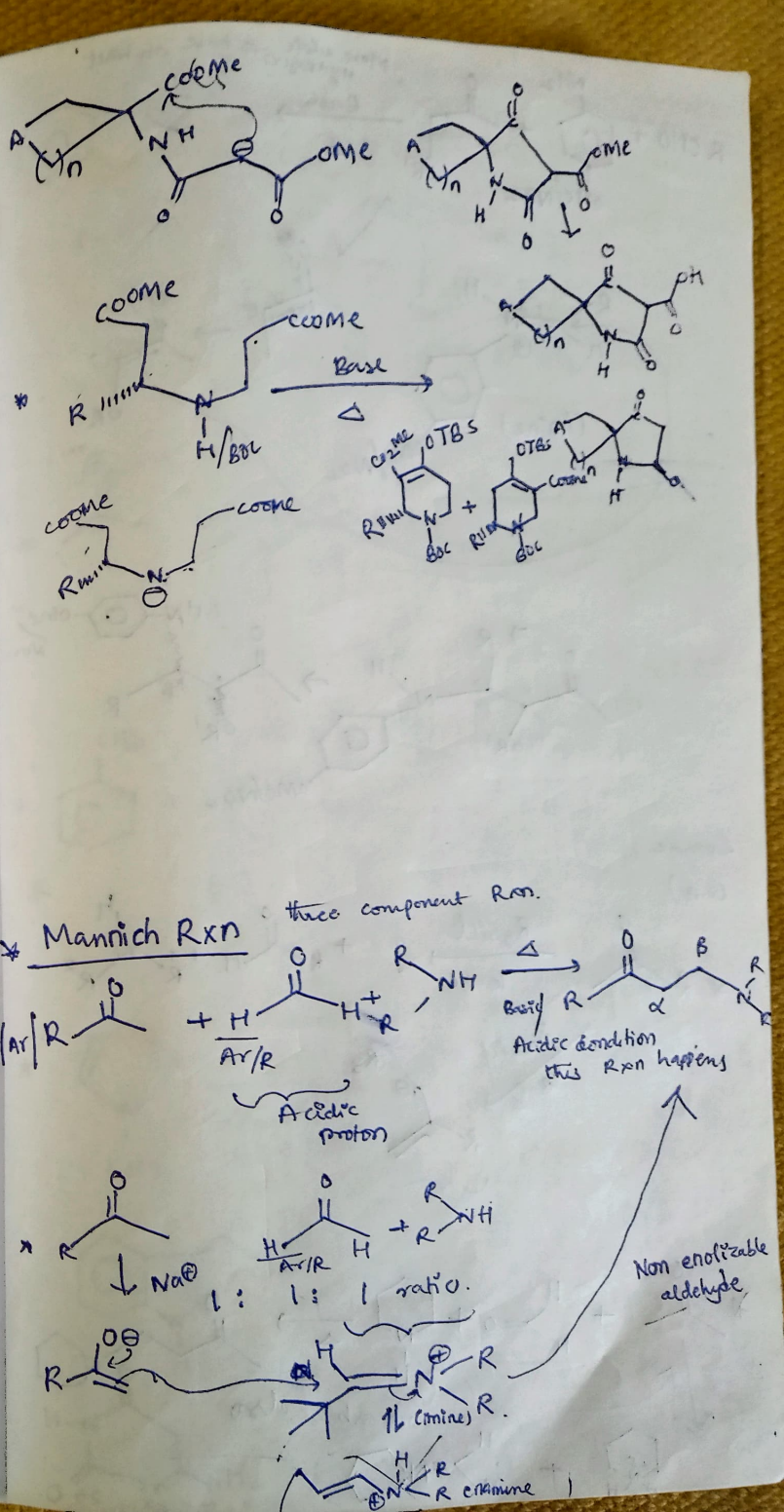


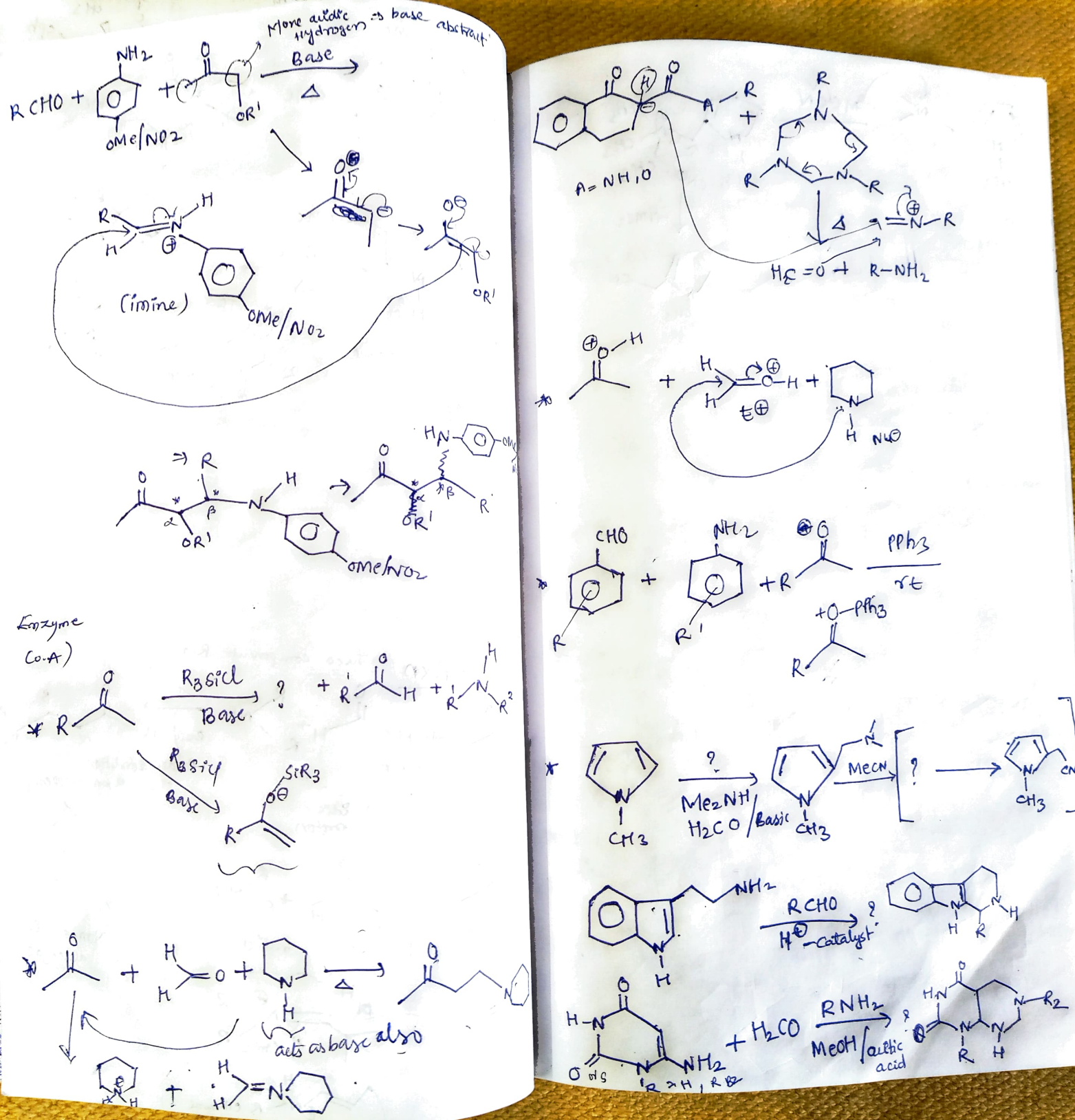


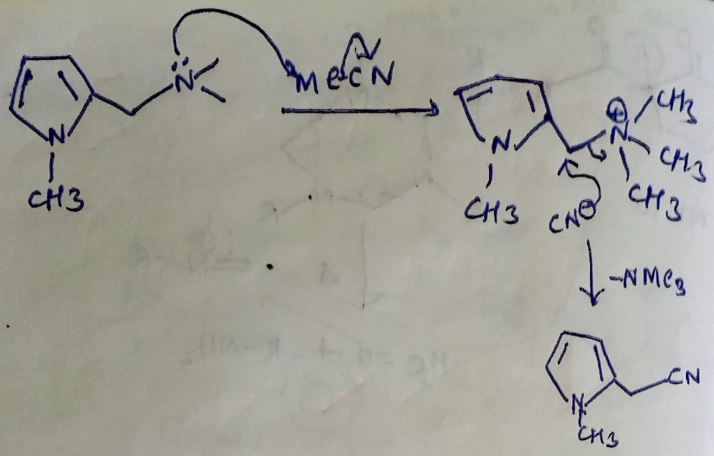

Base
-H2O
Resonance
Stabilized
Pearson
Soft hard
acid base
R×n.
coming from
polar protic solvent
Tautomerize
Na2CO3
H2O
-H2O
Py
H2O


Py
1,6 addition
KOH
Dieckmann condensation
Base
Hydrolysis
EtOH
decarboxylation
-CO2
Heat
Baeyer Villiger

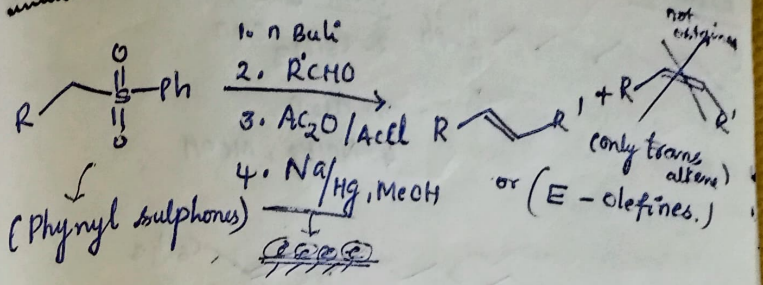

COOMe
Br
COOEt
Base
COOMe
COOEt
COOH
COOMe
COOMe
COOEt
COOH
COOMe
OMe
A
NH
n
H
Base
Δ
A = O, S, NH2
COOMe
NH
OMe
COOMe
A
n
NH
O
OMe

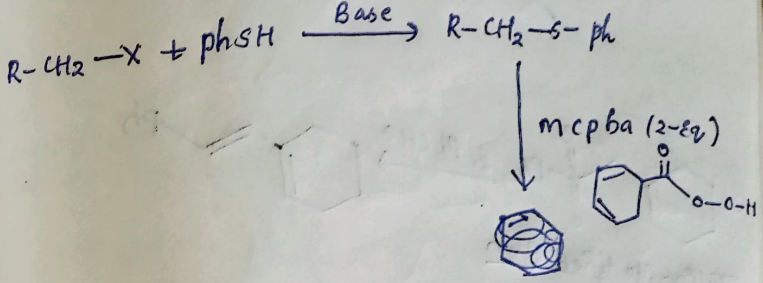

COOMe
A
n
NH
OMe
O
COOMe
A
n
N
H
OMe
O
COOMe
COOMe
R
N
H/Boc
Base
Δ
OH
COOMe
COOMe
R
N
O
OTBS
CO2Me
R
N
Boc
+
OTBS
COOMe
n
R
N
Boc
H
Mannich Rxn
three component Rxn.
H/Ar
R
O
+
H
Ar/R
O
H
+
R
NH
R
Acidic proton
Δ
Basic
Acidic condition this Rxn happens
B
R
R
R
α
N
R
Non enolizable aldehyde
R
O
NaO
1 : 1 : 1 ratio.
H
Ar/R
O
H
+
R
NH
R
O
R
H
N
R
R
(imine)
H
R
N
R
R imine

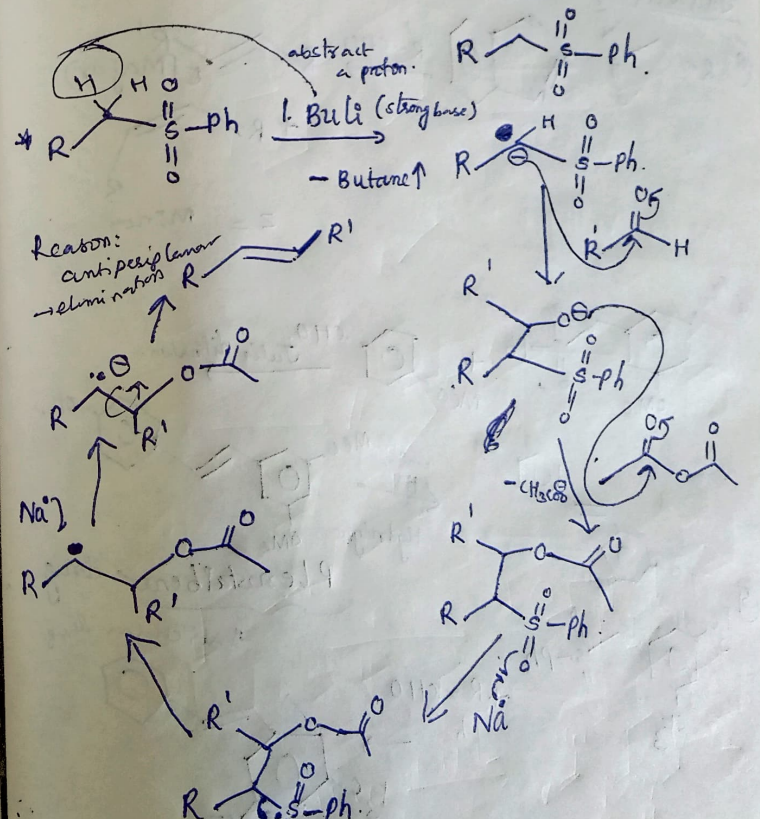

More acidic hydrogen
Base
OMe/NO2
(imine)
Enzyme
Co-A)
R3SiCl
Base
SiR3
acts as base also
RNH2
MeOH/acetic acid



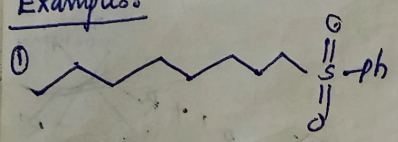
Julia Olifination:

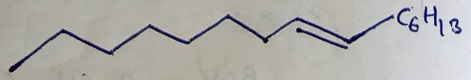


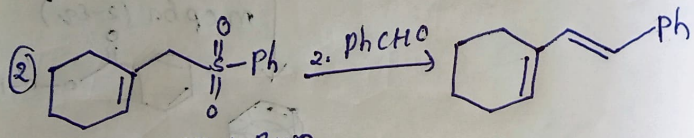




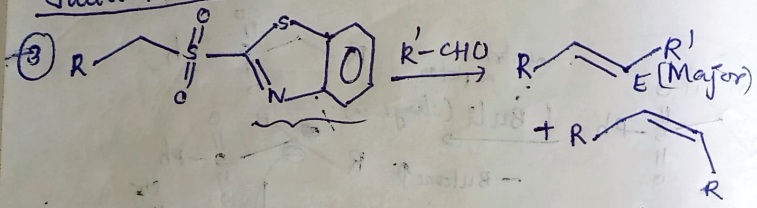
Examples:

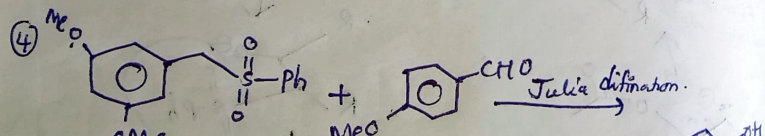


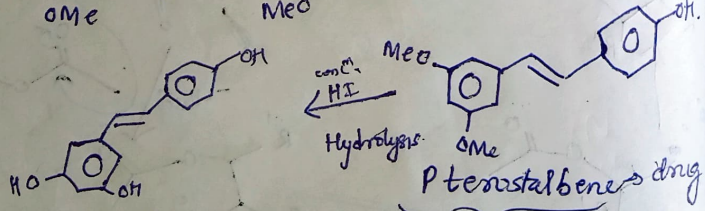


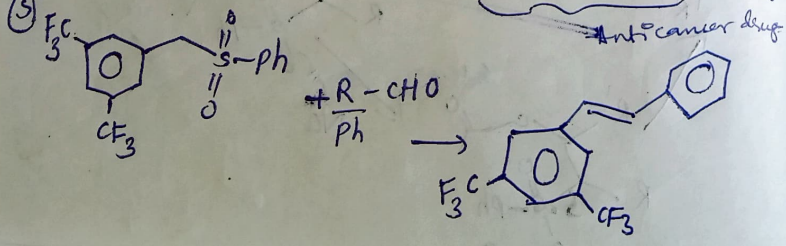


Julia-Modified Rxn



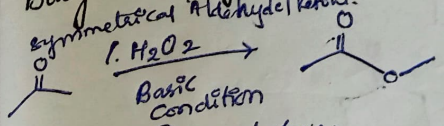




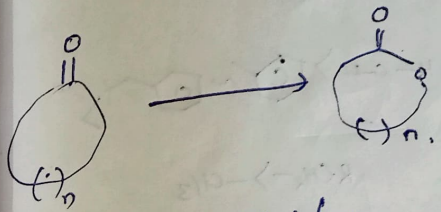


Baeyer Villiger Oxidation.

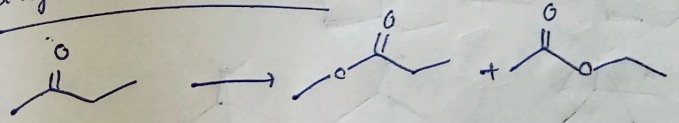
symmetrical Aldehyde/ketone.



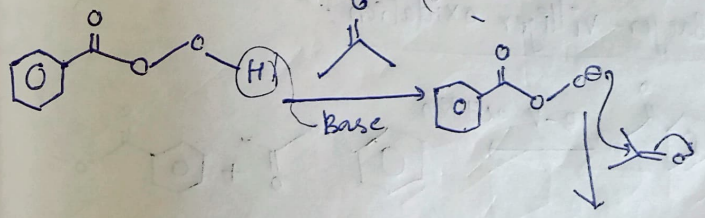
Acid peroxides can also be used.
- → MCPBA
- → acetic acid Peroxide
- → Trifluoro acetic acid
- → H_2SO_5
- → $PhCO_3H$.



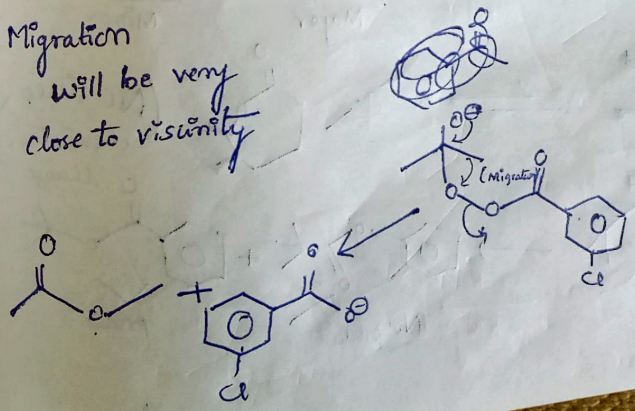
unsymmetrical Aldehyde/ketone

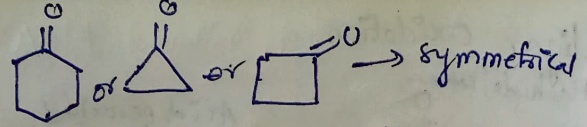


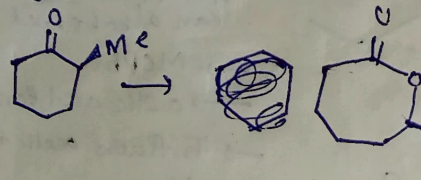
In Mechanism
insertion Rxn
Migration of group

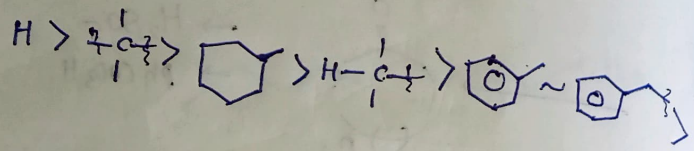


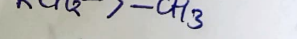
Migration will be very close to vicinity

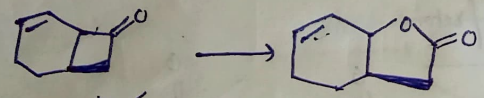


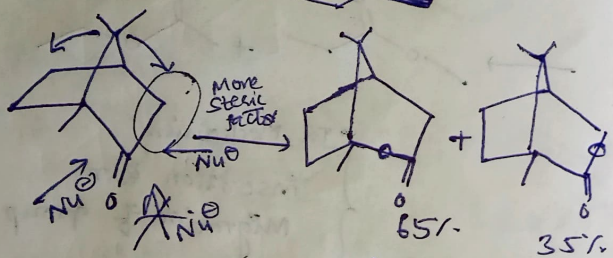




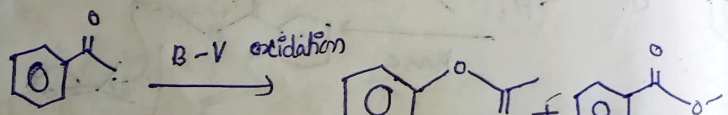


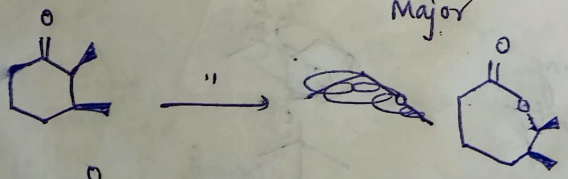


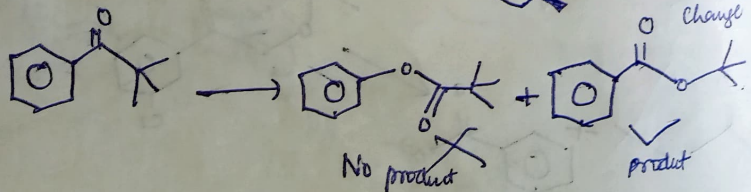


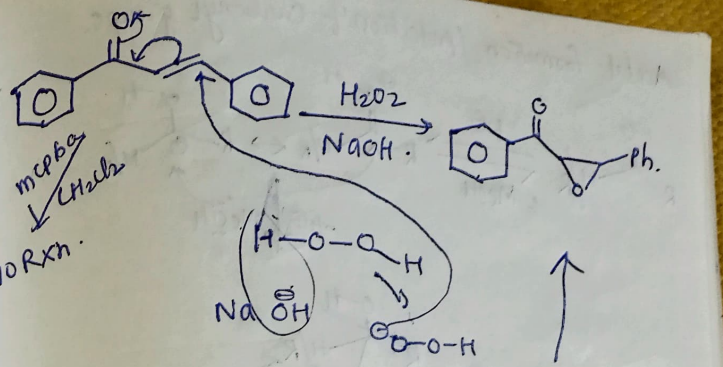


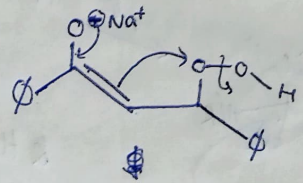
Baeyer-Villiger oxidation:

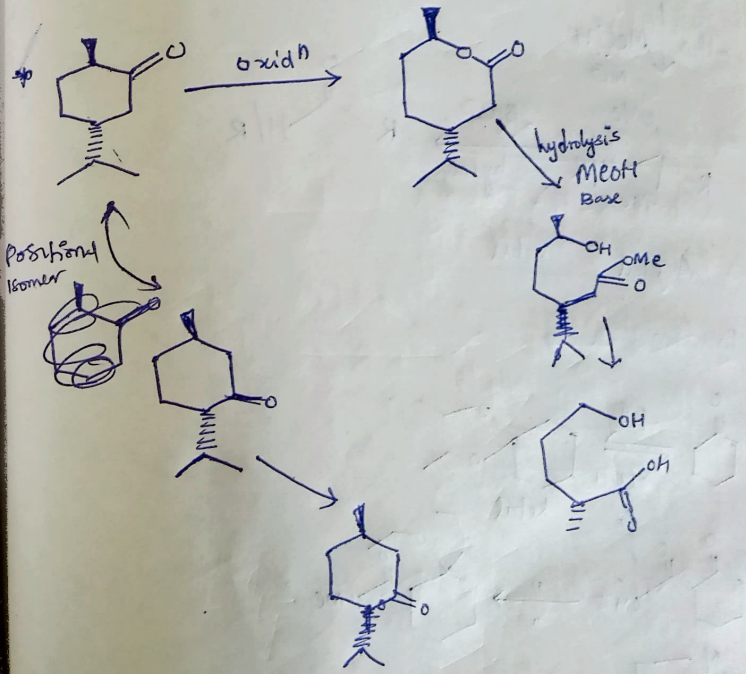




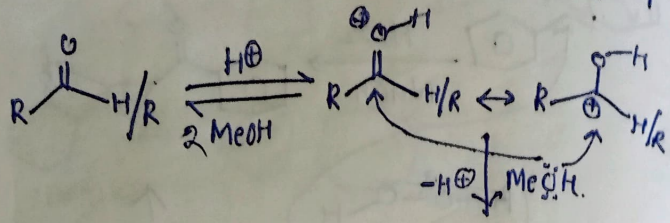


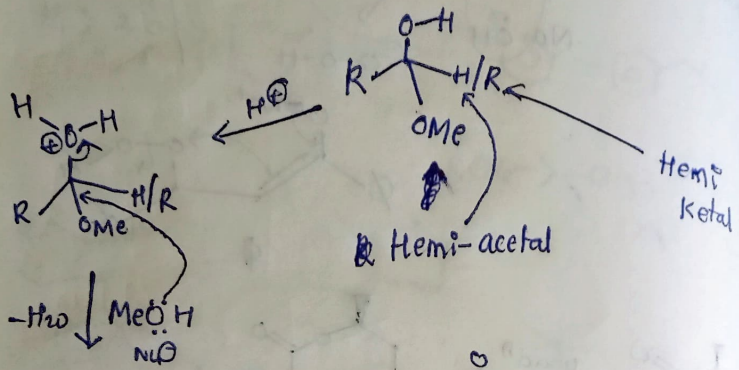


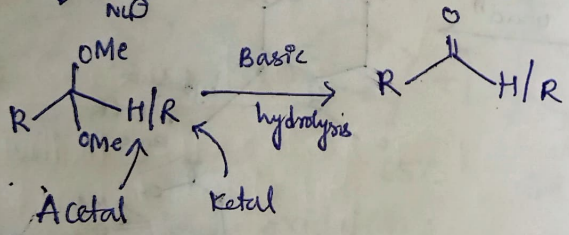




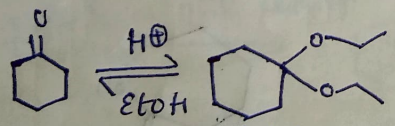
Acetal formation / protection of carbonyl groups.

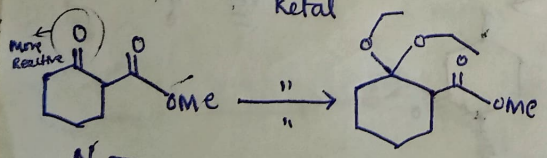


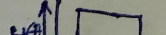


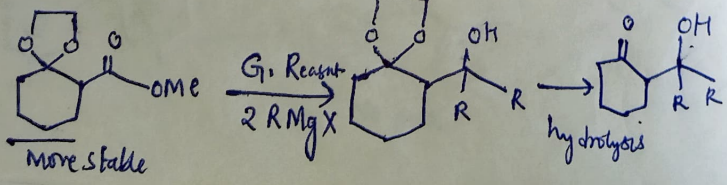


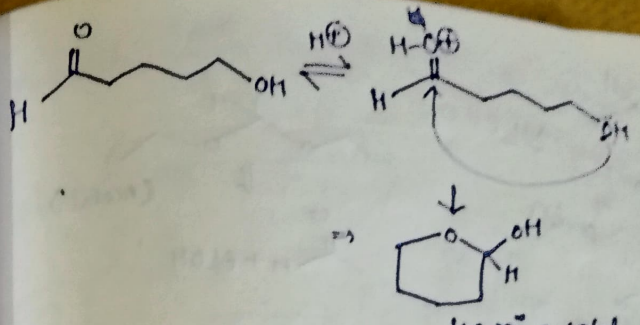
Protection of carbony.

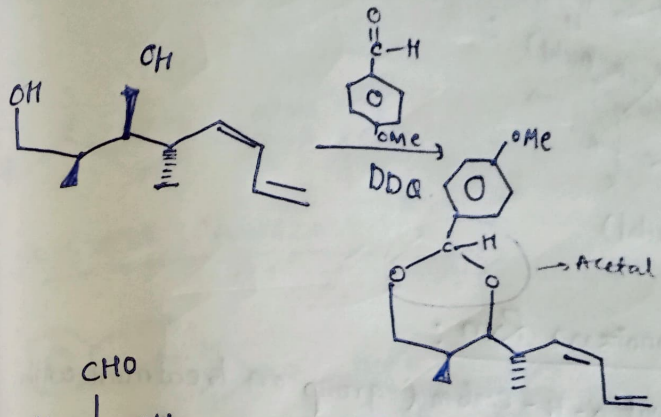


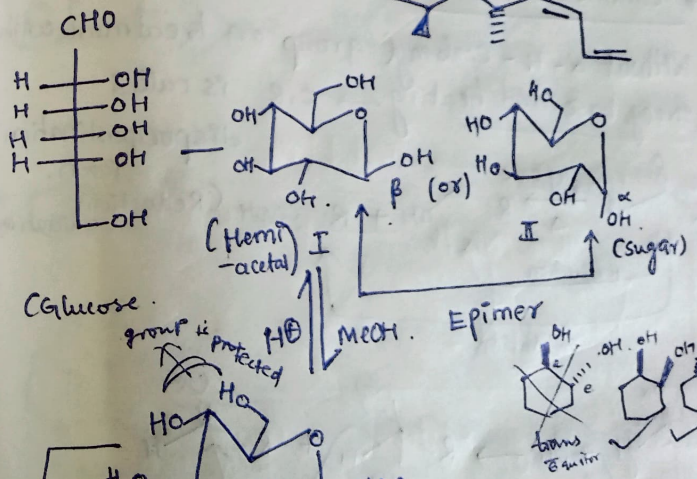


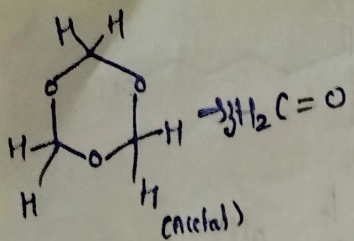


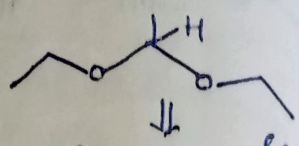


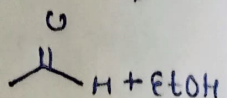


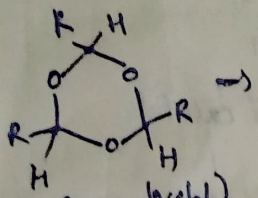


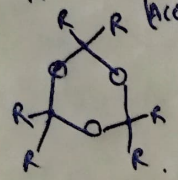






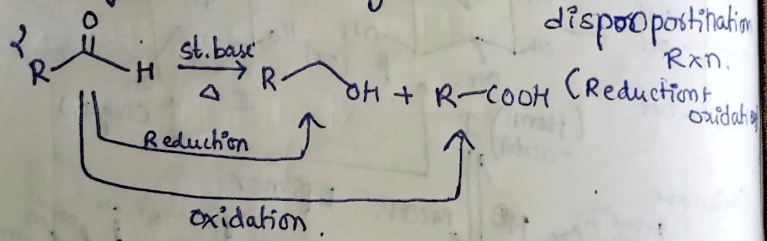


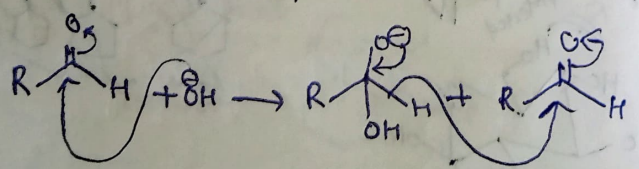


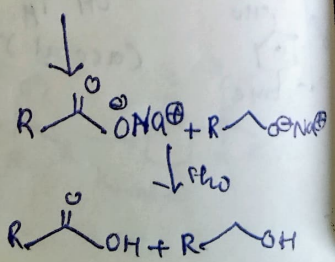


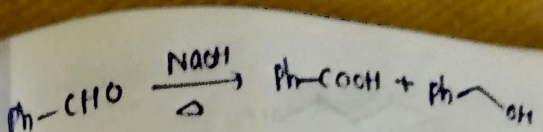
⇒ Cannizaro Rxn :

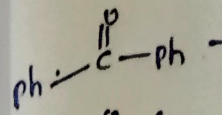
Without α-H-carbonyl group on treatment with strong base and heating → C.R is called disproportionation Rxn. (Reduction + oxidation)

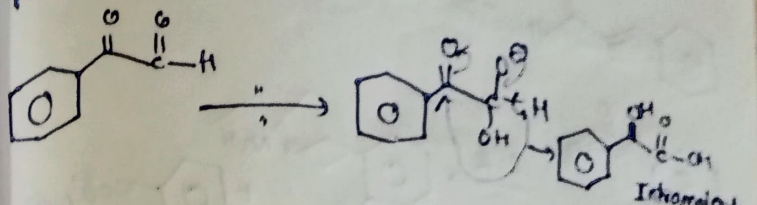


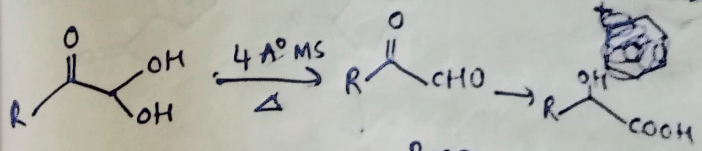




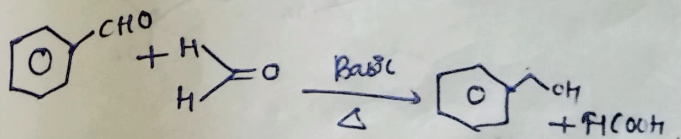


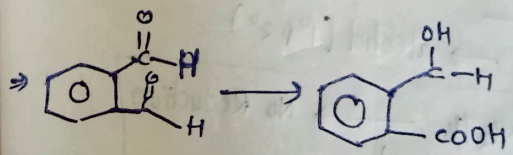


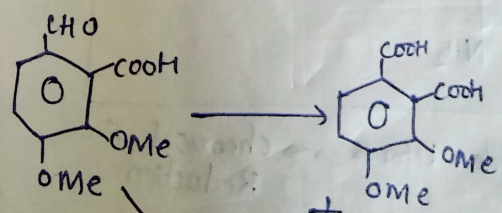


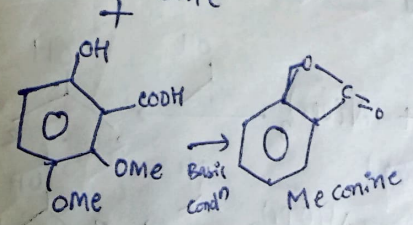


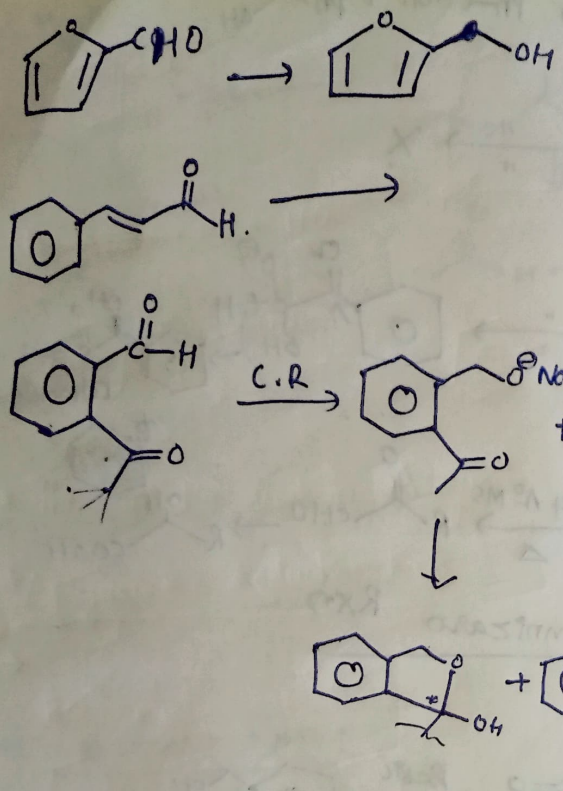
* Cross Cannizaro Rxn











* MPV – Reduction :

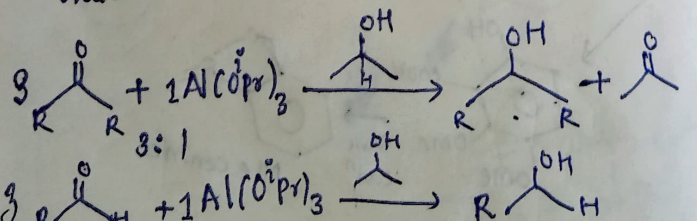
Aldehyde / Ketone ⟶ alcohol (1° & 2°)

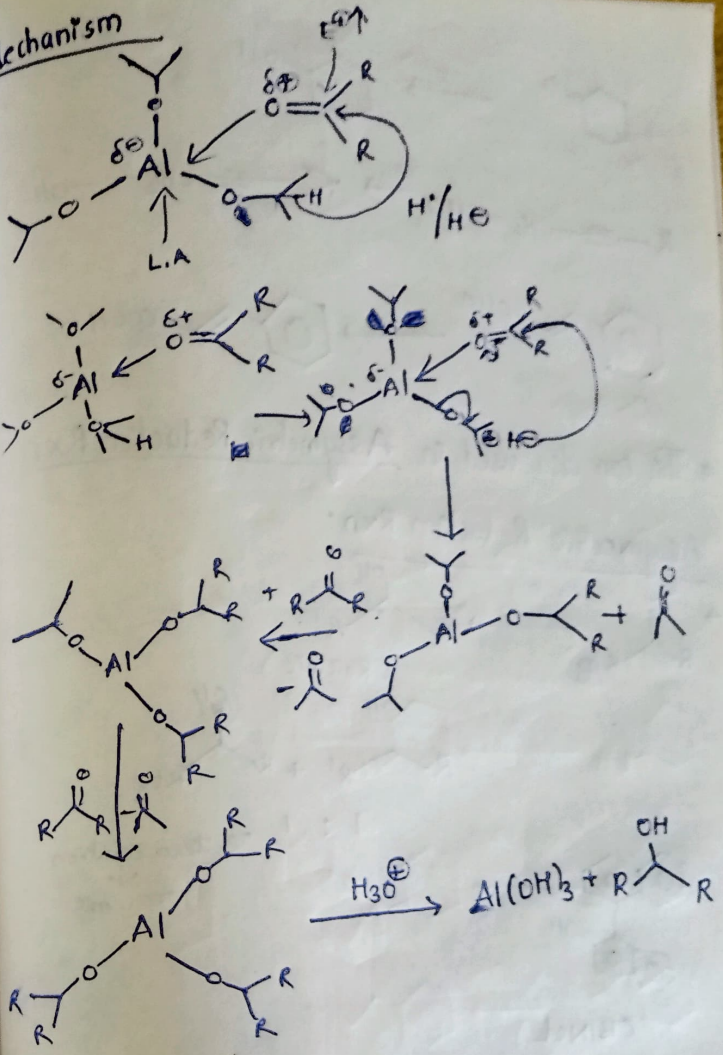
Alkene / Alkyne / NO_2 / X (Chalogen) ⟶ No Reduction

NH_2

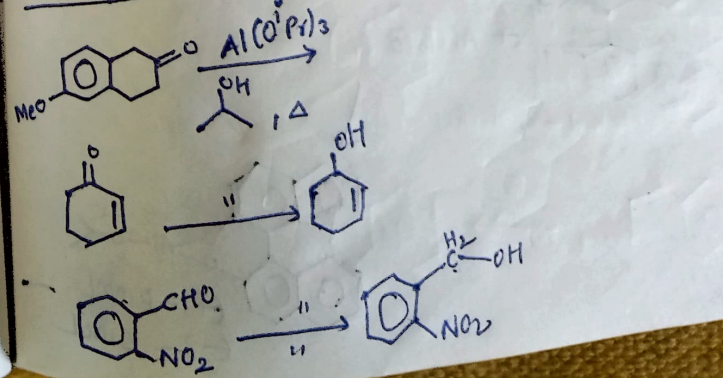
Hydrocarbon.

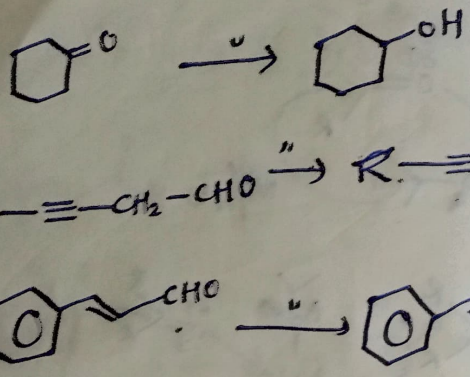
Reactivity order: aldehyde > ketones ⟶ chemoselective Reduction.





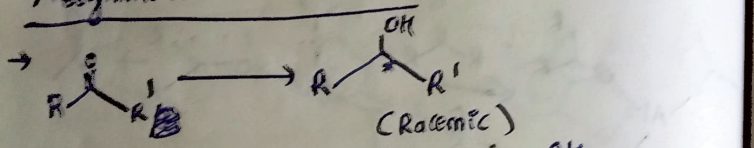
* Example :





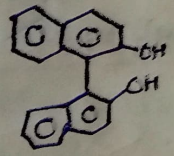
* This can also used in Assymetric Reduction Rxn.

Assymetric Reduction Rxn:

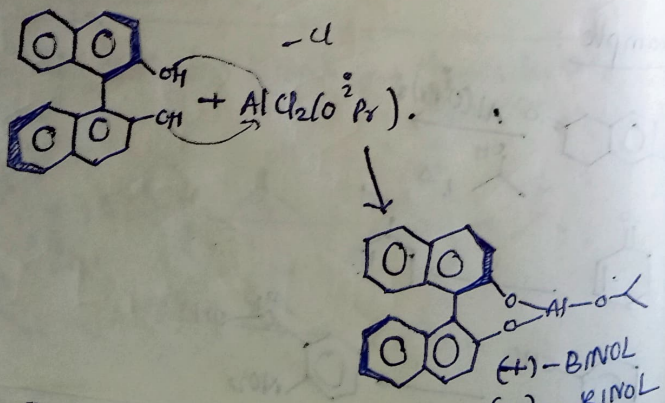


(Racemic)

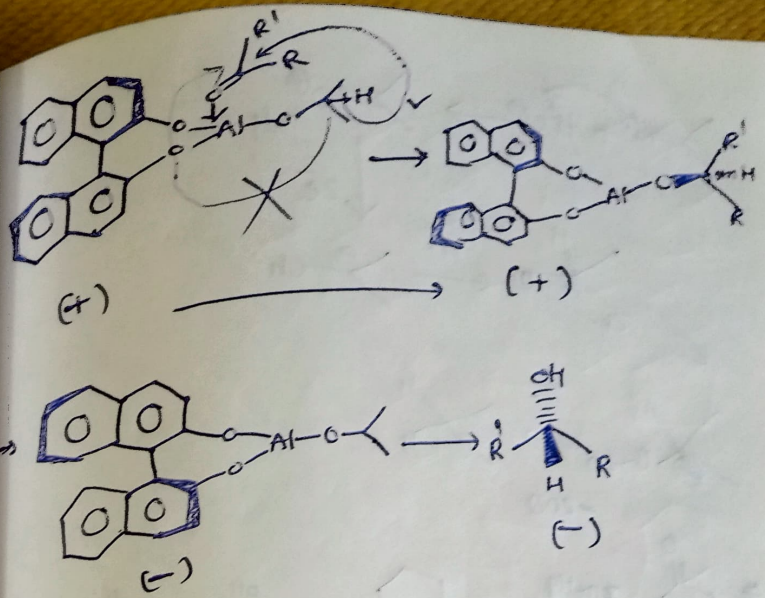
1 : 1 ⇒ Zero rotation → racemic



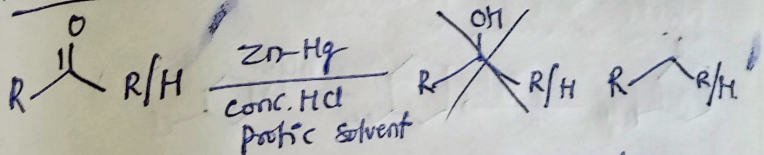
(BINOL)



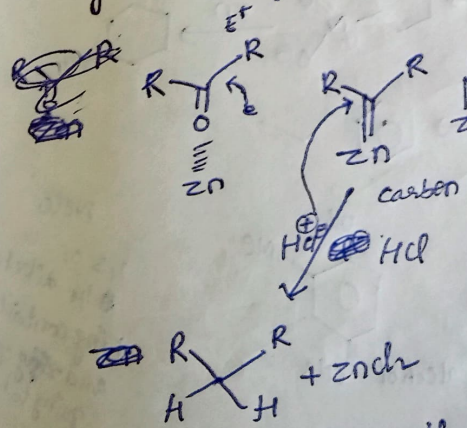
(+)-BINOL
(-)-BINOL



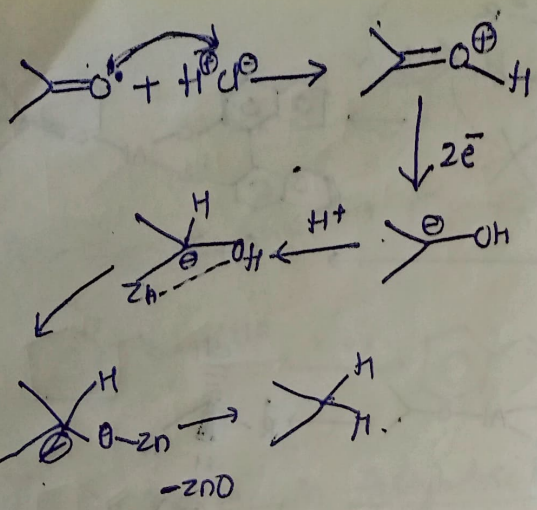
* Clemmenson Reduction/ Wolf kishner Reduction.

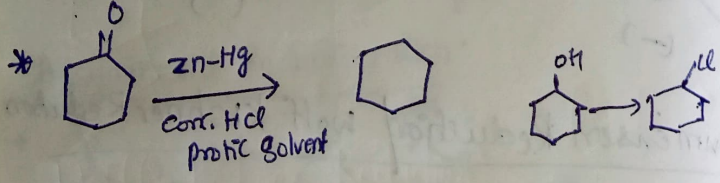


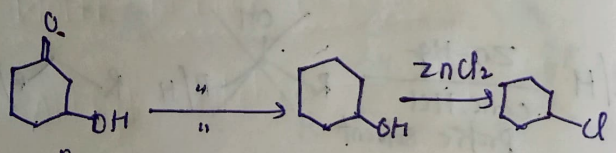
Zn-Hg → making colloid type soln → produce large surface area

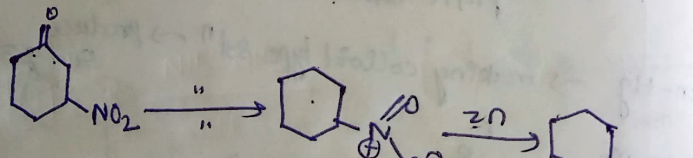


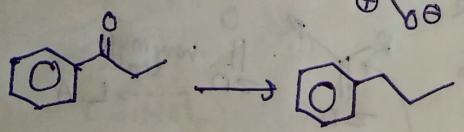
$ZnO + HCl \longrightarrow ZnCl_2 + H_2O$

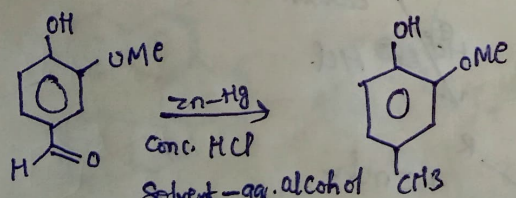


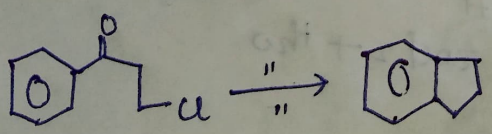






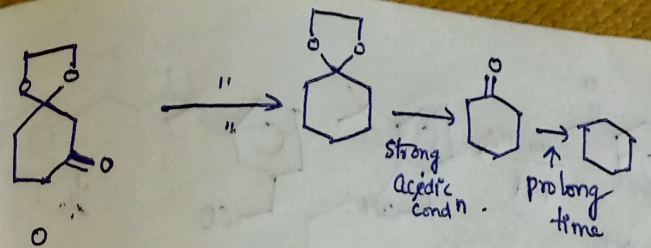


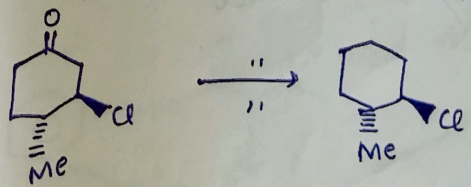


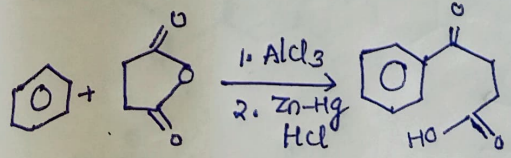


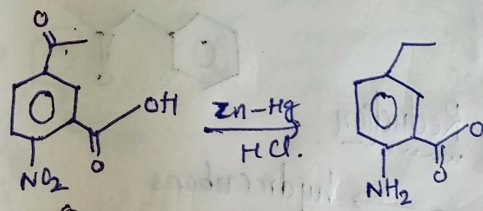
Note

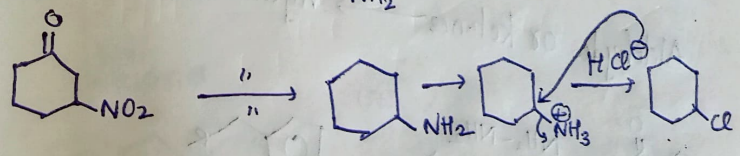
1,3 or β/γ diketone ring contraction and ring opening going to happen

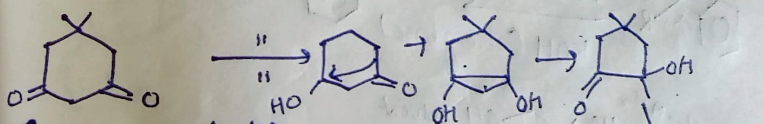


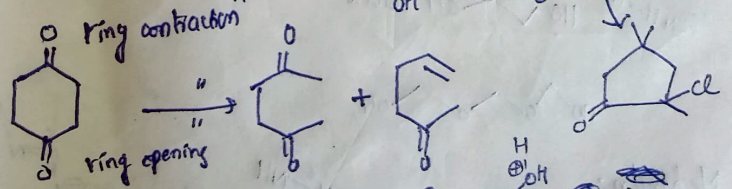


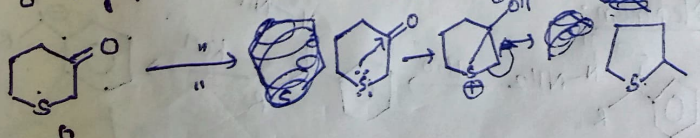


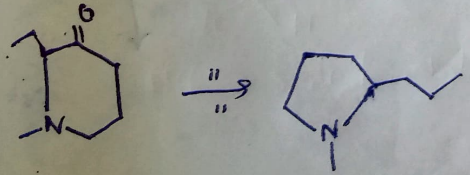


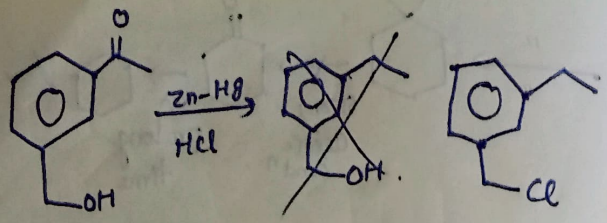


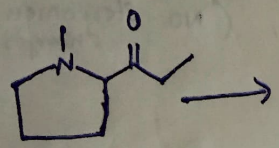


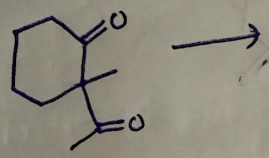


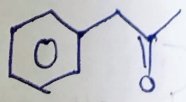






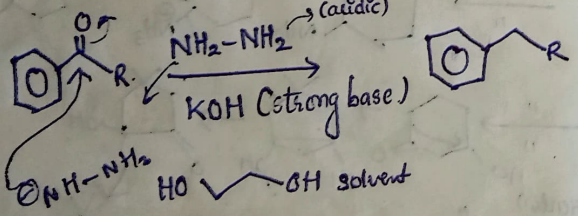


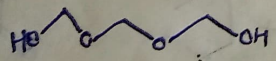




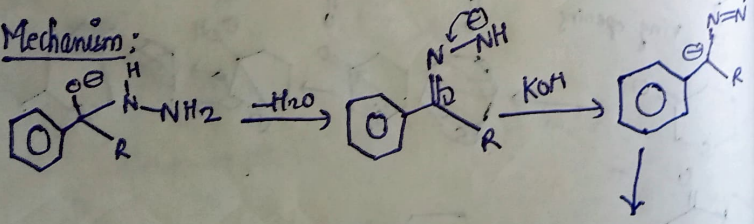
Wolff-Kishner Reduction

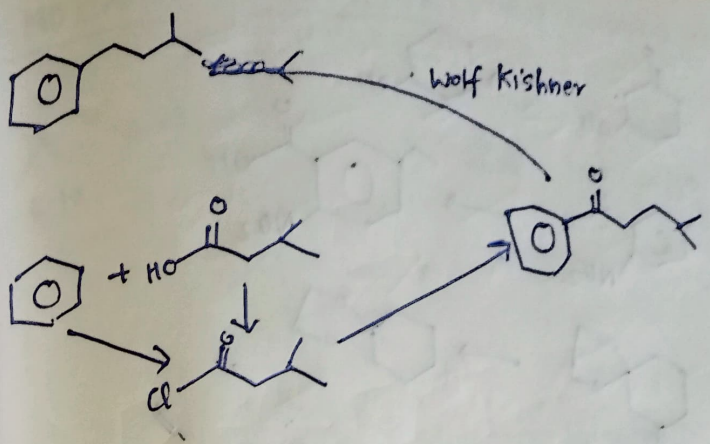
Aldehydes or ketones → hydrocarbons

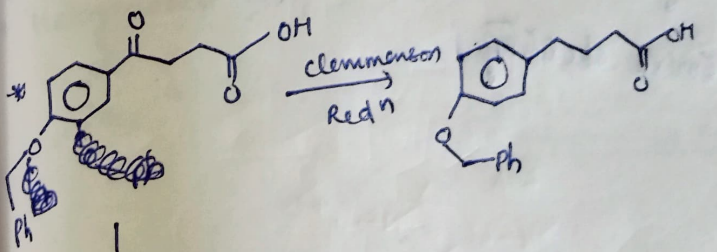


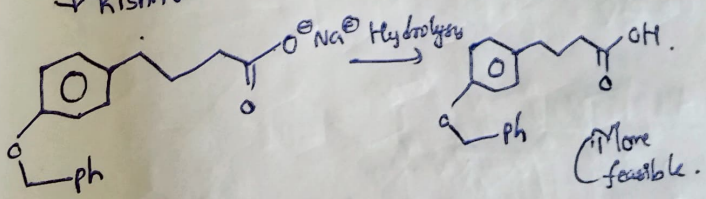


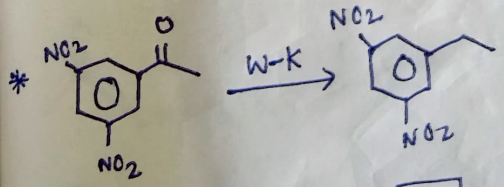
Mechanism:

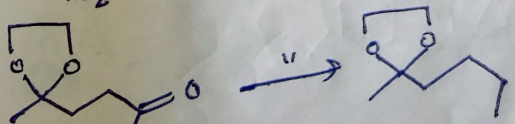


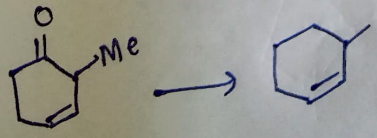


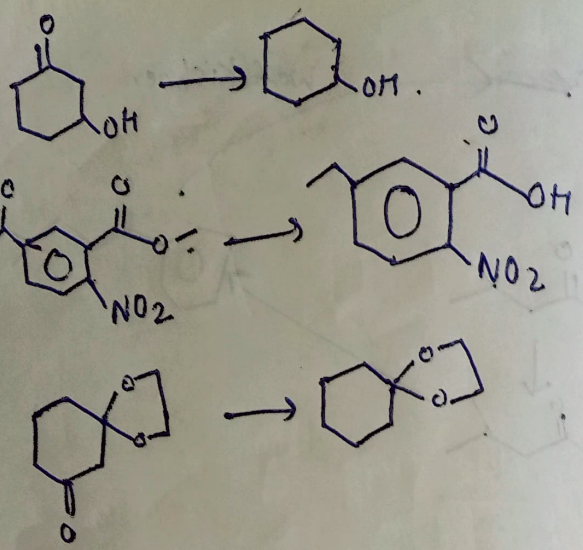






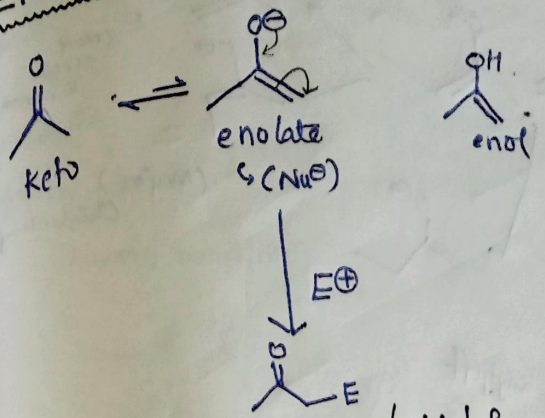




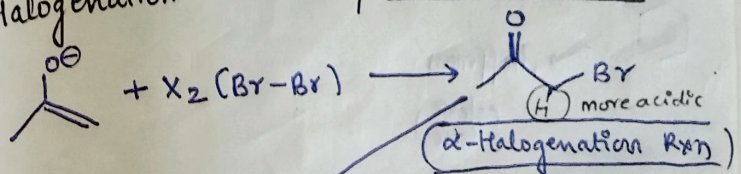


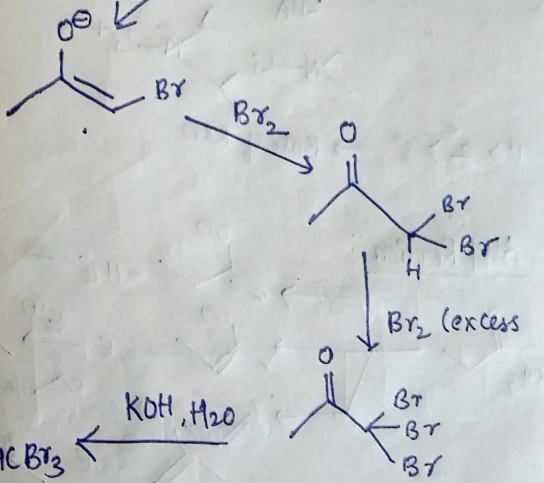
* Enolate chemistry.

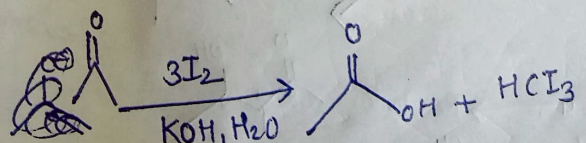
ENOLATE CHEMISTRY



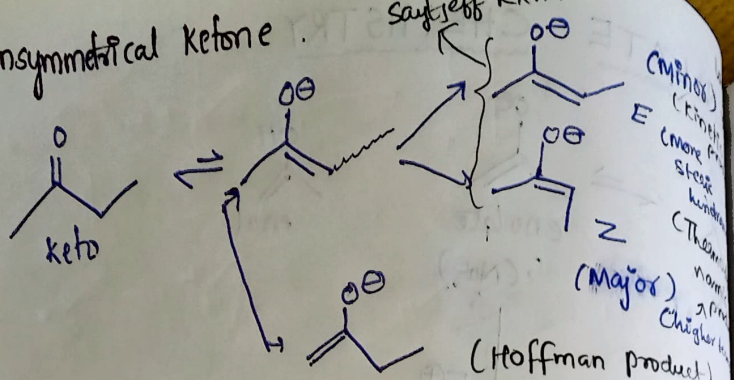
* Halogenation Reaction. / Haloform Reaction



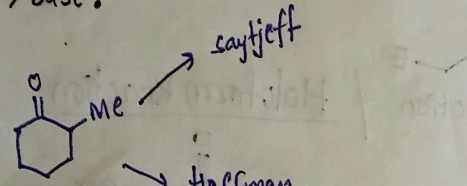




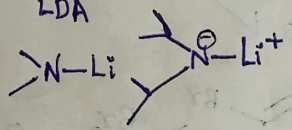
unsymmetrical Ketone.



→ base:

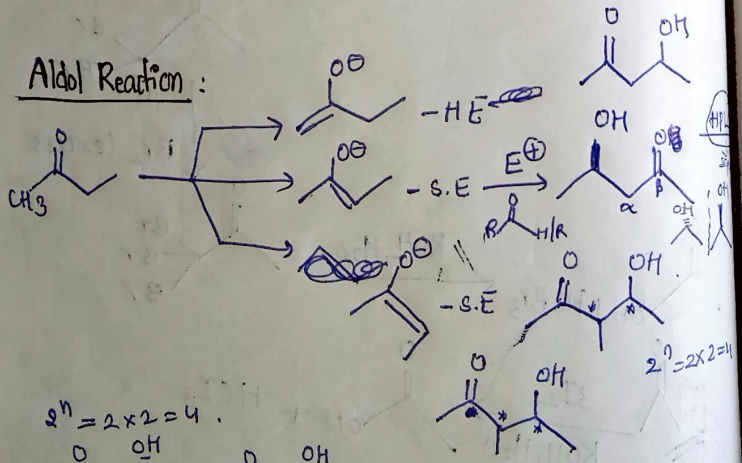


LDA

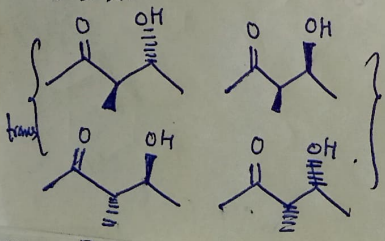


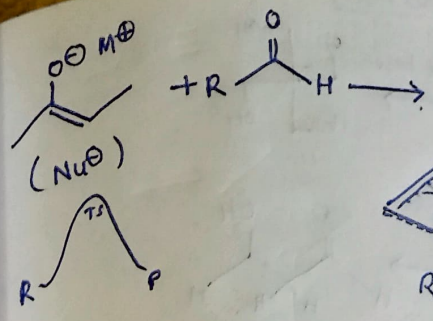
1° > 2° > 3° → Rate of RXN.

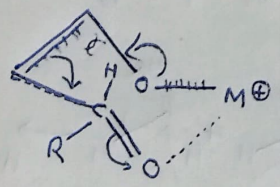
Aldol Reaction:



$2^n = 2 \times 2 = 4$.



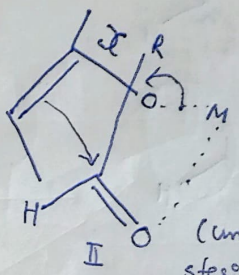




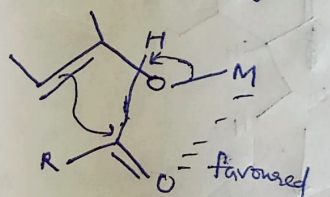
(favoured)

Ts-I → Major

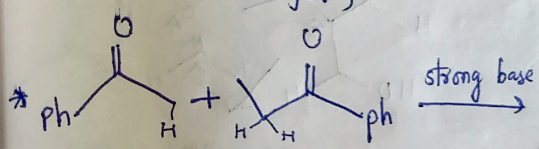
TS-II (unfavoured)



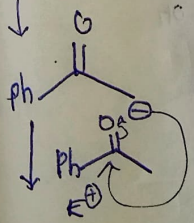
II (unfavoured sterically hindered.) → Minor.



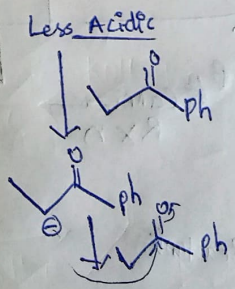
favoured (Major)

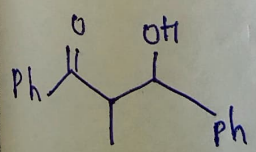


pka (More acidic)

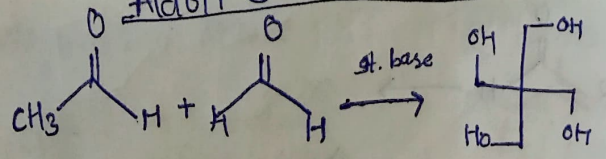


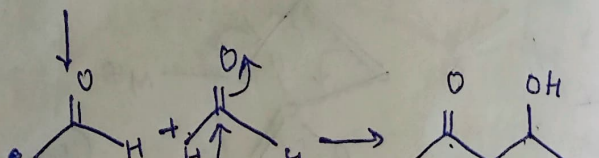
Less Acidic

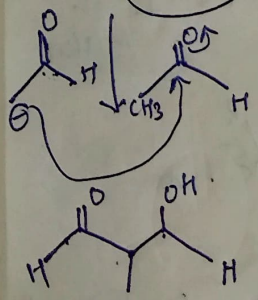


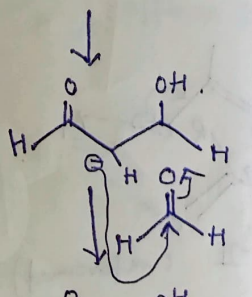


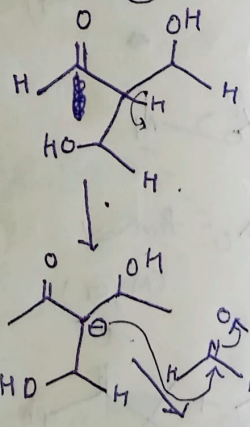
Aldol & Cannizaro Rxn

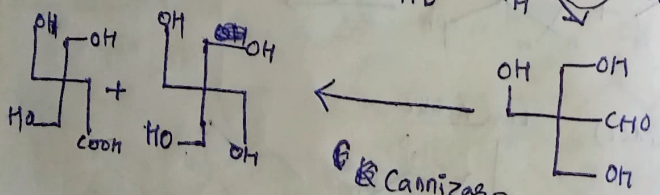


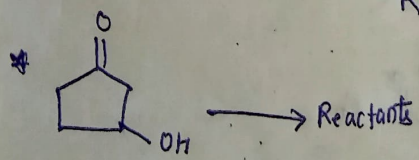


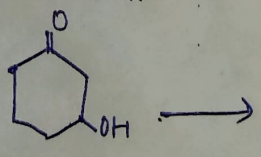


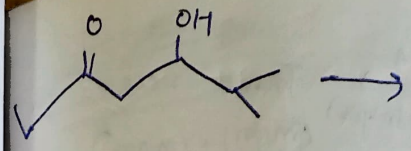


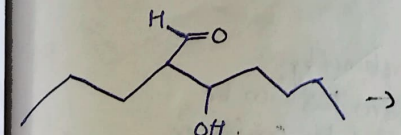


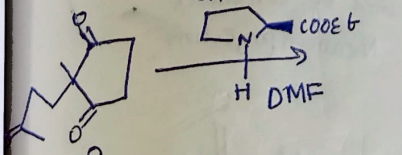


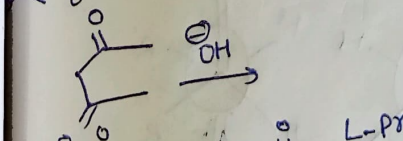


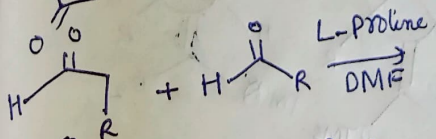


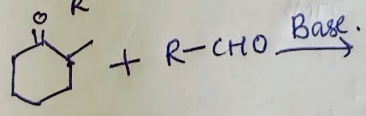




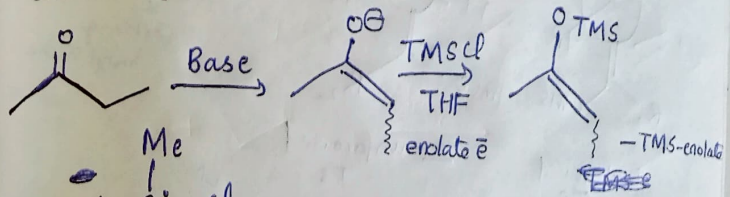


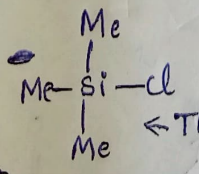


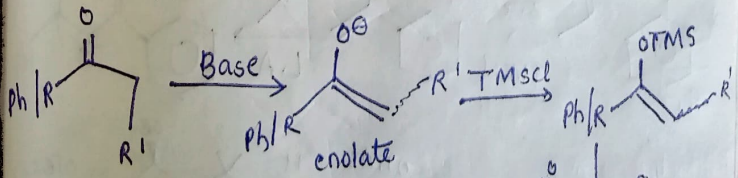


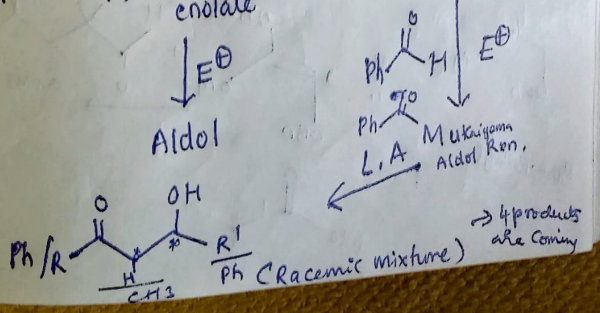


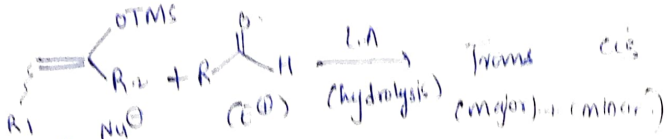
Mukaiyama Aldol Rxn:

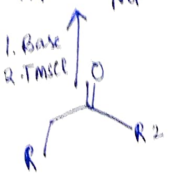




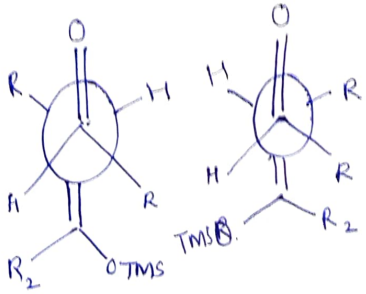


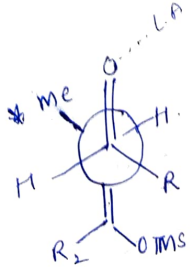


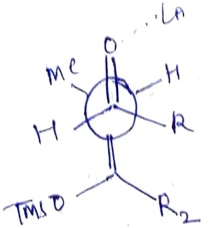




This could be explained by Chair boats. This can be explained by conformers Newman projections.

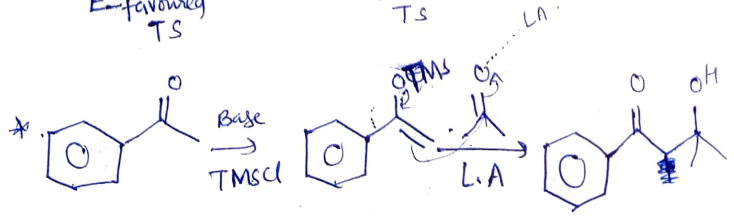


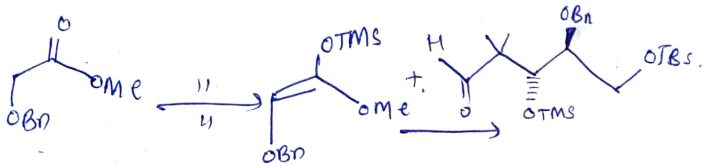




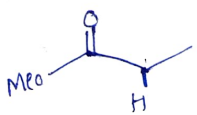
E-favoured TS

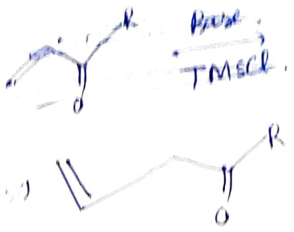
Z- unfavoured TS



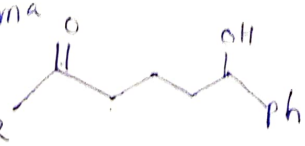


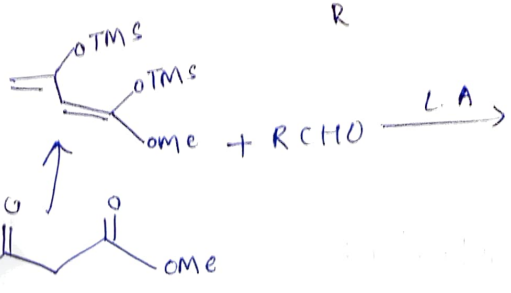
Bn → Benzyl

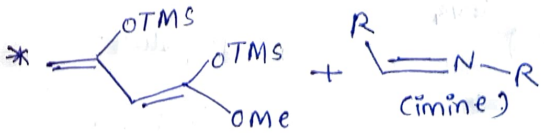


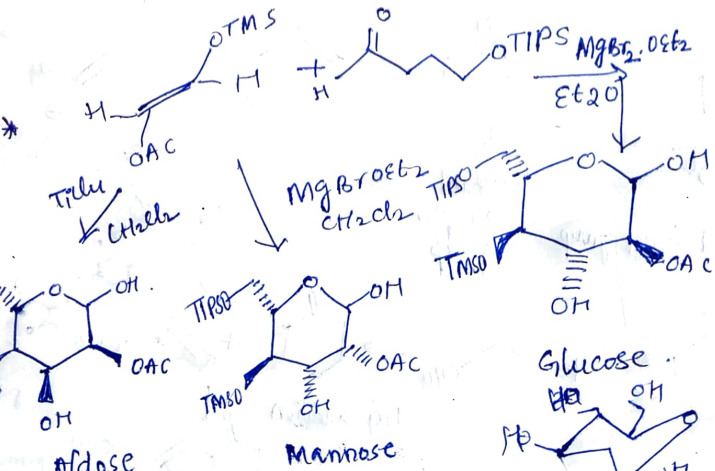


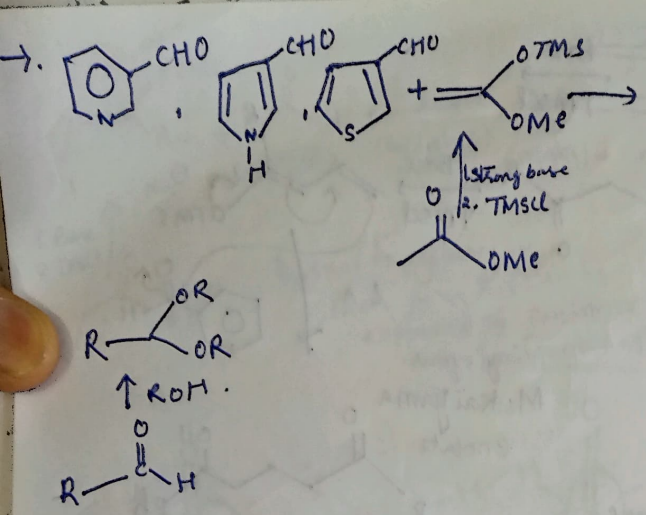
Vinylogous Mukaiyama enolate



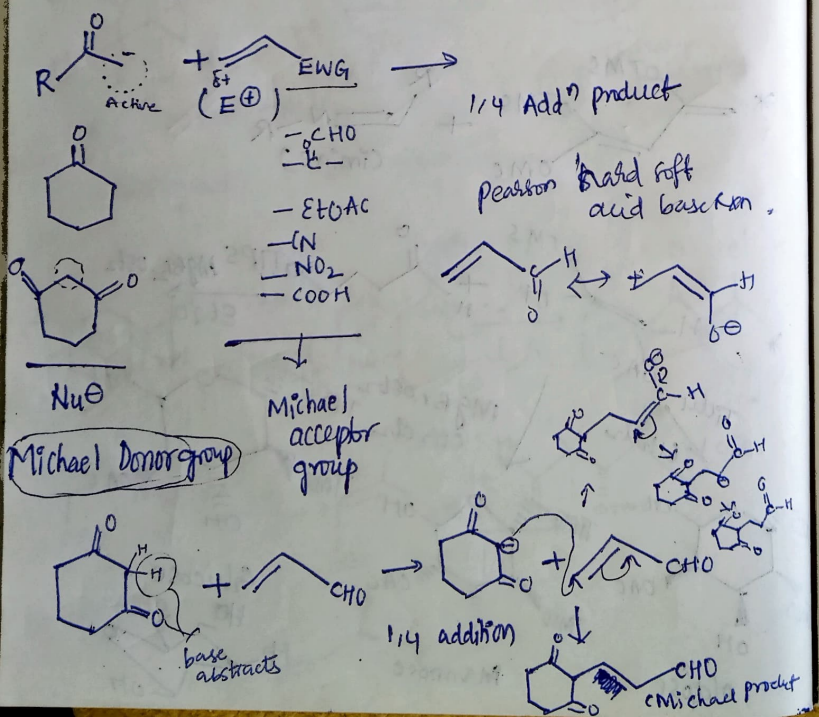


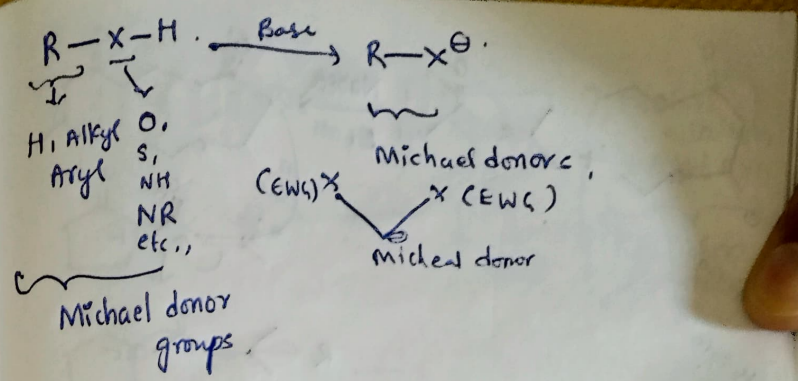


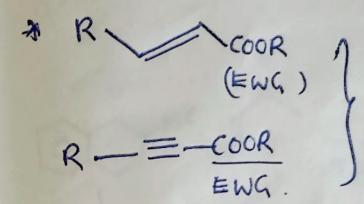




Michael Addition Reaction:





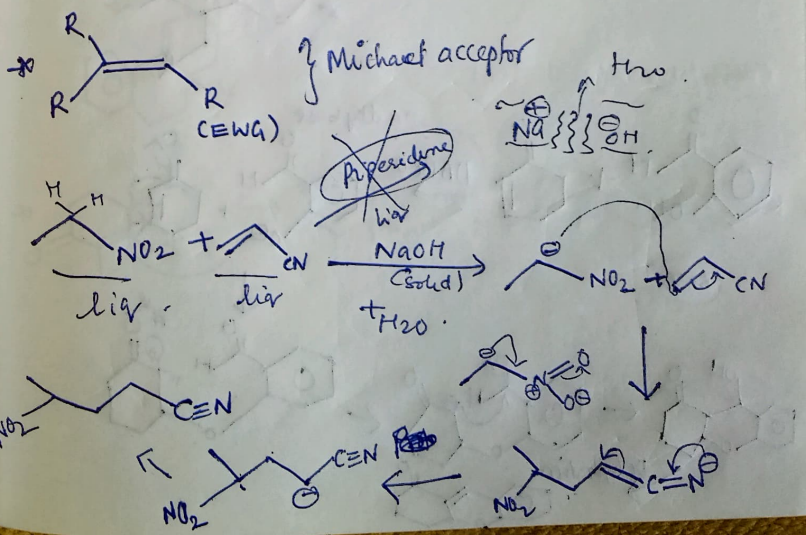


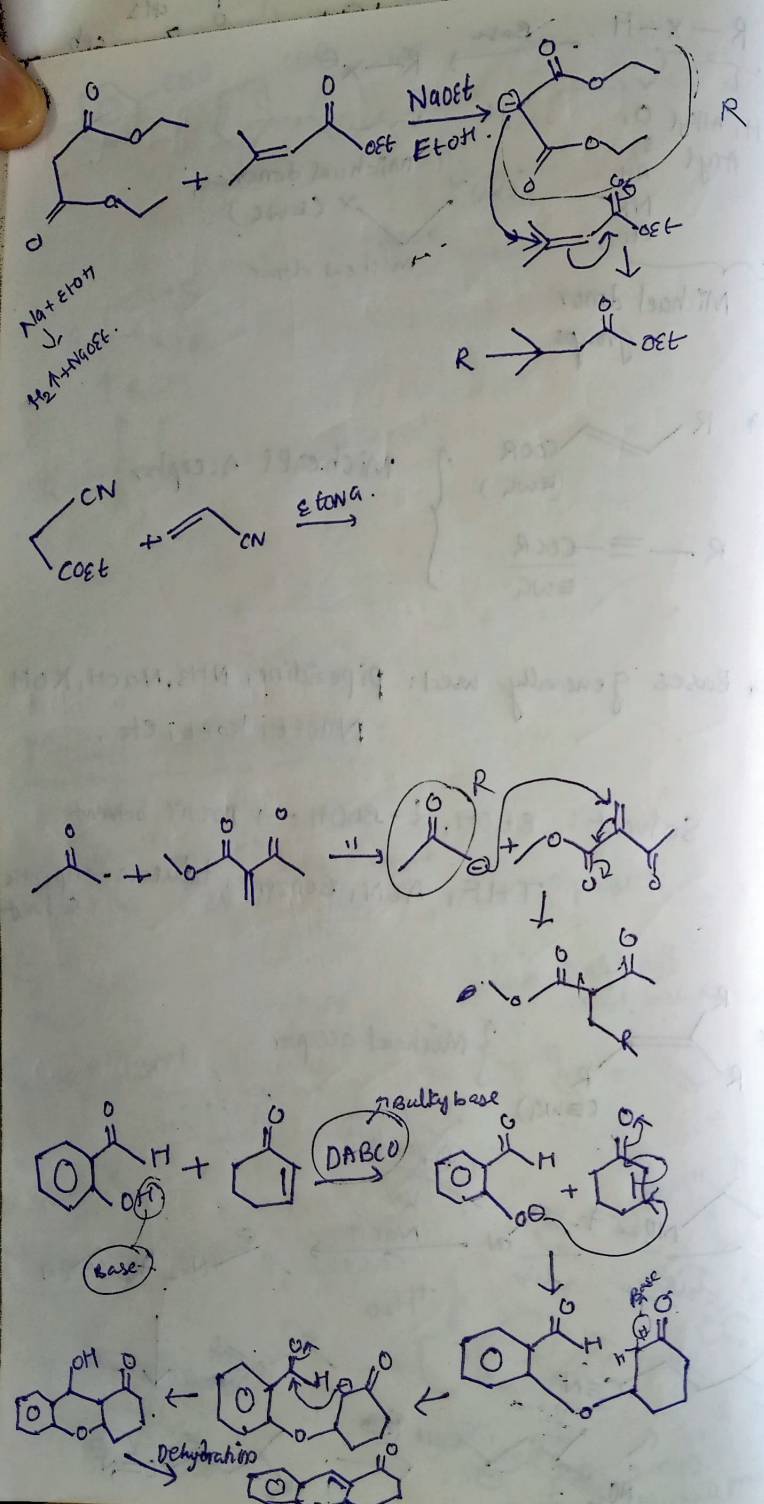
Michael Acceptor

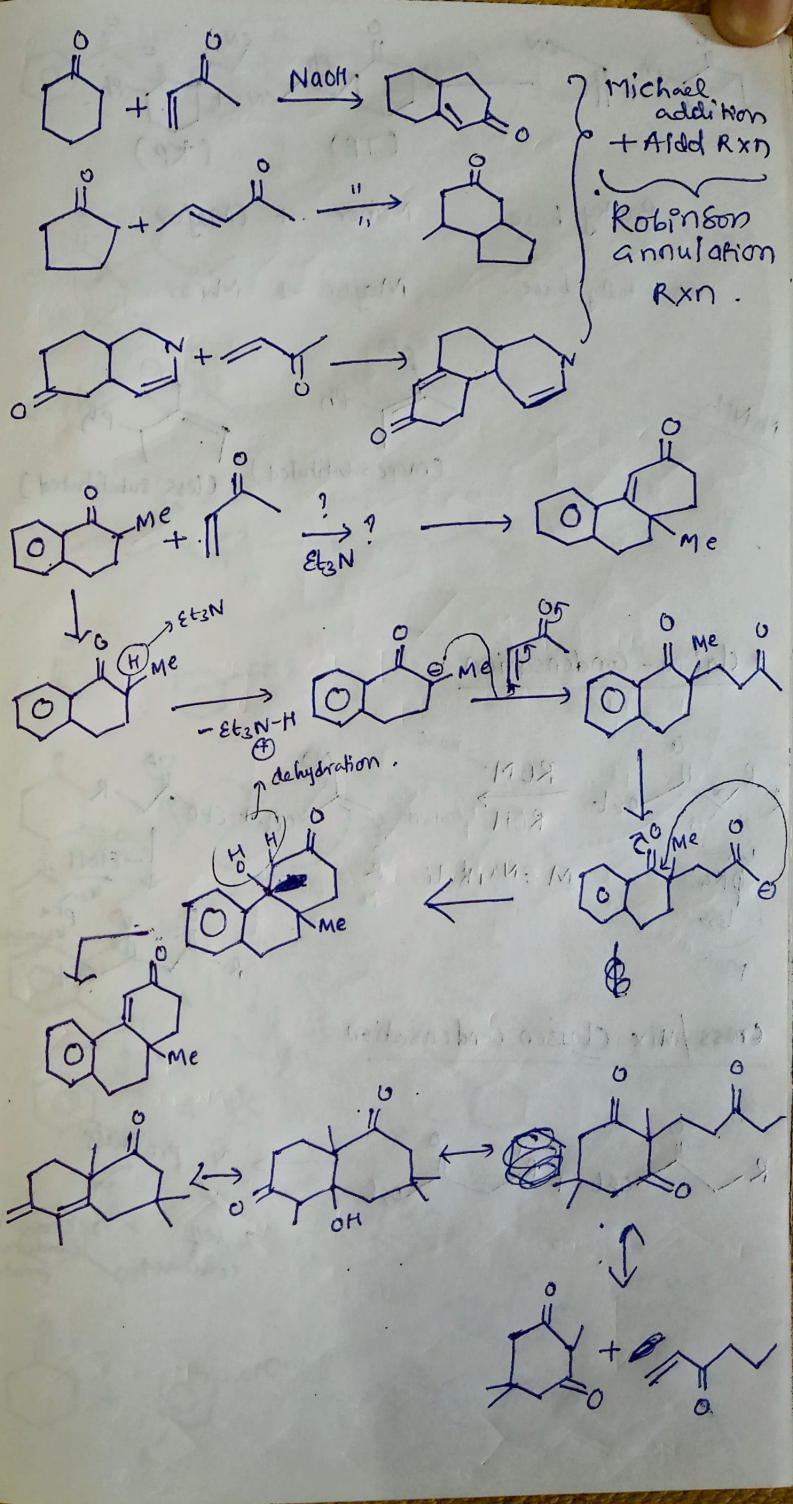
* Bases generally used: piperidine, NH_3, NaOH, KOH
NaOEt, KOEt, etc.,

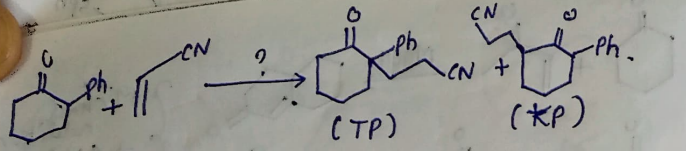
Solvent: EtOH, t-BuOH → protic solvent

THF, ACN, Benzene, toluene → Aprotic solvent



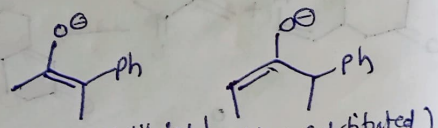

NaOEt
EtOH.
R
OEt
Na + EtOH
↓
Na⁺ + ⁻OEt.
CN
COEt
CN
EtONa.
Bulky base
DABCO
Base
OH
Dehydration


NaOH.
Michael addition
+ Aldol Rxn
Robinson annulation Rxn.
Me
?
Et₃N
?
Et₃N
Me
- Et₃N-H
dehydration.
Me
Me
OH



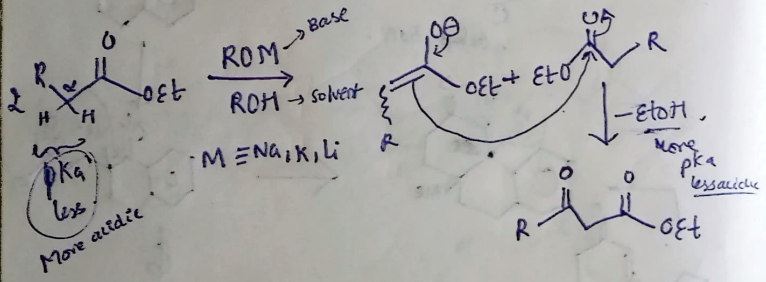
Bulky base. Minor + (Major.

non bulky base. Major + Minor

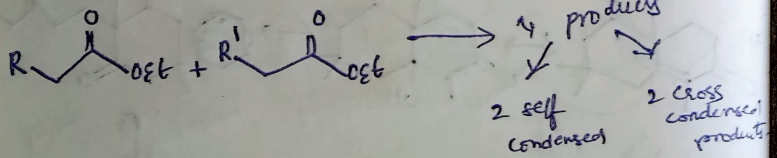


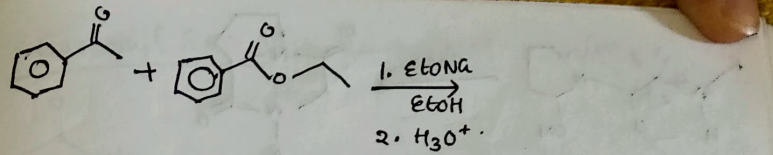
$NaNH_2$

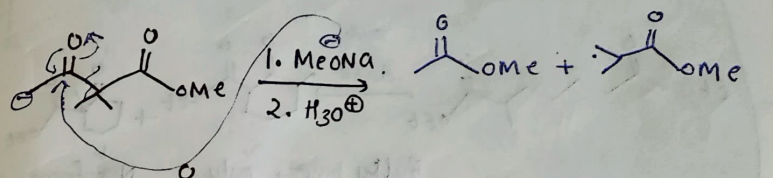
* Claisen - Condensation :

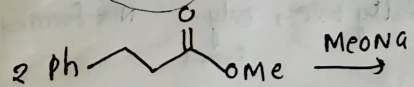


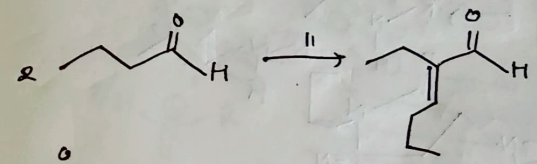
Cross / Mix Claisen condensation

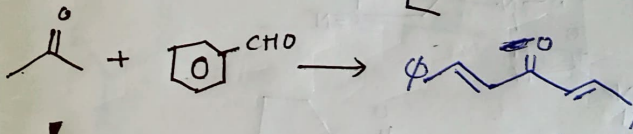


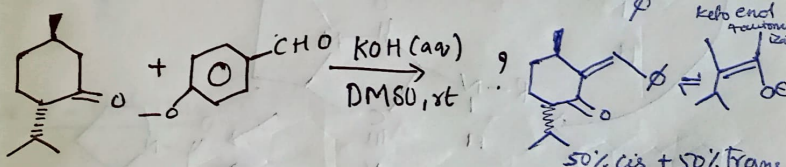


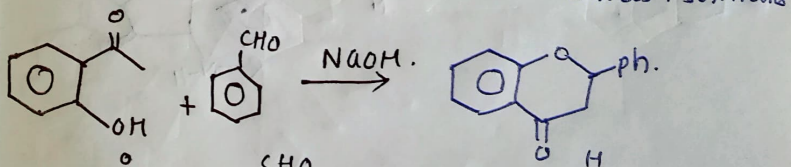


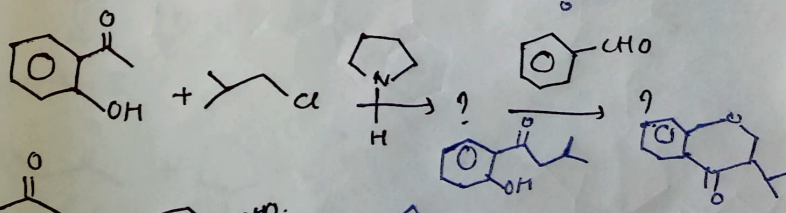


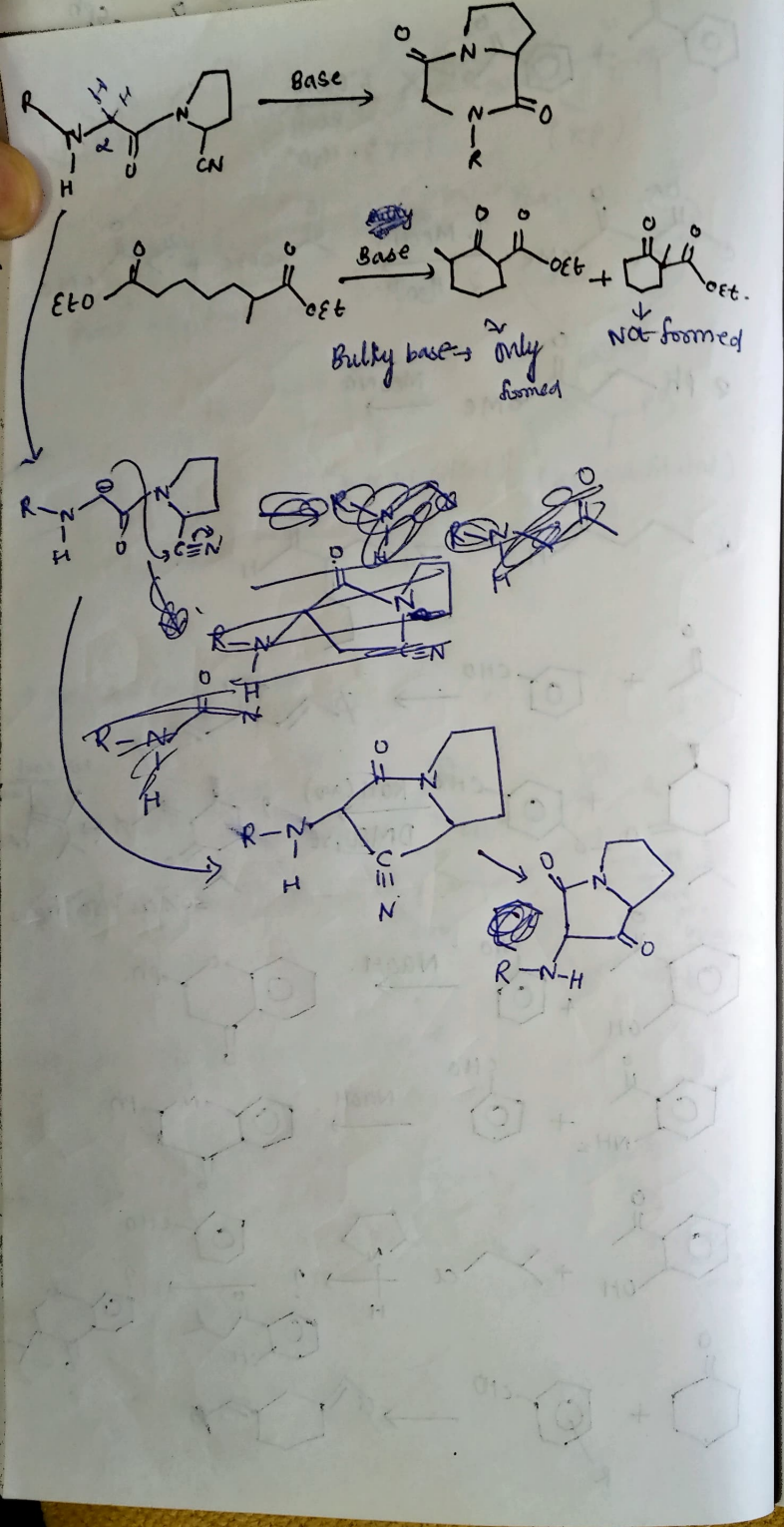




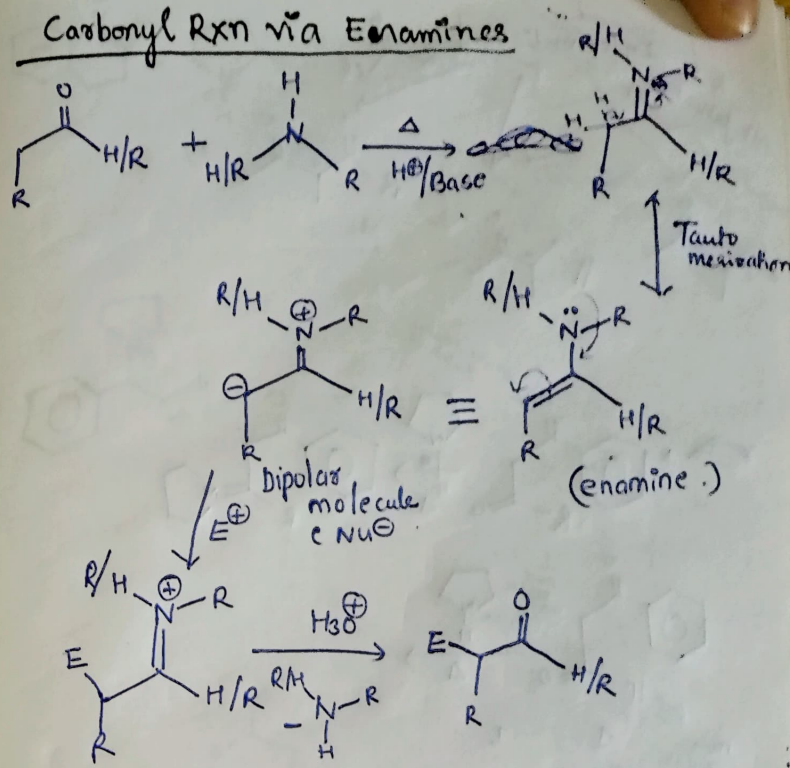




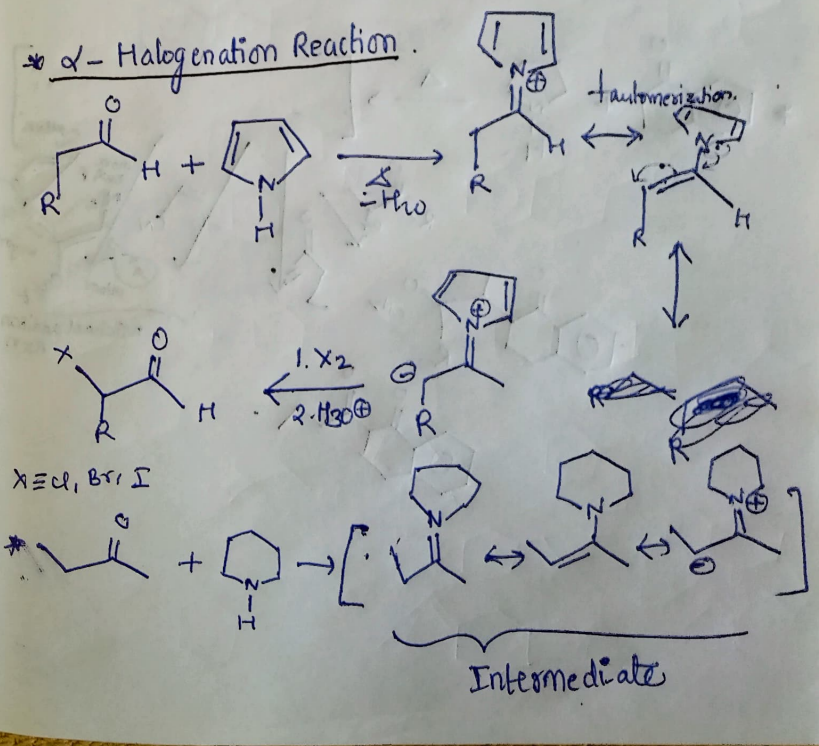


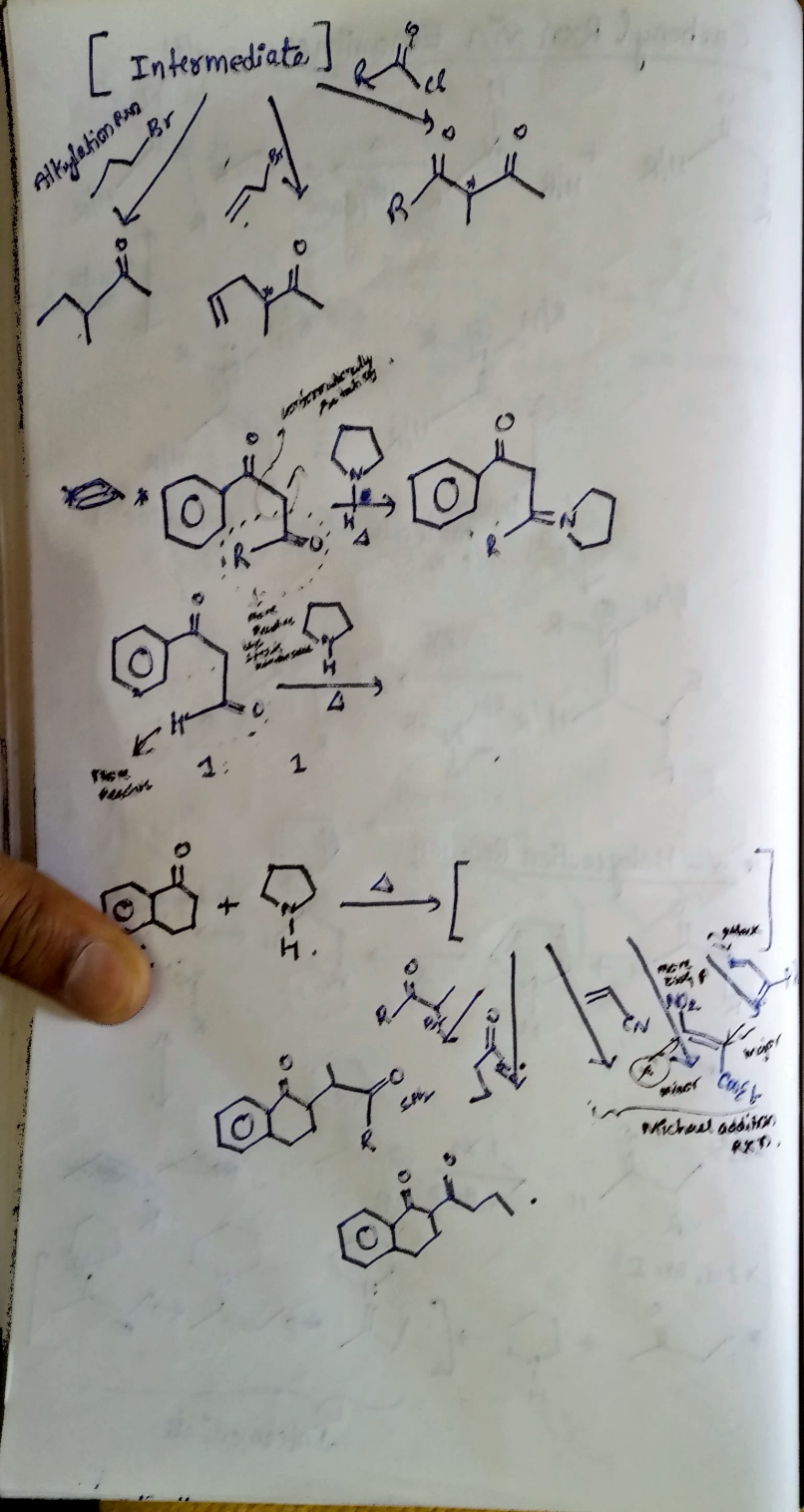


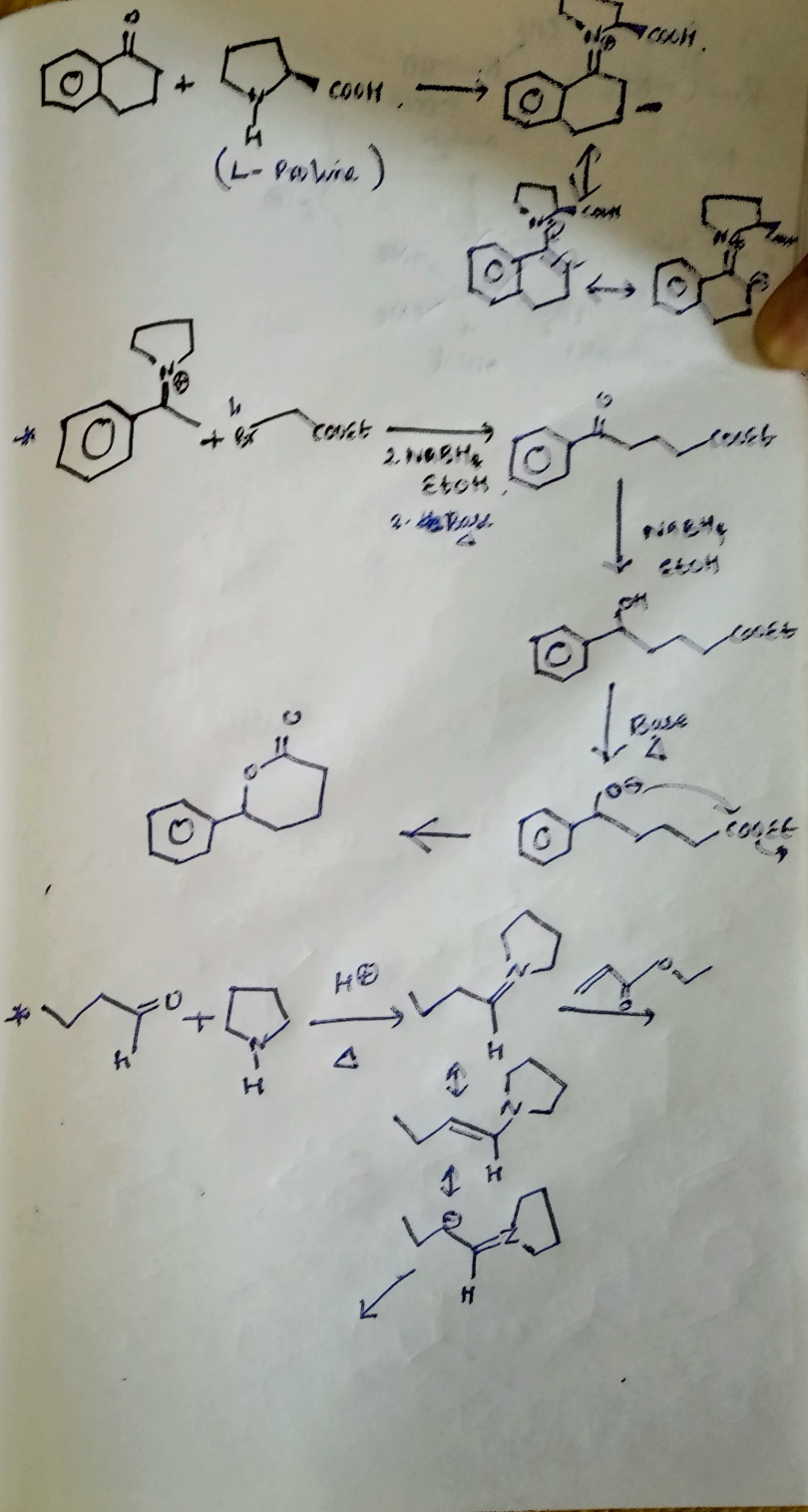
Carbonyl Rxn via Enamines

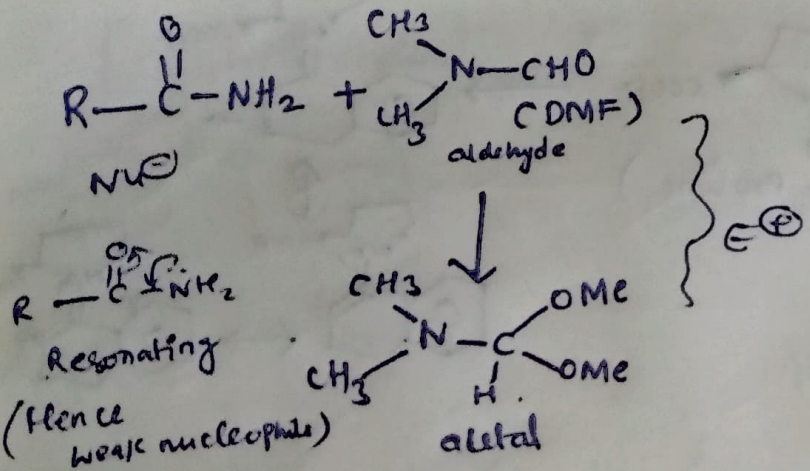


* α- Halogenation Reaction.




[Intermediate]
Alkylation Rxn
Br
Cl
1 : 1
Michael addition RXT


COOH
(L- Proline)
2. NaBH4 EtOH
Base
HO


R—C(=O)—NH2
NuΘ
CH3
N—CHO
CH3
(DMF)
aldehyde
R—C(=O)—NH2
Resonating
(Hence weak nucleophile)
CH3
N
C
OMe
OMe
CH3
H
aketal
EΘ