ALKYL HALIDE

27/04/2023

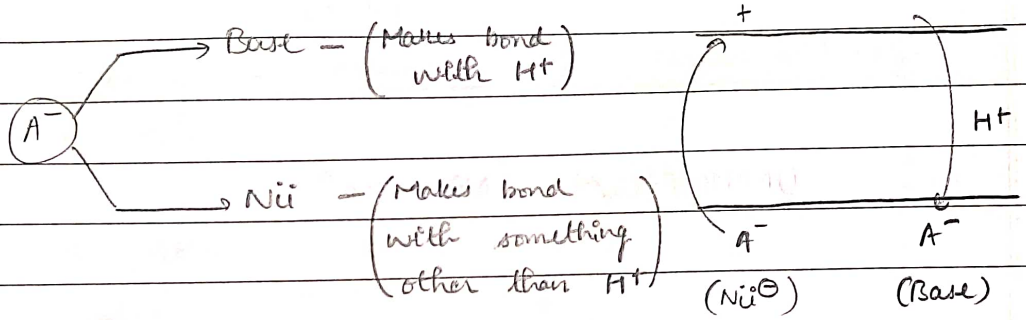
classmate Date Page 92

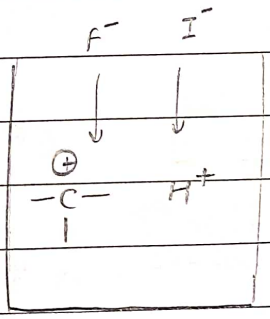
SUBSTITUTION REAⁿ

→ Aliphatic Nü Subⁿ

$$R-L \xrightarrow{Nü^{\ominus}} R-Nu + L^{\ominus}$$

Weak base is a good leaving grp.





$$H^+ + F^- \longrightarrow H-F$$

$$-\overset{|}{\underset{|}{C}}\oplus + F^- \longrightarrow -\overset{|}{\underset{|}{C}}-F$$

$$H^+ + I^- \longrightarrow H-I$$

$$-\overset{|}{\underset{|}{C}}\oplus + I^- \longrightarrow -\overset{|}{\underset{|}{C}}-I$$

1(193

• Retention — Preservation of the spatial arrangements of bonds to an asymmetric centre during a chem. rxn or transformation

Date
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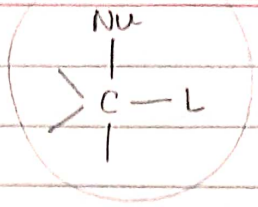
(I) $R-L \xrightarrow{Nu^{\ominus}}$  No rxn since 5 bonds on C

SN1

(II) $R-L \xrightarrow[rds]{} R^{\oplus} + L^{\ominus} \xrightarrow{Nu^{\ominus}} R-Nu$

(III) $Nu^{\ominus} + R-L \longrightarrow [Nu^{\ominus}---R---L] \longrightarrow Nu-R$

Transition state

SN1 : UNIMOLECULAR Nü SUBN

$$R-L \xrightarrow{Nu^{\ominus}} R-Nu + L^{\ominus}$$

Mechanism

Step-I : $R-L \underset{rds}{\rightleftharpoons} R^{\oplus}\,L^{\ominus} \xrightleftharpoons{H_2O} R^{\oplus} \,||\, L^{\ominus}$

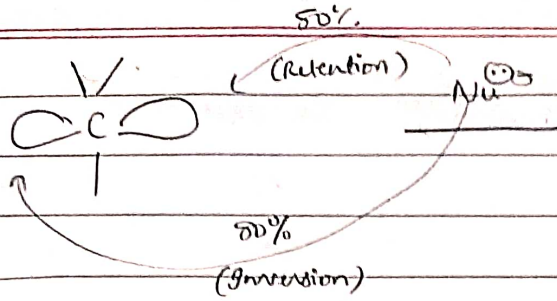
(Intimate ion-pair) (Polar protic solvent) (Solvent separate ion)

$\Downarrow\Uparrow$

R^{+}

Step-II : $R^{+} \xrightarrow[fast]{Nu^{\ominus}} R-Nu$

There is no rel^n b/w retention & inversion and (R), (S) & (d), (l).



☆ Retention & Inversion is defined on the basis of relative config.
i.e. (E)Z), (cis, trans), (syn, anti), (D, L)

NOTE: (i) RoR ∝ [R-L]
There is no meaning of Nucleophilicity for S_N1 rea^n

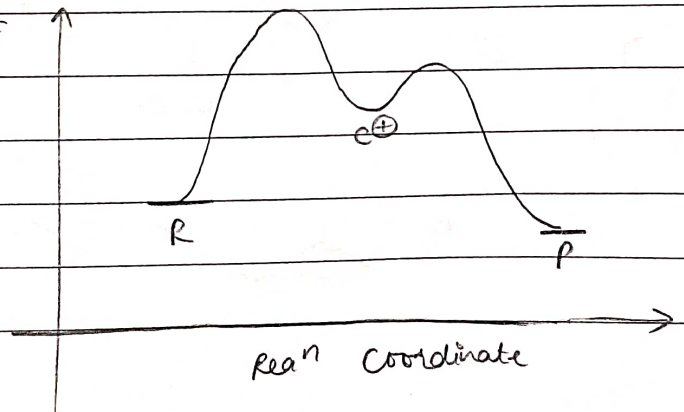
⇒ RoR ∝ (Stability of C⊕)
(PPS)
(Leaving grp)

(ii) 3° R–X → S_N1
1° R–X → S_N2
2° R–X → S_N1 (PPS)
2° R–X → S_N2 (PAS)

(iii) Racemisation occurs.

(iv) % product : Inversion > Retention

(v)



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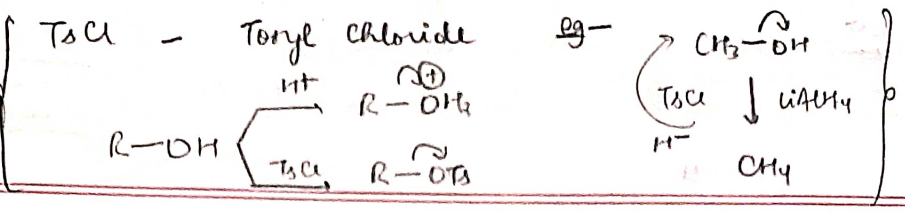
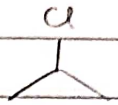
TsCl – Tosyl Chloride

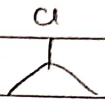


Q. Which gives SN1 with aq. KOH ?

1. CH_3-Cl ✗

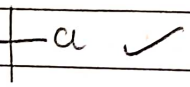
2.  ✗

3.  (PPS) ✓

4.  (PAS) ✗

5.  (PPS) ✓ (X)

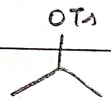
(F is bad leaving grp)

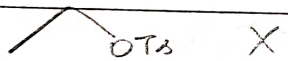
7.  ✓

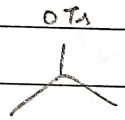
6.  (PAS) ✗

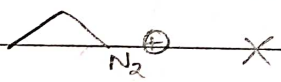
8.  ✓

9.  ✓

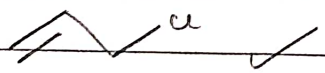
10.  (PAS) ✗

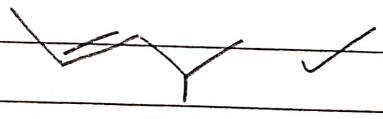
12.  ✗

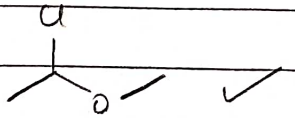
11.  (PPS) ✓

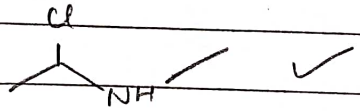
13.  ✗

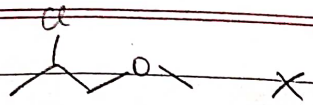
14.  ✗

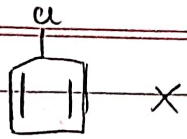
15.  ✓

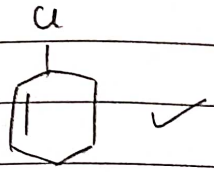
16.  ✓

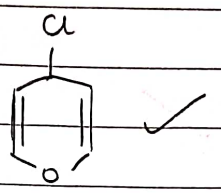
17.  ✓

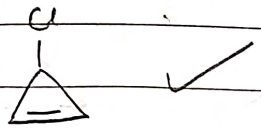
18.  ✓

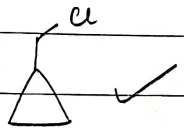
19. 

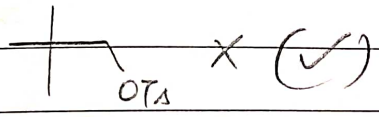
20. 

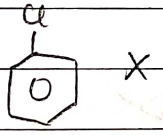
21. 

22. 

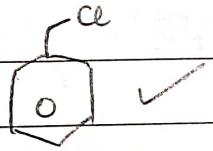
23 

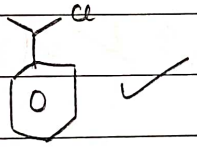
24. 

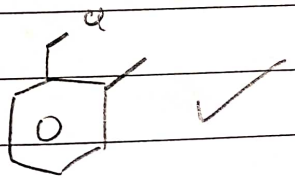
☆ 25. 

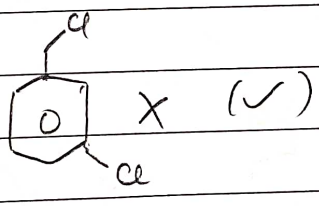
26. 

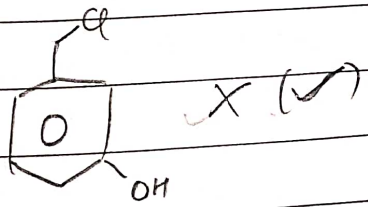
(High Steric Hindrance ⇒ No backside attack ⇒ No S_N2 ⇒ S_N1)

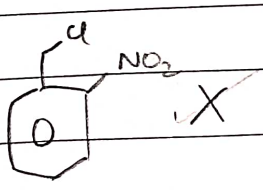
27. 

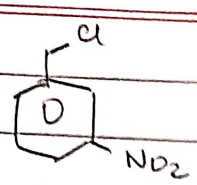
28 

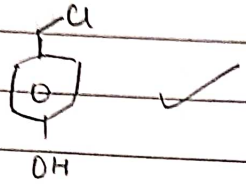
29. 

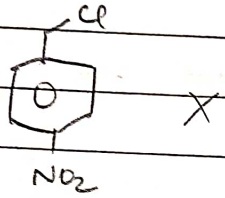
30. 

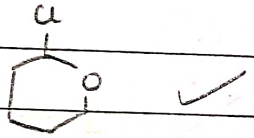
31 

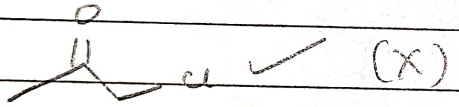
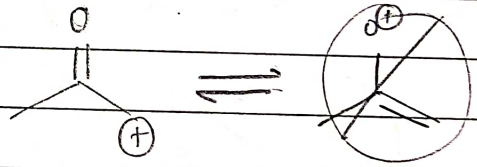
32. 

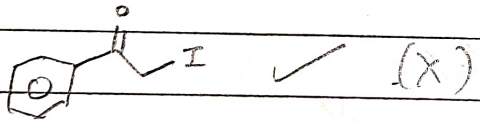
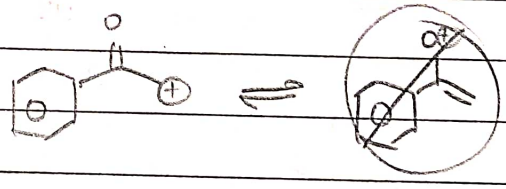
33.  ✗ (✓)

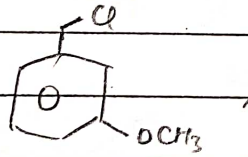
34. 

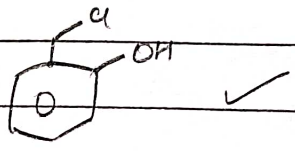
35.  ✗

36. 

37.  (✗) 

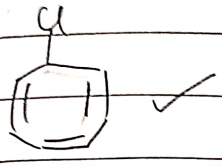
38.  (✗) 

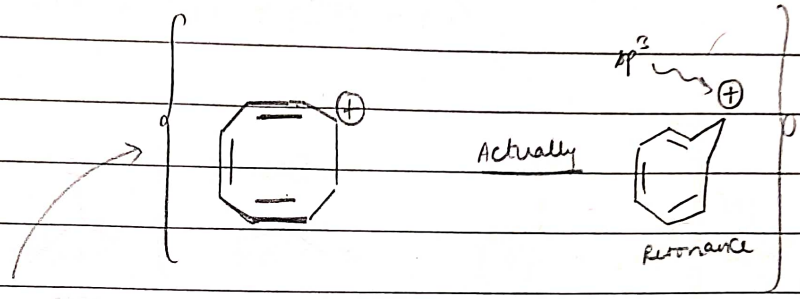
39.  ✗ (✓)

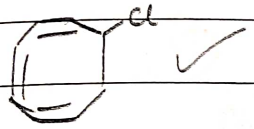
40. 

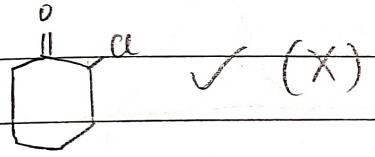
41.  ✓ (X)

42.  ✓ (X)

43.  ✓



★ 44  ✓

45.  ✓ (X)

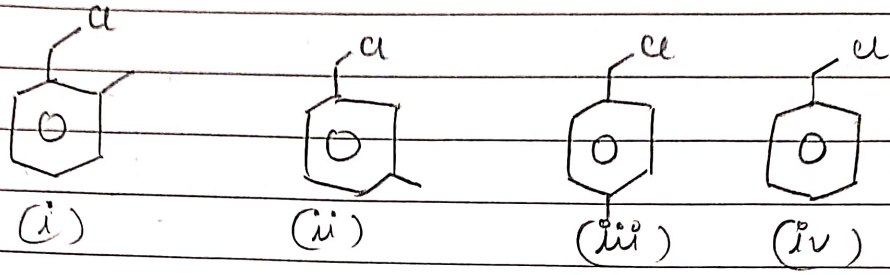
NOTE: Benzyl Chloride gives both S_N1 & S_N2.

Ortho & Para : EDG → S_N1
EWG → S_N2

Meta : Both S_N1 & S_N2

Q. Comparison of Rate of S_N1.

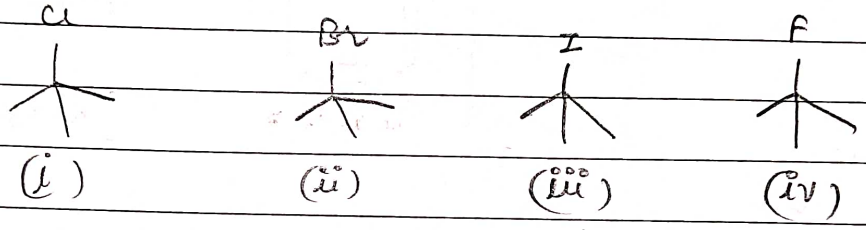
(i)



(i) (ii) (iii) (iv)

(i) > (iii) > (ii) > (iv)

(ii)



(i) (ii) (iii) (iv)

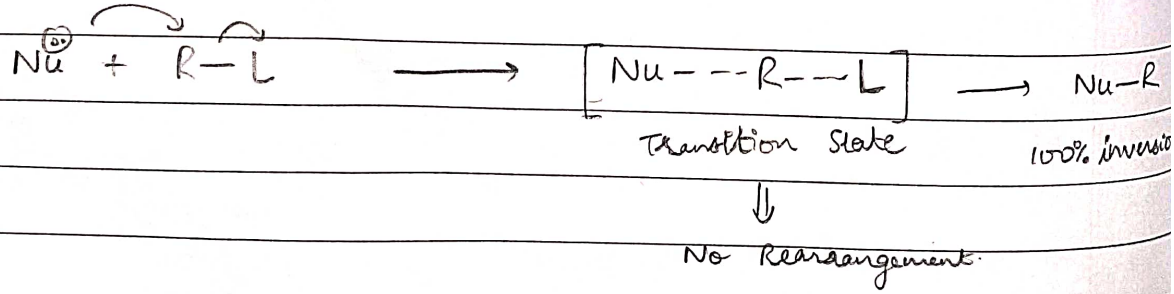
(iii) > (ii) > (i) > (iv)

28/04/2023

S_N2: BIMOLECULAR NU SUB^N

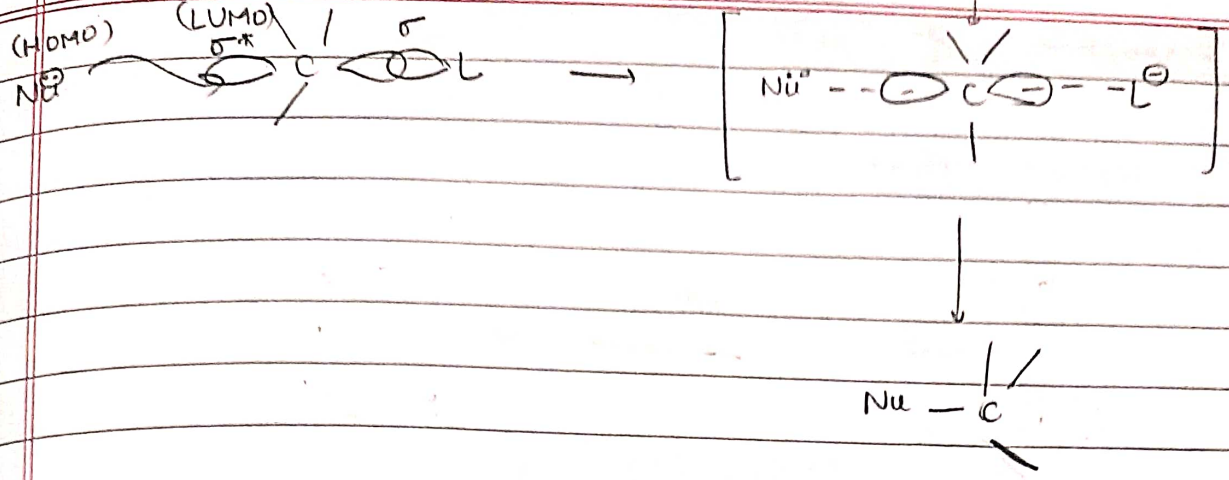
$$R-L \xrightarrow{Nu} R-Nu + L^{\ominus}$$

Mechanism



Bimolecular & unimolecular is due to molecularity, not order.

* Hyb of T.S = sp^2

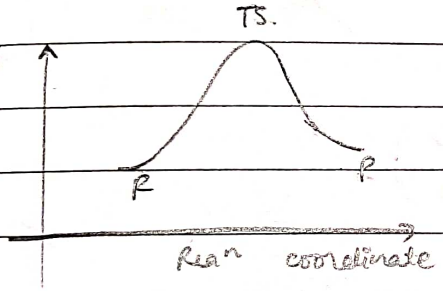


NOTE: (1) RoR $\propto$ [R-L][Nü]

Order = 2

For Nü in excess, order = 1 (since [Nü] ~ const)

(2)



(3) If more than one post. available for back attack, attack will be done from side where steric hinderance is lower.

(3) RoR $\propto \frac{1}{\text{(Steric Hinderance)}}$

$\propto$ Stability of TS

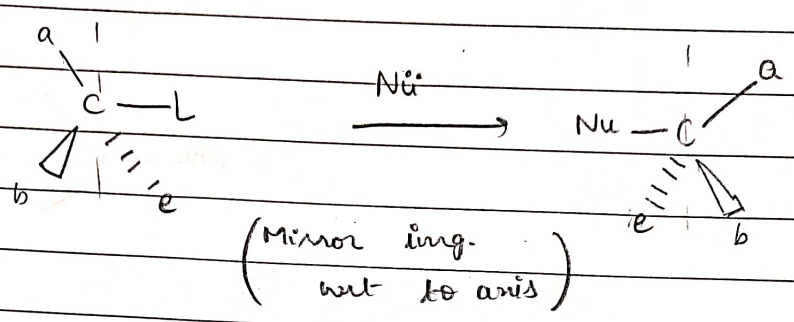
$\propto$ PAS

$\propto$ leaving grp.

$\propto$ Nucleophilicity of Nü

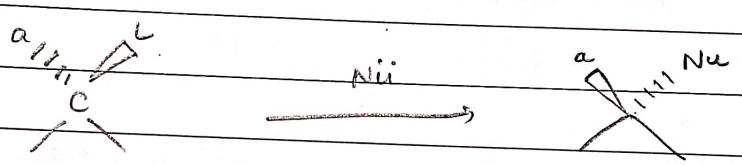
→ Stereochem. of S_N2

① L in plane



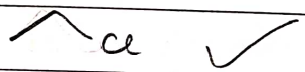
(Mirror img. wrt to axis)

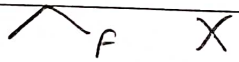
② L above or below plane

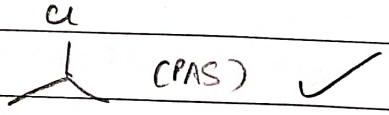


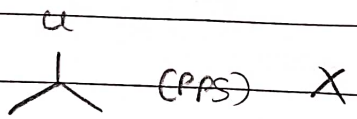
(Interchange wedges above & below plane)

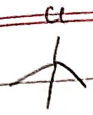
Q Which give S_N2.

1.  ✓

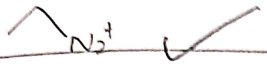
2.  X

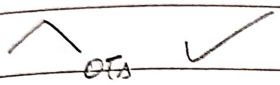
3.  ✓

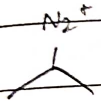
4.  X

5.  ✓ (X)

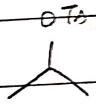
6.  X

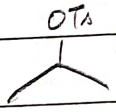
7.  ✓

8.  ✓

9.  (PAS) ✓

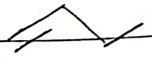
10.  (PAS) ✓

11.  (PPS) X

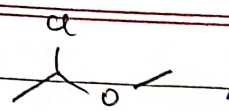
12.  (PPS)

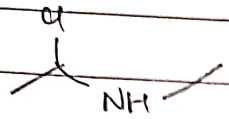
13.  X (✓)

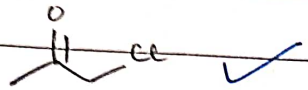
14.  (X)

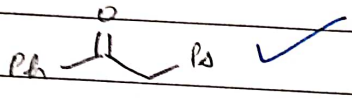
15.  X (✓)

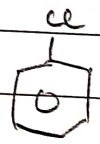
16.  X (✓)

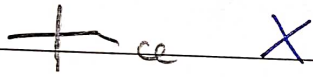
17.  X (✓)

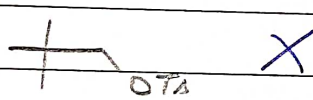
18.  X (✓)

19.  ✓

20.  ✓

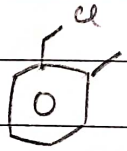
21.  (X)

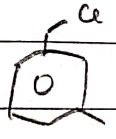
22.  X

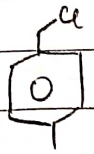
23.  X

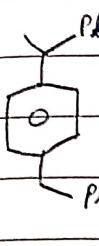
24  X (Steric hinderance)

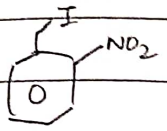
25.  

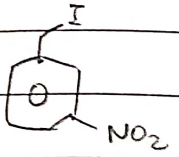
26.  X

27.  ✓

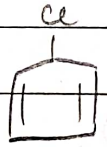
28.  ✗

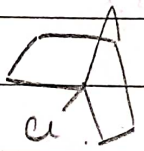
29.  (X) (DMSO) (✓)

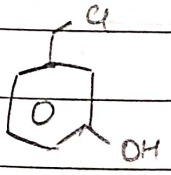
30.  ✓

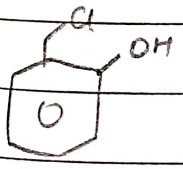
31.  ✓

32.  ✓

33.  ✗

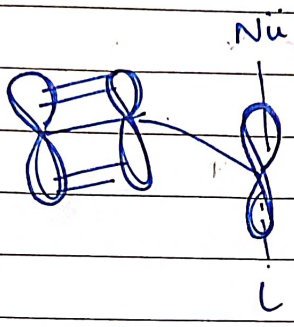
34.  ✗

35.  ✓

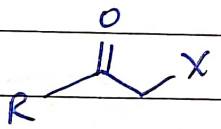
36.  ✗

NOTE: ① Any aliphatic comp. in which resonance stabilised $C^{\oplus}$ is formed gives both S_N1 & S_N2.

Reason: RoR (S_N2) $\propto$ Stability of TS.



Resonance stabilises TS also !

②  has exceptionally high rate of S_N2.

Reason : LUMO

Energy ~~Stability~~ $\pi^* + \sigma^*$ (New orbital formed.) $< \sigma^*$ (of $-X$) $< \pi^*$ (of $\overset{O}{\overset{\|}{C}}$)

So, Nü attacks at new LUMO.

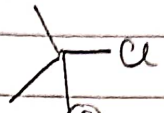
→ Order of Rate

SN1 (Solvation of R–Cl in 50% aq. ethanol

(I)

① (0.07)

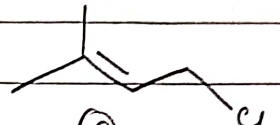
② (0.12)



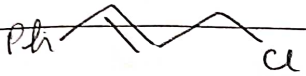
③ (1200)

④ (1)

⑤ (91)



⑥ (130000)

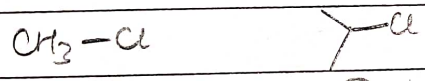


⑦ (1700)

⑥ > ③ > ⑦ > ⑤ > ④ > ② > ①

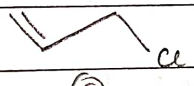
SN2 (R–X + I_2 → R–I)

(II)



① (200)

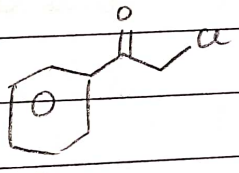
② (0.02)



③ (99)

④ (200)

⑤ (920)



⑥ (100000)

⑥ > ⑤ > ④ > ③ > ② > ①

$R-X \xrightarrow{Nu} R-Nu$

$\xrightarrow[(H^-)]{LiAlH_4} R-H$

$\xrightarrow[(H^-)]{NaBH_4} R-H$

$\xrightarrow[(R^-)]{R_2CuLi} R-R$

$\xrightarrow[(R^-)]{RLi} R-R$

$\xrightarrow[(R^-)]{R-MgX} R-R$

$\xrightarrow[(OH^-)]{aq.\ KOH} R-OH$

$\xrightarrow{KCN} R-CN + R-NC$

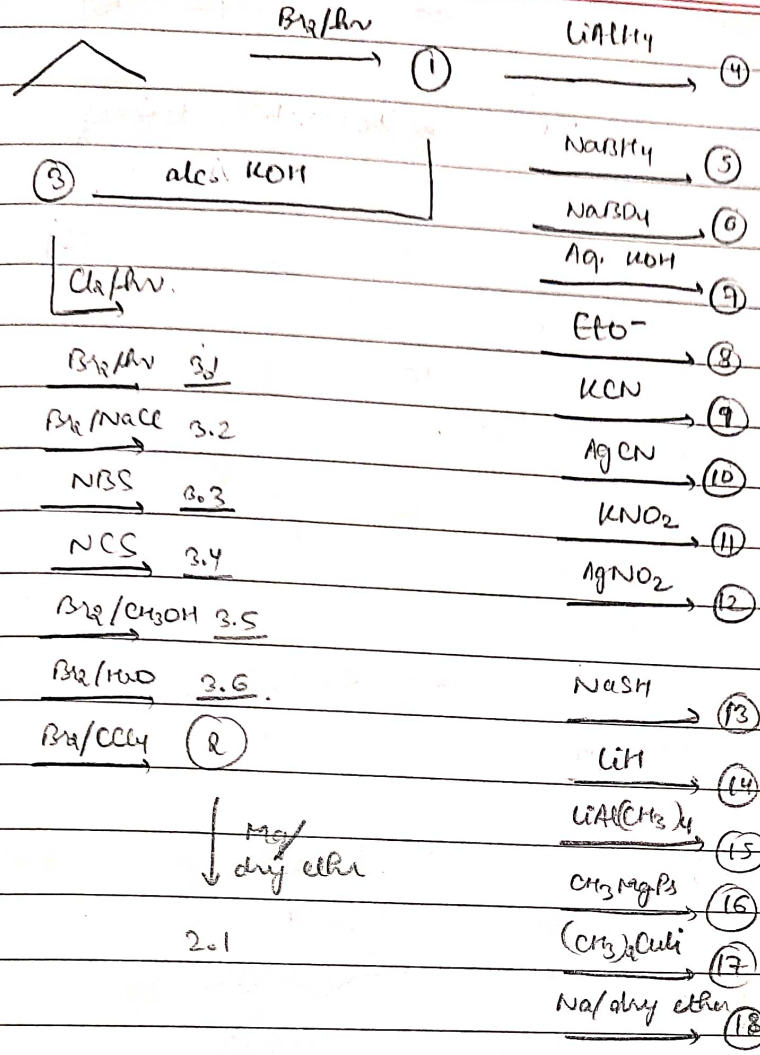
$\xrightarrow{AgCN} R-NC + R-CN$

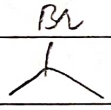
$\xrightarrow{KNO_2} R-ONO + R-NO_2$

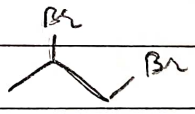
$\xrightarrow{AgNO_2} R-NO_2 + R-ONO$

$\xrightarrow[(low\ T)]{RO^-Na^+} R-OR$

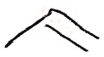
(high T) Elimination



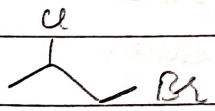
1. 

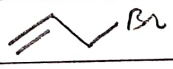
2. 

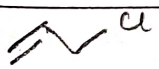
☆ 2.1 

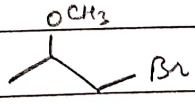
3. 

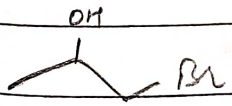
3.1 

3.2 

3.3. 

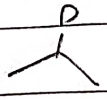
3.4 

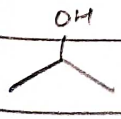
3.5 

3.6 

4. 

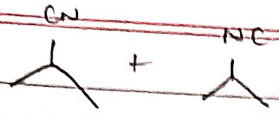
5. 

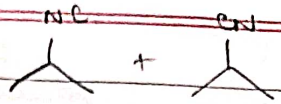
6. 

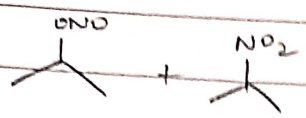
7. 

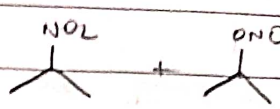
☆ 8. 

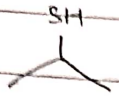
(⊖ ion first acts like a base)

9. 

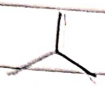
10. 

11. 

12. 

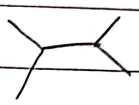
13. 

14. 

15. 

16. 

17. 

18. 

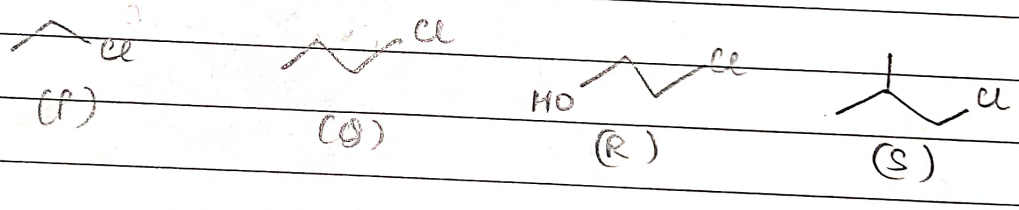
Himanshu Pandey

Alkyl halides (51 – 77)

51. Towards aq. KOH

S_N2:

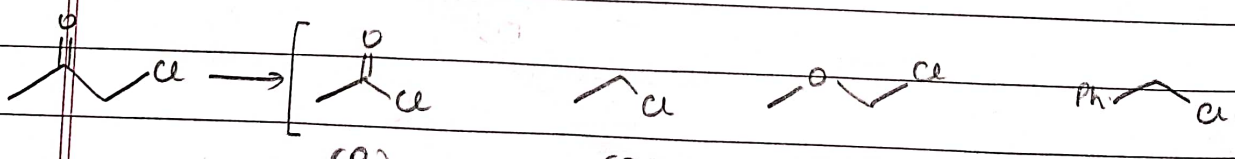
(Primary R–X)



(b) R > P > Q > S

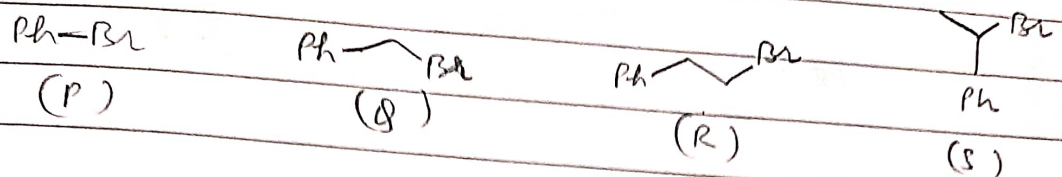
{ –I eff. of OH makes formation of TS easier }

52. S_N2 reaction order



(d) P > R > S > Q

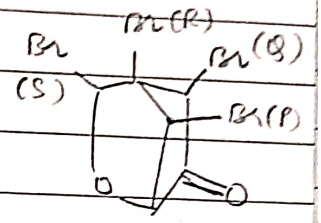
53. S_N1 reactivity order



(P) (Q) (R) (S)

a) S > Q > R > P

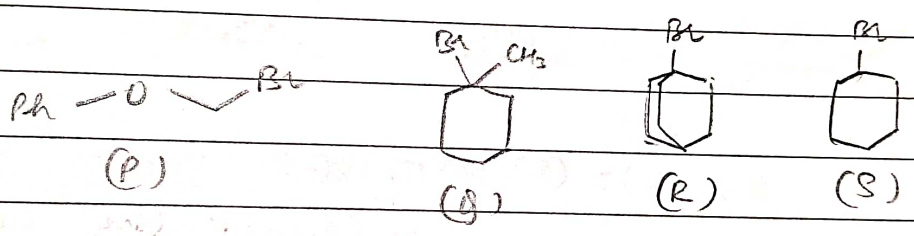
54. Reactivity of Br atoms towards NaSH



(Assuming S_N1)

(c) Q > S > P > R

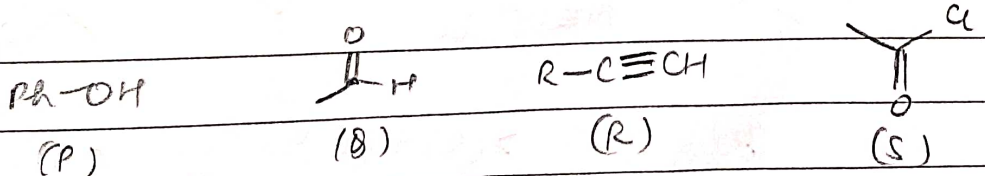
55. Towards aq. ethanol



(P) (Q) (R) (S)

(a) P > Q > S > R

56. Towards Ph–MgBr

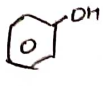


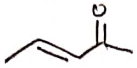
(P) (Q) (R) (S)

Base Nü

(c) P > R > S > Q

Ph^- acts first like Base, then Nü

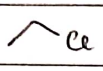
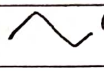
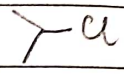
Acidity: (i)  > CH≡CH > 

(ii)  < 

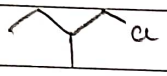
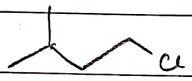
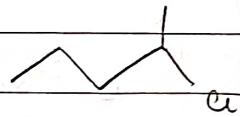
(iii) 

S_N2 reaⁿ order (57–65)

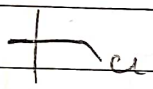
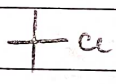
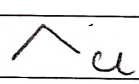
(P) (Q) (R) (S)

57. CH_3-Cl   

(b) (P) > (Q) > (R) > (S)

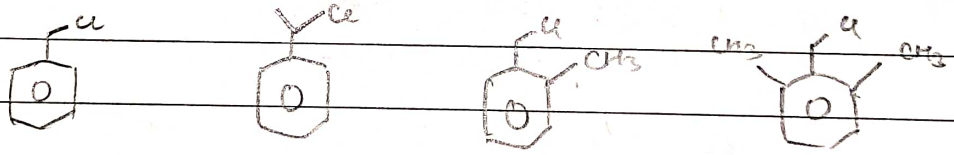
58.    

d) (R) > (Q) > (P) > (S)

59.    

a) (S) > (R) > (P) > (Q)

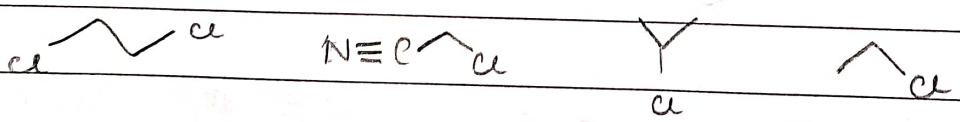
↳ (decreasing rate SN2 due to steric hindrance)

60. 

(b) ✗ (P) > (Q) > (R) > (S)

c) (P) > (R) > (Q) > (S)

R is primary

61. 

(b) (Q) > (P) > (S) > (R)

Stable TS.

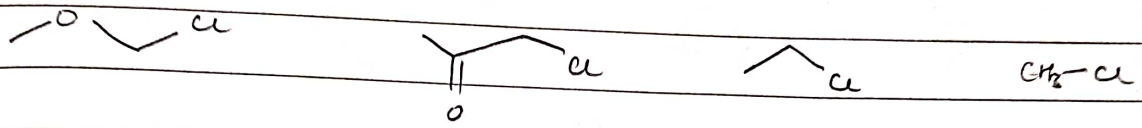
(TS easily formed due to ENG)

62. 

× (c) (Q) > (R) > (P) > (S)

(d) (R) > (Q) > (P) > (S)

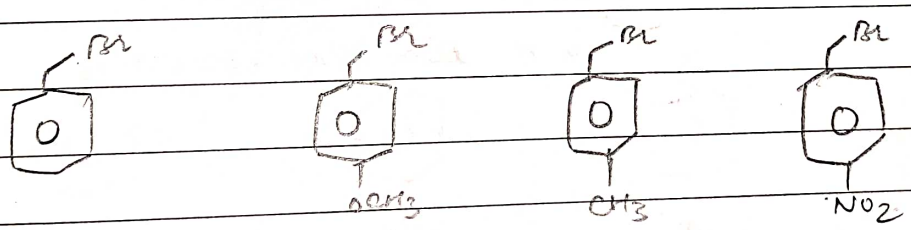
★ (data)

63. 

(a) (Q) > (P) > (S) > (R)

64. 

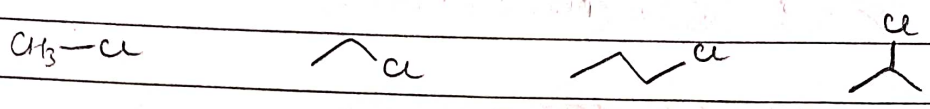
(b) (S) > (P) > (Q) > (R)

65. 

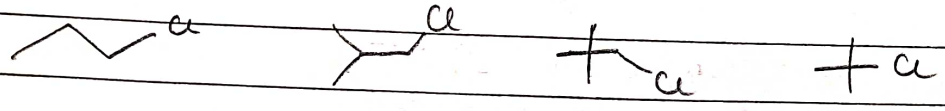
(d) (S) > (P) > (R) > (Q)

SN1 mein order (66-76)

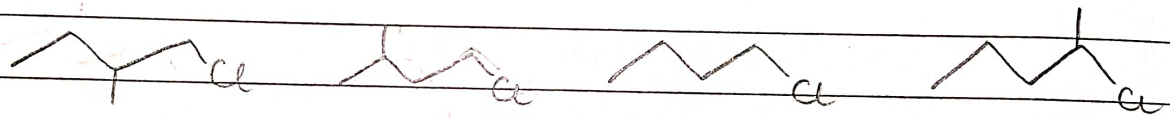
(P) (Q) (R) (S)

66. 

(a) (S) > (R) > (Q) > (P)

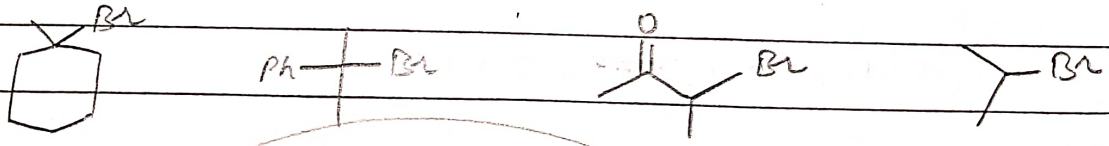
67 

(c) (S) > (R) > (Q) > (P)

68. 

(b) (S) > (P) > (Q) > (R)

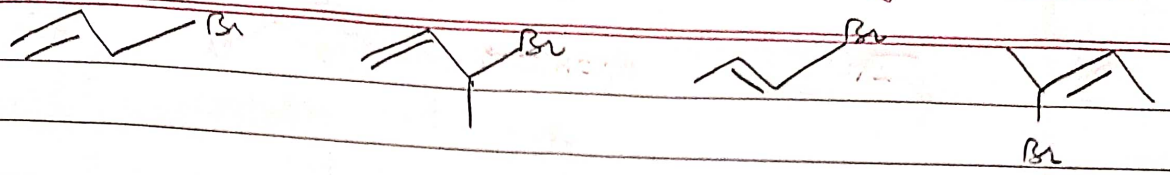
? α-H less than Q & R ?

70. 

(c) ? (Q) > (P) > (S) > (R)

Isme because exceptionally high SN2?

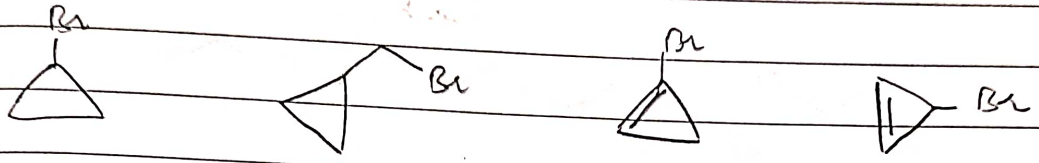
69.



(d) (Q) > (R) > (P) > (S)

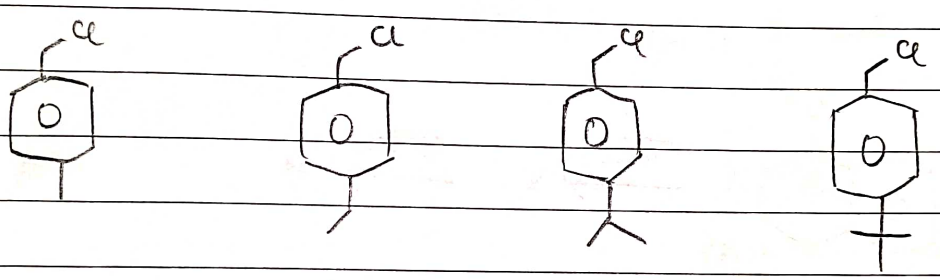
★ (data)

71.



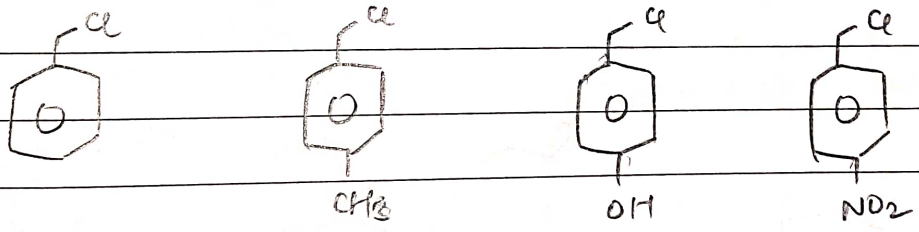
(c) (Q) > (S) > (P) > (R)

72.



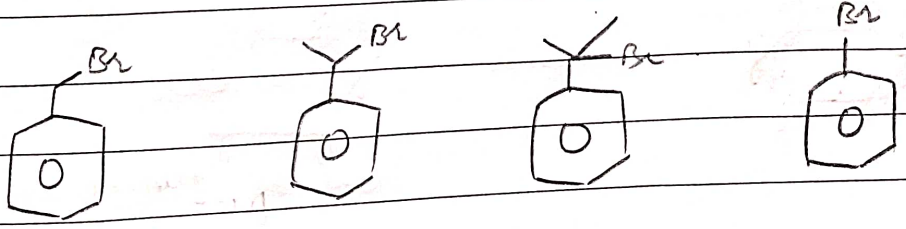
(d) (P) > (Q) > (R) > (S)

73.



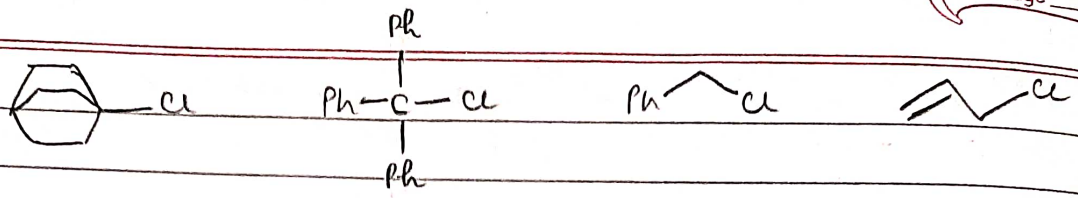
(b) (R) > (Q) > (P) > (S)

74.



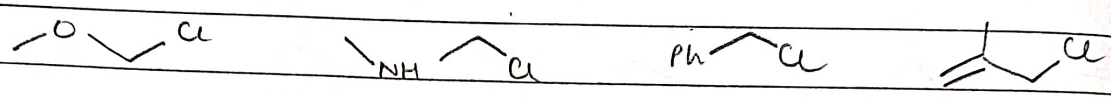
(c) (R) > (Q) > (P) > (S)

75.



(b) (Q) > (R) > (S) > (P)

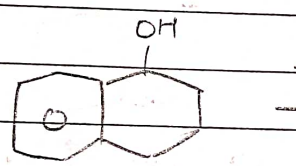
76.



(c) (Q) > (P) > (R) > (S)

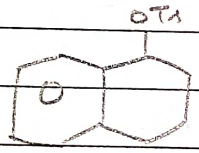
? How to compare?

77.

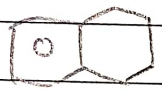


TsCl → X → LiAlH4 → Y. Find Y.

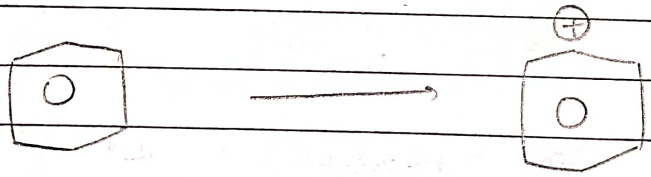
X =

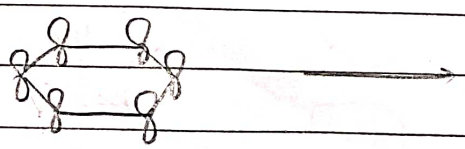


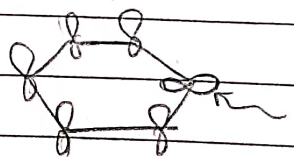
Y =



NOTE:







Loss of aromaticity

03/05/2023

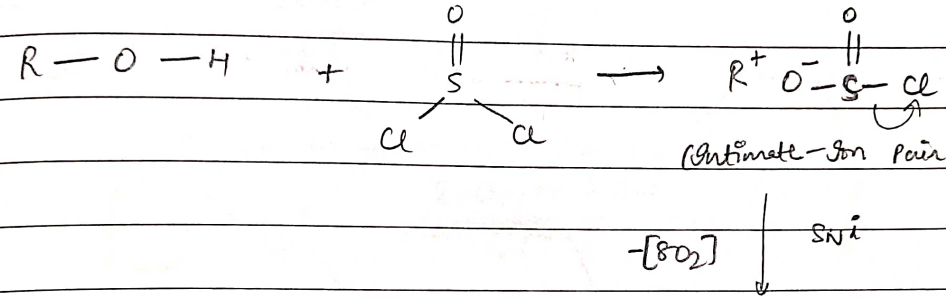
S_Ni: INTERNAL Nü SUBⁿ

$$R-OH \xrightarrow[\text{eg- ether.}]{SOCl_2\ [PAS]} R-Cl + SO_2\uparrow + H_2O\uparrow$$

$SOBr_2$ X

SOI_2 X

Mechanism



(Intimate-Ion Pair)

$-[SO_2]$ | S_Ni

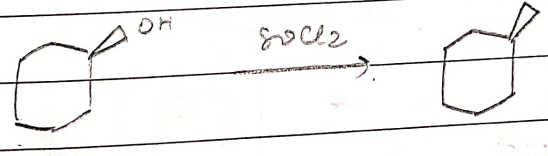
R—Cl

(Retention prod)

eg-(i) $R-OH \xrightarrow{SOCl_2} R-Cl + HBr + SO_2$

(Br leaves first since better leaving grp.)

(ii)



NOTE: (1) Only retention product formed.

(2) $C^{\oplus}$ NOT formed ⇒ no rearrangement

SN1

(3) $R-OH \xrightarrow[\text{[PPS]}]{SOCl_2} R^+ O^- \underset{\underset{O}{\|}}{S} -Cl$

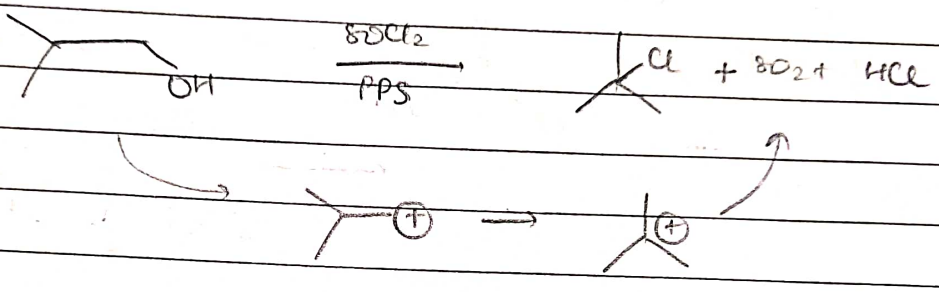
$\downarrow$

$R^+ + SO_2 \uparrow + Cl^-$

$\downarrow$ S_N1

$R-Cl$ (Racemic mix.)

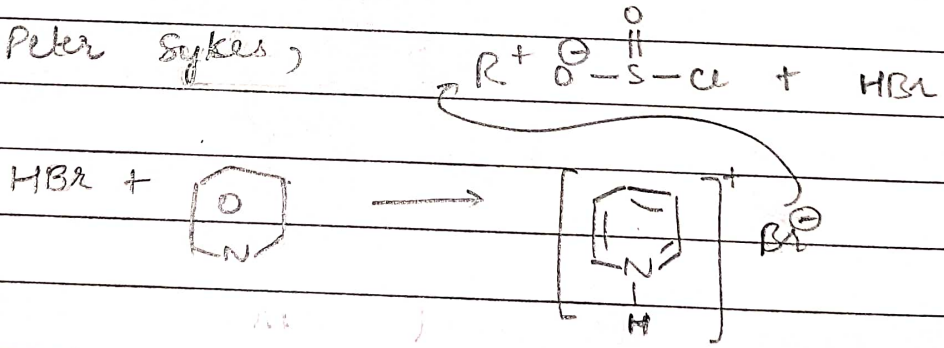
eg -



Basic Medium

(4) $R-OH \xrightarrow{SOCl_2}$ (Pyridine)

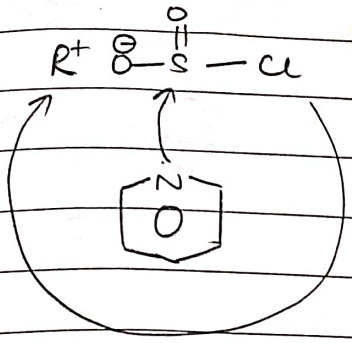
Acc. to Peter Sykes,



$\downarrow$ S_N2

$R-Br$

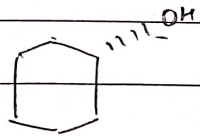
Acc. to Jerry March,



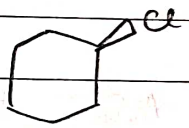
S_N2 ⟶ R–Cl

* Yield of inversion product is more.

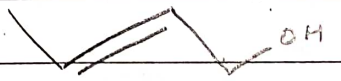
eg



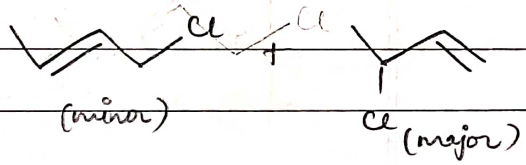
$SOCl_2$ / Weak Base ⟶



*Q.

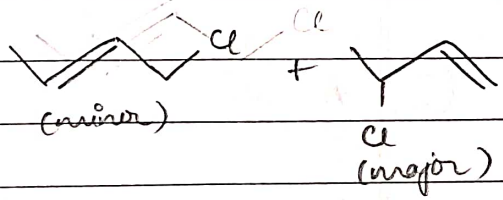


① $SOCl_2$ ⟶

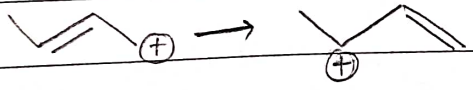


(SNi')

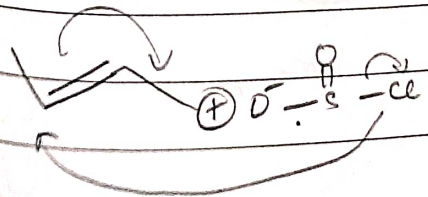
② $SOClBr$ ⟶



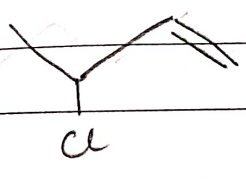
③ HI/Δ ⟶



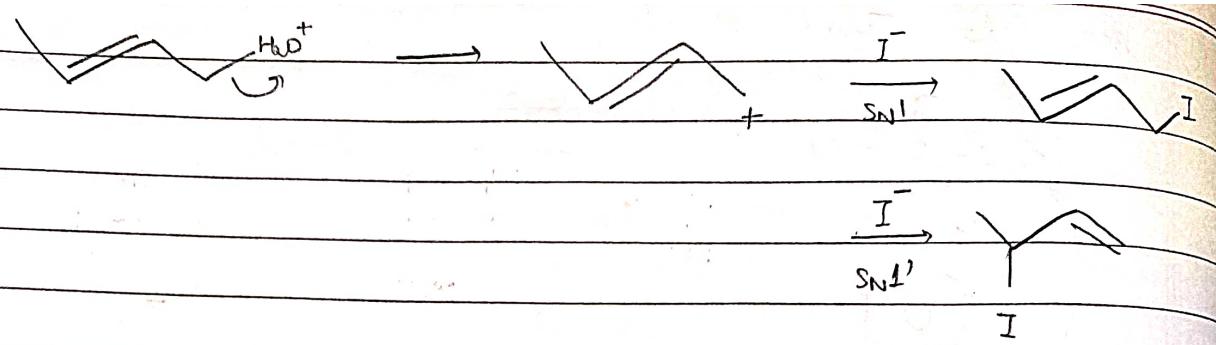
①



S_Ni' ⟶

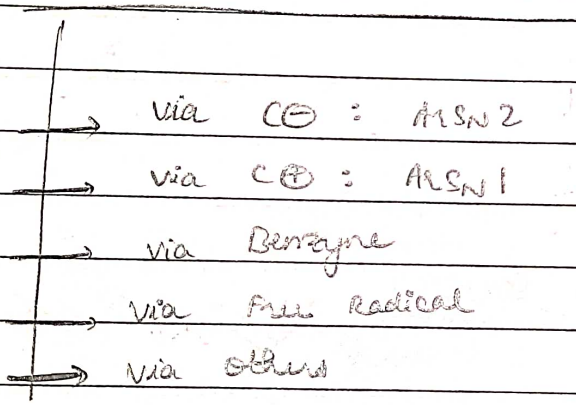


(3)



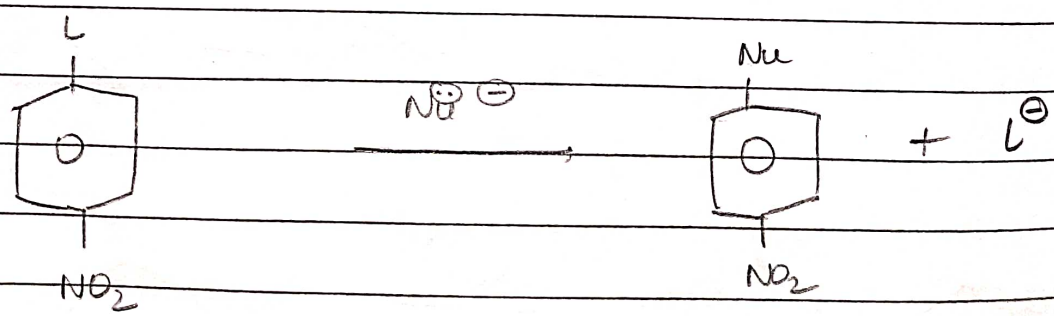
NOTE: Whenever allyl grp, $S_N1 \rightarrow S_N1'$
$S_N2 \rightarrow S_N2'$
$S_Ni \rightarrow S_Ni'$

04/05/2023 Ar_eS_N: AROMATIC Nü SUB^{n}

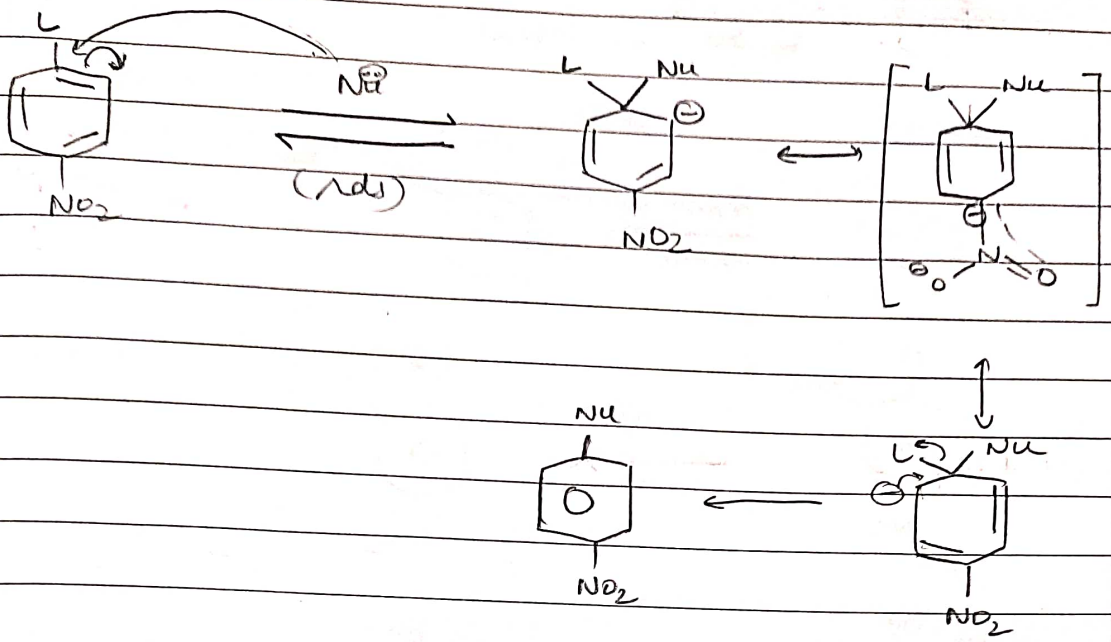


(I) ArSN2

Condⁿ: ENG(-M) should be present at -ortho or para post. wrt. L.G.

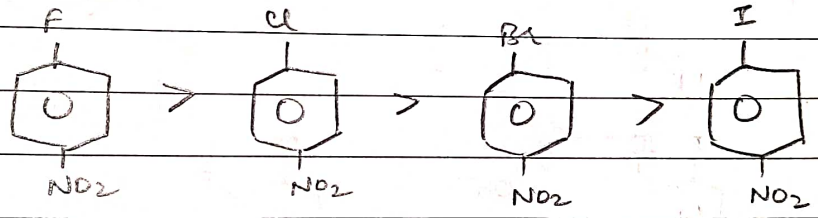


Mechanism

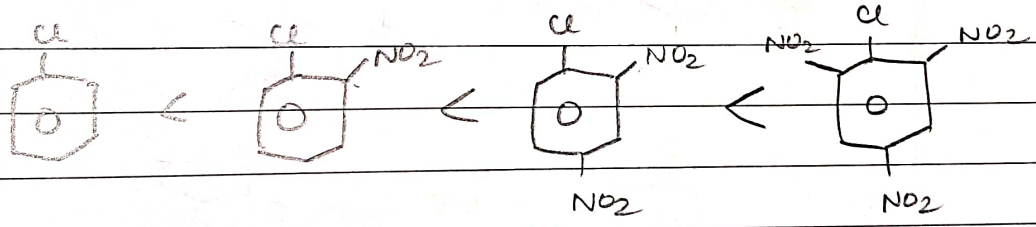


NOTE: (1) **ROR ∝ Stability of C⊖**

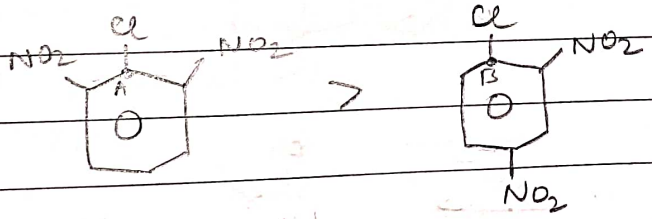
eg- (i)



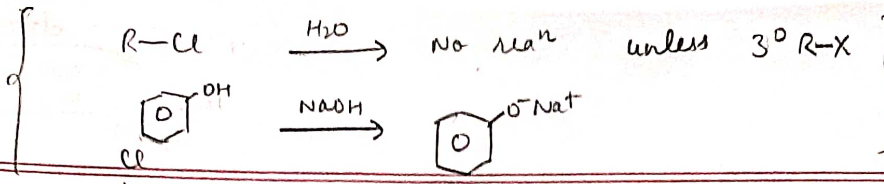
(ii)



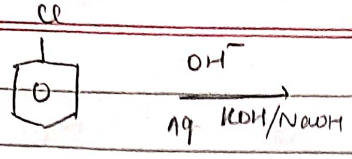
☆(iii)

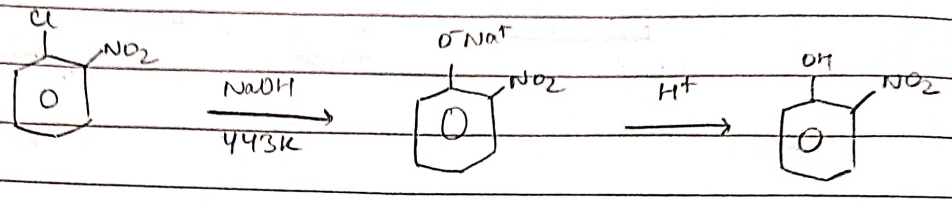


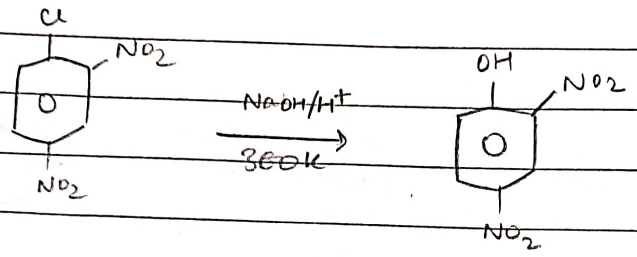
(Reason: A has less e⁻ density than B)

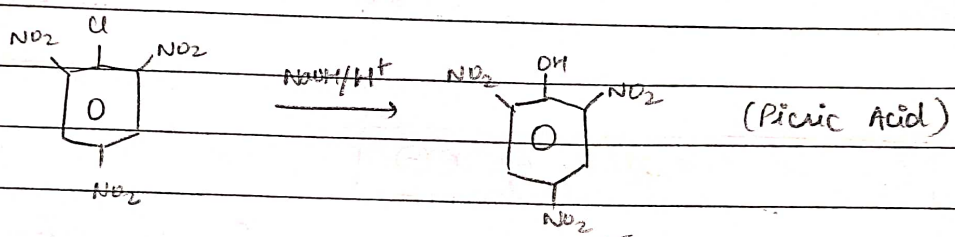

R–Cl
H2O
No rxn
unless 3° R–X
NaOH
O⁻Na⁺

(2)

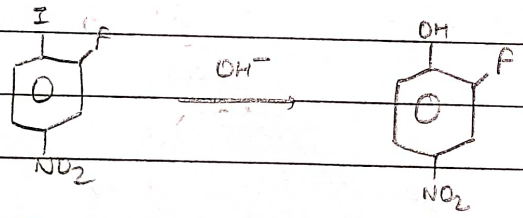

OH⁻
19 KOH/NaOH
No rxn


NaOH
443K
H+

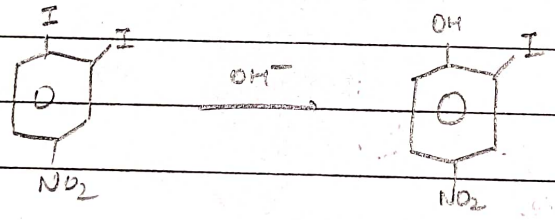

NaOH/H+
360K


NaOH/H+
(Picric Acid)

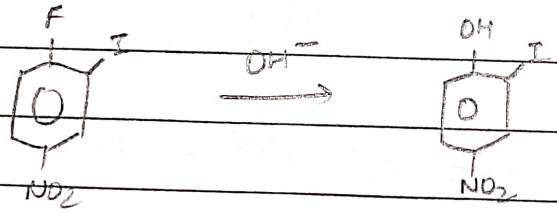
Q. (i)


OH⁻

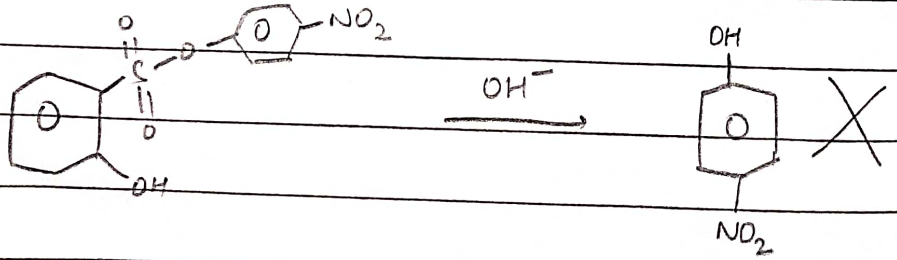
(ii)


OH⁻

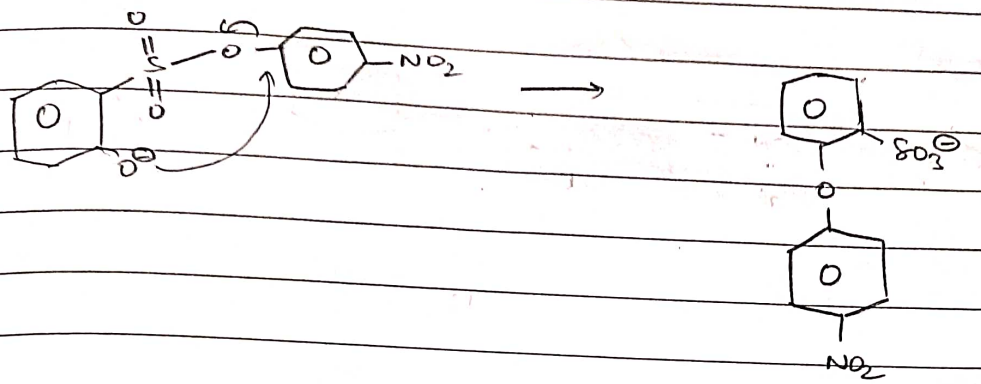
(iii)


OH⁻

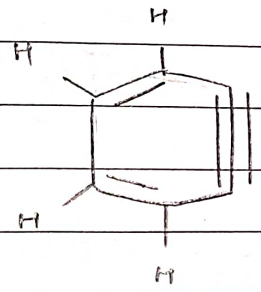
(iv)

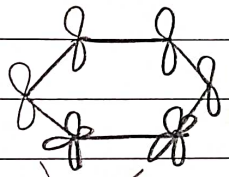

OH⁻

☆ OH^- first behaves like a base, so it snatches acidic-H first.



(II) Via Benzyne

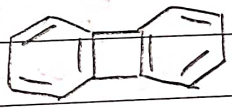




(involved in hybⁿ)

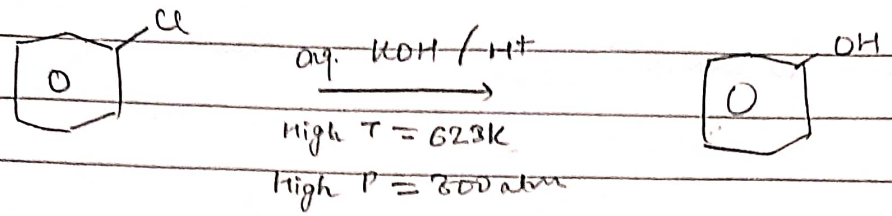
Bonds – $\sigma = 11$

$\pi = 3$

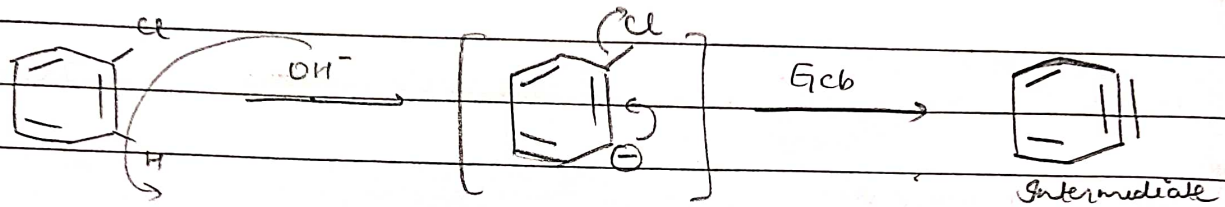


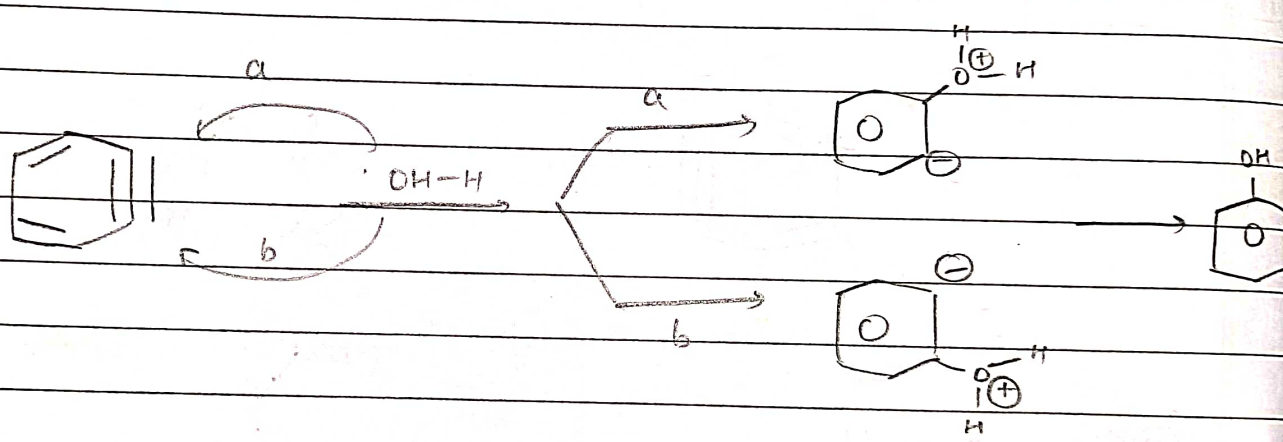
* Always give
* Aromatic yet Unstable

eg Dow's Process



Mechanism





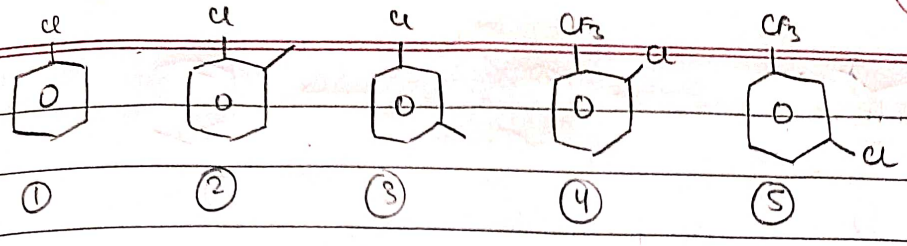
NOTE: (1) | RoR ∝ Stability of $C^{\ominus}$ |

(only I eff considered)

since ⊖ not delocalised

(2) Followed when EDG at ortho & para posts wrt. L.G.

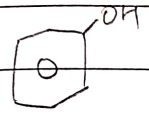
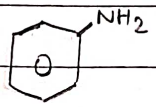
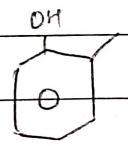
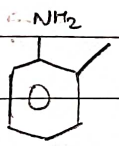
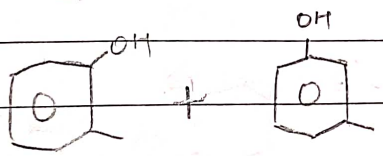
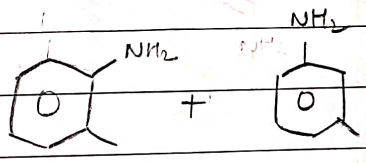
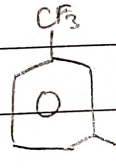
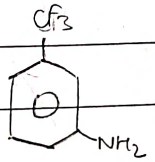
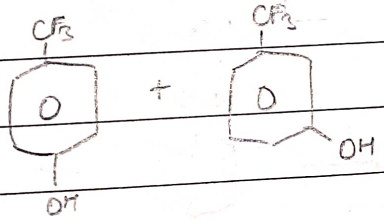
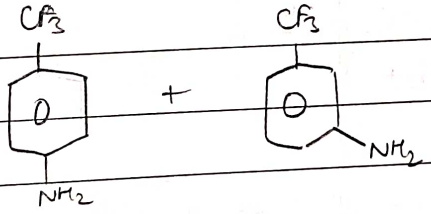
Q.



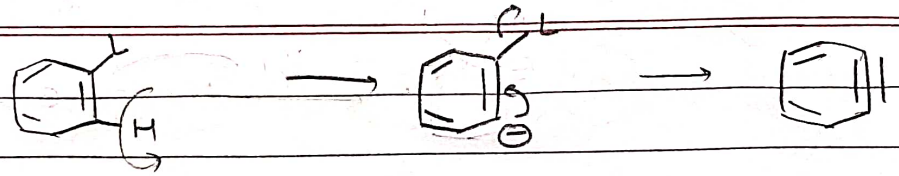
① ② ③ ④ ⑤

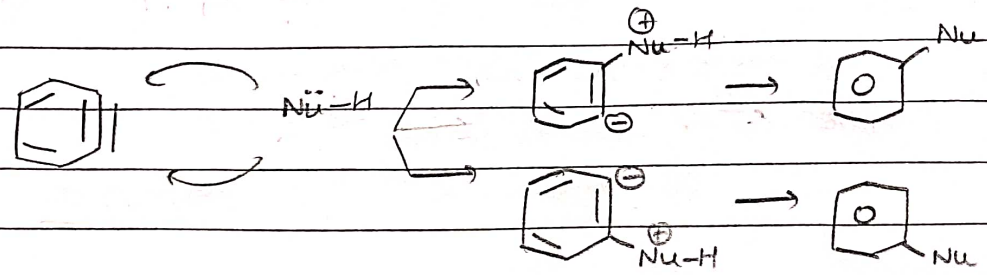
with aq. KOH (High P, T) & $NaNH_2/NH_3$.

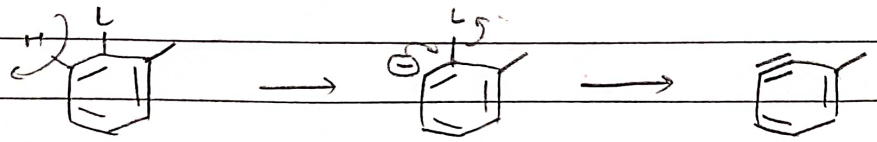
A.

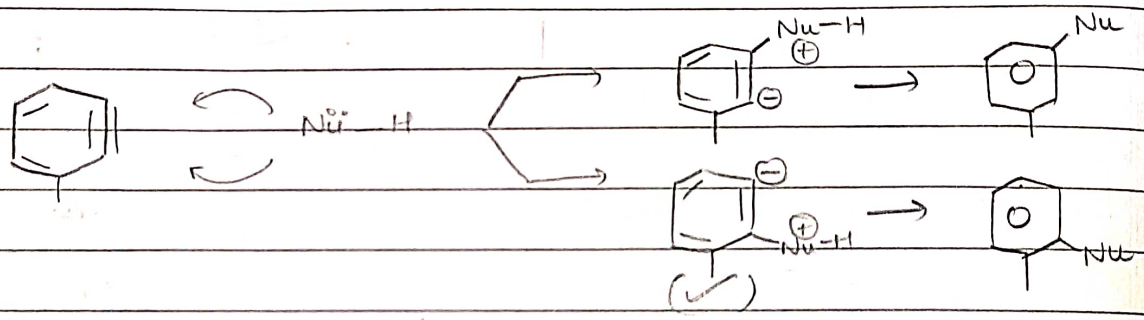
	aq. KOH (High P, T)	$NaNH_2/NH_3$
①		
②		
③		
④		
⑤		

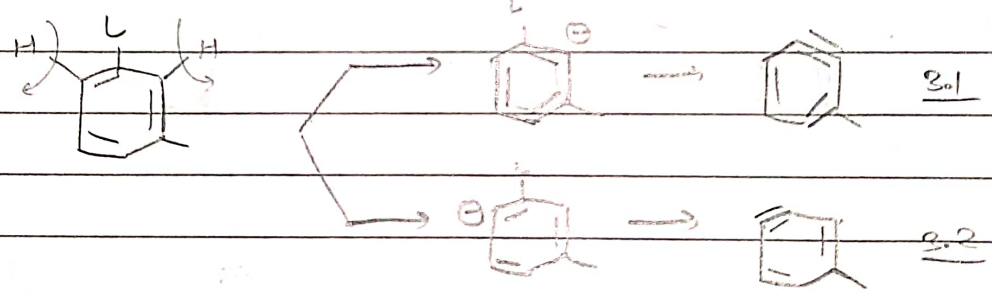
A.

① 



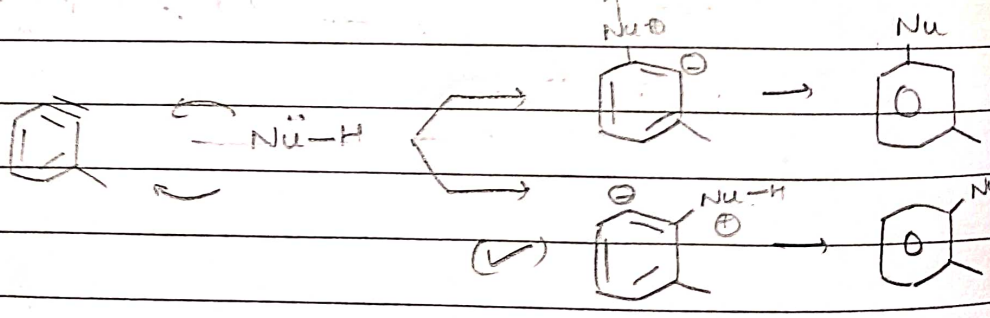
② 

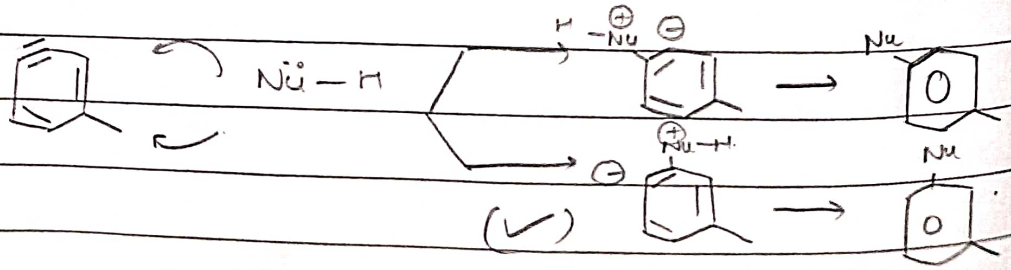


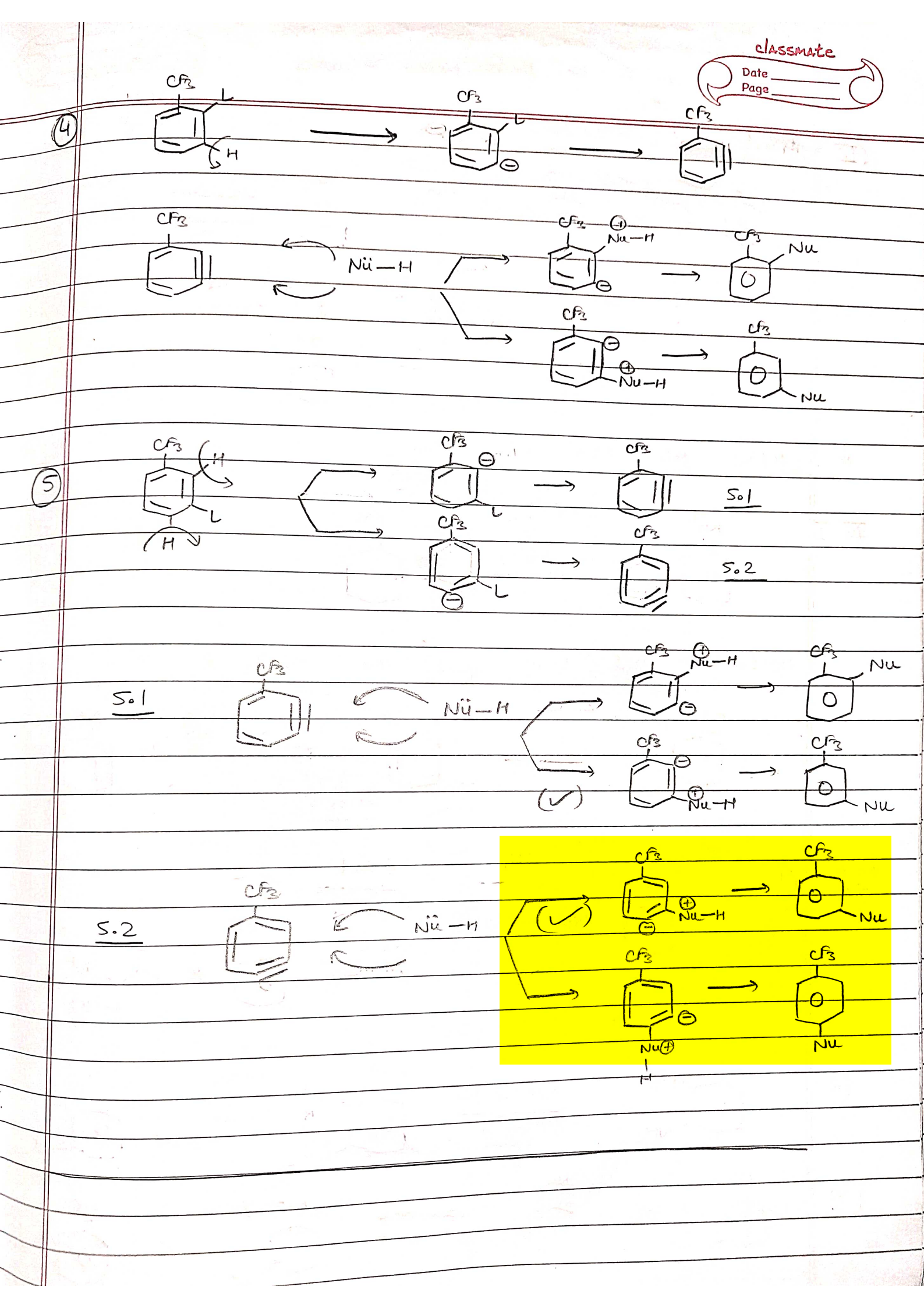
③ 

3.1

3.2

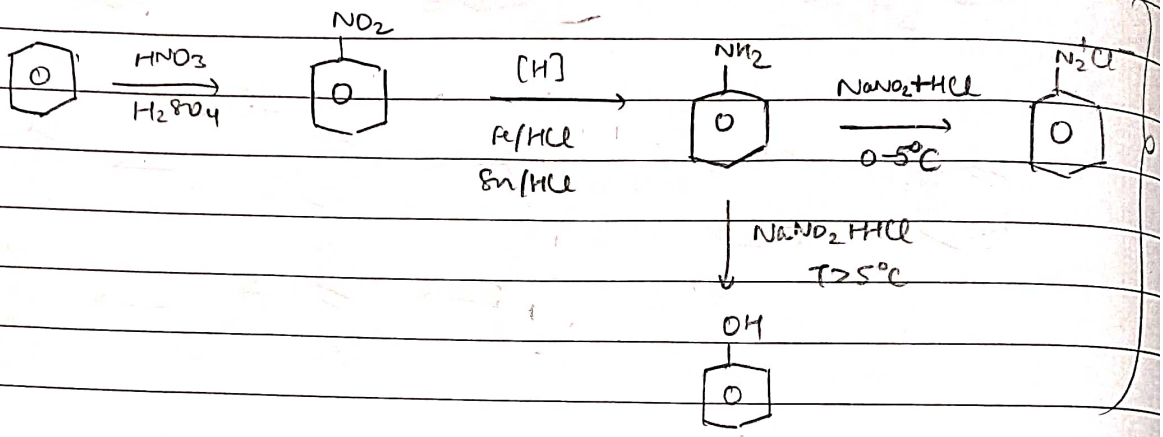





classmate
Date
Page
(4)
CF3
L
H
Nü—H
Nu—H
Nu
(5)
5.1
5.2
(✓)

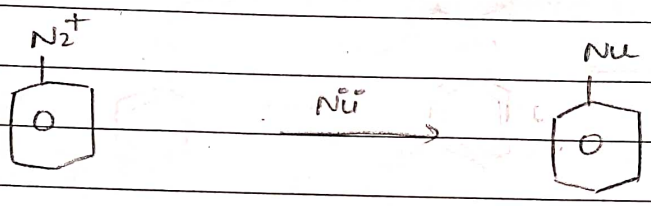
HNO_2 wherever used as reactant generally gives, disproportionation rxn to form HNO_3 & NO.
So to use it, we freshly prepare it, using $NaNO_2$ & HCl

(III) $Ar S_N1$

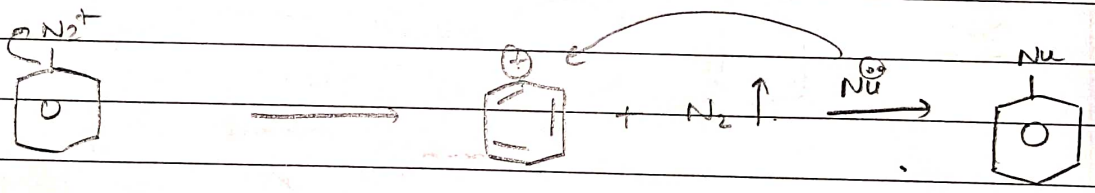


* Fe/HCl better than Sn/HCl

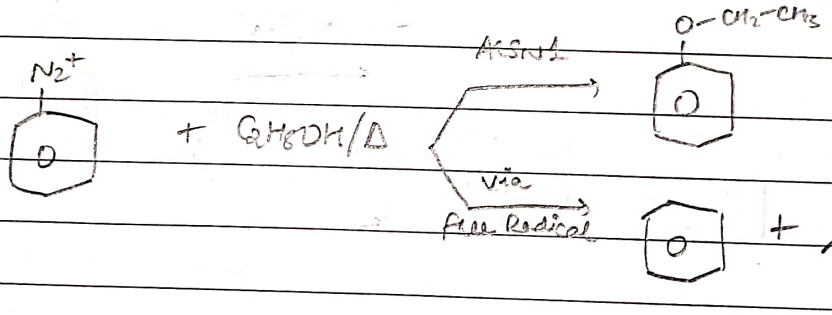
III.I



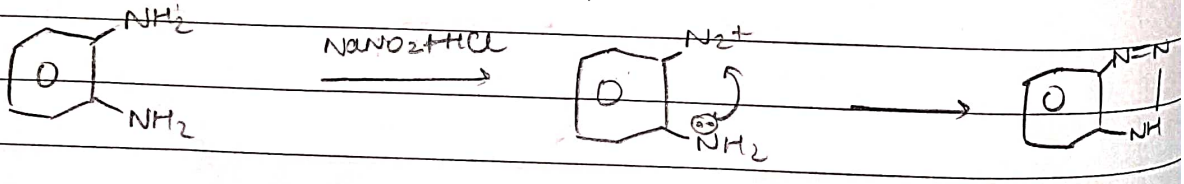
Mechanism



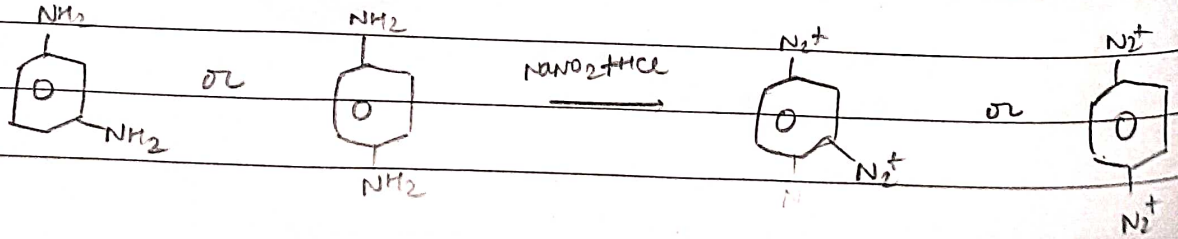
NOTE: (1)



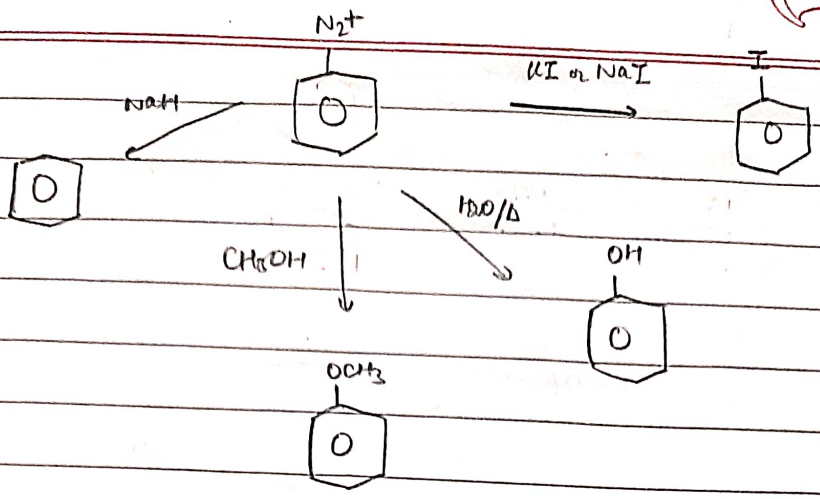
(2)



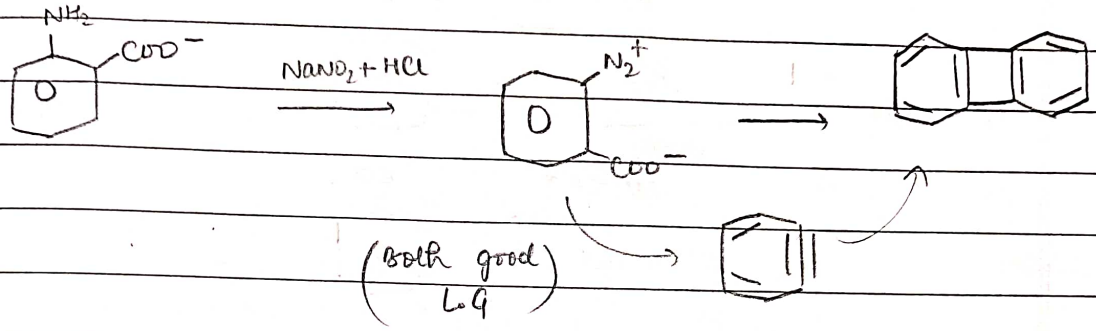
(3)



eg.

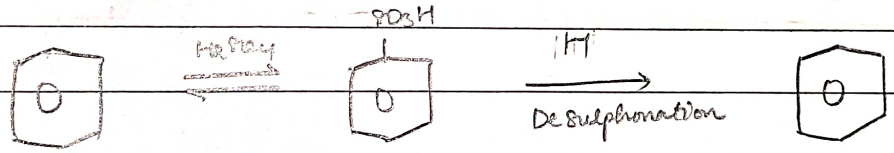


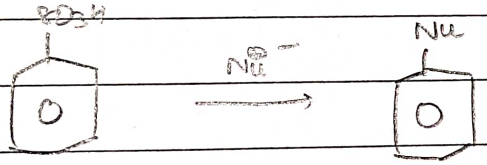
★ Q.



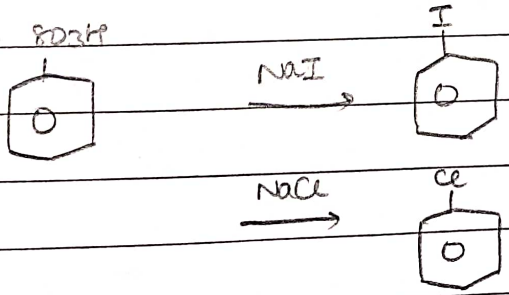
NOTE: COO^- & SO_3H are very good L.G.

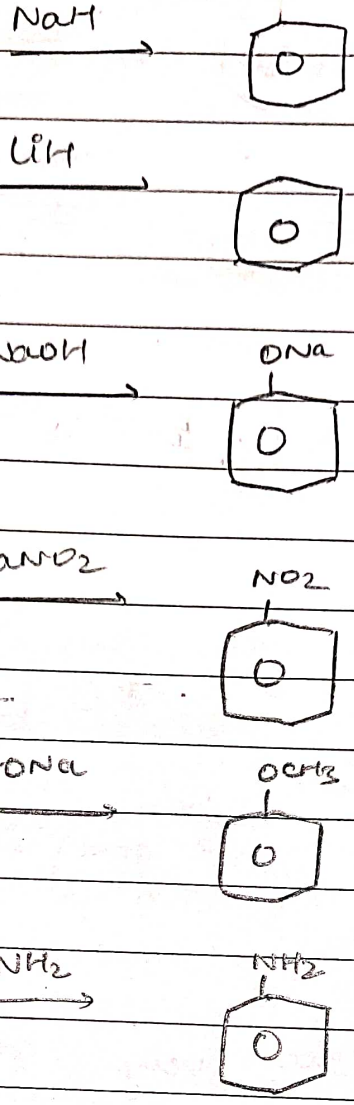
III. II



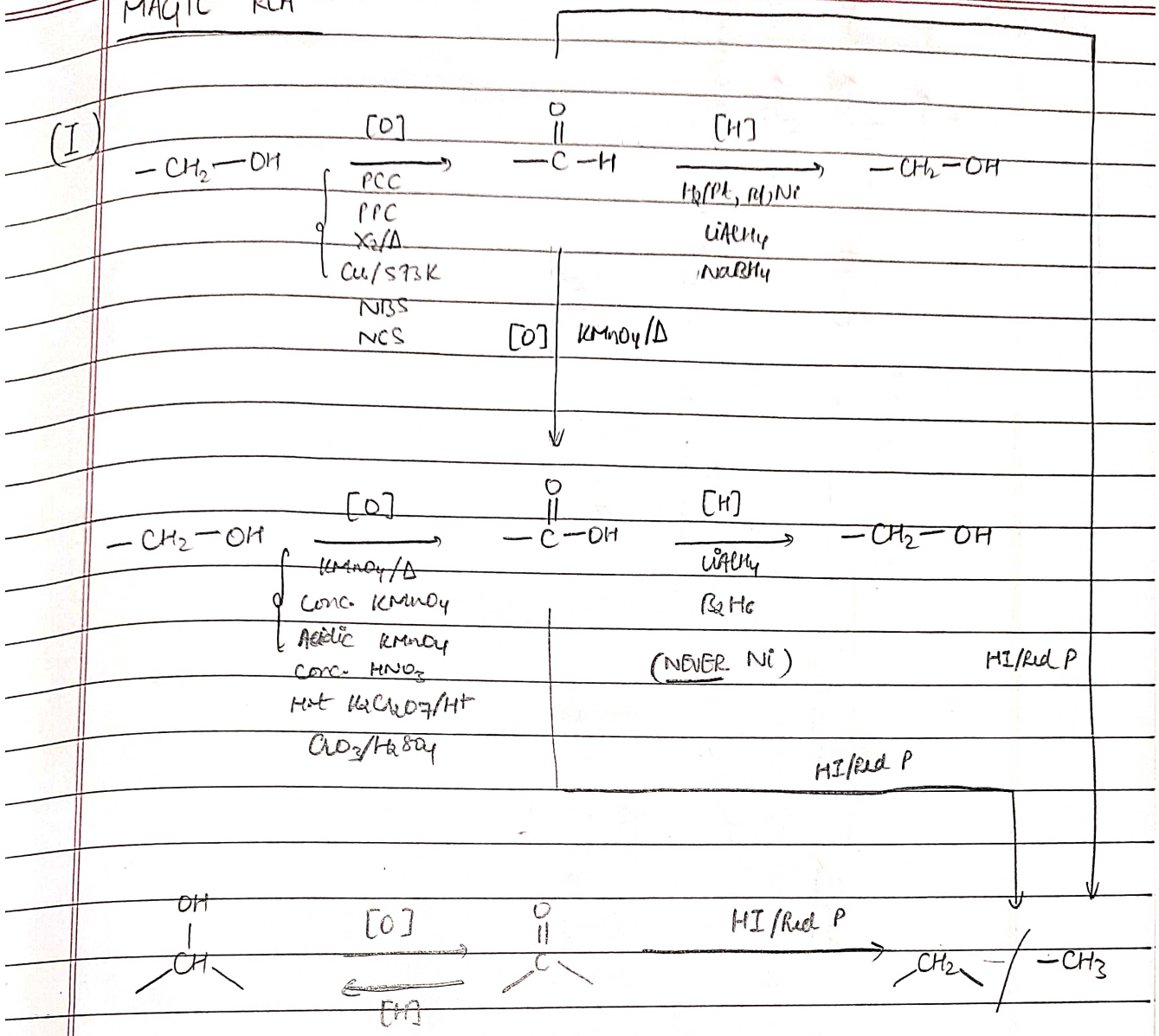


eg




NaH
LiH
NaOH
ONa
NaNO2
NO2
CH3ONa
OCH3
NaNH2
NH2

MAGIC REACTION



(I) & (II) valid for both aliphatic & aromatic comps.

(III) Aliphatic Amines (1°)

$R-NH_2 \xrightarrow{HNO_2} R-OH$

$R-OH \xrightarrow{HI/Red\ P} R-H$

$PCl_5/PCl_3/SOCl_2 \rightarrow R-Cl$

$P+Br_2/PBr_3 \rightarrow R-Br$

$P+I_2/PI_3 \rightarrow R-I$

$H^+/\Delta \rightarrow$ Alkene

$R-OH \xleftarrow{aq.\ KOH}$

Alkene $\xleftarrow{alc.\ KOH}$

$R-CN \xleftarrow{KCN}$

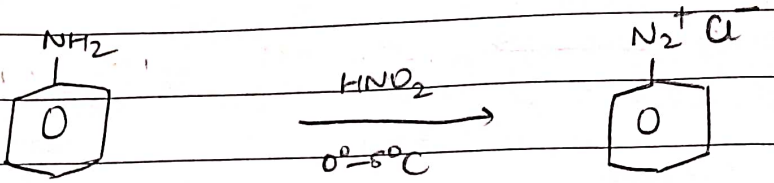
$R-NC \xleftarrow{AgCN}$

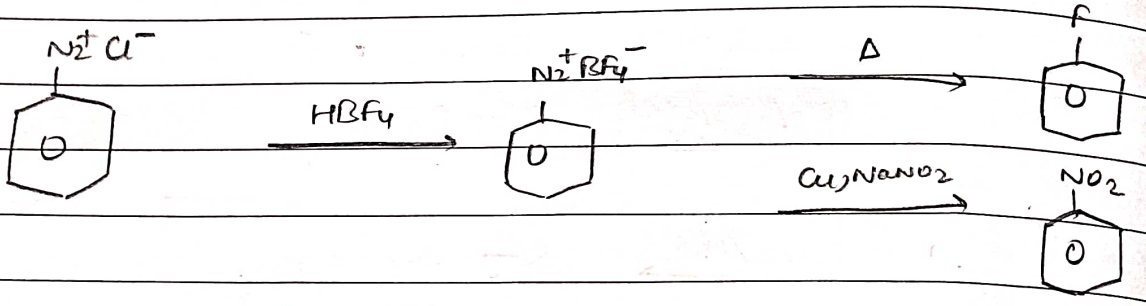
$R-ONO \xleftarrow{KNO_2}$

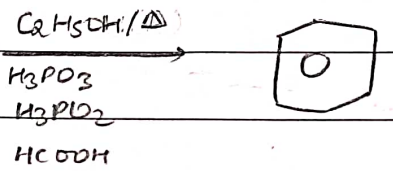
$R-NO_2 \xleftarrow{AgNO_2}$

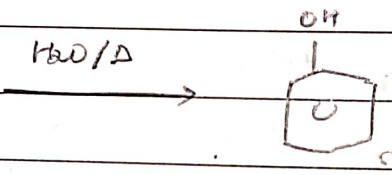
$R-H \xleftarrow{HI/Red\ P}$

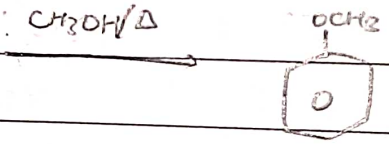
(IV) Aromatic Amines

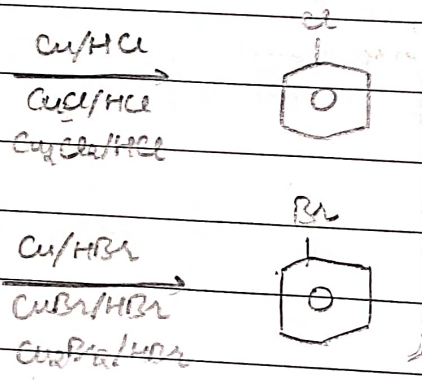


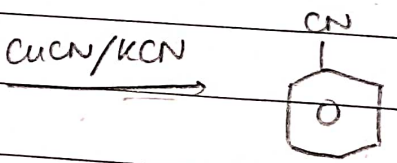












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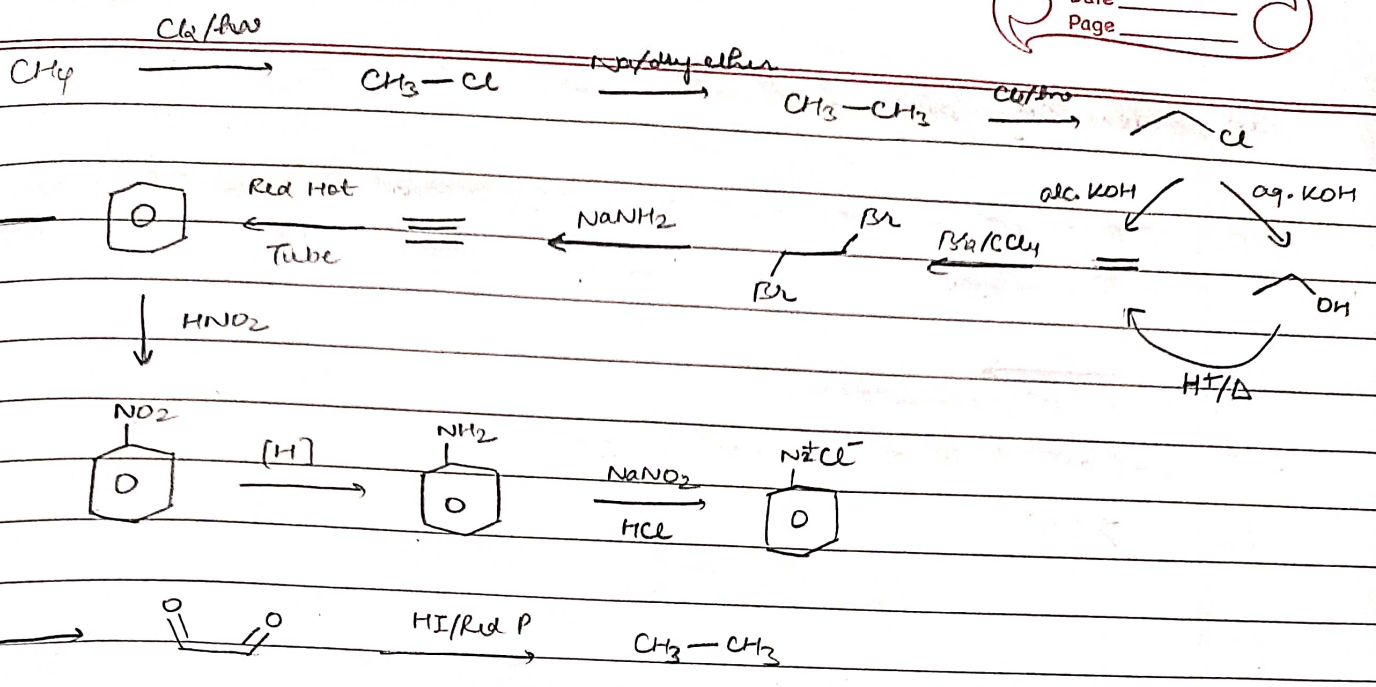
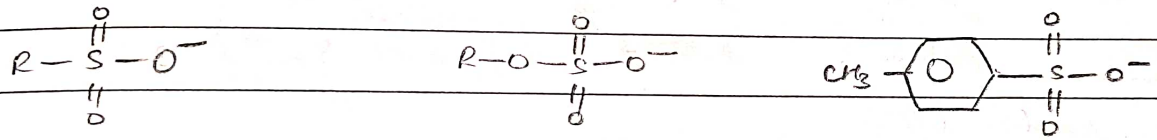


09/05/2023

→ LEAVING GROUPS (for aliphatic)

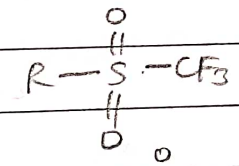


Alkane sulphate ion

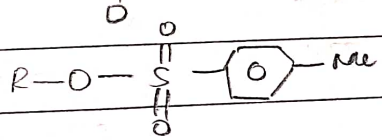
Alkyl sulphate

$CF_3-SO_3^-$ → very good L.G. (Triflate ion)

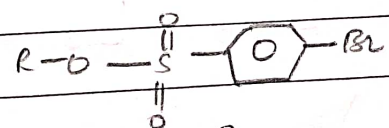
Triflate (OTf)



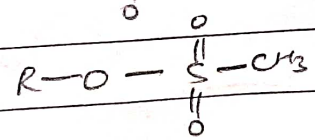
Tosifate (OTs)



Brosiflate (OBs)



Alkyl Mesylate (OMs)



→ Order of L.Gs (Factual)

① $OTf > OTs > OMs > I > Br > Cl > H_2O^+ > F > OAc > \overset{\oplus}{N}R_3 > OR \simeq OH > NR_2$

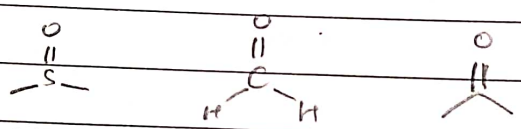
② $F^- > OH^- > NH_2^- > CH_3^-$

③ $R-COO^- > Ph-O^- > OH^- > OR^-$

④ $SH^- > OH^-$

→ Polar aprotic solvents

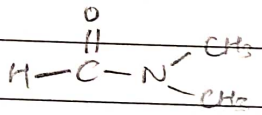
(μ ≠ 0 & No acidic H)



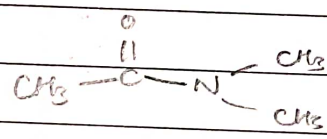
DMSO (Dimethyl sulphur oxide)

Methanal

Acetone * (sometimes PAS in some books)



DMF (Dimethyl formamide)

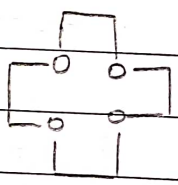


DMA (Dimethyl Acetamide)

Oxyrane

THF

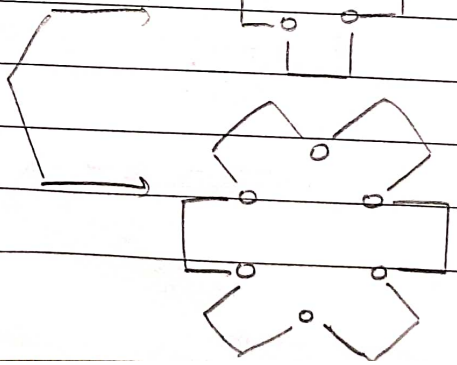
ethers (R–O–R)



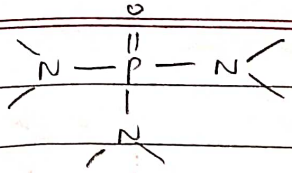
(#C) (#O)

12-Crown-4-ether

Crown ethers



18-Crown-6-ether



HMPA Hexa-methyl phosphoramide

→ Hard & Soft Nü

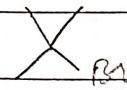
R–MgX, R–Li } R^- → Hard Nü, difficult to produce, give (1,2) addⁿ

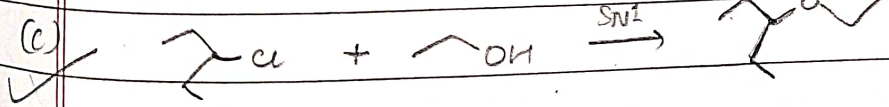
R_2CuLi, $RMgX + Cu$, $PhMgBr$ } R^- → Soft Nü, given (1,4) addⁿ

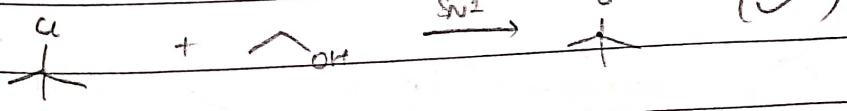
Q. Which gives S_N1 faster.

(a) $(CH_3)_3C-Cl + H_2O \xrightarrow{S_N1}$ 

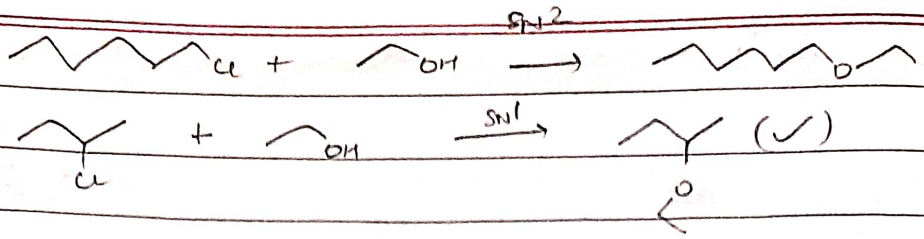
$(CH_3)_3C-I + H_2O \xrightarrow{S_N1}$  (✓)

(b)  $+ CH_3OH \xrightarrow{S_N1}$  (✓)

(c) 



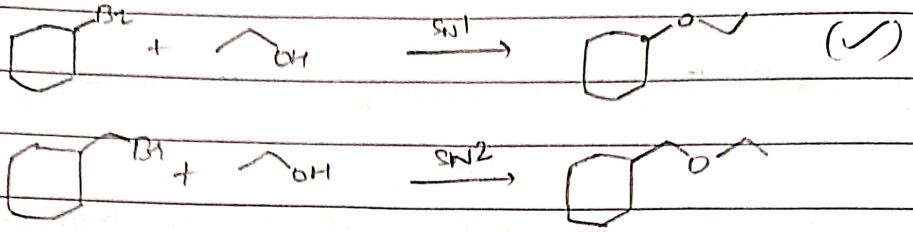
(d) ✓


SN2
Cl
OH
O

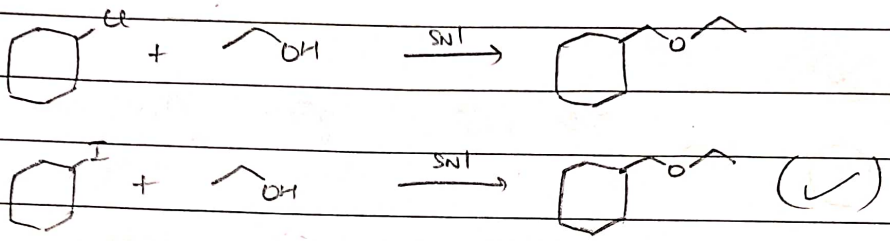
SN1
Cl
OH
O
(✓)


H
O

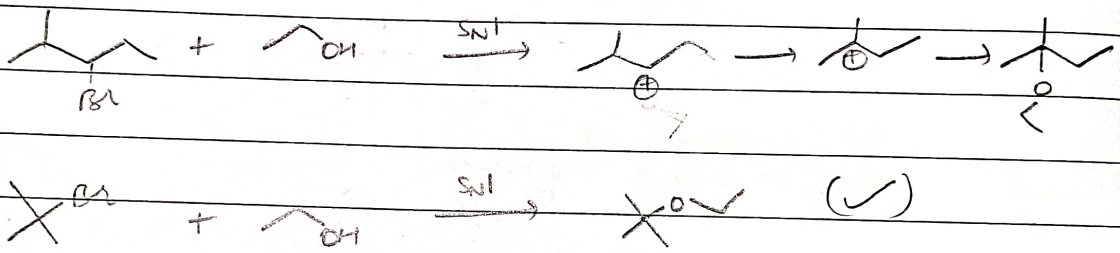
(e) ✓


Br
OH
SN1
O
(✓)
SN2

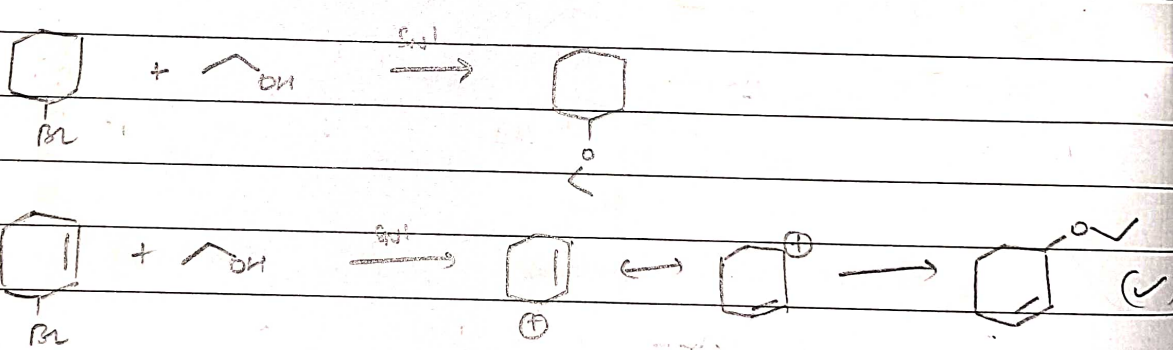
(f) ✓


Cl
OH
SN1
O
I
(✓)

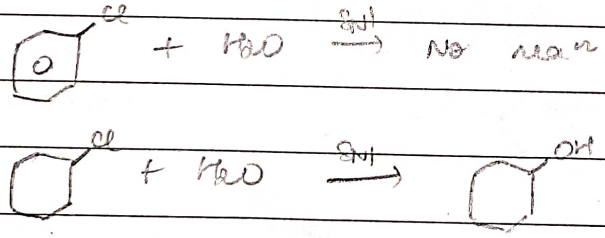
(g) ✓


Br
OH
SN1
O
(✓)

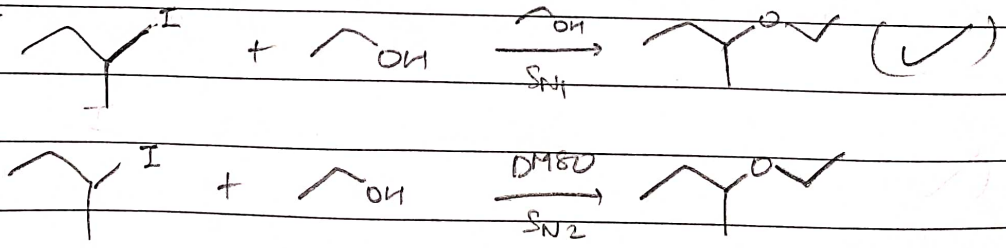
(h) ✓


Br
OH
SN1
O
(✓)

(i) ✓

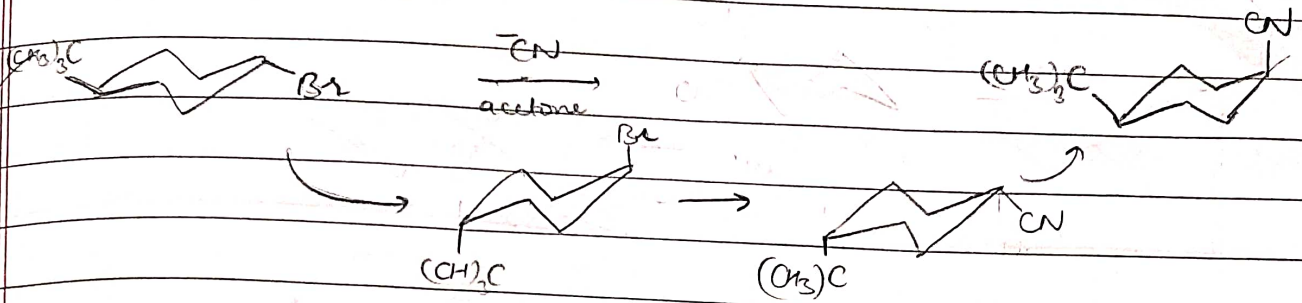

Cl
H2O
SN1
No reaction
OH
(✓)

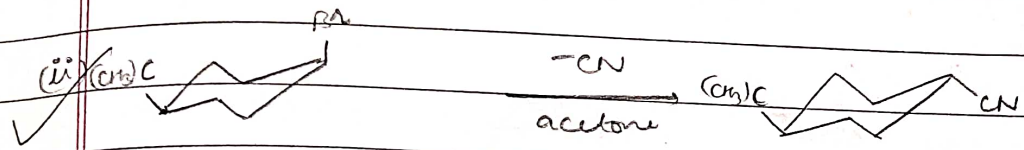
(j) ✓

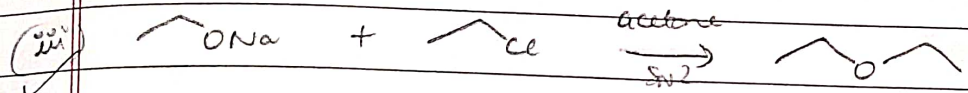

I
OH
SN1
(✓)
DMSO
SN2

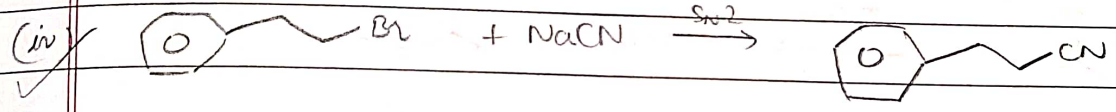
If solvent mentioned with $R-O^-$ (eg- DMF, DMSO) or low T → Sub^n
otherwise (eg- Δ) High T → Elimination

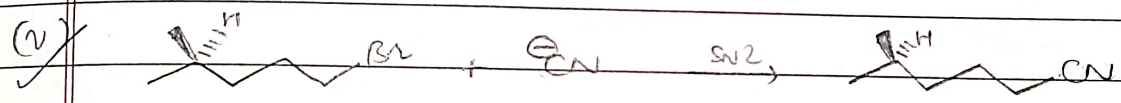
Q Complete the rxn's

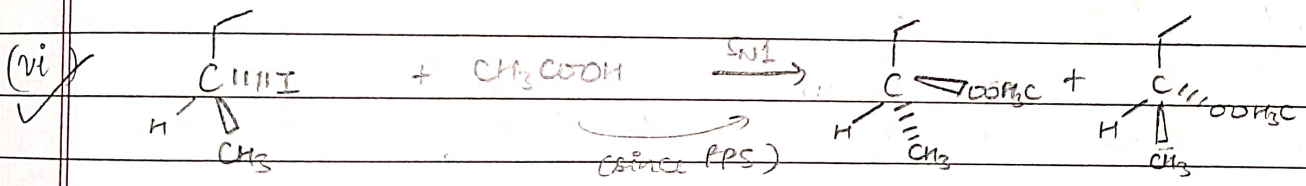
(i) 

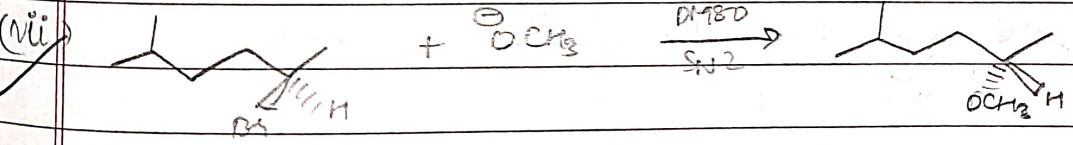
(ii) 

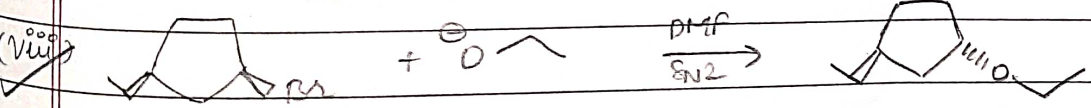
(iii) 

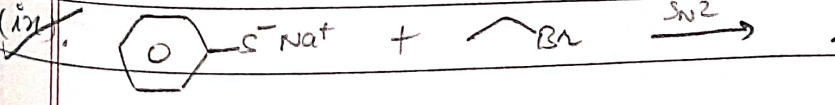
(iv) 

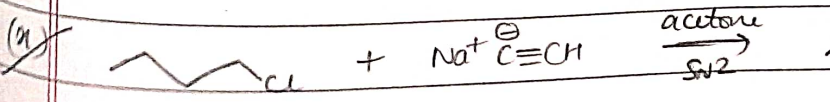
(v) 

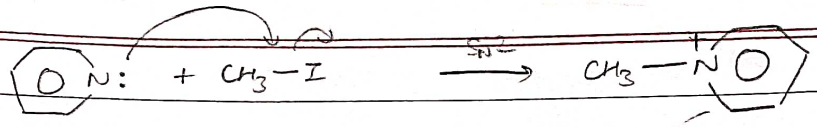
(vi) 

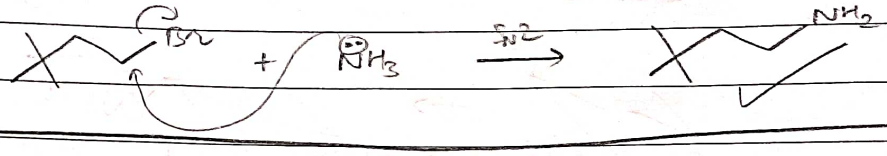
(vii) 

(viii) 

(ix) 

(x) 

(xi) 

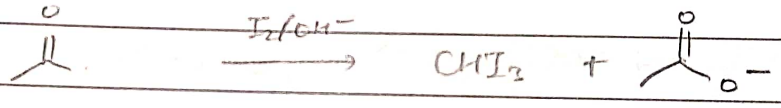
(xii) 

CONVERSIONS

→ Rean^s to be used

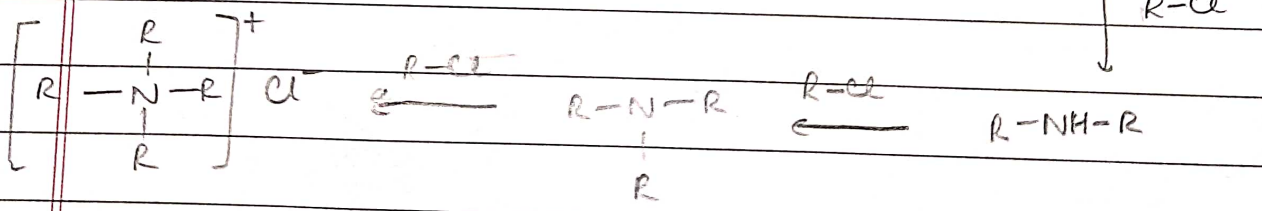
① $R-NH_2 \xrightarrow{CHCl_3 + OH^-} R-NC$

② Haloform xan^n

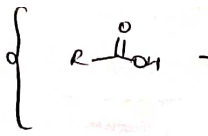


→ Ammonolysis

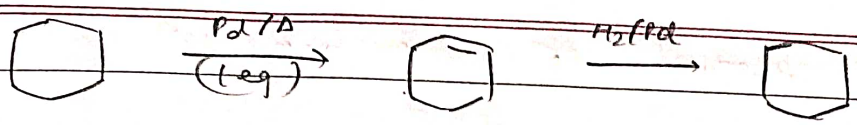
$R-Cl \xrightarrow{NH_3} R-\overset{\oplus}{N}H_3\,Cl^- \xrightarrow{\Delta} R-NH_2 + HCl$

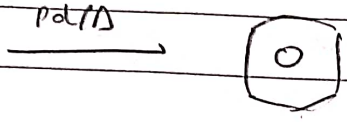


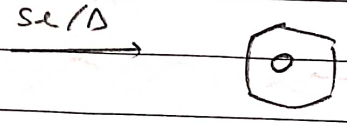
To form 1° $R-NH_2$, NH_3 to be in excess.



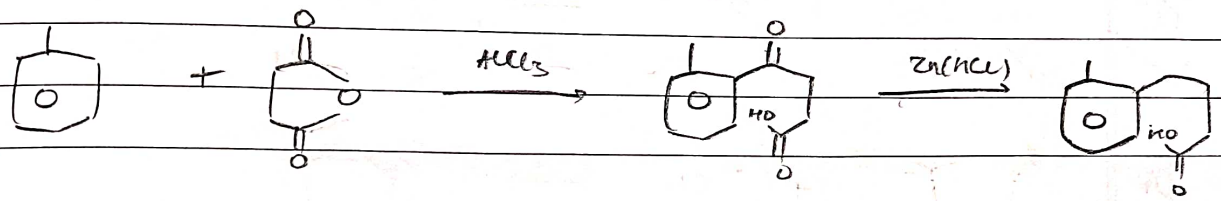
Making Aromatic Rings

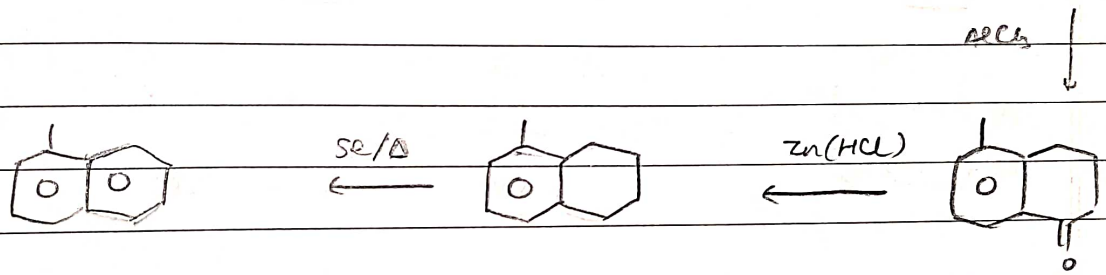






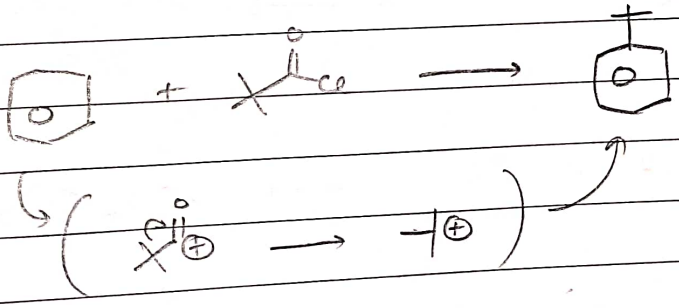
eg :- Making naphthalene from toluene



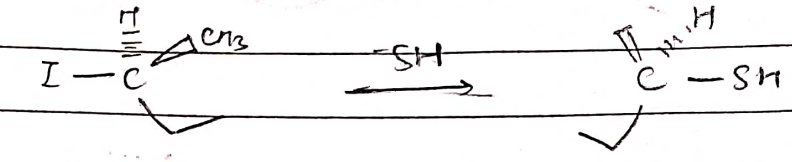


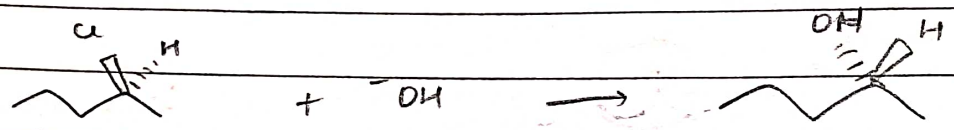
NOTE: Whenever R⊕ becomes stable after CO leaving, F.C Methylation instead of F.C Acylation

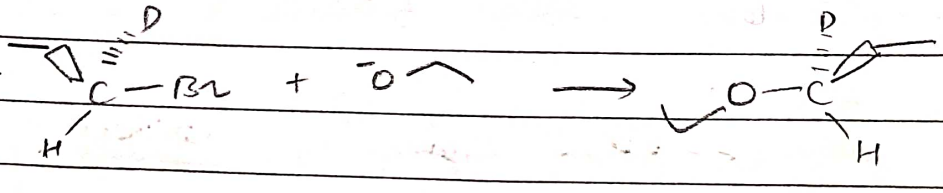
eg

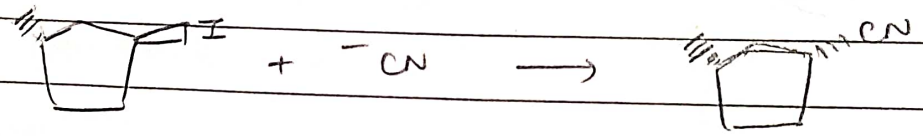


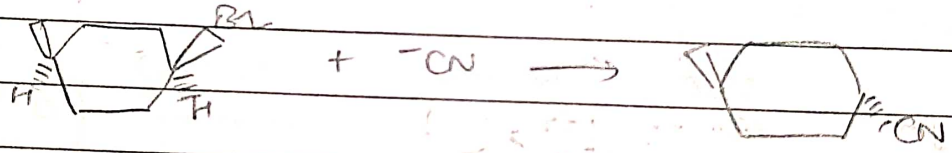
Q. Draw the product of each S_N2 reaction

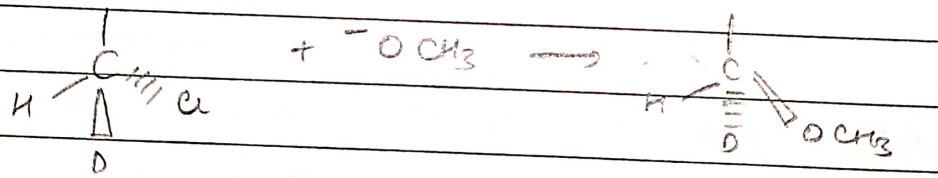
(i) 

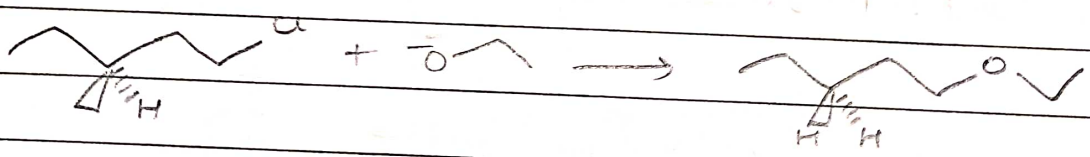
(ii) 

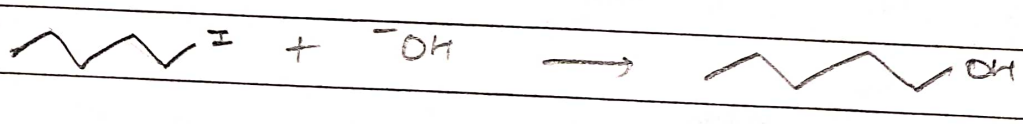
(iii) 

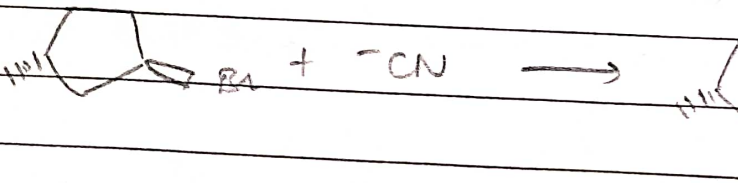
(iv) 

(v) 

(vi) 

(vii) 

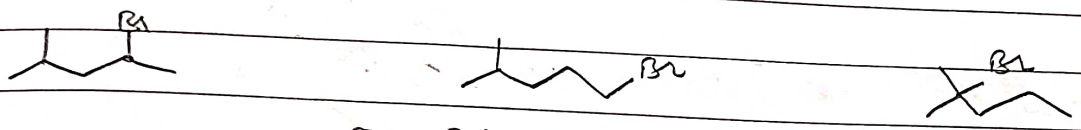
(viii) 

(ix) 

Q. Rank the alkyl halides in each group in order of increasing S_N2 reactivity.

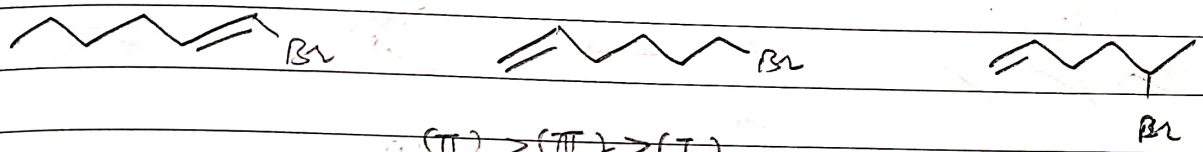
(I) (II) (III)

(i)



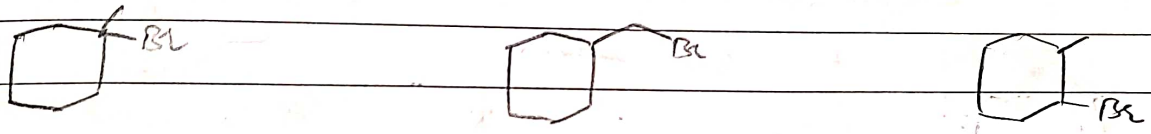
(II) > (I) > (III)

(ii)



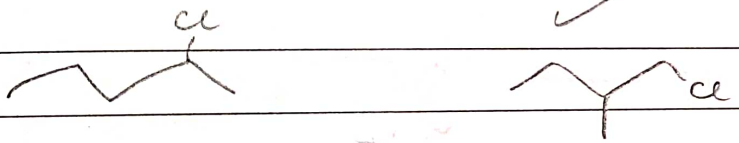
(II) > (III) > (I)

(iii)



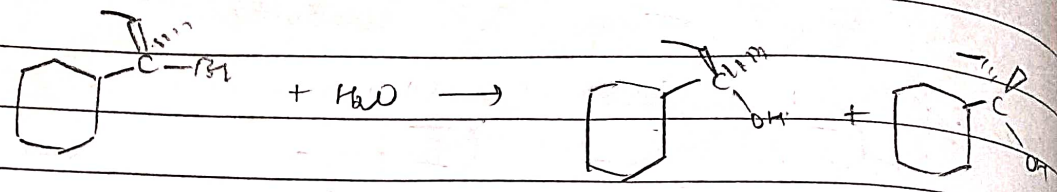
(II) > (III) > (I)

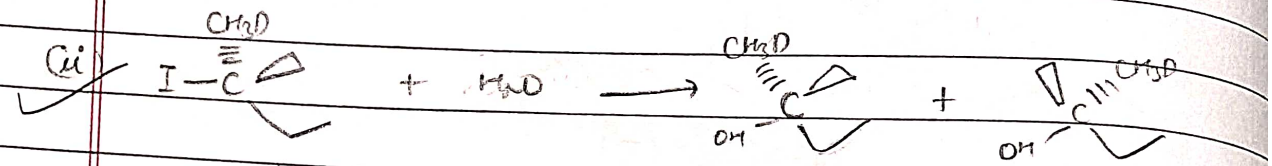
(iv)

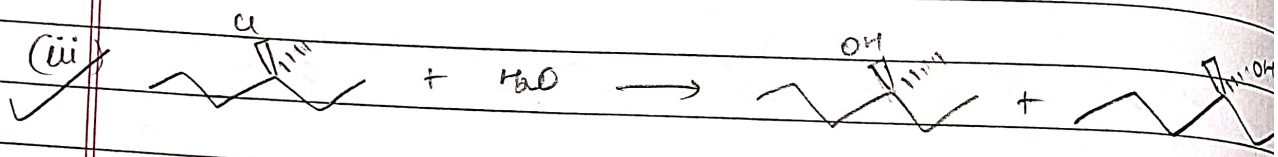


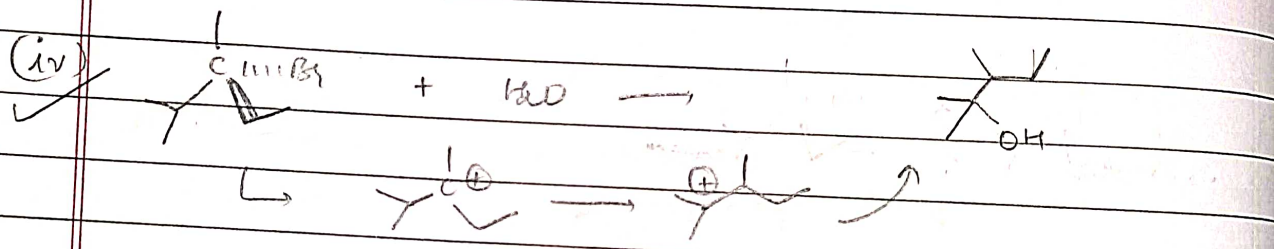
(II) > (I)

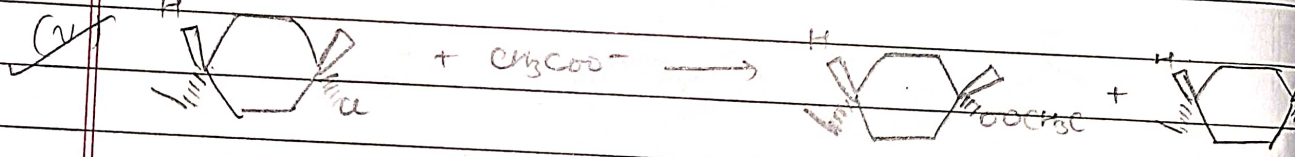
Q. Draw the products of each SN1 reaction

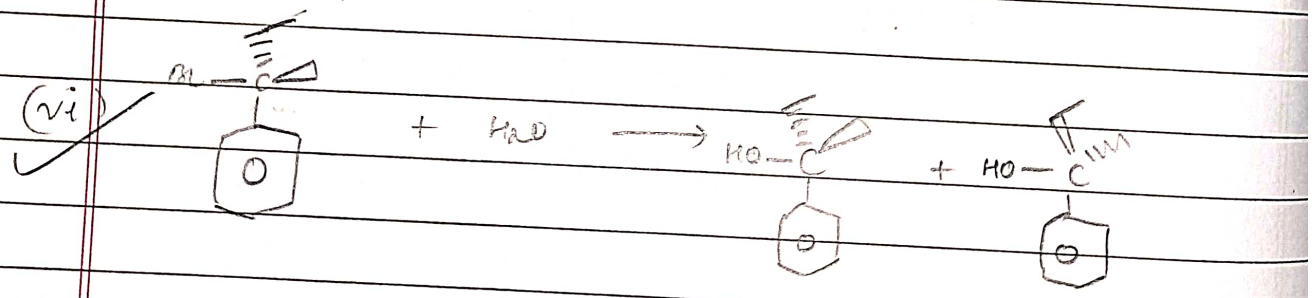
(i) 

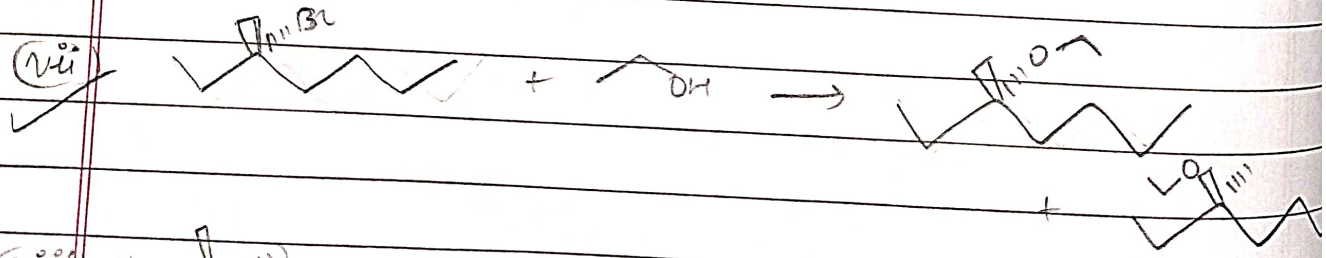
(ii) 

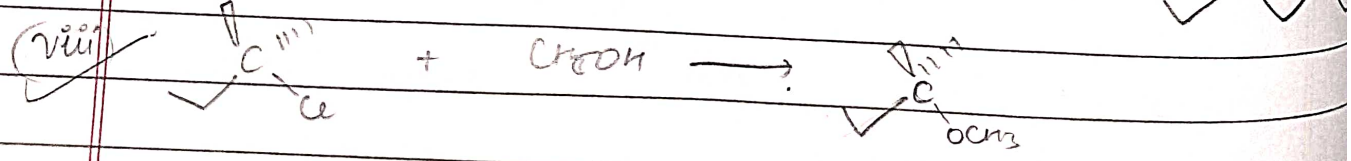
(iii) 

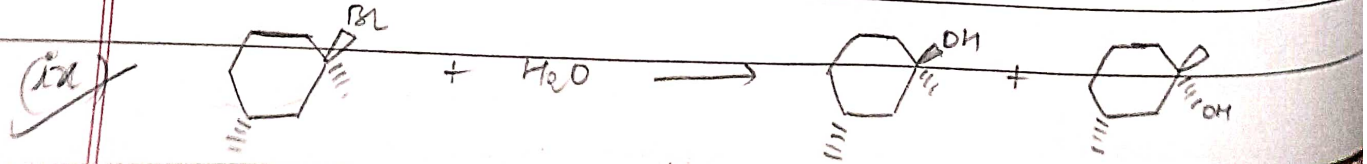
(iv) 

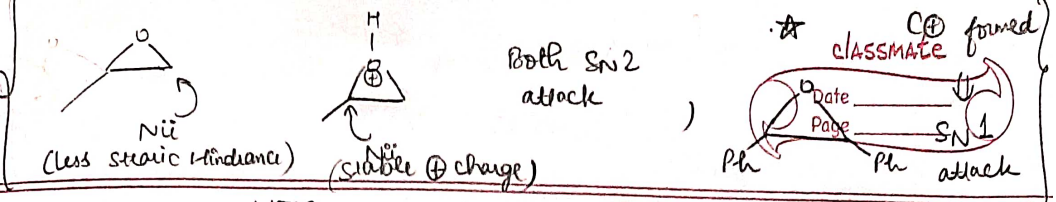
(v) 

(vi) 

(vii) 

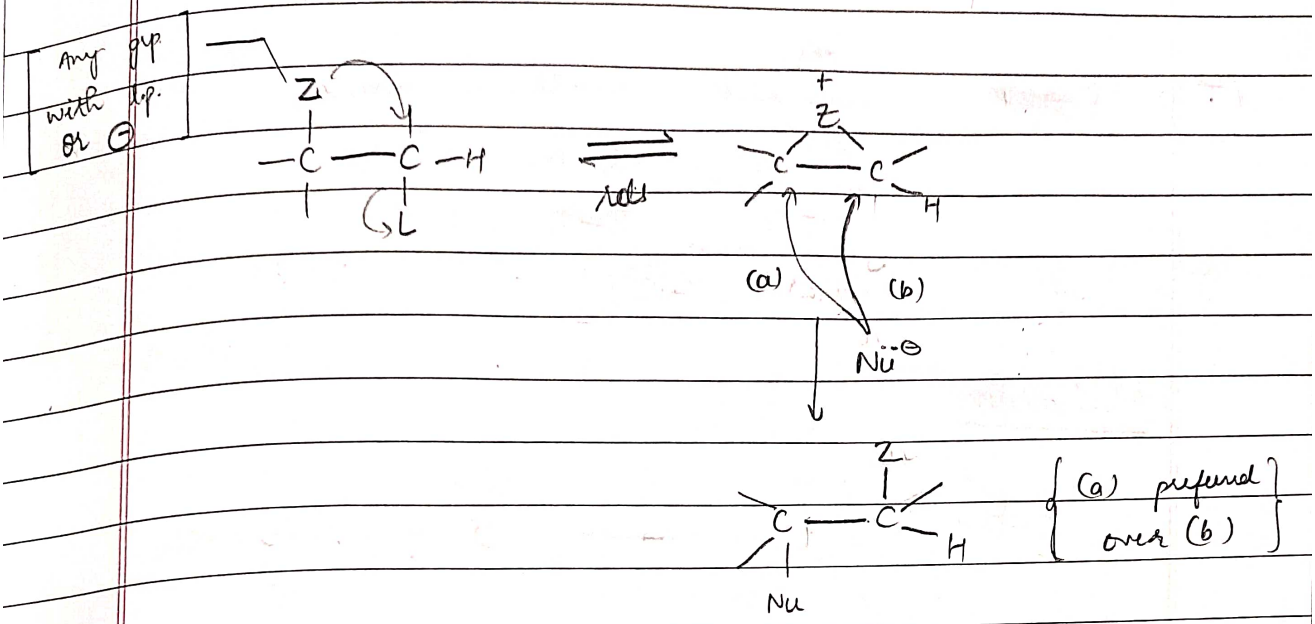
(viii) 

(ix) 



11/05/2023

S_N(NGP) : NEIGHBOURING GRP PARTICIPATION SUBⁿ

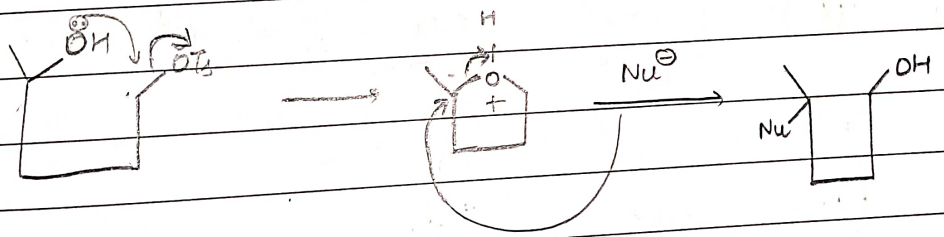


NOTE: ① Z & L must be anti-periplanar

② Retention product formed

17/05/2023

eg-



PREP^{n} of R–X

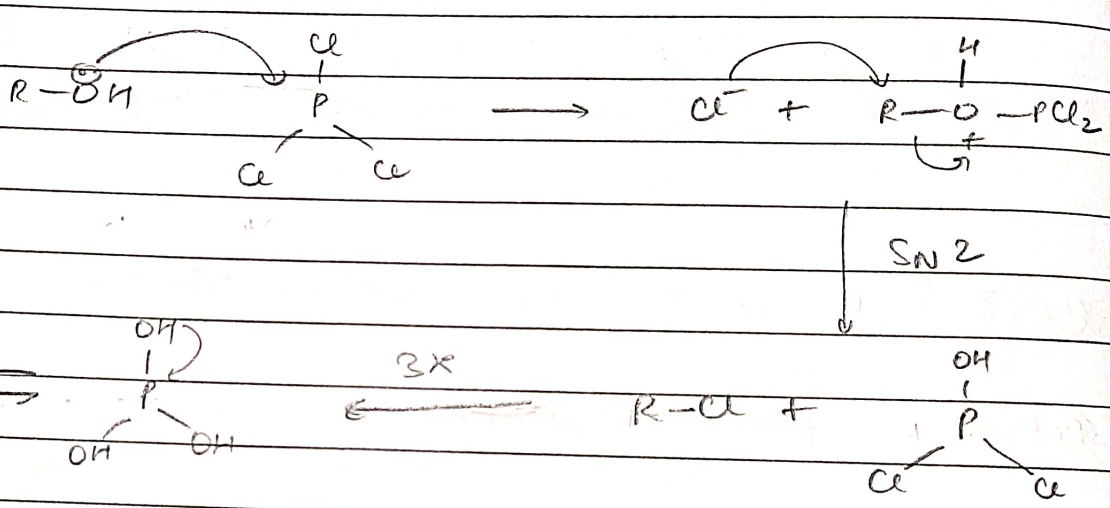
(I) $R-OH \xrightarrow{PCl_3} R-Cl + H_3PO_3$

$\xrightarrow{P+Br_2/PBr_3} R-Br + H_3PO_3$

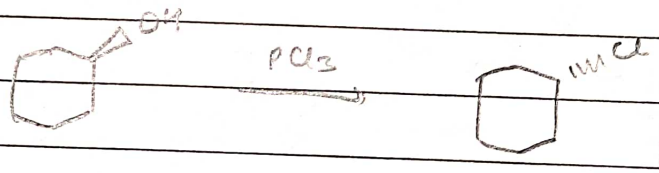
$\xrightarrow{P+I_2/PI_3} R-I + H_3PO_3$

(generally S_N2)

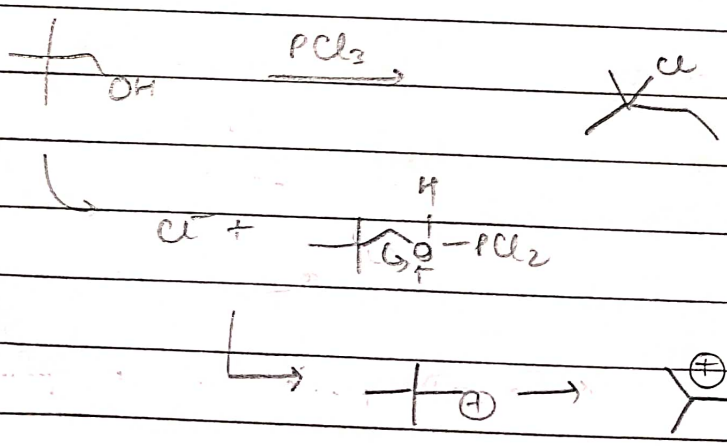
Mechanism



eg (i)



(ii)



★ During mech.,  has tendency to attack rather than PCl_3

(II) $R-OH \xrightarrow[(S_Ni)]{SOCl_2} R-Cl$

$\xrightarrow{PCl_5}$ (generally S_N2) $R-Cl + HCl + POCl_3$

Mechanism

$R-OH + PCl_5 \longrightarrow Cl^- + R-\overset{+}{O}(H)-PCl_4$

$\downarrow$

$R-Cl + HCl + POCl_3$

NOTE: (i) $R-O-H$, $Cl-PCl_3-Cl$ $\longrightarrow R-Cl + POCl_3 + HCl$

(ii) $R-O-R'$, $Cl-PCl_3-Cl$ $\longrightarrow R-Cl + R'Cl + POCl_3$

(iii) $R-C(=O)-O-H$, $Cl-PCl_3-Cl$ $\longrightarrow R-C(=O)-Cl + POCl_3 + HCl$

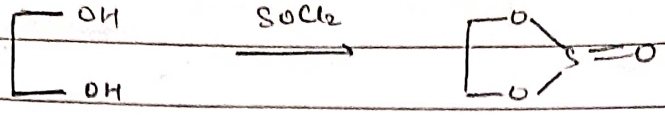
(iv) $R-C(=O)-O-R'$, $Cl-PCl_3-Cl$ $\longrightarrow R-C(=O)-Cl + POCl_3 + R'Cl$

(v) $Cl-PCl_3-Cl$, $R-C(=O)-H$ $\longrightarrow R-CCl_2-H + POCl_3$

(vi) $Cl-PCl_3-Cl$, $R-C(=O)-R'$ $\longrightarrow R-CCl_2-R' + POCl_3$

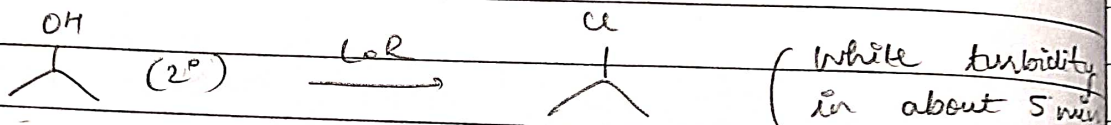
★ (vii)  $\longrightarrow$  (minor) + $RHO-\overset{O}{\overset{\|}{P}}(OR)-OR$ (major)

(viii)



(III) Lucas Test (Lucas Reagent - conc. HCl + $ZnCl_2$ + conc. H_2SO_4)

$R-OH$ (1°) $\xrightarrow{L.R}$ No rxn (or slow)



NOTE: (i) $R-OH$ $\xrightarrow{\text{conc HCl}}$ No rxn

$\xrightarrow{\text{conc HCl/A}}$ $R-Cl$

$R-OH \xrightarrow{L.R} R-\overset{\oplus}{O}H$ (complex formed)

$Cl-\underset{\ominus}{Zn}-Cl$ (Lewis acid)

(ii) $R-OH \xrightarrow[[H^+]]{H_2SO_4} R-\overset{\oplus}{O}H_2 \xrightarrow{NaBr} R-Br$

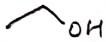
$\xrightarrow{NaCl} R-Cl$

(iii) $R-OH \xrightarrow{HI} R-\overset{\oplus}{O}H_2 \xrightarrow{I^-} R-I$

(no H^+ req. as HI strong acid)

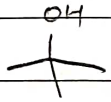
(iv) For comparing ROR (Lucas Test), check if CD favourable.
But rea^n follow S_N1 or S_N2 depending on R grp.

Q. Which give +ve Lucas Test.

1.  ✗

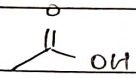
2.  ✗

3.  ✓

4.  ✓

5.  ✗

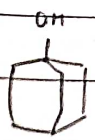
6.  ✗

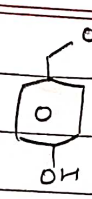
7.  ✗

8.  ✓

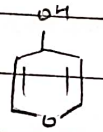
9.  ✓

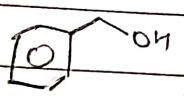
10.  ✓

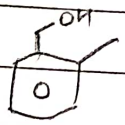
11.  ✗

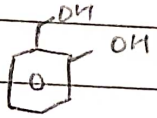
12.  ✓

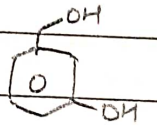
13.  ✗

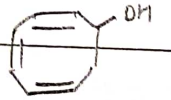
14.  ✓

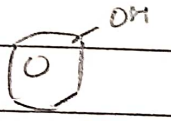
15.  ✓

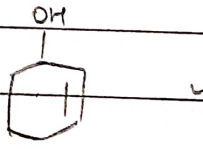
16.  ✓

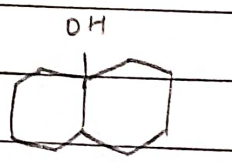
17.  ✓

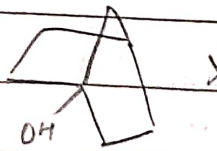
18.  ✗ (✓) [gives both S_N1 & S_N2 → ⊕ stable]

19.  ✓

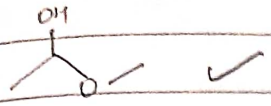
20.  ✗

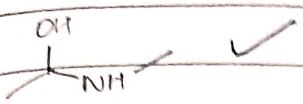
21.  ✓

22.  ✗ (✓) [#C in bridge = 0 → ⊕ stable]

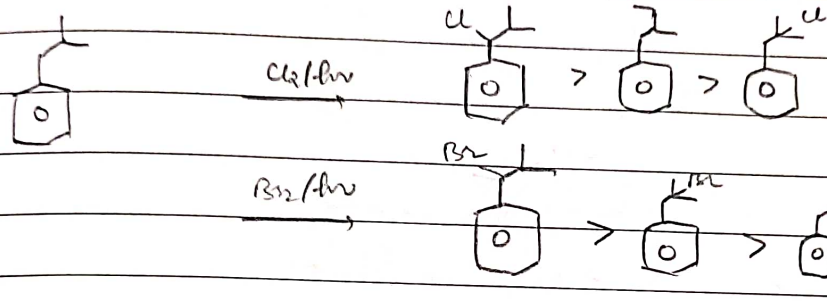
23.  ✗

{ selective halogenation followed in all reagents giving •X }

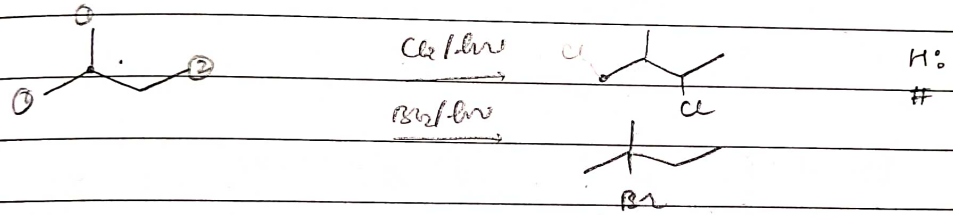
24. 

25. 

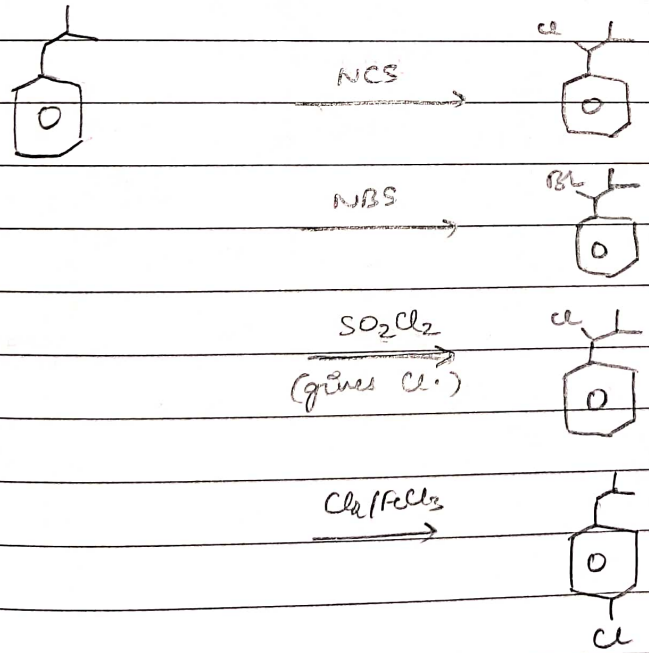
Q. Write major product

1. 

	1°	2°	3°
H:	6	2	1
#	1	4	5
	6	8	5

2. 

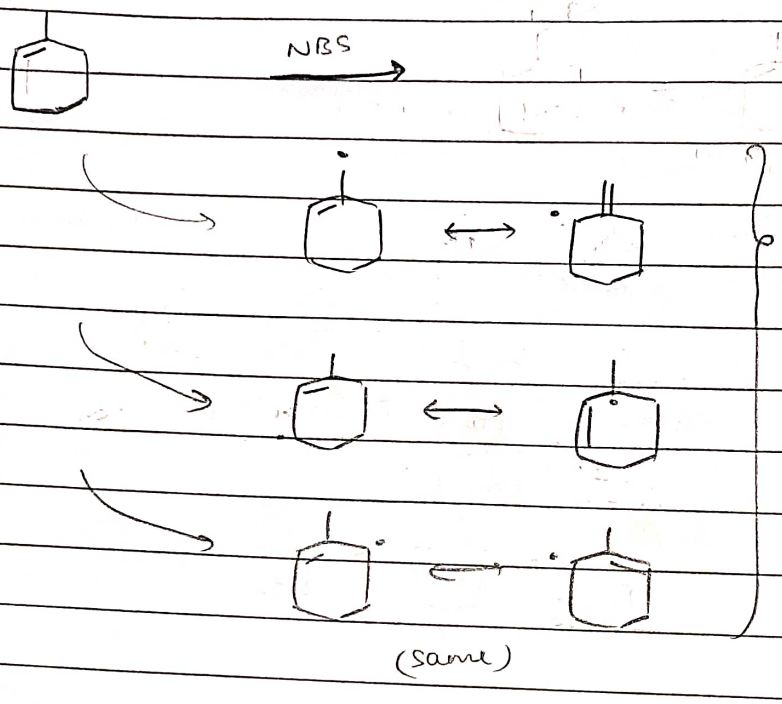
	1°	1°	2°	3°
H:	6	3	2	1
#	1	1	4	5
	6	6	8	5

3. 

4. 

[⊕ addn if PPS with NBS or NCS]

NBS → Br

5. 

(IV) Halogen Exchange

I. Finkelstein Rean

$$R-X + NaI \xrightarrow[(S_N2)]{\text{Dry acetone}} R-I + NaX\ (\downarrow)$$

(X = Cl, Br) (ppt)

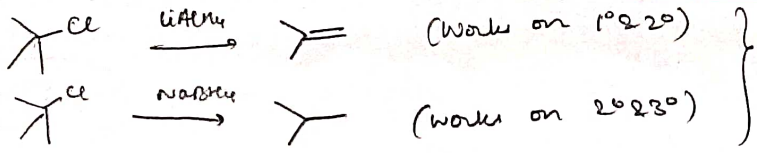
II. Swartz Rean

$$R-X \xrightarrow[(S_N2)]{AgF/Hg_2F_2/CoF_2/SbF_3} R-F$$

(X = Cl, Br, I)

Driving Force : Le Chatelier's Principle.

NaX precipitates ⇒ Rean goes fwd.



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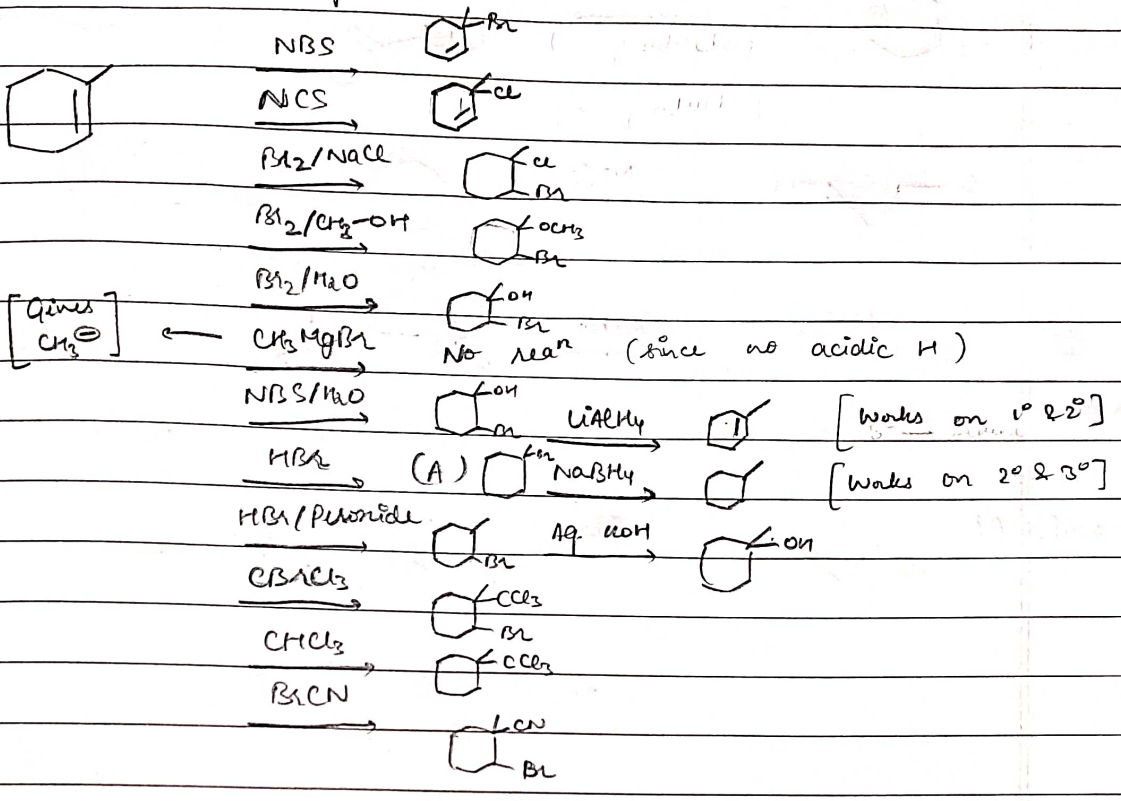
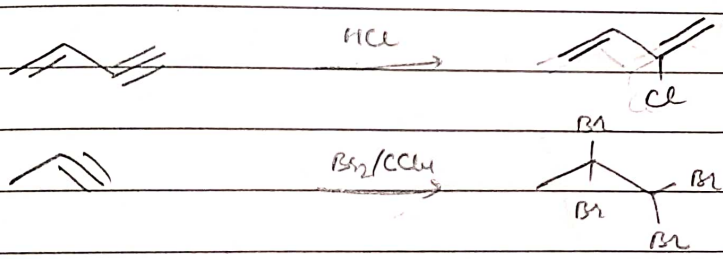
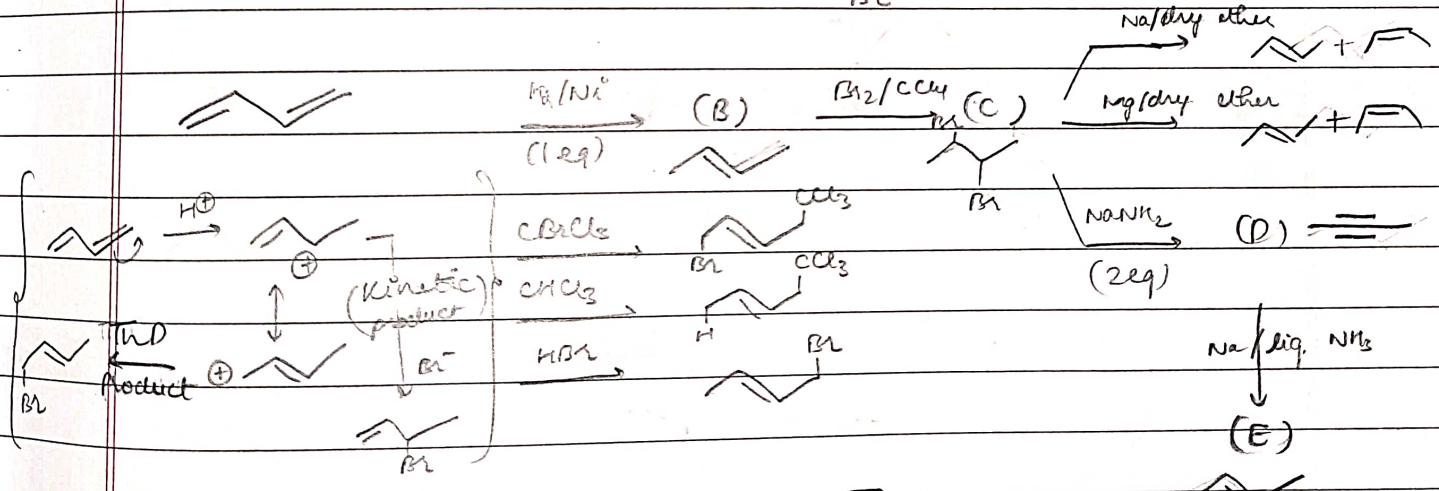
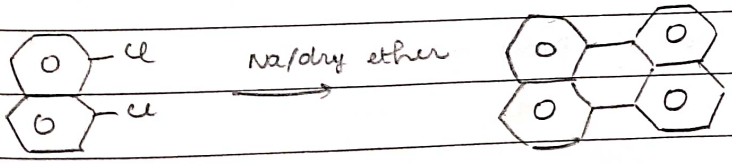
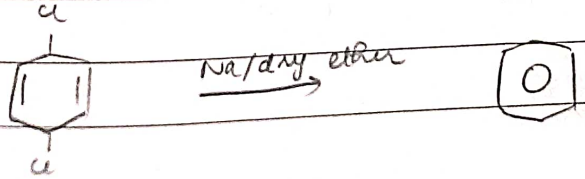
Q. Write the major product

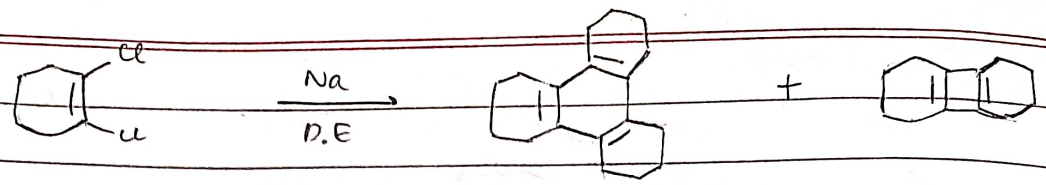


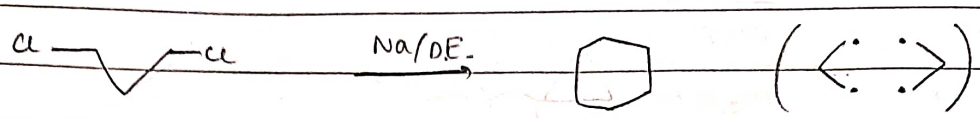


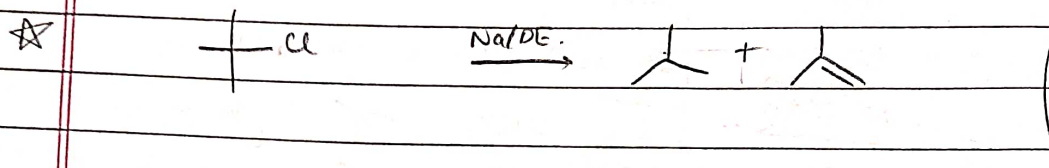




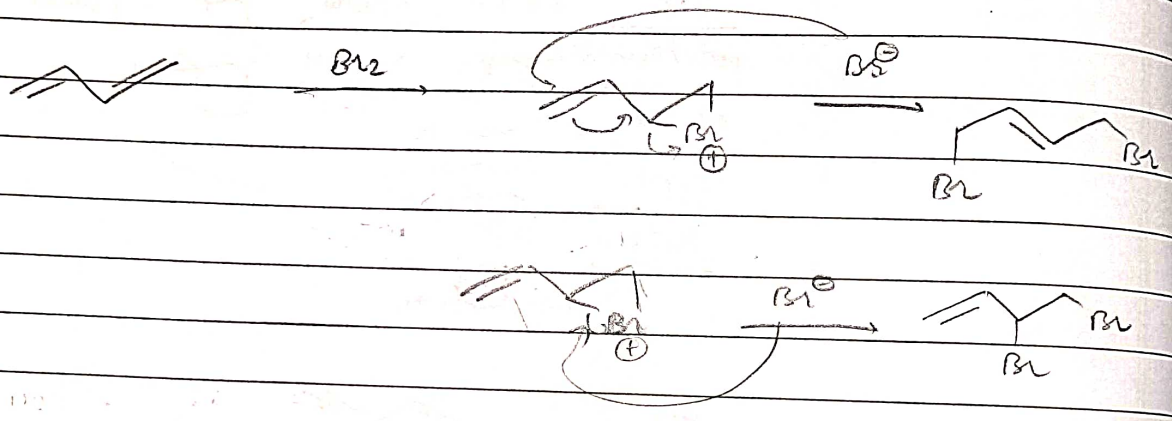




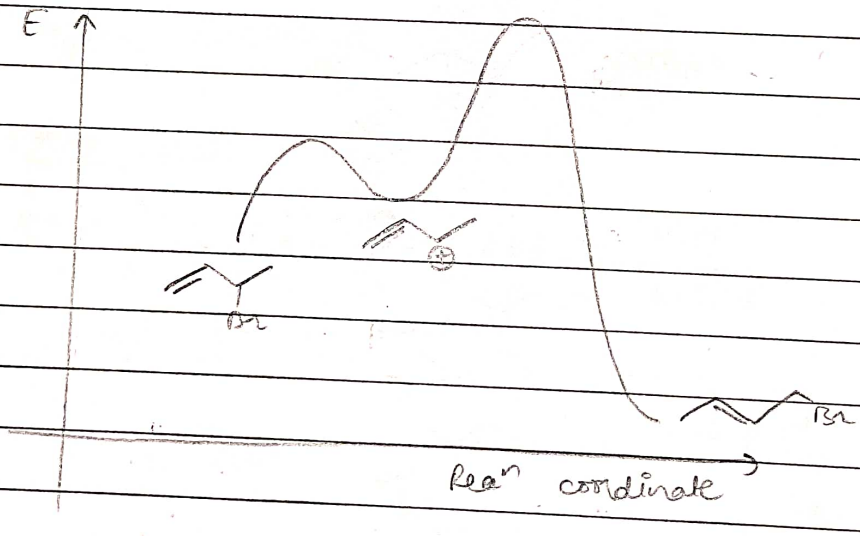




NOTE: (i)



(ii)



Thd Product (1,4 addn)	—	• (If nothing given) • High T • PPS
Kinetic Product (1,2 addn)	—	• Low T • PAS

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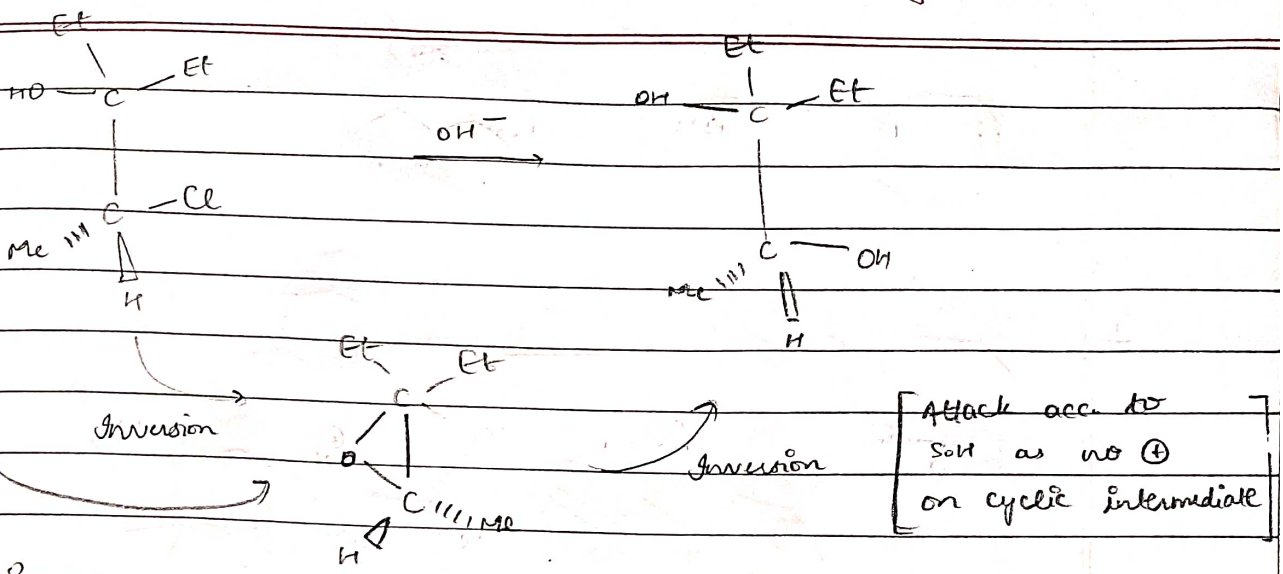
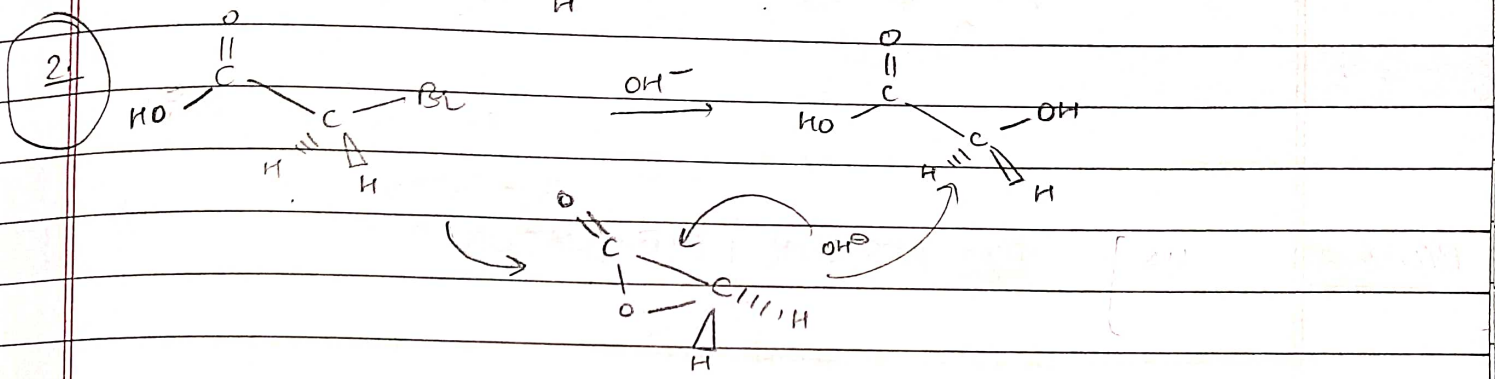
Q. 1.



[Attack acc. to SoM as no ⊕ on cyclic intermediate]

2.



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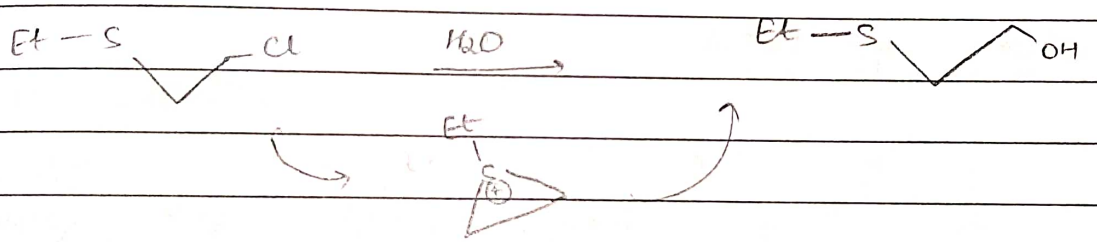

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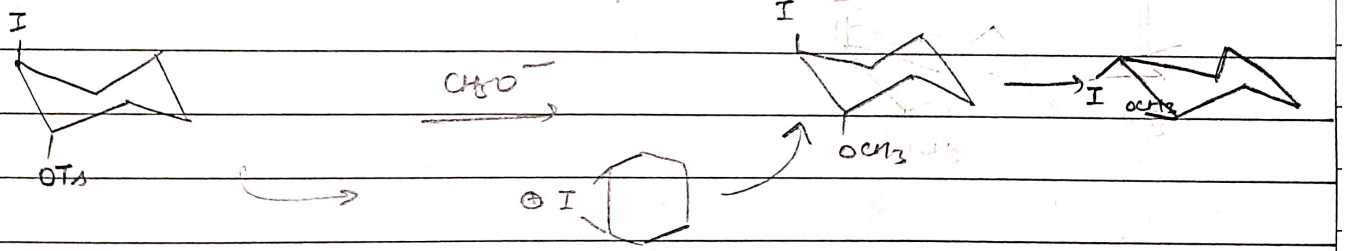

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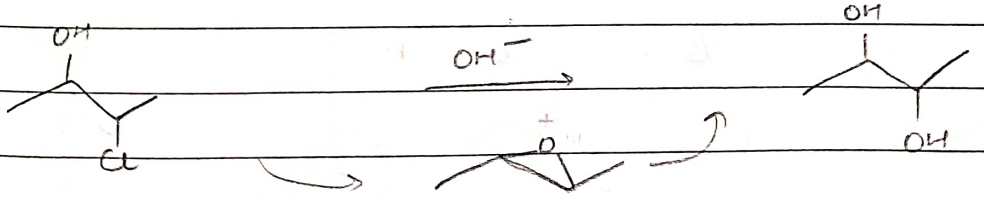
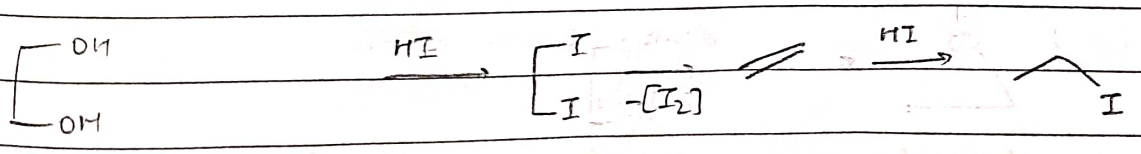
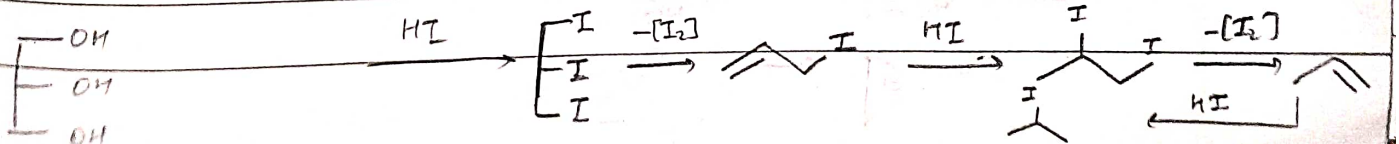
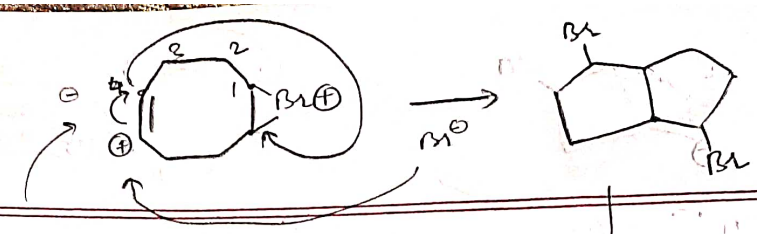


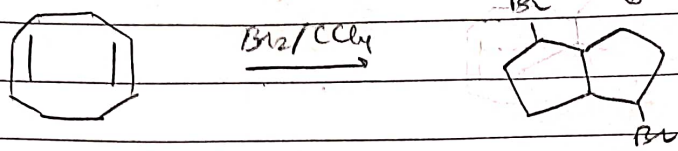
☆ 6.

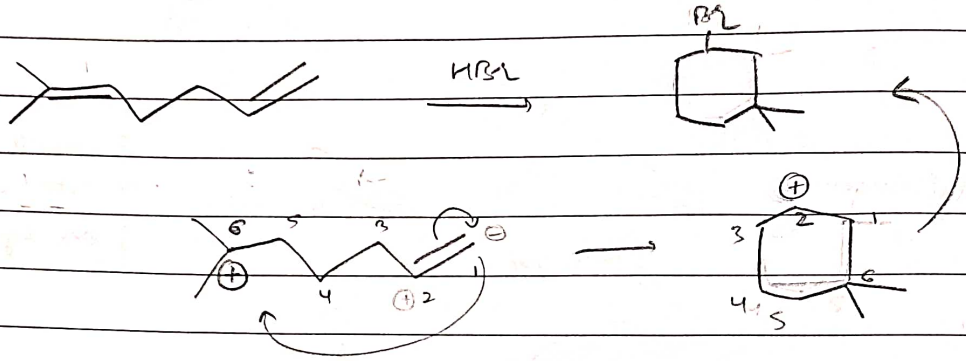


☆ 7.





8. 

9. 

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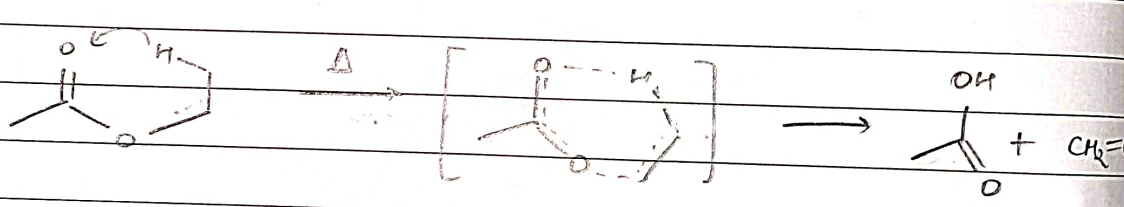
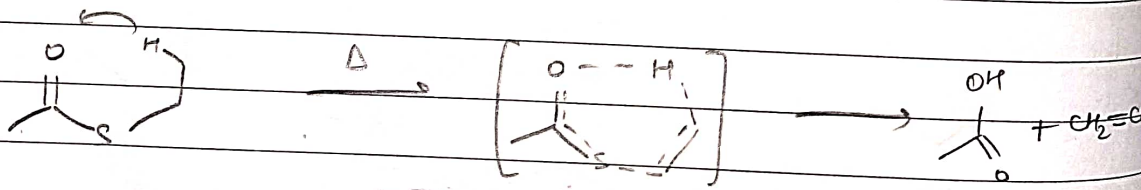
E_i: INTERNAL ELIMINATION

→ Pyrolysis of Ester



→ Pyrolysis of Xanthate



NOTE: (i) E_i is syn elimination

(ii) Hoffmann product formed

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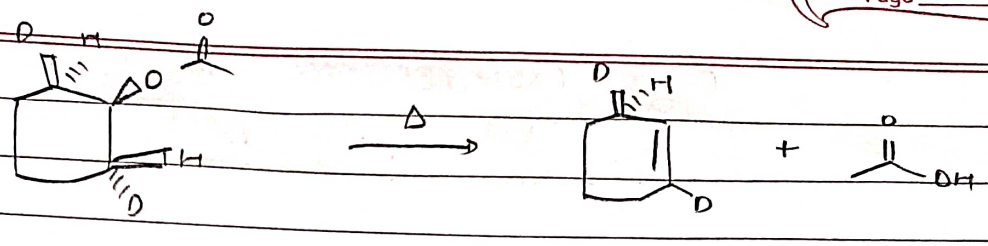
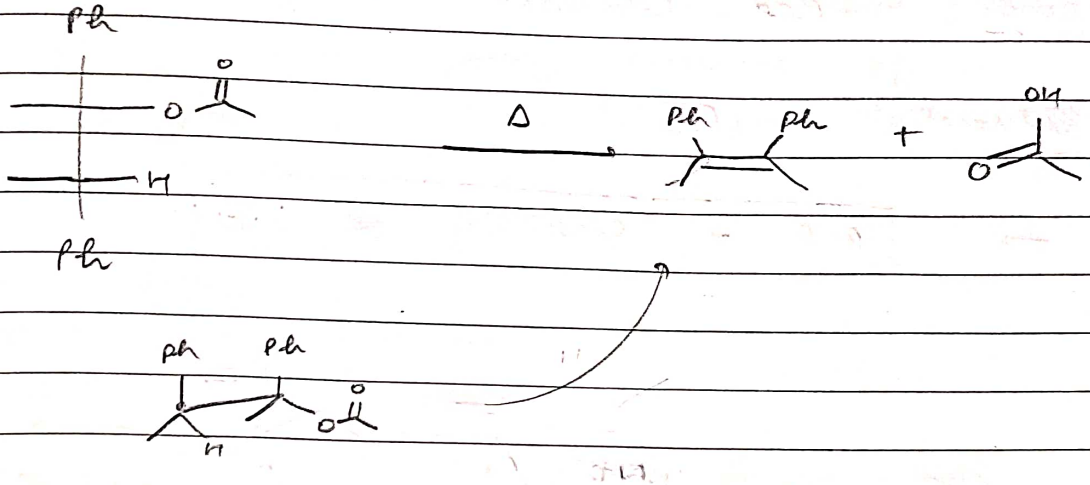
eg:- (i)

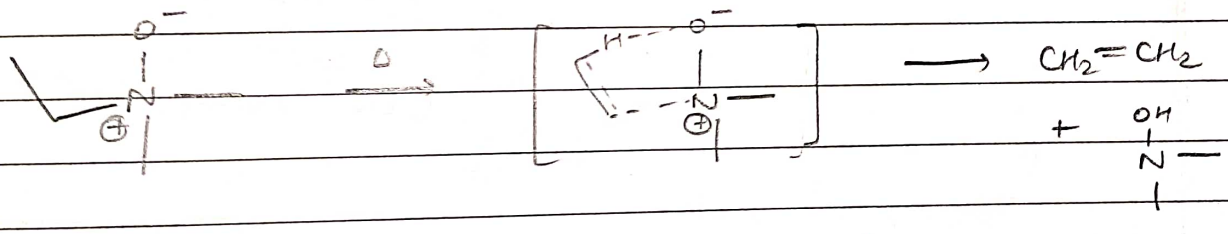


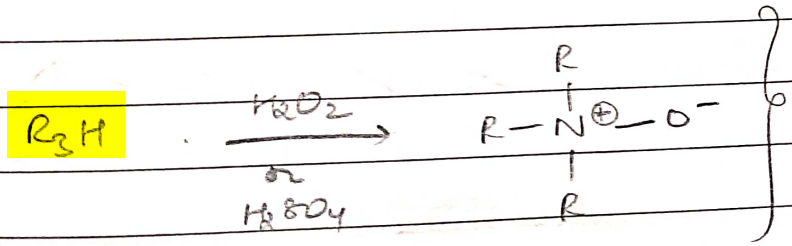
(ii)



→ Cope Elimination

Pyrolysis of tri alkylamine oxide



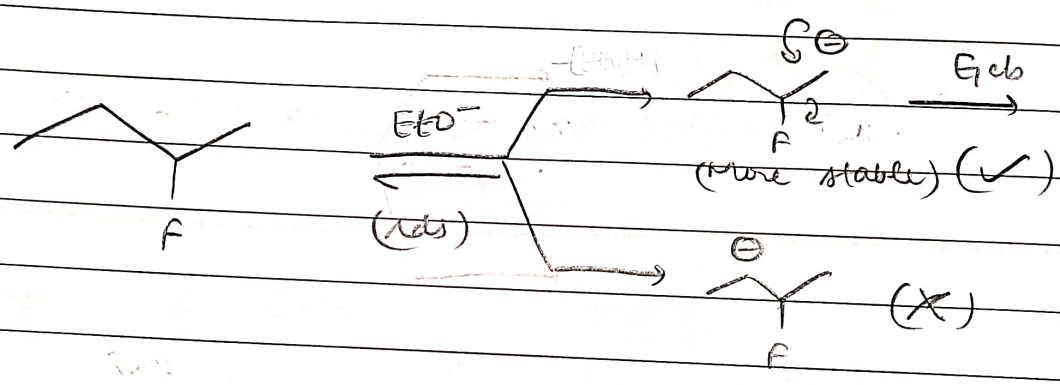


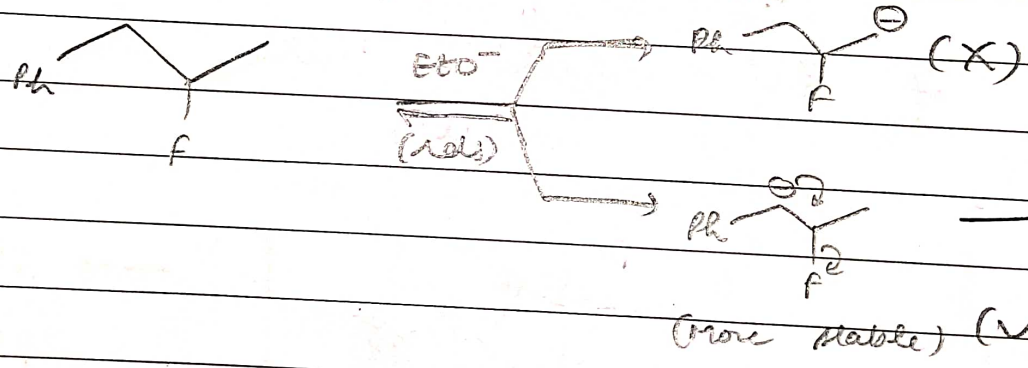
E_{1cb}: UNIMOLECULAR ELIM. VIA CONJ. BASE

Condⁿ: Bad L.G & Strong Base

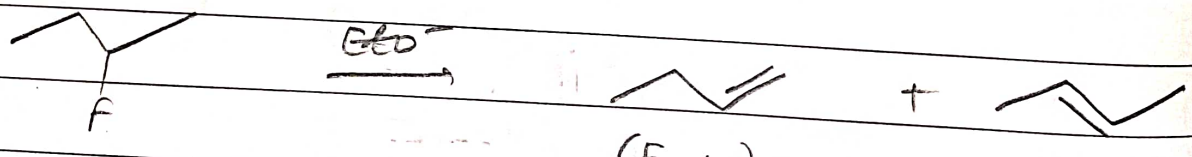
Intermediate: $C^{\ominus}$

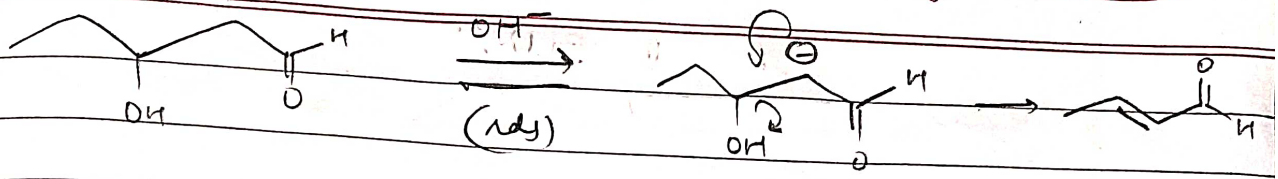
$\Rightarrow$ **RoR $\propto$ Stability of $C^{\ominus}$**





NOTE:

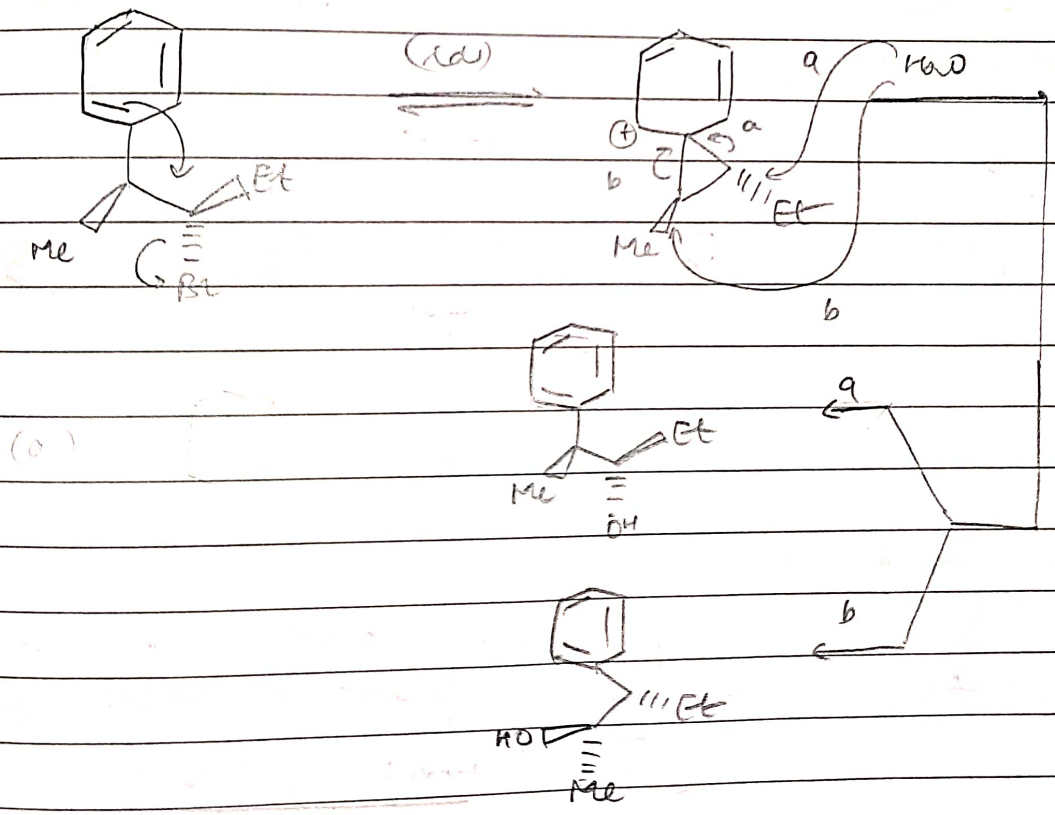


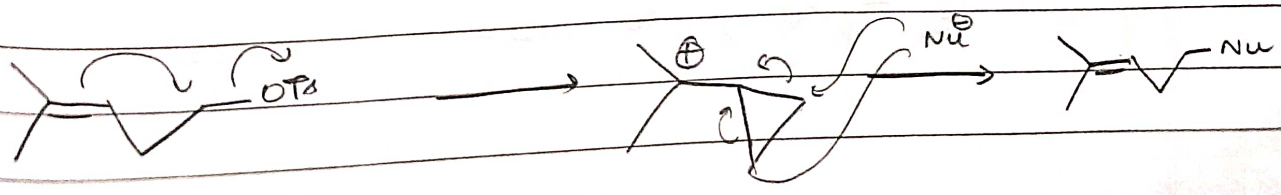


(Here, OH^- did not take acidic-H of -OH as $C^{\ominus}$ formed after removal of H of β-C ($\overset{O}{\underset{O}{\overset{\|}{C}}}-H$) got involved in resonance ⇒ it was ~~more~~ acidic)

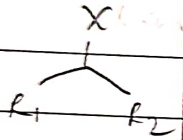
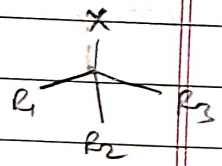
* Only for AITS

NGP via π-bond @ γ-post.



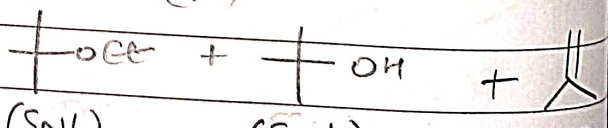


SUB^{n} & ELIM^{n}

Nu :	Good	Good	Poor	Poor
Base :	Weak	Strong	Strong	Weak
	(I^-)	(EtO^-)	($^+OH^-$)	(H_2O)
CH_3-X	S_N2	S_N2	S_N2	NO S_N2
R–X	S_N2	Low T – S_N2 High T – E_2	E_2	NO S_N2
	PPS – S_N1 PAS – S_N2	E_2	E_2	NO S_N2
	S_N1	E_2	E_2	S_N1

→ Data Based

①  $\xrightarrow[\text{20\% } H_2O]{\text{80\% EtOH}}$ $T < 25^\circ$

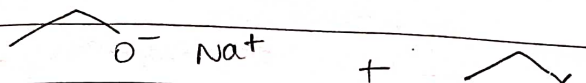


(SN1) (SN1) (E1)

(>) 83% 17%

(Not ⊖ prone, so behave like Nü majorly)

Date
Page

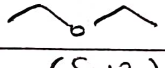
②  C_2H_5OH, $T = 55°C$ 

(S_N2)

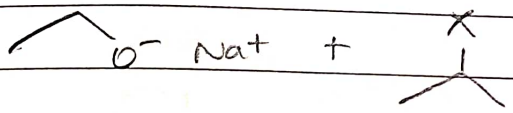
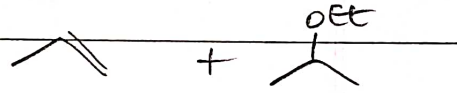
90%

+ $CH_2=CH_2$ (E_2)

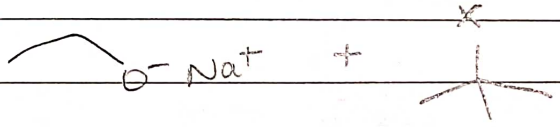
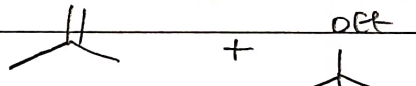
10%

$T > 55°C$ $CH_2=CH_2$ + 

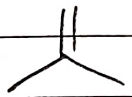
(E_2) (major) (S_N2) (Minor)

③  $T = 55°C$ 

(E_2) (major) (S_N2) (Minor)

④  $T = 25°C$ 

$(G + E_2)$ 91% (S_N1) 9%

$T = 55°C$  + 

$(G + E_2)$ 100%

(^-O took H from )

⑤ $CH_3-CH_2-(CH_2)_6-CH_2-Br$ $\xrightarrow[T=65^\circ C]{CH_3-O^-}$ $CH_3-CH_2-(CH_2)_6-CH_2-OCH_3$ (S_N2) 99%

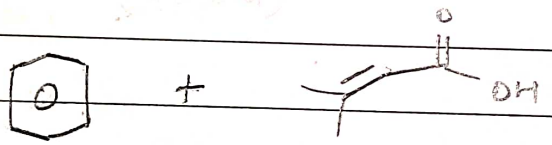
+ $CH_3-CH_2-(CH_2)_5-CH=CH_2$ (E2)

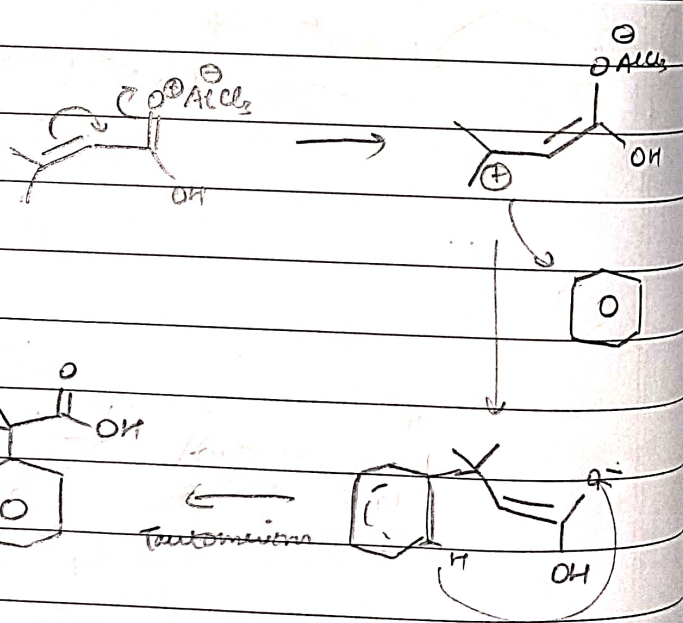
$\xrightarrow[T=45^\circ C]{+O^-}$ $CH_3-(CH_2)_6-CH=CH_2$ (E2) 65%

+ $CH_3-CH_2-(CH_2)_6-CH_2-O-$ (S_N2) 15%

23/05/2023

Q.





NUCLEOPHILICITY V/S BASICITY

- **Nucleophilicity** : Kinetic concept

  Depends on
  - Charge density
  - Steric factor

eg — (i) Neutral < Negative species

$H_2O < OH^-$

$NH_3 < NH_2^-$

$R-OH < R-O^-$

(ii) $\propto \left(\frac{1}{\text{Bulkiness}}\right)$ $\quad t\text{-}O^- < CH_3-O^-$

(iii) Down the grp

PPS: $I^- > Br^- > Cl^- > F^-$

(Charge density of F^- ↑
⇒ Bulky hydrated form)

PAS: $I^- < Br^- < Cl^- < F^-$
or Non polar

(iv) $\propto$ (# Nucleophilic centres) [in neutral species]

$NH_2-NH_2 > NH_3$

$HO-OH > H_2O$

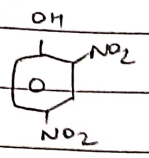
$R-O-O-R > R-OH$

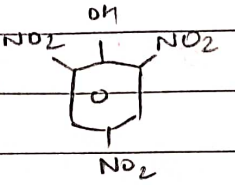
$HS-SH > H_2S$

If $\#NO_2 = 2$ in phenol

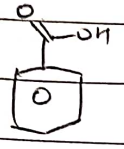
Acidic str: > Benzoic acid.

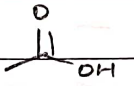
Q Compare acidic strength.

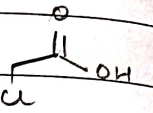
1. 

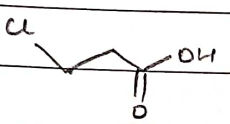
2. 

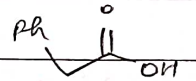
3. 

4. 

5. 

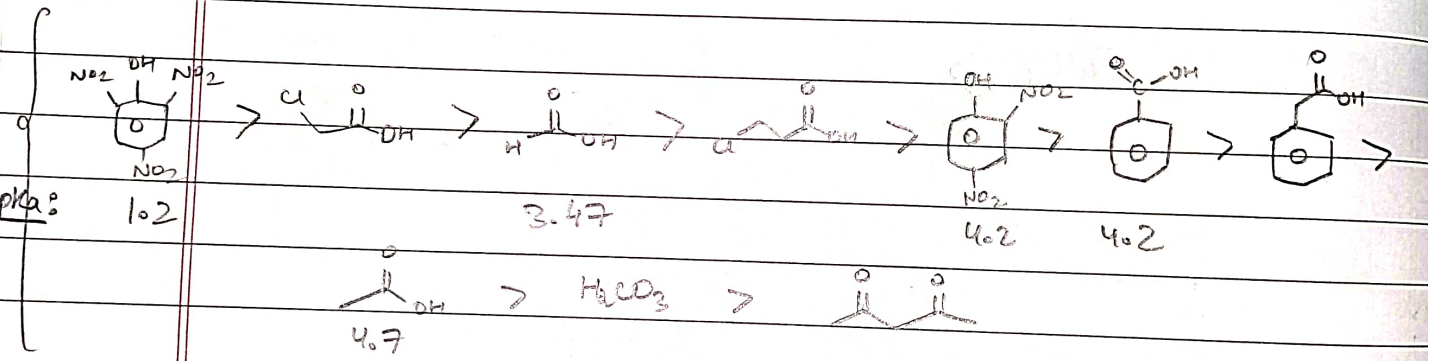
6. 

7. 

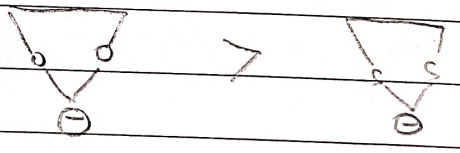
8. 

A. ✗ 3 < 2 < 1 < 4 < 5 < 8 < 7 < 6

Actual: 2 > 7 > 6 > 1 > 4 > 8 > 5 > 3



(v) $\propto \left(\frac{1}{\text{Resonance}}\right)$



(vi) Across Period [EN ↓ ⇒ Nu ↑]

PPS: $\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > O\overset{\ominus}{H} > \overset{\ominus}{F}$

PAS: $\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > O\overset{\ominus}{H} > \overset{\ominus}{F}$

NOTE: In period, solvent effect does not dominate. (since similar sites

CN

(PAS)

C act as Nü

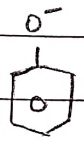
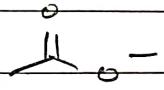
(EN: C < N)

(PPS)

N act as Nü

(EN_C ↑ ⇒ H^+ surround C ⇒ Bulkiness ↑)

Q. Compare nucleophilicity

1. CH_3-O^-  

① > ② > ③

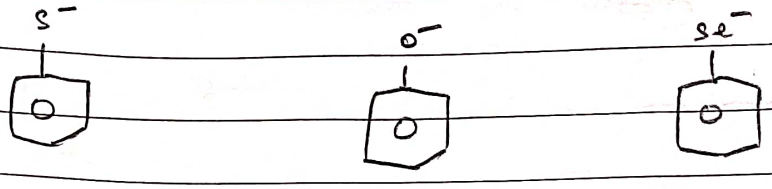
2. PH_3 NH_3

PAS: ② > ①

PPS: ① > ②

3. H_2S H_2O

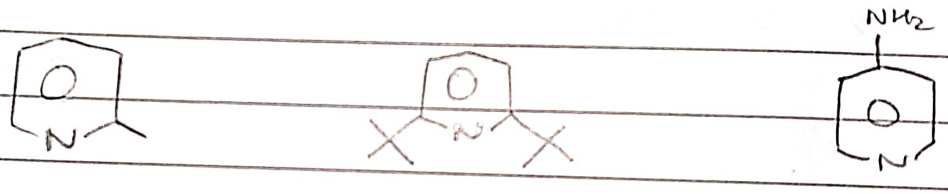
① > ②

4. 

PAS: ③ > ① > ②

(Resonance dominant. Best resonance
2p-2p > 3p > 2p > 4p-2p

PPS: ③ > ① > ②

5. 

③ > ① > ②

steric factor

6. CH_3-NH_2 CH_3OH CH_3-SH

PAS: ① > ② > ③

PPS: ① > ③ > ②

(Solvent factor not applicable in same period)

7. SH^- OH^- H_2O

PAS: ① > ② > ③

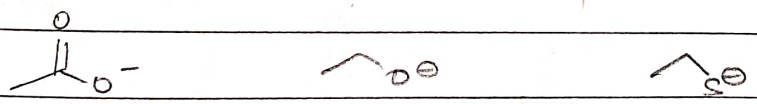
PPS: ② > ① > ③

8. OH^- F^- Cl^-

PAS: ① > ② > ③

PPS: ① > ③ > ②

(Solvent factor)

9. 

PPS: ③ > ② > ①

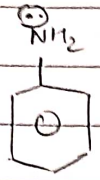
- **Basicity** : TRD Concept.

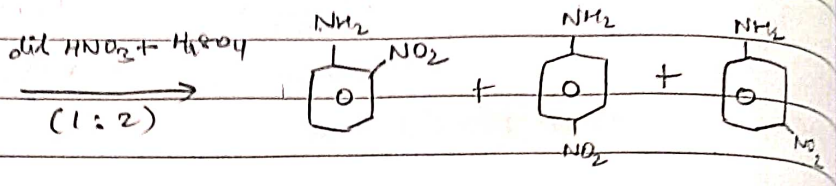
(Basicity) ∝ (charge Density)

Steric Hindrance does not matter.

NOTE

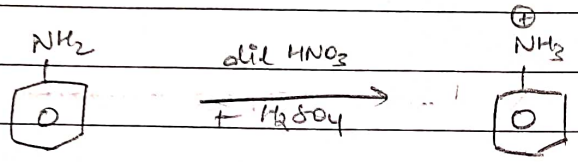
Nitration of Phenol & Aniline

(Highly activating) ⇝ 



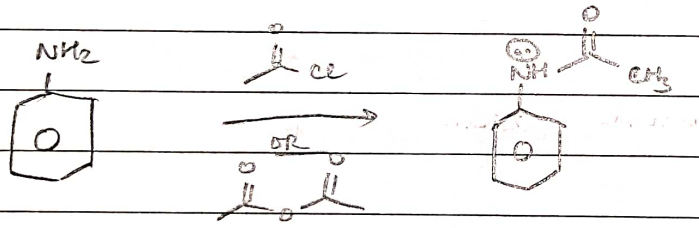
(51%) (47%)

Here, meta formed as,

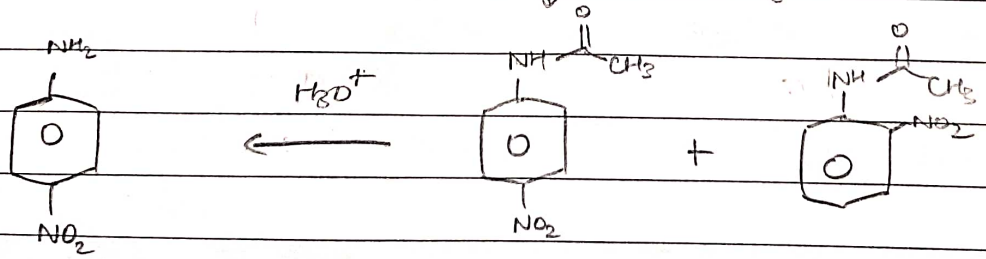


⇝ (deactivating) [due to −I]

So to avoid this, we use protecting gp.  (Acetic Anhydride)



Here, meta will not form as $\overset{\oplus}{N}H_2$ not formed due to resonance with both ring & 

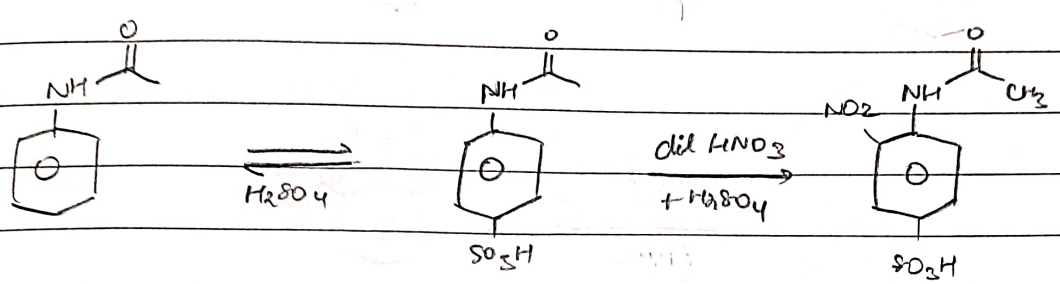


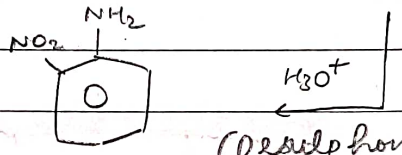
(Para) (99%) (1%)

[Steric Hinderance at ortho pos.]

NOTE: $R_1-C\equiv CH \xrightarrow{NaNH_2} R_1-C\equiv C^{\ominus}Na^{\oplus} \xrightarrow{(S_N1)\ R_2-I} R_1-C\equiv C-R_2$

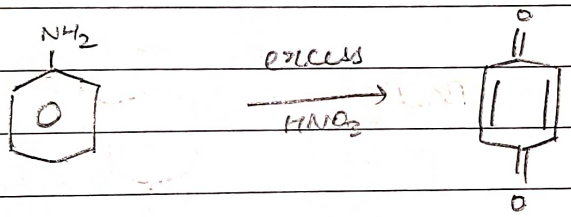
To form exclusively ortho product, we block para post. using $-SO_3H$.





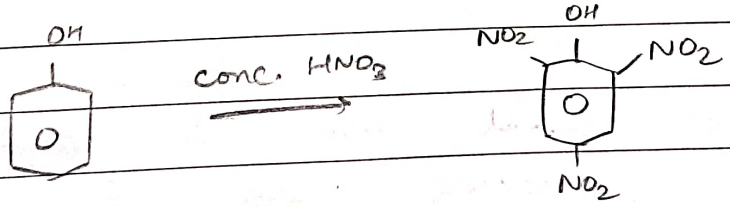
(Desulphonation)

Also,



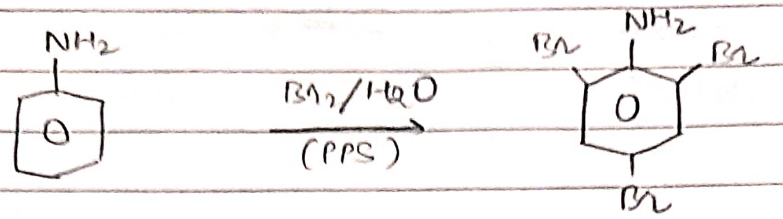
We do not need this in phenol with dil HNO_3.

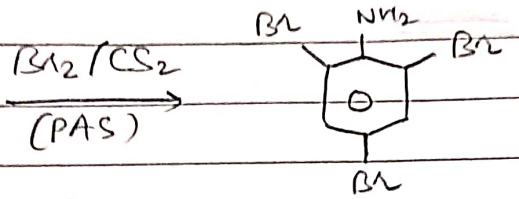
However, with conc. HNO_3



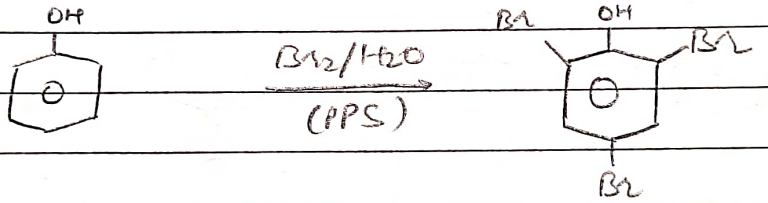
(Picric Acid)

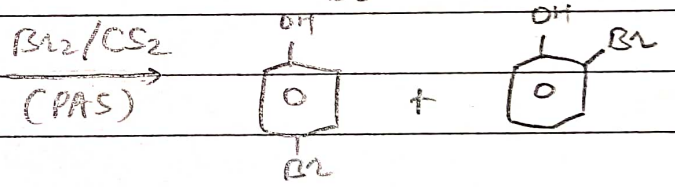
Bromination of Aniline & Phenol



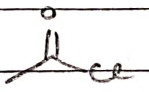
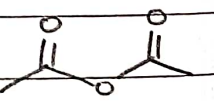


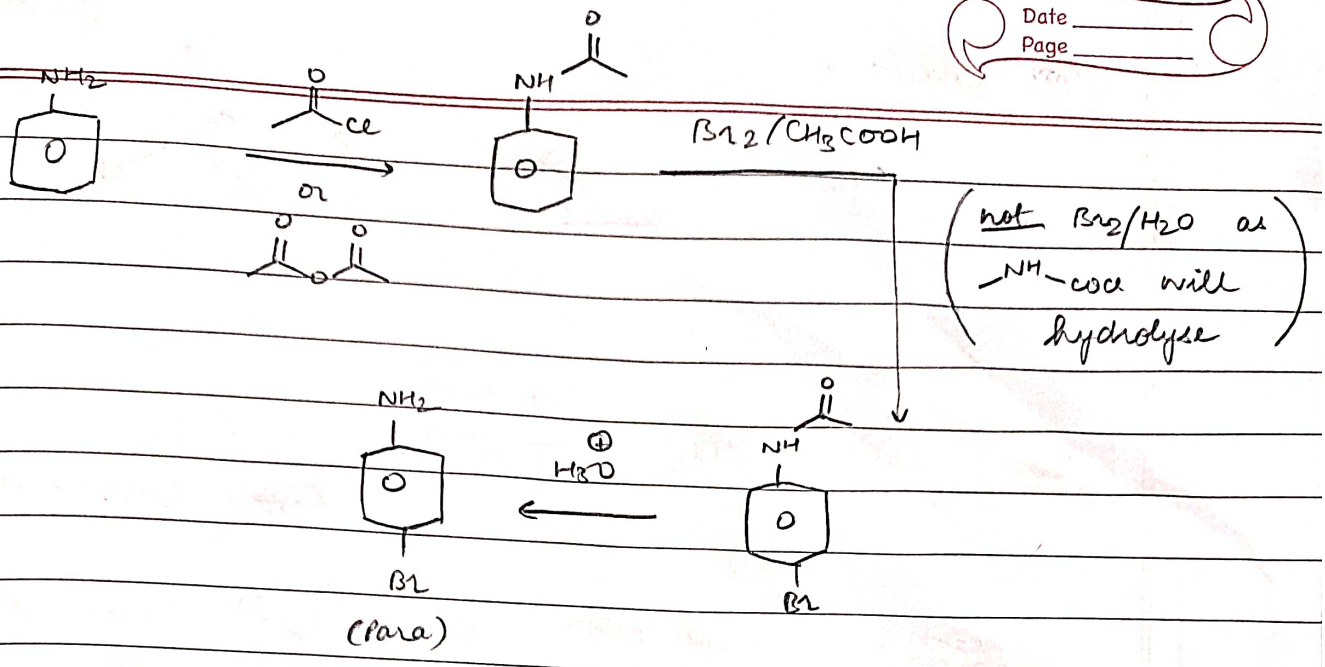
As $-NH_2$ highly activating.
Presence of PPS ↑ stability of EAS intermediate ($C^{\oplus}$)



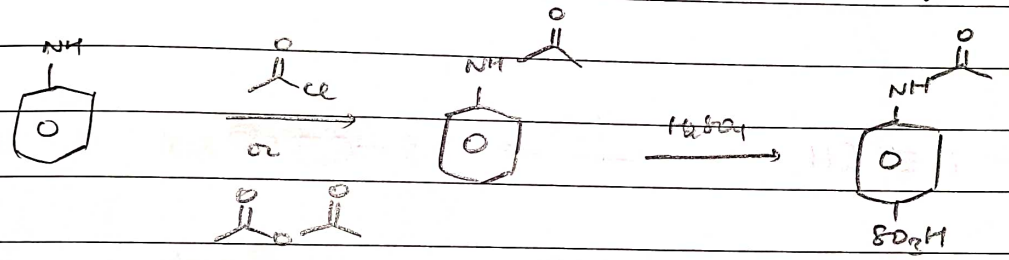


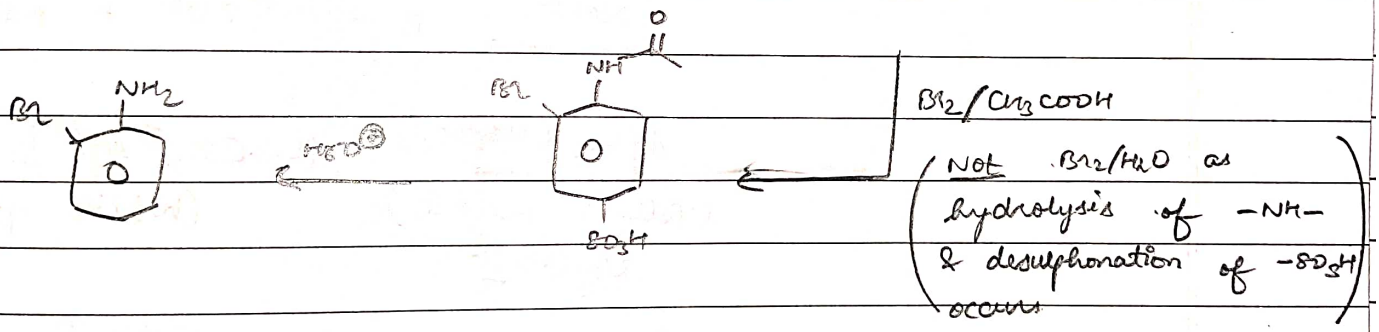
As $-OH$ activating, but <u>not</u> highly activating.

So to avoid this in Aniline, we use protecting grp  or 

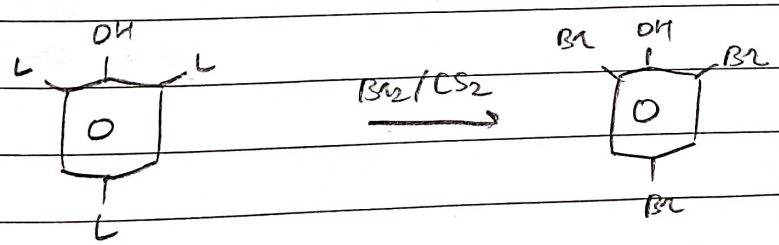


To form exclusively -ortho product, we block -para post. using SO_3H





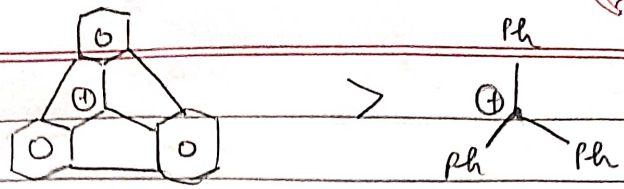
NOTE:



L = $-SO_3H$, $-COOH$, (any good L.G)

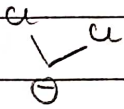
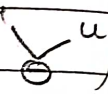
① Cross conj not considered in C⊕

② Stability :



③ $ClCH_2-CHCl_2 \xrightarrow[(1\,eq)]{alc\ KOH/\Delta} CH_2=CCl_2$

(NOT $CHCl=CHCl$)

Reason : H- more acidic as  more stable than 

TERMINAL ALKYNE DISTINCTION TESTS

$R-C\equiv CH \xrightarrow{Na} R-C\equiv C^{\ominus}Na^{+} + H_2$

$\xrightarrow{NaNH_2} R-C\equiv C^{\ominus}Na^{+} + NH_3$

$\xrightarrow[(Tollen's\ Reagent)]{AgNO_3 + NH_4OH} R-C\equiv C^{\ominus}Ag^{\oplus}\downarrow$ (White ppt.)

$[Ag(NH_3)_2]^{\oplus}$

$\xrightarrow{Cu_2Cl_2 + NH_4OH} R-C\equiv C^{\ominus}Cu^{\oplus}$ (Red ppt.)

$[Cu(NH_3)_2]^{\oplus}$ [due to Cu^{+}]