Organic Concepts Homework

Solutions to HomeWork-Sheet-2

HomeWork-Sheet-3

Based on Nucleophilic Substitution

1. In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?

faster

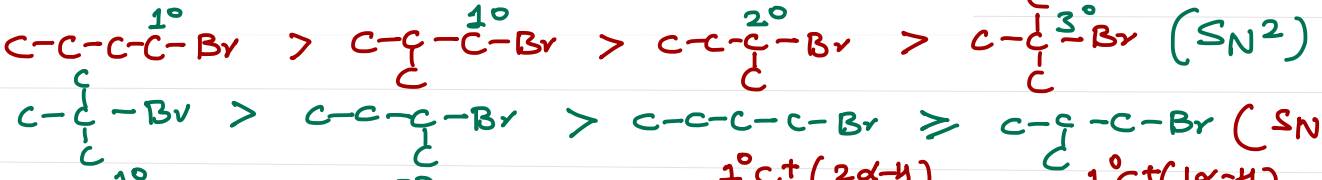
(In S_N2 path, steric hindrance is key factor)

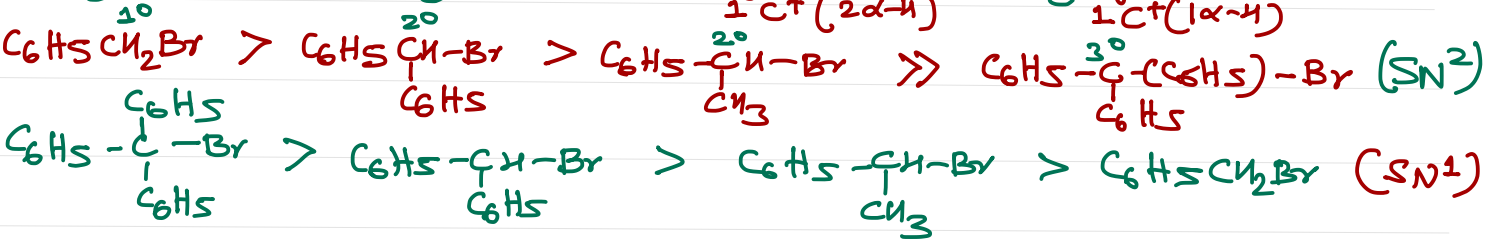
faster as I^- is better leaving group.

2. Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:

(i) The four isomeric bromobutanes

(ii) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

(i) 

(ii) 

3. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

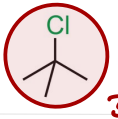
(i) $CH_3CH_2CH_2CH_2Br$ (1°) faster or $CH_3CH_2\underset{Br}{\underset{|}{C}}HCH_3$ (2°)

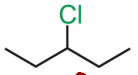
(ii) $CH_3CH_2\underset{Br}{\underset{|}{C}}HCH_3$ (2°) faster or $H_3C-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-Br$ (3°)

(iii) $CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2Br$ or $CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2Br$

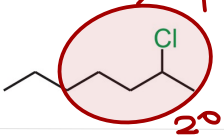
Observe steric hindrance at β-C'

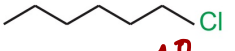
4. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction? → focus on stability of carbocation

(i) 

3° and 

2°

(ii) 

2° and 

1°

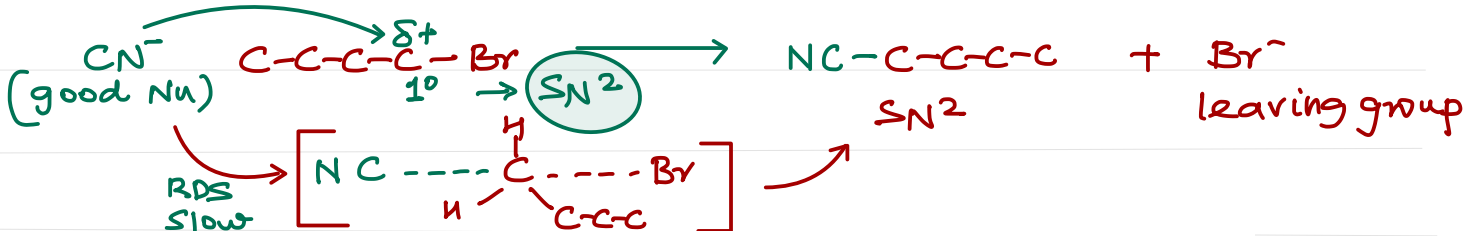
5. Which compound in each of the following pairs will react faster in S_N2 reaction with ^-OH?

(i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

I^-: better leaving group Me-Cl : has least steric hindrance

6. Write the mechanism of the following reaction:

$$nBuBr + KCN \xrightarrow{EtOH\text{-}H_2O} nBuCN$$

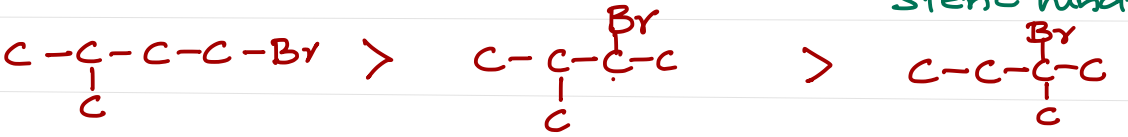


7. Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane

(i) 1-Bromopentane > 2-Bromopentane ≫ 2-Bromo-2-methyl butane
Steric hindrance

(ii) 

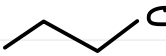
8. Identify the stronger nucleophile in each pair.

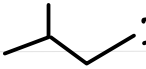
(i) Br^- & Cl^- in H_2O (ii) $\bar{S}H$ & Cl^- in MeOH (iii) $\bar{O}H$ & Cl^- in DMSO

(iv) H_2S & H_2O (v) PhO^- & PhOH (vi) PH_3 & NH_3

9. In which of the following pair of reactions; S_N2 path is faster.

I. (A)  + MeO^- $\xrightarrow{MeOH}$; (B)  + MeO^- $\xrightarrow{DMSO}$

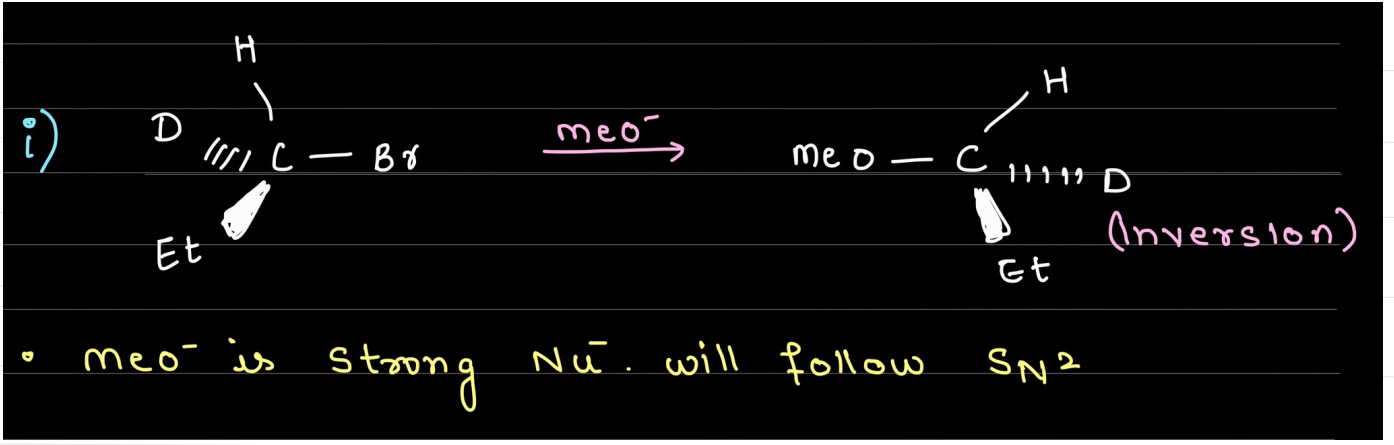
II. (A)  + $MeCOO^-$ $\longrightarrow$; (B)  + $NaOH_{aq}$ $\longrightarrow$

III (A)  + MeS^-Na^+ $\longrightarrow$; (B)  + MeS^-Na^+ $\longrightarrow$

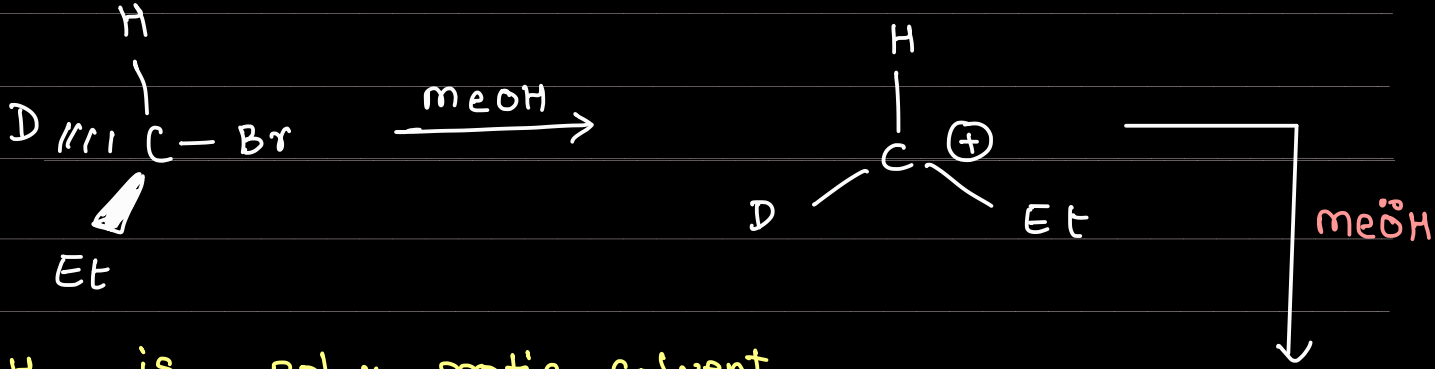
I: DMSO; Aprotic solvent favours S_N2 path

II/III: Better nucleophile increases rate of S_N2 path

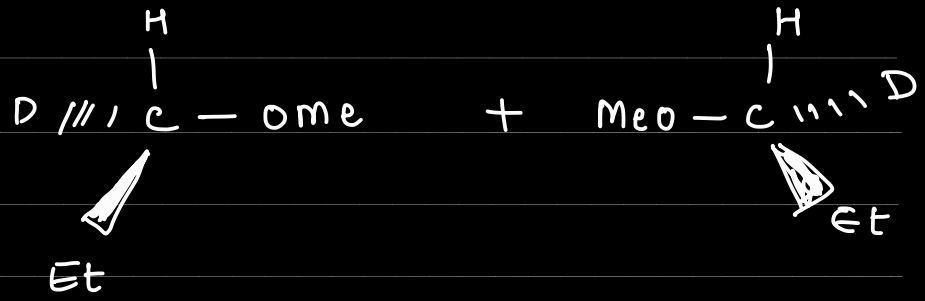
10.



(ii)

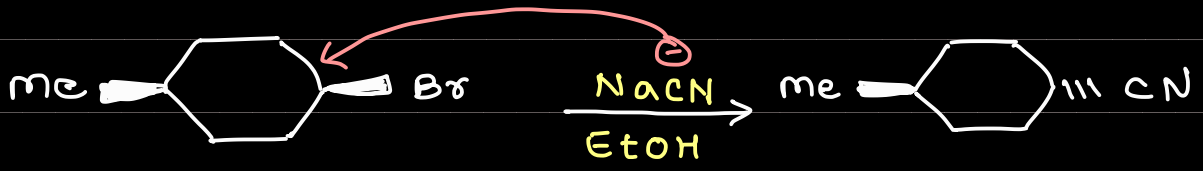


- MeOH is polar protic solvent
- MeOH is a weak Nucleophile, it will follow S_N1 Mechanism.



Racemic Product

iii)



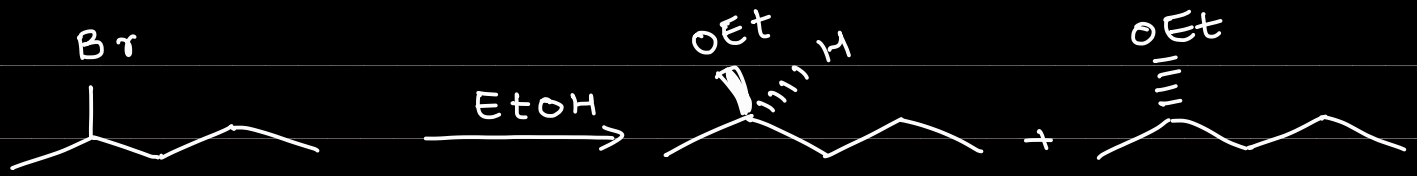
(Inversion Product)

- CN^- is a strong Nucleophile
- It will follow S_N2

iv)

- SH^- is a strong Nucleophile
- will follow S_N2.

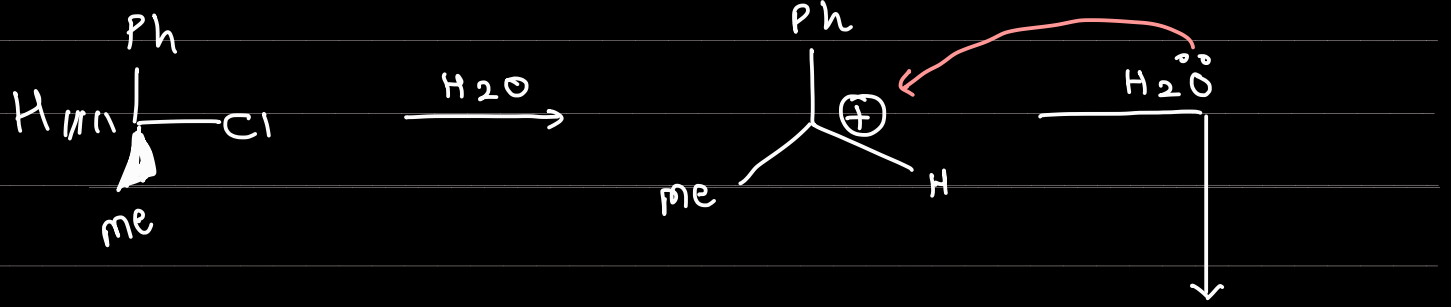
v)



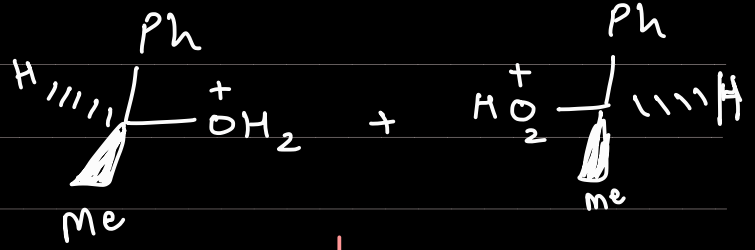
- EtOH is polar Protic Solvent
- EtOH is weak Nu^-, will follow S_N1 Mechanism

(Racemic Product)

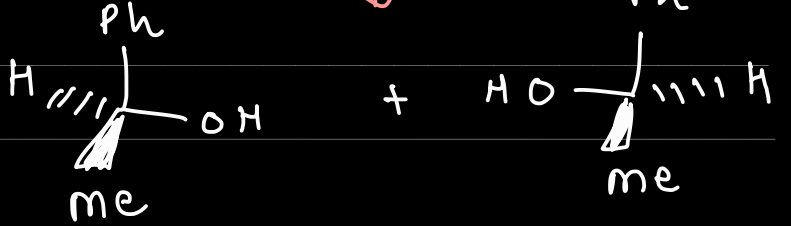
vi)



- H_2O is polar protic Solvent.
- It follow S_N1 path



(Racemic product)



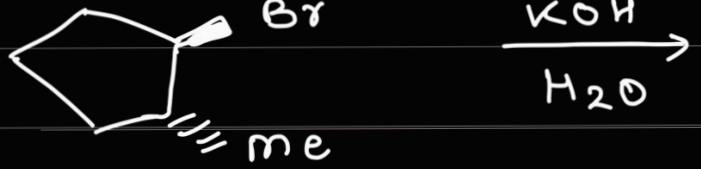
vii)

- EtOH is polar Protic Solvent.
- weak Nucleophile
- follow S_N1

Distereomers

viii)

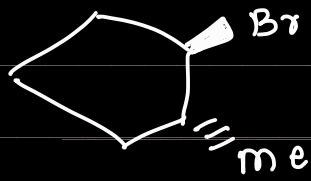
(Trans)



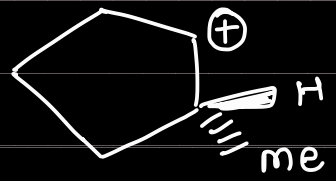
(cis)

$\bar{O}H$ is a strong Nu^- & hence S_N2 will be favoured.

ix)



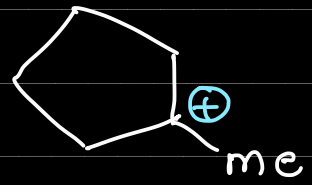
H_2O



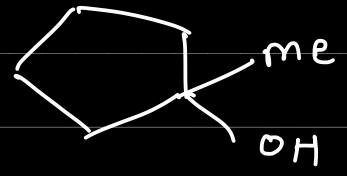
H_2O

1, 2 H^- shift

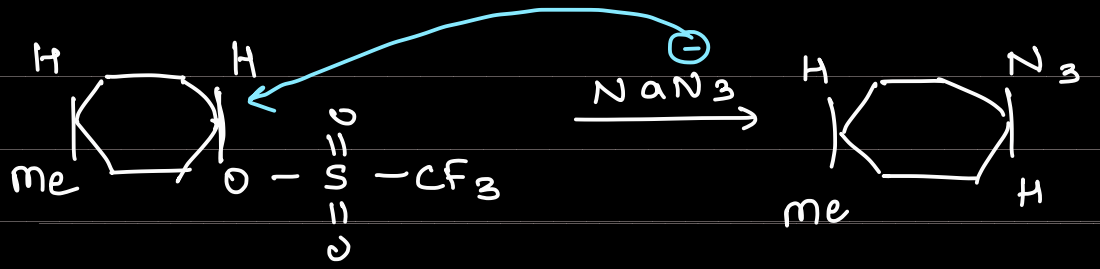
- H_2O is a polar protic solvent
- H_2O is weak Nucleophile
- It will follow S_N1



$H_2\ddot{O}$



x)



- N_3^- is Strong Nucleophile, follow S_N2

Observe : $CF_3SO_3^{\ominus}$ (Triflate ion) is a good leaving group.

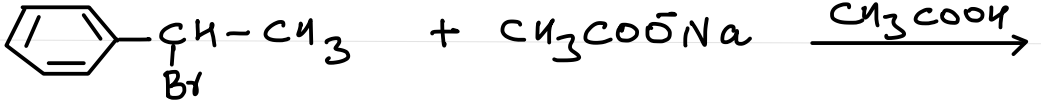
(I) Identify the product(s) & path of reaction. Identify Path.

1. $CH_3-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Br + H_2O \longrightarrow$

2. $Me_2\cdot N-CH_2Cl + MeOH \longrightarrow$

3. $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2Cl + H_2O \longrightarrow$

4. $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2Cl + KCN \xrightarrow{EtOH}$

5.  $\xrightarrow{CH_3COOH}$

6.  $\xrightarrow{EtOH}$

7.  $\longrightarrow$

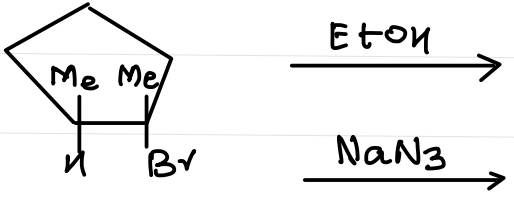
8. $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2Cl \xrightarrow{Na^+HS^-}$

9. $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2Cl \xrightarrow{H_2O}$

10. $CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3 \xrightarrow{NaN_3}$

II. a) Visualise the reaction mechanism of Finkelstein reaction.
b) Why it is a Reversible Reaction?
c) How can one force the reaction to go in forward direction

III.



comment upon stereochemistry of product also.

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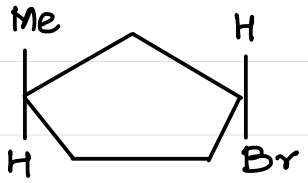
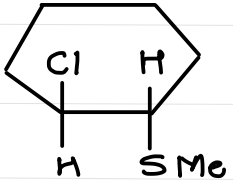
(IV)



EtOH

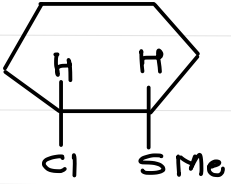
$CH_3COO^-Na^+$

(V)



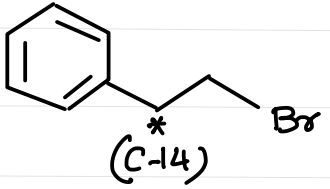
KOHaq.

(VI)

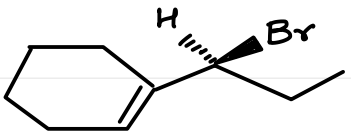


KOHaq.

(VII)

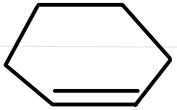


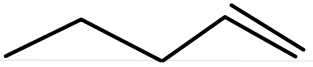
NaOH
aq.

VIII 

+ NaSH ⟶

NaOH / H_2O ⟶

IX.  Br_2 / H_2O ⟶ NaOH / Conc ⟶ MeMgBr / THF ⟶ H_2O ⟶

X.  Cl_2 / H_2O ⟶ $\bar{O}H$ / conc ⟶