Organic Concepts
Homework

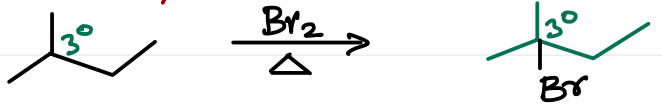
Solutions to HomeWork-Sheet-2

HomeWork-Sheet-2

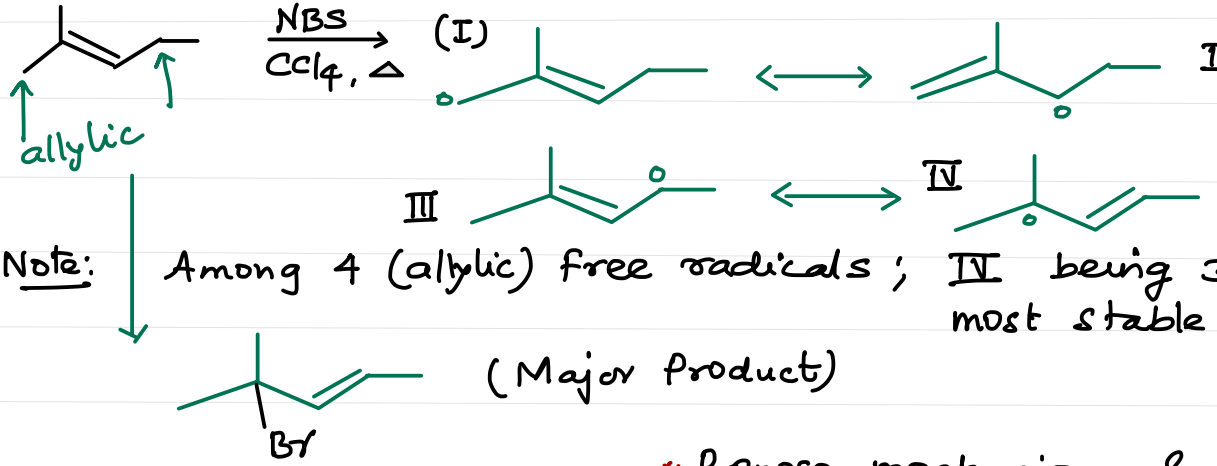
Based on Nucleophilic Substitution-II/III

(Solutions)

Q. Identify the MAJOR Product.

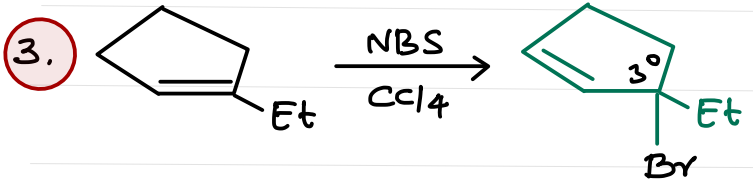
1. 

(Bromination is selective)
Free radical : $3^\circ_{FR} > 2^\circ_{FR} > 1^\circ_{FR}$

2. 

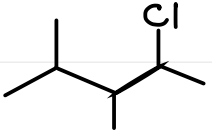
Note: Among 4 (allylic) free radicals ; IV being 3° allylic is most stable.

(Major Product)

3. 

(Major)

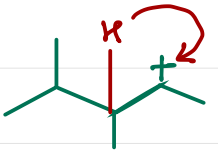
* Propose mechanism & visualise all possible products. Try Yourself on above lines

4. 

H_2O

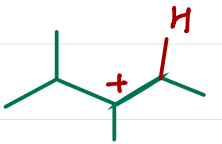
.Polar protic
. solvolysis: S_N1

(. H_2O: a weak Nu
so NO S_N2



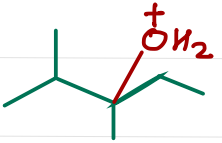
.2° carbocation
. fairly stable

H^- shift

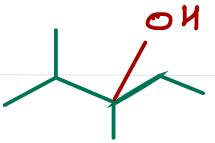


. 3° carbocation
. highly stable

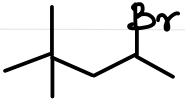
H_2O : Nu



$-H^+$



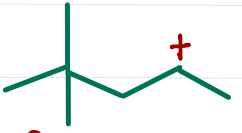
Major
(S_N1)

5. 

MeOH

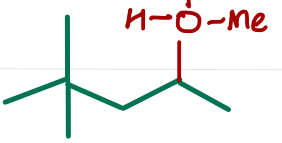
.Polar protic
. solvolysis: S_N1

(. MeOH : a weak Nu
So NO S_N2

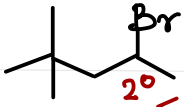


.2° carbocation
. fairly stable
. NO rearrangement
(Think Why?)

MeOH
Nu



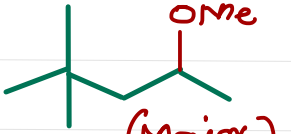
$-H^+$

6. 

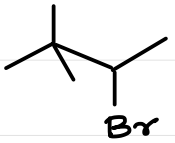
NaCN
DMSO

. Aprotic solvent
. CN^-; Strong Nu
. S_N2

only product
(S_N2)



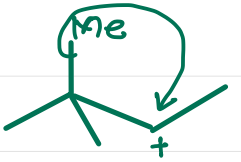
(Major)
S_N1

7. 

EtOH

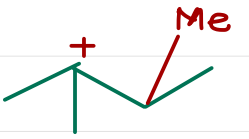
- Polar protic
- Solvolysis: S_N1

(- EtOH: a weak Nu
So NO S_N2)



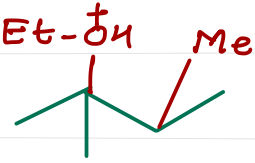
- 2° carbocation

Me^- shift

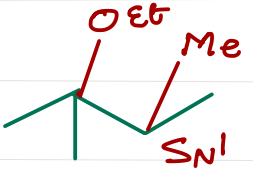


- 3° carbocation

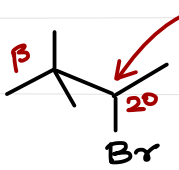
EtOH (Nu)



$-H^+$



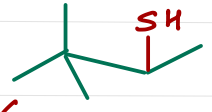
S_N1 (Major)

8. 

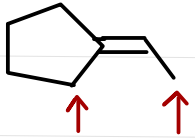
NaSH

- $\bar{S}H$: a strong Nu
- S_N2

- Slow S_N2 as there is steric hindrance at β-C



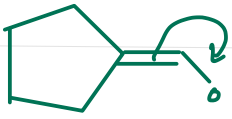
(S_N2 product)

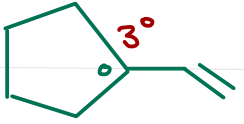
9. 

(allylic)

NBS

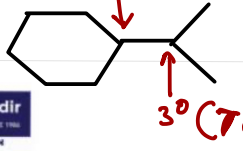
CCl_4, Δ





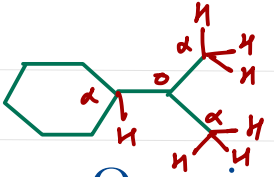
Br° or Br_2

(Major)

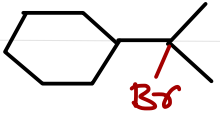
10. 

Br_2

Δ



7 α-H ≡ 7- hyperconjugative structure



(Major)

Organic Concepts

Q2. Arrange the following in decreasing order of:

1. PhO^-, $\bar{O}H$, $MeCOO^-$, MeS^- (Nucleophilicity)
2. F^-, $\bar{C}H_3$, MeO^-, $\bar{N}H_2$ (Basicity)
3. F^-, $\bar{C}H_3$, MeO^-, $\bar{N}H_2$ (Nucleophilicity)
4. F^-, Br^-, I^-, Cl^- Basicity in H_2O

1. MeS^- > $\bar{O}H$ > PhO^- > CH_3COO^-
   (MeS^-: large sized Nucleophilic atom)
   stronger base is better nucleophile

2. $\bar{C}H_3$ > $\bar{N}H_2$ > MeO^- > F^-
   conjugate base of weak acid is stronger

3. $\bar{C}H_3$ > $\bar{N}H_2$ > MeO^- > F^-
   Nucleophilicity decreases across a period from left to right

4. F^- > Cl^- > Br^- > I^-
   conjugate base of weak acid is stronger

5. F^-, Br^-, I^-, Cl^- Nucleophilicity in H_2O

6. F^-, Br^-, I^-, Cl^- Nucleophilicity in DMSO

7. CN^-, MeS^-, Cl^-, I^-, MeO^- Nucleophilicity in CH_3OH

8. 2-Bromopane , 1-Bromopropane, 2-Bromo-2-methylpropane, bromomethane

Ease of S_N2 reaction

(5.) $I^- > Br^- > Cl^- > F^-$

decreasing size of nucleophilic atom leads to decreasing polarizability

(6.) $F^- > Cl^- > Br^- > I^-$

smaller anion is poorly solvated by ion-dipole interaction with Aprotic solvent (DMSO)

(7.) $MeS^- > I^- > \bar{C}N > MeO^- > Cl^-$ (in MeOH: Protic)

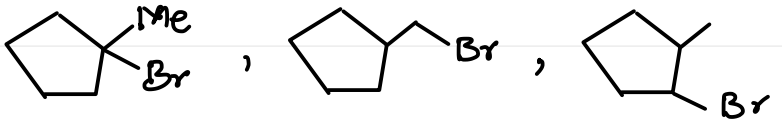
(learn as fact)

(8.) $CH_3Br > CH_3CH_2\overset{1^\circ}{C}H_2Br > CH_3-\overset{2^\circ}{C}H(Br)-CH_3 \gg CH_3-\overset{3^\circ}{C}(Br)(Me)-CH_3$

Zero steric hindrance → Increasing steric hindrance →

9. 2-Bromopentane, 2-Chloropentane, 3-Bromo-3-methyl pentane, 1-Chloropentane

Ease of S_N1 reaction

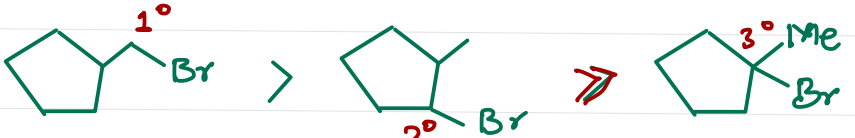
10. 

Ease of S_N2 reaction

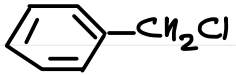
9. 

(∵ Br^- is better leaving group)

⟶ decreasing stability of carbocation

10. 

⟶ increasing steric hindrance from 1° → 2° → 3°

11.  + R_1 : KCN/alc ⟶

+ R_2 : NaSH/H_2O ⟶

+ R_3 : NaOH/H_2O ⟶

Ease of S_N2 reaction with respect to Reagents : R_1 , R_2 & R_3

11.  : 1° (benzyl chloride) + S_N2 conditions ⟶ S_N2 Path (R_1 , R_2 , R_3) very good nucleophiles.

Observe the decreasing ease of strength of nucleophiles --- thus decreasing ease of S_N2

$\bar{S}H > \bar{C}N > \bar{O}H$

hence decreasing ease of S_N2 ($R_2 > R_1 > R_3$)

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

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

(i) The four isomeric bromobutanes

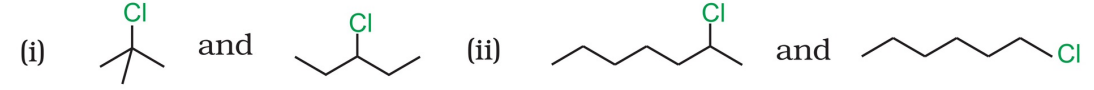
(ii) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

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

(i) $CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ (ii) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ or $H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-Br$

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

4. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?



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

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

8. Identify the stronger nucleophile in each pair.

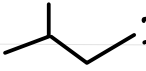
(i) Br^- & Cl^- in H_2O (ii) $\bar{S}H$ & Cl^- in MeOH (iii) $\bar{O}H$ & Cl^- in DMSO

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

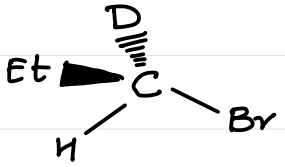
9. In which of the following pair of reactions; S_N2 path is faster.

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

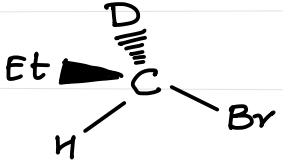
II. (A)  + $MeCOO^-$ $\longrightarrow$; (B)  + $NaOH_{aq}$ $\longrightarrow$

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

10. Write the structure of end product(s).

(i) 

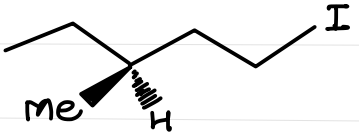
$\xrightarrow{MeO^-}$

(ii) 

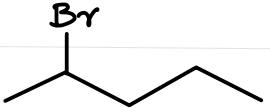
$\xrightarrow{MeOH}$

(iii) 

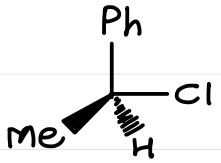
$\xrightarrow[EtOH]{NaCN}$

(iv) 

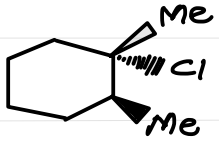
$\xrightarrow{Na^+ \bar{S}H}$

(v) 

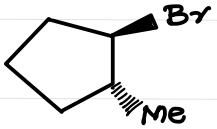
$\xrightarrow{EtOH}$

(vi) 

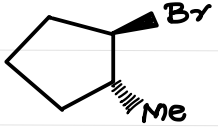
$\xrightarrow{H_2O}$

(vii) 

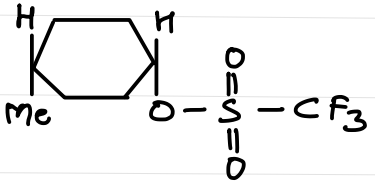
$\xrightarrow{EtOH}$

(viii) 

$\xrightarrow[H_2O]{KOH}$

(ix) 

$\xrightarrow{H_2O}$

(x) 

$\xrightarrow{NaN_3}$