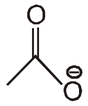
TOPIC : REACTION MECHANISM
EXERCISE # 1

SECTION (A)

5. CN^- is a nucleophile due to presence of negative charge.

7. On going left to right in period nucleophilicity decreases.

8. CN^- is an ambident nucleophile because it has two lone pair donar atom (C and N).

9.

is resonance stabilised.

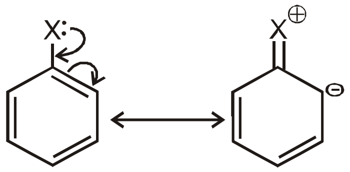
SECTION (B)

3. S_N1 reactions occur through the intermediate formation of carbocations.

4. S_N1 reactions are favoured by bulky groups on the carbon atom attached to the halogen atom.

7. $(C_6H_5)_3CCl$ give most stable carbocation.

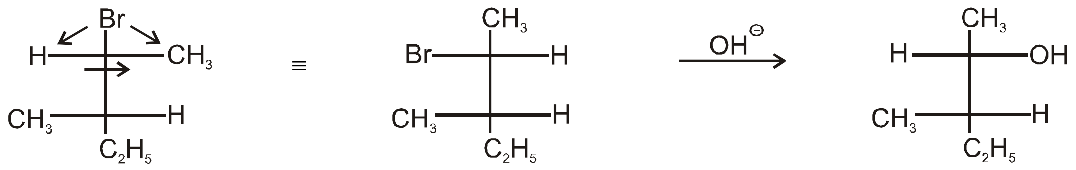
15. In aryl halides the C – X bond has partial double bond character due to resonance so the cleavage of C – X bond becomes difficult.



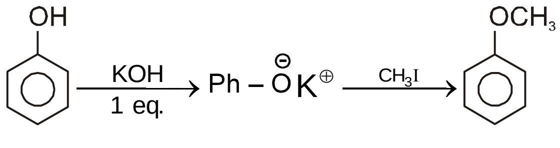
SECTION (C)

3. $R-X + KCN \xrightarrow{alcohol} R-C\equiv N$

4. $CH_3Br + AgCN \xrightarrow{alcohol} CH_3-N\equiv C$

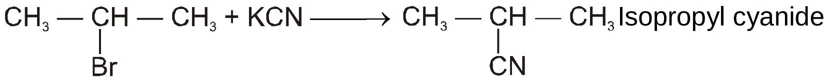
7.


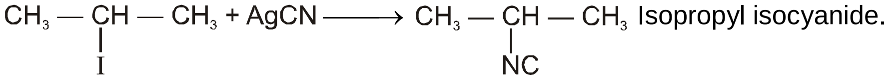
9. $CH_3-C\equiv CH \xrightarrow{Na} CH_3-C\equiv C^-Na^+ \xrightarrow{CH_3-CH_2-I} CH_3-C\equiv C-CH_2-CH_3$

10.


12. S_N2 mechanism is single step concerted process and transition state is fromed.

13. (1) $CH_3 — CH_2 — CH_2 — I + AgCN \longrightarrow CH_3 — CH_2 — CH_2 — NC$ n-propyl isocyanide.

(2) 
$CH_3 — \underset{Br}{CH} — CH_3 + KCN \longrightarrow CH_3 — \underset{CN}{CH} — CH_3$ Isopropyl cyanide

(3) 
$CH_3 — \underset{I}{CH} — CH_3 + AgCN \longrightarrow CH_3 — \underset{NC}{CH} — CH_3$ Isopropyl isocyanide.

(4) $(CH_3)_2\ CHCl + HCN \longrightarrow$ no. reaction.

14. 1, 2 and 4 are highly crowded molecules so they do not give S_N2 reaction.

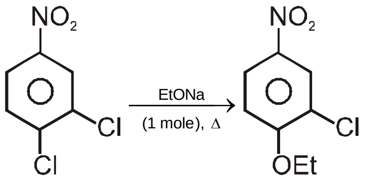
15. $C_2H_5Br + C_2H_5ONa \xrightarrow{S_N2} C_2H_5OC_2H_5$

SECTION (D)

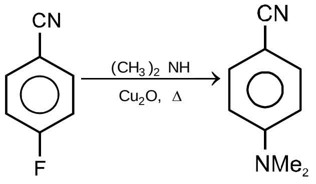
1. Because rate of S_N2 Ar is (–F > –Cl > –Br > –I) and –M groups at o/p- positions also increases rate of S_N2 Ar.

2. Electron withdrawing groups at ortho-para increases the reactivity of arylhalides

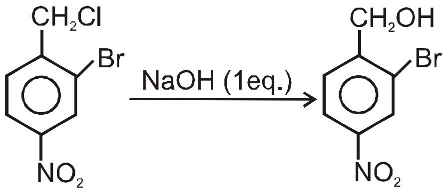
3. It is S_N2 Ar reaction. $F^{\ominus}$ is L.G., $CH_3O^{\ominus}$ is nucleophile.

4. 

[– M of $–NO_2$ at para position]

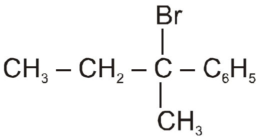
5. 

(S_N2 Ar)

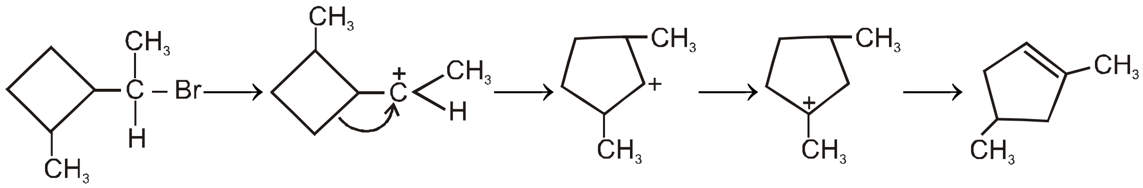
6. 

SECTION (E)

1. Elimination reaction generally occurs with the formation of one pi bond.

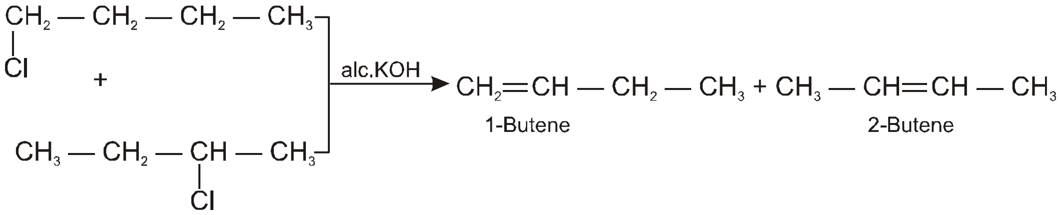
3. 
$CH_3 – CH_2 – \overset{Br}{\underset{CH_3}{C}} – C_6H_5$ produce most stable carbocation.

8. Carbocation of (1) is CPM which is most stable carbocation.

10. 

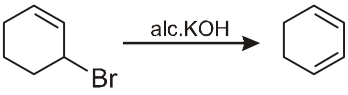
Section (F)

4.



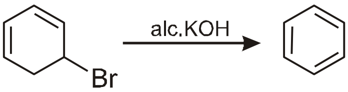
$$\left.\begin{array}{l} \underset{\displaystyle Cl}{CH_2} - CH_2 - CH_2 - CH_3 \\ + \\ CH_3 - CH_2 - \underset{\displaystyle Cl}{CH} - CH_3 \end{array}\right] \xrightarrow{alc.KOH} \underset{\text{1-Butene}}{CH_2{=}CH - CH_2 - CH_3} + \underset{\text{2-Butene}}{CH_3 - CH{=}CH - CH_3}$$

5. (1)



Stable by resonance and hyperconjugation

(2)

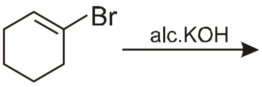


More stable product due to resonance of 6πe⁻

(3)

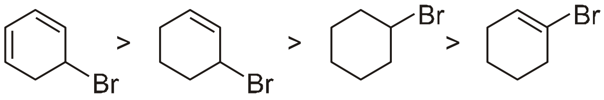
Stable by only hyperconjugation

(4)



No reaction

∴ Rate of de-bromination is



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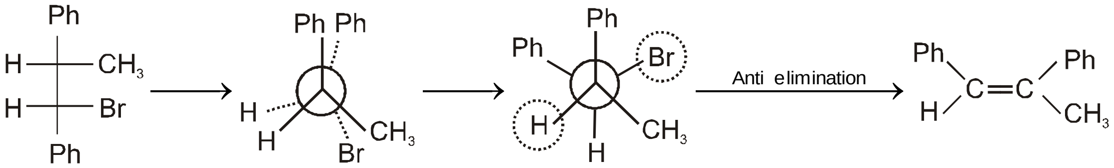
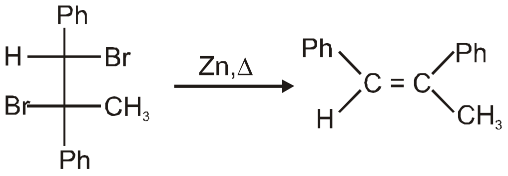
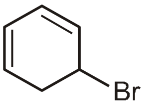


10.



(Anti–elimination)

15.

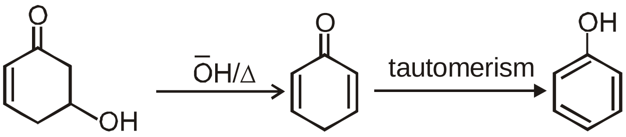


give benzene on elimination which is aromatic in nature.

16. But-2-ene is saytzeff's alkene.

SECTION (G)

5.



SECTION (H)

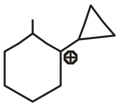
6. In Lucas test of alcohols, the appearance of cloudiness is due to the formation of alkyl chlorides

7. IV give most stable carbocation while I form least stable carbocation.

9. Thionyl chloride method is preferred over phosphorous pentachloride method for the preparation of alkyl chloride because, the by products being gases escape into the atmosphere leaving behind almost pure alkyl chloride.

10. It is S_Ni mech so retention of configuration take place in the product.

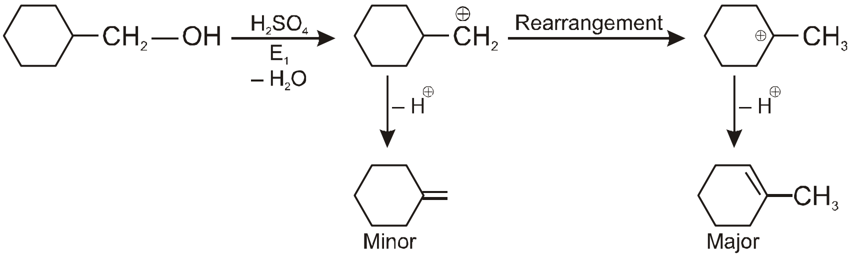
11. It is S_N2 mech so inversion of configuration take place in the product

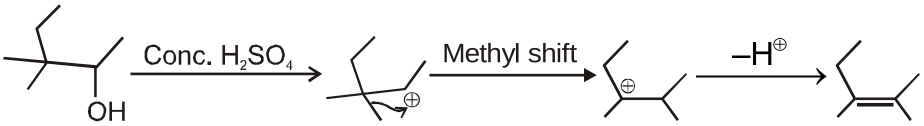
12.  (Most stable carbocation)

SECTION (I)

1. Dehydration of alcohol is an example of elimination reaction.

2. H_2SO_4, Al_2O_3 and H_3PO_4 all are dehydrating agent.

4. 

5. 

6. According to stability of carbocation.

SECTION (J)

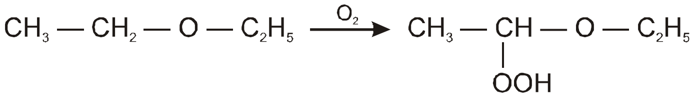
1. 1º R-X gives S_N2 reaction fastest and 3º R-X gives S_N1 reaction fastest.

2. $CH_2=CH–CH_2–Cl > CH_3–CH_2–CH_2–Cl > CH_3–CH=CH–Cl$

3. Rate of S_N2 reaction : 1º > 2º > 3º, as β-branching increases steric crowding increases in transition state so it makes less stable T.S.

SECTION (K)

1. $C_2H_5 - \boxed{I + Ag} - \underset{\text{Dry}}{O} - \boxed{Ag + I} - C_2H_5 \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5 - O - C_2H_5} + 2AgI$

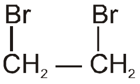
2. 

$CH_3 - CH_2 - O - C_2H_5 \xrightarrow{O_2} CH_3 - \underset{OOH}{\underset{|}{CH}} - O - C_2H_5$

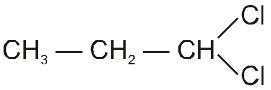
Ether peroxide

4. $CH_3 - CH_2 - CH_2 - O - CH_3 \xrightarrow{HCl\ (1eq)} CH_3 - CH_2 - CH_2 - OH + CH_3 - Cl$

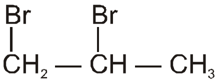
SECTION (L)

1. (1) 

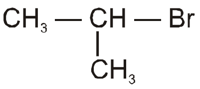
$\overset{Br}{\overset{|}{CH_2}} - \overset{Br}{\overset{|}{CH_2}}$ vicinal dihalides.

(2) 

$CH_3 - CH_2 - CH\begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$ gem dihalides.

(3) 

$\overset{Br}{\overset{|}{CH_2}} - \overset{Br}{\overset{|}{CH}} - CH_3$ vicinal dihalides.

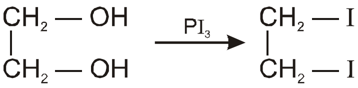
(4) 

$CH_3 - \underset{CH_3}{\underset{|}{CH}} - Br$ secondary alkyl halides.

2. $\underset{\text{Chloroform}}{CHCl_3} \xrightarrow[\text{light of sun}]{\text{Air}} \underset{\text{Phosgene}}{COCl_2}$

3. Impure chloroform give white ppt. of AgCl due to presence of HCl.

4. CHI_3 give yellow ppt. with $AgNO_3$ solution.

9. 

$\begin{matrix} CH_2 - OH \\ | \\ CH_2 - OH \end{matrix} \xrightarrow{PI_3} \begin{matrix} CH_2 - I \\ | \\ CH_2 - I \end{matrix}$

10. Alcohols form intermolecular hydrogen bonding so they have higher boiling points than hydrocarbon.

11. In option (3) all three hydoxy groups are directly attached to secondary carbon atoms.

12. It is fact.

EXERCISE # 2

2. $AlCl_3$ is electron deficient species thus it is a lewis acid.

3. $\overset{\oplus}{N}H_4$ do not have lone pair of electron.

4. Strength of nucleophile generally increases on going down a group in the periodic table, because polarising strength of anion increases.

5. Sulphur belongs to IIIrd period so it has maximum nucleophilicity.

6. Leaving group abilibity $\propto$ size of leaving atom.

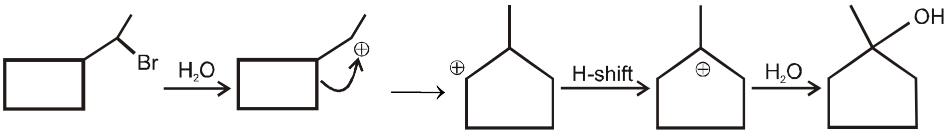
7. On going top to bottom in group nucleophilicity increases.

9. Reactivity of alkyl halides for S_N1 reaction is 3° > 2° > 1°.
So, option (4) is correct because it form more stable carbocation.

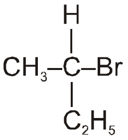
10. p-methoxy benzyl carbocation is most stable among these due to +M effect of $-OCH_3$.

11. S_N2 reaction involves transition state, there is no intermediate.

15.



16.

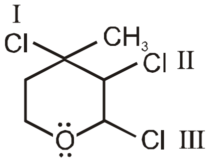


$CH_3-\overset{H}{\underset{C_2H_5}{C}}-Br$ give racemic mixture in S_N1 reaction because it has chiral carbon.

17. Ter-butyl carbocation is most stable among these so (1) give fastest S_N1.

19. Rate of solvolysis ∝ stability of carbocation

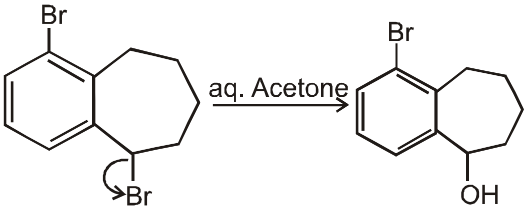
20.



$\xrightarrow{AgNO_3}$ S_N1 Reaction

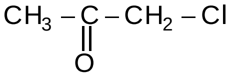
Reaction Intermediate — Carbocation :
III will give most stable carbocation ⇒ stabilised by +m effect of $-\ddot{\underset{..}{O}}-$
I will give stable carbocation $\longrightarrow$ 3° carbocation so order of reaction = III > I > II.

21.



In aryl halides the C–X bond has partial double bond character due to resonance so it will not give S_N1 reaction.

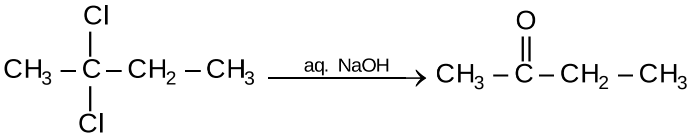
29.



$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-Cl$ is most reactive due to –I effect of C=O group.

30. It is S_N2 reaction.

31.

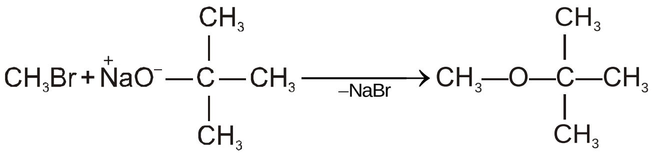


$$CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_2-CH_3 \xrightarrow{aq.\ NaOH} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

32. In S_N2 reaction the nucleophile always attack from back side therefore a single stereoisomer is formed with inverted configuration.

34. $CH_3-CH_3 \xrightarrow{Cl_2/h\nu} CH_3-CH_2-Cl \xrightarrow{KCN} CH_3-CH_2-CN$

35. t-butyl methyl ehter is a mixed ether and for the preparation of mixed ethers in high yield the essential condition is the use of primary alkyl halide.
Thus,



$$CH_3Br+\overset{+}{Na}O^{-}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow[-NaBr]{} CH_3-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

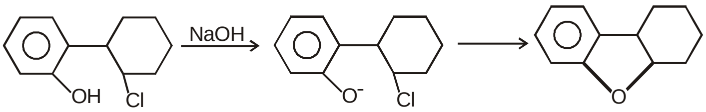
(This reaction is williamson's synthesis.)

t-butyl methyl ether

36. Inversion takes place in S_N2 reaction while configuration of nucleophile remains same.

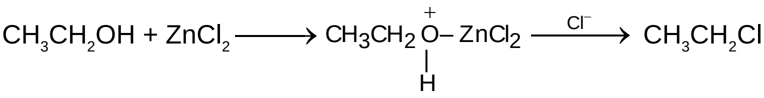
38. 1^o allyl halide gives most readily S_N2 reaction.

39. Intramolecular S_N2 reaction



41. $R-X+KCN \xrightarrow{alcohol} R-C\equiv N$

44.



$$CH_3CH_2OH + ZnCl_2 \longrightarrow CH_3CH_2\underset{H}{\overset{+}{O}}-ZnCl_2 \xrightarrow{Cl^-} CH_3CH_2Cl$$

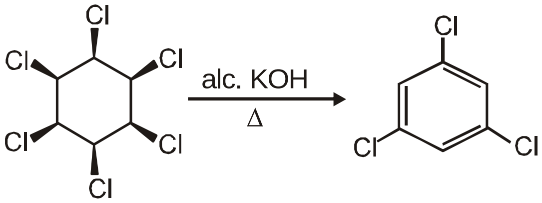
45. It is S_Ni reaction so retention takes place

46. It is S_N2 reaction so inversion takes place.

47. It is S_Ni reaction so retension takes place.

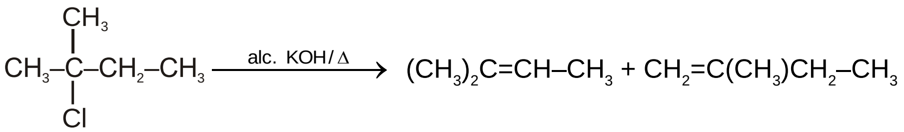
48. It is S_N1 reaction so racemisation occurs,

56.



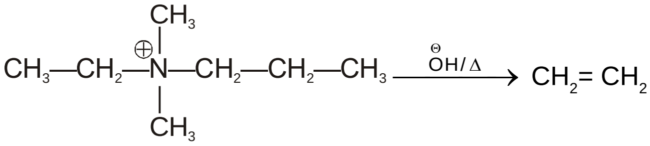
57. Bulky base give Hoffmann alkene as major product.

58.



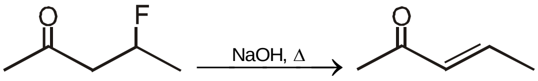
$$CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_2-CH_3 \xrightarrow{alc.\ KOH/\Delta} (CH_3)_2C=CH-CH_3 + CH_2=C(CH_3)CH_2-CH_3$$

59.

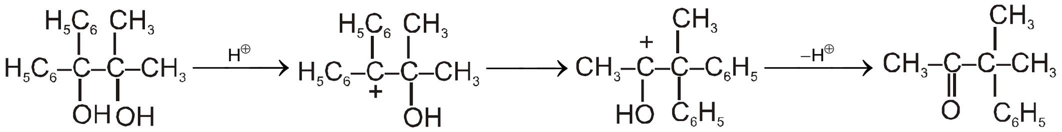


$$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{\oplus}{N}}}-CH_2-CH_2-CH_3 \xrightarrow{\overset{\ominus}{O}H/\Delta} CH_2=CH_2$$

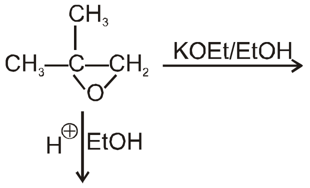
60. All the three have more acdic β–Hydrogen so in presence of strong base give product through E1cB reaction.

61.  (E1cB mechanism)

62. In dehydration of alcohol, β-hydrogen atom (sp^3 hybridised) must be present in compound.

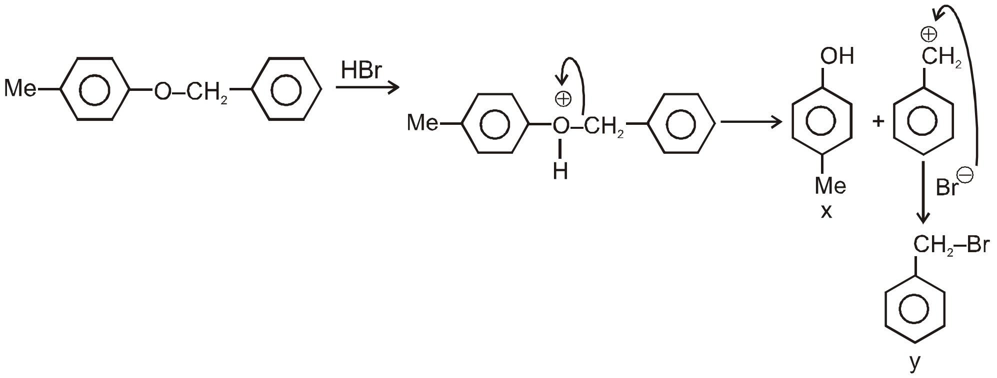
64. 

65. $PhCH_2CH_2OH \xrightarrow{TsCl} PhCH_2CH_2OTs \xrightarrow{KBr} PhCH_2CH_2Br \xrightarrow{alc.\ KOH} PhCH{=}CH_2$

70. 

In basic medium S_N2 product $Nu^{\ominus}$ attack at less crowded side.

In acidic medium S_N1 type product, $Nu^{\ominus}$ attack at crowded side.

71. 

72. Ethanol used to make Phosgene non-poisonous because it form diethyl carbonate with phosgene.

73. It is fact.

75. $CH_3CH_2\,Br + N{\oplus}a\ C{\ominus} \equiv CH \longrightarrow CH_3CH_2C \equiv CH + NaBr$

Ethylbromide sodium acetylide 1-butyne

EXERCISE # 3

PART - I

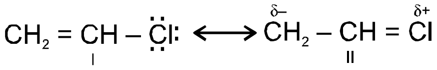
1. F, Cl, Br and I are the elements of VII A group. In A group atomic, radii increases from top to bottom and the bond dissociation energy decreases as -

R – F > R – Cl > R – Br > R – 1

So, during dehydrohalogenation R – I bond breaks more easily than R – F bond. Hence, order of reactivity will be -

R – I > R – Br > R – Cl > R – F

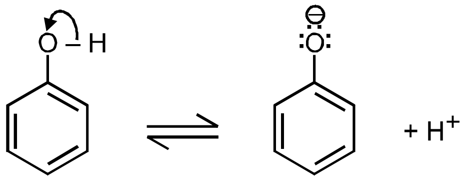
2. Chlorine of vinyl chloride (CH_2 = CHCl) is non-reactive (less reactive) towards nucleophile in nucleophilic substitution reaction because it shows the following resonating structure due to + M effect of – Cl atom.



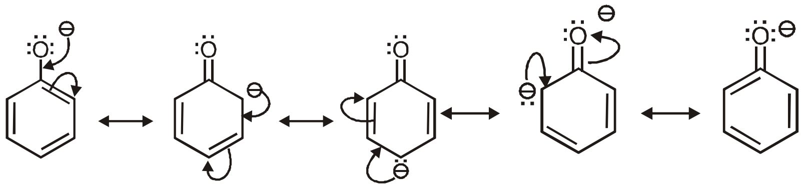
$$\underset{I}{CH_2=CH-\ddot{\underset{\cdot\cdot}{Cl}}:} \longleftrightarrow \underset{II}{\overset{\delta-}{C}H_2-CH=\overset{\delta+}{Cl}}$$

In structure II, Cl-atom have positive charge and partial double bond character with C of vinyl group, so it is more tightly attracted towards the nucleus and it does not get replaced by nucleophile in S_N reaction.

3. Phenols are much more acidic than alcohols, due to the stabilisation of phenoxide ion by resonance.



Phenoxide ion is stablized due to following resonating structures :



While in alcohols

$$R - \ddot{\underset{..}{O}}\!:\! - H \rightleftharpoons R - \ddot{\underset{..}{O}}\!:^{-} - H^{+}$$

Alcohol (not stabilized due to absence of resonance)

Ortho nitrophenoles most acidic because in it $-NO_2$ electron attracting group is attached on ortho position which helps in stabilizing of negative charge on the oxygen of phenoxide ion. Hence, due to this reason acidic character of phenol increased, while on attachment of $-CH_3$ group (electron donating group) acidic strength of phenol decreased in cresol due to destabilization of phenoxide ion.

5. $CH_3 - O - CH(CH_3)_2 + HI \xrightarrow{373\,K} H_3Cl + (CH_3)_2\ CHOH$

In case of unsymmertical ether, the alkyl halide is always formed from smaller alkyl group. This happen so, because I^- ion being larger in size approaches smaller alkyl group to avoid steric hindrance.

7. The relative reactivity of alkyl halides towards S_N2 reactions is an follows :

Primary > Secondary > Tertiary

However, if the primary alkyl halide or the nucleophile/base is sterically hindered the nucleophile will have difficulty to getting the back side of the carbon as a result of this, the elimination product will be predominant. Here CH_3CH_2Br is the least hindered, hence it has the highest relative rate towards S_N2 reaction.

8. Nucleophilic substitution reactions involve substitution (replacement) of a group or atom by a nucleophile.

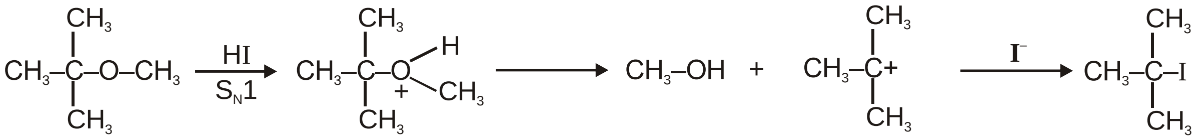
$$KOH \longrightarrow K^{+} + OH^{-}$$

$$RX + \underset{\text{nucleophile}}{OH^{-}} \longrightarrow R - OH + KX$$

Nucleophiles are either negative charge or lone pair of electrons bearing species, e, OH^-, $\ddot{N}H_3$ etc.

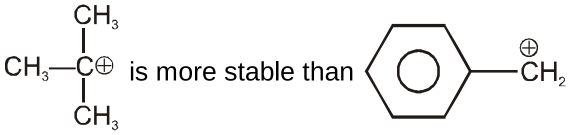
9. First reaction is S_N1 reaction because C_2H_5OH used as solvent which is a weak nucleophile.
Second reaction is S_N2 reaction because $C_2H_5O^-$ is strong nucleophile.

10.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3 \xrightarrow[S_N1]{HI} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{O}(H)CH_3 \longrightarrow CH_3-OH + CH_3-\overset{CH_3}{\underset{CH_3}{C}}{+} \xrightarrow{I^-} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-I$$

11.



12. It is Williamson-synthesis reaction

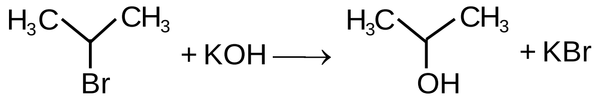
13. Lucas reagent in I & IV while S_N1 in III

15. Inversion product will be more than retention product due to close ion pair formation.

16. (a) $CH_3CH_2CH_2Br + KOH \longrightarrow CH_3CH=CH_2 + KBr + H_2O \longrightarrow$ Elimination reaction

Formation of π-bond and conversion of saturated compound into unsaturated compound by the removal of groups or atoms is known as Elimination reaction

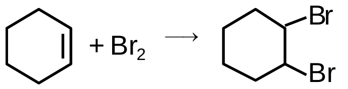
(b)



$\longrightarrow$ Substitution Reaction

Replacement of one group by other group known as Substitution Reaction

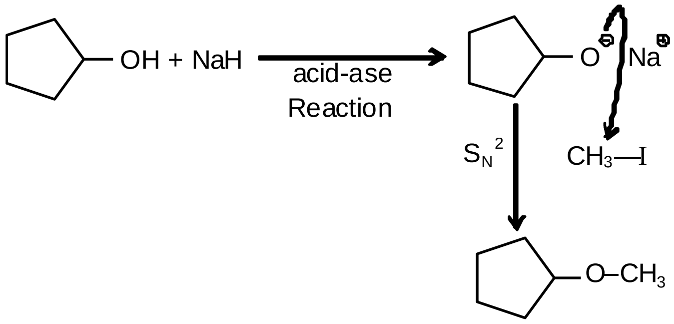
(c)



$\longrightarrow$ addition reaction

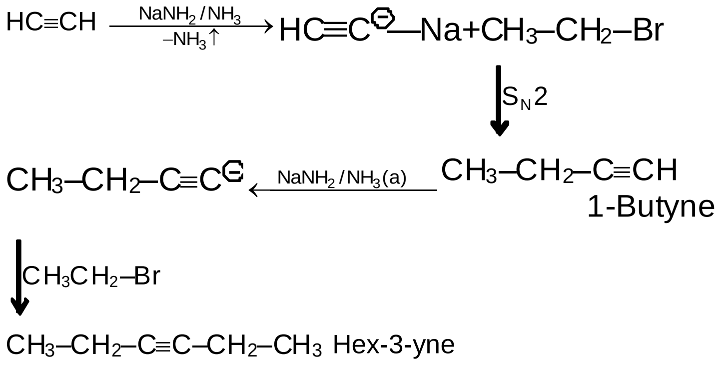
Conversion of unsaturated compound into saturated compound by the addition of groups or atoms is called as addition reaction.

17.



This williamson ether synthesis

18.



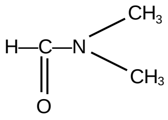
$HC\equiv CH \xrightarrow[-NH_3\uparrow]{NaNH_2/NH_3} HC\equiv C^{\ominus}—Na + CH_3-CH_2-Br$

$\downarrow S_N2$

$CH_3-CH_2-C\equiv C^{\ominus} \xleftarrow{NaNH_2/NH_3(a)} CH_3-CH_2-C\equiv CH$ 1-Butyne

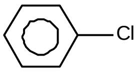
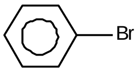
$\downarrow CH_3CH_2-Br$

$CH_3-CH_2-C\equiv C-CH_2-CH_3$ Hex-3-yne

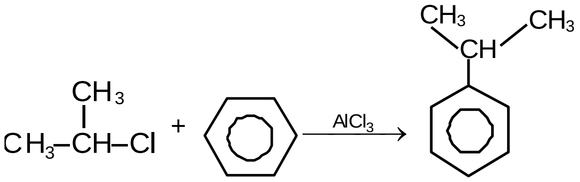
19.  (Polar aprotic solvent)

$CH_3—CH_2—CH_2—Br + NaCN \longrightarrow CH_3—CH_2—CH_2—CN + NaBr$

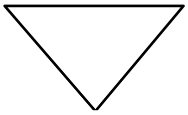
This is a S_N2 Reaction for which polar aprotic medium is suitable for faster rate of reaction.

20. $CH_2=CH–Cl$,  , 

Not suitable for friedal-craft Reaction in Benzene. Isopropyl chlrodie is suitable.



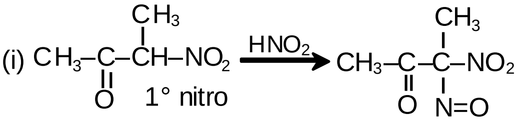
21. (i) $CH_3–CH_2–CH_2–Br \xrightarrow{\text{elimination}} CH_3–CH=CH_2$

(ii)  $\xrightarrow{\text{elimination}} CH_3–CH=CH_2$

(iii) $CH_3–CH_2–CH_2–OH \xrightarrow{HBr} CH_3–CH_2–CH_2–Br \xrightarrow{\text{elimination}} CH_3–CH=CH_2$

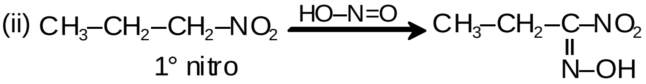
(iv) $CH_2=C=O \xrightarrow{HBr}$ No reaction.

22. 1° nitro compound, 2° nitrocompound react with HNO_2 acid but 3° nitro compound does not react with nitrous acid



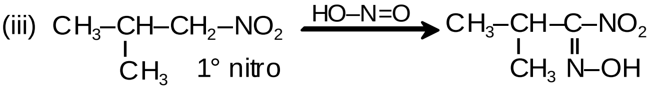
(i) $CH_3–\overset{\underset{\|}{O}}{C}–\overset{CH_3}{CH}–NO_2 \xrightarrow{HNO_2} CH_3–C(=O)–C(CH_3)(N=O)–NO_2$

1° nitro



(ii) $CH_3–CH_2–CH_2–NO_2 \xrightarrow{HO–N=O} CH_3–CH_2–C(=N–OH)–NO_2$

1° nitro



(iii) $CH_3–CH(CH_3)–CH_2–NO_2 \xrightarrow{HO–N=O} CH_3–CH(CH_3)–C(=N–OH)–NO_2$

1° nitro

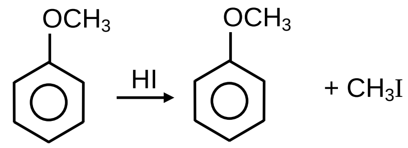
3° nitro $\xrightarrow{HNO_2}$ No reaction

23. Definition of electrophile

Example of positively charged electrophile is $NO_2^{\oplus}$ (nitronium ion)

Example of neutral electrophile is SO_3.

24.



Anisole Phenol Methyliodide

Phenyl-methyl ether

25.

$$\begin{tikzcd} A \arrow[r, "Na"] \arrow[d, "PCl_5"] & B \\ C & \end{tikzcd}$$

$B + C \longrightarrow$ diethyl ether

A is alcohol

$$\begin{tikzcd} R{-}OH \arrow[r, "Na"] \arrow[d, "PCl_5", "S_N2"'] & RO^-Na^+ \\ R{-}Cl & \end{tikzcd}$$

$RO^- + R{-}Cl \longrightarrow R{-}O{-}R$

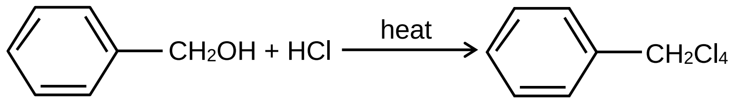
$$\begin{tikzcd} CH_3{-}CH_2{-}OH \arrow[r, "Na"] \arrow[d, "PCl_5", "S_N2"'] & CH_3CH_2O^-Na^+ \\ \underset{(C)}{CH_3{-}CH_2{-}Cl} & \end{tikzcd}$$

$CH_3{-}CH_2O^-Na^+ + CH_3{-}CH_2{-}Cl$

$CH_2{-}CH_2{-}O{-}CH_2{-}CH_3$
Diethyl ether

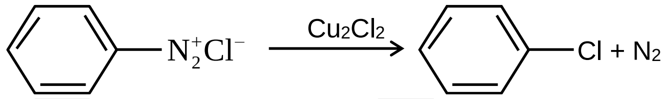
A = $CH_3{-}CH_2{-}OH$
B = $CH_3{-}CH_2O^-\ Na^+$
C = $CH_3{-}CH_2{-}Cl$

26. (1)



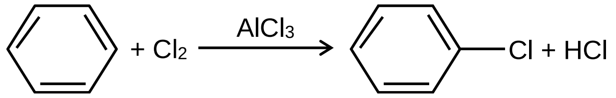
[NSR]

(2)



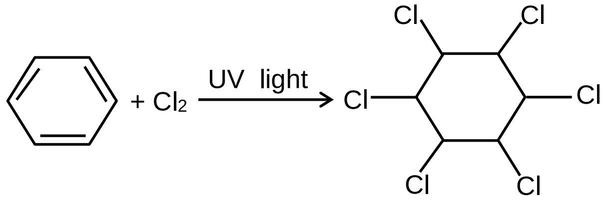
[NSR]

(3)



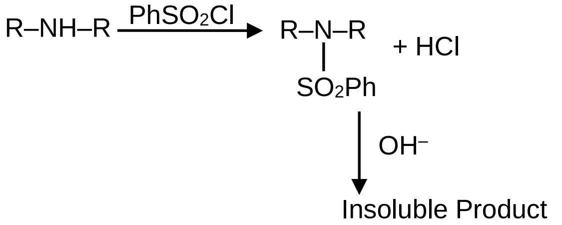
[ESR]

(4)



[FAR]

27. 2º amine form salt with Hinsberg reagent ($PhSO_2Cl$) which remain Insoluble in alkali :



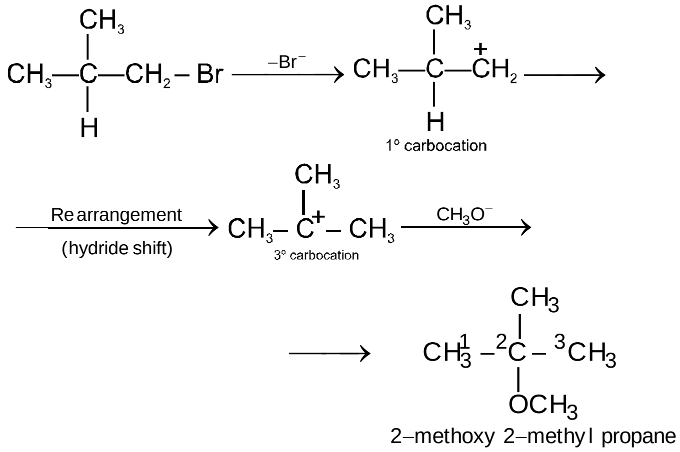
$$\begin{tikzcd} R{-}NH{-}R \arrow[r, "PhSO_2Cl"] & \underset{\substack{|\\ SO_2Ph}}{R{-}N{-}R} + HCl \arrow[d, "OH^-"] \\ & \text{Insoluble Product} \end{tikzcd}$$

PART - II

1. The most reactive nucleophile is $(CH_3)_3CO^-$ because of three electron donating $-CH_3$ groups (+ I effect) attached which tends to increase the electrons density no O atom.

$\xrightarrow[\text{decreasing order of reactivity of nucleophile}]{}$

5. The reaction is an example of nucleophilic substitution reaction. The mechanism is as follows :

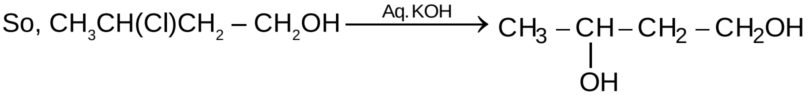


6. The relative stability of alkyl carbocation is due to inductive effect and hyperconjugation, while that of stable carbocation is due to resonance. The order is :

$CH_3CH_2X < (CH_3)_2CH-X < CH_2 == CH-CH_2X < PhCH_2-X.$

7. It is an example of nucleophilic substitution reaction.

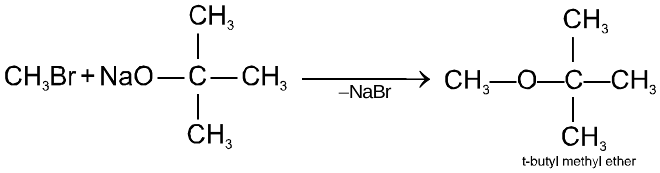
$R-\boxed{X+K}\,OH \longrightarrow R-OH+KX$



$$\text{So, } CH_3CH(Cl)CH_2-CH_2OH \xrightarrow{\text{Aq. KOH}} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2OH$$

8. t-butyl methyl ehter is a mixed ether and for the preparation of mixed ethers in high yield the essential condition is the use of primary alkyl halide.

Thus,

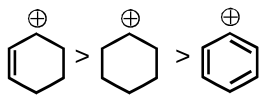


$$CH_3Br+NaO-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3 \xrightarrow[-NaBr]{} CH_3-O-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

t-butyl methyl ether

This reaction is williamson's synthesis.

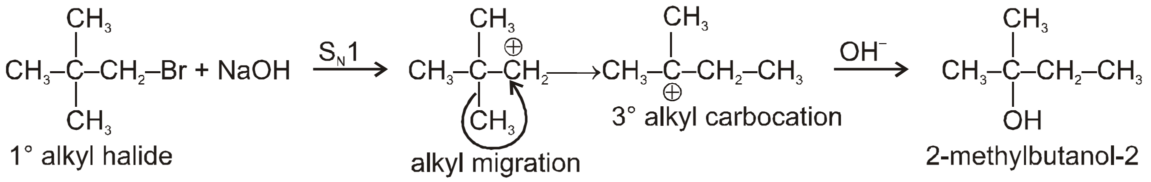
9. Rate of hydrolysis $\propto$ stability of formed carbocation intermediate

$(CH_3)_3C^+ >$ 

12. S_N2 reaction readily occurs on less sterically hindered substrate.

13. Presence of excess of HI favours substitution reaction in ethers.
Thus the product for given reaction are $C_6H_5CH_2I$, CH_3CH_2I, $HOCH_2 - CH_2OH$.

14. (1)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Br + NaOH \xrightarrow{S_N1} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{CH_3}{\underset{\oplus}{C}}-CH_2-CH_3 \xrightarrow{OH^-} CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2-CH_3$

15. Williamson's synthesis occurs by S_N2 mechanism and primary alkyl halides are most reactive in S_N2 reactions.

17. 1º alkyl halides (i.e. CH_3 Br) undergo S_N2 reaction with strong nucleophile.

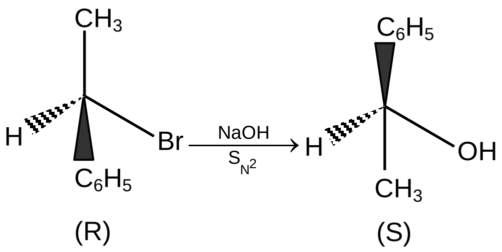
18. **(3)** $C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl + POCl_3 + HCl$

$C_2H_5Cl + AgNO_2$ $C_2H_5NO_2 + AgCl$

19. Asseration is false, because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon– chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles.

25. A major factor in determining the reactivity of acyl derivatives is leaving group ability which is related to acidity. Weak bases are better leaving groups than strong bases.
The reactivity acyl compound towards nucleophiles decreases as the basicity of the leaving group increases.

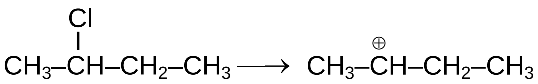
27.



inversion of configuration

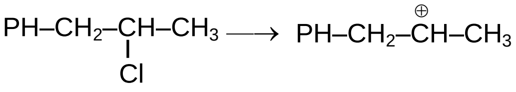
29. Rate of SN1 α stability of carbocation
α +I, +M, HC effect

(i)



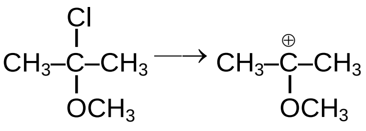
$CH_3-\overset{Cl}{C}H-CH_2-CH_3 \longrightarrow CH_3-\overset{\oplus}{C}H-CH_2-CH_3$

(ii)



$PH-CH_2-\underset{Cl}{C}H-CH_3 \longrightarrow PH-CH_2-\overset{\oplus}{C}H-CH_3$

(iii)



$CH_3-\overset{Cl}{\underset{OCH_3}{C}}-CH_3 \longrightarrow CH_3-\overset{\oplus}{\underset{OCH_3}{C}}-CH_3$

(iv) $CH_3-CH_2-CH_2-Cl \longrightarrow CH_3-CH_2-CH_2^+$

30. Order of nucleophilicity

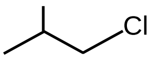
$OH^-, HS^-, Ph-O^-, C_2H_5O^- = \quad HS^- > C_2H_5O^- > OH^- > Ph-O^-$

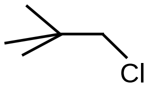
On increasing delocalization of e^- nucleophilicity decrease

31. Rate of S_N2 α – I, – M effect

$$\alpha \ \frac{1}{\text{steric crowding}}$$

$CH_3-CH_2-CH_2-Cl$ $\quad$ $Ph-CH_2-CH_2-Cl$

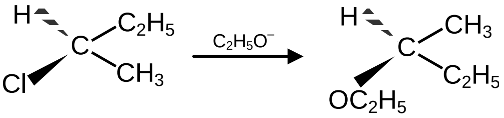




(I) (II) (III) (IV)

Rate of S_N2 = II > I > III > IV

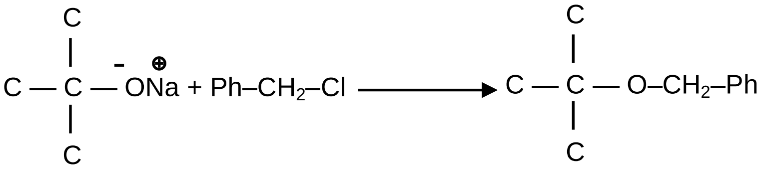
32.



(R) (S)

This is a S_N2 Reaction, and walolen inversion take place in which configuration become opposite

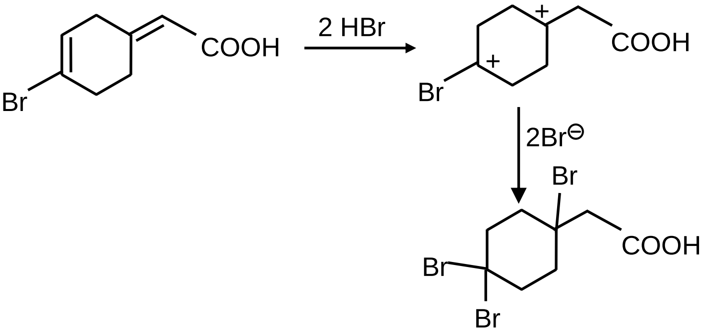
33.



$$C-\overset{\displaystyle C}{\underset{\displaystyle C}{C}}-\overset{-}{O}\overset{\oplus}{Na} + Ph-CH_2-Cl \longrightarrow C-\overset{\displaystyle C}{\underset{\displaystyle C}{C}}-O-CH_2-Ph$$

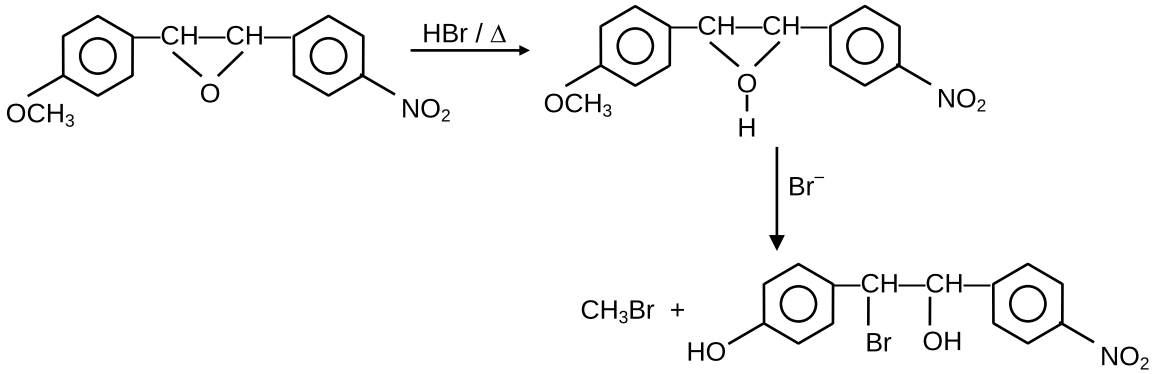
This is a Williamson ether synthesis in which alkylhalide should be either 1º/2º

34.



This is a electrohilic addition reaction reaction by markownikoff rule depond upon stability of carbocation.

35.



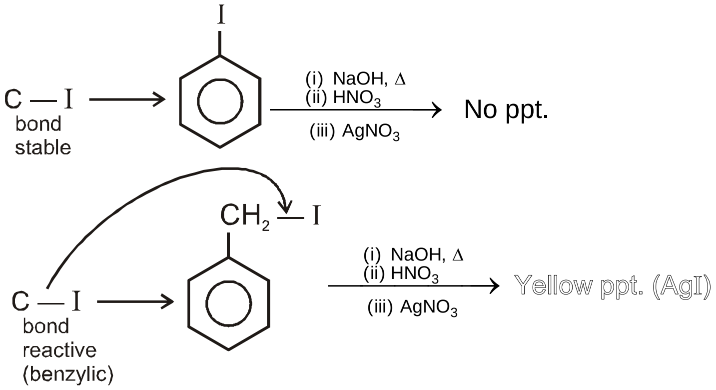
PART - III

1. $(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$

It is S_N1 reaction

2. S_N1 reaction $\propto$ stability of carbocation

3.

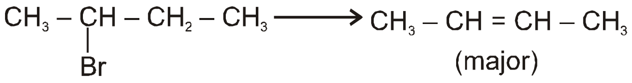


4. $R - OH \xrightarrow{H^{\oplus}} R - \overset{\oplus}{O}H_2$ this step is initiation step.

5. According to stability of carbocation.

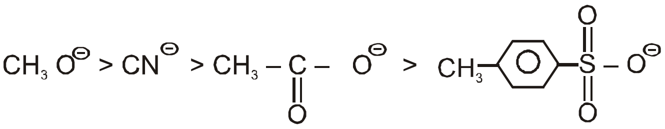
6. Steric hinderence.

7.

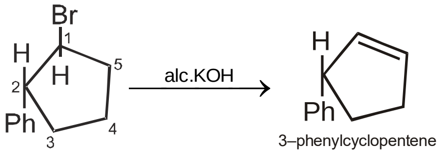


$$CH_3 - \underset{\displaystyle Br}{\underset{|}{C}H} - CH_2 - CH_3 \longrightarrow \underset{\text{(major)}}{CH_3 - CH = CH - CH_3}$$

8. Nucleophilicity order



9.



It is anti elimination reaction so hydrogen atom from second carbon will not eliminated as it is in syn-position rather hydrogen atom from 5th carbon will be eliminated.

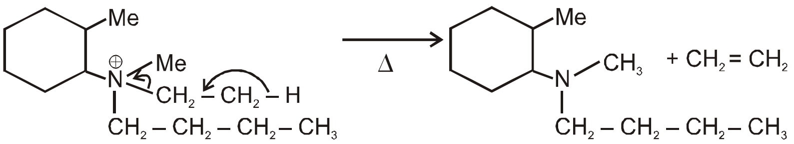
10. Since this reaction will follow S_N2 pathway so stronger the base better its nucleophilicity.

The correct order of nucleophiles would be :

$CH_3O^- > OH^- > PhO^- > AcO^-$

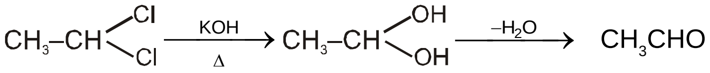
11. In aryl halides the C–X bond has partial double bond character due to resonance so it will not give S_N reaction

12.

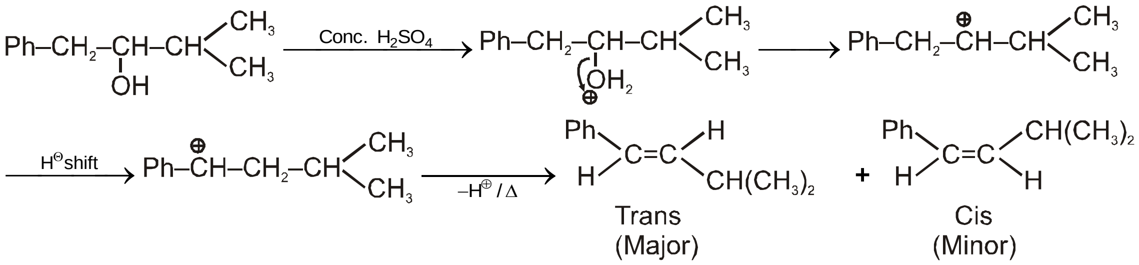


13. The reactivity of a compound towards S_N2 reaction decreases as the crowding at the C-atom containing leaving group increases.

14.



15.



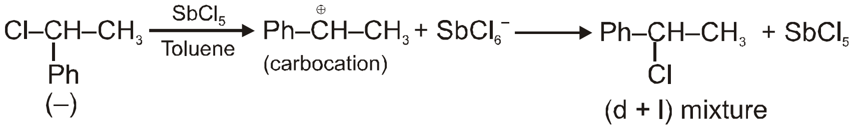
16. Reaction of alcohol with HCl and anhydrous $ZnCl_2$ is an S_N reaction.

3° alcohol react faster with HCl and anhydrous $ZnCl_2$ since it forms more stable carbocation intermediate.

17. Rate of S_N1 reaction $\propto$ stability of carbocation

18. $RS^{\ominus}$ is more nucleophilic than $R–O^{\ominus}$ due to larger size of orbitals and polarization but $RS^{\ominus}$ is less basic than $R–O^{\ominus}$ as the negative charge get stabilized due to larger size of sulphur atom.

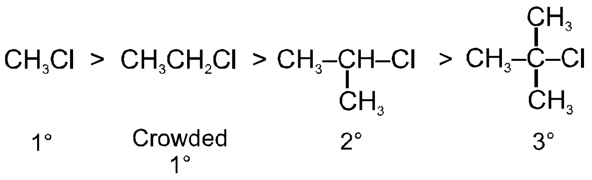
19.



$$\underset{\underset{(-)}{Ph}}{Cl-\underset{|}{C}H-CH_3} \xrightarrow[\text{Toluene}]{SbCl_5} \underset{\text{(carbocation)}}{Ph-\overset{\oplus}{C}H-CH_3} + SbCl_6^- \longrightarrow \underset{\text{(d + l) mixture}}{Ph-\underset{\underset{Cl}{|}}{C}H-CH_3} + SbCl_5$$

20. The reaction of alcohol with lucas reagent is mostly an S_N1 reaction and the rate of reaction is directly proportional to the carbocation stability formed in the reaction, since 3° R–OH forms 3° carbocation hence it will react fastest.

21. Rate of $S_N2 \propto \dfrac{1}{\text{Steric crowding of } \alpha\text{'C'}}$



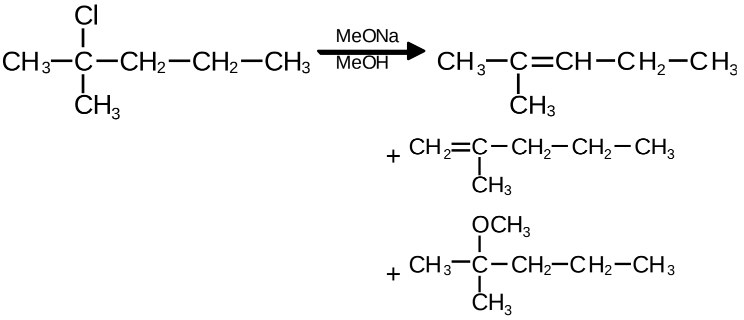
$$\underset{1°}{CH_3Cl} > \underset{\text{Crowded } 1°}{CH_3CH_2Cl} > \underset{2°}{CH_3-\underset{\underset{CH_3}{|}}{C}H-Cl} > \underset{3°}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl}$$

22.

$$2CH_3-CCl_3 \xrightarrow[\Delta]{6Ag} \underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3} + 6AgCl$$

23. R–X + AgF ⟶ R–F + AgX (Swarts reaction)

24.



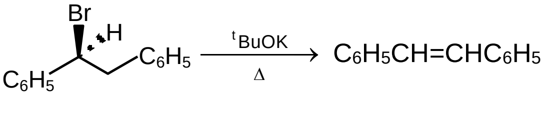
$$CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-CH_3 \xrightarrow[MeOH]{MeONa} CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_3$$

$$+\ CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH_3$$

$$+\ CH_3-\overset{\overset{OCH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-CH_3$$

Elimination dominate over substitution in the given reaction but all the products are possible.

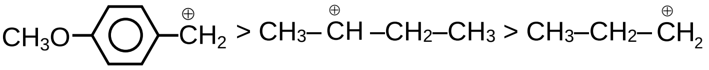
25.



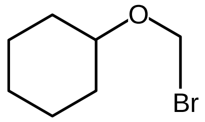
It is E-2 reaction.

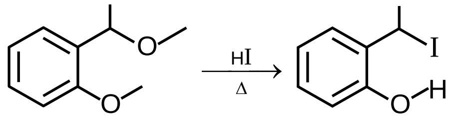
26. Reactivity towards S_N1 reaction $\propto$ stability of carbocation.

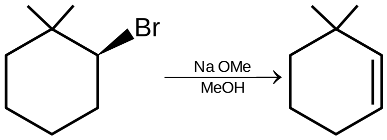
II < I < III

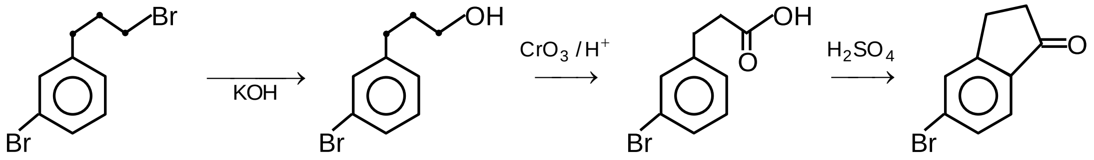


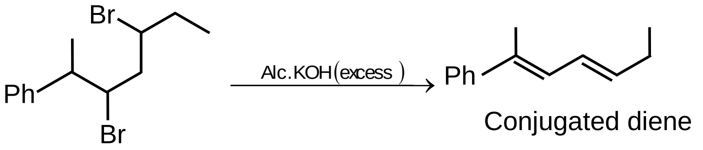
[Stability order of carbocation]

27. With  , alkene can not be produced with t-BuONa. Hence the product will not decolourise the bromine water.

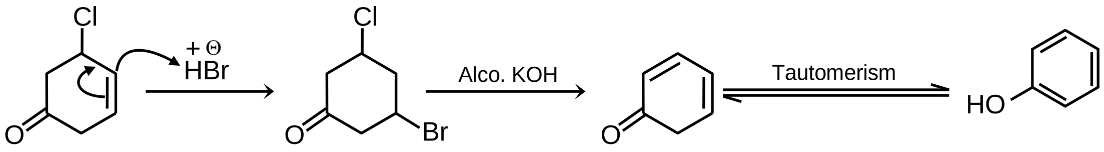
28. 

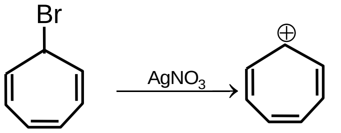
29.  (E$_2$) (Major) भत्रृस

30. 

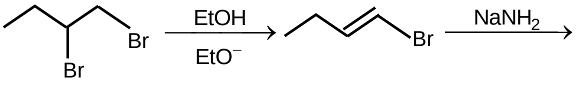
31. 

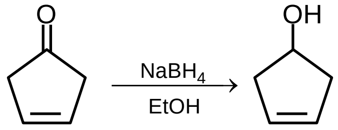
Conjugated diene

32. 

33.  + AgBr(Yellow ppt)

Intermediate carbocation is resonance stabilised and aromatic.

34.  $CH_3-CH_2-C\equiv\bar{C}\,Na^{\oplus}\xrightarrow{H^{\oplus}}CH_3-CH_2-C\equiv CH$

35. 

$NaBH_4$ does not reduce