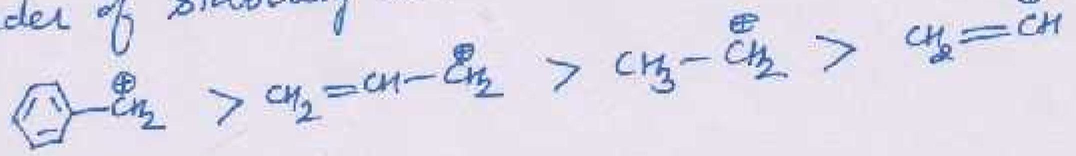
Home Assignment-1

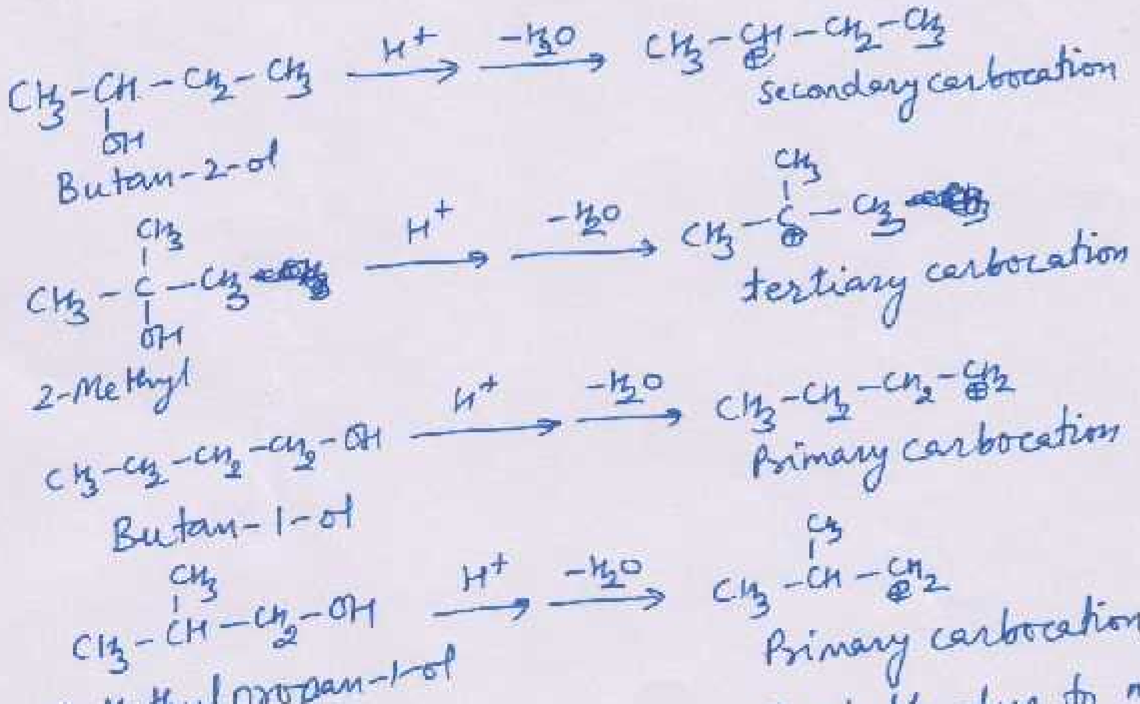
1. Benzyl and allyl carbocations are stabilized by resonance. Benzyl carbocation is more stable than allyl carbocation due to more resonating structures in former. Ethyl carbocation is more stable than vinyl carbocation due to lesser number of hyperconjugation effects as well as more electronegativity of sp hybrid carbon in the later. Therefore, the correct order of stability is:



$C_6H_5-\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 > CH_3-\overset{\oplus}{C}H_2 > CH_2=\overset{\oplus}{C}H$

∴ (a)

2.



$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow{H^+} \xrightarrow{-H_2O} CH_3-\underset{\oplus}{CH}-CH_2-CH_3$

Butan-2-ol

Secondary carbocation

$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow{H^+} \xrightarrow{-H_2O} CH_3-\underset{\oplus}{\overset{CH_3}{\overset{|}{C}}}-CH_3$

2-Methyl

tertiary carbocation

$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{H^+} \xrightarrow{-H_2O} CH_3-CH_2-CH_2-\overset{\oplus}{C}H_2$

Butan-1-ol

Primary carbocation

$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-OH \xrightarrow{H^+} \xrightarrow{-H_2O} CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{\oplus}{C}H_2$

2-Methylpropan-1-ol

Primary carbocation

Tertiary carbocation will be most stable due to more positive inductive effects as well as more positive hyperconjugation.

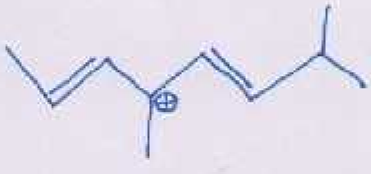
∴ (b)

3. NaCl will not give addition reaction with alkenes because Na^+ has negligible tendency to form covalent bonds and can not act as electrophile. Alkenes, themselves, do not react with nucleophile as such.

∴ (d)

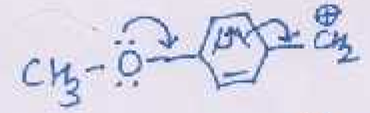
4. Tertiary carbocation will be most stable.

∴ (b)

5. 

The given carbocation is tertiary as well as stabilized by resonance with π bond from both sides.

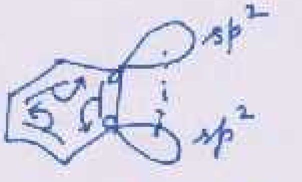
∴ (a)

6. 

will be most stable due to positive resonance effect of $CH_3-\ddot{O}-$ group.

∴ (c)

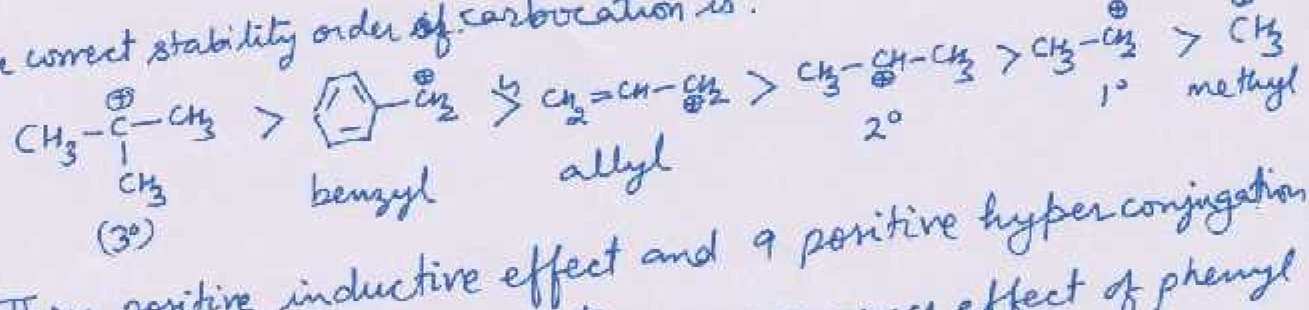
7. Additional π bond of benzyne is formed by sideways overlapping of sp^2 hybrid orbitals of carbon as shown below:



delocalized π bond is formed by sideways overlapping of p orbitals.

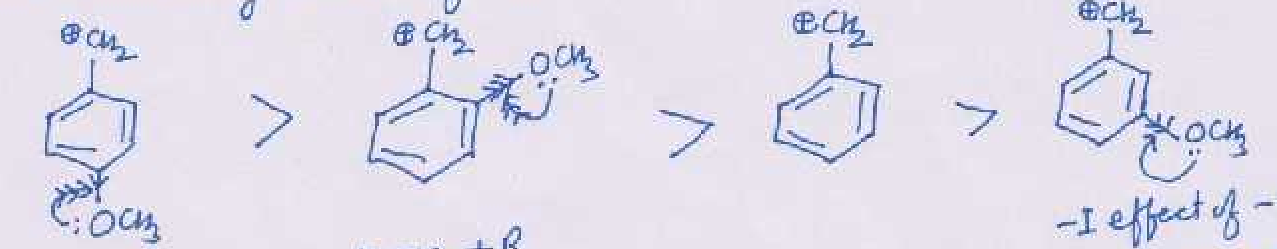
∴ (d)

8. The correct stability order ~~of~~ carbocation is:



Three positive inductive effect and 9 positive hyperconjugation effects collectively dominate over resonance effect of phenyl and vinyl groups in benzyl and allyl carbocation, respectively. However, in free radicals the positive inductive effects matter very little and tertiary radical is less stable than benzyl and allyl free radical. ∴ (a)

9. The stability order of resultant carbocation will be:



more +R
less −I

more +R
more −I

−I effect of $-OCH_3$ group is more than its +R effect from meta position.

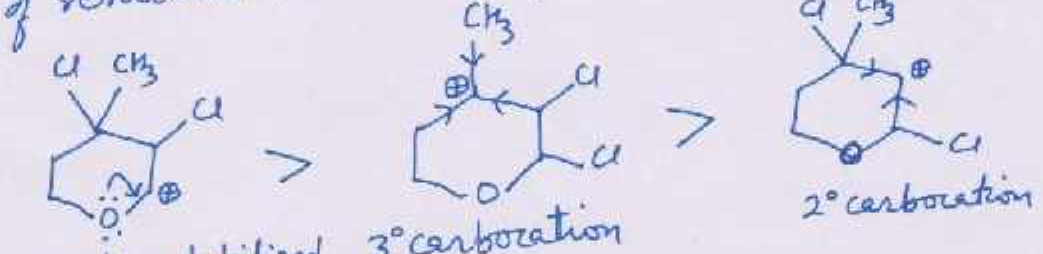
More the stability of resultant carbocation, easier will be its formation and lesser will be bond dissociation energy of C−Cl bond.

∴ (b)

10. Testiary carbocation is more stable than benzyl ⊕ and allyl carbocation due to collective effect of 3 +I effect and 9 +h effects.

∴ (d)

11. Stability of resultant carbocation formed by removal of Cl^- is



Carbocation stabilized by resonance of lone pairs.

3° carbocation

2° carbocation

More the stability of carbocation faster will be removal of Cl^-.

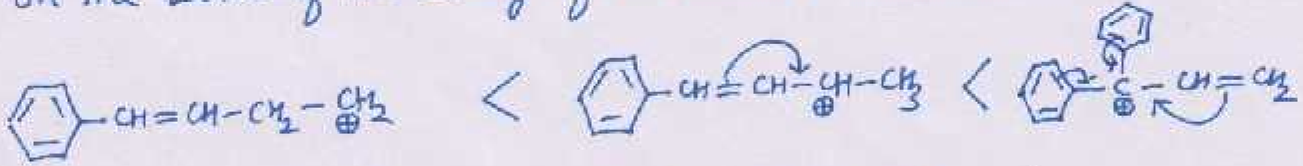
∴ (c)

12. $ZnCl_2$, being Lewis acid, help in ionization of alcohol to form carbocation. The stability of resultant carbocations is:

More the stability of carbocation, faster will be reaction of alcohol

∴ (C)

13. Compound (iii) has partial double bond character of C–Cl bond due to resonance. Hence, removal of this Cl^- will be most difficult. Reactivity of remaining can be explained on the basis of stability of resultant carbocation as below:



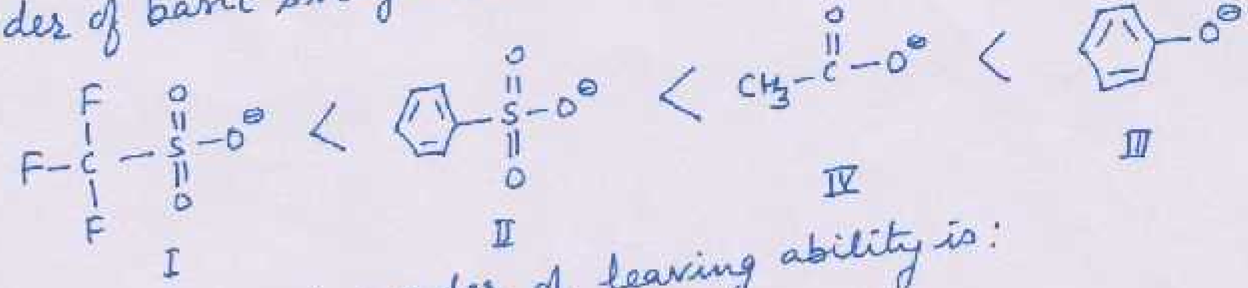
∴ Reactivity order is III < I < II < IV

∴ (C)

14. Bond (q) will migrate to form more stable carbocation which is tertiary as well as six membered ring.

Subjective:

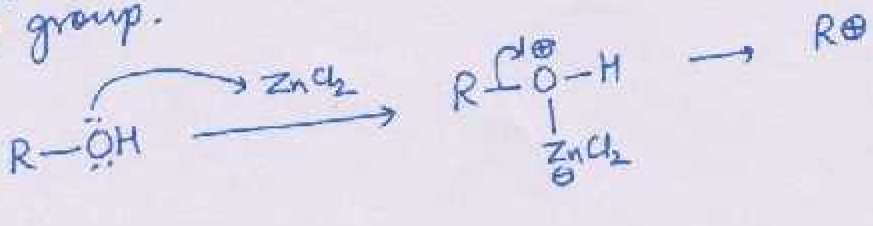
1. Order of basic strength is



Therefore, decreasing order of leaving ability is:

I > II > IV > III

2. Being Lewis acid, anhydrous $ZnCl_2$ helps in removal of –OH group.



Home Assignment-2

1. Weaker base is better leaving group.

Basic strength: $OH^{\ominus} > H_2O$

$OH^{\ominus} > \overset{\ominus}{S}H$

$CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} < CH_3-CH_2-O^{\ominus}$

$Cl^{\ominus} > I^-$

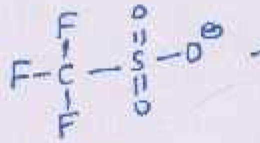
leaving ability: $OH^- < H_2O$

$OH^{\ominus} < \overset{\ominus}{S}H$

$CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} > CH_3-CH_2-O^{\ominus}$

$Cl^- < I^-$

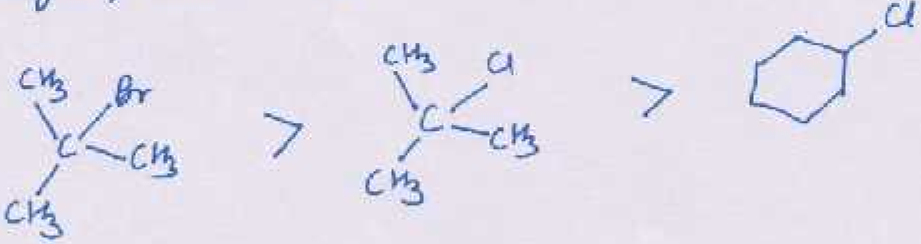
∴ (C)

2. 

$CF_3-SO_2-O^{\ominus}$ is weakest base and hence best leaving group.

∴ (d)

3. Br^- is better leaving group than $Cl^{\ominus}$. Moreover, tertiary carbocation is more stable than secondary carbocation.
There fore, reactivity order will be

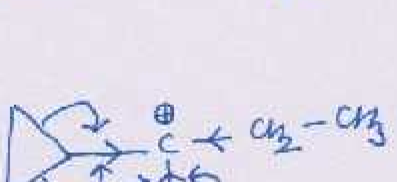


∴ (C)

4. I^- will be better leaving group than $Br^{\ominus}$ and tertiary carbocation is more stable.

∴ (d)

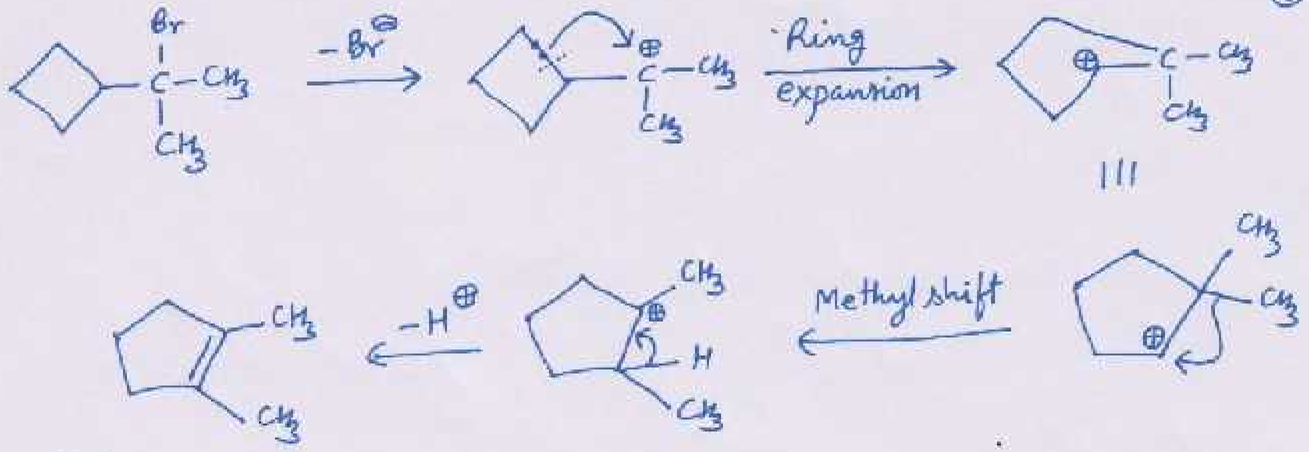
5. Stability of carbocation by cyclopropyl group is much more due to +R effect of τ (tau) bonds of cyclopropyl group as well as +I effect.



(most stable carbocation)

∴ (a)

6.

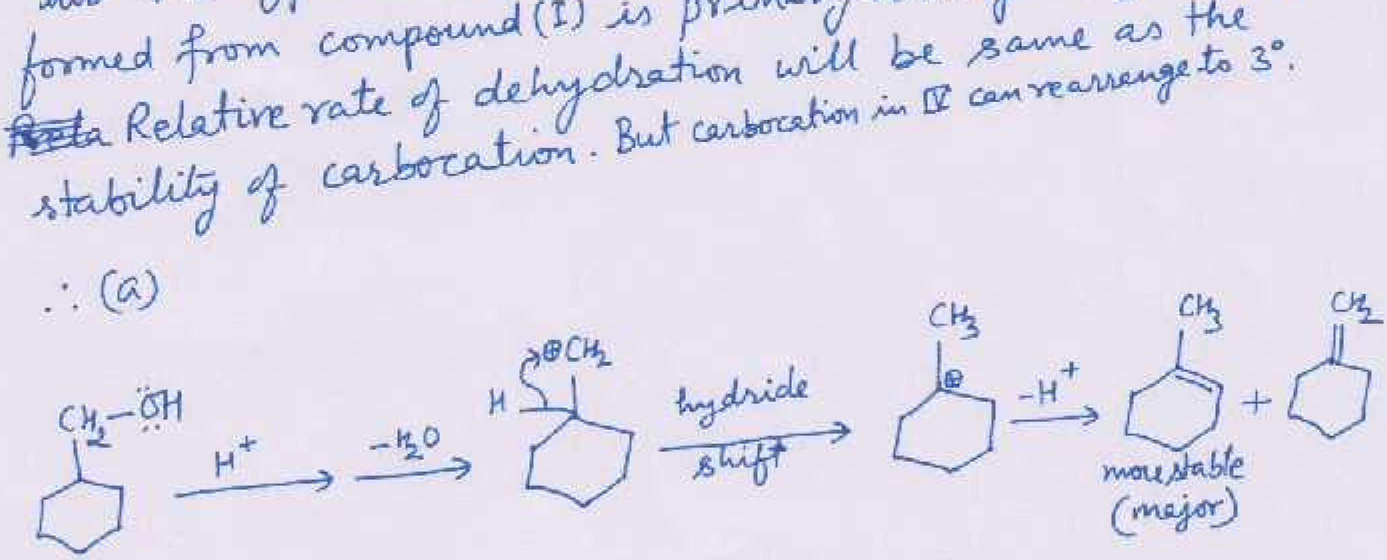


∴ (c)

7. Compound (III) gives most stable carbocation which is tertiary as well as stabilized by +R effect of phenyl group. Carbocation formed by compound (I) is secondary, carbocation formed by compound (II) is primary which is stabilized by two +ve hyperconjugation effects. Primary carbocation formed from compound (I) is primary having no hyperconjugation. ~~Rata~~ Relative rate of dehydration will be same as the stability of carbocation. But carbocation in IV can rearrange to 3°.

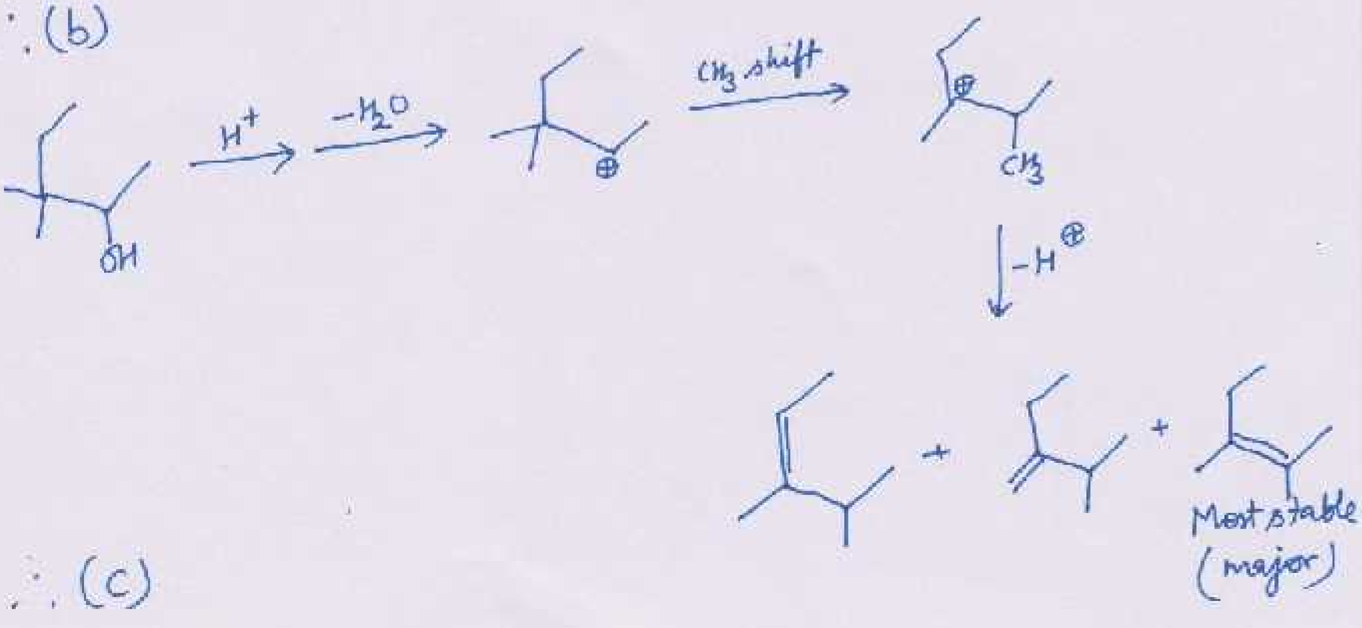
∴ (a)

8.



∴ (b)

9.

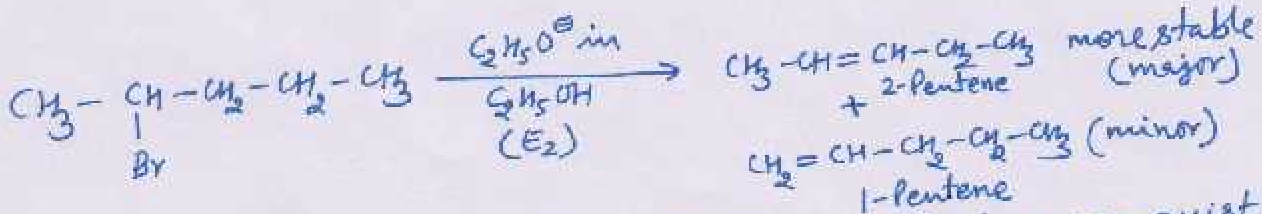


∴ (c)

10. Compound (c) has no β-hydrogen and can not undergo E_2 elimination.

∴ (c)

11.

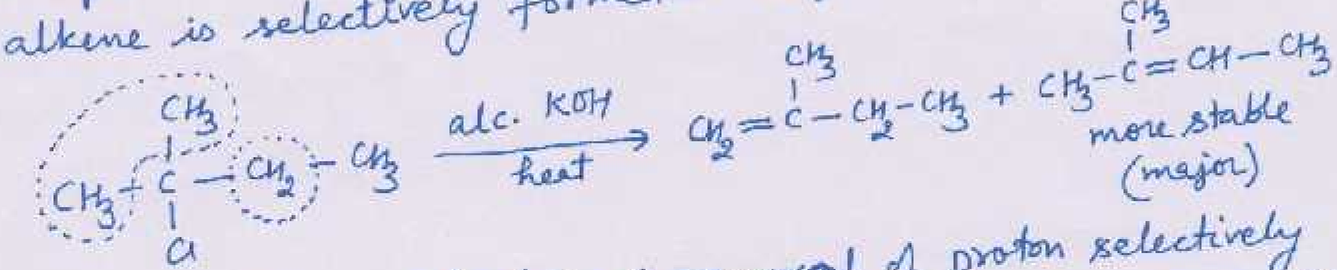


$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow[\substack{C_2H_5OH \\ (E_2)}]{C_2H_5O^{\ominus}\ \text{in}} \underset{\text{2-Pentene}}{CH_3-CH=CH-CH_2-CH_3}\ \text{more stable (major)} + \underset{\text{1-Pentene}}{CH_2=CH-CH_2-CH_2-CH_3}\ \text{(minor)}$$

2-Pentene is more stable than 1-Pentene. 2-Pentene can exist in cis and trans isomer out of which trans-2-Pentene is more stable. Therefore, trans-2-Pentene is formed in maximum amount.

∴ (d)

12. Compound (c) contains different β-hydrogen. More stable alkene is selectively formed in major amount



$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3 \xrightarrow[\text{heat}]{\text{alc. KOH}} CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3 + \underset{\text{more stable (major)}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3}$$

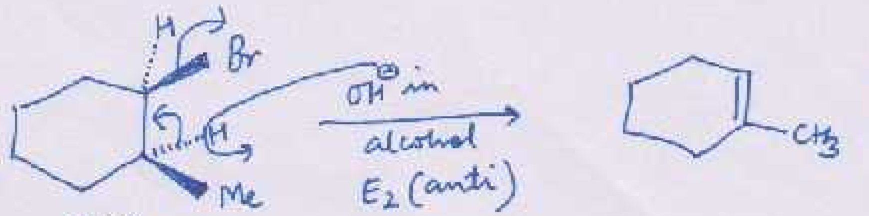
Regioselection is selection of removal of proton selectively more from one position over removal of proton from other position. In compound (a) and (b) all β-hydrogen are identical and hence no regioselection. Compound (d) has no β-hydrogen and will undergo 1,1-Elimination (α-elimination) having no regioselection possible.

∴ (C)

13. Compound (c) is most stable due to conjugated π bonds

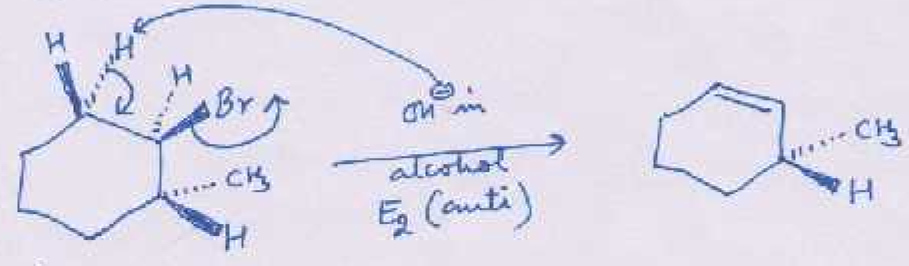
∴ (c)

14.

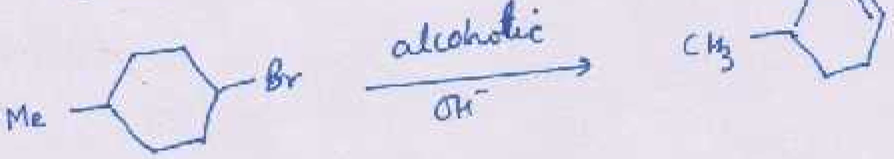
(a) 

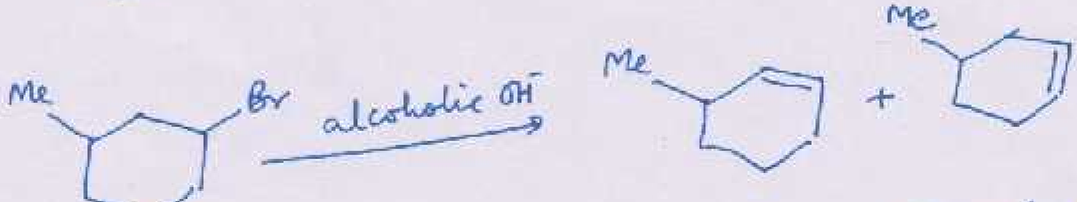
(cis)

(most stable)

(b) 

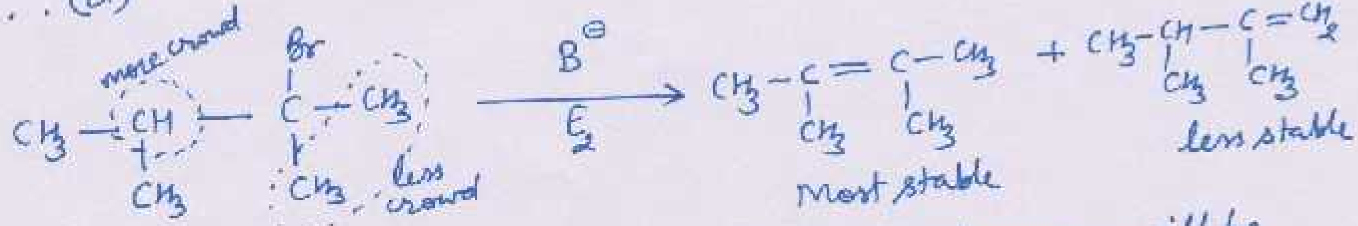
(trans)

(c) 

(d) 

Compound (a) gives most stable alkene. Therefore, it will undergo fastest E_2 elimination.

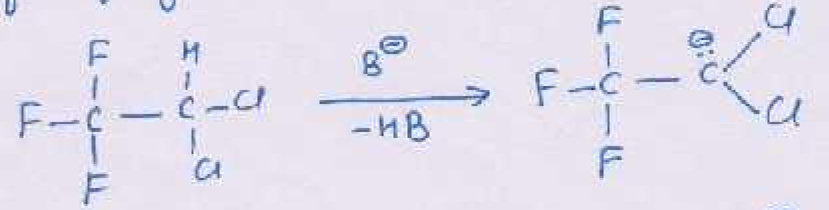
∴ (a)

15. 

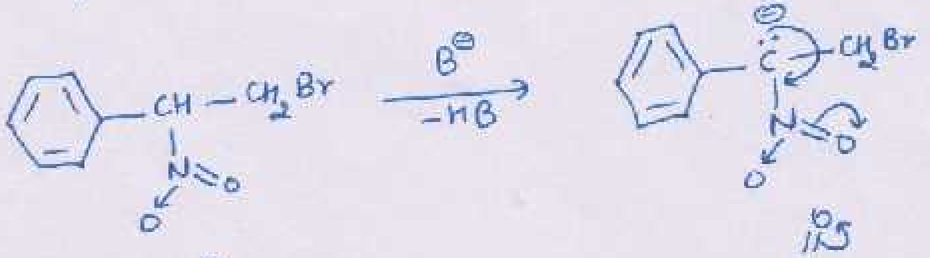
$CH_3-O^{\ominus}$ is small base. Therefore, steric hindrance will be negligible and more stable compound is major. On the other hand $Me_3CO^{\ominus}$ is bulky base. Therefore, steric hindrance is very large and dominating resulting in formation of other product as major. Therefore, most stable compound is 'X' while the other product is Y.

∴ (a)

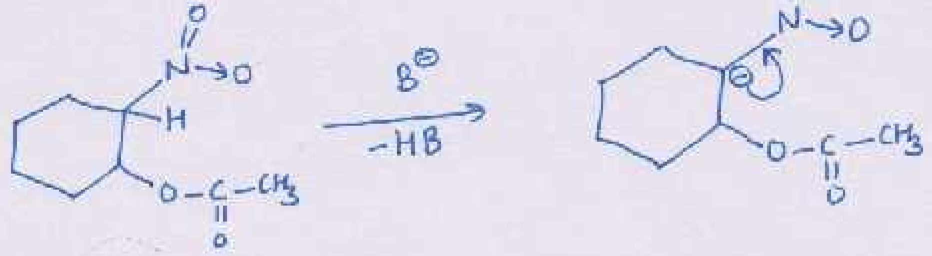
16. All of these can undergo E_{1cB} elimination due to formation of highly stable carbanion.



highly stable



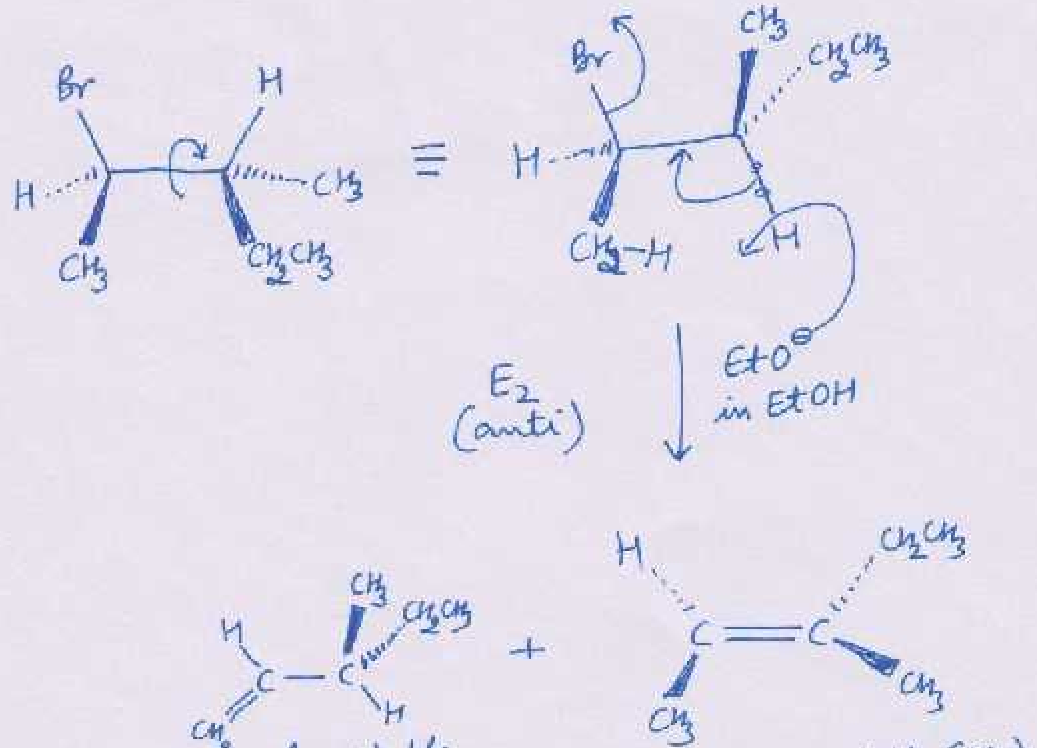
highly stable



highly stable

∴ (d)

17.



less stable

more stable (cis)

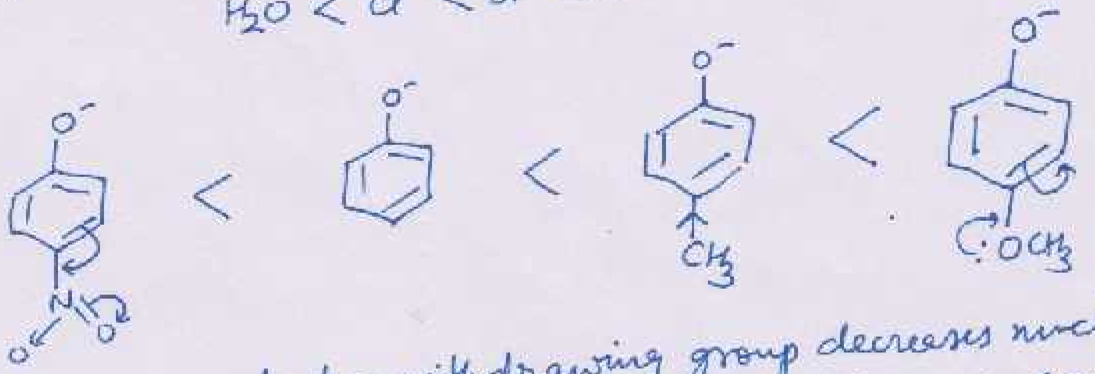
∴ (c)

Home Assignment - 3.

1. Nucleophilicity increases from top to bottom in a group.

$H_2O < Cl^- < Br^- < I^-$

2.

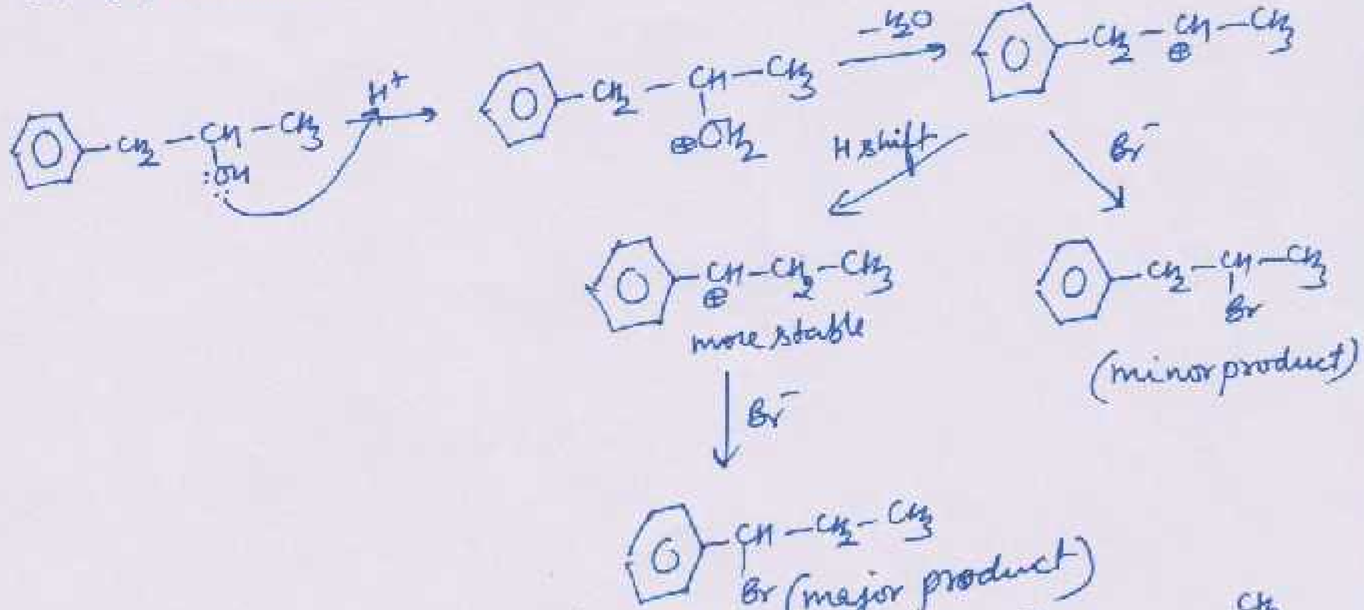


Presence of electron withdrawing group decreases nucleophilic strength while presence of electron donating group will increase nucleophilic strength.

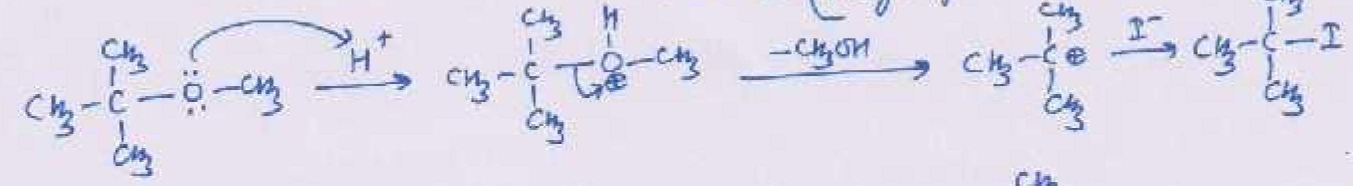
4. Rate of S_N1 reaction of $(CH_3)_3CBr$ with $CH_3OH = k[(CH_3)_3COH]$

∴ (a) doubled (b) tripled.

9.

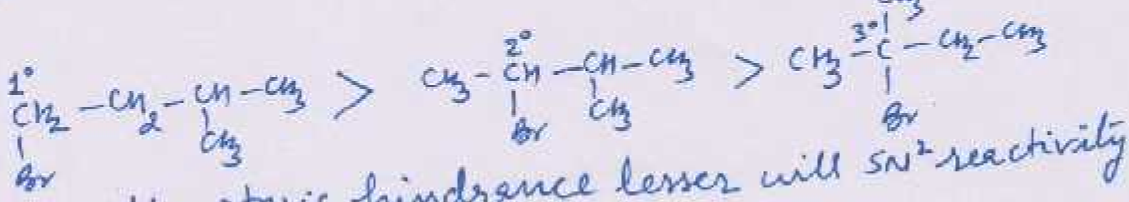


10.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\ddot{O}-CH_3 \xrightarrow{H^+} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{\oplus}{O}}-CH_3 \xrightarrow{-CH_3OH} CH_3-\overset{CH_3}{\underset{CH_3}{C}}\oplus \xrightarrow{I^-} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-I$$

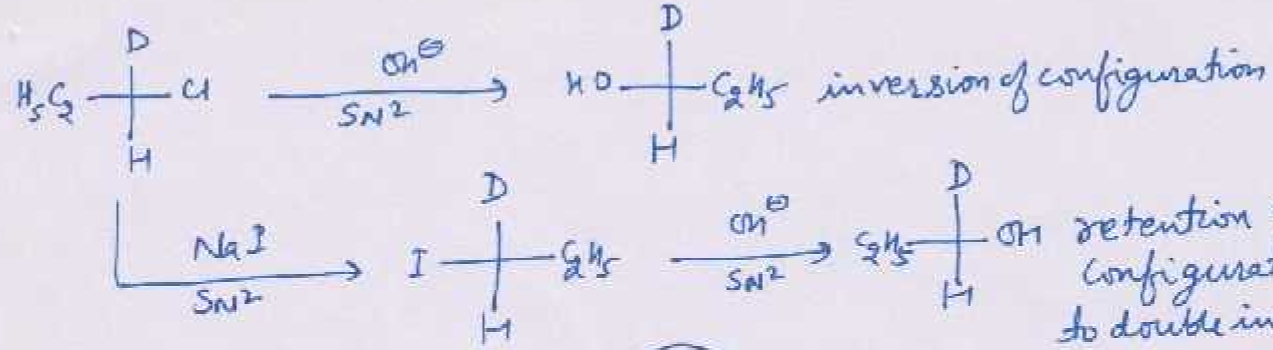
11. (b)



$$\overset{1^\circ}{\underset{Br}{CH_2}}-CH_2-\underset{CH_3}{CH}-CH_3 > CH_3-\overset{2^\circ}{\underset{Br}{CH}}-\underset{CH_3}{CH}-CH_3 > CH_3-\overset{CH_3}{\underset{Br}{\overset{3^\circ}{C}}}-CH_2-CH_3$$

More the steric hindrance lesser will S_N2 reactivity.

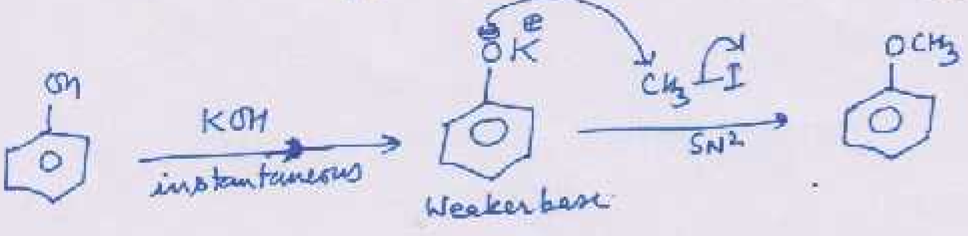
16.



inversion of configuration

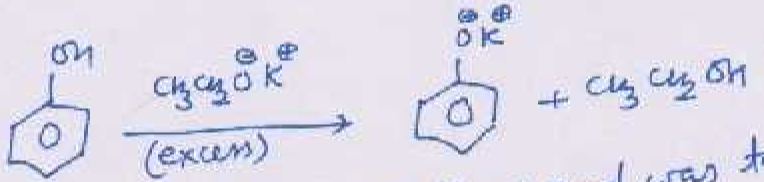
retention of configuration due to double inversion.

18. (a)

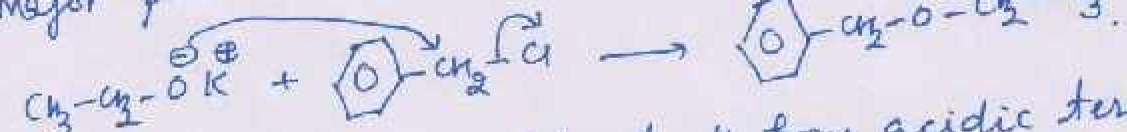


Weaker base

(b)



But $CH_3CH_2O^{\ominus}$ is still there and was taken in excess. Now $CH_3CH_2O^{\ominus}$ is stronger nucleophile than $C_6H_5-O^{\ominus}$. Therefore, major product is formed by nucleophilic attack of $CH_3CH_2O^{\ominus}$.



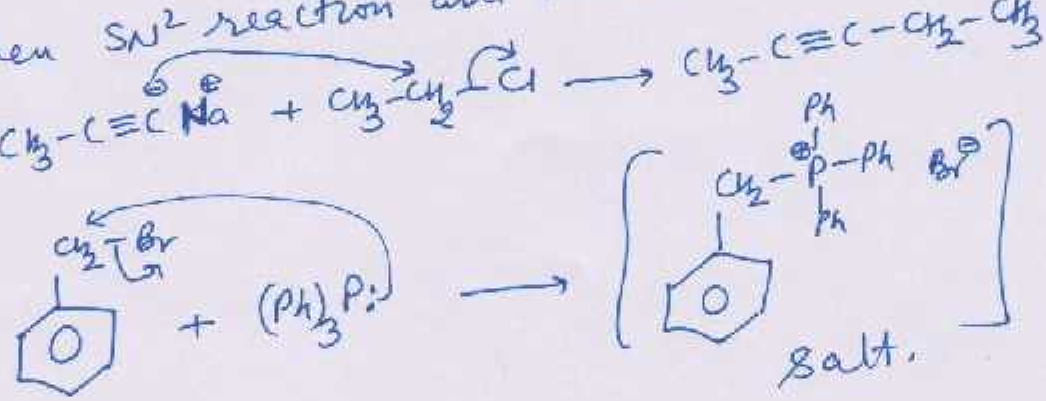
(C) Active metal, Na, will liberate H_2 from acidic terminal alkyne.

$$CH_3-C\equiv CH + Na \longrightarrow CH_3-C\equiv \overset{\ominus}{C}\overset{\oplus}{Na} + \frac{1}{2}H_2\uparrow$$

Then S_N2 reaction will occur with CH_3-CH_2-I

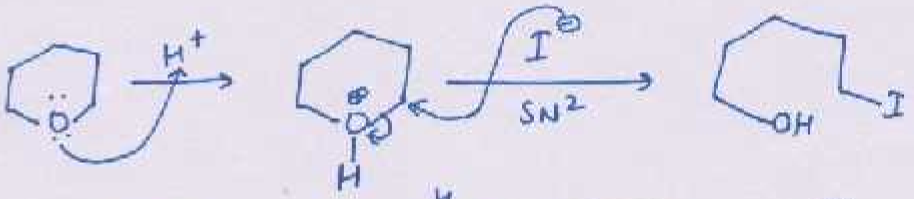
$$CH_3-C\equiv \overset{\ominus}{C}\overset{\oplus}{Na} + CH_3-CH_2-Cl \longrightarrow CH_3-C\equiv C-CH_2-CH_3$$

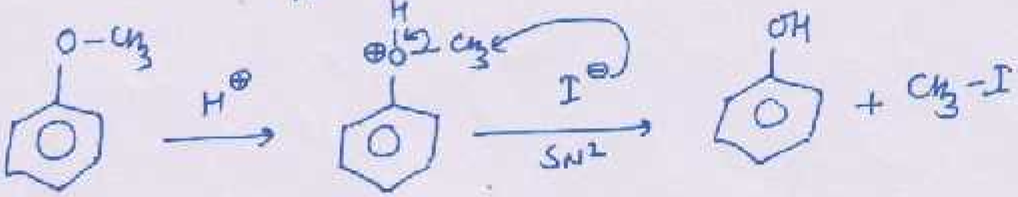
(d)

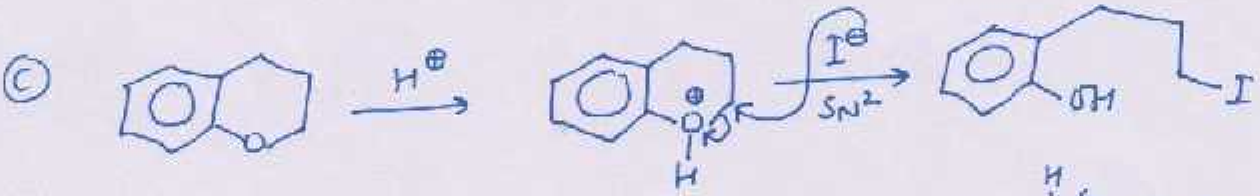


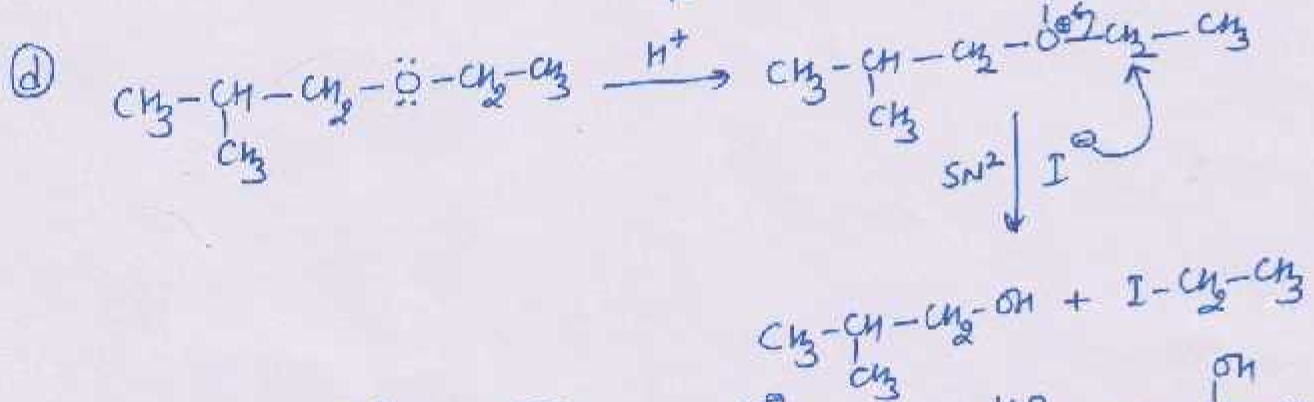
salt.

19.



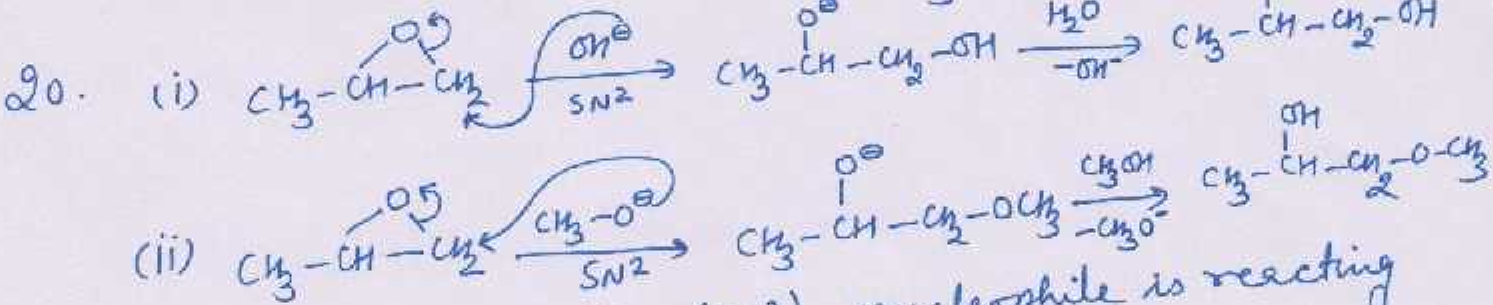






$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\ddot{O}-CH_2-CH_3 \xrightarrow{H^+} CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{H}{\overset{|}{O^{\oplus}}}-CH_2-CH_3 \xrightarrow[SN^2]{I^{\ominus}} CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-OH + I-CH_2-CH_3$$

20.

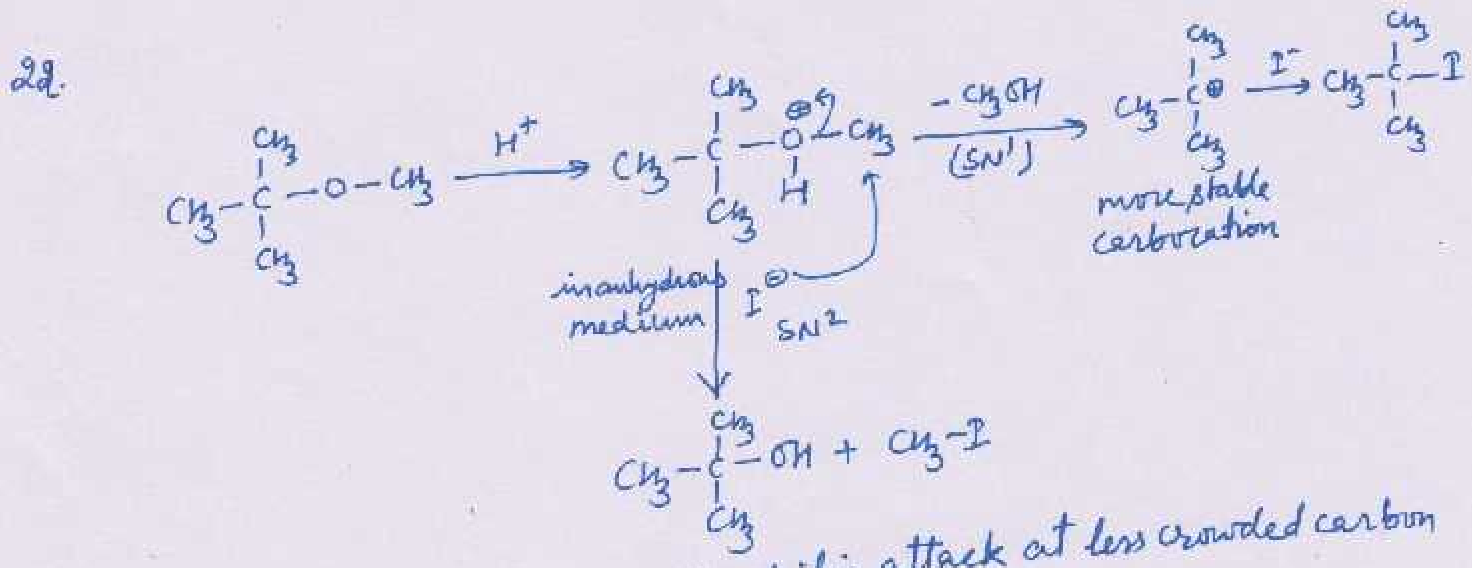


$$\text{(i)}\quad CH_3-CH\overset{O}{-}CH_2 \xrightarrow[SN^2]{OH^{\ominus}} CH_3-\overset{O^{\ominus}}{\overset{|}{CH}}-CH_2-OH \xrightarrow[-OH^{\ominus}]{H_2O} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-OH$$

$$\text{(ii)}\quad CH_3-CH\overset{O}{-}CH_2 \xrightarrow[SN^2]{CH_3-O^{\ominus}} CH_3-\overset{O^{\ominus}}{\overset{|}{CH}}-CH_2-OCH_3 \xrightarrow[-CH_3O^{\ominus}]{CH_3OH} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-O-CH_3$$

In both above reactions (SN^2), nucleophile is reacting at less sterically hindered site.

22.



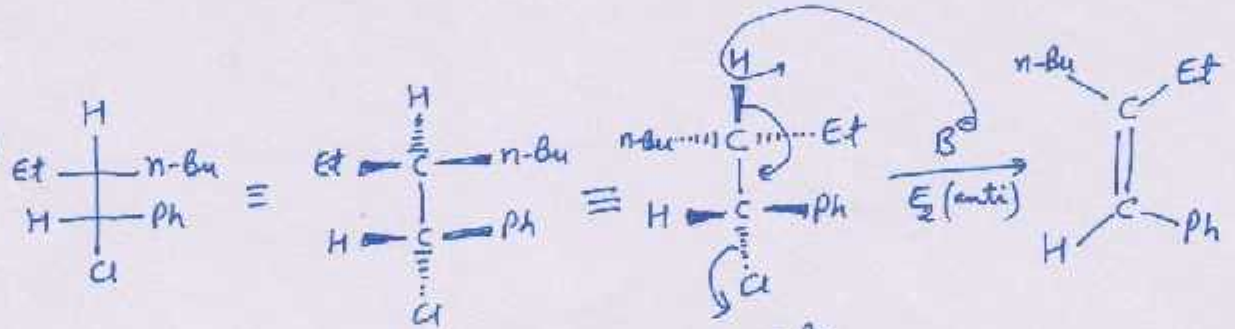
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 \xrightarrow{H^+} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{O^{\oplus}}-CH_3 \xrightarrow[(SN^1)]{-CH_3OH} CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} \xrightarrow{I^-} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

$$\xrightarrow[SN^2]{I^{\ominus}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + CH_3-I$$

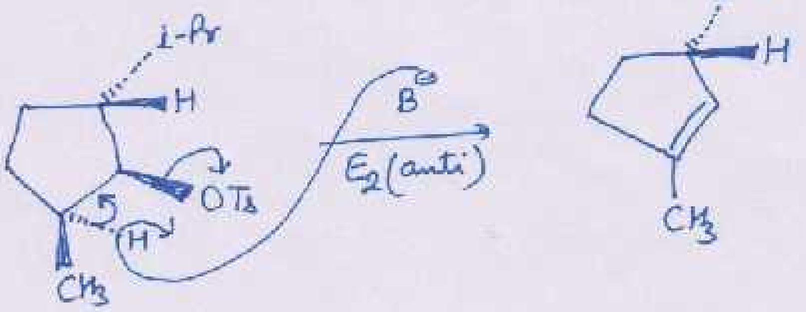
Nucleophilic attack at less crowded carbon

23.

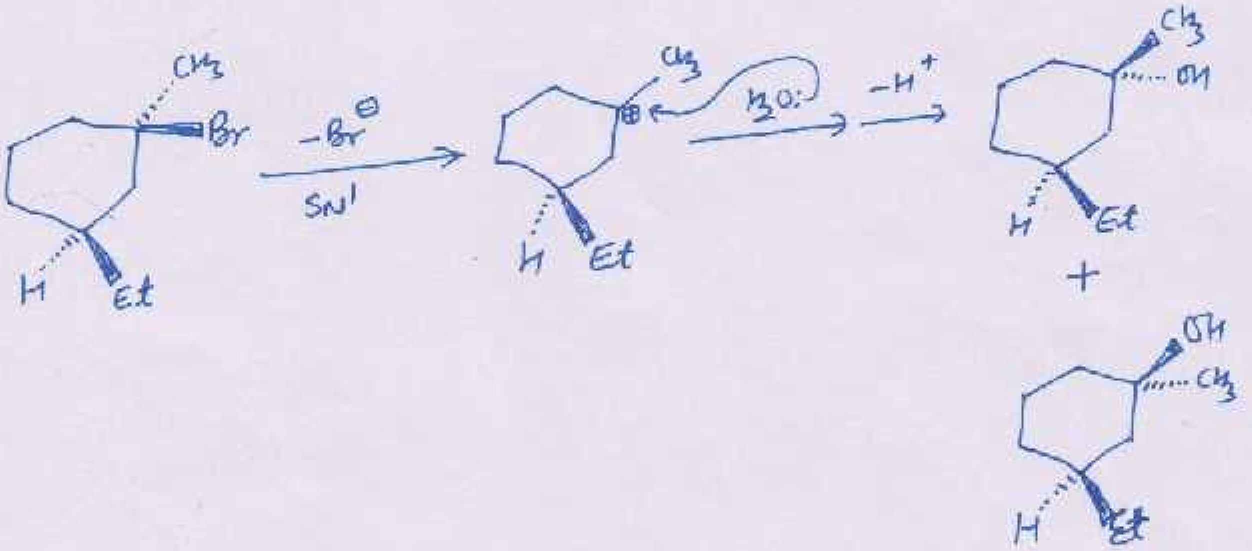
(a)


H
Et
n-Bu
H
Ph
Cl
≡
H
Et
C
n-Bu
H
C
Ph
Cl
≡
H
n-Bu
C
Et
H
C
Ph
Cl
B⊖
E2(anti)
n-Bu
Et
C
C
H
Ph

(b)


i-Pr
H
OTs
H
CH3
B⊖
E2(anti)
i-Pr
H
CH3

(c)


CH3
Br
H
Et
-Br⊖
SN1
CH3
⊕
H
Et
H2O:
-H+
CH3
OH
H
Et
+
OH
CH3
H
Et

24. When nucleophilic site belongs to same period, nucleophilicity decreases from left to right in the period.

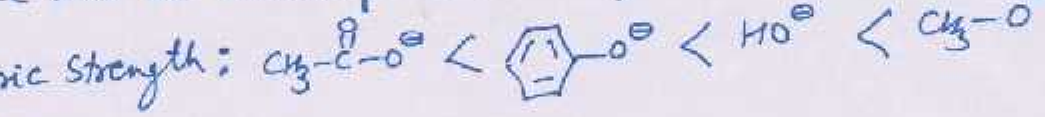
∴ (a)

24. Conjugate base is a stronger nucleophile. Moreover, nucleophilicity decreases from left to right in the period but increases from top to bottom in the group.

∴ (a)

26. When nucleophilic site is same, more the basic strength more will be nucleophilic strength.

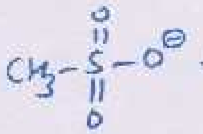
Basic Strength:



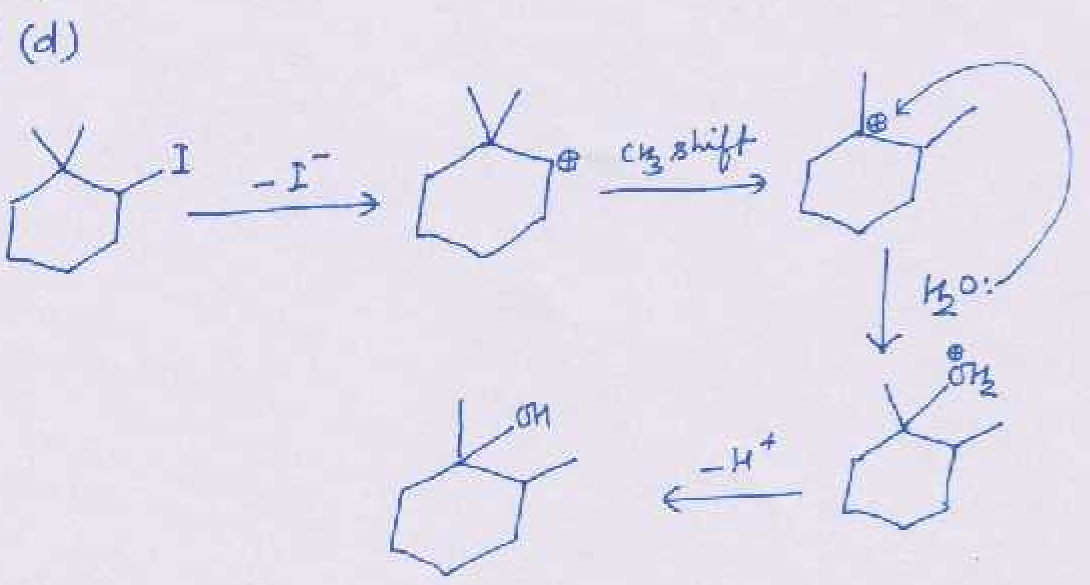
∴ (d)

27. Nucleophilicity increases from top to bottom in a group. For same nucleophilic site, stronger base is stronger nucleophile. Conjugate base is stronger nucleophile. Hence, correct order of nucleophilicity will be:

∴ (b)

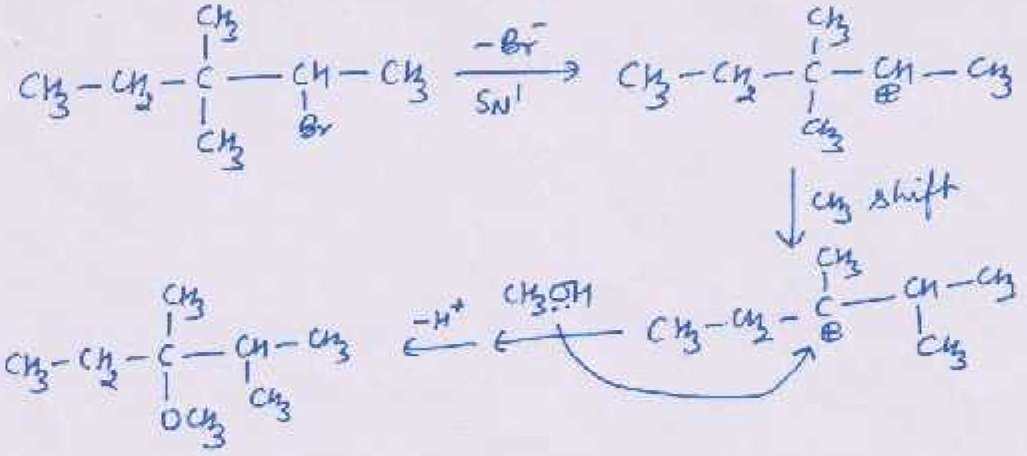
28. 
$CH_3-SO_2-O^{\ominus}$ will be weakest base and best leaving group

∴ (d)

29. 

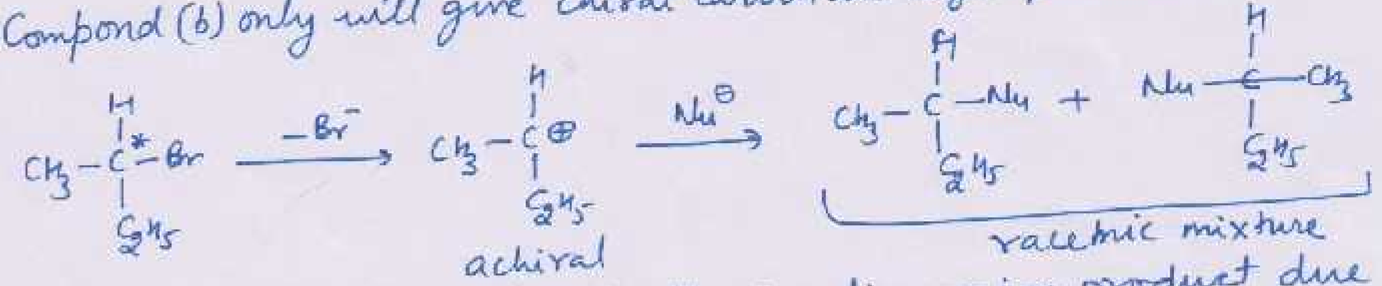
∴ (a)

30.

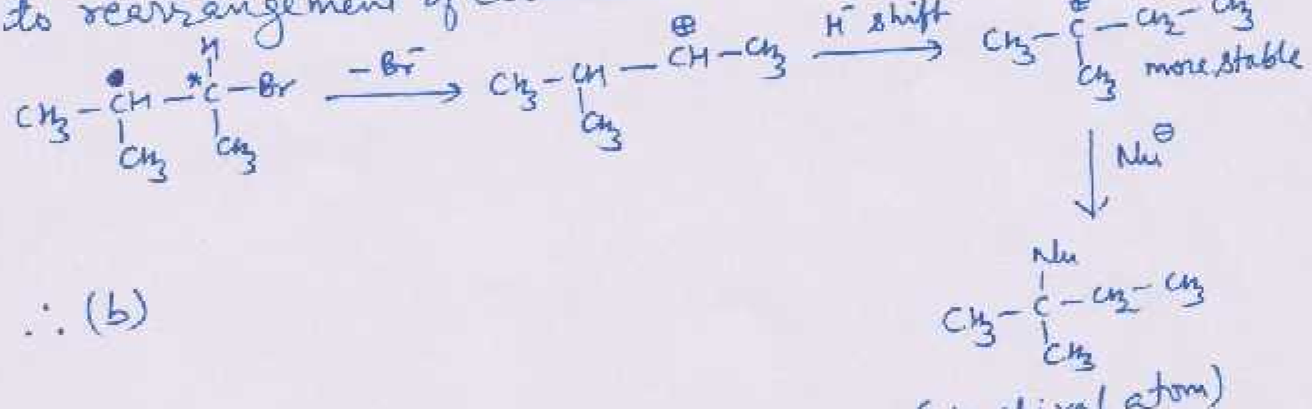


∴ (C)

31. Compond (b) only will give chiral carbon in major product.

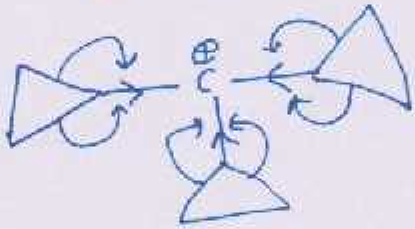


Compound (d) will give optically inactive major product due to rearrangement of carbocation.



∴ (b)

32. Cyclopropyl group when attached to carbocation increases stability to very large extent due to presence of τ (tau) bond.

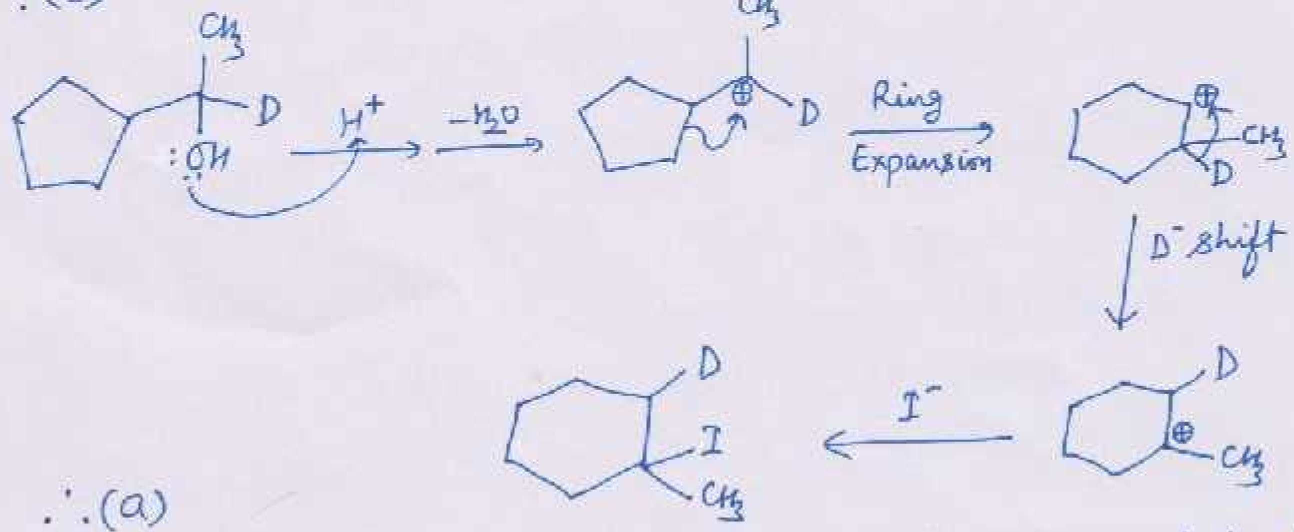


∴ (d)

33. Tertiary alcohols will undergo S_N' reaction in acidic medium. Such S_N1 reaction at chiral atom will lead to formation of racemic mixture.

∴ (c)

34.



∴ (a)

35. Bromine attached to benzene will not be removed due to partial double bond character. Ony benzyl position will undergo substitution reaction.

∴ (a)

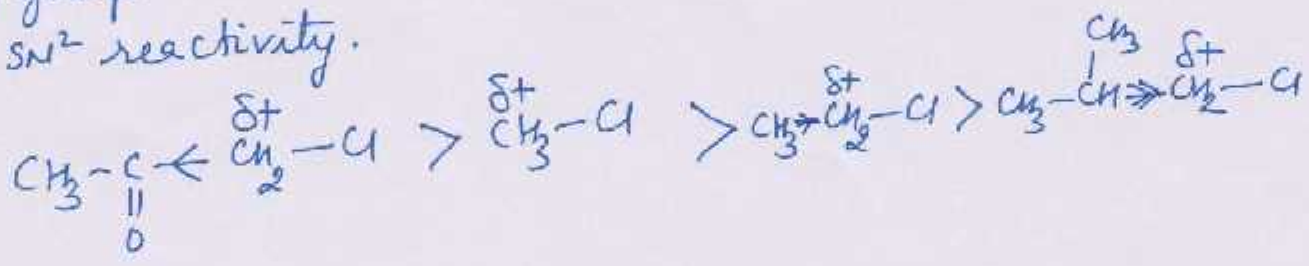
36. Rate of S_N2 reaction $= k\,[R-X][Nu^{\ominus}]$

$$\text{Rate} = k\ C_1 \times C_2$$

$$\text{New Rate} = k \times 3C_1 \times \frac{C_2}{2} = 1.5\ k\ C_1 C_2$$

∴ (C)

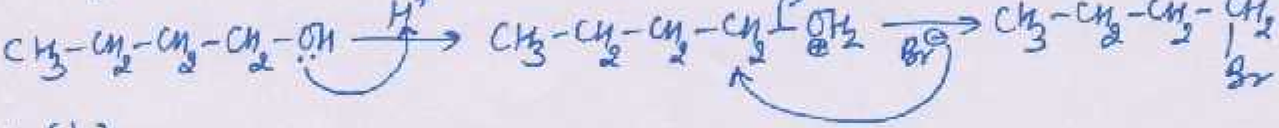
37. Electron withdrawing acetyl group will increase S_N2 ↑reactivity of compound (ii). On the other hand electron donating alkyl groups will decrease the +ve charge that will decrease S_N2 reactivity.



$$CH_3-\underset{\underset{O}{\|}}{C} \leftarrow \overset{\delta+}{CH_2}-Cl > \overset{\delta+}{CH_3}-Cl > CH_3 \rightarrow \overset{\delta+}{CH_2}-Cl > CH_3-\overset{CH_3}{\overset{|}{CH}} \Rightarrow \overset{\delta+}{CH_2}-Cl$$

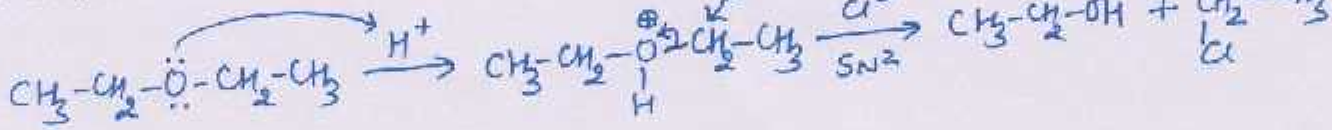
∴ (C)

38. Due to very less stability of carbocation, normal 1° alcohols undergo S_N2 reaction even if medium is acidic.



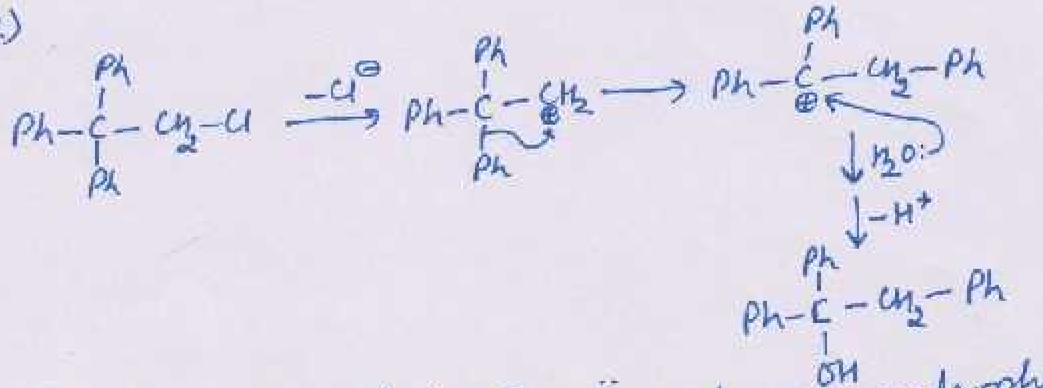
∴ (b)

39.

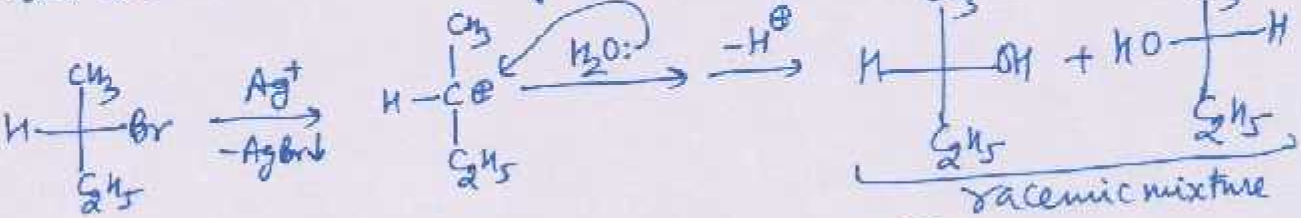


∴ (a)

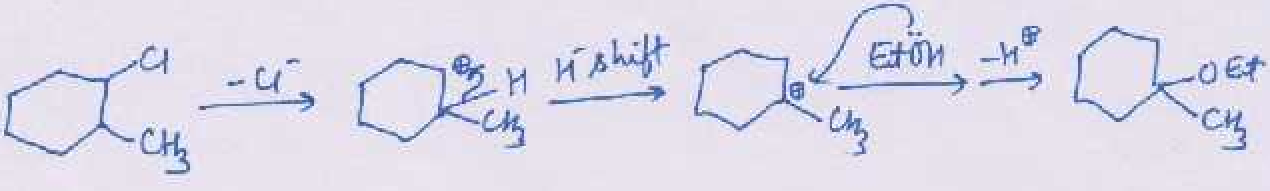
40. (a)



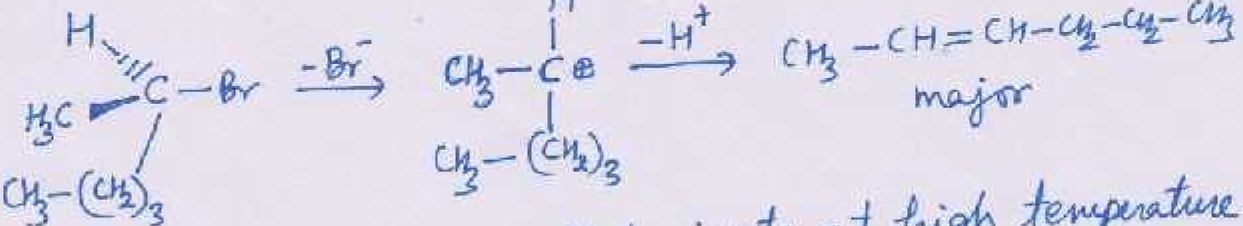
(b) Ag^+ help in removal of Br^-. $H_2\ddot{O}$: acts as nucleophile during the S_N1 reaction leading to racemic mixture of alcohols.



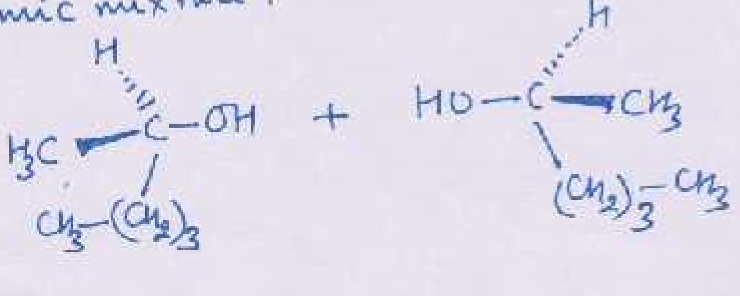
(c)



(d)



elimination reaction will dominate at high temperature. but S_N1 reaction will dominate at low temperature, which gives racemic mixture.



41. Nucleophilic strength of C^- is more than that of O^-.
-ve charge at 3rd will be involved in resonance.
∴ (d)

42. More the stability of carbocation, lesser will energy required for ionization of alkyl halide, lesser will be activation energy of SN' reaction and faster will be rate of SN^1 reaction.
∴ (d)

1. (a) will give achiral carbon
(b) is already achiral and product will also be achiral
(c) will undergo elimination (E_2) reaction having no chiral atom.
(d) will ~~not~~ give only single optically active product due to SN^2 reaction.

∴ (d)

2. SN^2 reaction at chiral atom will lead to inversion of ~~reaction~~ configuration but the stereochemistry of other chiral atom will remain unaltered.

∴ (b)

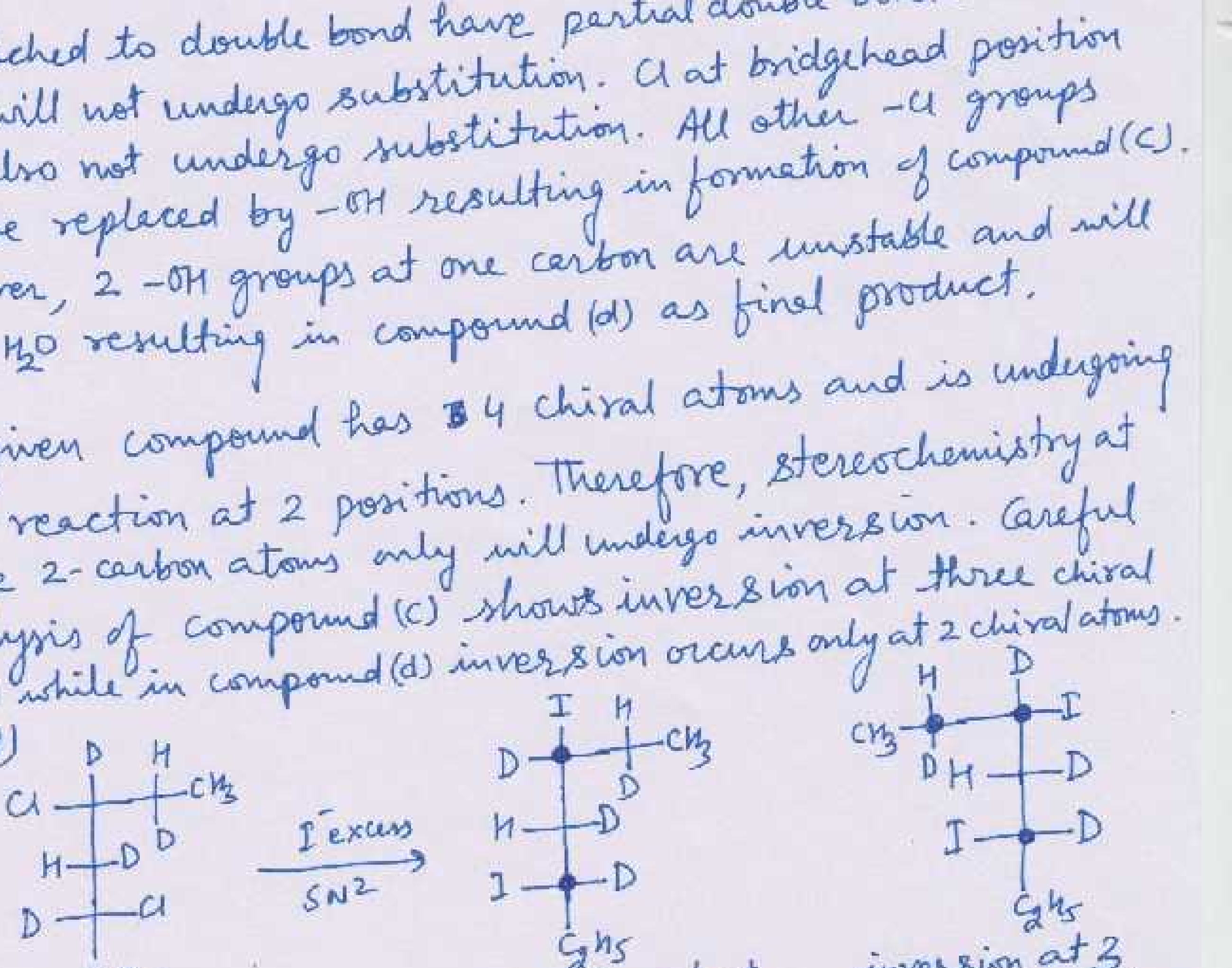
3. SN^2 reaction at chiral atom will result in inversion of configuration but stereochemistry of other carbon will remain unaltered.

∴ (b)

4. Cl attached to double bond have partial double bond character and will not undergo substitution. Cl at bridgehead position will also not undergo substitution. All other –Cl groups will be replaced by –OH resulting in formation of compound (c). However, 2 –OH groups at one carbon are unstable and will lose H_2O resulting in compound (d) as final product.

5. The given compound has ~~3~~ 4 chiral atoms and is undergoing SN^2 reaction at 2 positions. Therefore, stereochemistry at these 2-carbon atoms only will undergo inversion. Careful analysis of compound (c) shows inversion at three chiral atom while in compound (d) inversion occurs only at 2 chiral atoms.

∴ (d)

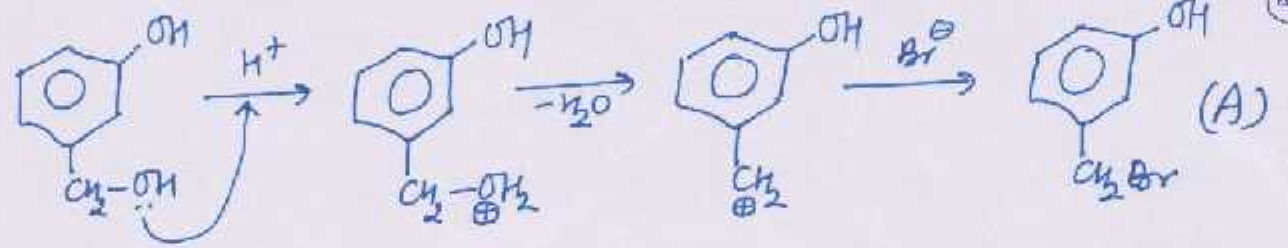


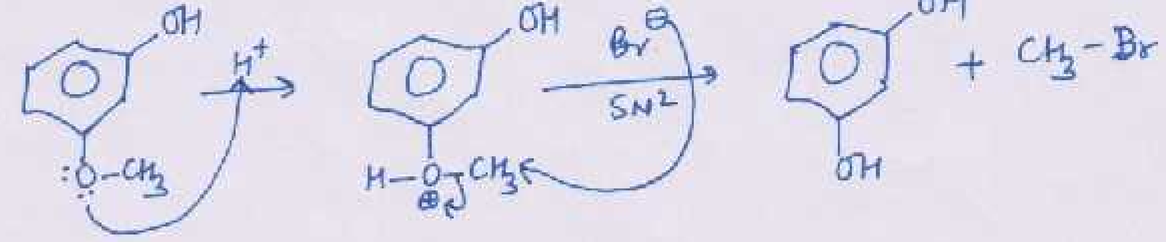
reaction

inversion only at marked 2 chiral atom.

inversion at 3 marked chiral atom.

6.





∴ (a)

7. More the positive charge at carbon more will be S_N2 reaction rate. However, S_N2 reaction at bridgehead position will be most difficult.

∴ (a)

8. A bulky base Et_3N: will do Hoffmann elimination leading to removal of hydrogen from least hindered position.

∴ (b)

9. Lesser the steric hinderence more will be S_N2 reaction and more will be S_N2/E_2 ratio.

∴ (a)

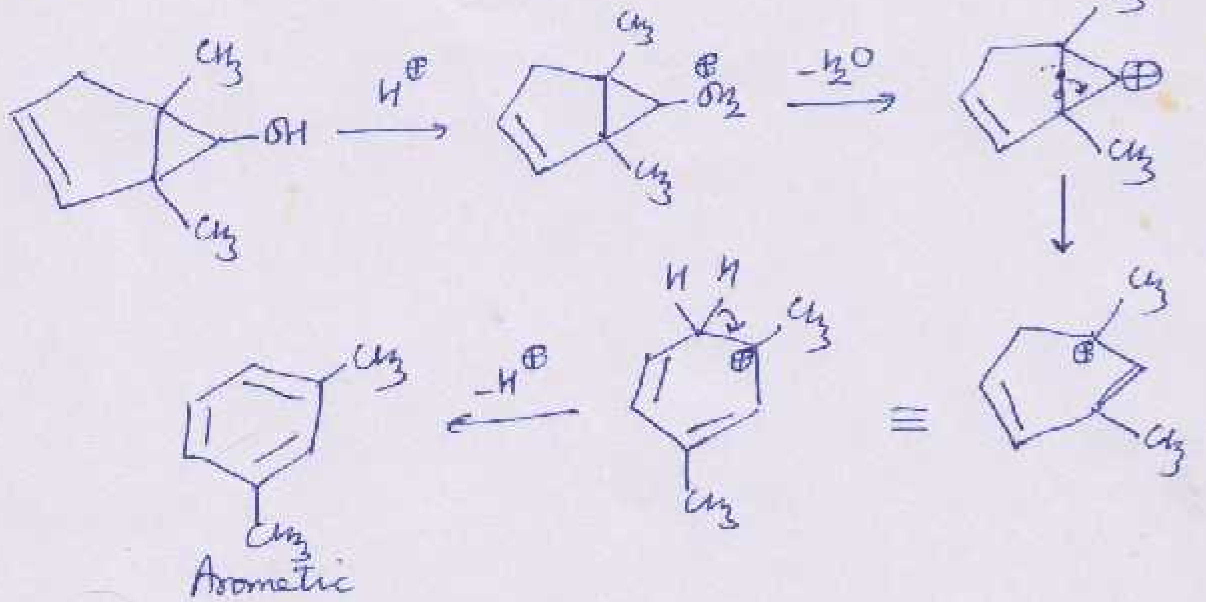
10. S_N2 reaction will lead to inversion of configuration. The optical activity of product molecules will be opposite the reactant. Therefore, optical activity of other same number of reactant molecules will also be cancelled by product molecules. Therefore, a, b and (c) statements are correct. However final solution will have radioactive iodine as well as non radioactive iodine. Therefore, incorrect statement will be (d).

∴ (d).

11. As we move from CH_3-X to $3°R-X$ rate of S_N1 will increase due to increased stability of carbocation while rate of S_N2 will decrease due to more steric hindrance.

∴ (b)

12.



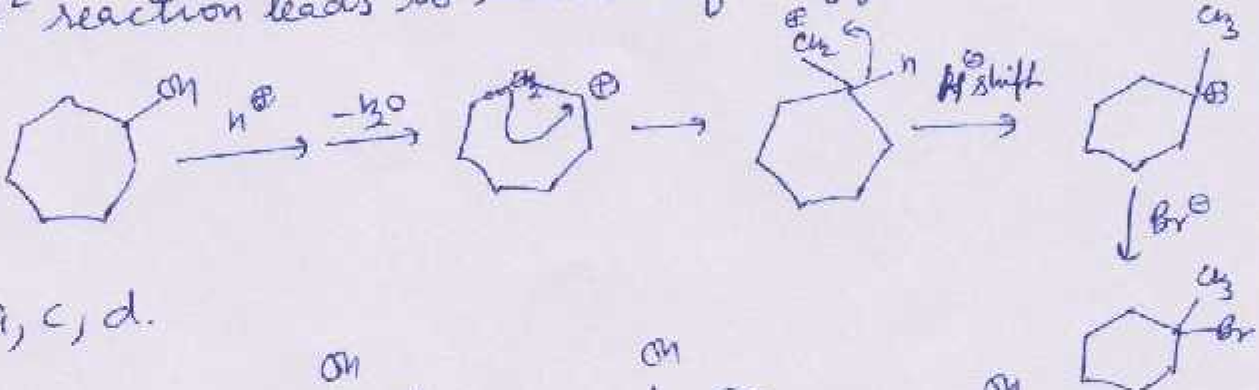
∴ (b)

13. (a) S_N2 reaction leads to inversion of configuration

(b) Cl attached to benzene will not be replaced because of partial double bond character.

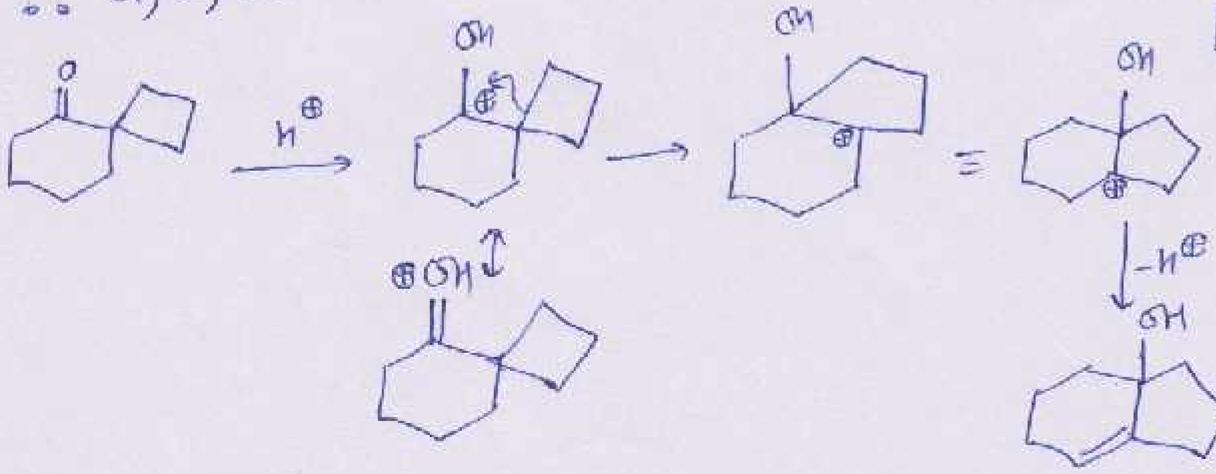
(c) S_N2 reaction leads to inversion of configuration.

(d)



∴ a, c, d.

14.



∴ a, b, d

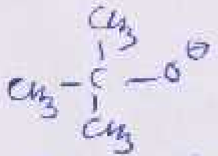
15. Nucleophile is electron rich species.

$\therefore$ (a), (b), (d)

16. Conjugate base is a stronger nucleophile. Nucleophilic strength decreases along a period and increases along a group.

$(CH_3)_3CO^{\ominus} < \overset{\ominus}{C}H_3$ $\quad$ $CH_3-S^{\ominus} > CH_3-\ddot{S}H$

$(CH_3-CH_2)_3N: < (CH_3-CH_2)_3P:$ $\quad$ $CH_3-CH_2-CH_2-O^{\ominus} >$



$CH_3-C(CH_3)_2-O^{\ominus}$

less nucleophilic due to more steric hindrance.

$\therefore$ b, d

17. Weaker base is better leaving group.

$\therefore$ (a), (b),

18. More the stability of resultant carbocation, faster will be solvolysis. When different leaving groups are attached, better the leaving group faster will be solvolysis.

$\therefore$ (a), (b), (c)

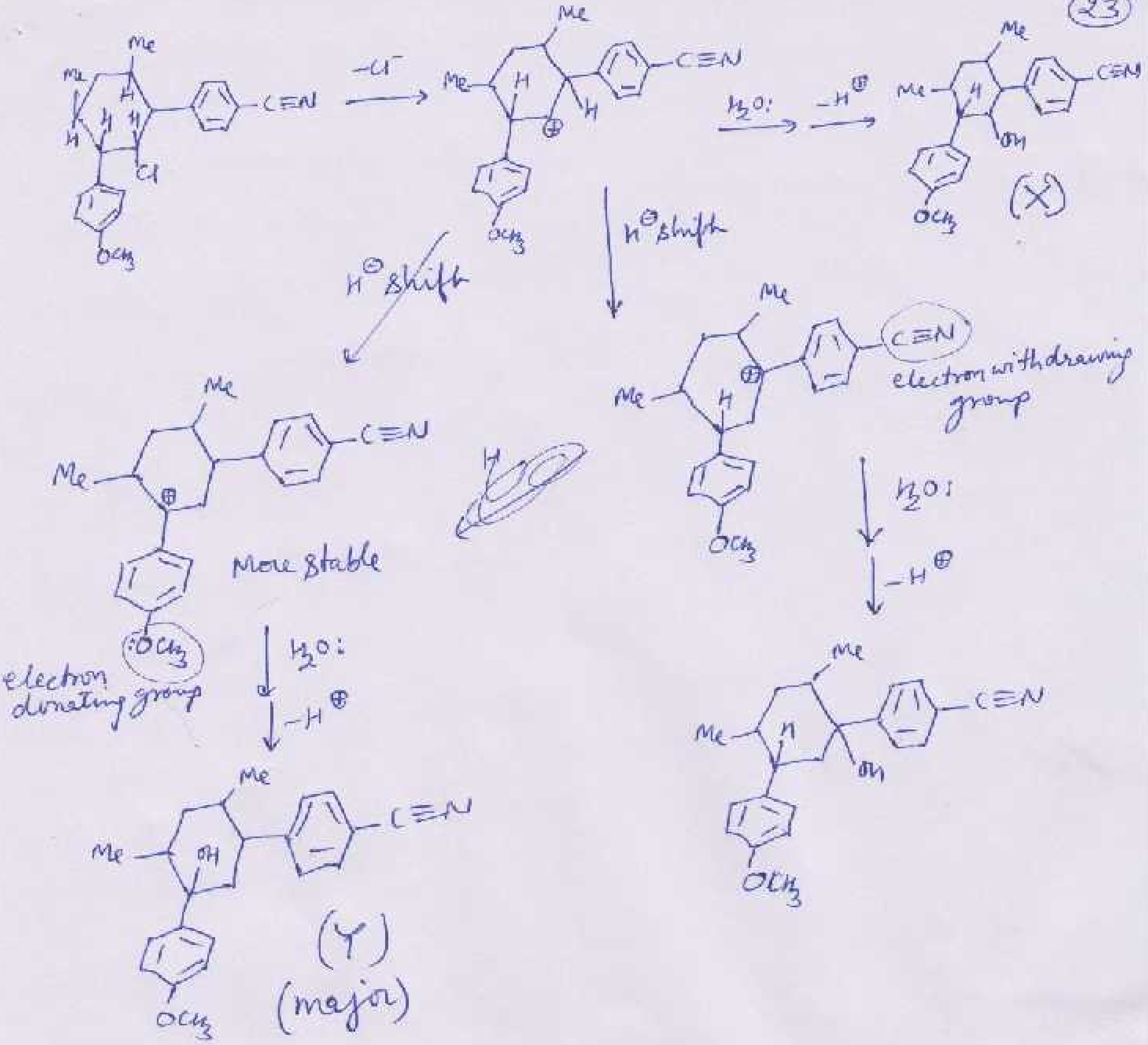
19. S_N1 reaction occurs in at least two steps.

Rate of $S_N1 = k[R-X]$

S_N1 reaction is favoured by polar solvents and for 3° alkyl halides.

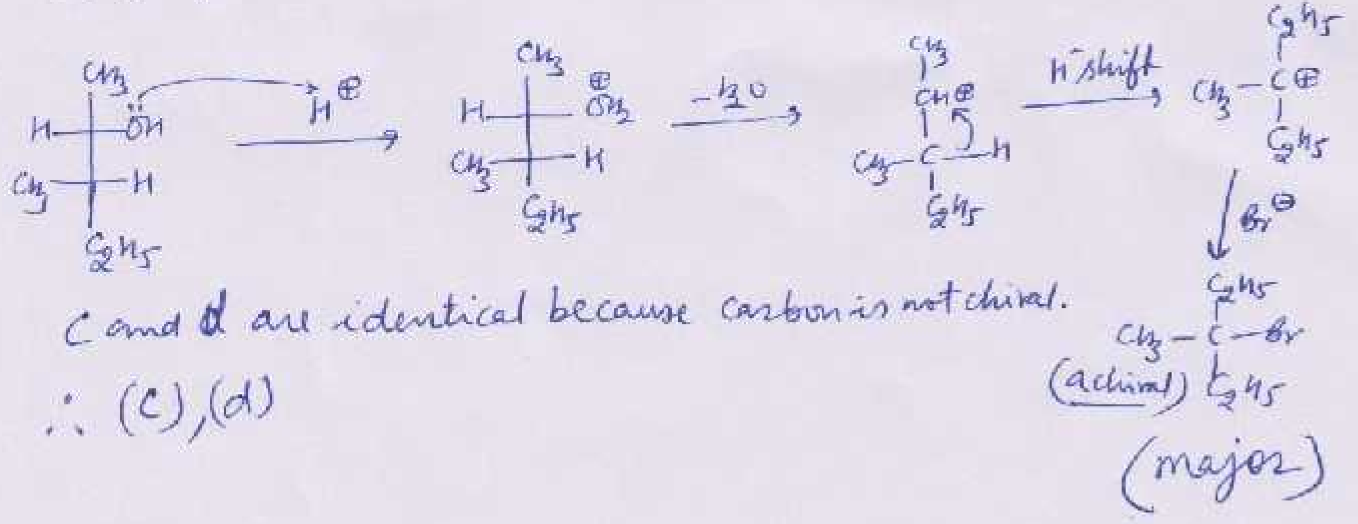
$\therefore$ (b), (c), (d).

20.



∴ (B), (D)

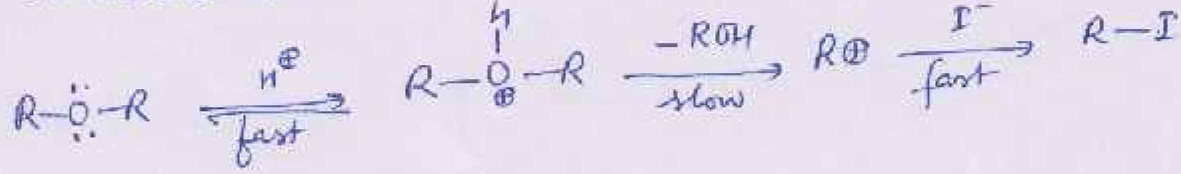
21.



C and d are identical because carbon is not chiral.

∴ (C), (d)

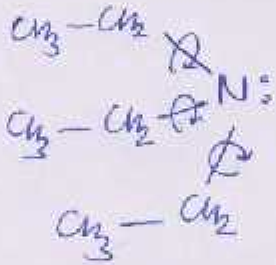
22. In SN^1 mechanism:



$$R-\ddot{O}-R \underset{fast}{\overset{H^{\oplus}}{\rightleftharpoons}} R-\overset{H}{\underset{\oplus}{O}}-R \xrightarrow[slow]{-ROH} R^{\oplus} \xrightarrow[fast]{I^-} R-I$$

∴ (b), (C)

23



C–N bonds can rotate that will increase steric hindrence and rate of SN^2 reaction will decrease.

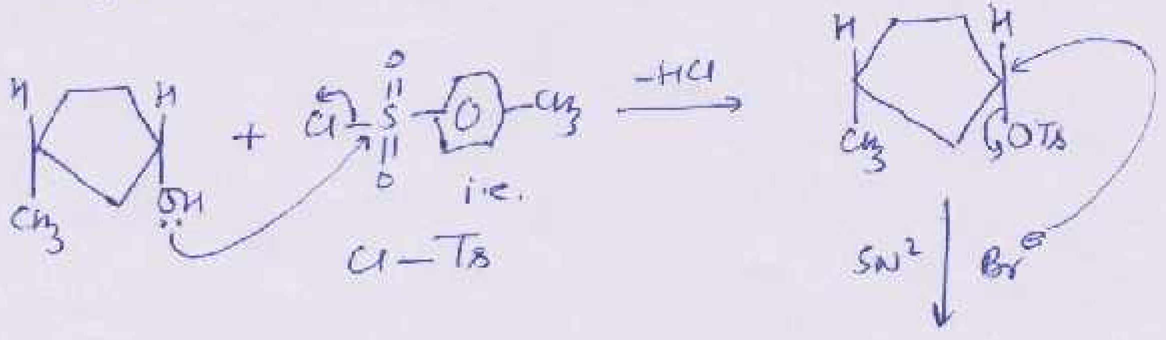
C–N bonds can not rotate due to ~~steric~~ ~~hindrance~~ cyclic structure, steric hindrance will be lesser. SN^2 rate will be more.

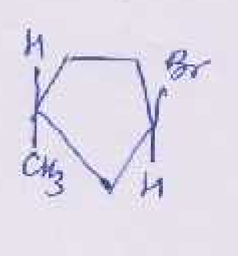
CH_3-I will react faster than $CH_3-\underset{I}{CH}-CH_3$ in SN^2 reaction due to more steric hindrance in later.

∴ a, b.

24. Br^- is better leaving group and will be mainly replaced. Due to SN^2 mechanism, inversion of configuration will occur.
∴ (a), (c)

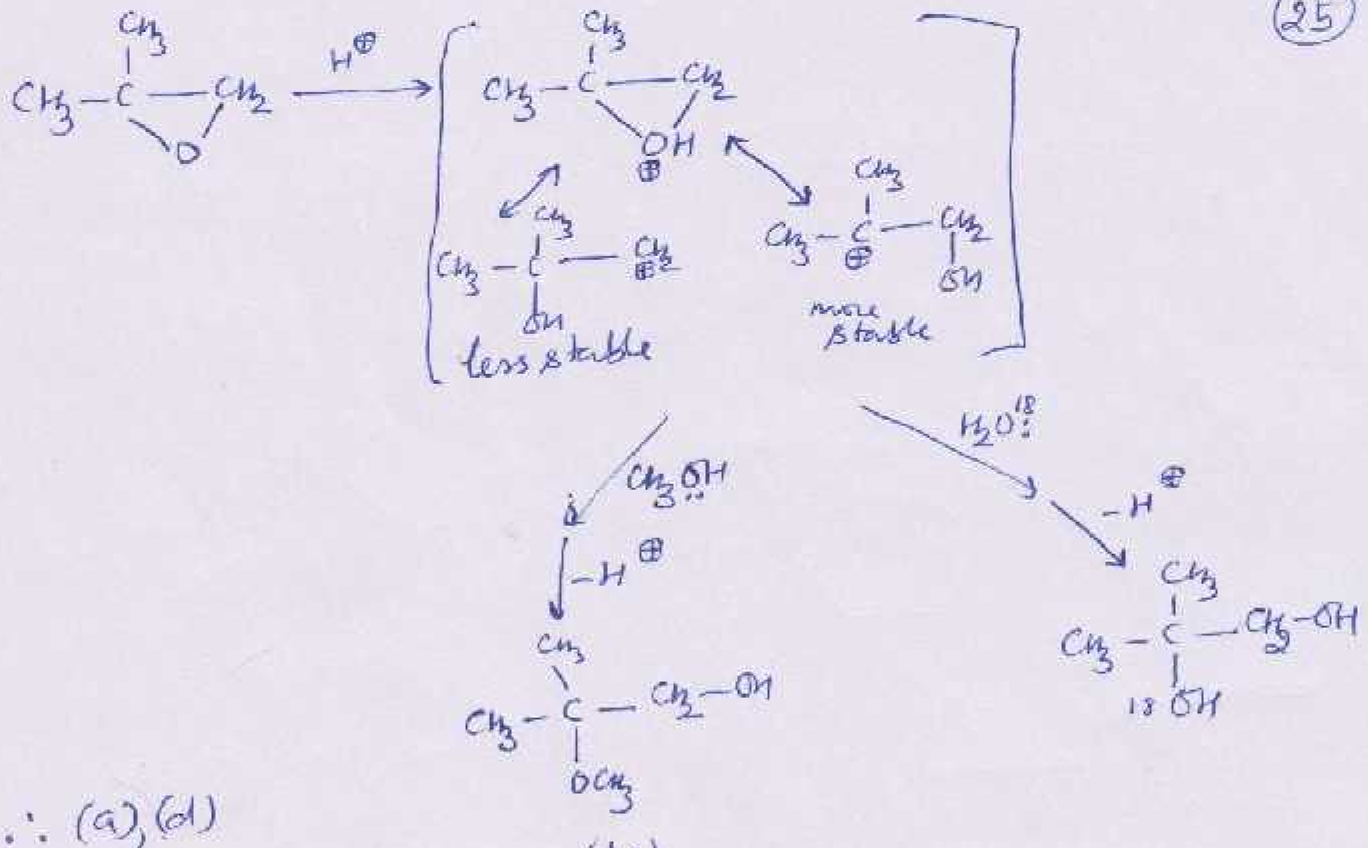
25.





∴ (a), (b)

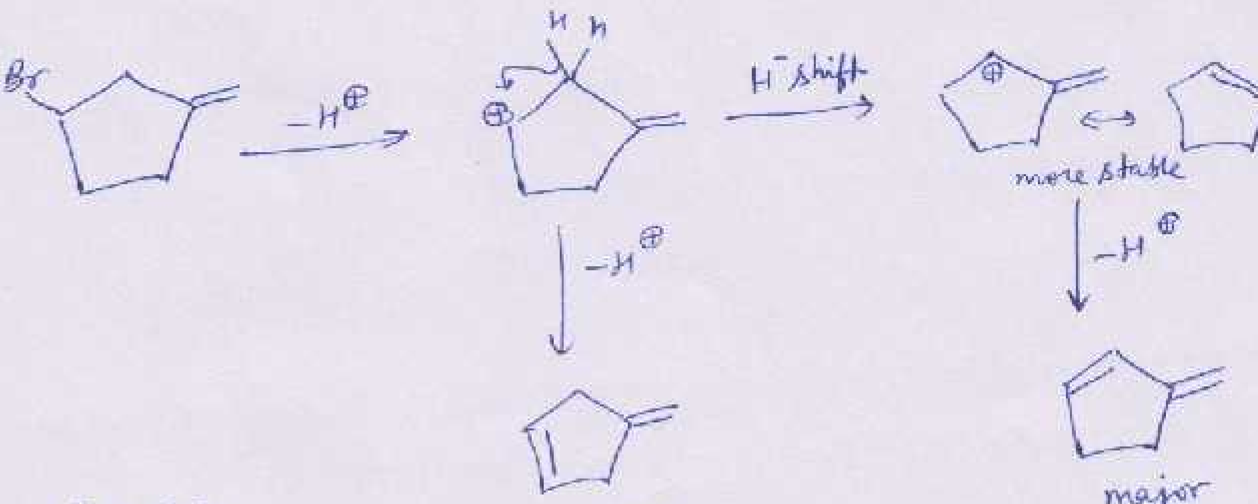
26.



(Y)

∴ (a), (d)

27.

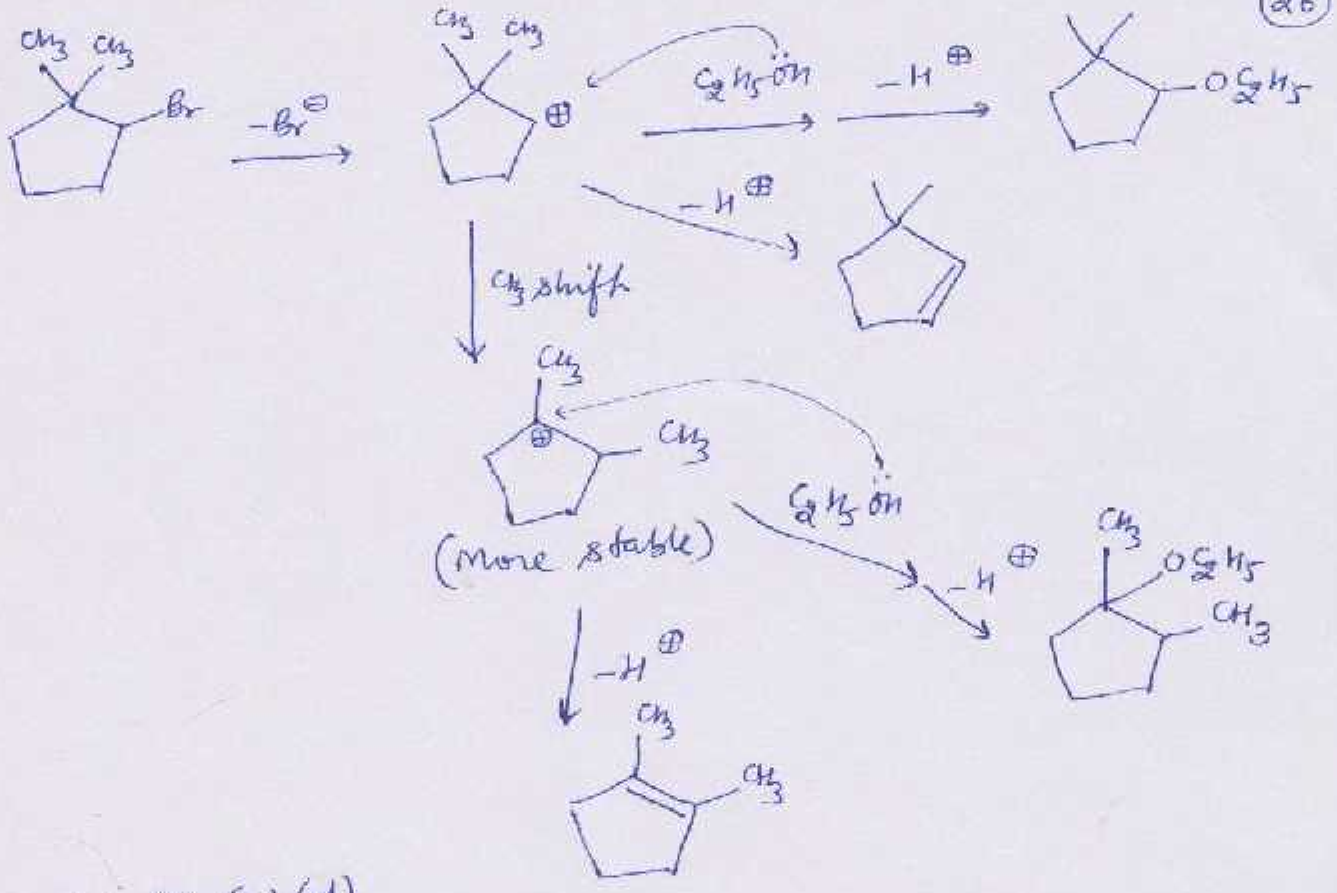


∴ (b), (c)

28. Carbocation prefers to form σ bond so SN' reaction is favoured over E_1. Branching at β-carbon will increase stability of alkene formed by removal of H^+ from β-carbon. This will favour elimination. High temperature favours elimination due to +ve ΔS. Weaker base and polar solvents favour E_1 reaction.

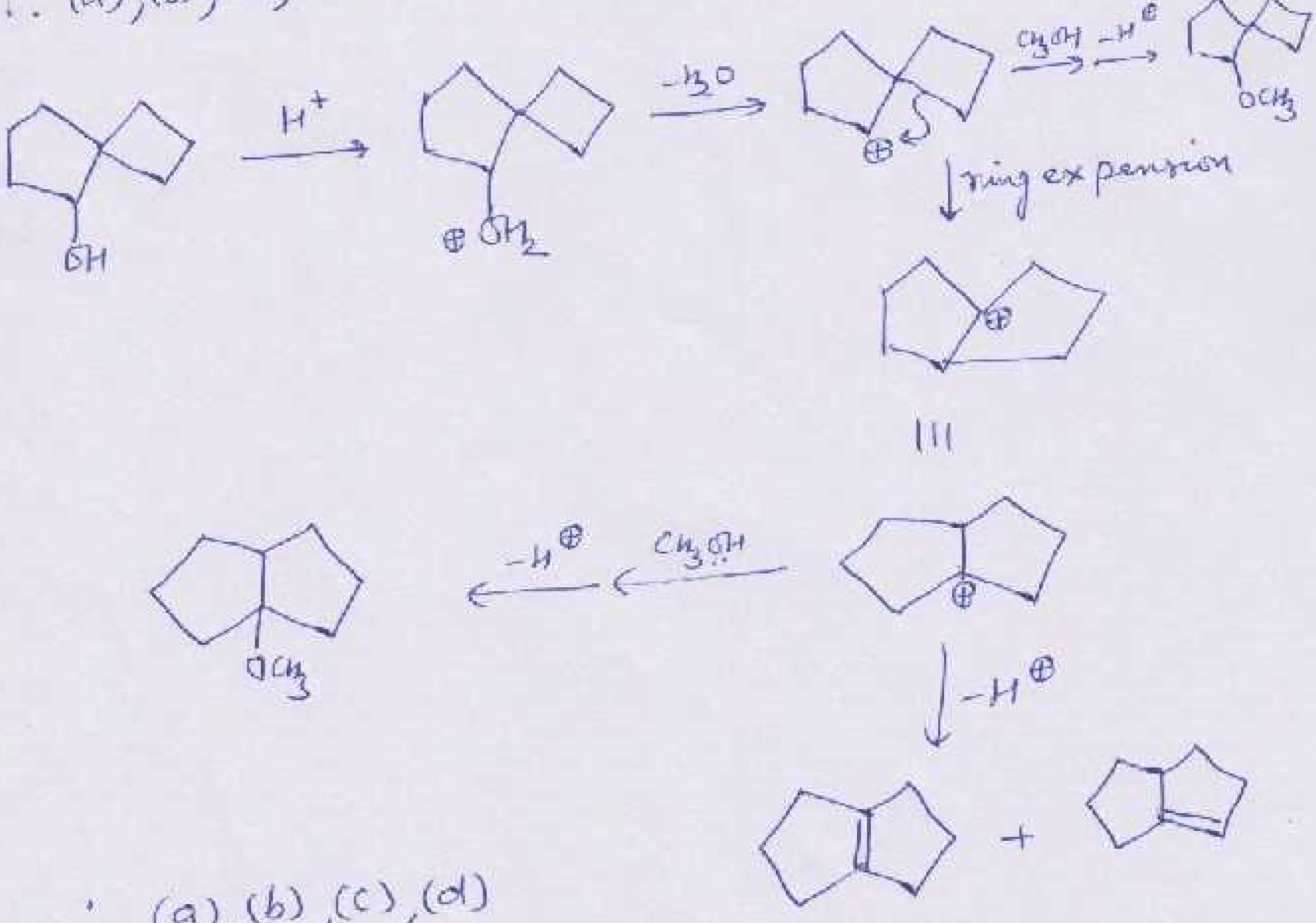
∴ a, b, c, d.

29.



∴ (a), (b), (c), (d)

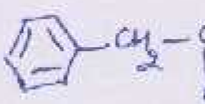
30.

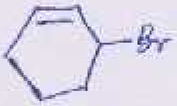


∴ (a), (b), (c), (d)

31.

(a) Incorrect because Br^- is better leaving group.

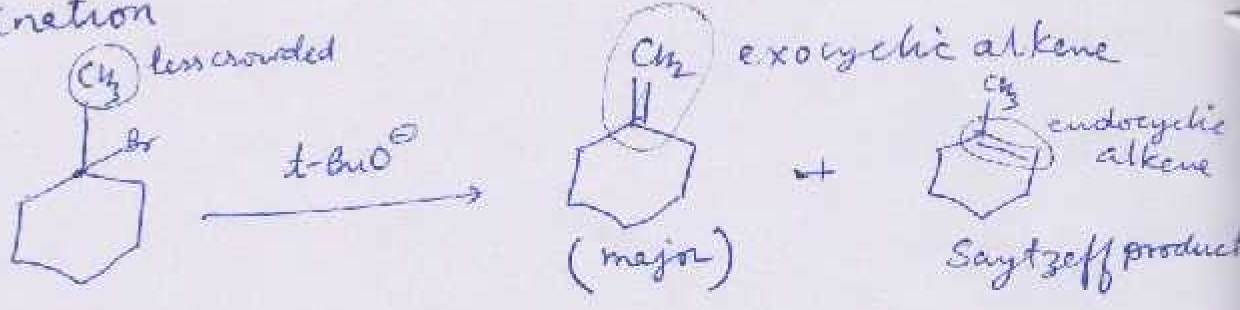
(b)  will give more stable conjugated alkene and will react faster than 

(c)  react faster due to partial C–Br bond and more stable alkene (diene) than  .

(d) $CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-CH_2-CH_3$ will give more stable alkene (more substituted) and will react faster than $CH_3-\underset{Br}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

∴ (b), (c), (d)

33. tert. butoxide is a bulky base and will do Hoffmann elimination

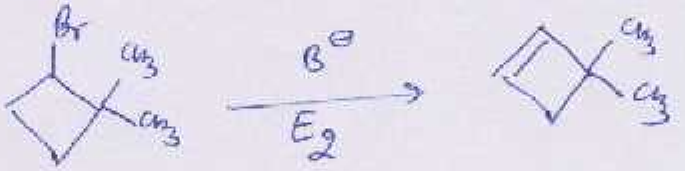


a, b, d

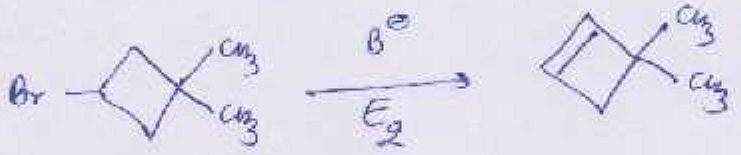
34. t-BuO$^\ominus$ is bulky base and will give Hoffmann Product as major while Et–O$^\ominus$ is smaller base and gives saytzeff product as major

∴ a, d.

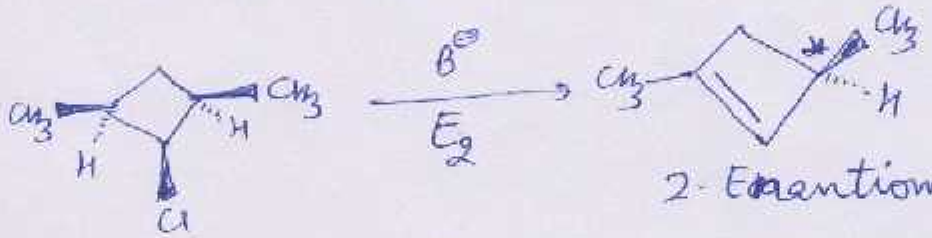
35. Strong base will result in E_2 elimination.

(a)


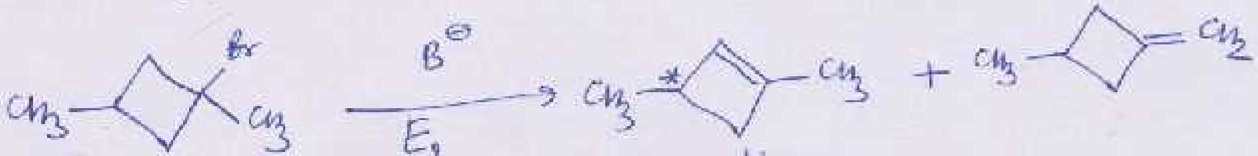
1 product

(b)


1 product

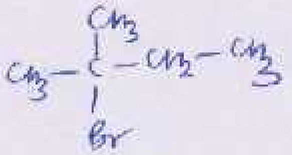
(c)


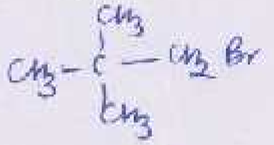
2 Enantiomers

(d)


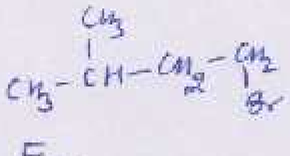
2 enantiomers

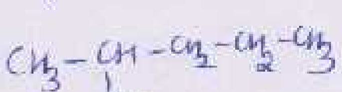
∴ a, b

36.
(a)

$CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$ react fastest in E_1

(b)

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Br$ is unable to react in E_2 due to absence of β hydrogen.

(c)

$Br-CH_2-\overset{CH_3}{CH}-CH_2-CH_3$,

$CH_3-\overset{CH_3}{CH}-CH_2-\underset{Br}{CH_2}$, $CH_3-CH_2-CH_2-CH_2-CH_2-Br$ can give single alkene in E_2.

(d)

$CH_3-\underset{Br}{CH}-CH_2-CH_2-CH_3 \xrightarrow{E_2} \underset{\text{1-isomer}}{CH_2=CH-CH_2-CH_2-CH_3} + \underset{\text{2 geometrical isomers}}{CH_3-CH=CH-CH_2CH_3}$

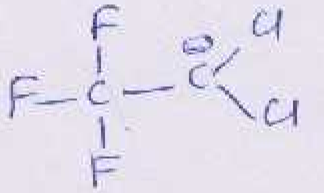
∴ (a), (c), (d)

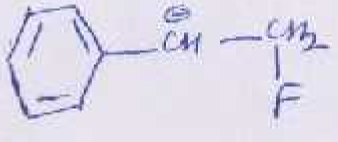
37. (a) Due to bulky base elimination will be as per Hoffmann's rule leading to 1-Butene.

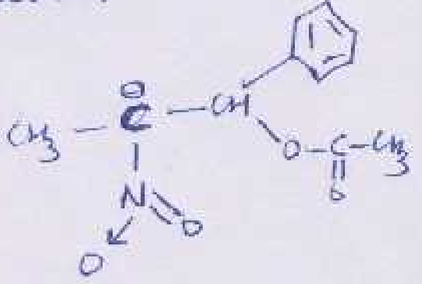
(b), (c), (d) Due to poorer leaving group reaction will proceed by E_{1CB} like mechanism in which more acidic β-hydrogen is mainly removed to give Hoffmann product 1-Butene as major

∴ (a), (b), (c), (d).

38. (a), (b) and (c) will react through E_{1CB} mechanism due to ~~resonance~~ highly stable conjugate bases.







39. a, b, d are correct.

c is incorrect because electron withdrawing group –X will stabilize the carbanion.