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Substitution Reaction — 1

Substitution Reaction

S_N1
substitution nucleophilic unimolecular

S_N2
substitution nucleophilic bimolecular

S_Ni
Internal Nucleophilic substitution

S_N1 (Substitution Nucleophilic Unimolecular):

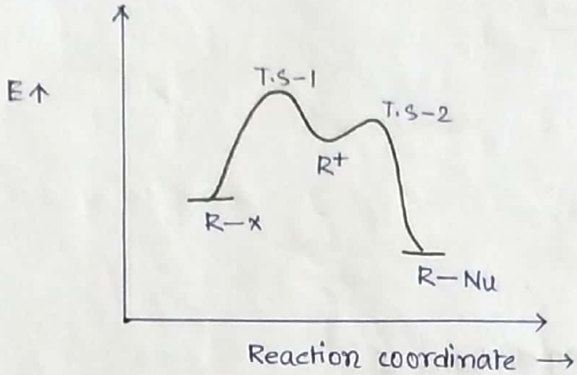
$C(CH_3)_3-X$

i. 1st Step (Slow step): $R-X \overset{r.d.s}{\rightleftharpoons} R^+ + X^-$

ii. 2nd Step (Fast step): $R^+ \xrightarrow{Nu^-} R-Nu$

$\text{rate} \propto [R-X]$

$\text{rate} = K[R-X]$ K = rate constant

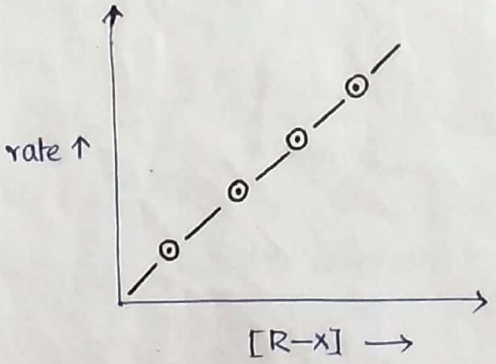


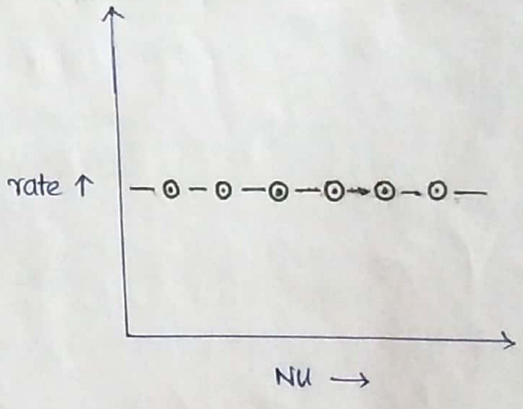
$R-X \rightarrow [\overset{\delta+}{R} \cdots\cdots \overset{\delta-}{X}]^{\neq}$

R^+ (intermidiate)

S_N1 reaction rate depends upon the following factor —

(I) effect of the substrate R–X
(II) Stability of the carbocation
(III) Leaving group ability.
(IV) Solvent Polarity.





Transition state -1

$R-X \rightarrow [\overset{\delta+}{R} \cdots\cdots \overset{\delta-}{X}]$ X = Leaving group

Bond Breaking

Transition state - 2

$\overset{+}{R} \;\; Nu^- \rightarrow [\overset{\delta+}{R} \cdots\cdots\cdots \overset{\delta-}{Nu}]$ Nu = Nucleophile

Bond Making

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Effect of the substrate and stability of the carbocation :

(I) (A) $MeS-CH_2-Cl \rightleftharpoons Me\ddot{S}-\overset{+}{C}H_2 \rightleftharpoons Me-\overset{+}{S}=CH_2$ (A) 3p-2p overlap

(B) $MeO-CH_2-Cl \rightleftharpoons Me\ddot{O}-\overset{+}{C}H_2 \rightleftharpoons Me-\overset{+}{O}=CH_2$ (B) 2p-2p overlap

The S_N1 reactivity order : B > A.

As 2p-2p overlap is better than 3p-2p overlap. Since, the carbocation genarated by the 2nd compound is more stable than compound 1.

(II)

— Which carbocation is more stable ?

(A)

Eqivalent resonating structure

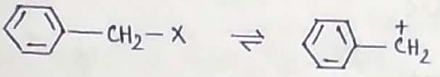
(B)

Hyperconjugation stability

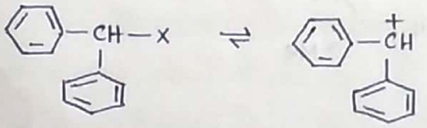
As the carbocation (A) has two equivalent resonating structure while 2nd carbocation has only hypereconjugation stability. So carbocation of compound A is more stable carbocation of compound B.

(III) $Ph-CH_2-X$ Ph_2-CH-X Ph_3-C-X

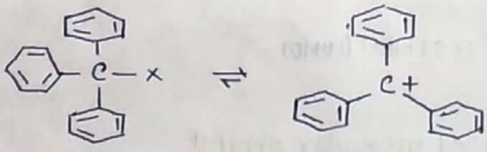
— Which carbocation is more stable?



A



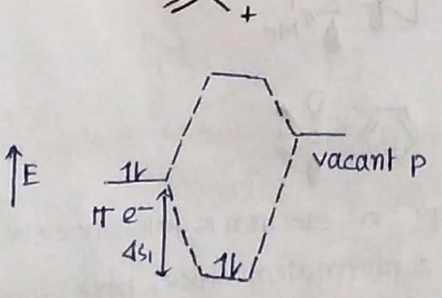
B

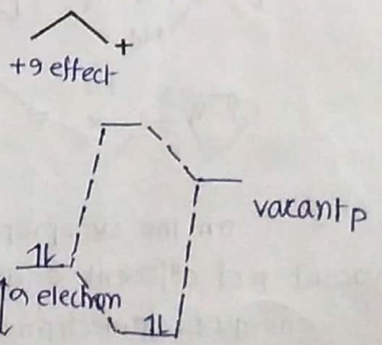


C

With increasing the number of phenyl group the delocalization of positive charge also increases and the stability also increases.

S_N1 reactivity order : (C) > (B) > (A)





ΔS_1 = Stabilization energy

Since, $\Delta S_1 > \Delta S_2$

i.e. $r_1 > r_2$

Substitution reaction

(IV)

— Which carbocation is more stable?

Homoaromatic A

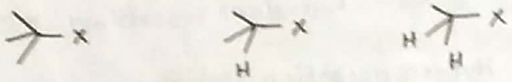
Antiaromatic B

Aromatic C

Stability order: $C > A > B$.

As, Aromatic > Homoaromatic > Antiaromatic.

(V)



Which carbocation is more stable?

A

9 hyperconjugative structure + I effect of three –Me group

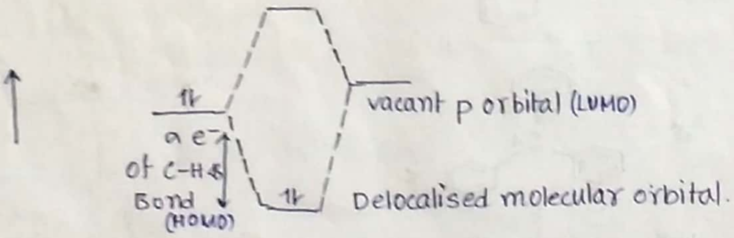
B

6 hyperconjugative structure + I effect of two –Me group

C

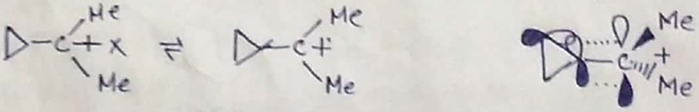
3 hyperconjugative struture + I effect of –Me group.

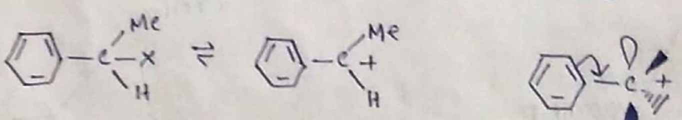
stability order: $A > B > C$.



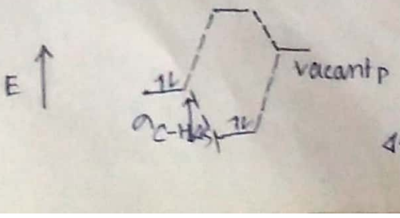
(VI)

— Which carbocation is more stable?



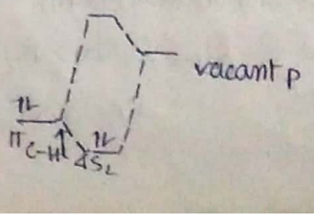


In the cyclopropyl cation high energy σ–electron is delocalized with the vacant p of adjecent C-atom in the bisecting conformation. Since, here energy of σ electron > energy of π - electron



$\Delta S_1 > \Delta S_2$

$r_1 > r_2$



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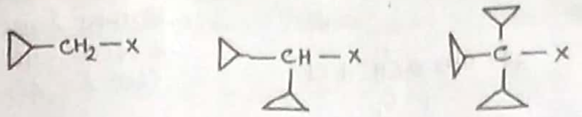
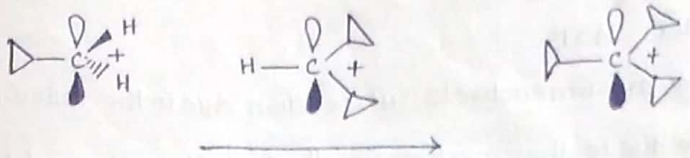
(VII)



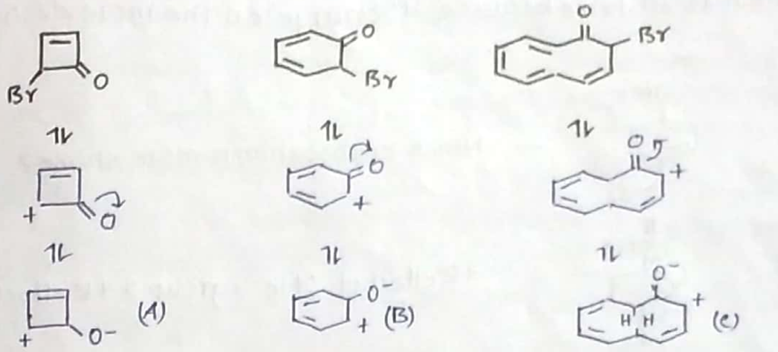
Which carbocation is more stable?



S_N1 reactivity increases

As the number of cyclopropyl ring increases the stability of the carbocation and SN1 reactivity also increases.

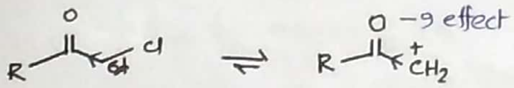
(VIII)



Arometic Antiarometic Non arometic

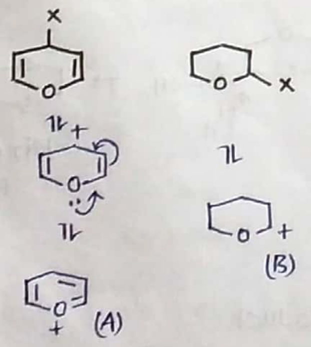
The stability order will be (A) > (C) > (B)

(IX)



This cation is unstable due to strong electron withdrawing group adjecent to the positive charge.

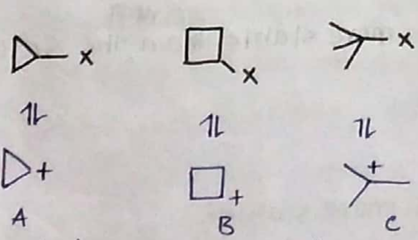
(X)



— Which carbocation is more stable?

carbocation A is more stable (because) due to arometicity according to Huckel's rule.

(XI)



— Which carbocation is more stable?

3° carbocation + 9 hyperconjugative structure + 3 +I effect of −Me group.

Angle strain
$= \frac{1}{2}(120-60)$
$= 30^\circ$

Angle strain
$= \frac{1}{2}(120-90)$
$= 15^\circ$

Stability order : C > B > A.

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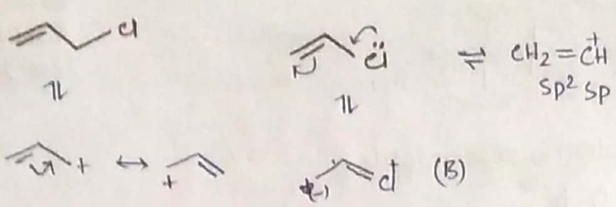
(XII)



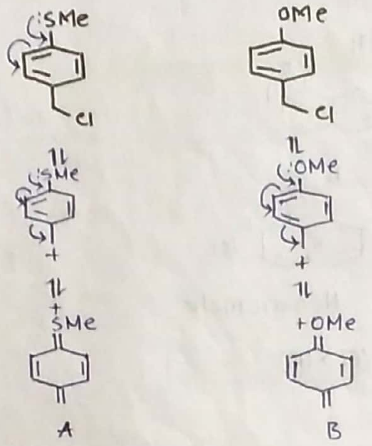
Stability order: A>B

Vinyl halides are unreactive to S_N1 reaction due to the following reason–

(i) In vinyl chloride due to the mesomeric effect of Cl, C–Cl bond become partial double bond character which is not possible in allyl chloride. Thus C–Cl Bond in vinyl is stronger than allyl chloride.

(ii) Again vinyl cation is unstable because '+' charge on the more electronegative sp carbon atom.

(XIII)

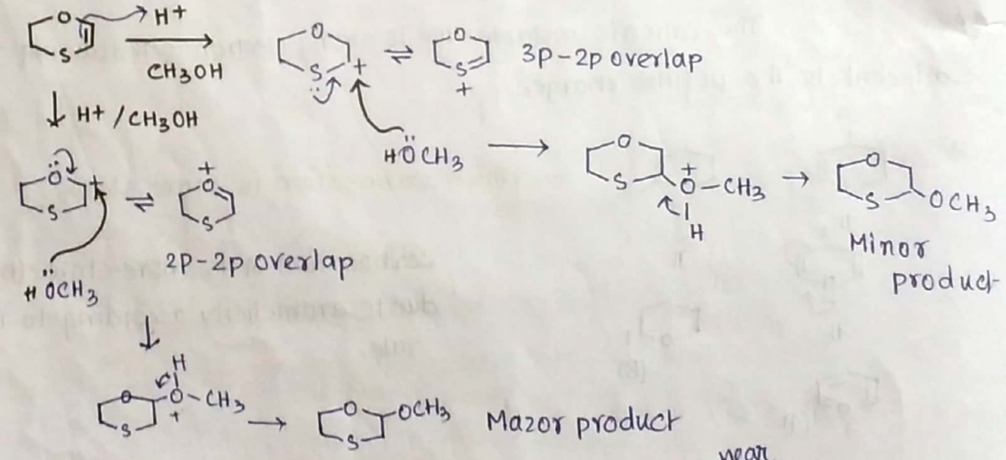


— Which carbocation is more stable?

+R effect of OMe group > +R effect of -SMe group

Stability order: B>A.

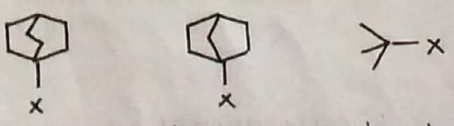
(XIV)



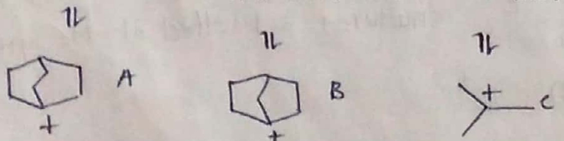
Mazor product

+ve charge near O atom is more stable than near the S atom

(XV)

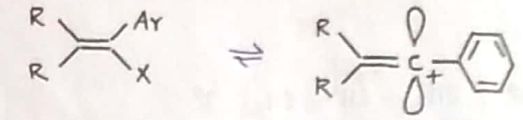


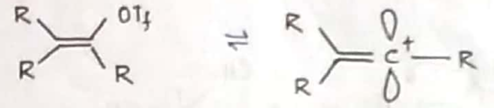
Which carbocation is more stable?



Here all the halides are 3° halides. So, solvolysis through SN1 reaction is expected. Tartiary butyl chloride undergoes S_N1 reaction and the tartiary cation is stabilized by the 9 hyperconjugative structure and +I effect three –Me group. carbocation A and B are quite unstable because '+' charge on the bridge head position which violates the Bredt's rule. Between (2) and (1) 2 (1) is slightly stable because of extra $-CH_2$ group. So, the stability order is — C>A>B.

Modification to increase the reactivity of the S_N1 reaction :

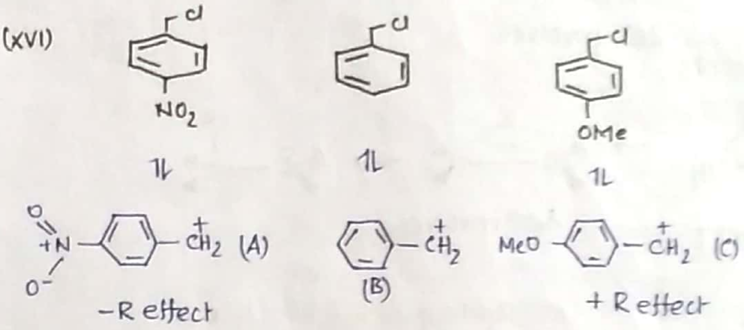
(I)


(II)


Vinyl substrate are in general unreactive to S_N1 reaction but they connot be met to do so in two ways —

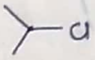
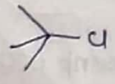
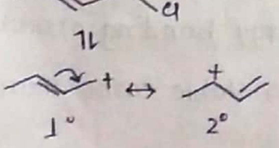
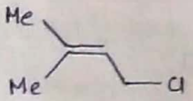
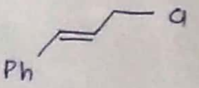
(I) By the use of a group that stabilize the vinyl group.

(II) Even without stabilization by the use of very good leaving group like triflet, tosylate, $\overset{+}{N_2}$ etc.

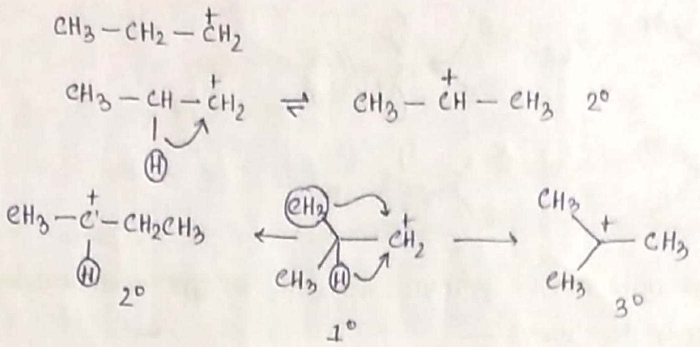
(XVI)


Stability order : C > B > A

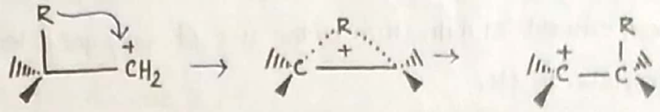
carbocation (1) is distabilized by the -R effect of the NO_2 group.

	Substrate	Reactivity
1.		Mainly S_N2 reaction occur S_N1 reactivity rate 0.07
2.		S_N1 reactivity rate 0.12, it is 2n secondary chloride undergoes S_N1 reaction but not so good. (Both S_N1 and S_N2).
3.		Very good for S_N1 reaction. rate = 2100,
4.		Reaction rate 91. Allylic cation is secondary at one end.
5.		Reaction rate $= 1.3 \times 10^5$ Allylic cation is tartiary at one end.
6.		Reaction rate 770 Primary carbocation is both benzylic and allylic.

Explain why less stable carbocation can undergoes to more stable carbocation but free radical does not. — Why?

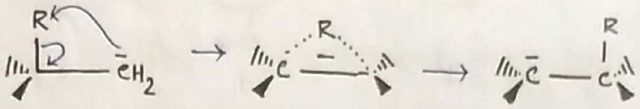


Cationic Rearrangement:



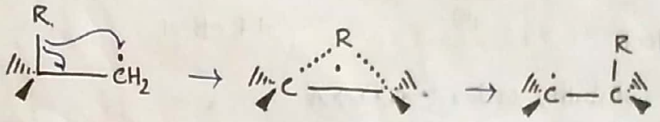
2e⁻ involves

Anionic Rearrangement:

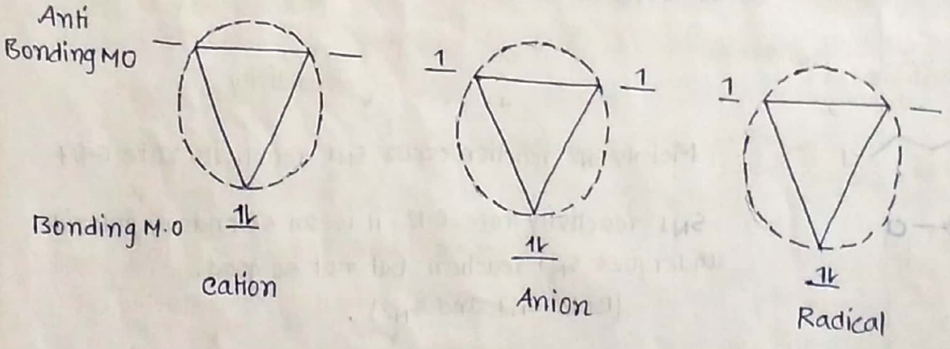


4e⁻ involves

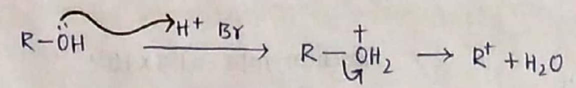
Radical Rearrangement:



3e⁻ involves

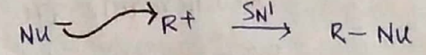


In case of anionic and radical rearragement e⁻ goes to the higher energy antibonding orbital, which is energitically unfavouable but in case of cationic rearrangement e⁻ goes to the lower energy bonding orbital which is energatically favourable process. That is why less stable carbocation undergoes rearrangement but radical does not.

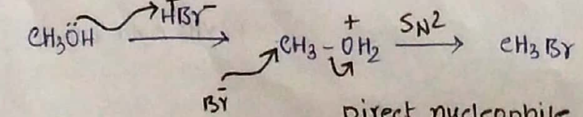


$R-\ddot{O}H \xrightarrow{H^+\ Br} R-\overset{+}{O}H_2 \rightarrow R^+ + H_2O$

$-OH^-$ is bad leaving group But $-\overset{+}{O}H_2$ is a good leaving group.
Weak base is good leaving group.



$Nu^- \quad R^+ \xrightarrow{S_N1} R-Nu$



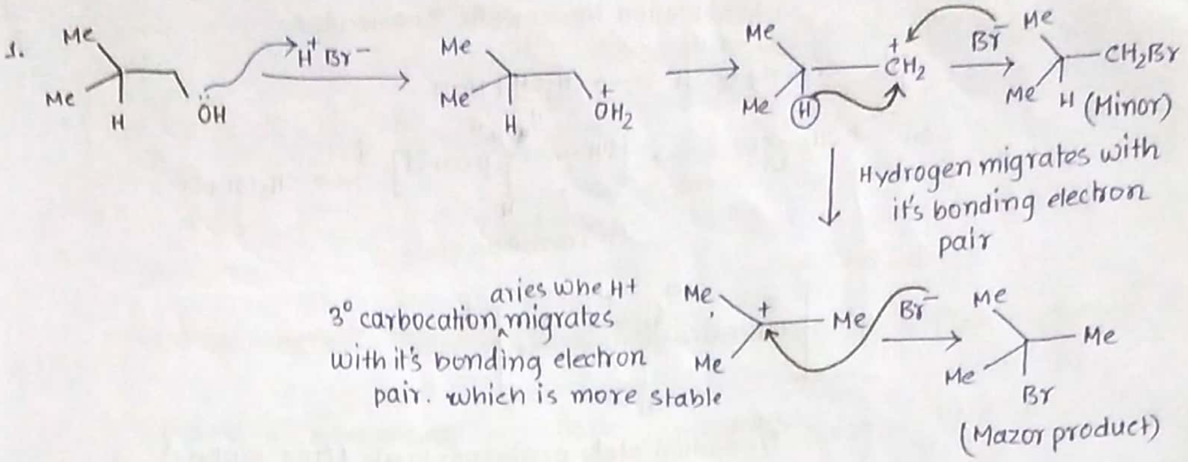
$CH_3\ddot{O}H \xrightarrow{HBr} CH_3-\overset{+}{O}H_2 \xrightarrow{S_N2} CH_3Br$

Br^-

Direct nucleophile attack

Rearrangement Reaction also occur in S_N1 reaction:

1.



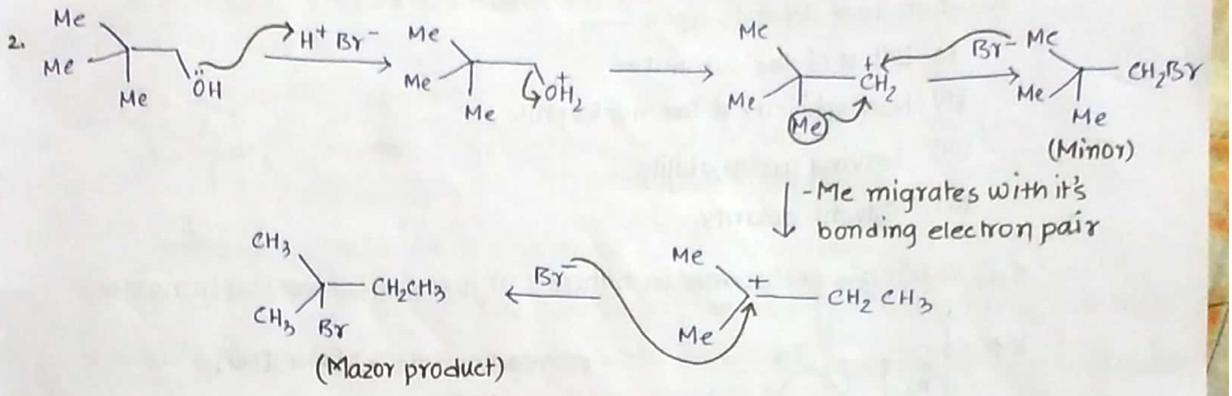
(Minor)

Hydrogen migrates with it's bonding electron pair

3° carbocation aries whe H+ migrates with it's bonding electron pair. which is more stable

(Mazor product)

2.

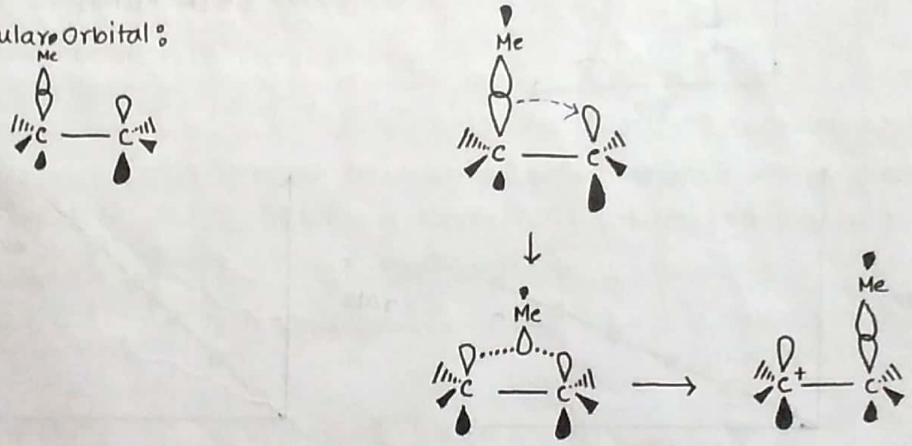


(Minor)

-Me migrates with it's bonding electron pair

(Mazor product)

Molecular Orbital:



$Me_2S: \xrightarrow{Br-Br}$

$Me_2S: \xrightarrow{CH_3-CH_3}$