

SN^1 & SN^2 Reactions:- [Nucleophilic addition Reaction]

SN^1 \Rightarrow Unimolecular Nucleophilic Substitution Reaction.

SN^2 \Rightarrow Bimolecular Nucleophilic Substitution Reaction.

Nucleophilic Substitution Reaction - A nucleophilic substitution reaction in which an atom or group of an atom is replaced by from substrate by a nucleophile.

- The substitution can occur one or two steps.

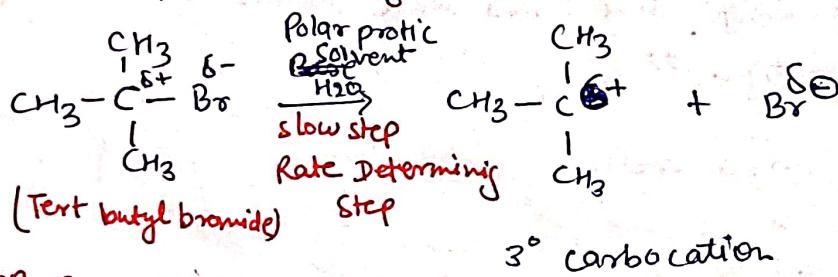
- Nucleophilic substitution reactions mainly occurs in alkyl halides.

SN^1 Reaction :- It is also known unimolecular nucleophilic substitution reactions.

- The reaction follows the first order kinetic.
- The reaction occurs in the weak nucleophile.
- Order of reactivity of carbocation - $3^\circ > 2^\circ > 1^\circ$

Mechanism :-

Step 1 - formation of carbocation -



In step 1 \rightarrow The polarized $\text{C}^{\delta+}-\text{Br}^{\delta-}$ bond undergoes slow cleavage to produce carbocation (Intermediate)

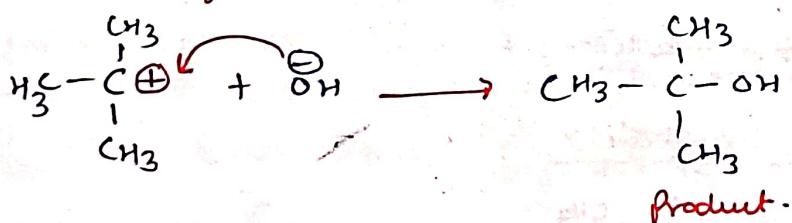
In step 2 \rightarrow Carbocation formed is now attacked by nucleophile to complete substitution Rxn:

$$\text{Rate} = k [\text{substrate}]^1$$

order = 1

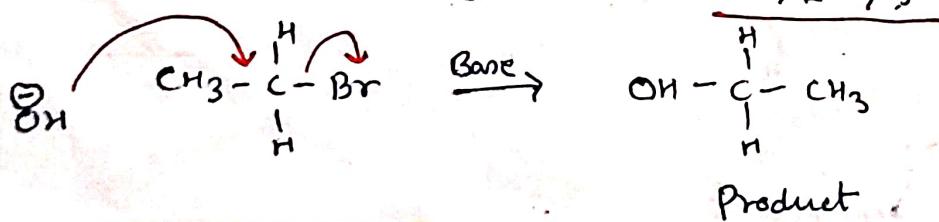
Molecularity = 1

Step 2 Attack of Nucleophile on carbocation -



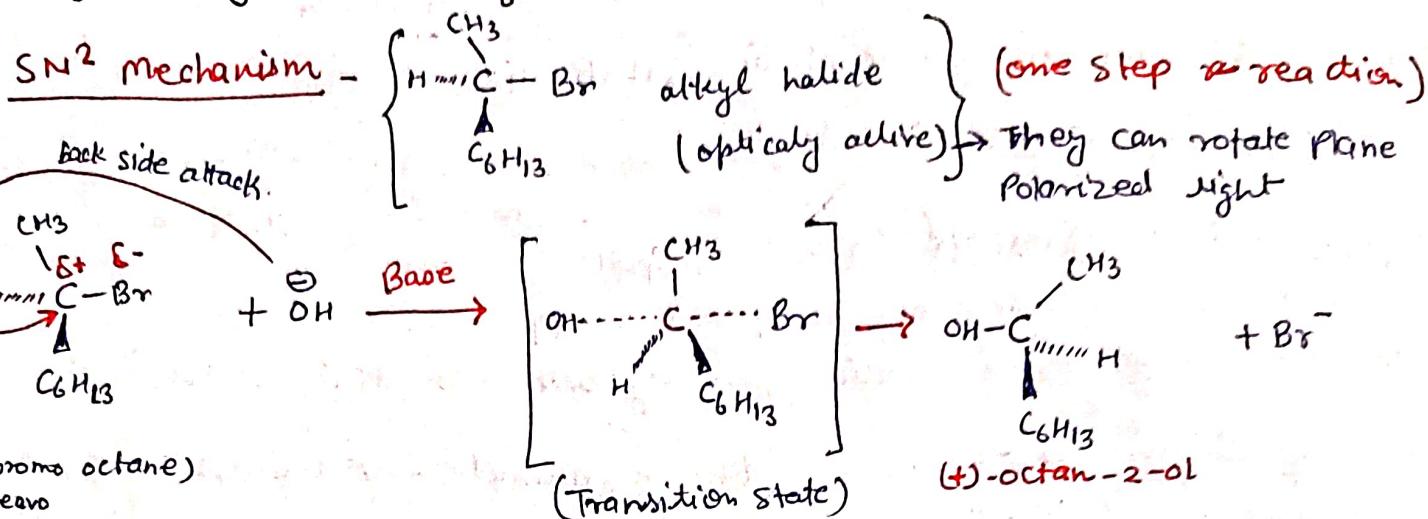
SN^2 Reaction :-

- It is also known as bimolecular nucleophilic substitution reaction.
- It is one step reaction.
- The reaction follows the second order kinetic.
- Carbocation reactivity order - $3^\circ > 2^\circ > 1^\circ$.



Stereochemistry in S_N^1 & S_N^2 Mechanism:-

- [by taking example of optically active Alkyl halides]



- when optically active Alkyl halide is attacked by a nucleophile (OH^-) by S_N^2 mechanism, the product will have inverted configuration as compared to the reactant.
- Because here in S_N^2 , nucleophile (OH^-) will attack from opposite side w.r.t. halogen ($-\text{Br}$) present. due to repulsion between halogen atom and nucleophile.

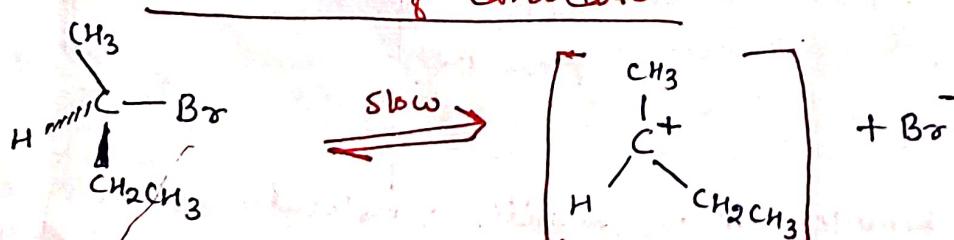
Result: " S_N^2 reactions of optically active halo alkyl halide are accompanied by Inversion of configuration "

Inversion \rightarrow like inversion in umbrella

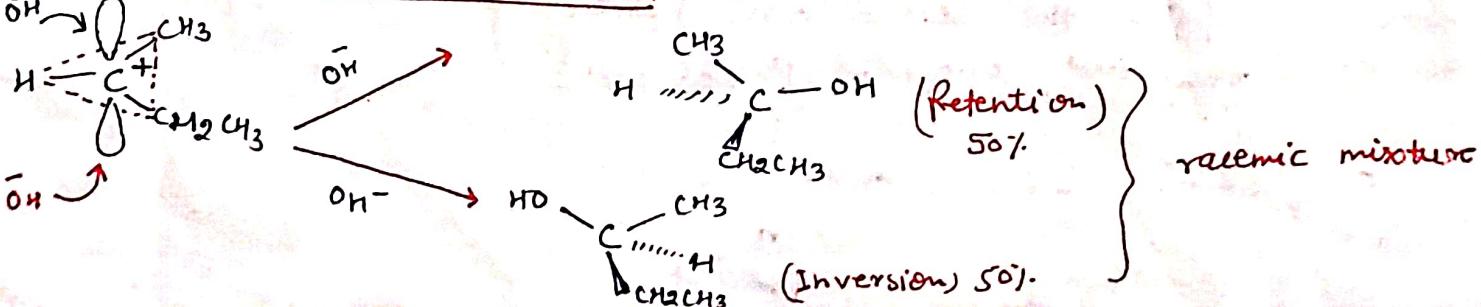


S_N^1 Mechanism :- Two step reaction :-

Step 1 :- Generation of carbocation



Step 2 \rightarrow Nu⁻ Attack on carbocation - (carbocation) Sp², Planar



SEPTEMBER - 2020

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1	2	3	4	5	6	7	8	9	10	11	12	13	
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WK 34 (232-134)

AUGUST

WEDNESDAY

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Step 1 :- optically active halide will produce carbocation. This carbocation is sp^2 hybridized and planar.

Step 2 :- Since, carbocation is planar, so Na^+ can attack in two ways. One attack can be from top & other attack can be from back.

so, we will have two products.

→ one product on which - OH attacking on the same position as halide ion.

→ second product on which - OH attacking on the other opposite side to halide ion.

So, In S_{N}^1 , one product is retention product other product is inversion product

Result

So, in S_{N}^1 we will get racemic mixture.

Difference between S_{N}^1 & S_{N}^2 Reactions:-

 S_{N}^1 S_{N}^2

nucleophile

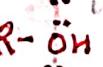
① Unimolecular substitution reaction

② molecularity = 1

③ order of reaction = 1

④ Rate law expression = $\text{Rate} = \text{K}[\text{R-X}]$

⑤ weak nucleophiles used
(neutral with lone pair) e.g. H_2O



① Bimolecular Nucleophilic substitution reaction.

② molecularity = 2

③ order of reaction = 2

④ Rate law expression = $\text{K}[\text{R-X}][\text{Nu}]$

⑤ strong nucleophile used
[negatively charged] e.g. OH^-
(NaOH)

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(233-133) WK 34

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THURSDAY

protic = H^+ give.
 Aprotic = Not release H^+

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- (6) It's a two step reaction
 (7) Solvent is polar protic solvent
 e.g. H_2O , CH_3COOH

- (8) Intermediate is formed
 \hookrightarrow carbocation

- (9) Stability of carbocation is main factor here

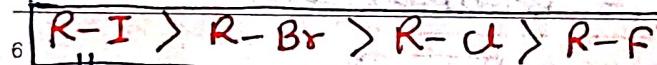
- (10) Rate of reaction with respect to Alkyl halide (substrate)



because rate of reaction \rightarrow

- Rate of reaction \propto stability of carbocation

- (10) Rate of reaction w.r.t. leaving group. ($-X$) (halogen)



\downarrow
 good leaving group.

- (11) If alkyl halide is optically active.

Then for $S_N^2 \rightarrow$ Racemic mixture will form

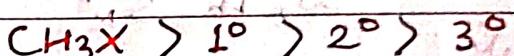
which is optically inactive.

- (6) Single step reaction
 (7) Solvent is polar aprotic
 e.g. Acetone, DMSO

- (8) No intermediate formed

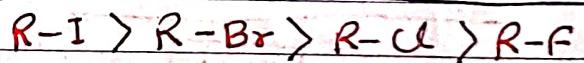
- (9) Less steric hindrance around carbon is main factor here

- (10) Rate of reaction w.r.t. alkyl halide



- Rate of reaction $\propto \frac{1}{\text{steric hindrance}}$

- (10) Rate of reaction w.r.t. leaving group. ($-X$) halogen



- (11) If alkyl halide is optically active : Then for $S_N^2 \rightarrow$ Inversion will be observed. (Walden)

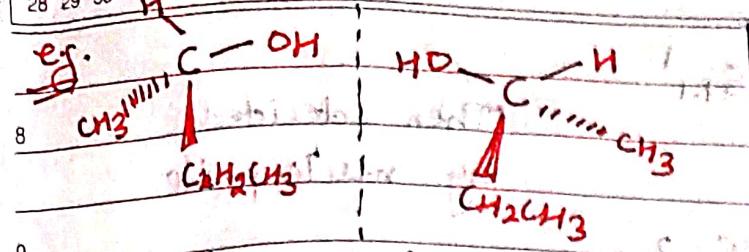
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WK 34 (234-132)

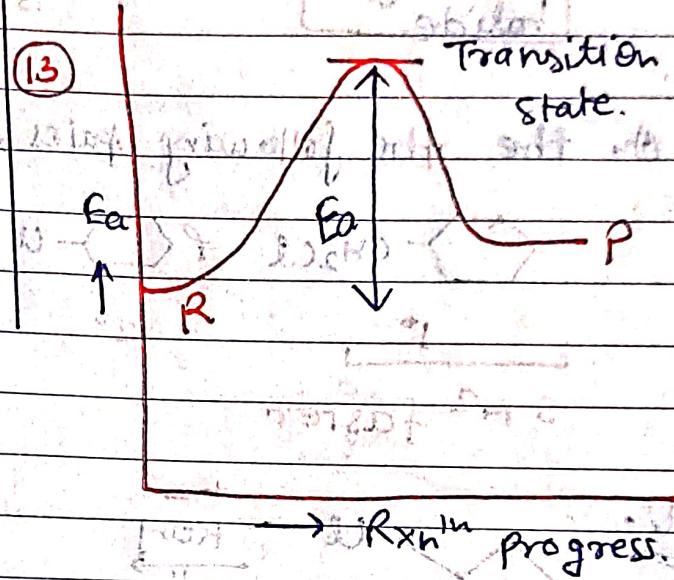
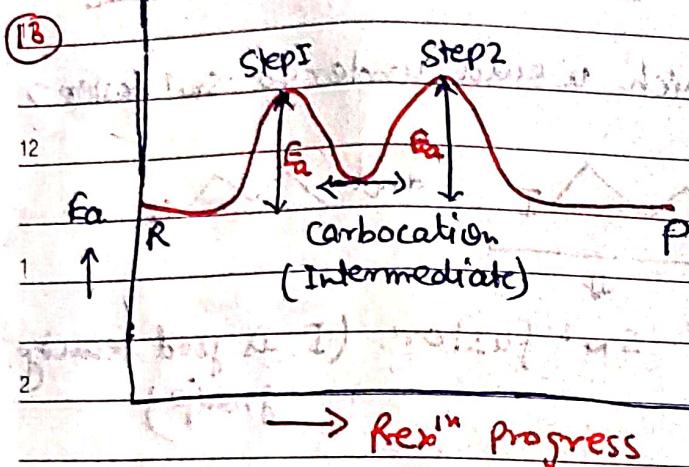
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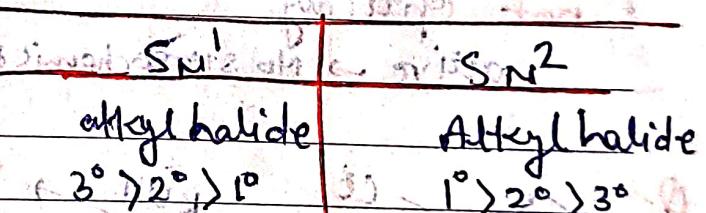
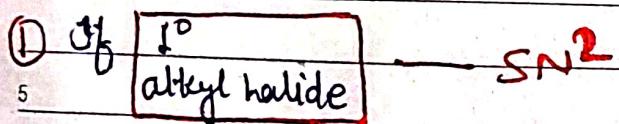


(Retention) (Inversion) Walden

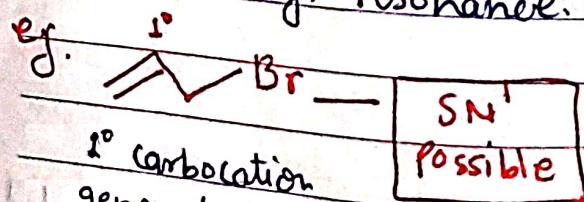
Racemic mixture



Trick to solve $\text{S}^{\text{N}}1$ & $\text{S}^{\text{N}}2$ Questions :-



Exception $\rightarrow \text{S}^{\text{N}}1$ possibility only when 1° carbocation is stabilized by resonance.



Racemic mix (If Alkyl halide optically active) inversion (If alkyl halide optically active.)

weak Nu^- Strong Nu^-
Neutral $\rightarrow \text{H}_2\text{O}$: Negative (-)

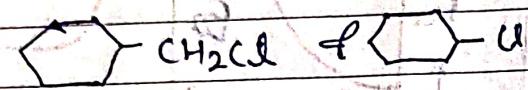
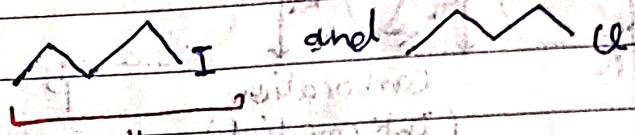
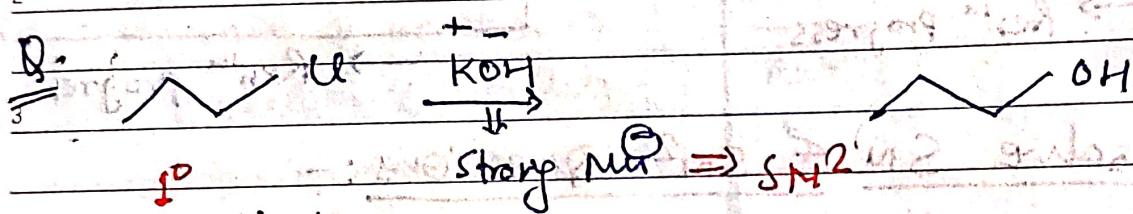
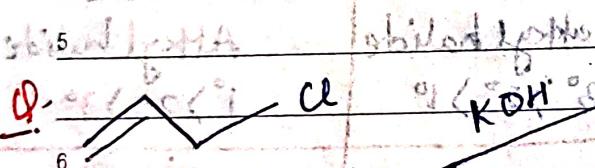
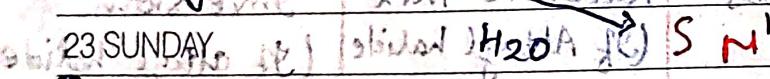
Polar protic solvent - $\text{H}_2\text{O}, \text{R-OH}$ Polar Aprotic solvent - $\text{DMF}, \text{Acetone}$

If we have both $\text{S}^{\text{N}}1$ & $\text{S}^{\text{N}}2$ Possibility then it is decided by Nu^-

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SATURDAY13 14 15 16 17
27 28 29 30 31(2) for 2° alkyl halide S_N^1

Then decided by nucleophile.

Two possibilities and
at last decided by M_N^- S_N^2 (3) for 3° alkyl halide S_N^1 Always S_N^1 whatever
the nucleophile.Q. On the following pairs, which would undergo S_N^2 faster? S_N^2 faster S_N^2 faster (I is good leaving group.)not optically
active \rightarrow no stereochemistry $KOH \Rightarrow S_N^2$  3° Alkyl halide $KOH \Rightarrow S_N^2$ 23 SUNDAY $\Rightarrow H_2O \Rightarrow S_N^1$ possibility for both S_N^1 & S_N^2 Note:- Usually 1° alkyl halides give S_N^2 Rex^n , but if 1° generatedis stabilized by resonance, it can give S_N^1 Rex^n too

2020

- CH_3CH_2Cl : $CH_3CH_2^+$ Cl^-
nitrobenzene NO_2 : NO_2^- , Cl^-

S_N^1 $CH_3CH_2^+$ Cl^- is strong and very Rex^n
with Cl^- less stable, so it need

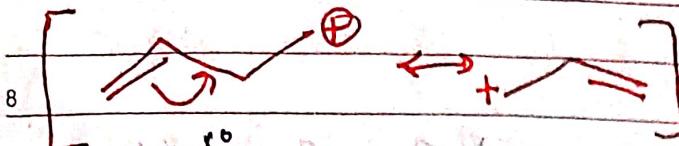
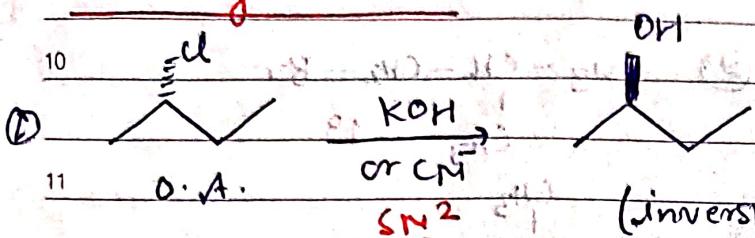
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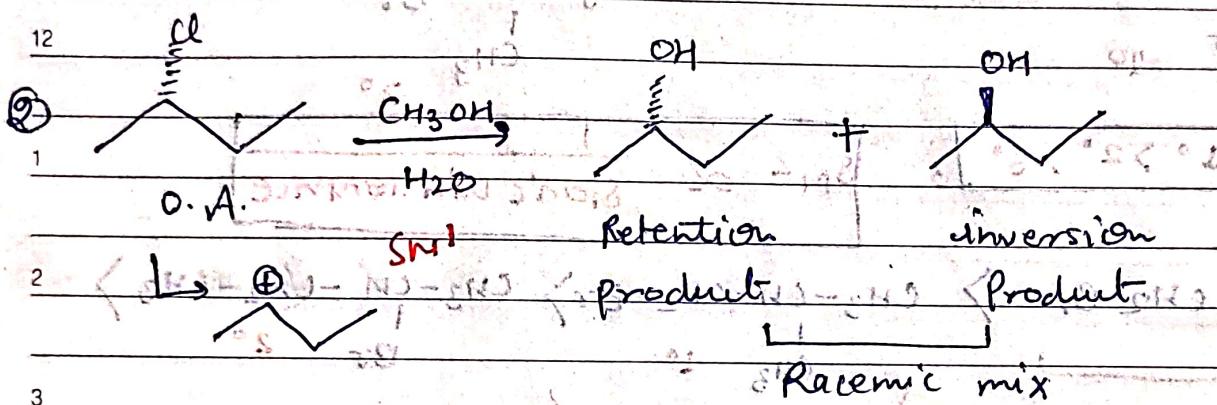
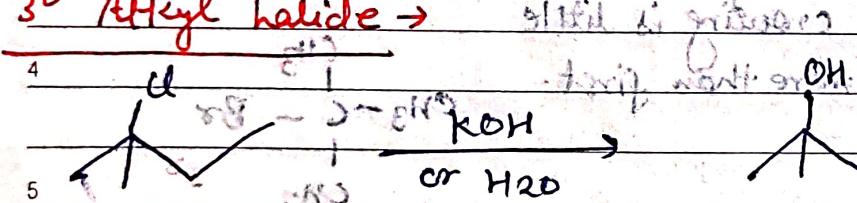
WK 34 (230-136)

AUGUST
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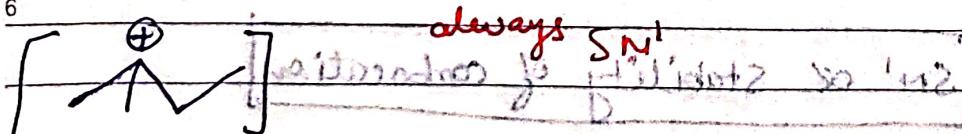
17

2° Alkyl halide:-

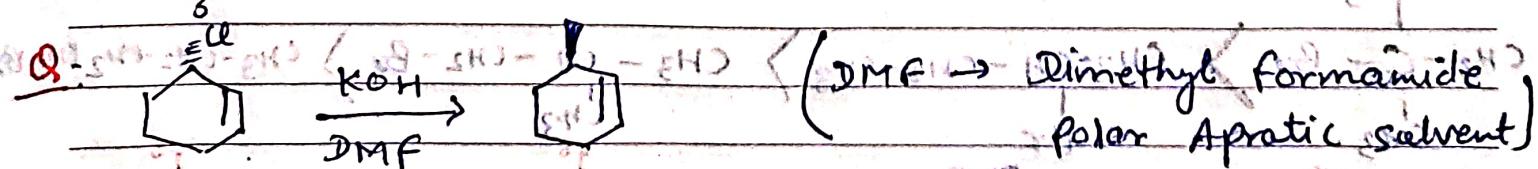
(Inversion product)

3° Alkyl halide →

3° Alkyl halide C angle

always SN¹

3°



2°

SN² It + et al.Inversion product (DMSO \rightarrow Dimethyl sulfide.)

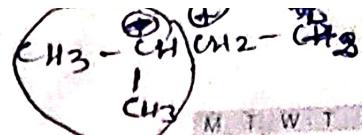
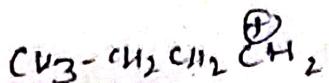
H

Strong bases

Chiral-C

2020

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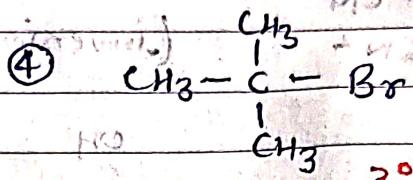
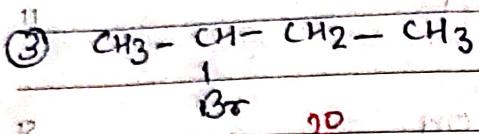
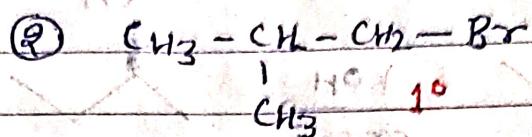
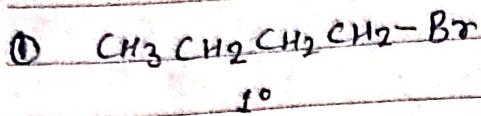
(231-135) WK 34
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TUESDAY

JULY - 2020

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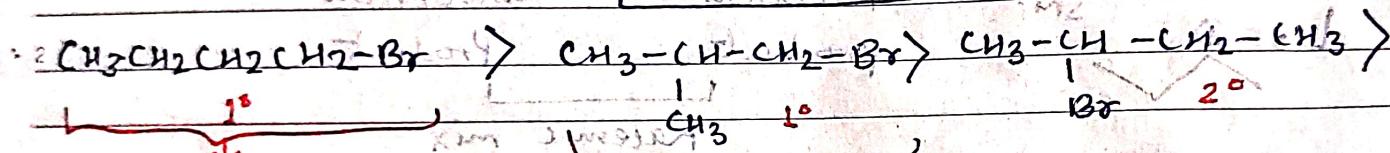
 $\text{S}^{\text{N}} \text{ } \text{S}^{\text{N}} \text{ } \text{Question:}$

Q. Predict order of reactivity in $\text{S}^{\text{N}} \text{I}$ & $\text{S}^{\text{N}} \text{2}$ reactions for four isomeric bromobutanes.



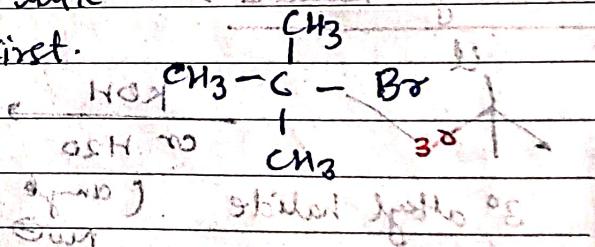
1. $\text{S}^{\text{N}} \text{2} \Rightarrow [1^\circ > 2^\circ > 3^\circ]$

$\text{S}^{\text{N}} \text{2} \propto$ steric hindrance



Among 1° molecules will give $\text{S}^{\text{N}} \text{2}$ rxn faster b/c less crowding.

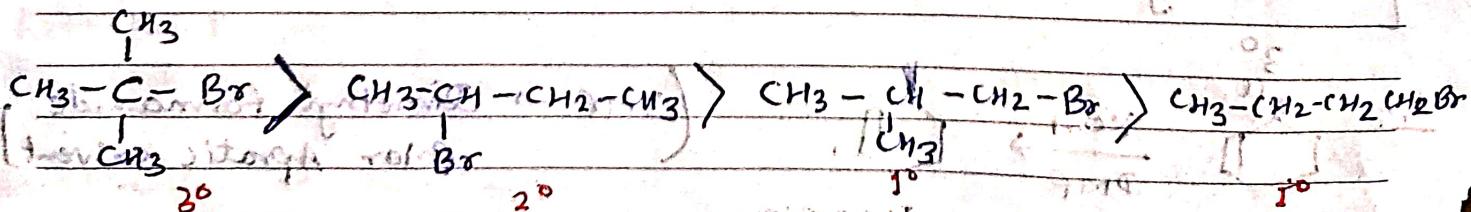
Crowding is little more than first.



$\text{S}^{\text{N}} \text{I}$

$[3^\circ > 2^\circ > 1^\circ]$

$\text{S}^{\text{N}} \text{I} \propto$ stability of carbocation



3°

2°

1°

3°

2020

shiroishi

due to $+ \text{I} = \text{H}_2$
effect more.

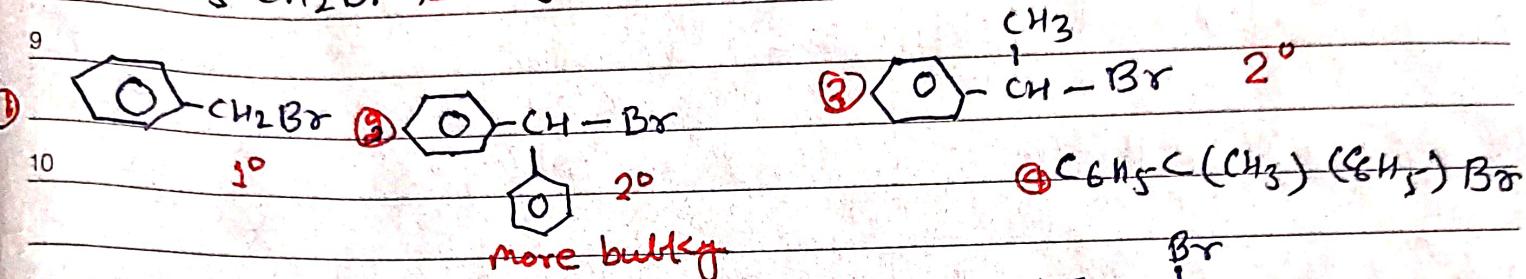
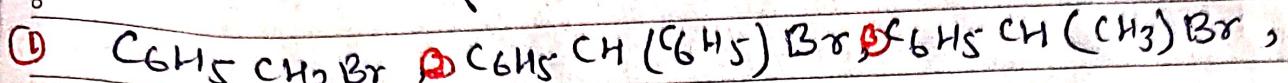
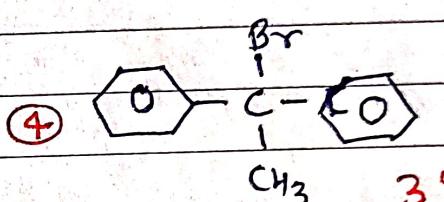
SEPTEMBER - 2020

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WK 35 (237-129)

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Q: Predict order of $SN1$ & $SN2$ in following $SN2$ 

(Ph $>$ CH_3 more bulky)

 $SN1$ 