

(परीक्षार्थी द्वारा भरा जाए)

(To be filled by the Candidate)

First Periodical Test, July-December, 2021

परीक्षा का नाम (Name of Examination)..... First Periodical Test, July-

December, 2021.....

अनुक्रमांक अंकों में(In figures) 2141991

अनुक्रमांक(शब्दों में)(Roll No. in Words) Twenty one lakh forty one thousand
nine hundred and ninety one

नामांकन संख्या (Enrollment No.).....

ई-मेलआई.डी. (E-mail ID.) lsmsc21031_sakriti@banasthali.in

विषय(Subject)..... CHEMISTRY.

प्रश्न पत्र कोड सहित (Paper withCode)..... CHEM 406 - Organic Chemistry

परीक्षा दिवस और दिनांक (Day and Date of Examination). 8th SEPTEMBER 2021

MONDAY

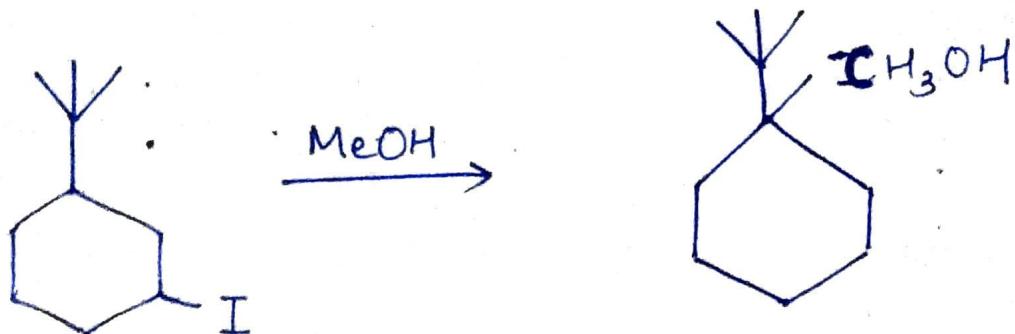
Total Number of Pages excluding this page: _____ 16 _____

Question	1	2	3	4	5	6
Write NA for questions not attempted		NA		NA		

Signature of the Student

Ques
1a

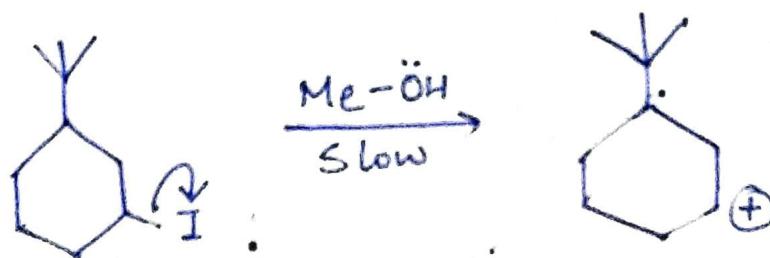
Give the product and mechanism



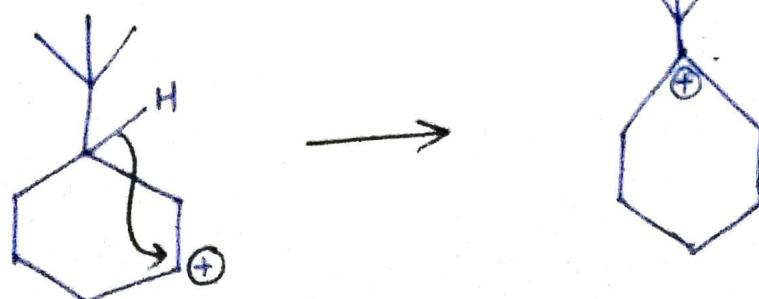
This reaction takes place via S_N1 mechanism.

MeOH is a poor nucleophile but I⁻ is a good leaving group.
(Best leaving) - can best stabilise S_N1 Reactions via two steps. a negative charge.

step 1. Formation of a carbocation



Rearrangement of carbocation via hydride shift.

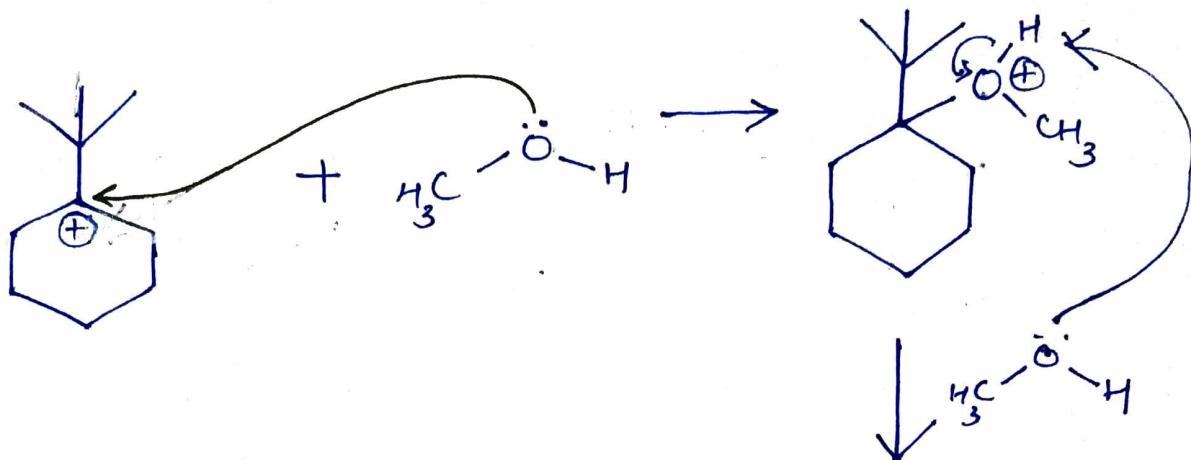


3° carbocation
(more stable)

[Rate Determining Step]

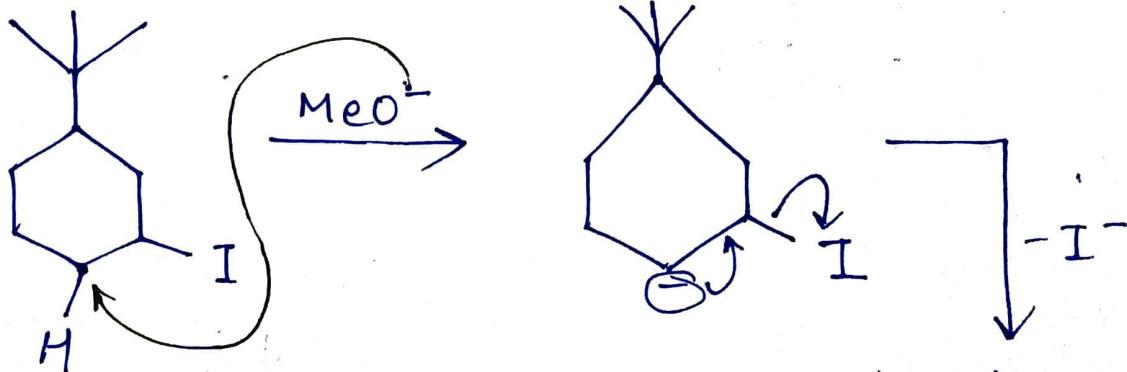
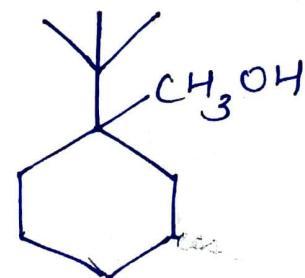
Aakriti Mehrotra
2141991

Step 2 - Reaction between nucleophile and carbocation

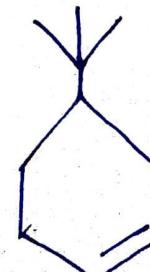


In this reaction

S_N1 or $E1$ Mechanism $H_3O^+ +$
 can occur if competes hydronium
 with S_N1 but ion.
 80% of the product
 is S_N1 mechanism. Usually S_N1 predominates

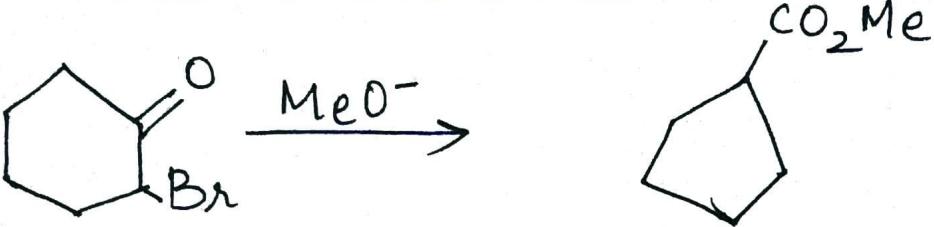


1-iodo-3-isopropyl
cyclohexane

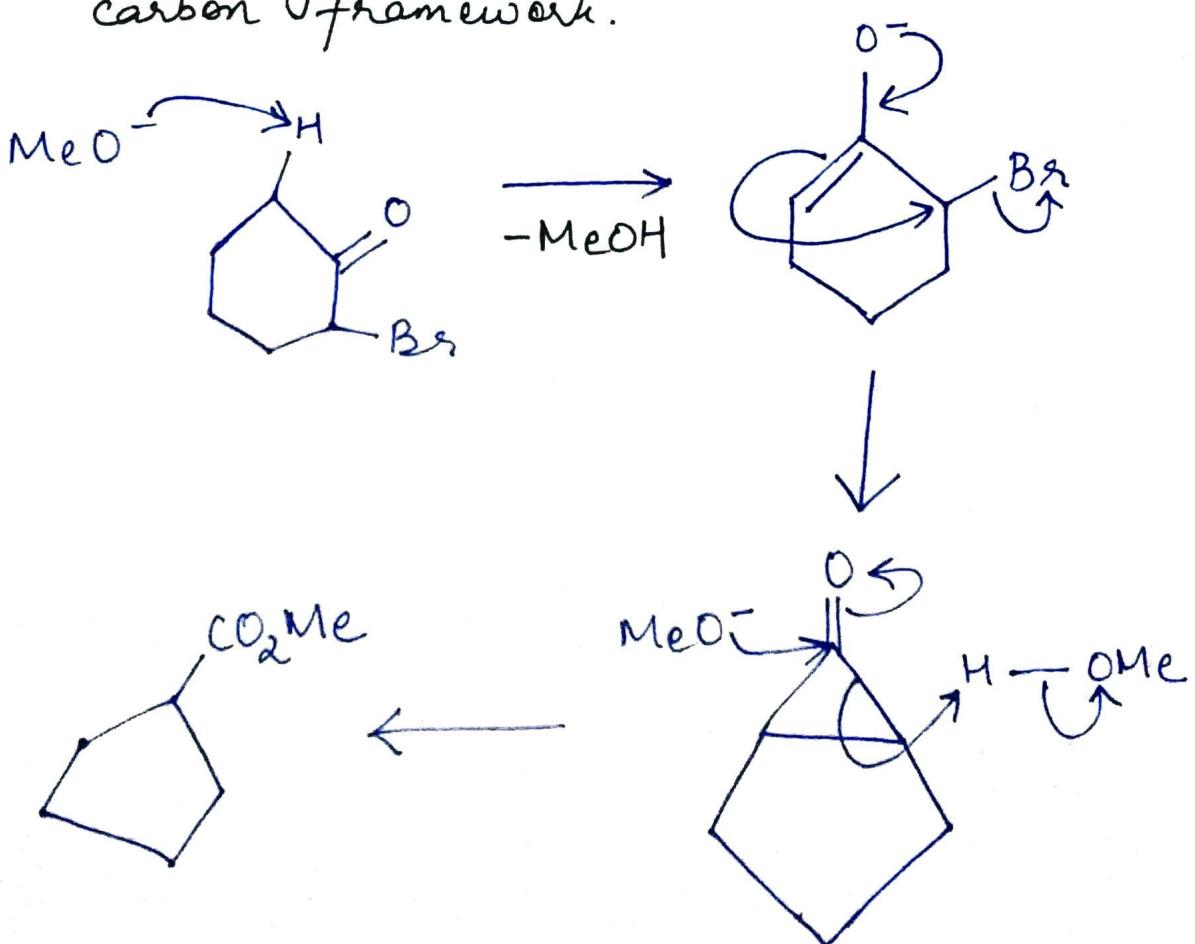


This Reaction proceeds with $E2$ mechanism
 As the substrate was hindered so the
 S_N2 reaction is not possible

(1b)



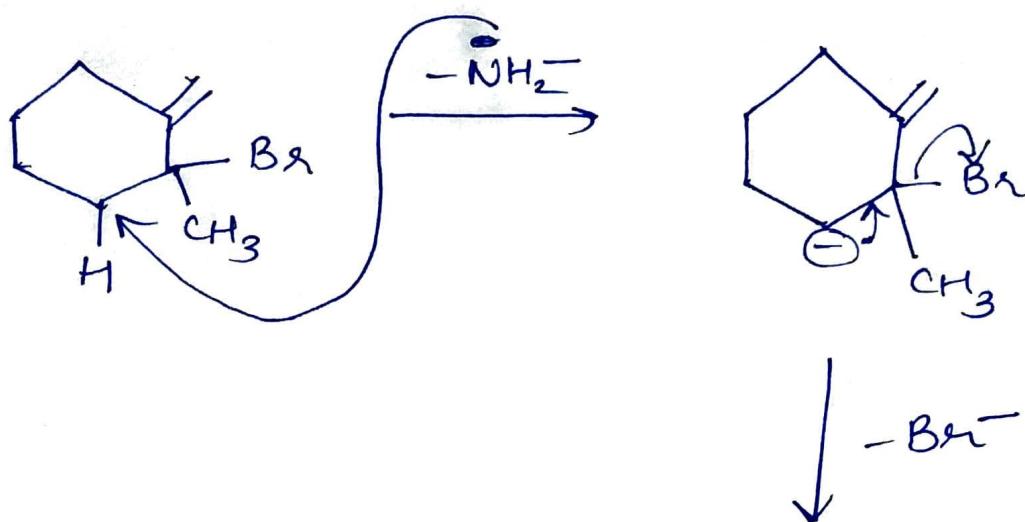
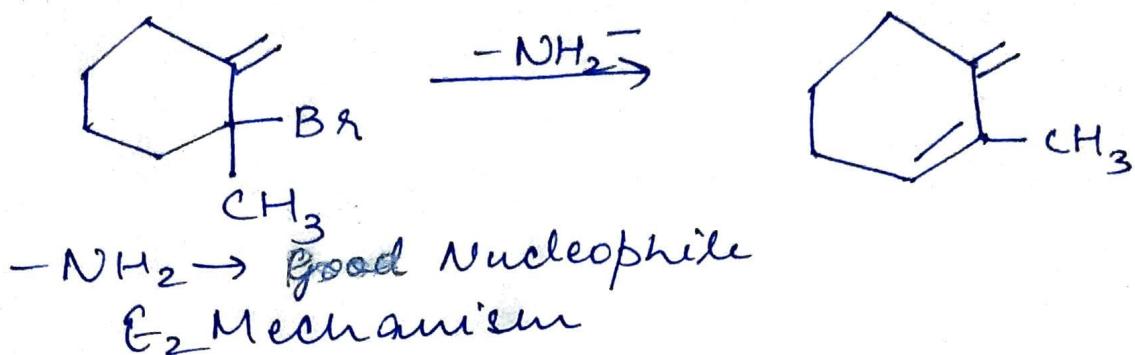
α -haloketones when treated with a strong base (generally alkoxides) lead to the formation of esters with rearrangement of the carbon framework.



The name of the mechanism is Favorskii rearrangement.

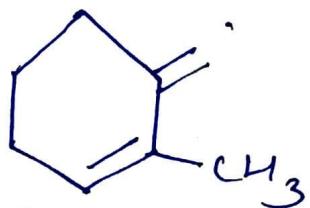
In this an alkyl group is transferred from one side of a carbonyl group to other.

(c)



The Reaction proceeds
via E_2 Mechanism.

S_ND Reaction not possible.

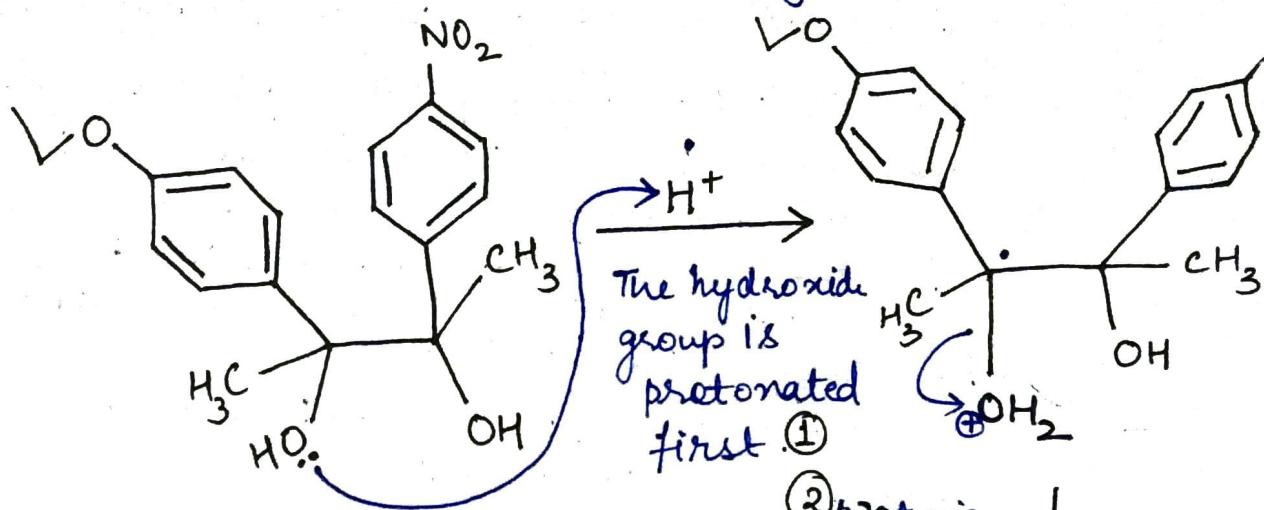


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Q3.

Give the mechanism of following reactions.

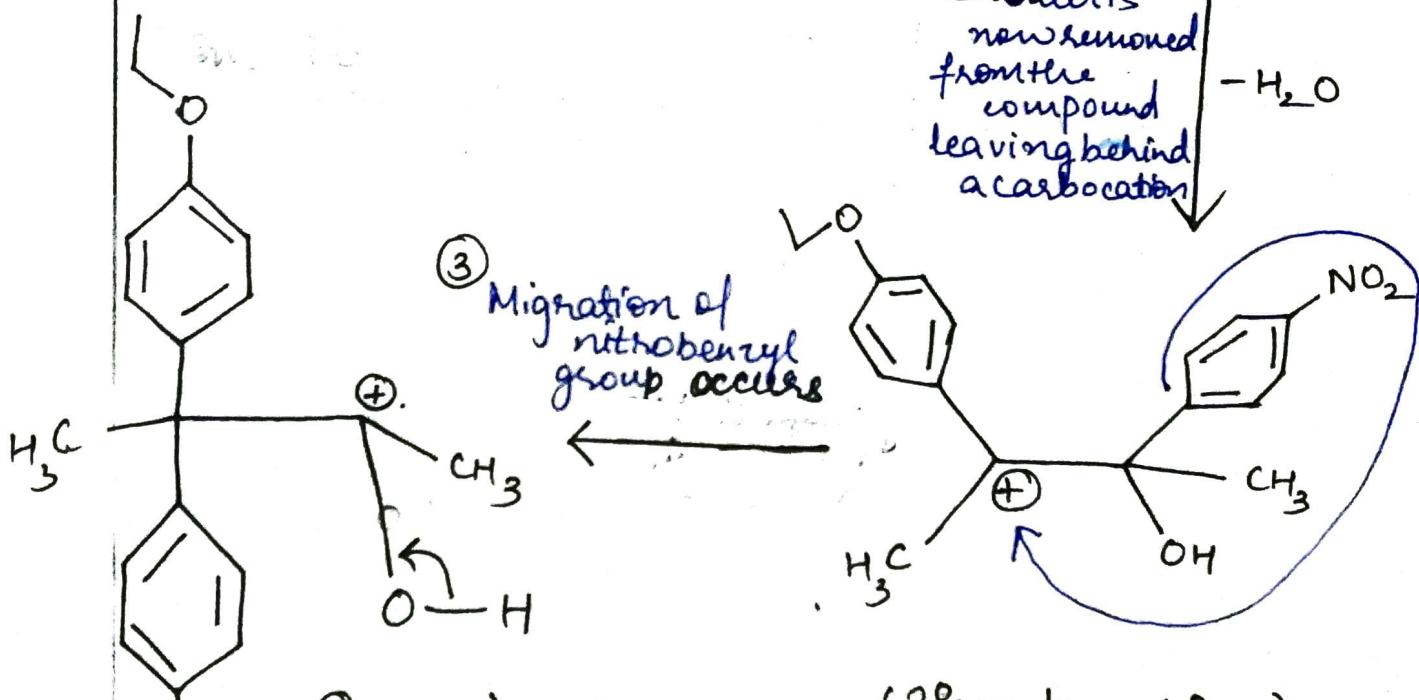
(A)



② Water is now removed from the compound leaving behind a carbocation.

-H₂O

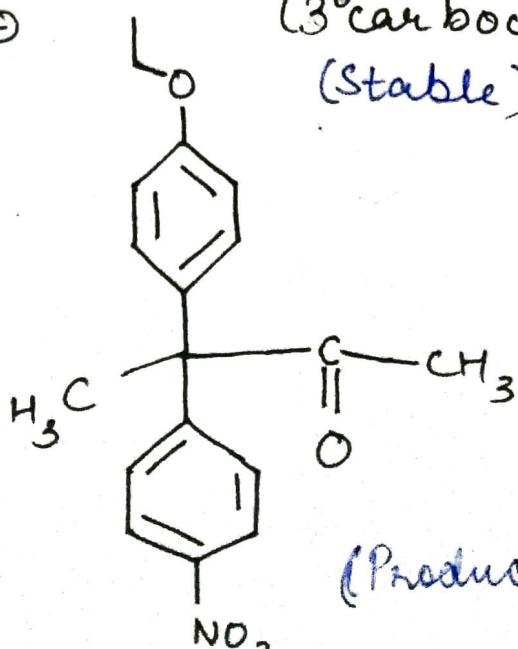
③ Migration of nitrobenzyl group occurs.



④ loss of proton from oxygen gives a stable ketone.

-H⁺

(3° carbocation)
(Stable)



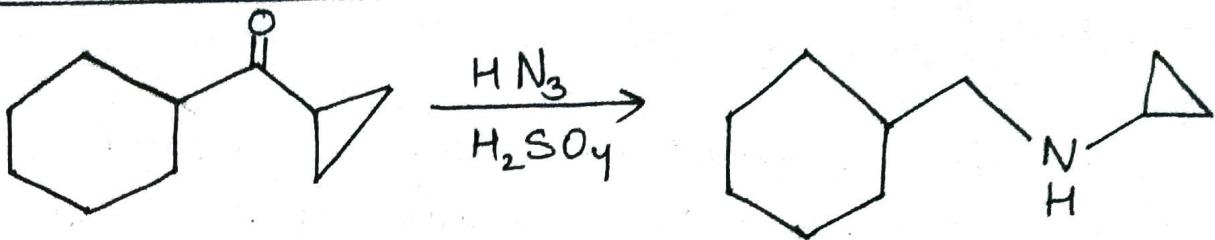
This Rearrangement is called Pinacol - Pinacolone Rearrangement

The Rearrangement or the mechanism
is Pinacols - Pinacolone Rearrangement.

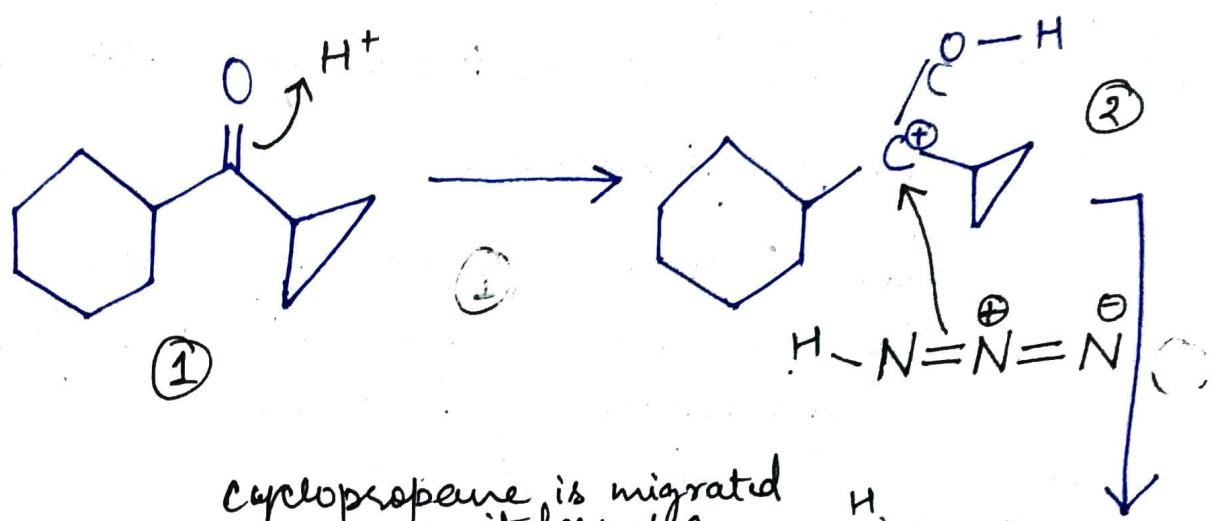
In the ① step shown, where the OH group is
protonated. The OH group selected for
protonation is stabilised by the OEt group
but which is not stabilized by NO_2 group.

As NO_2 is the meta directing group
(it is an electron with drawing group.)
so it cannot stabilize the carbocation
if formed in the OH attached
to that "group."

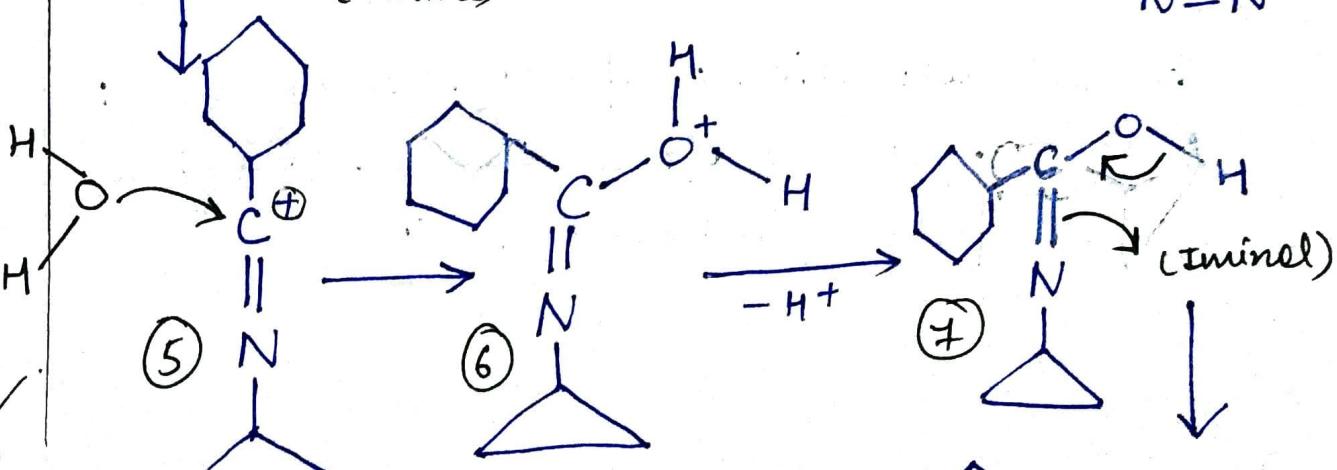
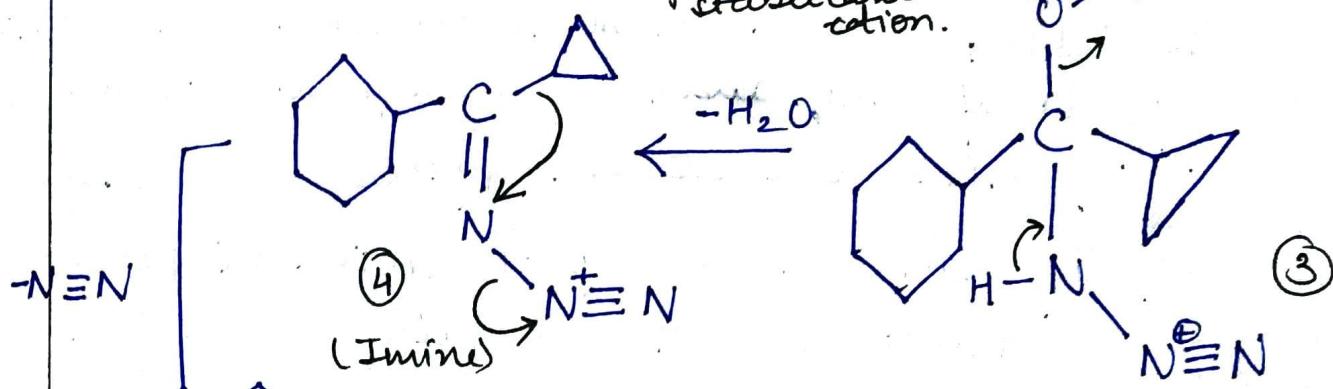
(B)



This is Schmidt Reaction



cyclopropane is migrated because it forms a stable carbocation.

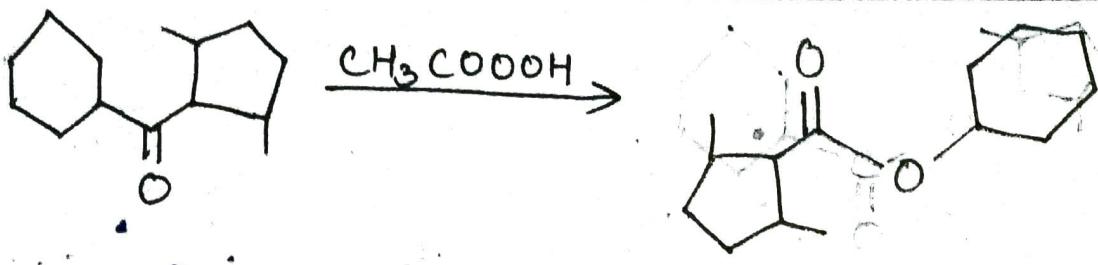


Mechanism:-

1. This mechanism begins with the protonation of the ketone, leading to the formation of O-H bond.
2. The subsequent nucleophilic addition of the azide leads to the formation of an intermediate.
3. Water is now removed from this intermediate via an elimination reaction, forming a temporary imine.
4. This results in the elimination of dinitrogen.
5. Now, water is used to attack the resulting compound.
6. The subsequent deprotonation yields a tautomer of the required amide.
7. The relocation of a proton belonging to the tautomer of the amide gives the final product.

Vineet

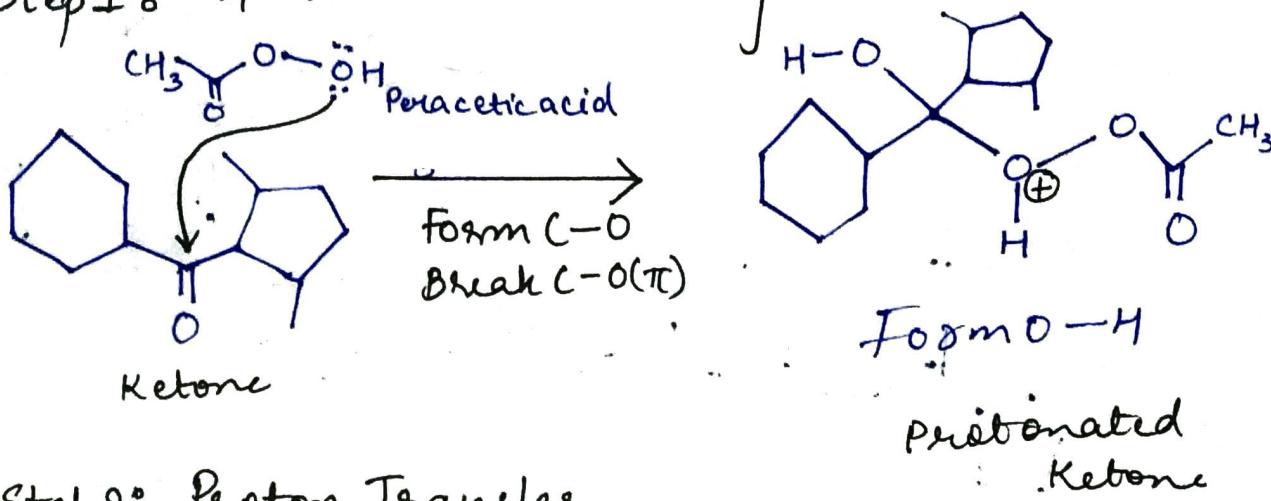
(c)



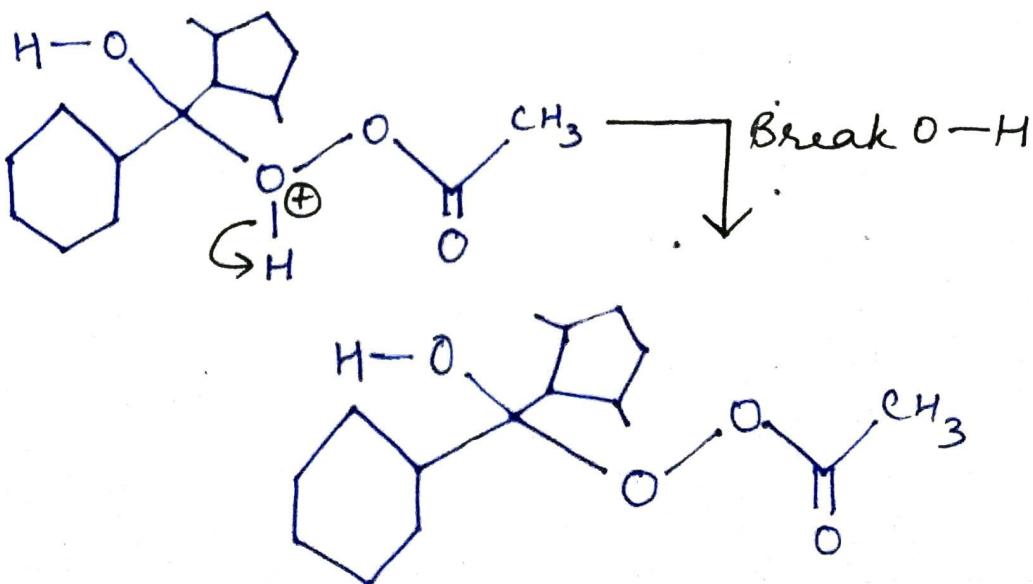
Ester

This is Baeyer - Villiger Oxidation

Step 1: Addition to Carbonyl

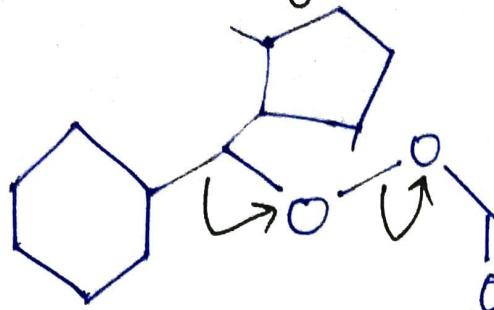


Step 2: Proton Transfer



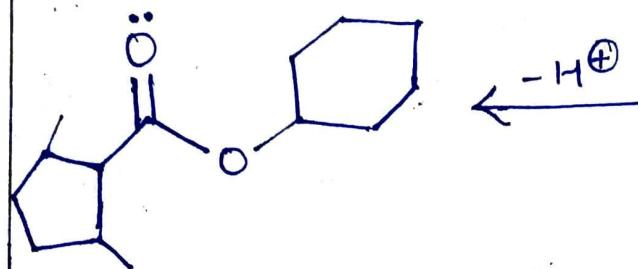
Ans

Step 3: Migration

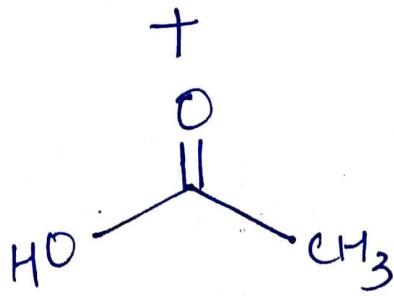


form C-O
Break C-C
Break O-O

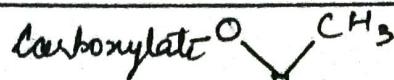
Step 4: Deprotonation



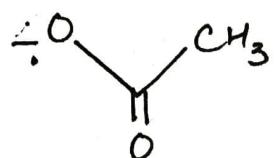
Ester



Acetic Acid



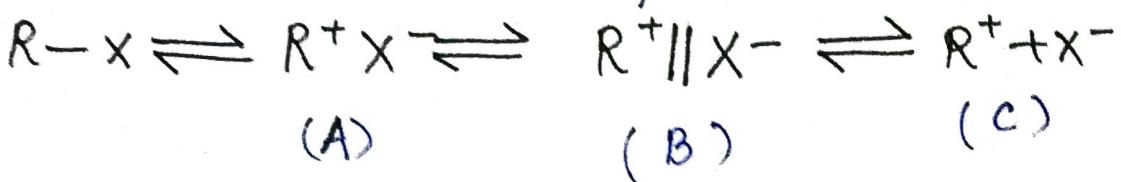
Resonance



Carboxylate

05 a)

* Give the product formation in the following reactions with nucleophile.



A = an intimate, contact or tight ion pair

B = a loose, or solvent separated, ion pair

c = the dissociated ions (each surrounded by molecules of solvent).

The reaction in which the intimate ion pair recombines to give the original substrate is referred to as internal return.

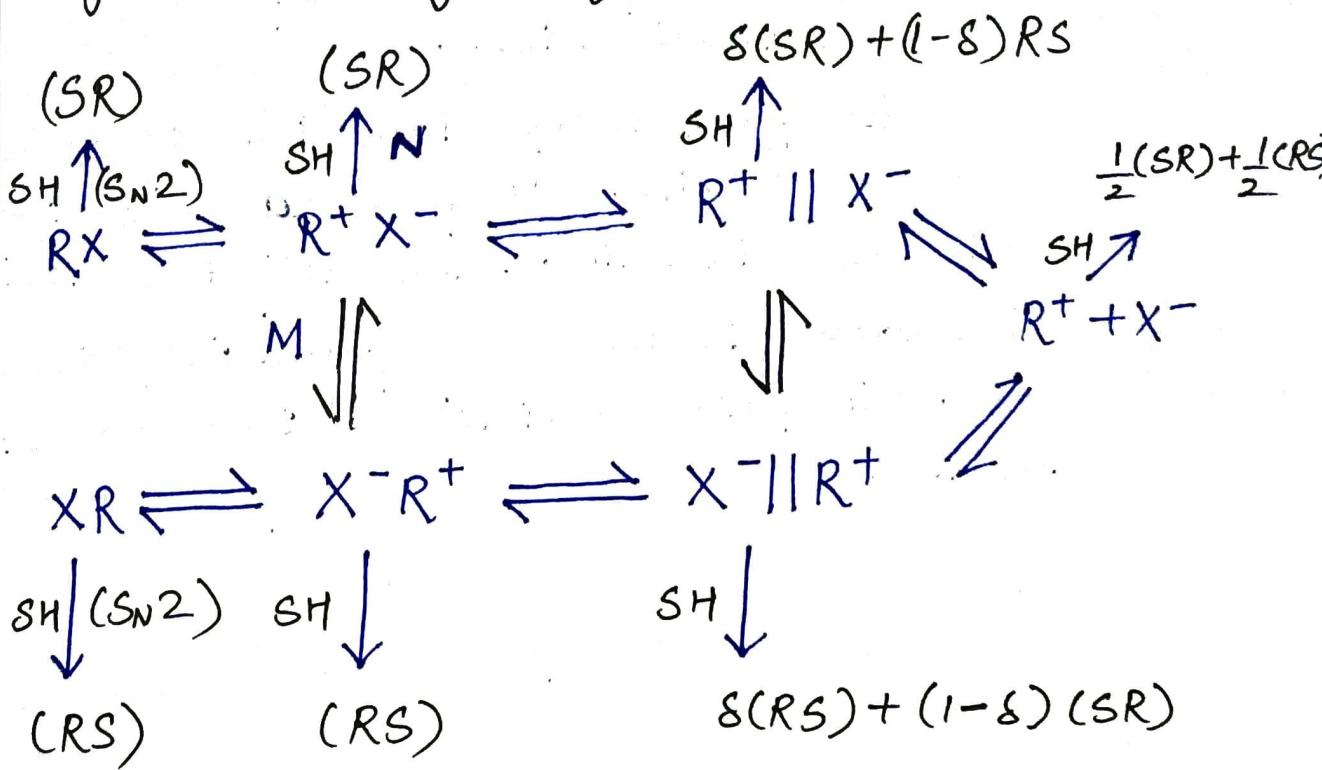
The reaction products can result from attack by the nucleophile at any stage.

In the intimate companion (A), R⁺ does not behave like the free cation of (C)

There is probably significant bonding between R^+ and X^- and asymmetry will be maintained.

Here, X^- solvates the cation on the side from which it is departed, while solvent molecules near (A) can only solvate it from the opposite side. Nucleophilic attack by a solvent molecule on (A) thus leads to inversion.

A complete picture of possibilities for solvolysis reactions in a solvent SH is represented by the following diagram,



In this RS and SR represent enantiomers and so on, and s represents some fraction.

The following are the possibilities

- 1) Direct attack by SH on RX gives SR (complete inversion) in a straight S_N2 mechanism.
- 2) If the intimate ion-pair R^+X^- is formed, the solvent can attack at this stage. This leads to total inversion if reaction (M) does not take place or to a combination of inversion and racemization if there is competition between M and N .
- 3) If the solvent separated ion-pair is formed, SH can attack here.

The stereochemistry is not maintained as tightly

13

and more racemization (perhaps total) is expected

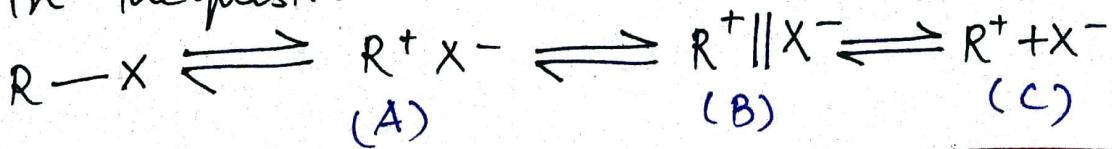
- 4) Finally, if free R⁺ is formed, it is planar and attack by SH gives complete racemization.

The ion-pair concept thus predicts that S_N1 can display either complete racemization or partial inversion. The fact that this behaviour is generally found is evidence that ion pairs are involved in many S_N1 reactions. In S_N1 Reaction the optical activity is zero as 50% retention and 50% inverted like kinetic evidence, stereochemical evidence formed for the S_N1 mechanism is less clear than it is for the S_N2 mechanism.

If there is a free carbocation, it is planar and the nucleophile should attack with equal facility from either side of the plane resulting in incomplete racemization. Although many first order substitutions give complete racemization, many others don't. Typically there is 5-20% inversion, although in few cases a few amount of retention of configuration has been found.

In many S_N1 reactions at least some of the products are not formed from free carbocations but rather from ion pairs.

According to this concept S_NT Reactions proceed in the manner given in the question.



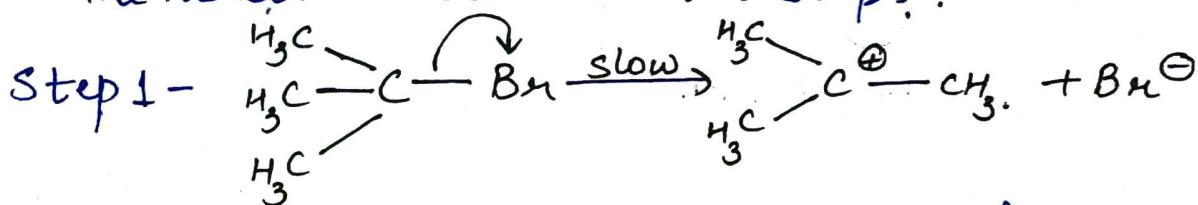
5(b) Give the energy profile diagram for S_N1 and S_N2 reaction with taking suitable examples.

Energy Profile Diagram for S_N1 Reaction

S_N1 Reaction

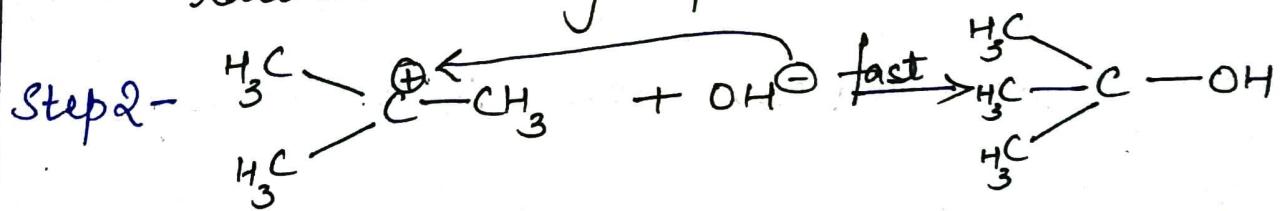
(Substitution Nucleophilic Unimolecular
Unimolecular reaction)

The reaction occurs in two steps.



In this step leaving group liberates from the substrate (t-butyl bromide) to form stable carbocation.

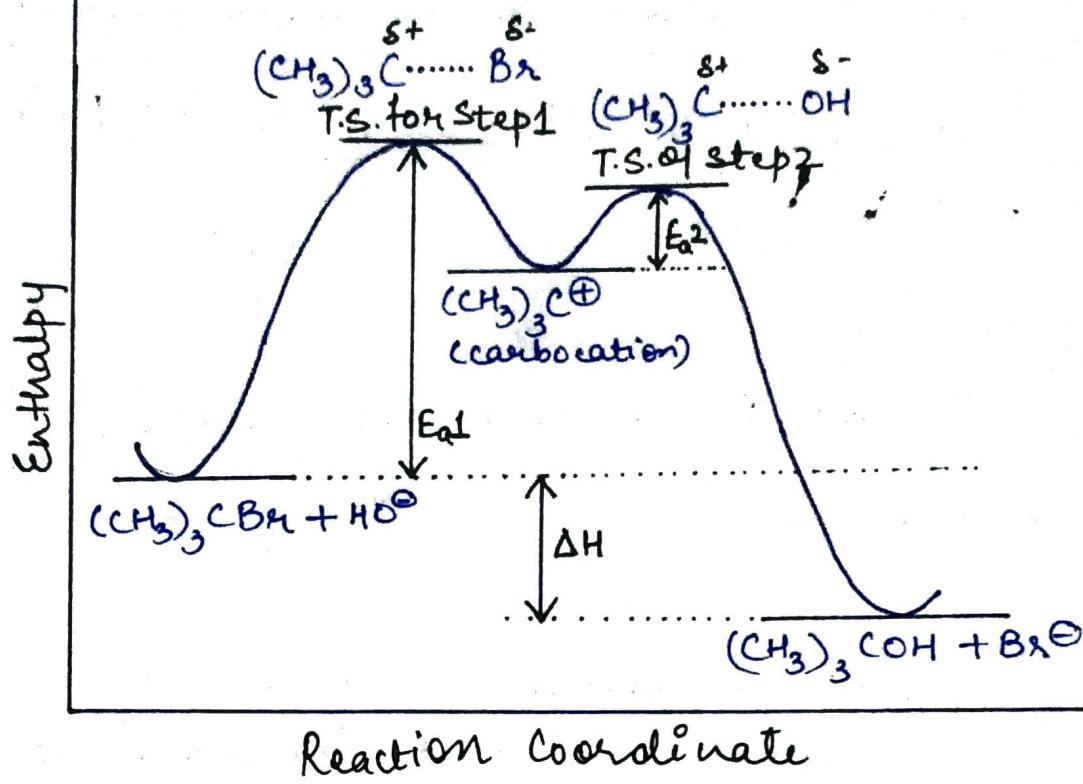
This is the slowest step. and so is the rate determining step.



In this step nucleophile (hydroxide ion) attack to the carbocation.

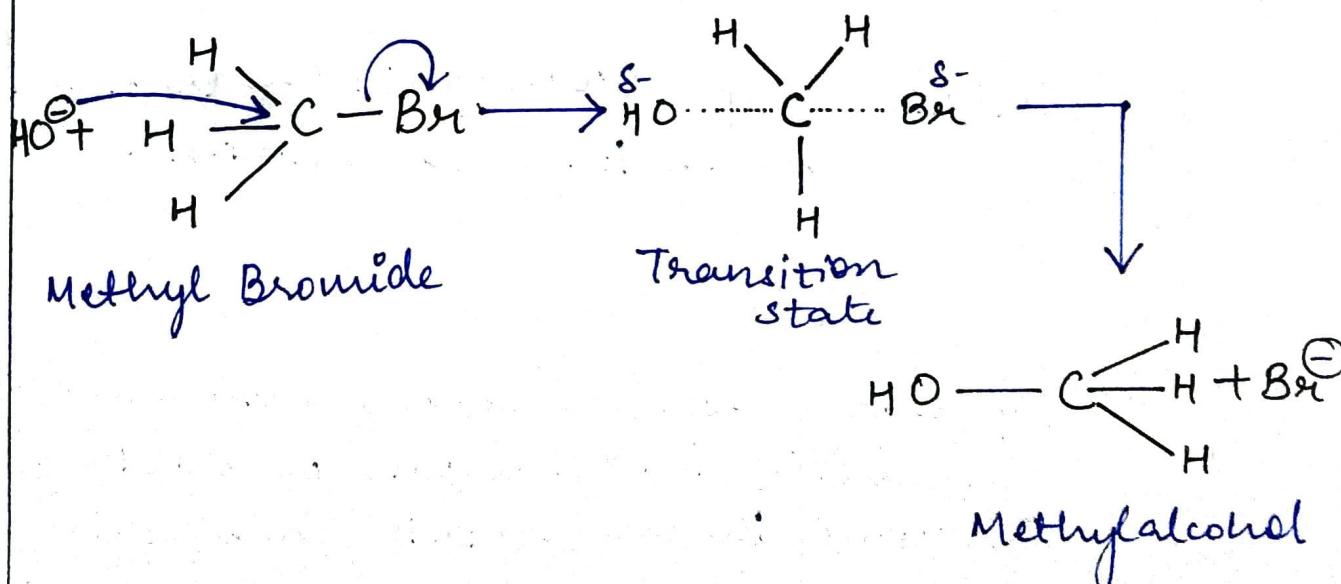
Energy Profile Diagram

An energy level diagram shows whether a reaction is exothermic or endothermic. It shows the energy in the reactants and products, and the difference in energy between them.



$\text{S}_{\text{N}}2$ Reaction (Substitution Nucleophilic Bimolecular)

This Reaction occurs in Single step -

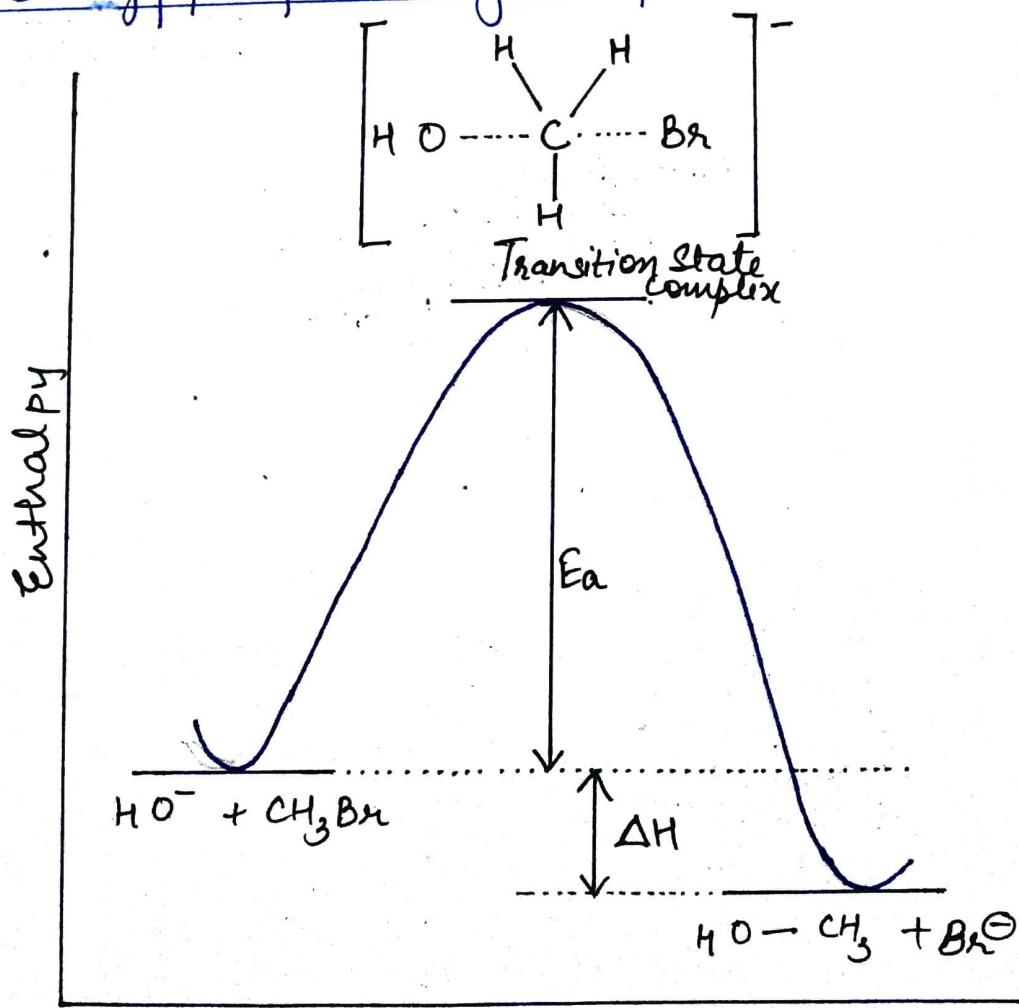


Ansari

The approaching of nucleophile and liberation of the leaving group occurs simultaneously in one step. Nucleophile approached the substrate to the opposite side with respect to the leaving group. So only one product is obtained with inversion of stereochemistry when a chiral molecule is taken as a substrate.

The rate of the reaction depends on both substrate concentration as well as concentration of nucleophile.

Energy profile Diagram for S_N2 Reaction



Reaction Coordinate