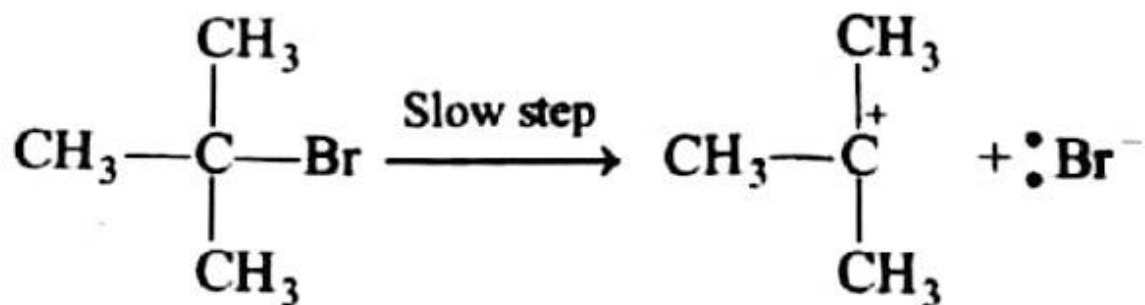


(b) S_N1 Reactions : S_N1 stands for **unimolecular reaction**. When the rate of nucleophilic substitution reaction depends only on the concentration of the substrate, the reaction is of first order change and is represented as S_N1

Rate [Substrate]

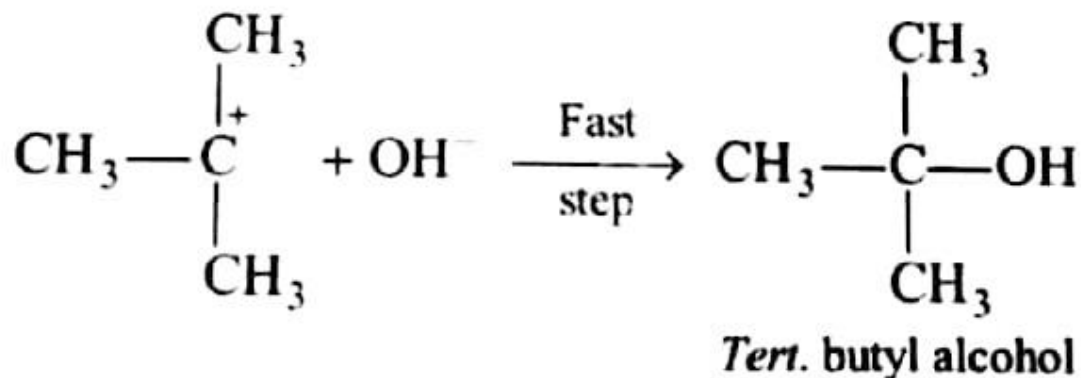
The hydrolysis of tert. -butyl bromide is an example S_N1 reaction. The reaction consists of two steps:

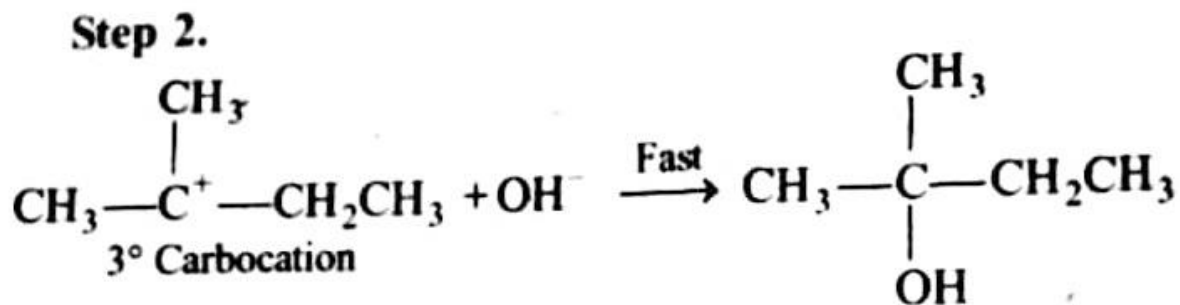
Step 1. The substrate undergoes heterolytic fission forming a carbocation. This is the slow process and rate determining step.



The carbocation is planar as the central positively charged carbon atom is sp²-hybridized.

Step 2. The nucleophile (OH⁻) can attack the planar carbocation from either side to form tert. -butyl alcohol and the low concentration of OH⁻ favours S_N1 reaction.

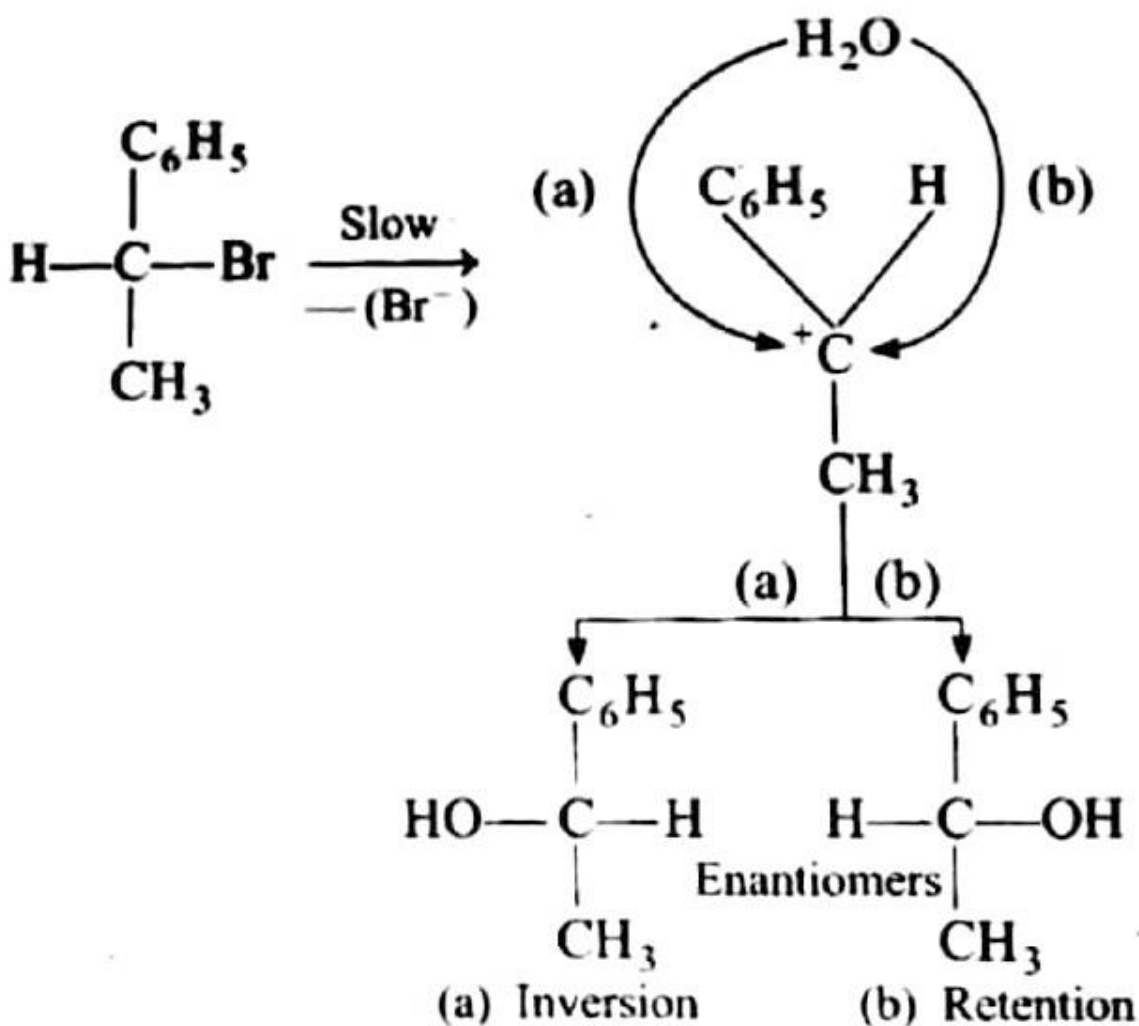




As a result of S_N1 reaction, there can be **racemisation** and **inversion**. The racemisation is due to inverting nucleophilic displacement of halogen atom from the alkyl halide by the halide in solution.

For example, when (-) 2-bromo butane having chiral centre is treated with low concentration of nucleophile (OH^-), it forms (+) 2-butanol. There is also loss in optical activity due to formation of d- and l-isomer (racemic) because of S_N1 reaction. The more stable the carbocation, the greater is the proportion of racemisation.

In another example of 1-bromo-1-phenylethane [$\text{C}_6\text{H}_5, \text{CH}(\text{Br})\text{CH}_3$], the S_N1 reaction involves racemisation plus inversion.



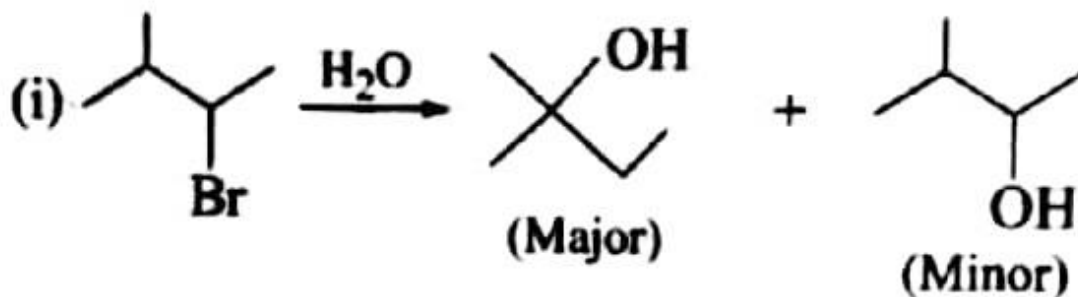
The nucleophilic reagent attacks both (a) the back side and (b) the front side of the carbocation. Back side attack (a) predominates. The two enantiomers constitute the racemic modification.

Thus, in S_N1 reaction, racemization as well as inversion is observed, while in case of S_N2 completes

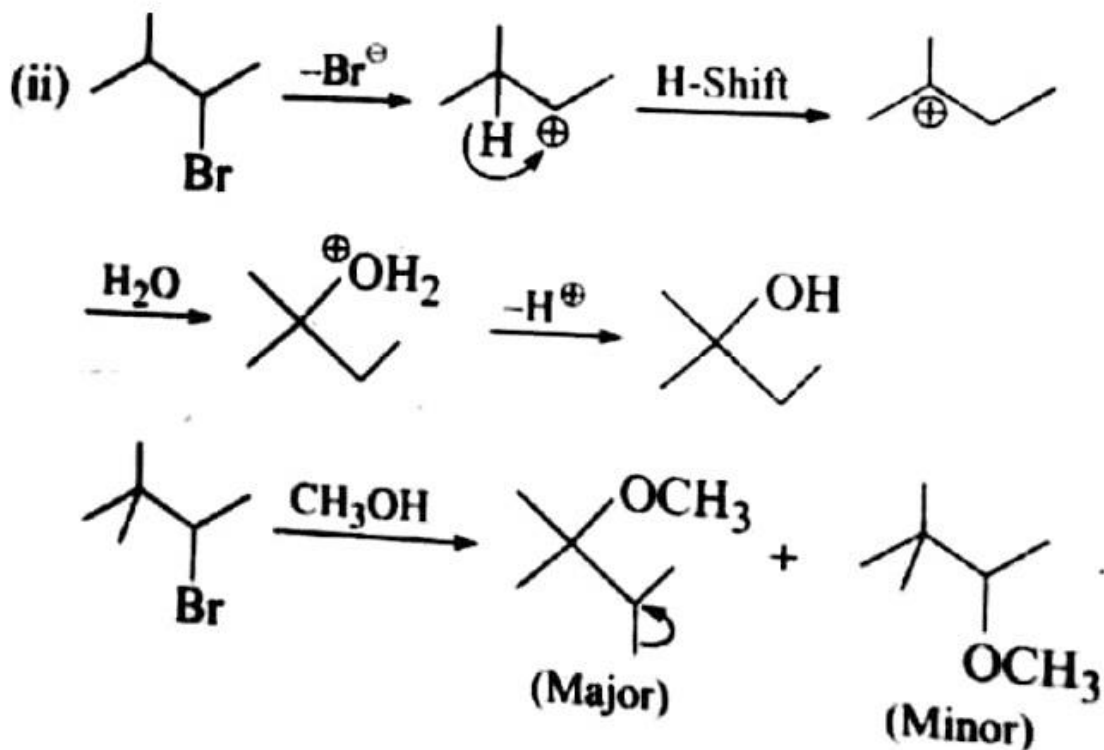
inversion takes place (where chiral carbon exist).

Carbocation rearrangement

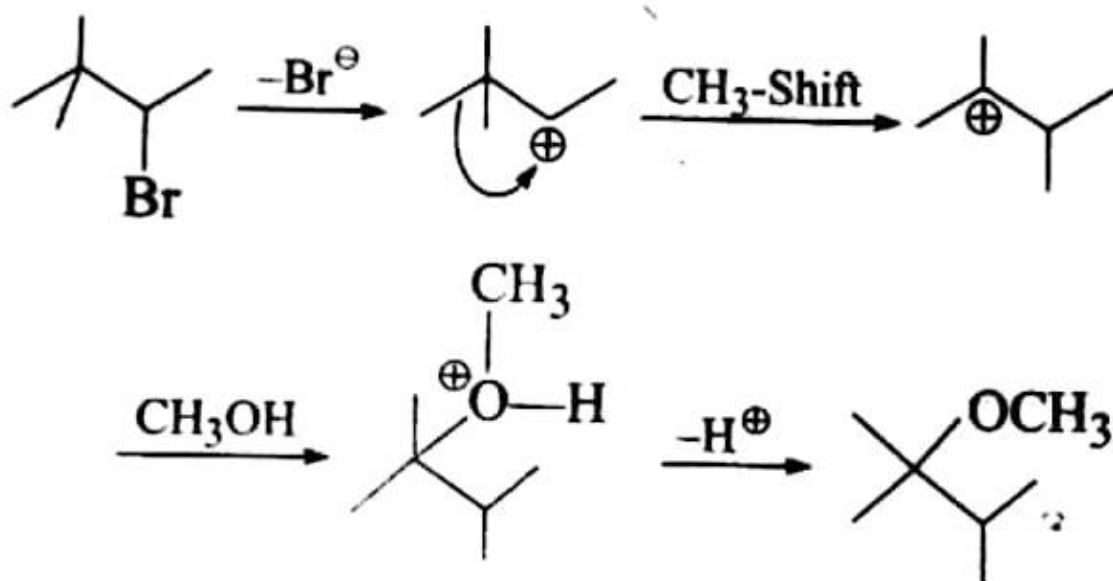
A carbocation intermediate formed in S_N1 reaction will rearrange if it becomes more stable in the process and the same alkyl halide can produce different structural isomers as product, e.g.,



Mechanism :



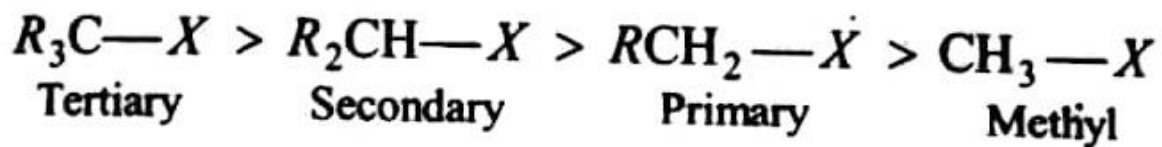
Mechanism :



Factor affecting rate of S_N1 reaction

S_N1 reaction is favoured by heavy (bulky) groups on the carbon atom attached to halogens; i. e., the order of reactivity

is:



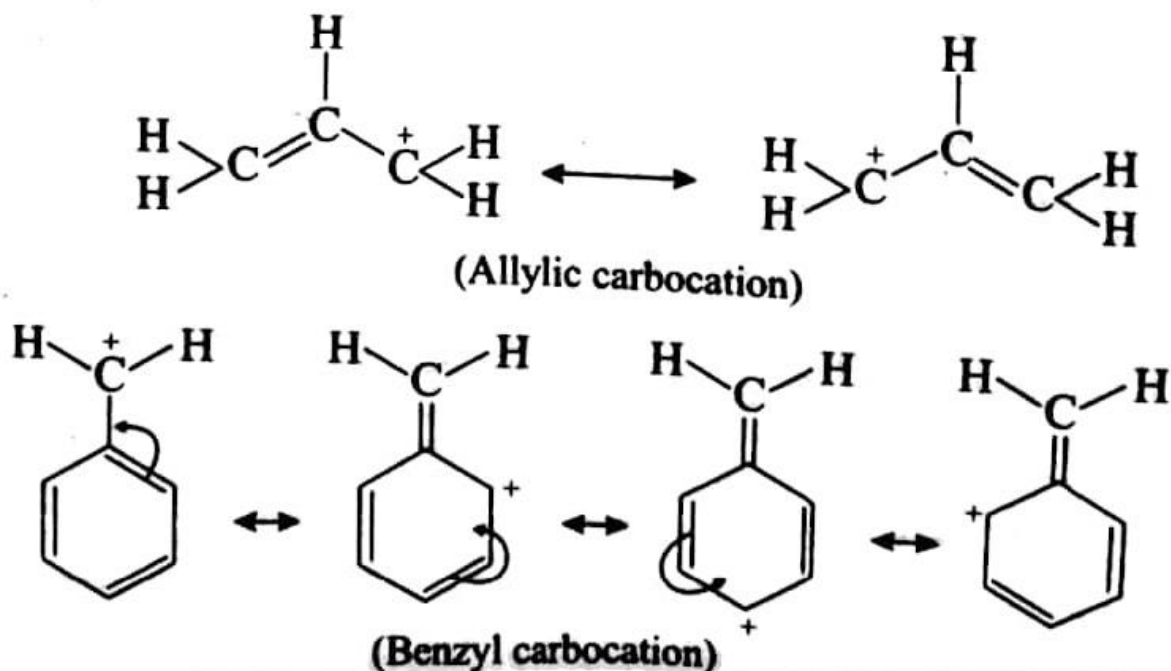
and nature of carbocation (**decreasing stability**) in substrate

is:

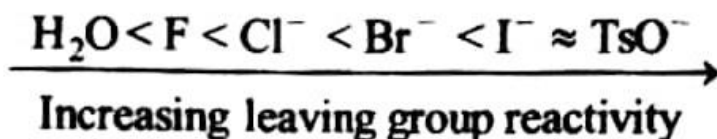
Benzyl > allyl > tertiary > secondary > primary

> methyl halides (S_N1 order)

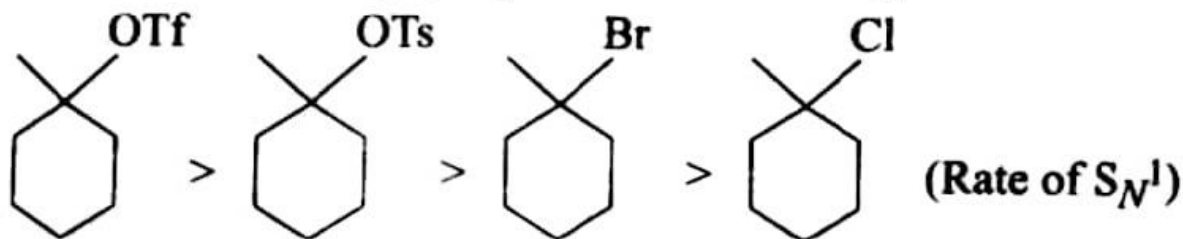
Allylic and benzylic carbocations are resonance stabilized.



Leaving group reactivity for $\text{S}_{\text{N}}1$ reaction may be given as,



A better leaving group increases rate of $\text{S}_{\text{N}}1$ reactions.



The best leaving group should be those that are most stable that is conjugate bases of strong acids. An identical reactivity order is found for $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$ reaction. In $\text{S}_{\text{N}}1$ reaction it is very important because leaving group is directly involved in rate determining step.

Solvent effect in $\text{S}_{\text{N}}1$ reaction: $\text{S}_{\text{N}}1$ reaction takes place much more rapidly in polar solvents than in non-polar solvents. In the reaction of 2-chloro-2-methylpropane, for example, a rate increase of 1,00,000 is observed on going from ethanol to water. The rate increase on going from hydrocarbon solvents to water are so large that they cannot be measured accurately.

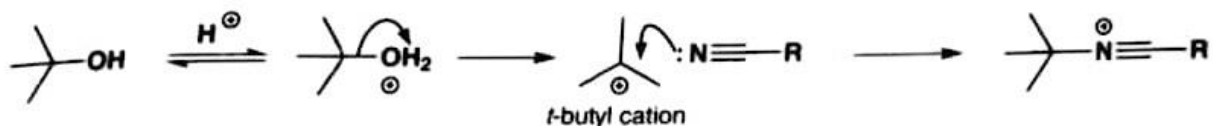
$$(\text{CH}_3)_3\text{C}-\text{Cl} + \text{ROH} \longrightarrow (\text{CH}_3)_3\text{C}-\text{OR} + \text{HCl}$$

Solvent	CH_3COOH	$\text{C}_2\text{H}_5\text{OH}$	CH_3OH	HCOOH	HOH
Relative reactivity (increasing)	< 1	1	4	5,000	1,00,000
Dielectric constant (ϵ)	6	7	33	58	78

Dielectric constant is a measure of the ability of a compound. Polar solvents have high dielectric constant... The positive and negative charged species are best separated in a medium with higher dielectric constant. The standard dielectric is a vacuum ($\epsilon = 1$).

A very bad nucleophile in a good $\text{S}_{\text{N}}1$ reaction: the Ritter reaction

An interesting result of the unimportance of the nucleophile to the rate (and therefore the usefulness) of an $\text{S}_{\text{N}}1$ reaction is that very poor nucleophiles indeed may react in the absence of anything better. Nitriles, for example, are very poorly basic and nucleophilic because the lone pair of electrons on the nitrogen atom is in a low-energy sp orbital. However, if *t*-butanol is dissolved in a nitrile as solvent and strong acid is added, a reaction does take place. The acid does not protonate the nitrile, but does protonate the alcohol to produce the *t*-butyl cation in the usual first step of an $\text{S}_{\text{N}}1$ reaction. This cation is reactive enough to combine with even such a weak nucleophile as the nitrile.



The resulting cation is captured by the water molecule released in the first step and an exchange of protons leads to a secondary amide. The overall process is called the Ritter reaction and it is one of the few reliable ways to make a C-N bond to a tertiary centre

