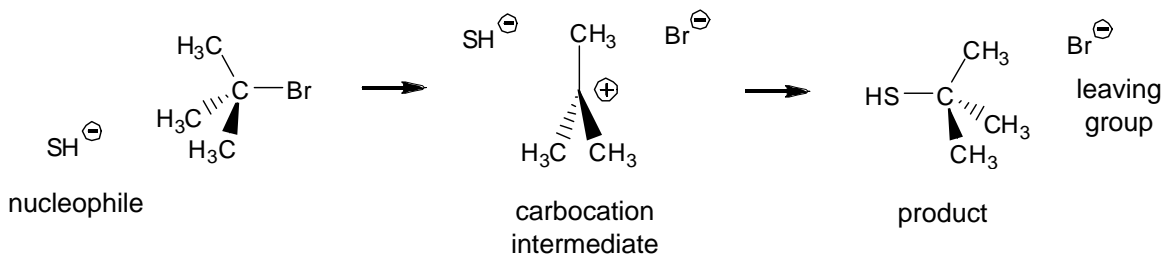


1st Order Nucleophilic Substitution (S_N1)



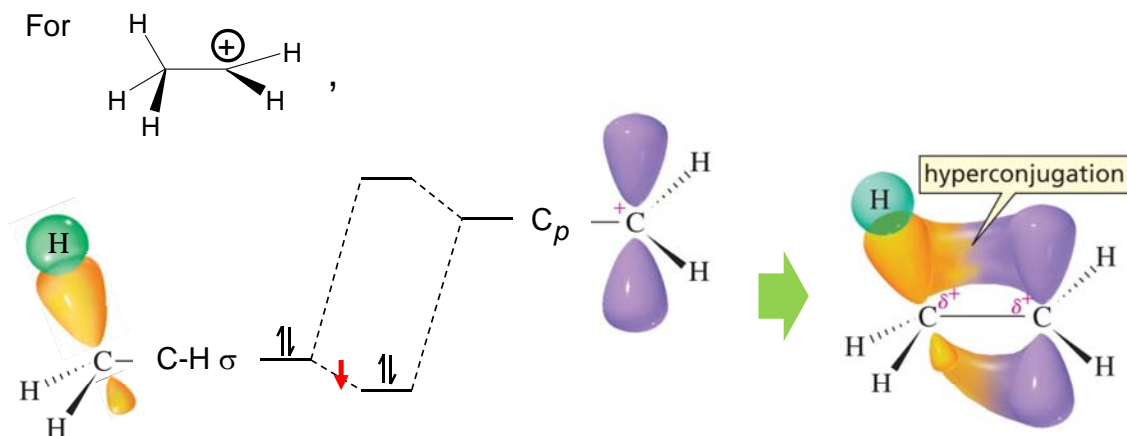
1st Order because only electrophile involved in rate expression:

$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$$

- In **S_N2**, departure of leaving group and arrival of nucleophile were **concerted**.
- In **S_N1**, mechanism is **stepwise**. Leaving group departs to form discrete intermediate, then nucleophile adds.

S_N1 Occurs When Carbocation Intermediate is Stable

Carbocations are stabilized by **hyperconjugation**.

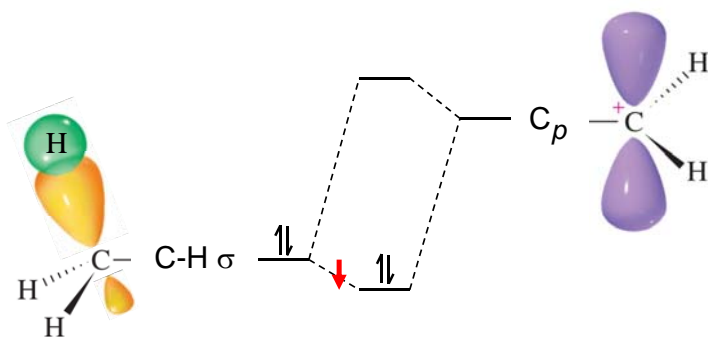


Each neighboring C-H σ **stabilizes** empty C_p orbital in cation. (C-C σ also stabilizes.)

The more C-H/C-C's there are, the more stable the cation is.

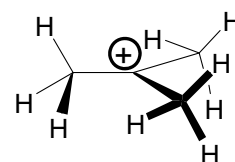
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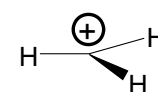


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So,



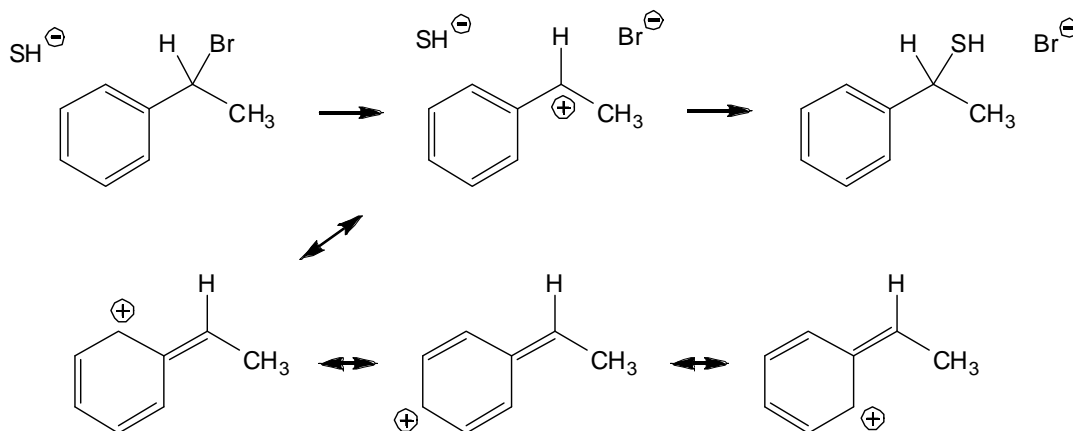
more stable than



Stability trend for R_3C^+ :
 $3^\circ > 2^\circ > 1^\circ > CH_3$

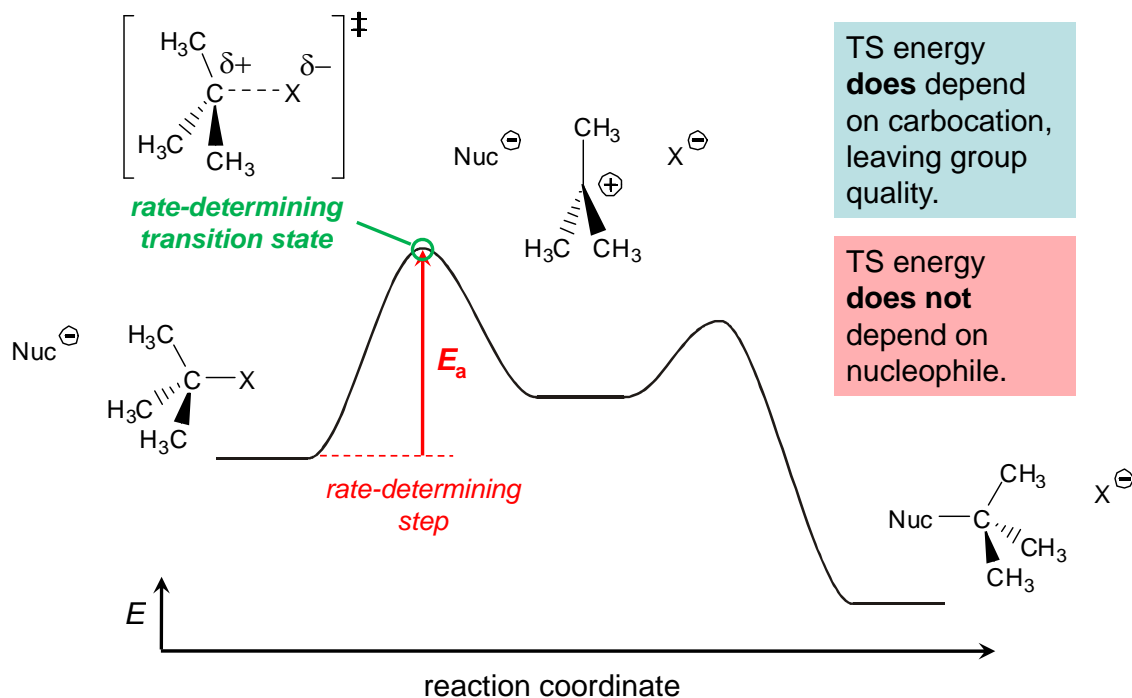
S_N1 Occurs When Carbocation Intermediate is Stable

Carbocations also stabilized by resonance.

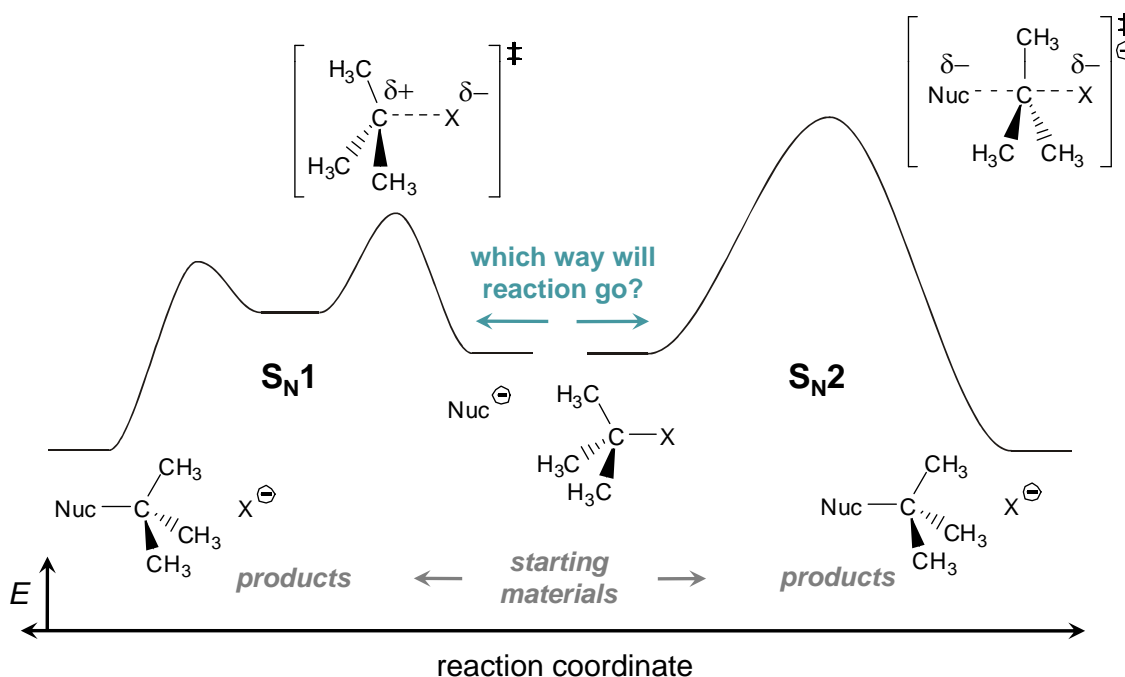


So, because cation stabilized by resonance,
 S_N1 mechanism operates here.

Potential Energy Diagram for S_N1



Substitution Reactions Choose S_N1 or S_N2 (or Both)



Substitution Reactions Choose S_N1 or S_N2 (or Both)

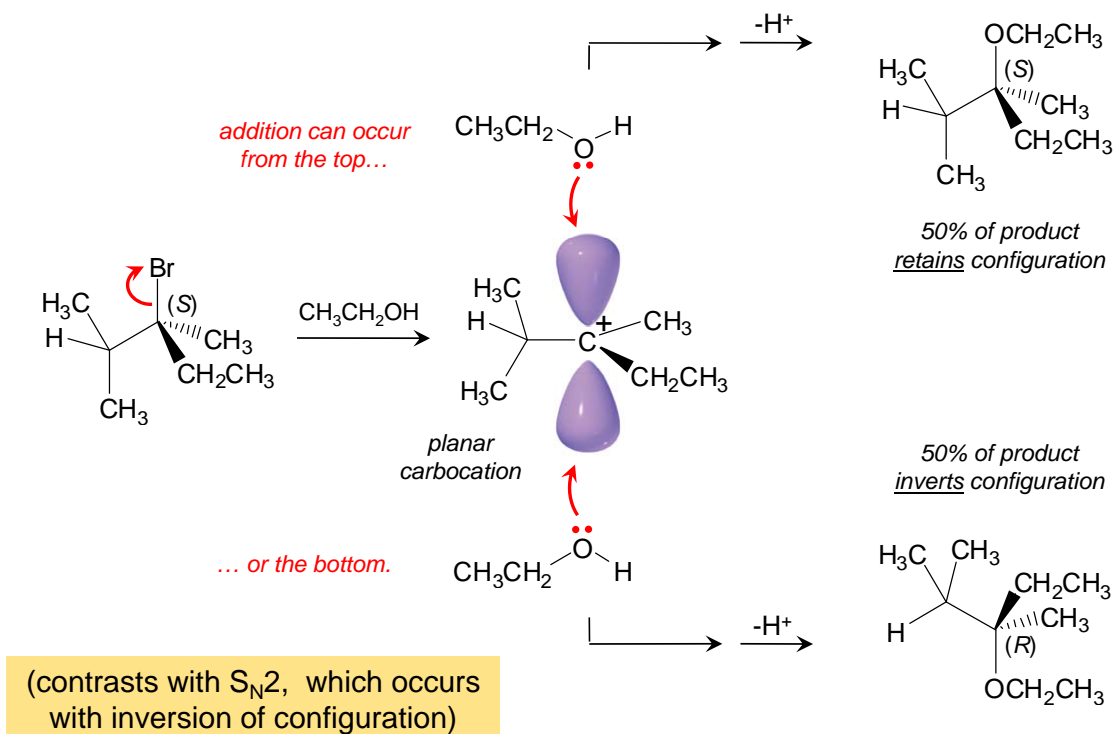
Promoting factors:

	S_N1	S_N2
nucleophile	weak nucleophile OK high concentration helps	strong nucleophile required
substrate	$3^\circ > 2^\circ$	$CH_3 > 1^\circ > 2^\circ$
leaving group	good leaving group required	good leaving group required
solvent	very polar solvent helps	polar, but not too polar

Proposing Multistep Reaction Mechanisms ("Electron Pushing")

- Focus on getting from starting materials to products.
- Make sure each step is balanced; atoms, electrons and charge should be conserved.
- Don't draw multiple steps as one. Each step (including acid-base exchange) creates new, discrete species.
- Make sure intermediates are compatible with reaction conditions.

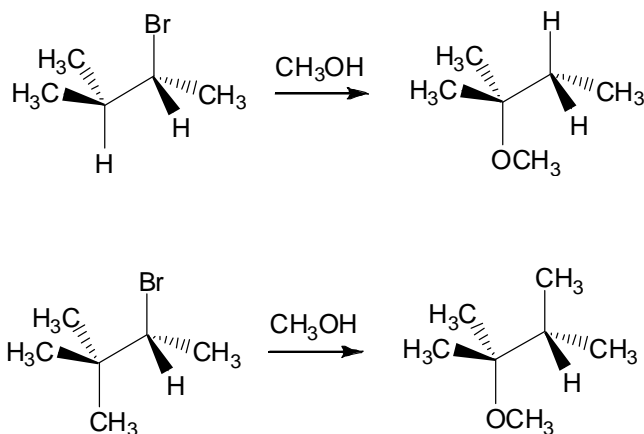
S_N1 Reactions Produce Racemates



Carbocation Rearrangements

A carbocation will rearrange (by hydride or alkyl shift) if it can form a more stable carbocation.

Explains:



S_N1 and S_N2 Occur at sp^3 -Hybridized Carbon Only

