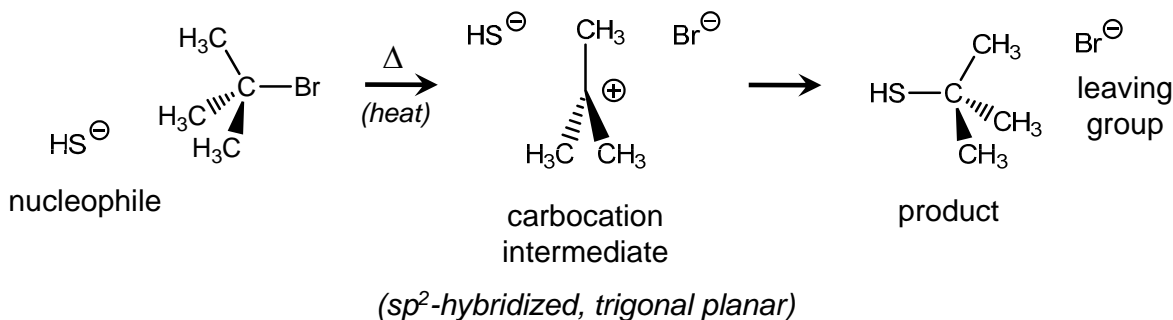


# 1<sup>st</sup> Order Nucleophilic Substitution (S<sub>N</sub>1)

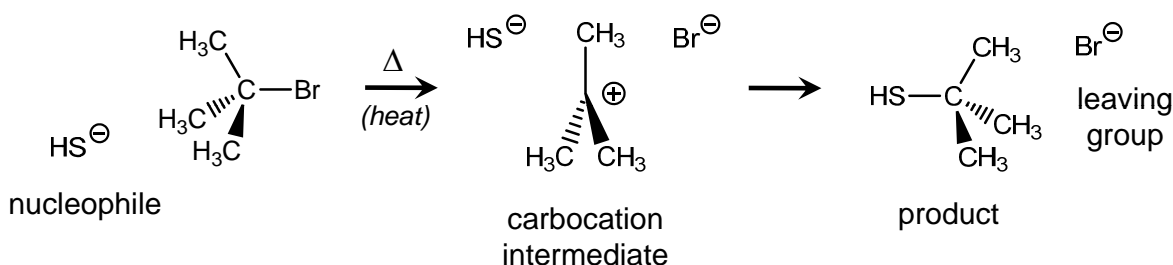
Like S<sub>N</sub>2, S<sub>N</sub>1 is another reaction mechanism that substitutes one functional group for another.



The outcomes of S<sub>N</sub>2 and S<sub>N</sub>1 reactions are the same. So,

- What are the differences between the two mechanisms?
- How do we know which mechanism is preferred?

## Features of S<sub>N</sub>1

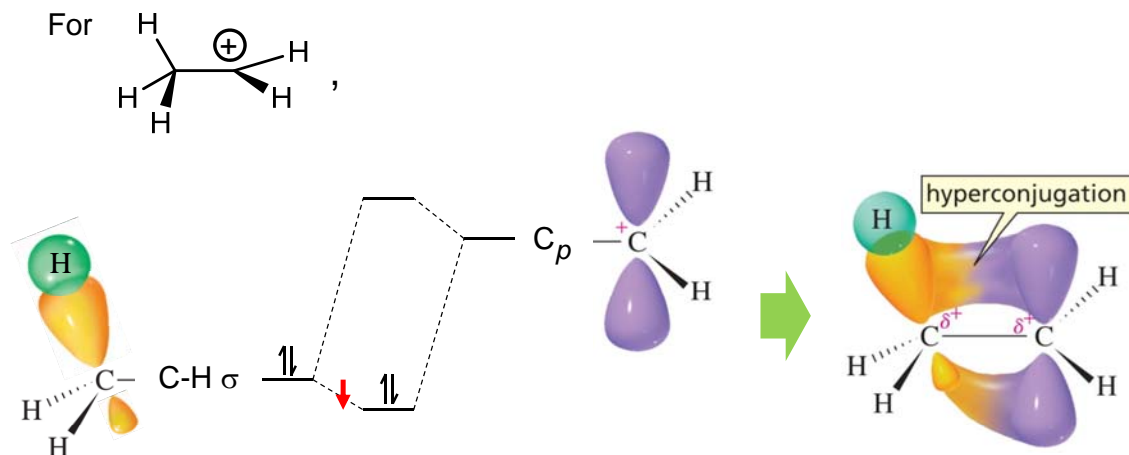


1<sup>st</sup> Order because only electrophile involved in rate expression:

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

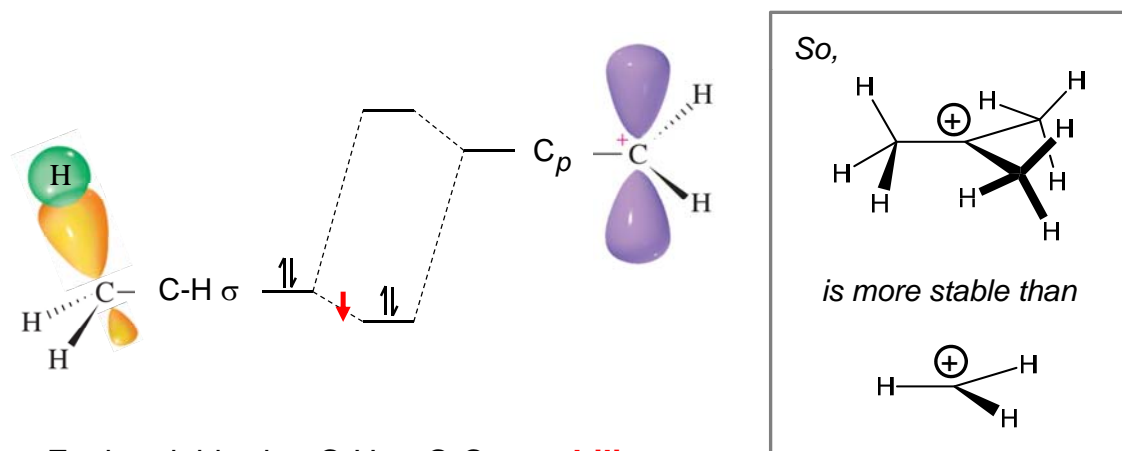
- In S<sub>N</sub>2, departure of leaving group and arrival of nucleophile are **concerted**.
- In S<sub>N</sub>1, mechanism is **stepwise**. Leaving group departs to form discrete intermediate, then nucleophile adds.

# Carbocations Are Stabilized by Hyperconjugation



Each neighboring C-H  $\sigma$  **stabilizes** the empty  $C_p$  orbital in a carbocation. (C-C  $\sigma$  also stabilizes.)

# More Substituted Carbocations Are More Stable



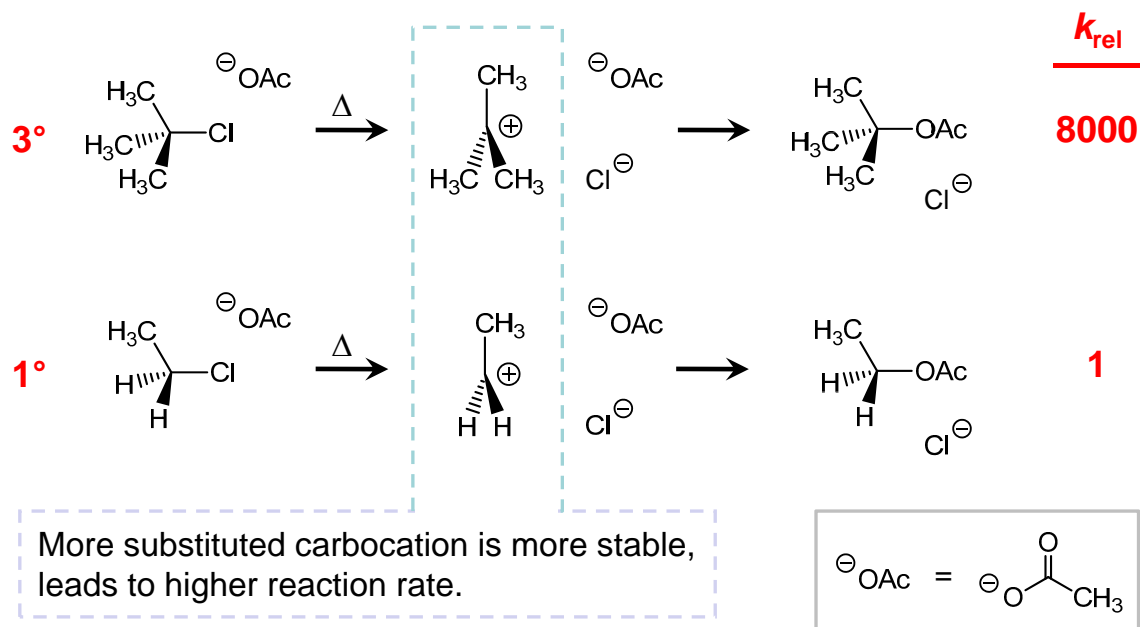
Each neighboring C-H or C-C  $\sigma$  **stabilizes** the empty  $C_p$  orbital in a carbocation.

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

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

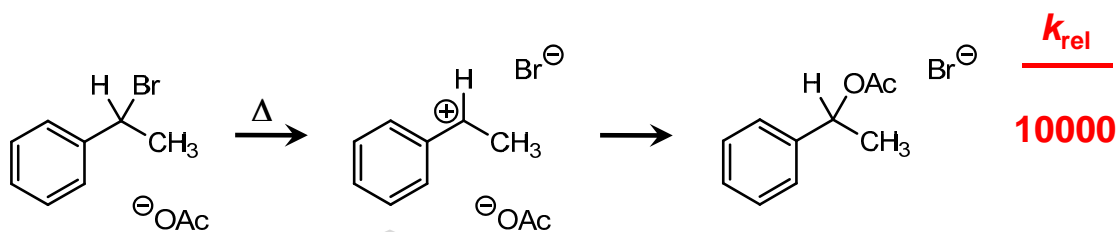
## S<sub>N</sub>1 Occurs When the Carbocation Intermediate is Most Stable

Relative rates of S<sub>N</sub>1 reactions:



## S<sub>N</sub>1 Occurs When the Carbocation Intermediate is Most Stable

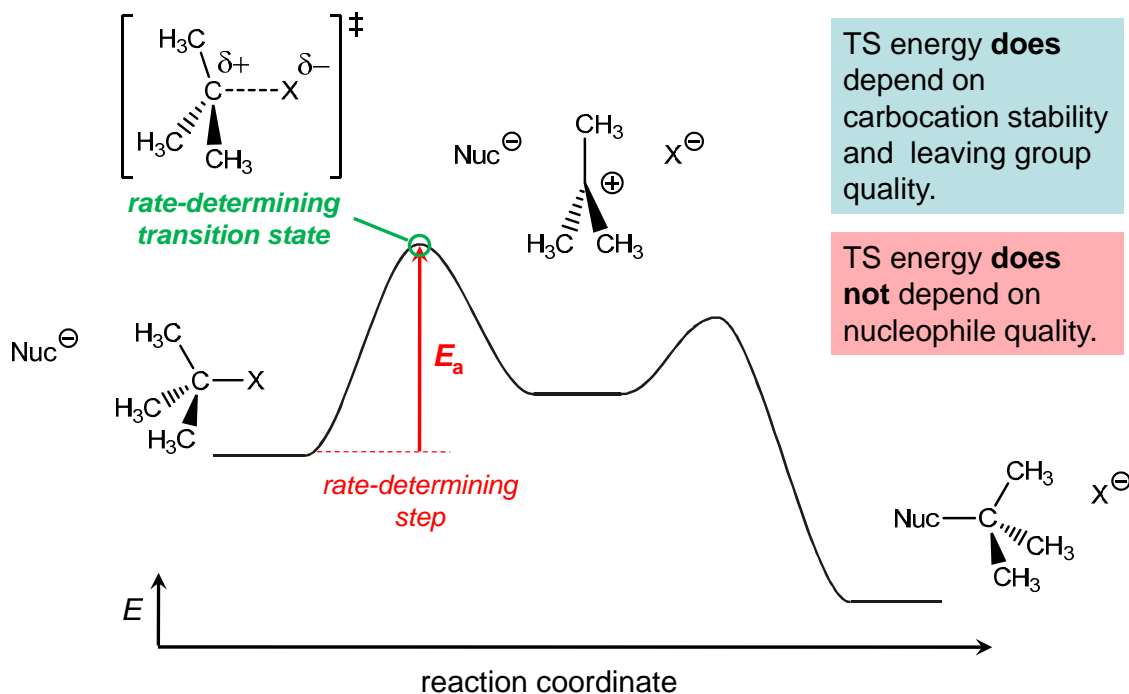
Carbocations also stabilized by resonance.



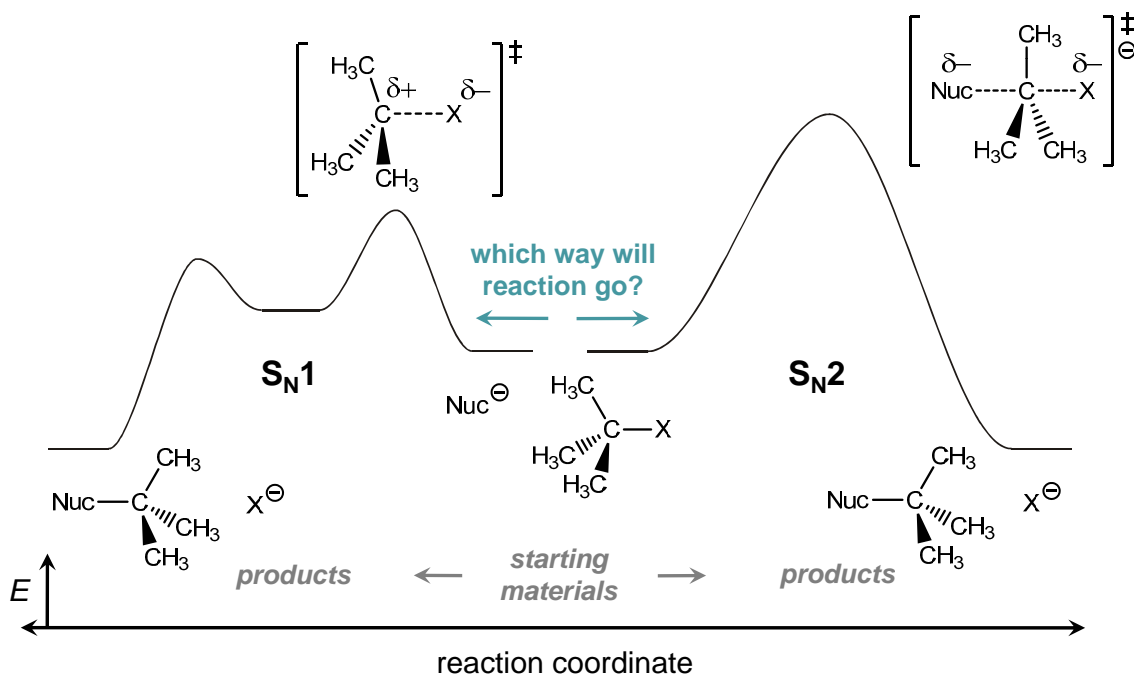
resonance structures?

Cation is stabilized by resonance, so S<sub>N</sub>1 mechanism operates here.  
Resonance is usually even more important than substitution.

# Potential Energy Diagram for S<sub>N</sub>1



# Substitution Reactions Choose S<sub>N</sub>1 or S<sub>N</sub>2 (or Both)



# Substitution Reactions Choose $S_N1$ or $S_N2$ (or Both)

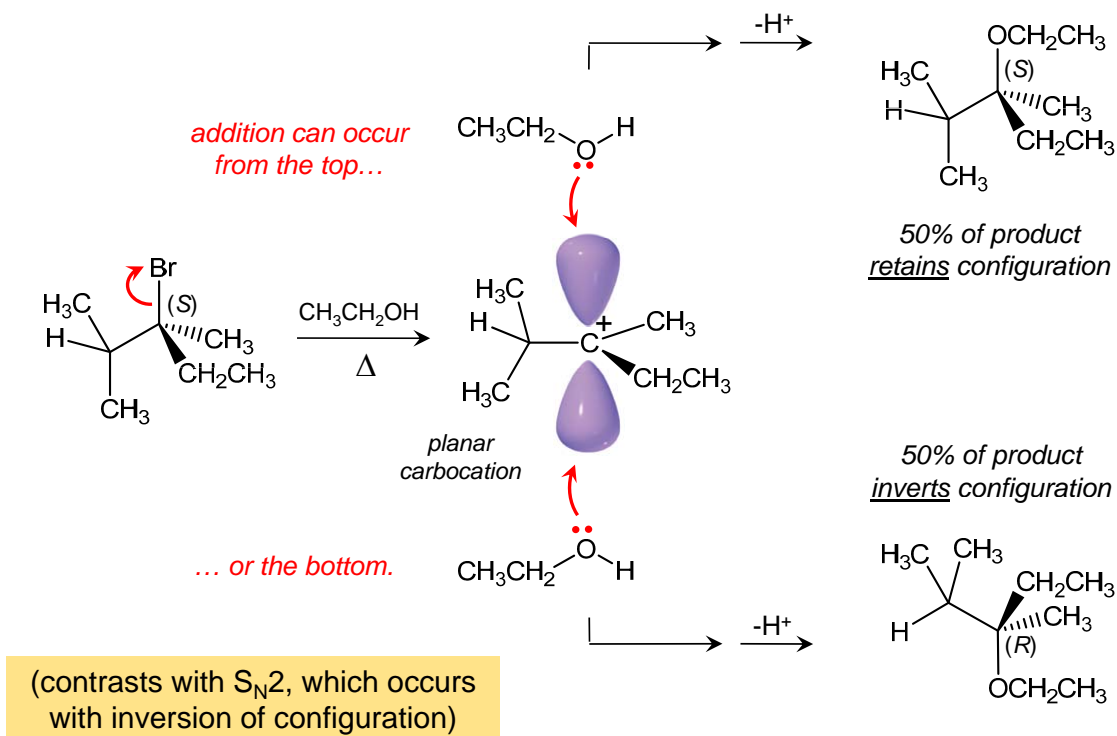
Promoting factors:

	$S_N1$	$S_N2$
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 ( $H_2O$ , DMF, DMSO, $CH_3CN$ )	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.

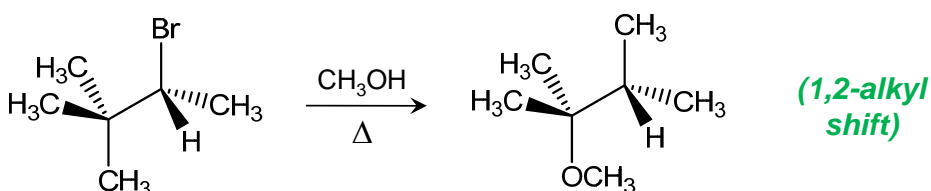
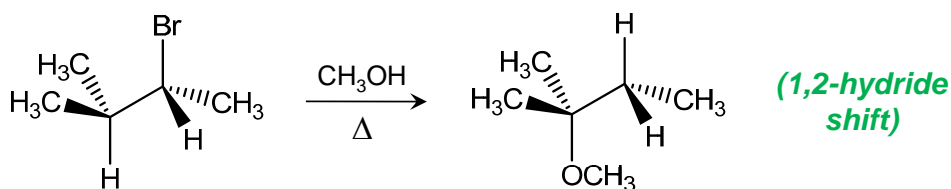
# S<sub>N</sub>1 Reactions Produce Racemates



## 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 Carbons Only

