



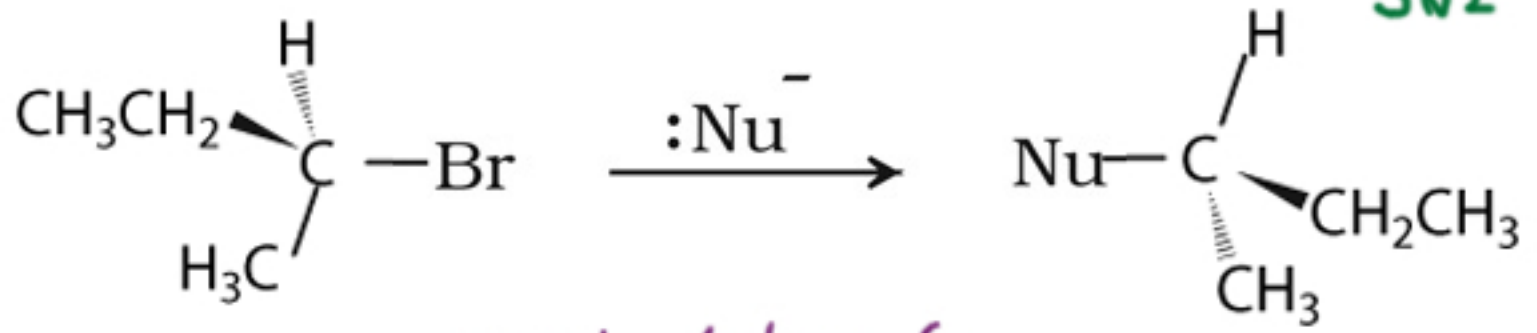
Substitution vs. Elimination

Session Slides with Notes

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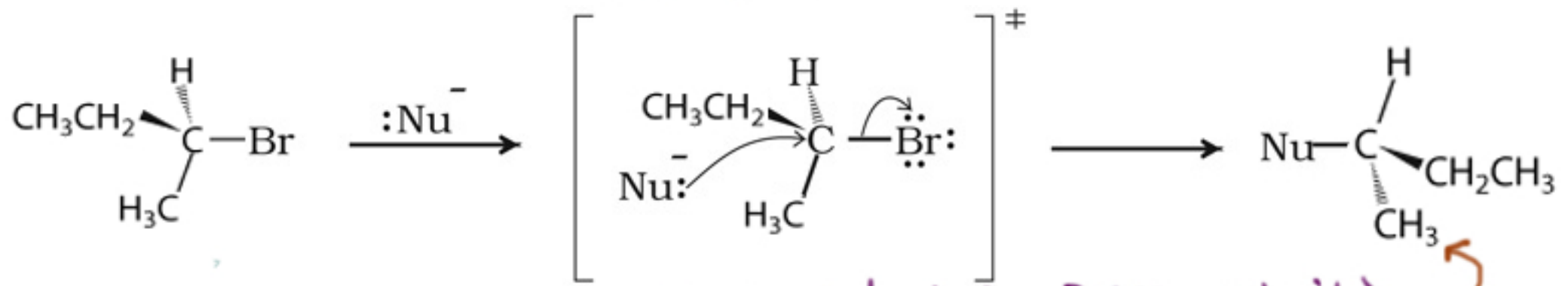
SN2 Substitution



Alkyl halide

Substitution product

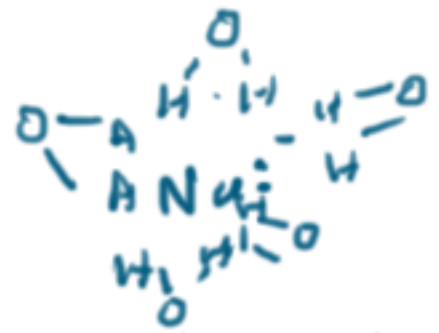
- reaction of choice for primary alkyl halides
- prefers unhindered substrate and nucleophile
- unless strong, bulky, hindered base - for 1° - tert-butoxide then E2 elimination



• polar aprotic solvent like DMSO, acetonitrile

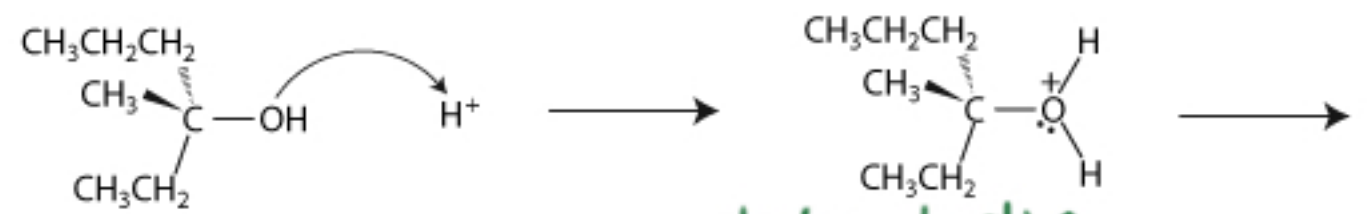
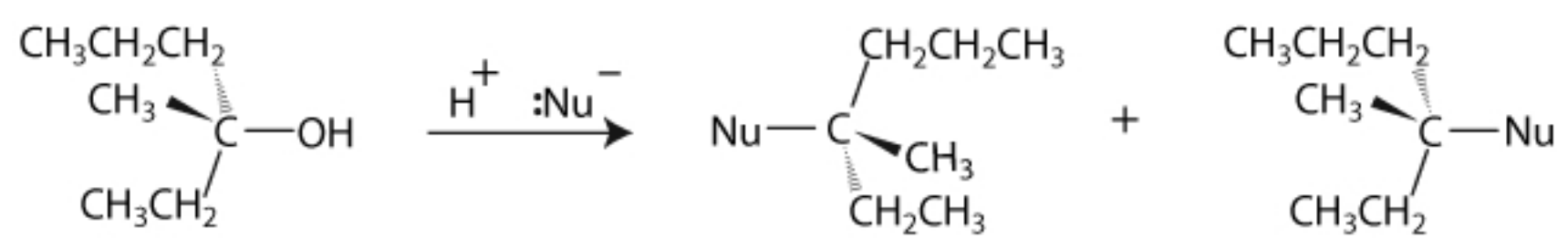
stereospecific for inversion of configuration

$$\text{rate} = k [\text{Nu}] [\text{RX}]$$



Why is a protic solvent a bad idea? Overstabilizes the nucleophile.

S_N1 Substitution



electron donating by induction

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



rate determining

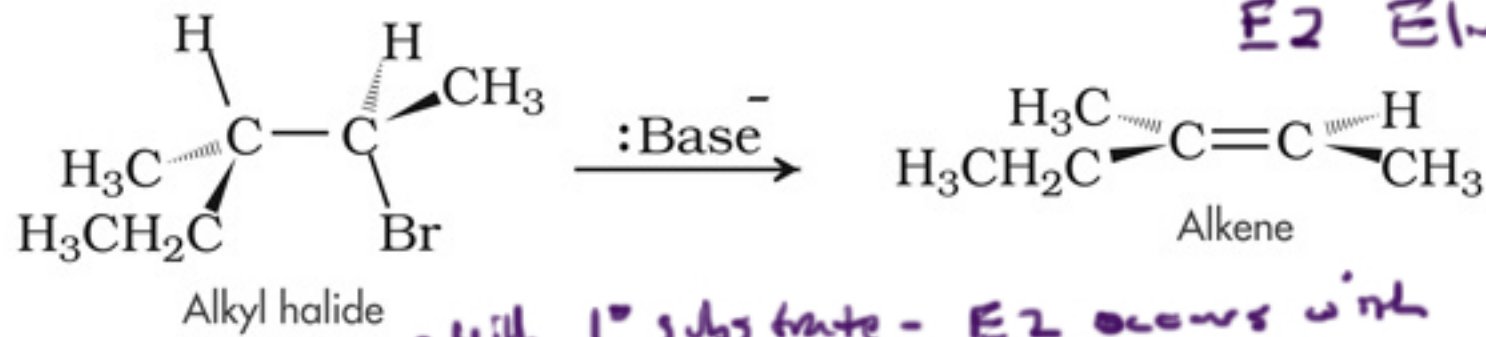
carbocation might rearrange.



racemic mixture

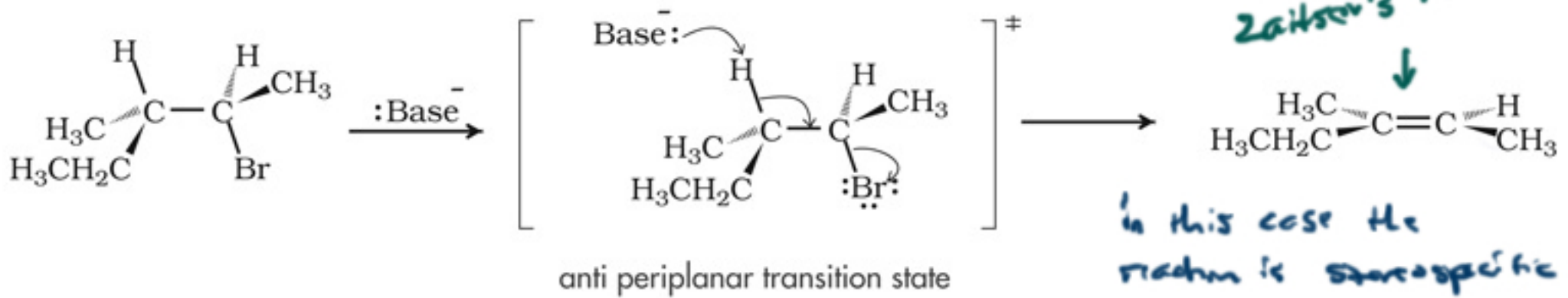
rate = k [RX]

E2 Elimination



- With 1° substrate - E2 occurs with a bulky hindered base
- with 2° - strong bases

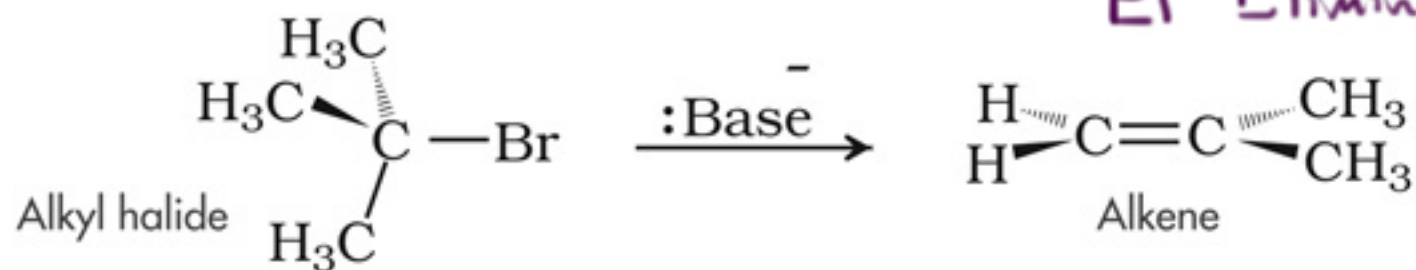
more substituted double bond is favored
Zaitsev's rule



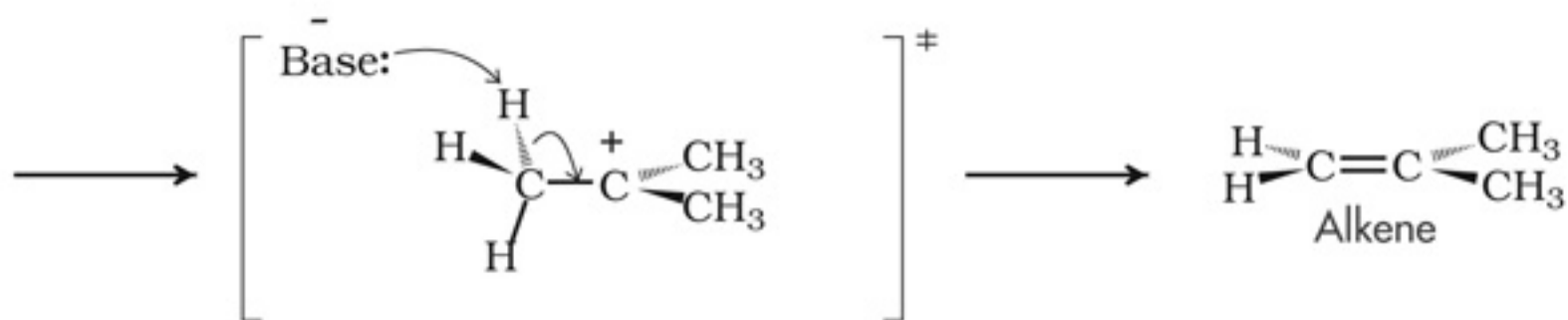
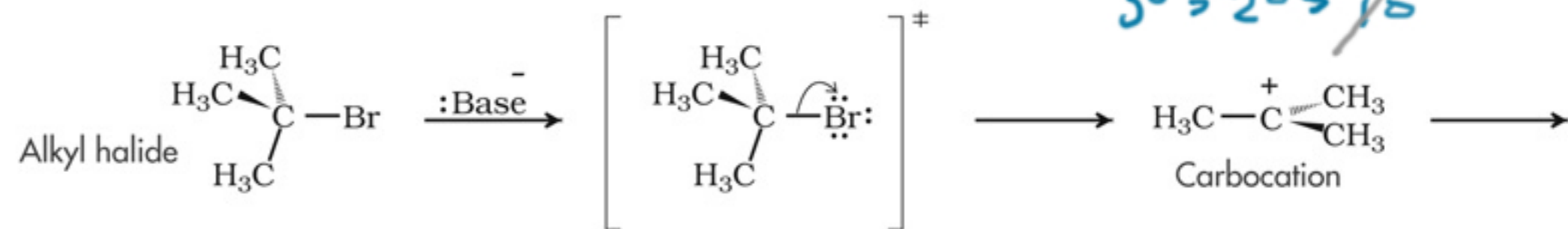
In this case the reaction is stereospecific for cis.

(anti-periplanar transition state)

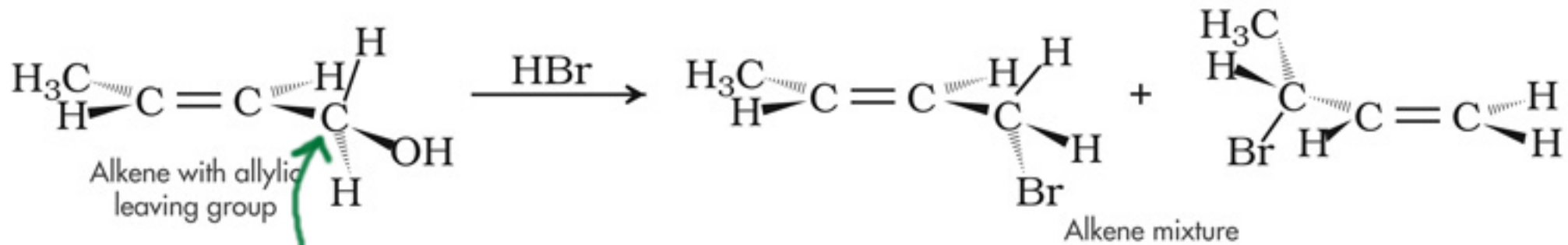
E1 Elimination



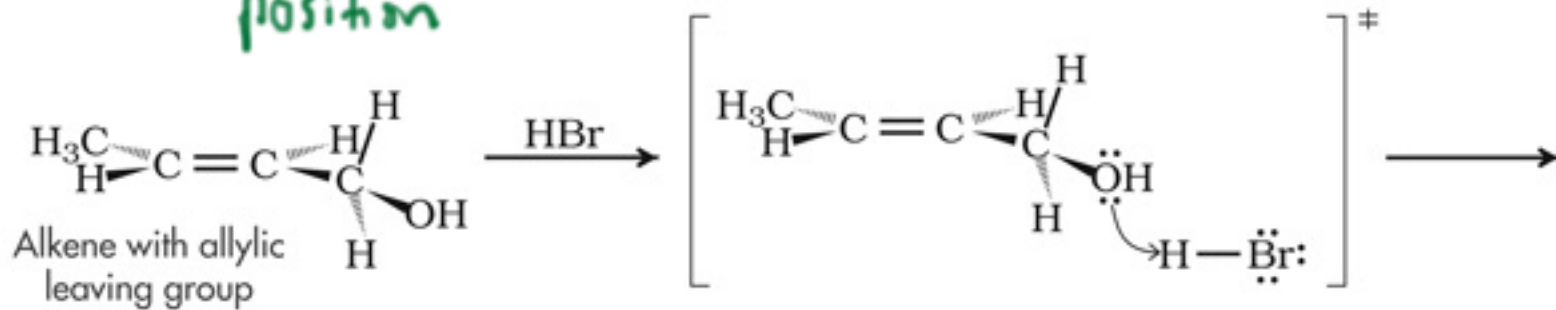
3° > 2° > 1°



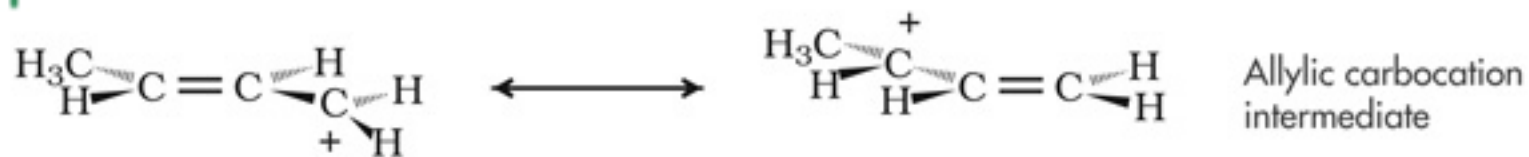
Often in mixture with SN1



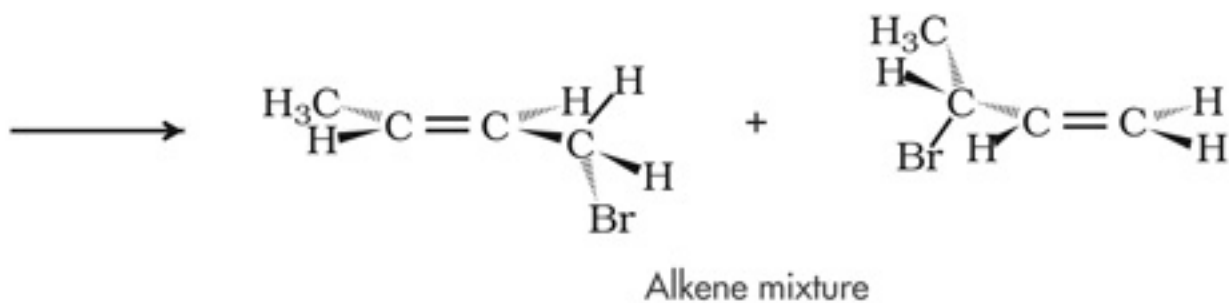
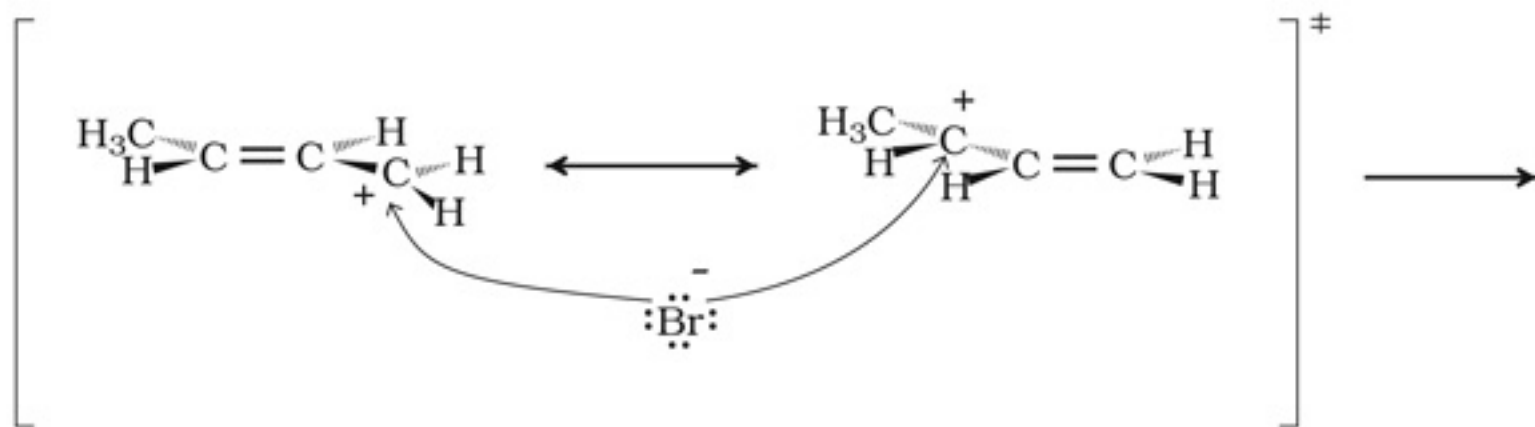
allylic position



allylic > 3° > 2° > 1°



benzylic



Substrate

If the substrate is a primary alkyl halide, the reaction will almost certainly be SN2.
Exceptions: A bulky hindered base like tert-butoxide will tend to react with E2.
Watch out for allylic primary alkyl halides.
If the substrate is tertiary, the reaction cannot be SN2.

Nucleophile Charged nucleophiles/bases will favor SN2/E2. Deciding between SN2 & E2, look at the basicity. Strong bases with secondary substrates will favor E2. Weak bases like Cl⁻, CN⁻ favor SN2.
Uncharged nucleophiles/bases favor SN1/E1.

Solvent

SN2 substitution is favored by polar, aprotic solvents like DMSO, acetonitrile, diethyl ether etc.

Temperature If the choice is between E1 and SN1, high temperature favors elimination.