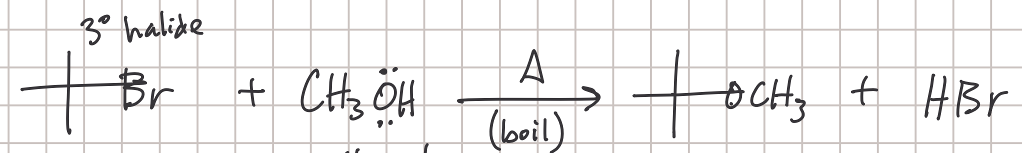
# Ch 6

Note Title 11/8/2005

## $S_N1$ reaction



t-butylbromide

methanol (solvent)

methyl-t-butyl ether (MTBE)

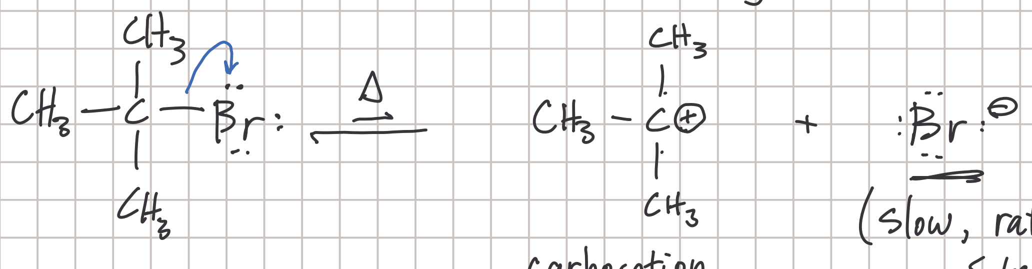
Solvolysis reaction : solvent reacts w/ substrate

$rate = k\,[+Br]$

only dependent on $[RX]$

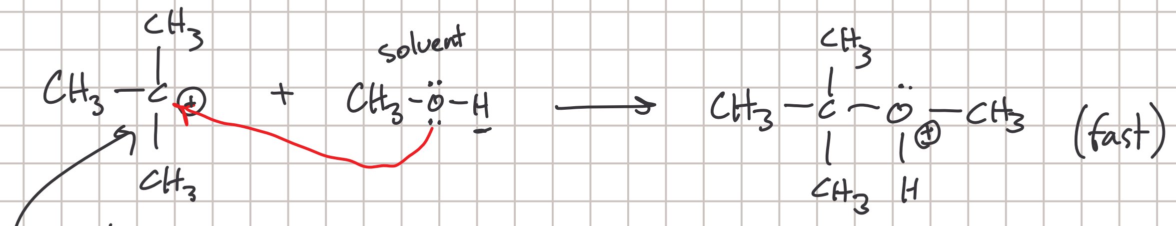
1st order overall → $S_N1$

Substrate only involved in rate-limiting step

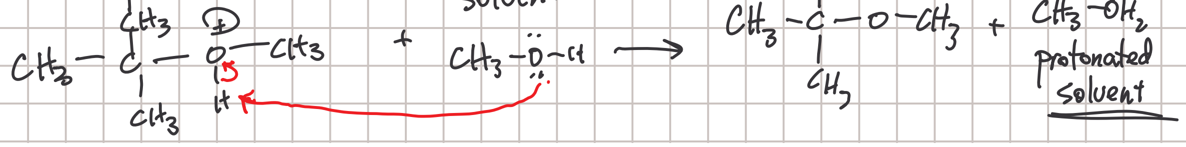


carbocation

(slow, rate-limiting step)



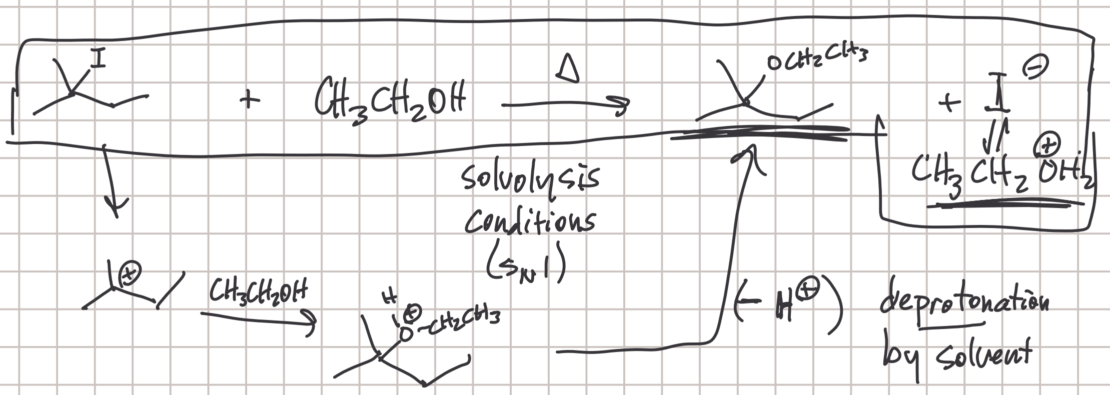
v. strong electrophile



protonated solvent

# $S_N1$ reaction

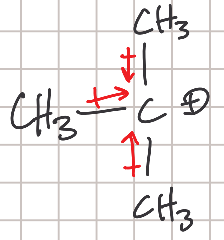
1. leaving group leaves to form carbocation (slow)
2. carbocation attacked by solvent (or other nuc.) (fast)
3. +-charged product is deprotonated by solvent, if necessary (fast)



## Substrate effects

stability of carbocation ↙

$$\underline{3^\circ} > 2^\circ > 1^\circ >>> {}^{\oplus}CH_3$$


$(CH_3)_3C^{\oplus}$

extra C's on $C^{\oplus}$ will donate $e^-$ density → stabilize $C^{\oplus}$

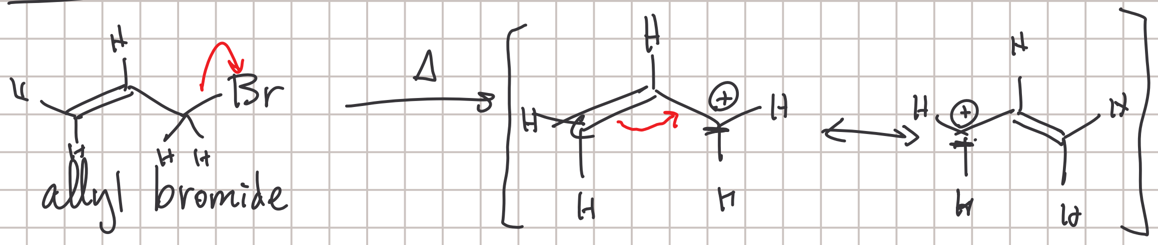
3° R-X reacts v. fast by $S_N1$

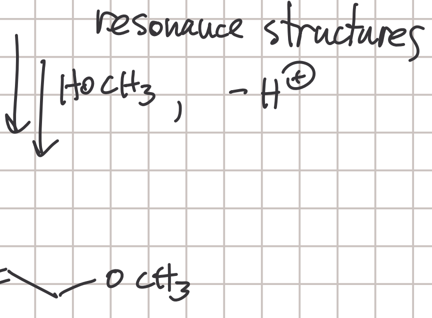
2° R-X ~ moderate

1° or $CH_3X$ = difficult by $S_N1$

] rearrangements

## resonance adds stability





compounds that make resonance-stabilized carbocations react faster in $S_N1$

## Leaving group

$S_N1$ requires a <u>strong</u> L.G.

(part of rate-limiting step)

$AgNO_3$ added to solution will <u>force</u> <u>ionization</u>

$$R{-}X + AgNO_3 \longrightarrow \underline{R^+} + NO_3^- + AgX\downarrow$$

precipitate

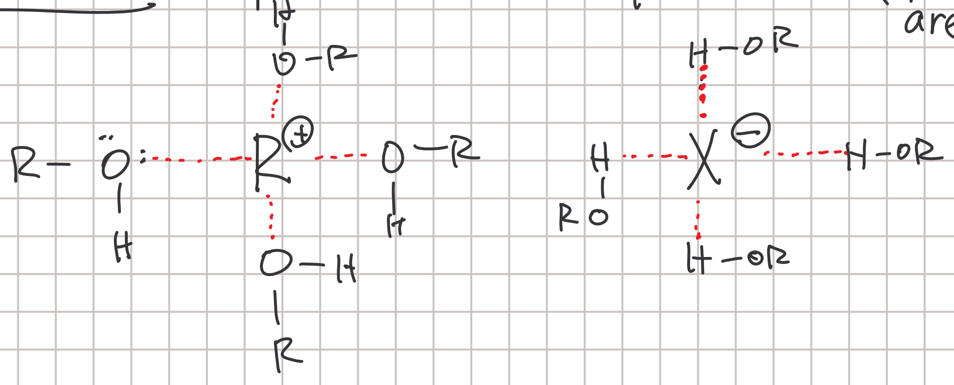
## Solvent

Polar solvent required (protic solvents are best)

↓

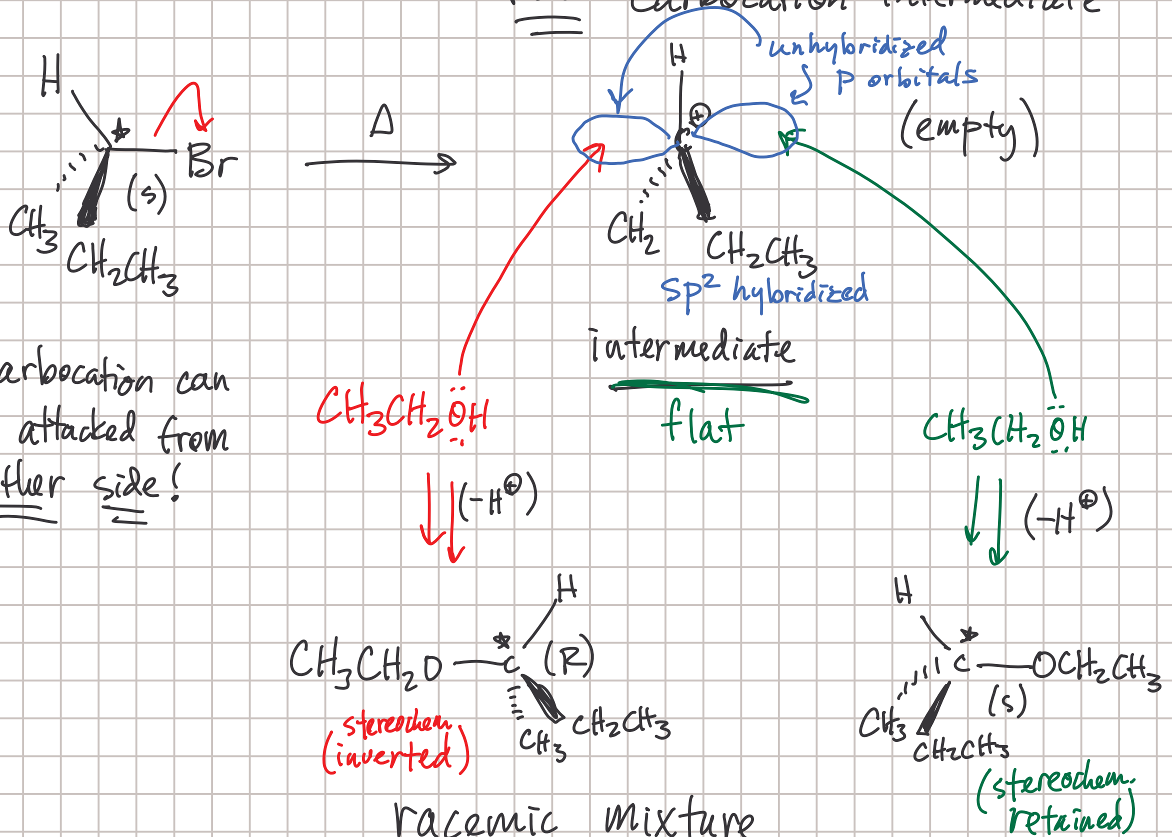
H-bonding

$H_2O$, R-OH



## Stereochemistry

$S_N1$ reacts by way of **flat** carbocation intermediate



carbocation can be attacked from either side!

racemic mixture

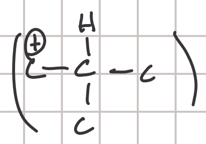
"scrambling"

(~ equal amounts of each enantiomer)

## Rearrangements

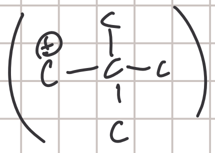
carbocations readily rearrange to make themselves more stable

① $C^{\oplus}$ next to 3° C, there will be a **hydride shift** (~H)



$$\left(\overset{\oplus}{C}-\underset{C}{\overset{H}{C}}-C\right)$$

② neopentyl $C^{\oplus}$ ($C^{\oplus}$ next to 4° C) will undergo **methyl shift** ($\sim CH_3$)



$$\left(\overset{\oplus}{C}-\underset{C}{\overset{C}{C}}-C\right)$$