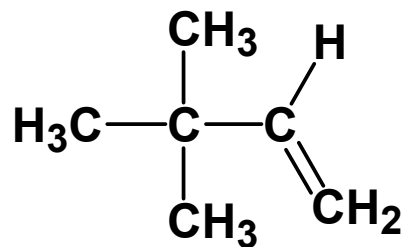
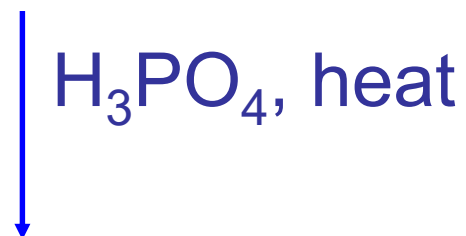
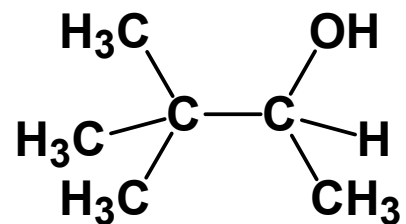


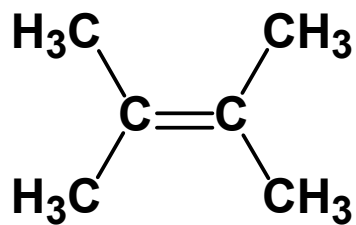
## Chapter 7 End:

### Competition Between Elimination and Substitution

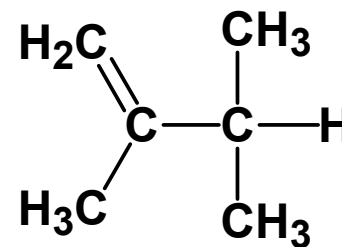
- E1 vs. E2
- SN1 vs. SN2
- SN2 vs E2/ SN1 vs. E1



+



+

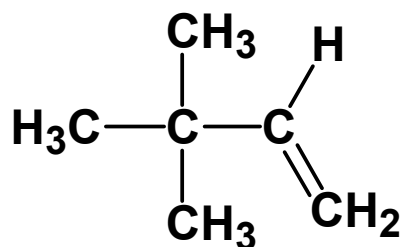
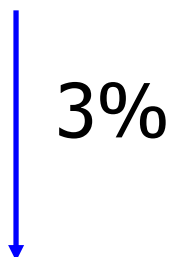
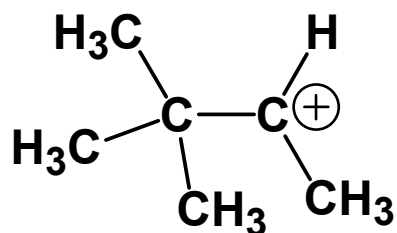


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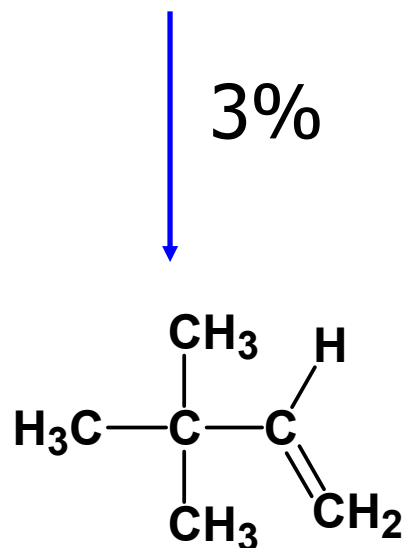
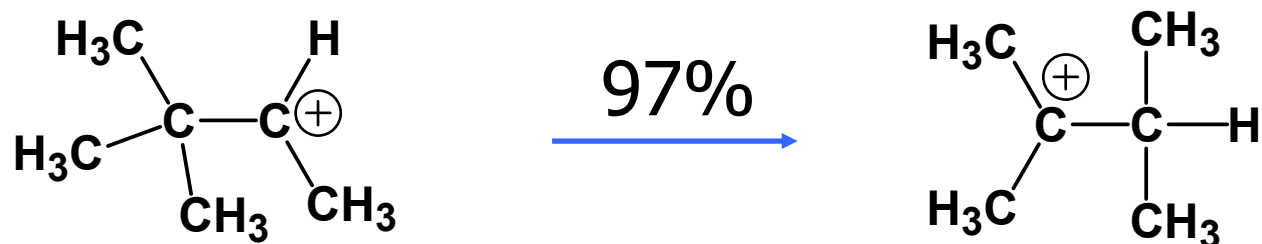
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# Rearrangement involves alkyl group migration



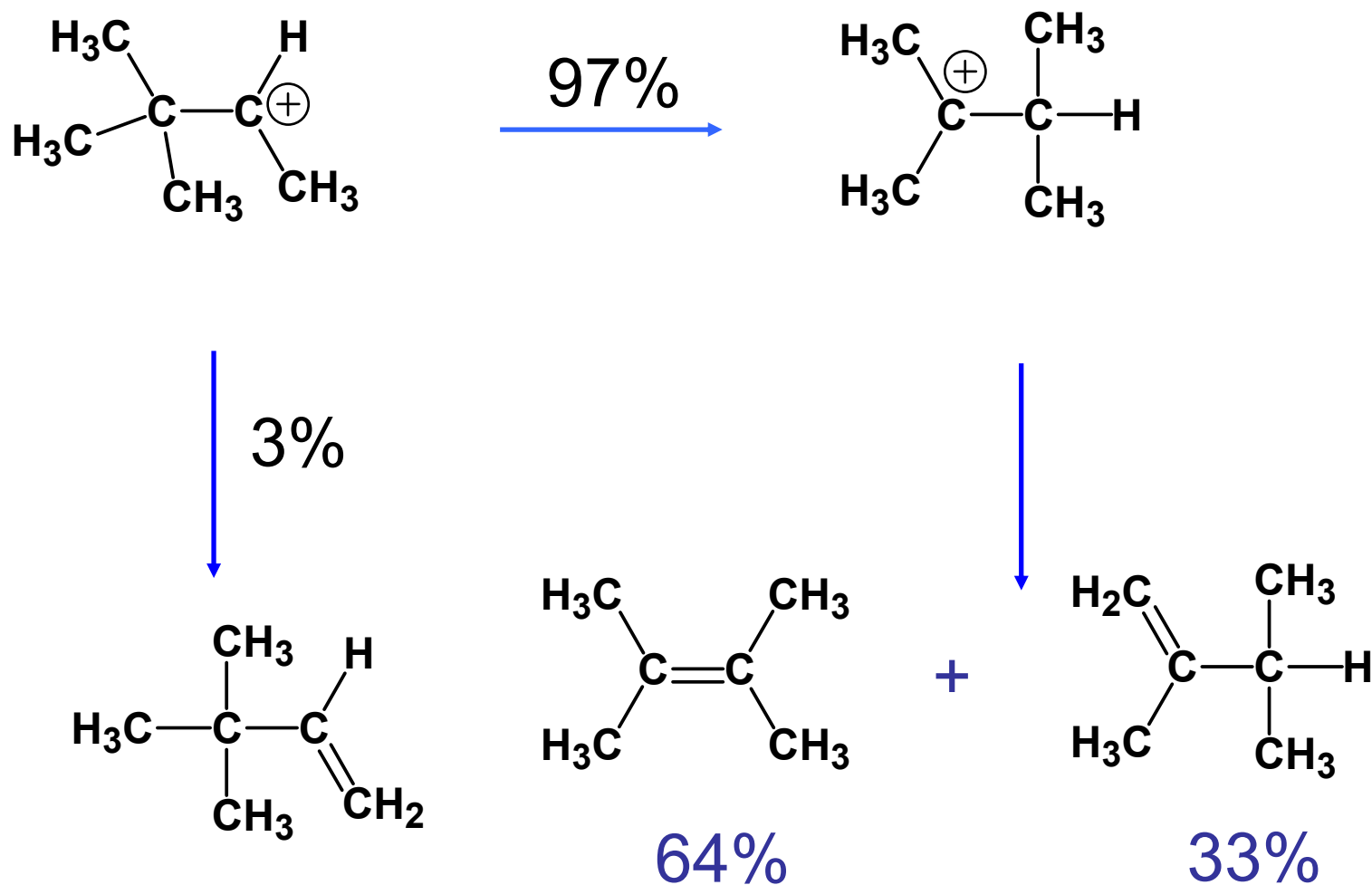
- carbocation can lose a proton as shown
- or it can undergo a methyl migration
- CH<sub>3</sub> group migrates with its pair of electrons to adjacent positively charged carbon

# Rearrangement involves alkyl group migration



- tertiary carbocation; more stable

# Rearrangement involves alkyl group migration



# Carbocations can...

- react with nucleophiles
- lose a proton from the  $\beta$ -carbon to form an alkene
- rearrange (less stable to more stable)

Because *carbocations are intermediates in E1 reactions, rearrangements are possible.*

## *Characteristics of the E1 mechanism*

- First order kinetics:  $\text{rate} = k[\text{RX}]$ 
  - unimolecular rate-determining step
- carbocation intermediate
  - rate follows carbocation stability
  - rearrangements sometimes observed
- Reaction is regiospecific
  - more substituted alkene is still preferred product
  - reaction is not stereospecific

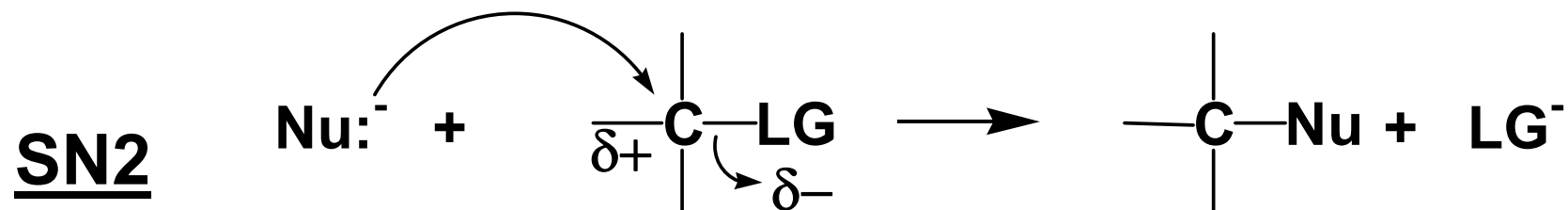
# Competition Between E2 and E1 Reactions

- Primary Alkyl Halides – E2 Only
- Secondary Alkyl Halides – E1 or E2
- Tertiary Alkyl Halides – E1 or E2

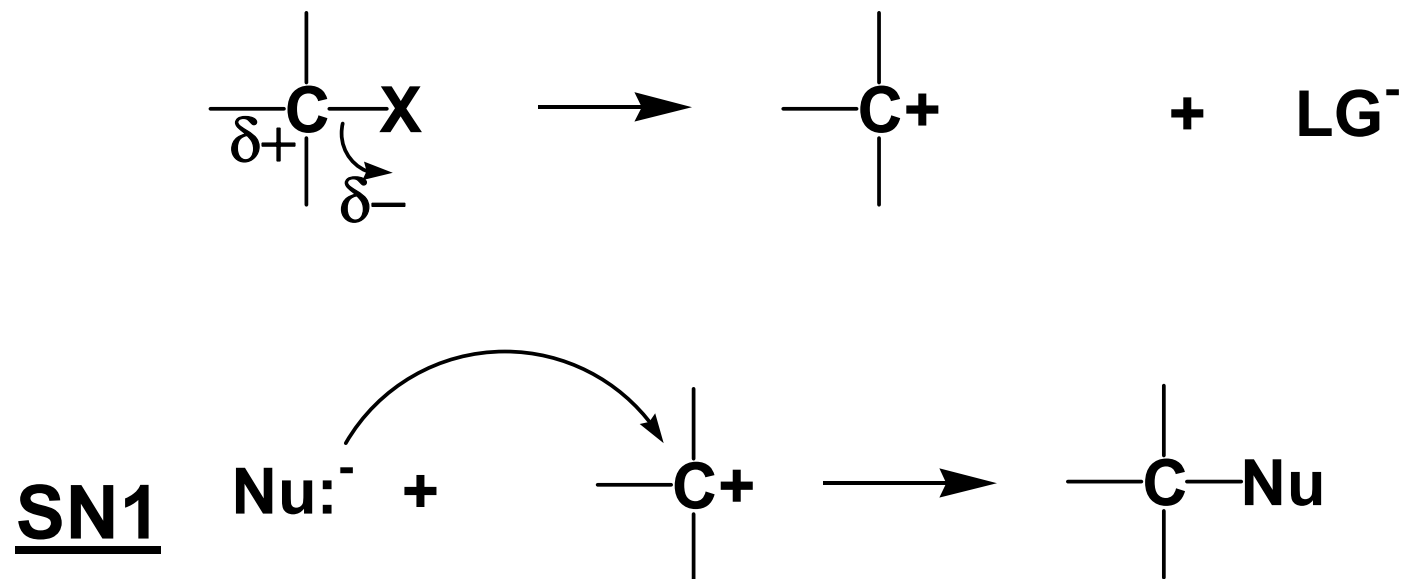


# SN2 vs. SN1

Substitution Nucleophilic *Bimolecular*



Substitution Nucleophilic *Unimolecular*





# Experimental Evidence

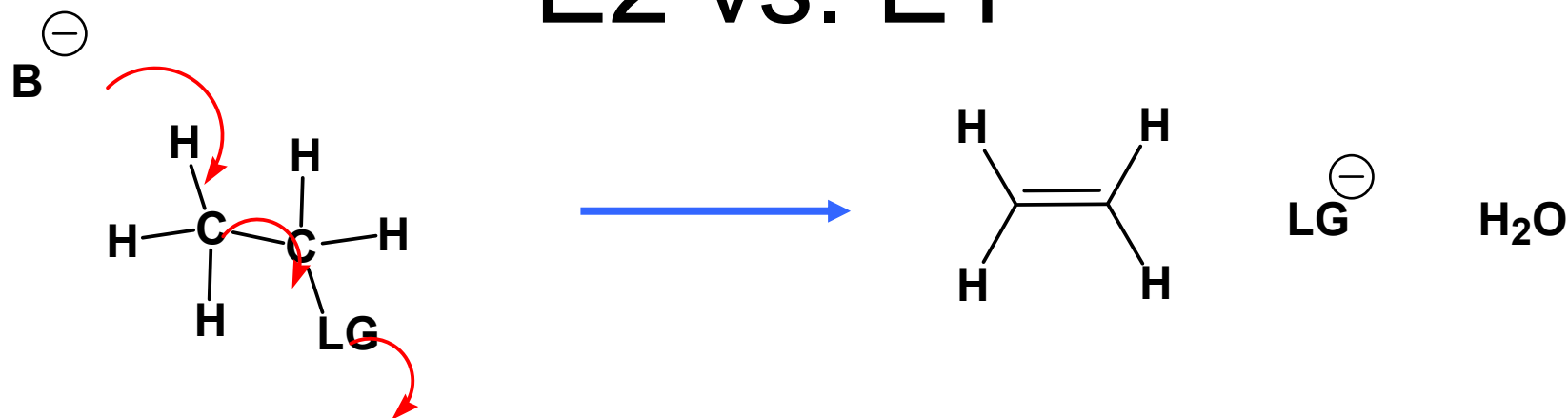
## SN2

1. The rate of the reaction is dependent on the concentration of the alkyl halides and the nucleophile
2. The rate of the reaction with a given nucleophile decreases with increasing size of the alkyl halides
3. The configuration of the substituted product is inverted compared to the starting material

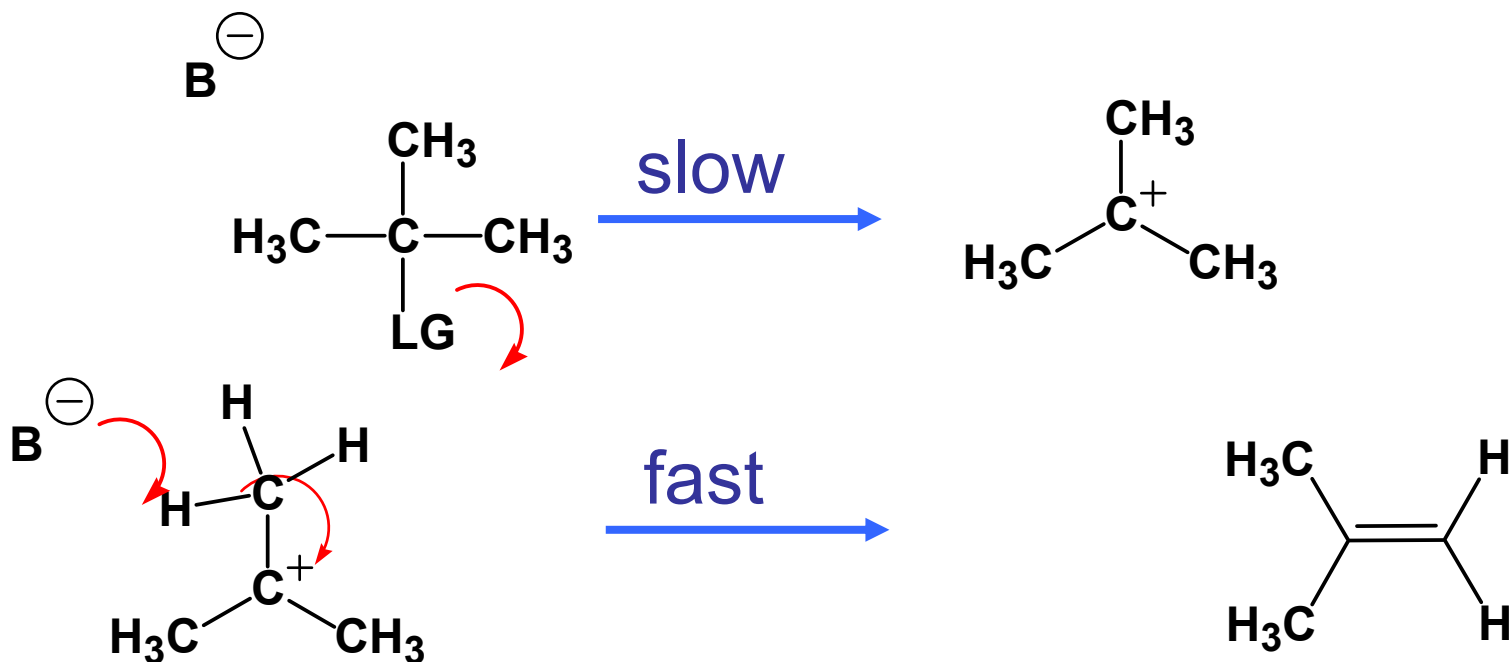
## SN1

1. The rate of the reaction depends only on the concentration of the alkyl halide
2. The rate of the reaction is favored by the bulkiness of the alkyl substituent.
3. In the substitution of a chiral alkyl halide, a racemic mixture of product is obtained

# E2 vs. E1



## E2 - Elimination *Bimolecular*



## E1 - Elimination *Unimolecular*

# Competition Between Substitution and Elimination

Alkyl halides can undergo  $S_N2$ ,  $S_N1$ , E2 and E1

1) decide whether the reaction conditions favor  $S_N2$ /E2 or  $S_N1$ /E1

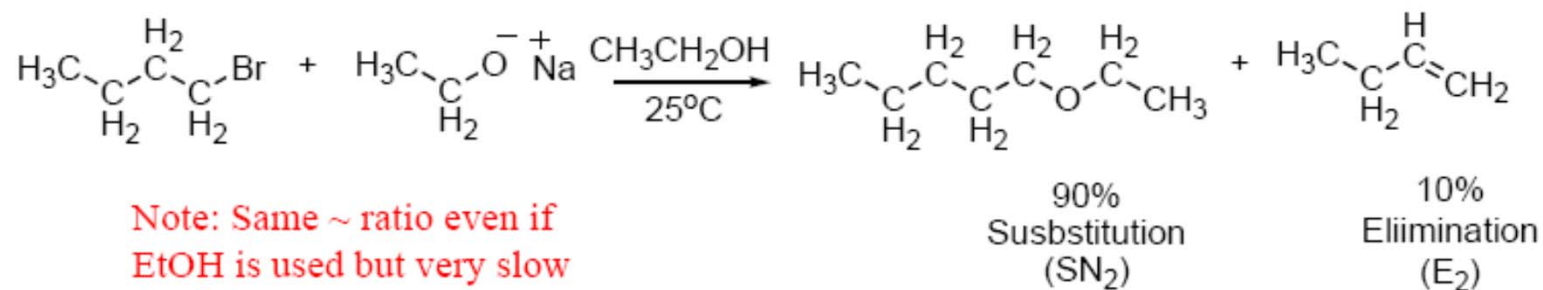
- $S_N2$ /E2 reactions are favored by a high concentration of nucleophile/strong base

- $S_N1$ /E1 reactions are favored by a poor nucleophile/weak base

2) decide how much of the product will be the substitution product and how much of the product will be the elimination product

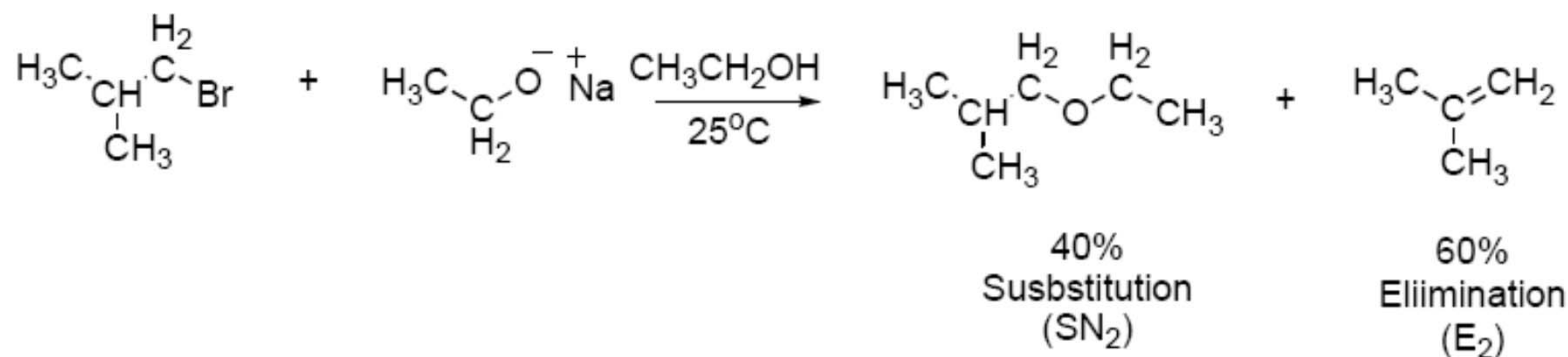
Some experimental data:

1. Primary alkyl halide as starting material (SM); base as “nucleophile”

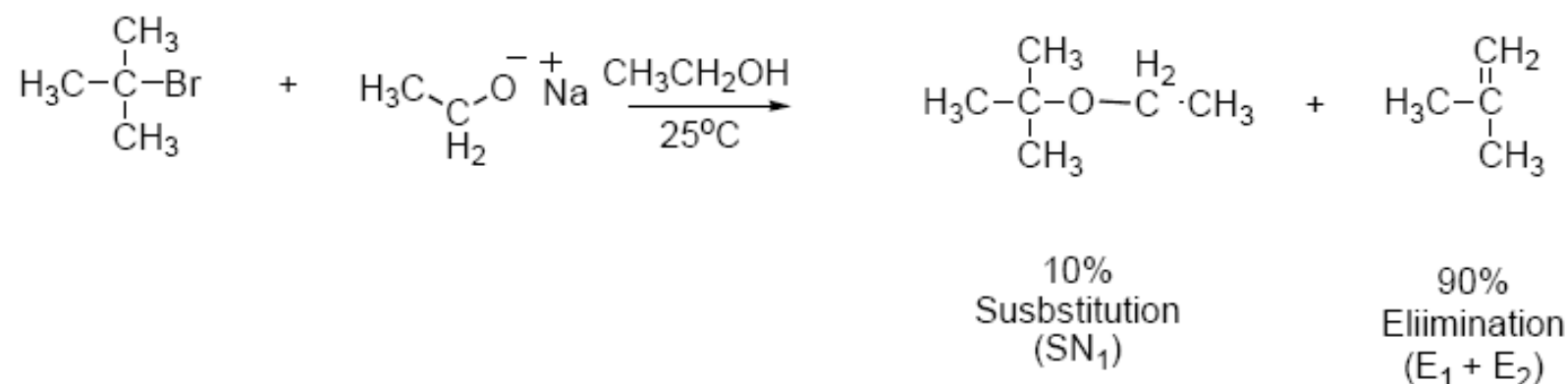


Note: Same ~ ratio even if  
EtOH is used but very slow  
(10<sup>-5</sup> times)

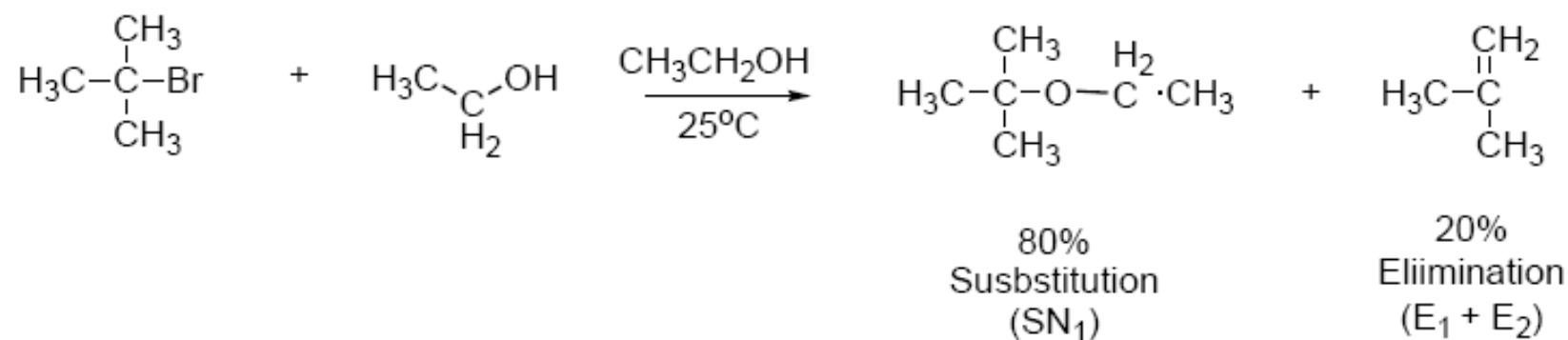
2. Secondary alkyl halide as starting material (SM); base as “nucleophile”



### 3. Tertiary alkyl halide as starting material (SM); base as “nucleophile”



### 4. Tertiary alkyl halide as SM; neutral alcohol as “nucleophile”



# List of Factors/Concepts:

Steric effects: slows  $\text{SN}_2$ , helps  $\text{E}_2$

Basicity: helps  $\text{SN}_2$  but helps  $\text{E}_2$  more

Nucleophilicity: kinetic idea Polarizability: helps  $\text{SN}_2$  (and  $\text{SN}_1$  2nd step)

Leaving Group Charge: Leaving group - leave as neutral if possible

Attacking group - negative if possible

Concentration: high base concentration helps  $\text{E}_2/\text{E}_1$

Solvent: can help  $\text{SN}_2$

Temperature: all reactions increase but  $\text{E}_2 > \text{SN}_2$

Stability of possible carbocation: if good enough  $\text{SN}_1$  and  $\text{E}_1$

Also will want to consider stereochemical consequences

Inversion for  $\text{SN}_2$

loss of chirality for  $\text{SN}_1$

Anti-periplanar for  $\text{E}_2$



# For Next Time....

Suggested Homework Problems Chapter 7

#1,14,21,26, 31, 36,38,41,44,50,52,53,59,64,65

Exam#2 → Wednesday OCTOBER 25th!