

# Chap 6

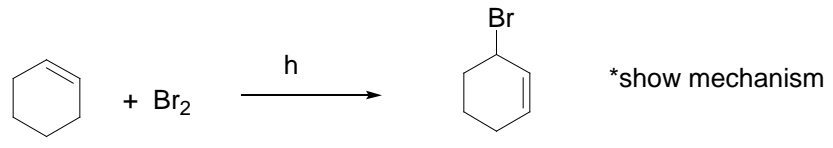
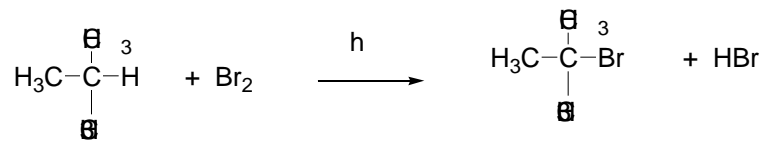
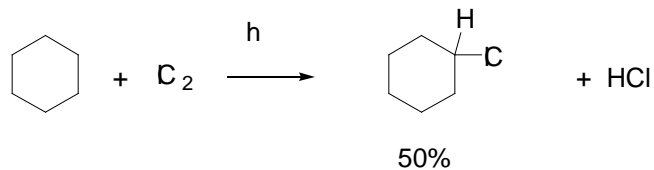
## Alkyl Halides

1. alkyl Halide- halogen bound to a  $sp^3$  carbon atom.

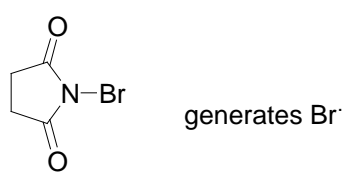
vinyl halide

1. Preparation of Alkyl Halides.

A) Free radical halogenation

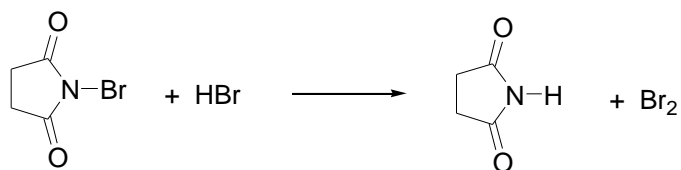


or can use



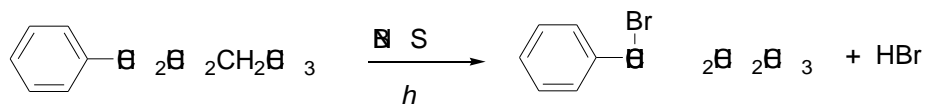
N-bromosuccinimide

NS



helps keep the concentration of  $\text{Br}_2$  low and constant so bromine doesn't add to the double bond.

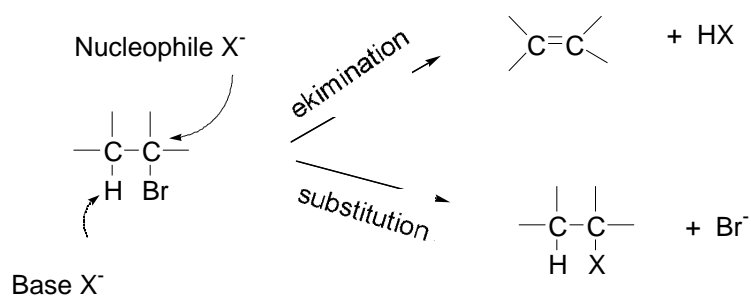
**Ex. 6-1.** Predict the product of the following reaction.



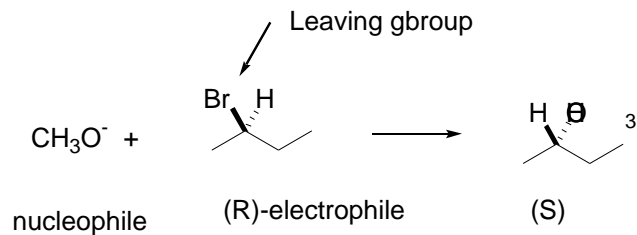
## 2. Substitution and Elimination reactions.

A negative charged species can have two functions.

Base or a nucleophile



Ex.



A. Evidence of Rxn.

1. rate =  $k[\text{OCH}_3^-][2\text{-(R)-bromobutane}]$  2<sup>nd</sup> order reaction, bimolecular.

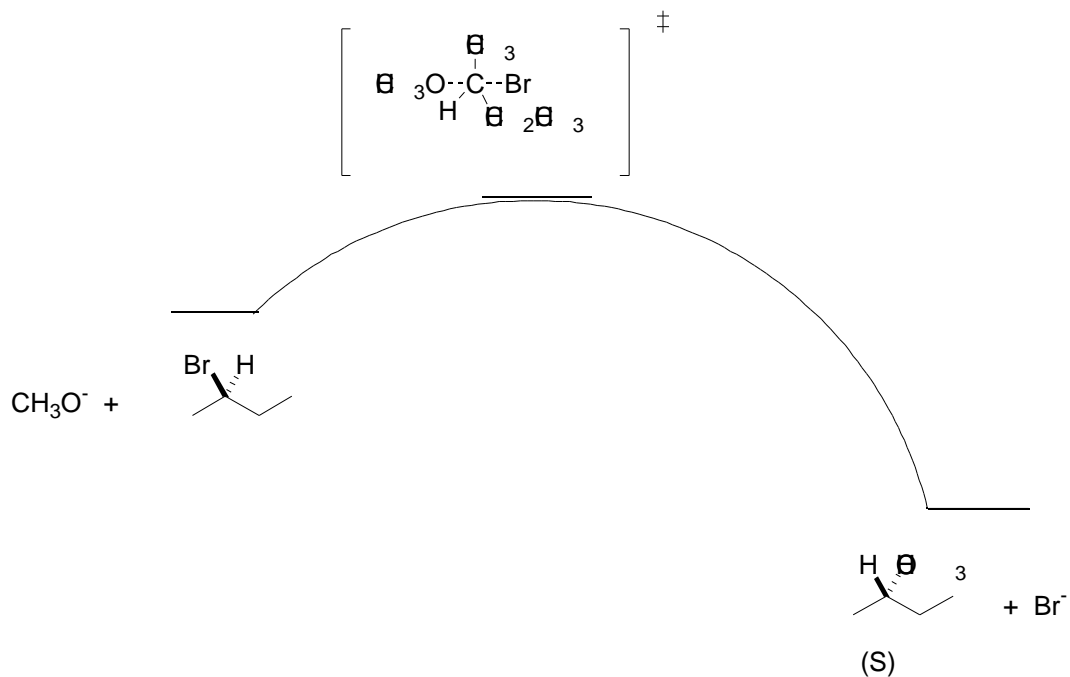
2. Inversion of stereochemistry.

B. Explanation.

1. Needs to have a transition state that involves both species.

(CONCERTED)

2. LV group and Nuc must be on opposite sides.



called  $S_N^2$  rxn- substitution nucleophilic bimolecular

C. Strength of Nucleophiles- ability to donate e', less steric hinderance.

A) Nucleophilicity usually follows strength of basicity.

strong base = strong nucleophile

but not the same property, basicity leads to elimination.

B) Polarizability- ability of e' to move more freely. Leads to stronger bonding in transition state.

C) Examples of Nucleophiles.

1. Negative charges  $OH^- > H_2O$   $-SH > (H_2S)S$

2. Decrease from left to right across periodic table, electronegativity.

$OH^- > F^-$   $NH_3 > H_2O$   $(CH_3CH_2)_3P > (CH_3CH_2)_2S$

3. Polarizability.

$I^- > Br^- > Cl^- > F^-$   $SeH^- > SH^- > OH^-$

$(CH_3CH_2)_3P > (CH_3CH_2)_3N$

D) Solvent effects on Nucleophilicity.

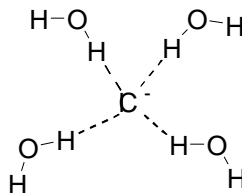
First need a polar solvent in order to solvate the nucleophile.

Aprotic solvents- no H on N, O, F.

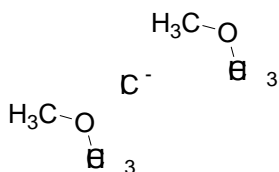
Protic- H on N, O, F.

Must break the bonds from solvent to nucleophile.

Protic solvent

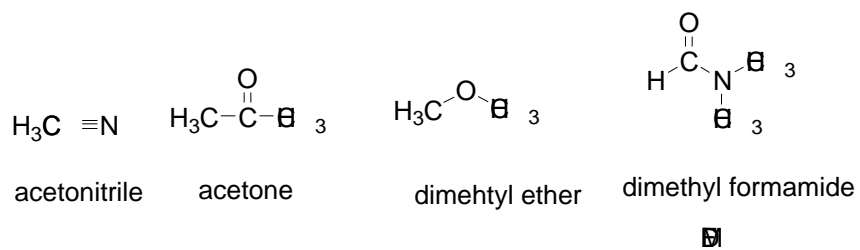


Polar aprotic solvents-



Easier to attack but harder to solvate strong nucleophiles.

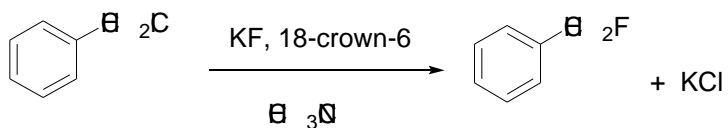
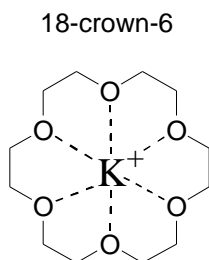
Examples of Polar aprotic solvents



E) Phase transfer catalysts.

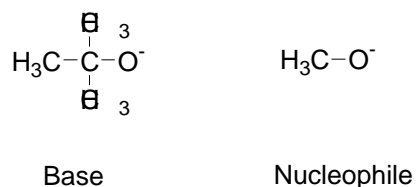
Two phases, nucleophile in aq. and substrate in organic.

Phase transfer catalyst takes nucleophile into organic layer.



#### F) Steric Effects of Nucleophile

Bulky nucleophiles act as a base.



Base about the same strength. H is small so bulkiness does not effect it.

#### G) Leaving group.

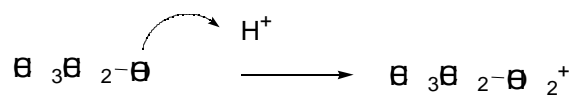
should be,

1. e' withdrawing, make C more positive.
2. resulting species stable.
3. polarizable, for transition state.

e' withdrawing, high electronegativity

good leaving group is a weak base. can be stabilized by resonance.

leave as neutral



F) Substrate effects- steric effects

Rate of Sn2  $CH_3X > 1 > 2 > 3$

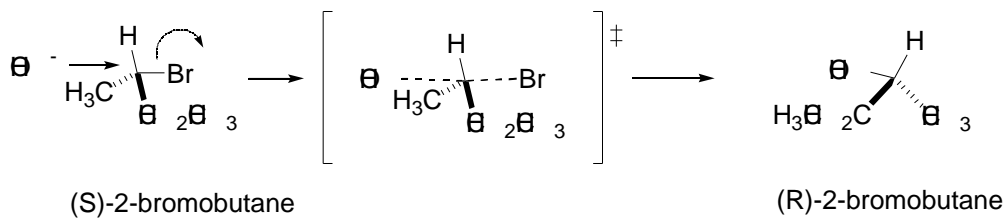
less sterically hindered the easier the attack.

$CH_3CH_2Br + ^-OCH_3$  faster

$(CH_3)_2CHBr + ^-OCH_3$  slower

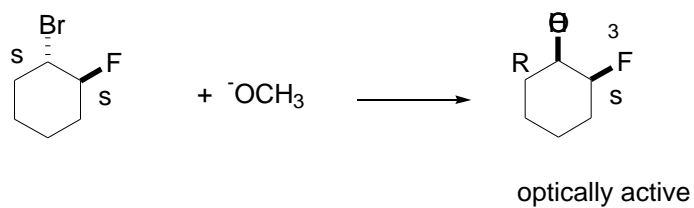
H) Stereochemistry of Sn2

Backside attack- opposite of leaving group.

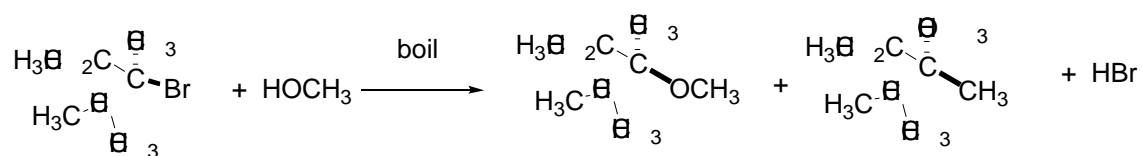


inversion of configuration

Ex. 6-3. Predict the product.



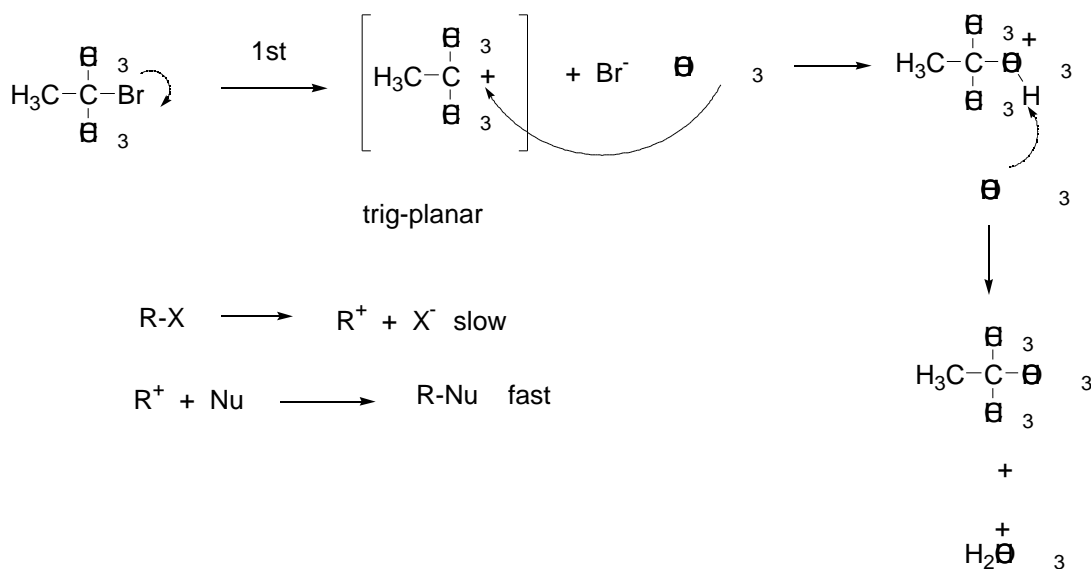
3. Sn1 Rxn.



Evidence of Rxn.

1. rate =  $k[\text{substrate}]$
2. racemic mixture in products.

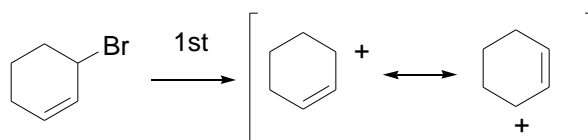
$\text{S}_{\text{N}}1$  = substitution, nucleophilic, unimolecular



A) substrate-

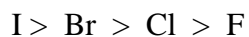
$\text{S}_{\text{N}}1$  reactivity -  $3 > 2 > 1 > \text{CH}_3\text{X}$  same as carbocation stability,  
opposite  $\text{S}_{\text{N}}2$

allyl position same rate as 3

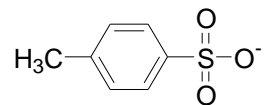


B) Leaving group-

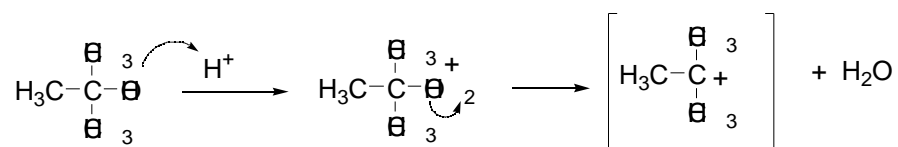
1. Highly polarizable



2. Stabilize negative charge, resonance, induction.



TsOH tosylate = a common leaving group.



C) Solvent effects-



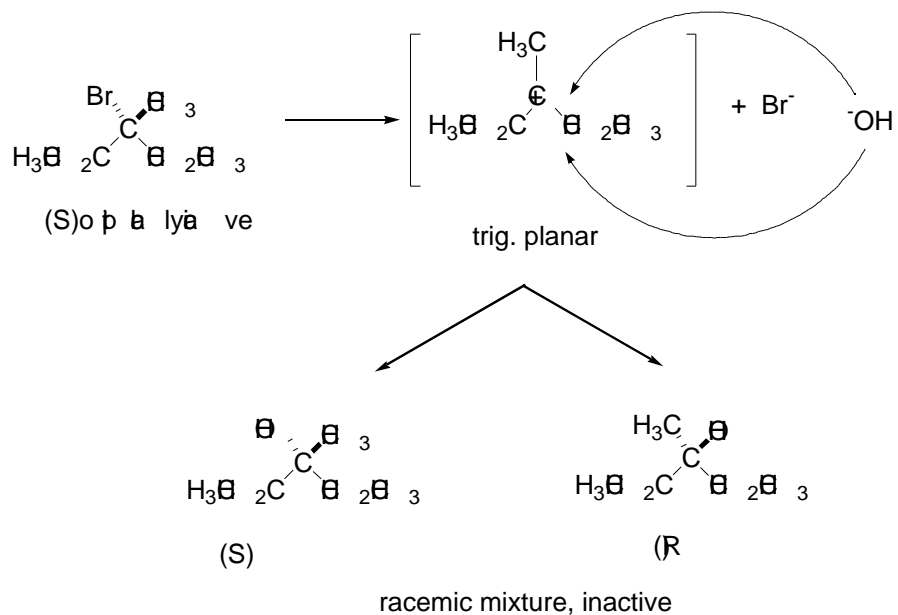
Polar solvent will help stabilize polar carbocation intermediate.

More polar the better.

dielectric constant,  $\epsilon$ , the higher the number the greater the polarity of the solvent.

		Relative rate
water	78	8000
ethanol	24	200
hexane	2.0	< 0.0001

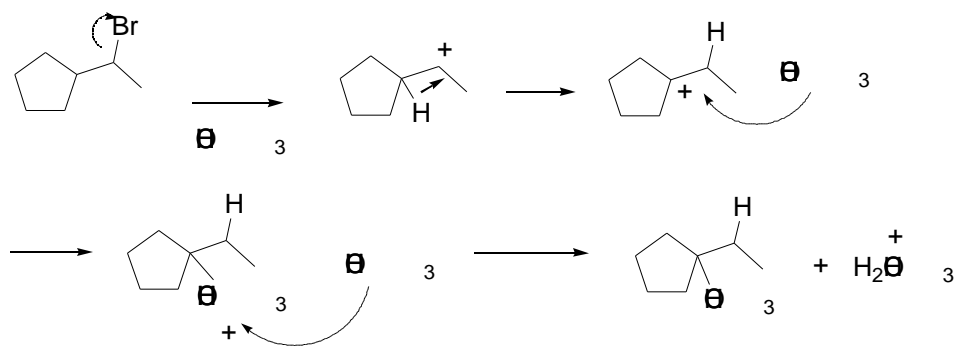
D) Stereochemistry of Sn1



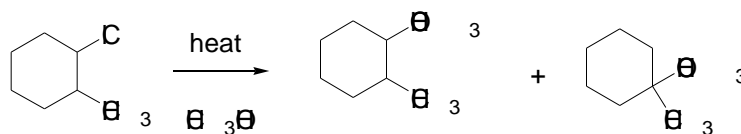
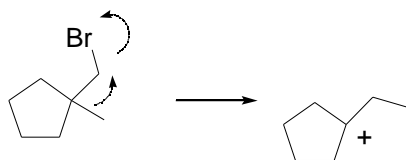
Not exactly racemic leaving group blocks one side to a small degree.

### E) Rearrangement of $S_N1$ rxns.

#### 1) Hydride shift: $H^-$



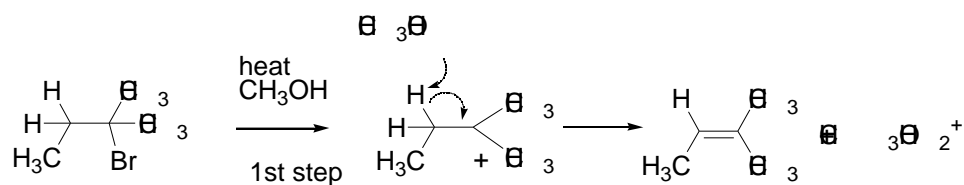
#### 2) Methyl shift: $CH_3^-$



1. Elimination Rxns: Remove a H and a leaving group.

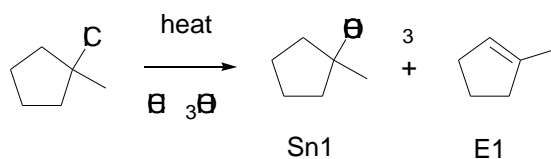
A) E1

$X^-$  can act as a base (elimination) or a nucleophile ( $S_N1$ ,  $S_N2$ )

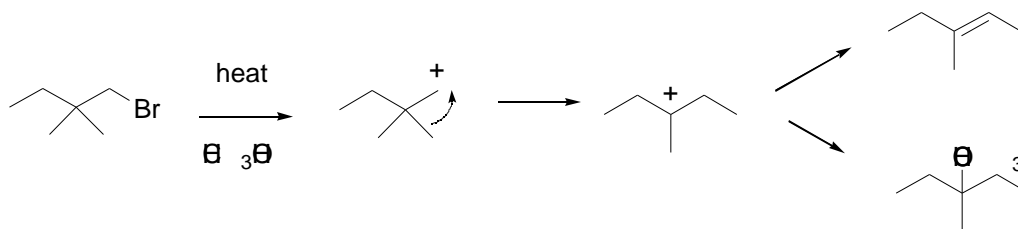


rate =  $k[\text{substrate}]$

competes with  $S_N1$ , weak base favors E1 compared to E2.

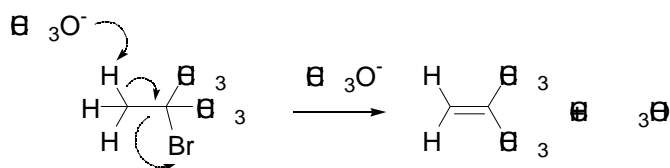


Rearrangement-



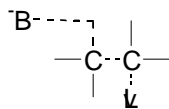
B) E2, bimolecular rxn. Prefers strong base.

1)



no Sn2, 3 on carbon with LV group

rate = k[substrate][base] bimolecular

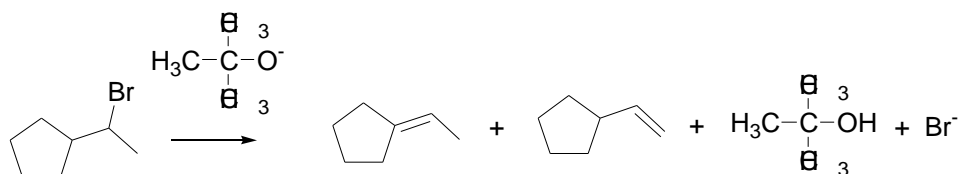


Transition state

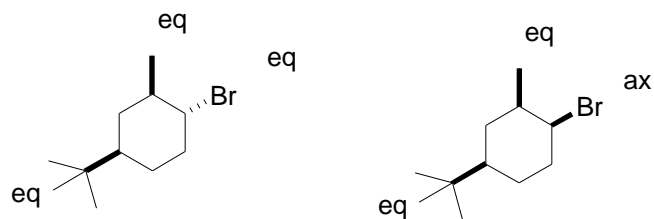
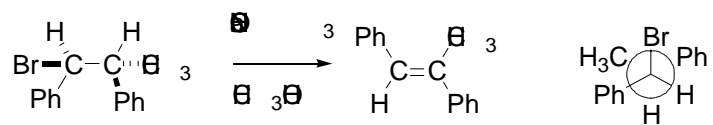
E2 favors strong bases that are sterically hindered.

(CH3)3C-O^- not CH3OH

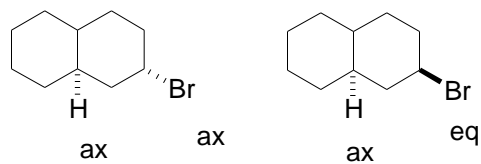
2) Sometimes can get more than one product.







H and Lv group need to be trans-diaxial



Summarize rxns with overhead and handout.