#### The Electrophile

- Recall that electrophile means "electron- loving."
- When considering substitution and elimination reactions we must consider the carbon attached to the leaving group. Is it a primary, secondary, or tertiary carbon?

Electrophile Type	Favors	Disfavors
Methyl	S <sub>N</sub> 2	S <sub>N</sub> 1, E1, E2
Primary	S <sub>N</sub> 2, E2	S <sub>N</sub> 1, E1
Secondary	S <sub>N</sub> 1, S <sub>N</sub> 2, E1, E2	
Resonance Stabilized Primary	S <sub>N</sub> 1, S <sub>N</sub> 2	E1, E2
Tertiary	S <sub>N</sub> 1, E2, E1	S <sub>N</sub> 2



# The Electrophile: $S_N^1$ and E1 Reactions, Carbocation Stability

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- The first step in a  $S_N 1$  and E1 reaction is to form a carbocation. If the carbocation is too unstable, then regardless of how good the leaving group is the carbocation will not form.
- To determine the stability of a carbocation we must consider inductive and resonance effects



#### Examining the Leaving Group and Electrophile



#### The Leaving Group and the Electrophile: Examples

The leaving group here would be OH<sup>-</sup>, a **bad** leaving group No reaction is likely to take place here without further modifying the the substrate.

The leaving group here would be Cl<sup>-</sup>, a **good** leaving group The electrophile is a secondary electrophile, SN1, SN2, E1, and E2 are all possible



Haloalkane produced by red algea

The leaving group here would be Br<sup>-</sup>, a **good** leaving group. However, it is attached to an Sp2 carbon, no substitution or elimination reaction will occur here.

#### **Practice Question**

Which substrate will undergo the fastest  $S_N^2$  reaction?



# The Nucleophile

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- Recall that nucleophile means "nucleus loving" or "positive-charge loving"
- □ Nucleophiles donate a pair of electrons to an electrophile. (Lewis base!)
- When the nucleophile donates a pair of electrons to a proton it is called a Bronsted base or simply a base. The proton is acting like an electrophile.

Nucleophile Type	Favors	Disfavors
Strong Nuc/Strong Base	S <sub>N</sub> 2, E2	S <sub>N</sub> 1, E1
Strong Nuc/ Weak Base	S <sub>N</sub> 2	S <sub>N</sub> 1, E1, E2
Weak Nuc/ Strong Base	E2	S <sub>N</sub> 1, S <sub>N</sub> 2, E1
Weak Nuc/Weak Base	S <sub>N</sub> 1,E1	S <sub>N</sub> 2, E2

#### The Nucleophile: Factors That Affect Nucleophilicity and Basicity

- How do we know if a nucleophile is acting as a nucleophile or a base?
  - Consider the following properties:



#### The Nucleophile: Charge and Electronegativity

#### Charge

- The greater the electron density on the nucleophile the greater its nucleophilicity
- Increased electron density results in an increased desire to donate those electrons; ie: increased nucleophilicity



- Electronegativity
  - Electronegativity relates how "tightly" held a pair of electrons are. The more tightly they are held the less the ability for them to be donated is.

$$H_3C^{\ominus} > H_2N^{\ominus} > H^{\ominus}_2N^{\ominus} > H^{\ominus}_2N^{\ominus} > H^{\ominus}_2N^{\ominus}_2 > H^{\ominus}_2N^{\ominus}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N^{\Box}_2N$$



#### Rank the Following Nucleophiles in Order of Increasing Nucleophilicity (1 being the weakest 5 being the strongest)



# The Nucleophile: Steric Hindrance

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- Nucleophilicity decreases with increasing steric bulk
  - Nucleophiles generally are reacting at electrophilic carbon. The orbitals that participate in the reactions are less accessible than those orbitals on hydrogen.



If your nucleophile is bulky then its electrons may not be able to "reach" the antibonding orbitals at the carbon

### **Practice Question**

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□ t-butoxide has the following structure.



Based on what you know about nucleophilicity what type of reaction or reactions are favored?

A. Both S<sub>N</sub>1, E1
B. Both S<sub>N</sub>2, E2
C. Primarily E1
D. Primarily E2

E1 or  $S_{\rm N}1$  unlikely as this is a charged nucleophile (not A or C)

bulky nucelophiles do not allow for  $S_N^2$  (not B)

# Solvent Effects: The Electrophile

Solvent Type	Favors	Disfavors	Polar protic – has hydrogen bound to
Polar Protic	S <sub>N</sub> 1, E1		Eg. H <sub>2</sub> O Polar aprotic – no hydrogens, but still contains a dipole Eg. CH <sub>2</sub> Cl <sub>2</sub> Non-polar – has no dipoles Eg. hexanes, benzene
Polar Aprotic	S <sub>N</sub> 2, E2	S <sub>N</sub> 1, E1	
Non-Polar		S <sub>N</sub> 1, S <sub>N</sub> 2, E1, E2	

 $S_N 1$  and E1 reactions proceed more quickly in polar protic solvents 

Intermediates are solvated through hydrogen bonding 









Polar protic solvents favour  $S_N 1$  and E1 reactions because the intermediates are solvated

# Solvent effects: The Nucleophile

- Nucleophilicity can be affected by solvent
- Polar protic solvents cause nucleophilicity to increase going down the periodic table



Polar aprotic solvents cause nucleophilicity to decrease going down the periodic table



# Solvent Effects: The Nucleophile



 $\uparrow$  interaction with solvent =  $\checkmark$  nucelophilicity

#### Can you rank the following nucleophiles in order of increasing nucleophilicity? (1 being the weakest 5 being the strongest)

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How would the rate of the reaction change if the solvent was changed from methanol to DMF.



The protic solvent can interact with the nucelophile and keep it from reacting with the alkyl bromide. Therefore, DMF increases the rate of reaction.

#### **Temperature Effects**

When all else is equal increased temperatures will favor elimination reactions over substitution reactions

Temperature	Favors	Disfavors
High	E1, E2	S <sub>N</sub> 1, S <sub>N</sub> 2
Low	S <sub>N</sub> 1, S <sub>N</sub> 2	E1, E2



 $\Delta G < 0$  reaction is spontaneous  $\Delta G > 0$  reaction is non-spontaneous  $\Delta G = 0$  reaction is in equilibrium



Elimination reaction produces more products, this is favoured in the presence of heat as it increases the universe's entropy.

# Mind Map

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### **Practice Question**

- What is the most likely reaction to occur under the following conditions?
- What is the most likely product of the following reaction.

Which product is formed? C or D?

**Recall Zaitsey's Rule!** 

The most stable product is C.



- 1. LG? OH or Br Br is a better LG
- Electrophile? 3°
   S<sub>N</sub>1, E1, E2 possible
- Nucleophile? Strong favours S<sub>N</sub>2, E2
- 4. Solvent? N.A.
- 5. Temperature? Yes eliminations preferred

Therefore, E2 reaction occurs (not A or B)



# Substitution and Elimination Reactions







so SN1 Reaction



What Reaction Is occuring? Which Isomer will undergo the fastest reaction?



# **Additional Practice Questions**

- Textbook Problems Solomons+Fryhle+Snyder (12 edition )
- Leaving Group and Electrophile
  - **Q**. 6.20, 6.22
- Nucleophile and Solvent Effects
  - **Q**.6.21, Q6.29
- Deciding between SN1 and SN2
  - **Q**. 6.28, 6.35, 6.40
- Challenge Problems

**6.41, 6.42, 6.46, 6.47** 

Group Discussion Problems