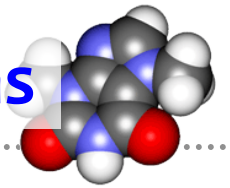
CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

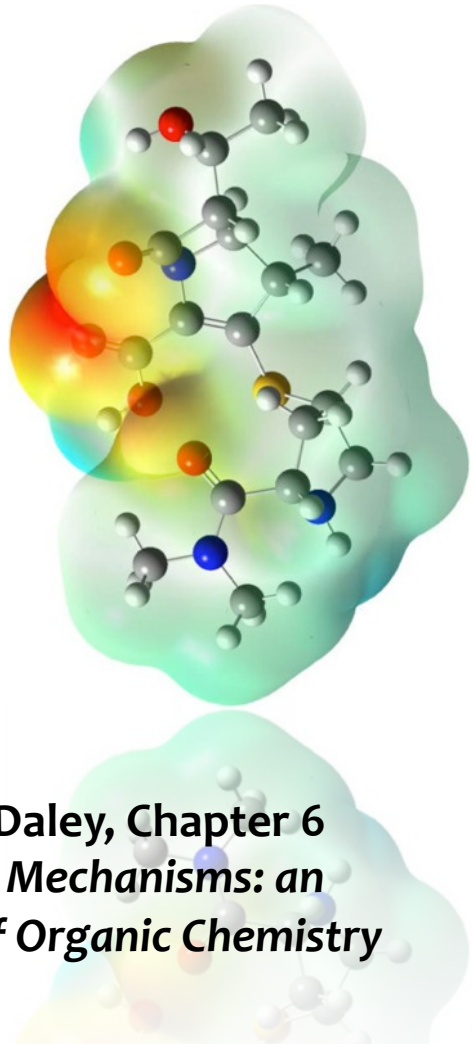
7.4 Substitution reactions

7.5 Addition reactions

7.6 Elimination reactions

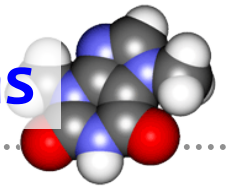
7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions



Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry

CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

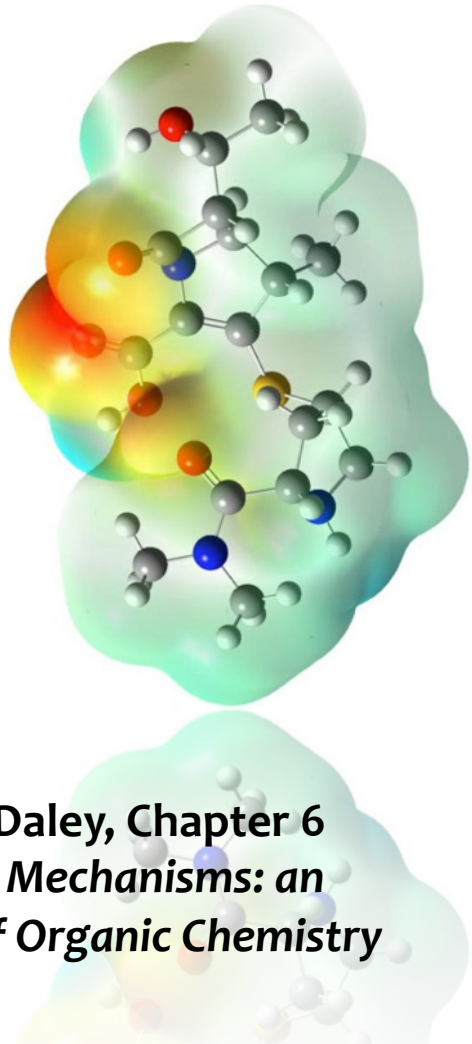
7.4 Substitution reactions

7.5 Addition reactions

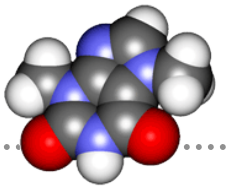
7.6 Elimination reactions

7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions



Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry



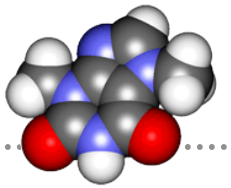
Reaction energies & transition states

Reactions run to the lowest energy state.

Transitions states are temporary unstable 'midpoints'.

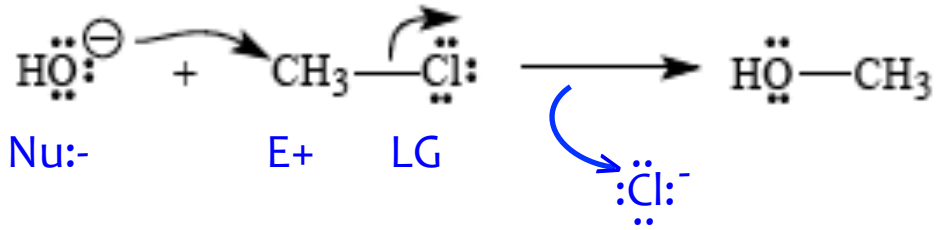
Activation energy pushes reactants to transition states.

Reaction mechanism



Reaction mechanism: *balanced chemical equation that shows the movement of electrons that causes the chemical change and all reactants & byproducts using a formalized structure*

The methyl chloride – hydroxide ion reaction mechanism shown below uses arrows to show movement of electron pairs between reactants:



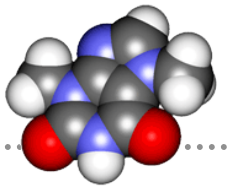
This one-step reaction mechanism is called a type 2 nucleophilic substitution (SN2).

- Nu:- is the hydroxide ion;
- E+ is the dipolar positive carbon of the methyl chloride
- The chloride ion that's released is called a leaving group.

This reaction does have a **transition state** (or "intermediate") that is not shown in this reaction mechanism.

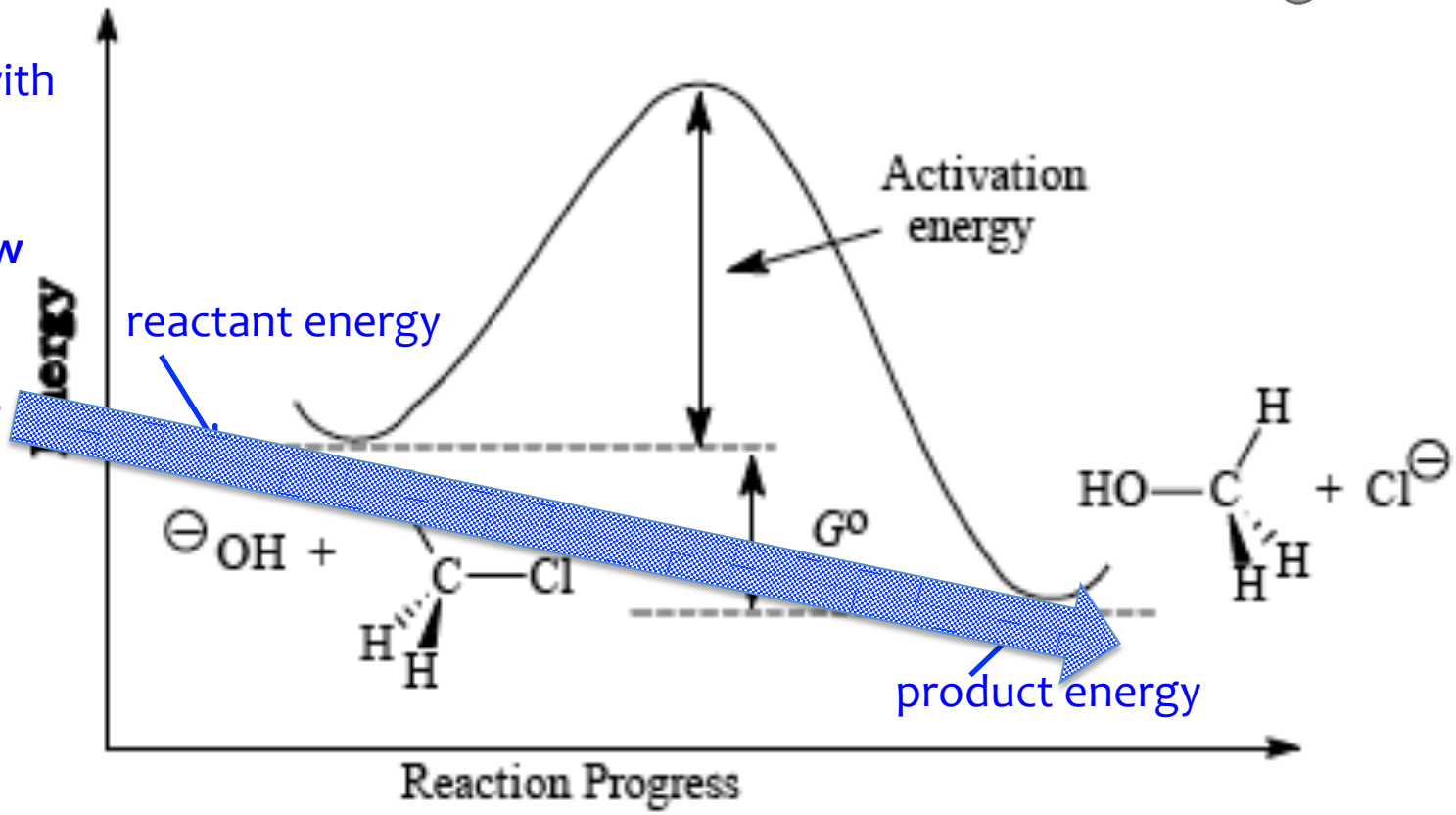
D&D, p.256 - 7

Reaction profiles: energy vs. chemical change



So, what's with the **hill**?

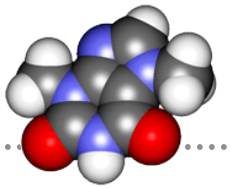
Why not flow directly downhill to products?



The equilibrium of chemical reactions flows towards the **lower energy state.**

- Here the energy of the products is lower than the energy of the reactants.
- Therefore equilibrium favors the products.

Transition states & activation energy

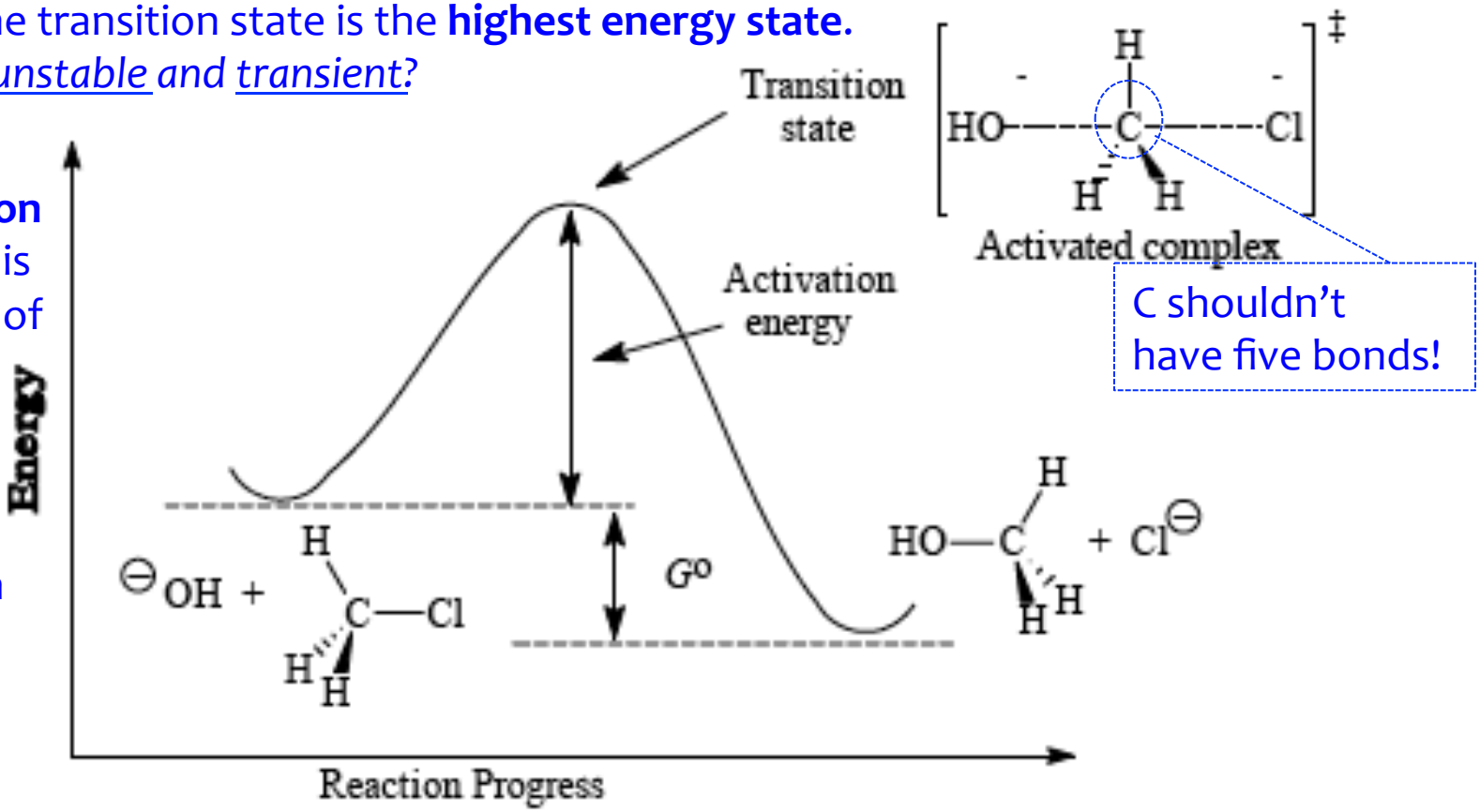


Transition state: *the least stable state formed during the reaction; a structure that the reactant molecule passes through on its way to becoming a product*

Note that the transition state is the **highest energy state**.
Why is it so unstable and transient?

The **activation energy** (Ea) is the amount of energy required to covert reactant to transition state.

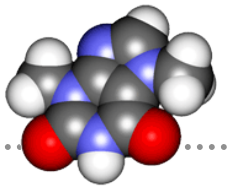
- heat
- light
- movement



C shouldn't have five bonds!

D&D, p.2 54 - 5

Mechanisms can be more complex

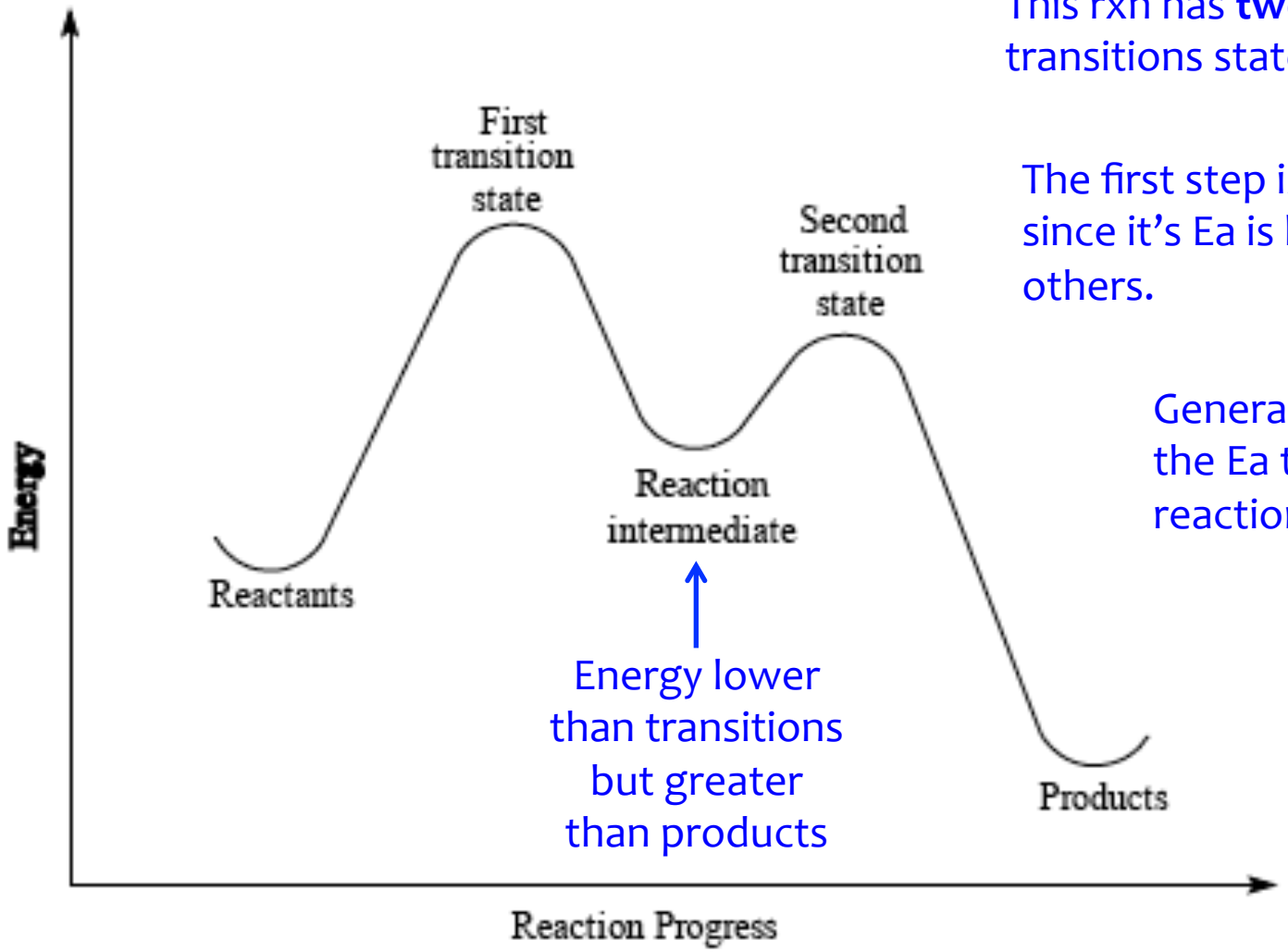


Here you see a **reaction profile** of a reaction that has two transition states, and a **reaction intermediate** between them.

This rxn has **two** steps & two transitions states.

The first step is **rate-limiting**, since it's Ea is higher than all others.

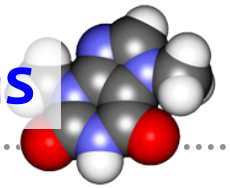
Generally, the higher the Ea the **slower** the reaction.



Energy lower than transitions but greater than products

D&D, p.256 - 7

CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

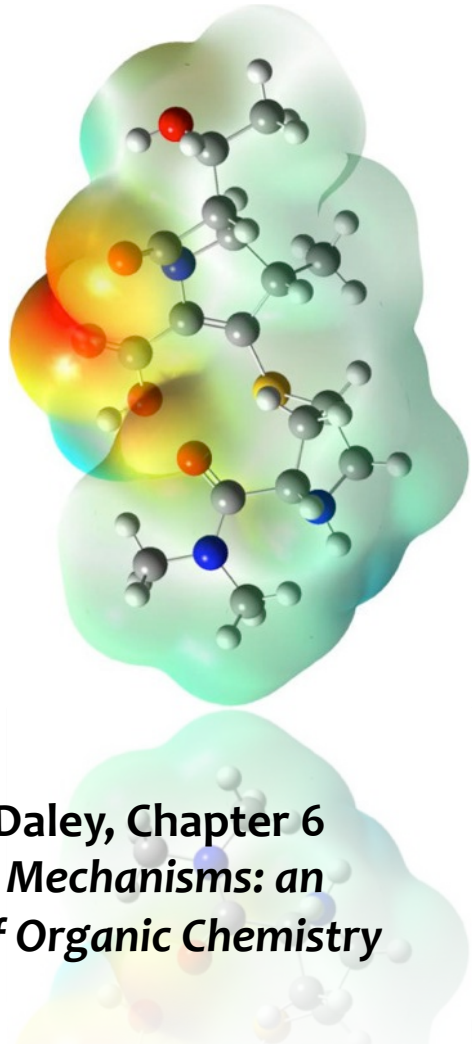
7.4 Substitution reactions

7.5 Addition reactions

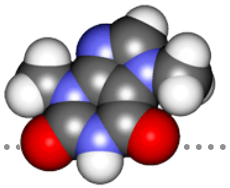
7.6 Elimination reactions

7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions



Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry



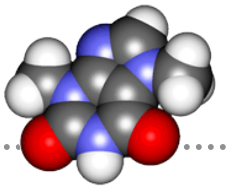
Review of acid-base reaction mechanisms

Nucleophiles & electrophiles

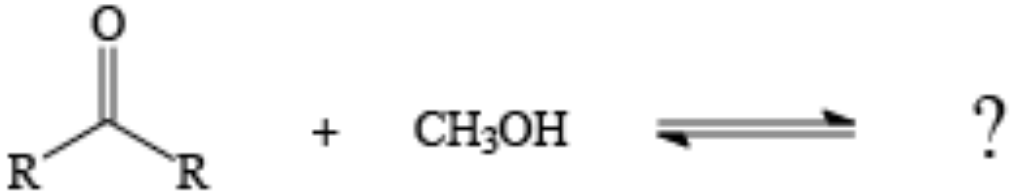
Equilibrium constants

Most likely reactions

Review of acid base reactions



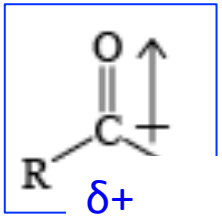
Most of the reactions we will study this semester are **acid-base reactions.** So it's critical that you learn to identify acids and bases in reactions.



Aldehyde or ketone

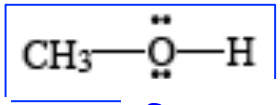
Methanol

Writing complete Lewis dot structures of each reactant helps to determine who's the Nu: & who's the E+.



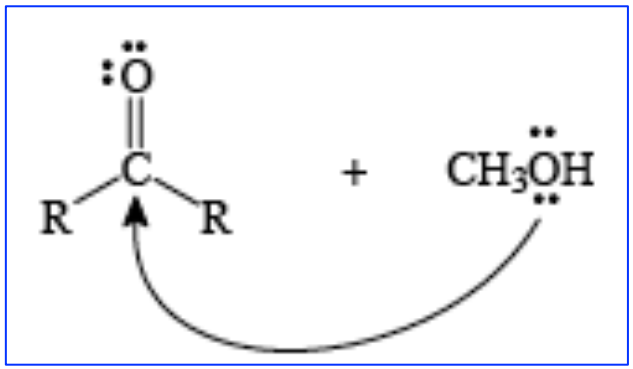
δ+

E+/Lewis acid



δ-

Nu:/Lewis base

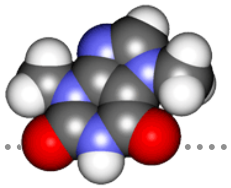


So what happens next?

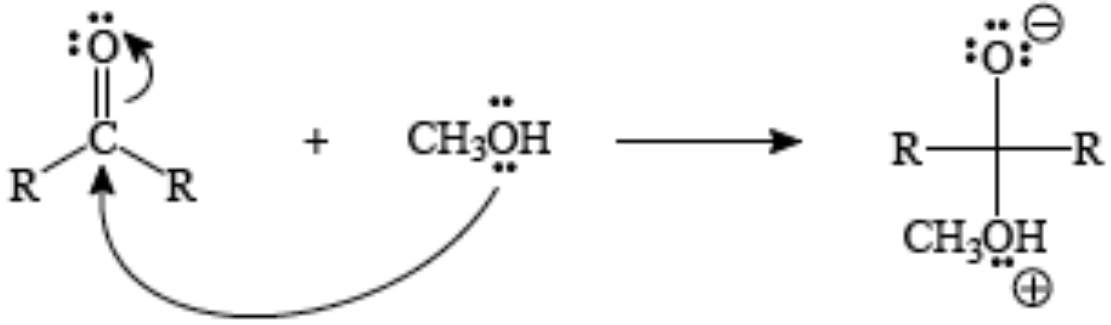
What products form?

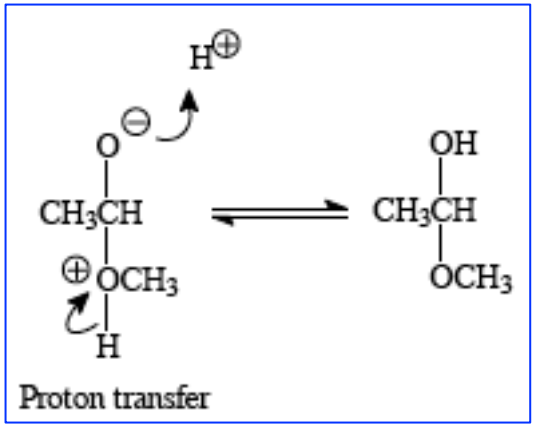
D&D, p.258 - 9

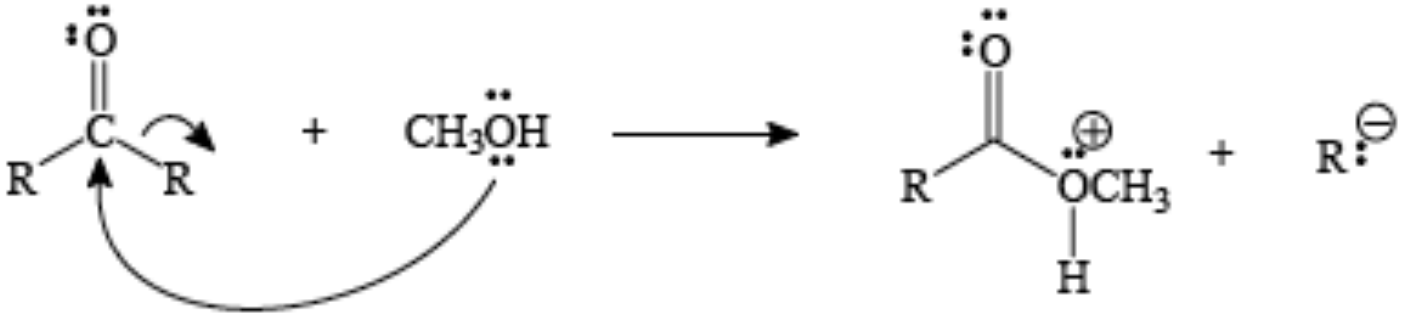
Which products are formed?



Here we see two possible sets of products. Which is correct?
How do you evaluate & make a decision?



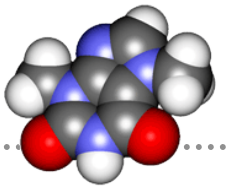




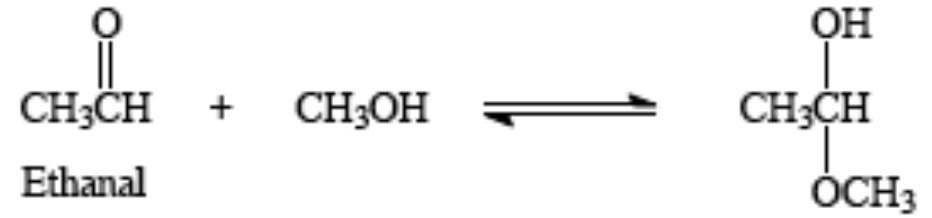
- Both products have a positive charge on an oxygen atom.
- The negative charge's location differs. Generally (-) belongs on the more en atom.
  - So, the first set of products are much more likely.
- A last proton transfer step produces the final product, hemiacetal (on way to sugar).

D&D, p.258 - 9

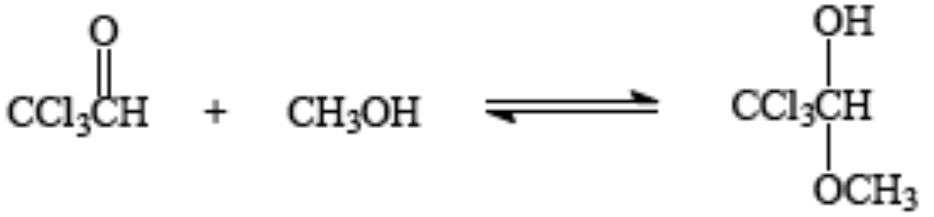
How good will the yield be?



Here we see two possible sets of products. Which is correct?
How do you evaluate & make a decision?



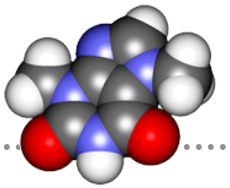
The *K* (equilibrium constant) value shows that the ketone with the Cl favors products more.



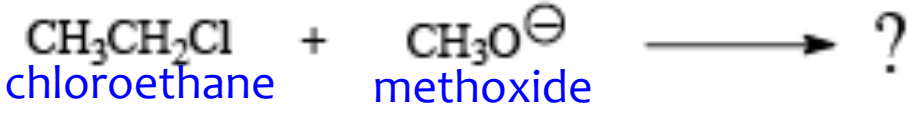
Why?

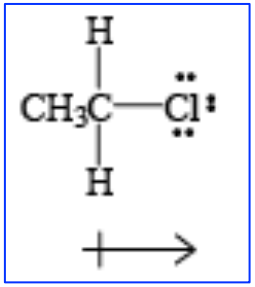
- The Cls have a higher en than H & C and pulls e-.
- So the central carbonyl C is more dipolar + in the second reaction than the first.
- So the second reaction is more likely to favor products.

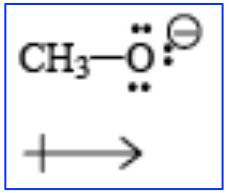
Another example



Who's the Nu: and E+ here? What are the product(s)?



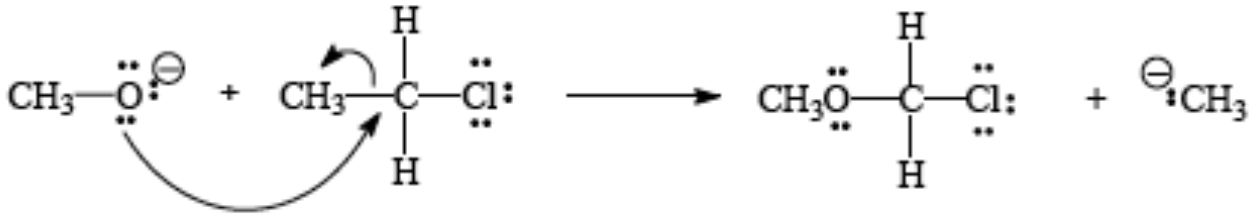


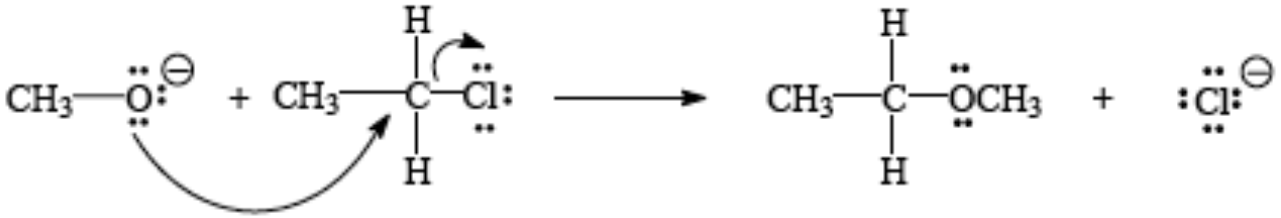


Neg O = Nu:-

Central C = E+

Which of these 3 reactions is most likely? And why?



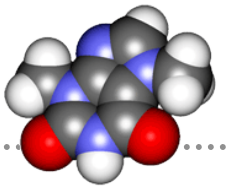


3rd reaction occurs:

- C can't have 5 bonds
- The most en atom takes the : & is the leaving group.

D&D, p.258 - 9

What's a leaving group?



Leaving group: *an atom (or group) that leaves a molecule & takes the electron pair bonding it to the molecule with it*

- LGs may or may not be negatively charged;
- Weak bases make the best LGs since the LG must takes its : with it
  - Strong bases want to donate their :

So, **good LGs** have:

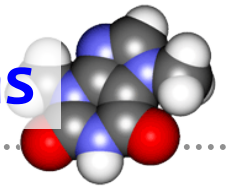
- High EN values (motivation to take :)
- Large atomic radii (space for :)
- Resonance (stabilizes negative charge)

Rank these LGs:

worst $-:CH_3$ $-:NH_2$ $-:\ddot{O}H$ $-:\ddot{F}:$ best

best I Br Cl F worst

CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

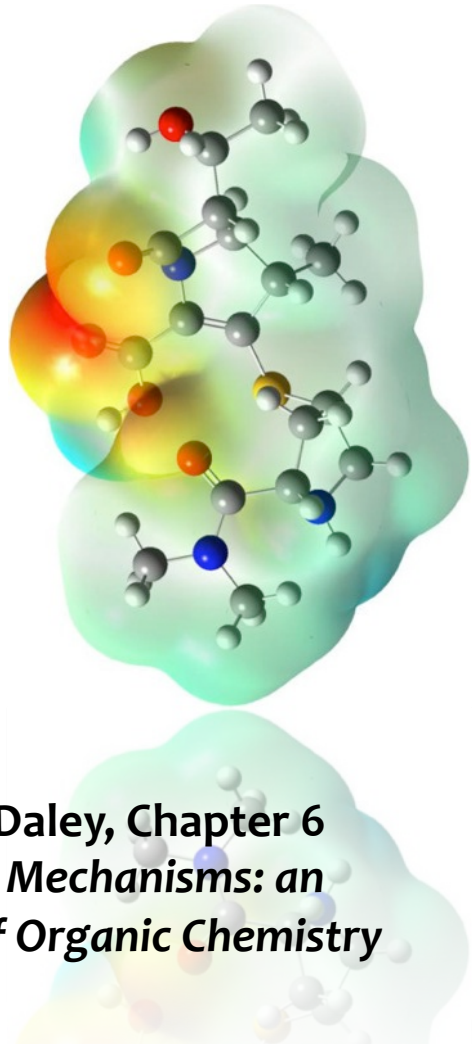
7.4 Substitution reactions

7.5 Addition reactions

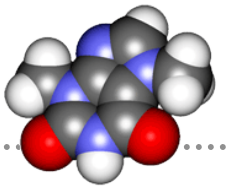
7.6 Elimination reactions

7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions

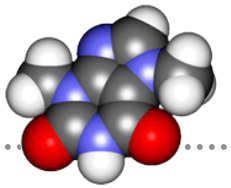


Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry



Writing reactions as transformations

Writing organic reactions as 'transformations'

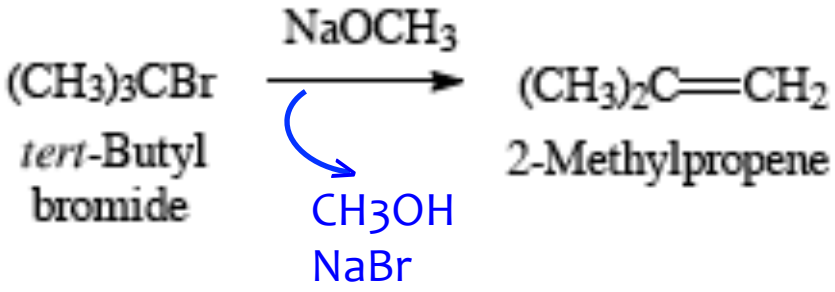


When not concerned about reaction mechanism, organic chemists write chemical reactions in a form of shorthand sometimes referred to as a **transformation.**

$(CH_3)_3CBr$ + $NaOCH_3$ ⟶ $(CH_3)_2C{=}CH_2$ + CH_3OH + $NaBr$

tert-Butyl bromide — Sodium methoxide — 2-Methylpropene — Methanol — Sodium bromide

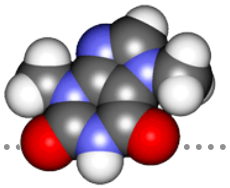
reagents — Intended product — by-products



Transformation shows the reagent (or reactant) that the chemist is trying to transform, the product goal, and the chemical that must be added to make the change happen.

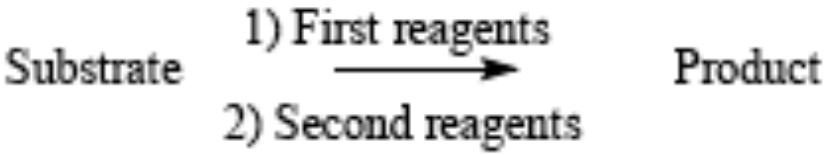
D&D, p.263 - 5

Including reaction conditions

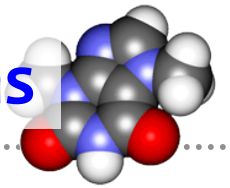


Some reactions require specific conditions like:

- *+/- air*
- *+/- light (shown as hv)*
- *Added temperature (shown as Δ)*
- *A series of reactants*
- *A catalyst (shown in transformations, not BCE)*



CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

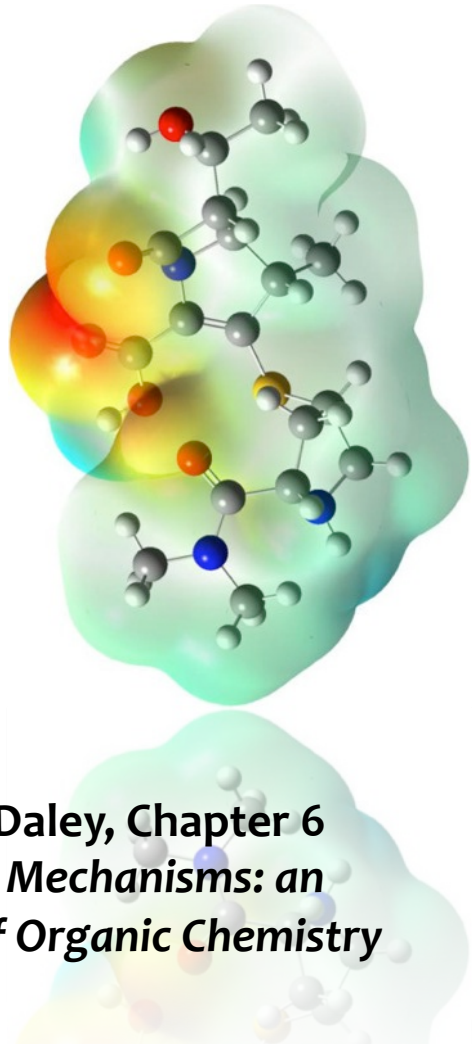
7.4 Substitution reactions

7.5 Addition reactions

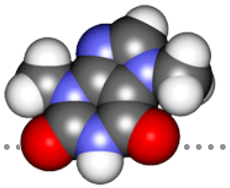
7.6 Elimination reactions

7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions

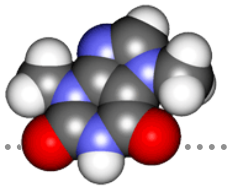


Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry



Substitution reactions

Substitution reactions



Substitution: *a reaction in which an atom (or group) from a reactant takes the place of an atom (or group) on the substrate*

- A new group is substituted for an existing one

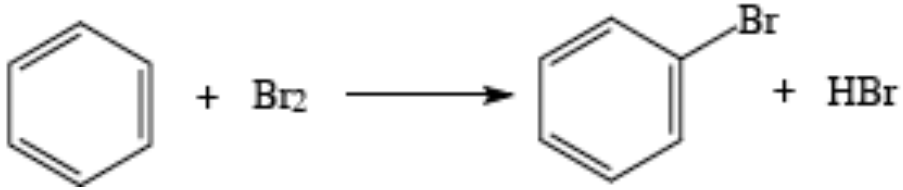
(1) $CH_3CCl + CH_3OH \longrightarrow CH_3COCH_3 + HCl$

(2) $CH_3Br + {}^{\ominus}OH \longrightarrow CH_3OH + Br^{\ominus}$

(3) $(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$

nucleophilic substitution

Nu: is reagent
E+ is substrate

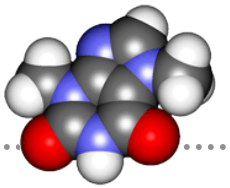
(4)  + Br_2 → + HBr

electrophilic substitution

Substrate (Nu:) provides the : to make the new bond

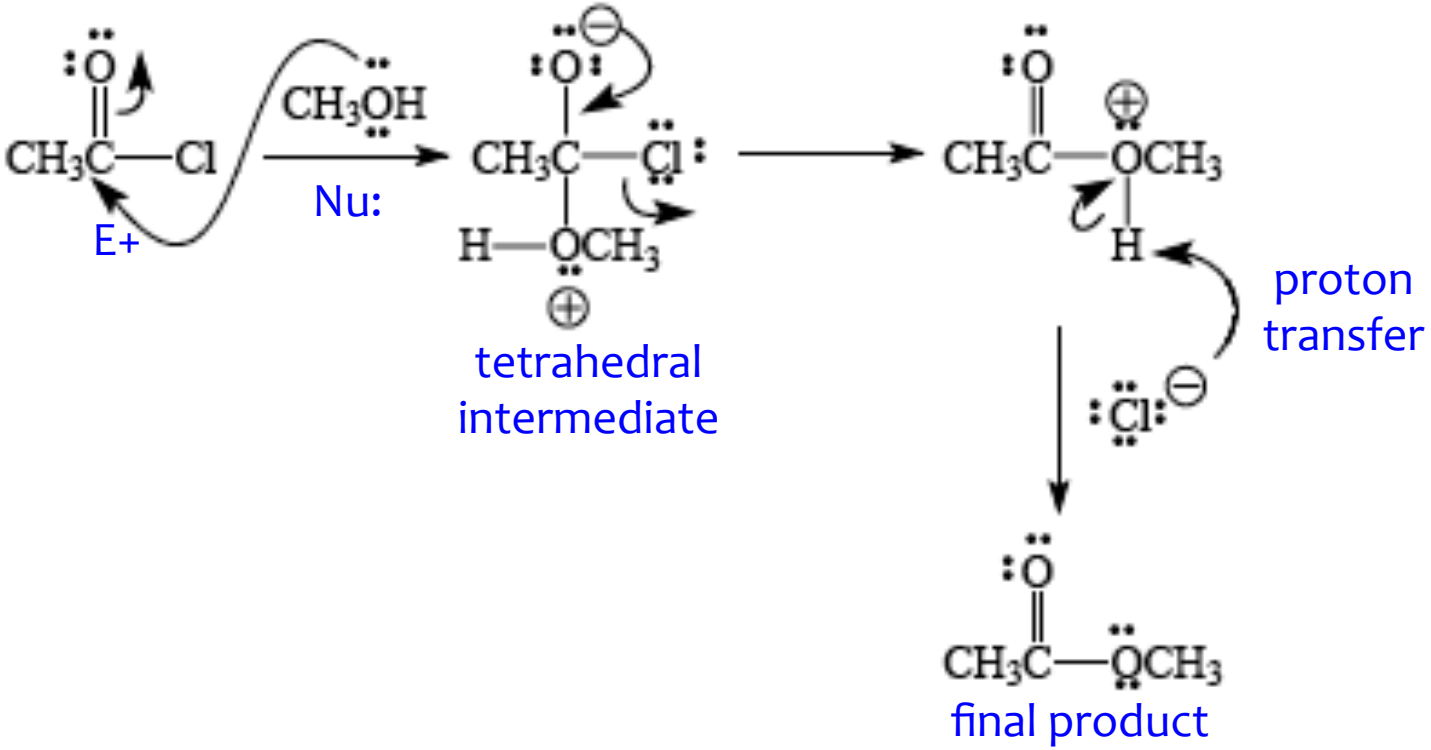
D&D, p.276 - 7

Nucleophilic substitution mechanism (SN1)



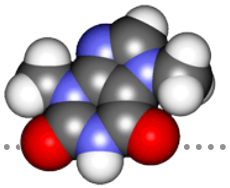
SN1 – two step reaction with intermediate

- Secondary or tertiary E+
- Weak Nu:



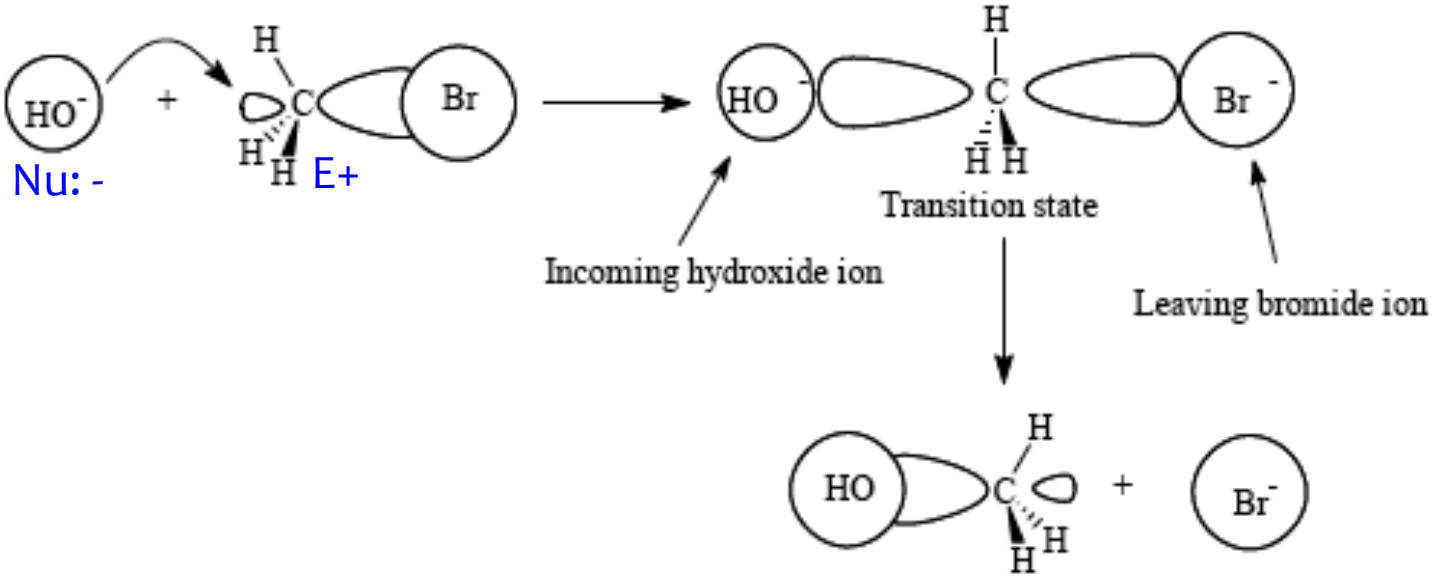
D&D, p.276 - 7

Nucleophilic substitution mechanism (SN2)



SN2 – aka <u>concerted mechanism</u>

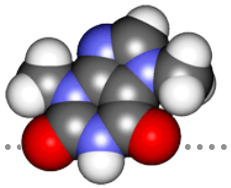
- No intermediates
- Strong Nu:
- Primary E+
- Causes stereochemical inversion of the product



final product

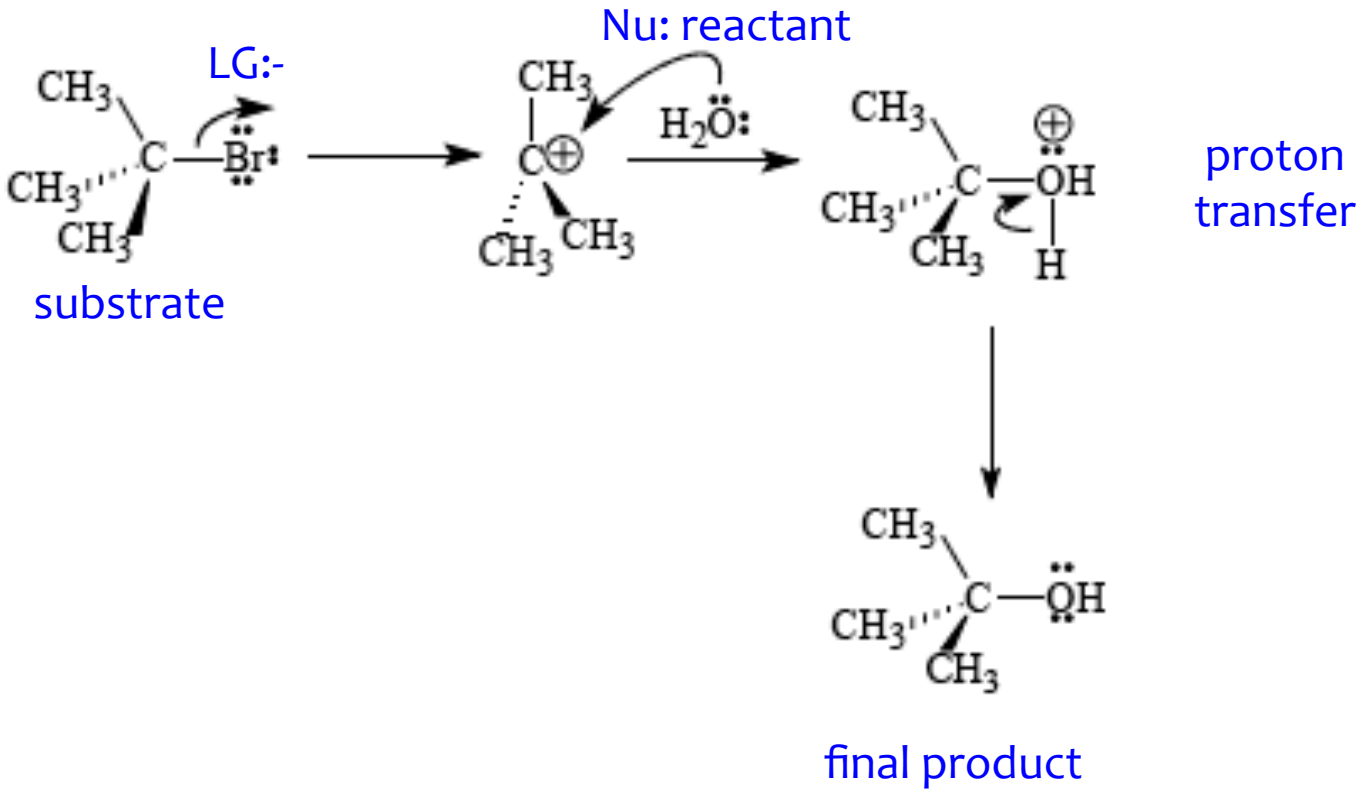
D&D, p.276 - 7

Nucleophilic substitution example

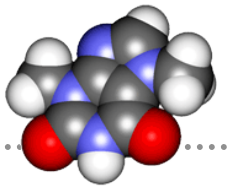


Which type of nucleophilic substitution is this? SN1

- *Label each component & process.*

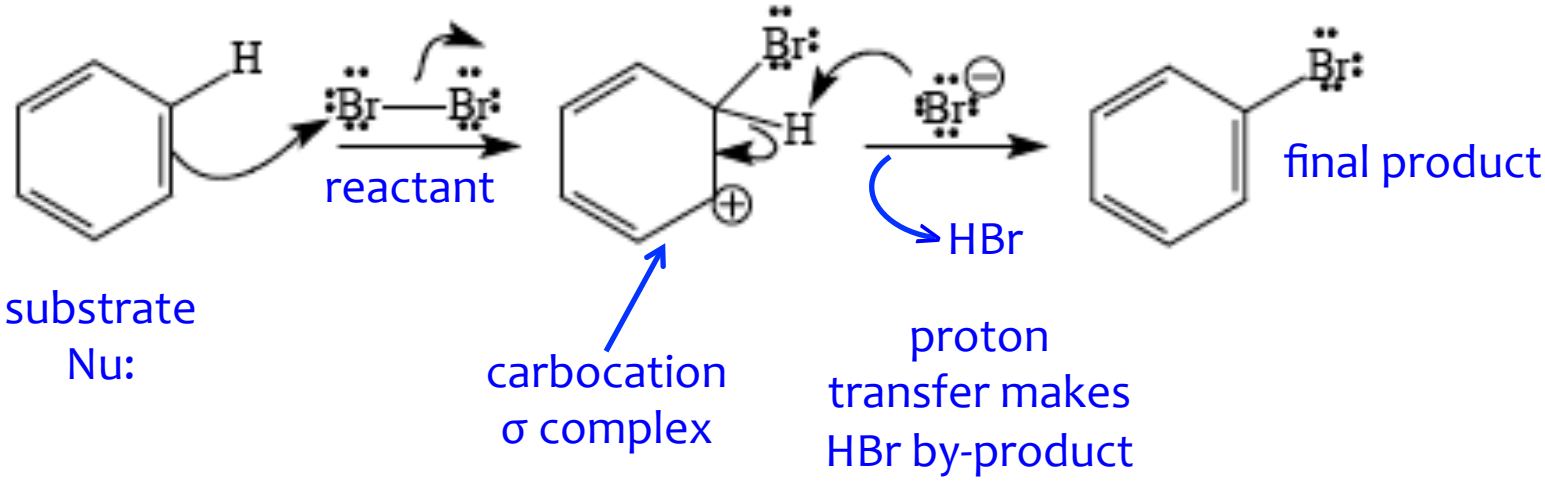


Electrophilic substitution

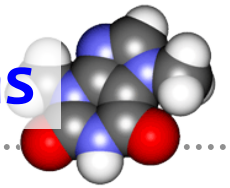


Electrophilic substitution: the substrate is the actor

- Substrate is a Nu:
- Substrate supplies : to create the bond with the reactant
- Intermediate is a stable **carbocation** called a **σ complex**
- Both of theses steps are 1,3 electron pair displacements



CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

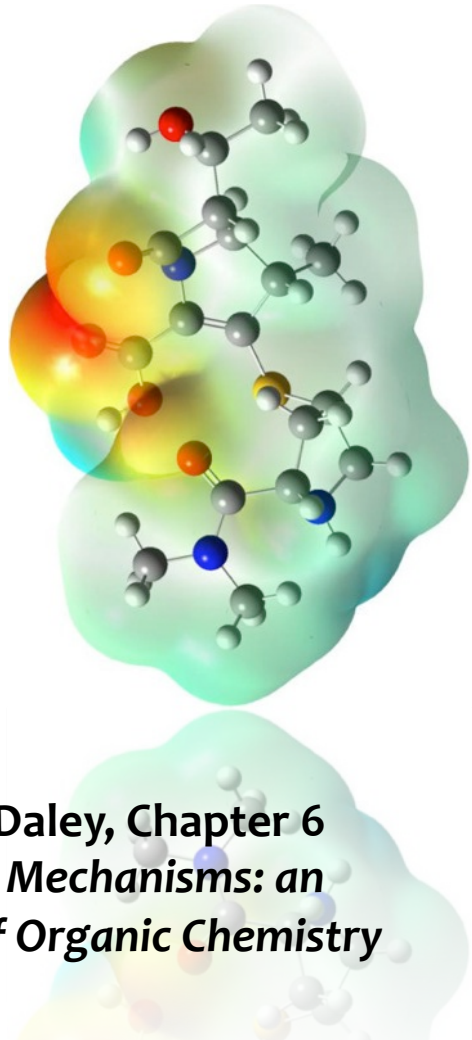
7.4 Substitution reactions

7.5 Addition reactions

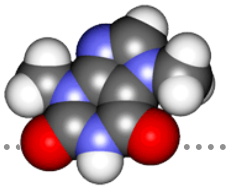
7.6 Elimination reactions

7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions

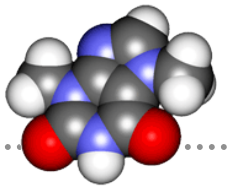


Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry



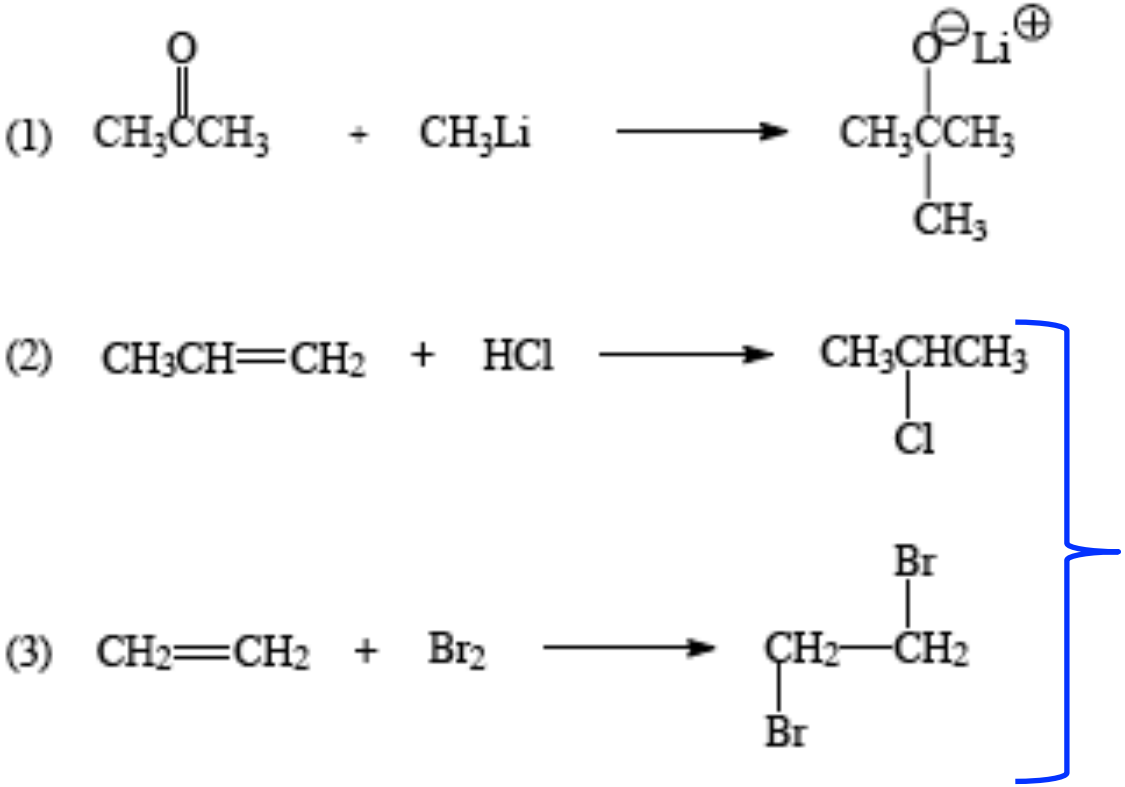
Addition reactions

Addition reactions



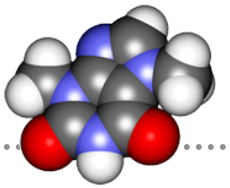
In **addition** reactions *the substrate gains atoms (or groups) from the reactant but doesn't lose any.*

- Substrate is unsaturated (Has multiple bond(s))
- Occur easily & quickly because σ-bonds are more stable than the π bonds they replace

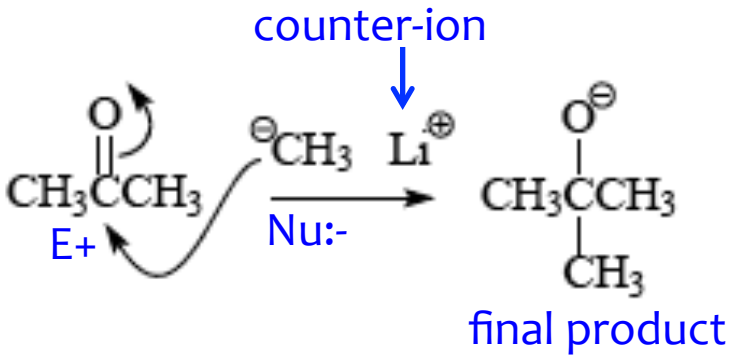


D&D, p.279 - 81

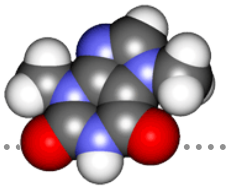
Nucleophilic addition



Nucleophilic addition: *a Nu:- attacks the electrophilic carbonyl carbon of the substrate and adds to the substrate.*

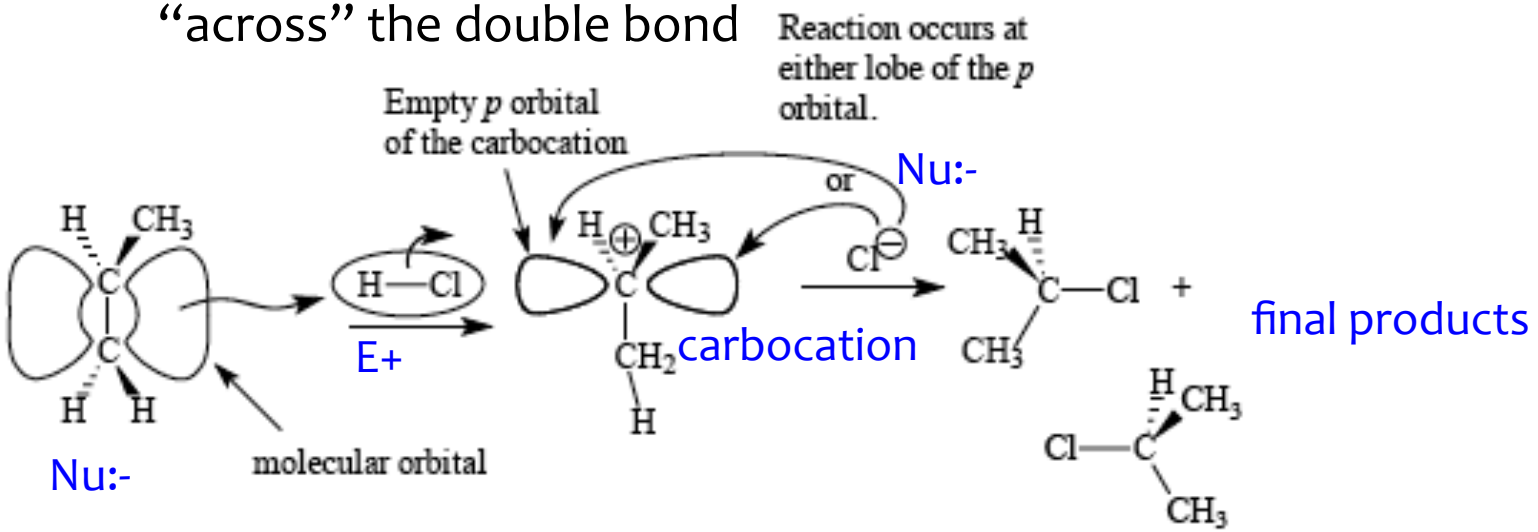


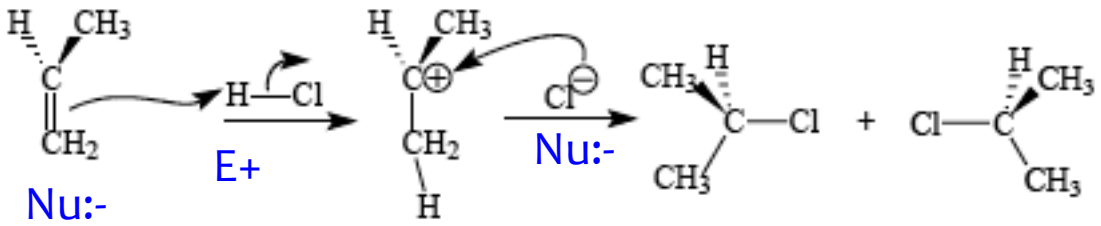
Electrophilic addition



Electrophilic addition: *an alkene or alkyne serves as the Nu: and donates :*
to the electropositive atom of a molecule, typically an acid

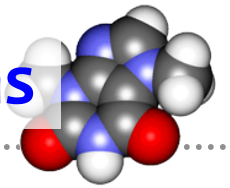
- Substrate is unsaturated
- Reactant is often an acid
- The two halves (electropositive & electronegative) are both added "across" the double bond





D&D, p.279 - 81

CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

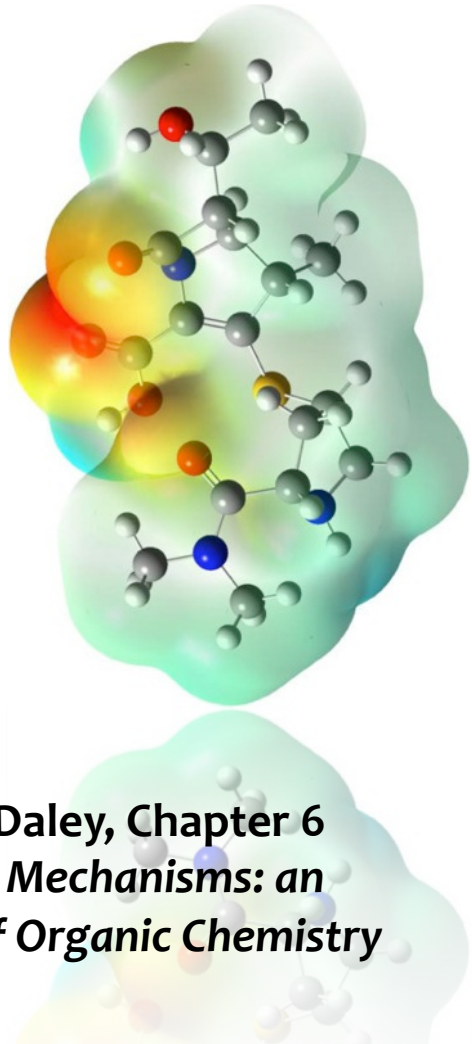
7.4 Substitution reactions

7.5 Addition reactions

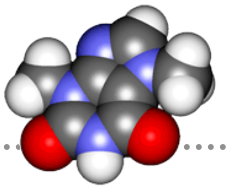
7.6 Elimination reactions

7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions

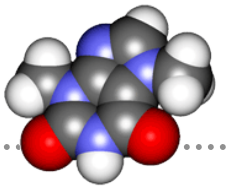


Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry



Elimination Reactions

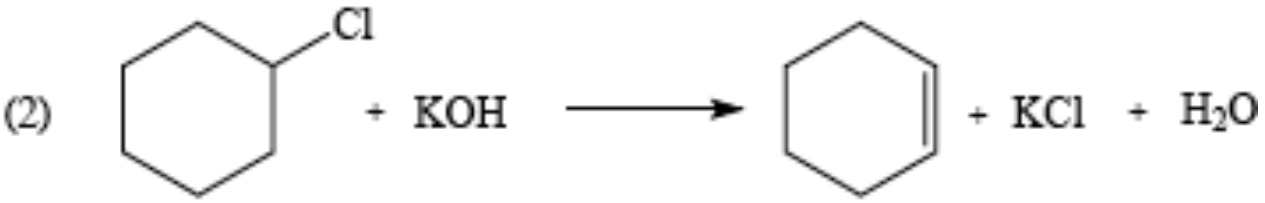
Elimination reactions



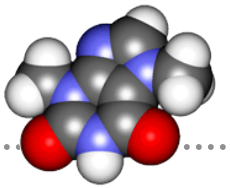
Elimination reaction: *removes two atoms (or groups) from the substrate to produce a product with a multiple bond or ring*

- Eliminated groups can be on adjacent carbons (=) or on distant carbons (ring)

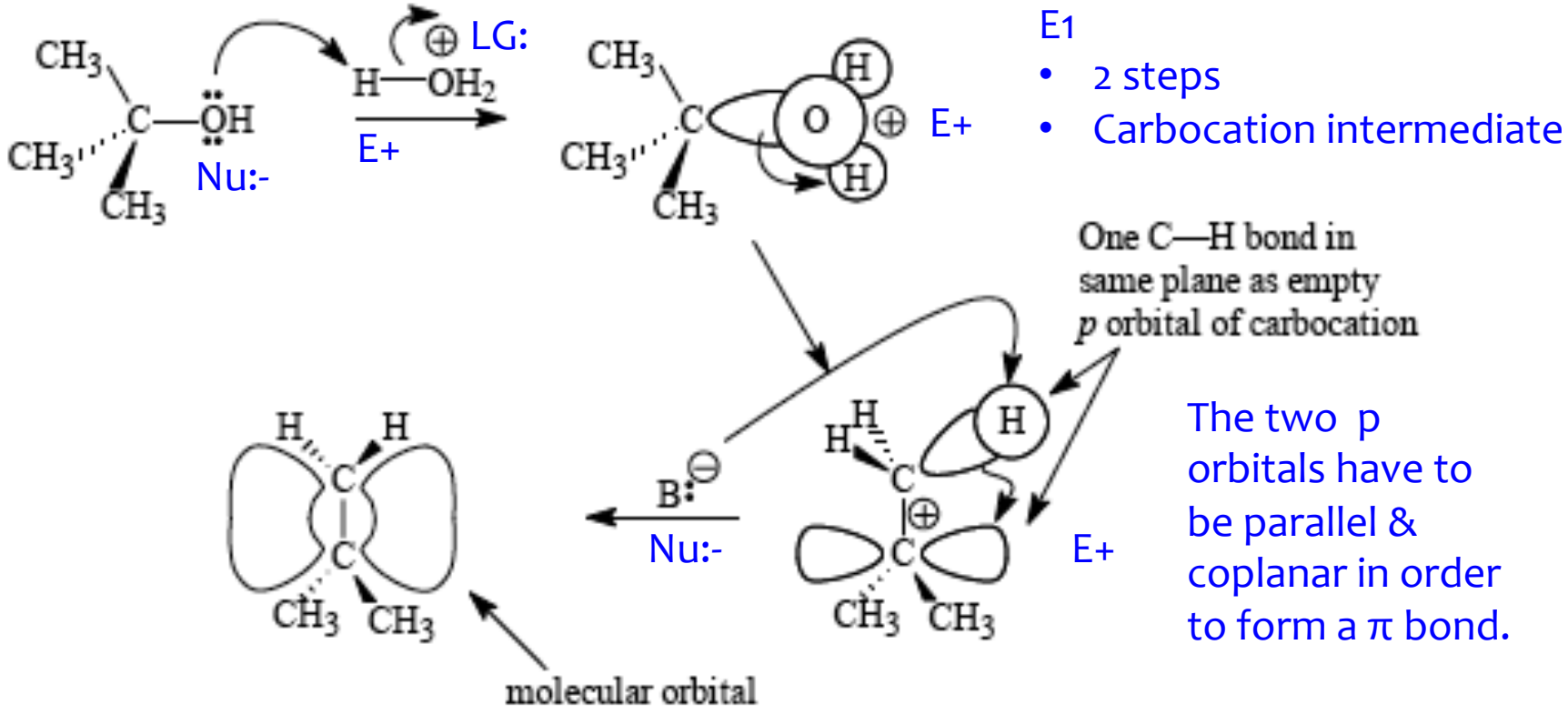
(1) $(CH_3)_3COH \xrightarrow[2)\ {}^{\ominus}OH]{1)\ H_3O^{\oplus}} (CH_3)_2C{=}CH_2 + H_2O$

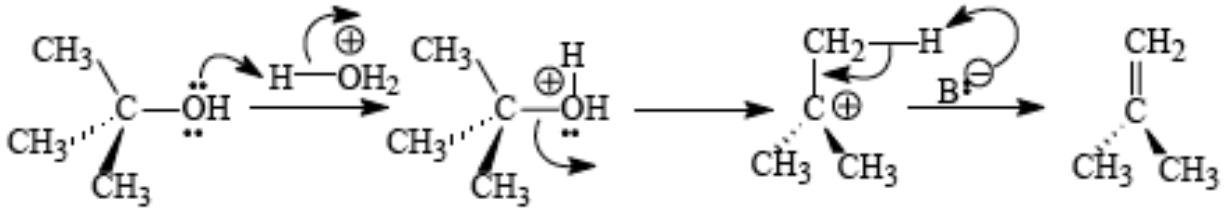
(2) 

Elimination mechanism (E1)



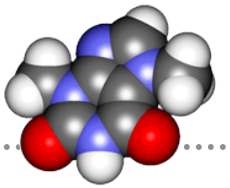
Elimination reaction: this example begins with electron abstraction, then heterocyclic bond cleavage, finally 1,5 electron pair displacement





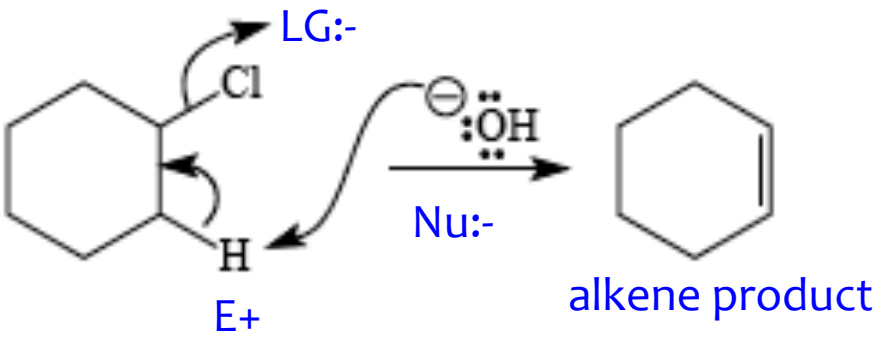
D&D, p.282 - 4

Elimination mechanism (E2)

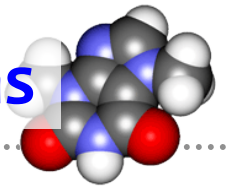


Elimination E2 mechanism: *is a one-step (or concerted) mechanism*

- Creates multiple bonds, changing sp3 to sp2 or sp hybridization
- No intermediates
- Requires a strong Nu:
- E2 competes with SN2



CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

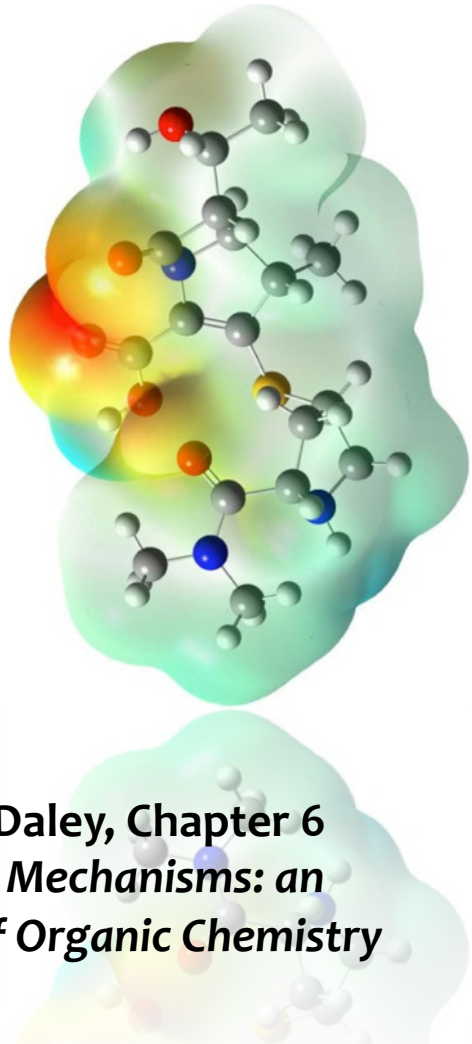
7.4 Substitution reactions

7.5 Addition reactions

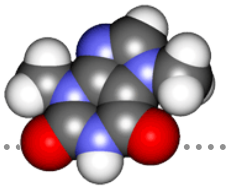
7.6 Elimination reactions

7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions

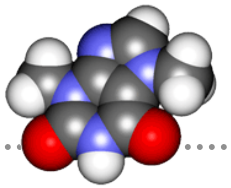


Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry



Competition between substitution, addition & elimination reactions?

Carbocations: a common intermediate…



… for some substitution, addition & elimination reactions allows them to compete with one another.

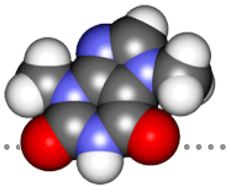
- So how do you be sure you create the reaction you want?

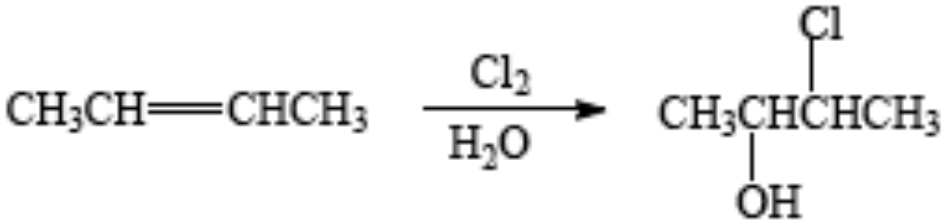
By careful choice of substrate, reactant and conditions!

- **Substrate** decides between addition & elimination reactions.

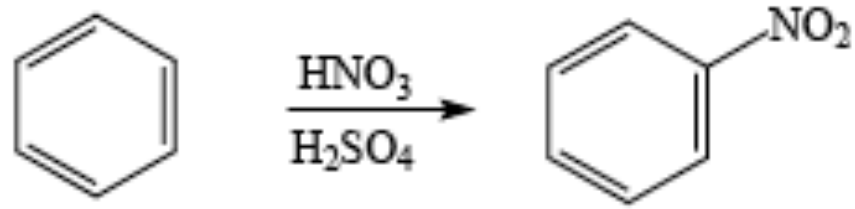
- **Nucleophile** decides between substitution & elimination reactions.
  - Sulfuric or phosphoric acids → elimination
  - Hydrochloric → substitution

Which reactions are these?

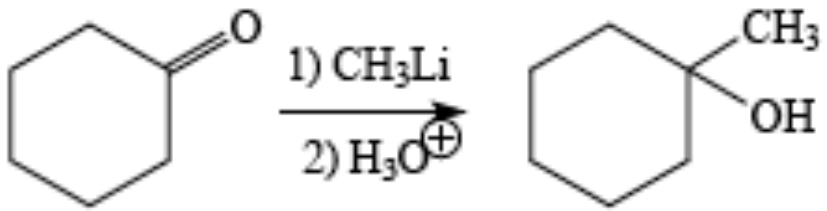




Electrophilic addition



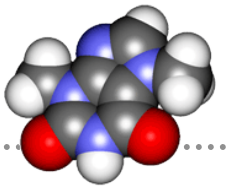
Substitution of NO2 for H

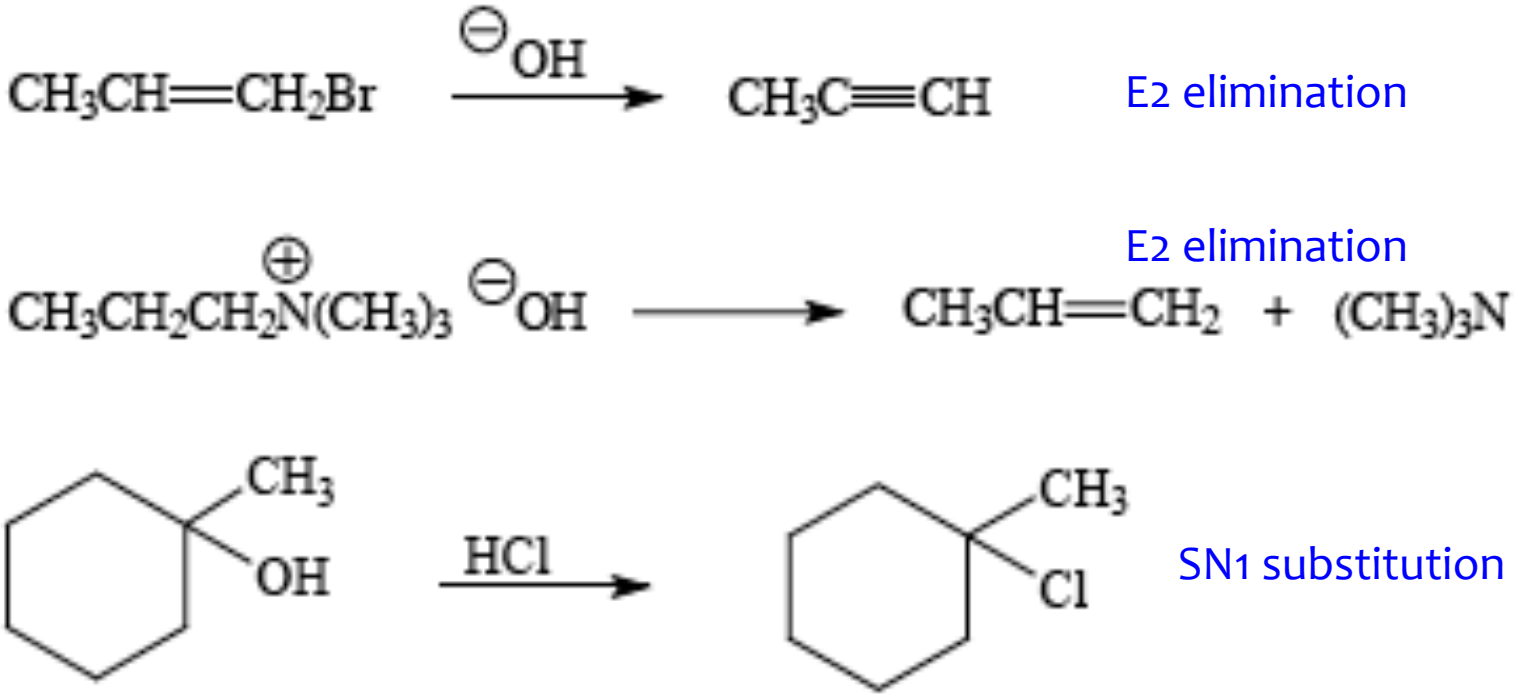


Electrophilic addition

D&D, p.282 - 4

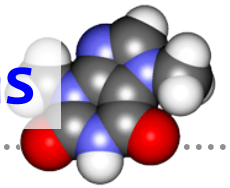
Which reactions are these?





D&D, p.282 - 4

CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

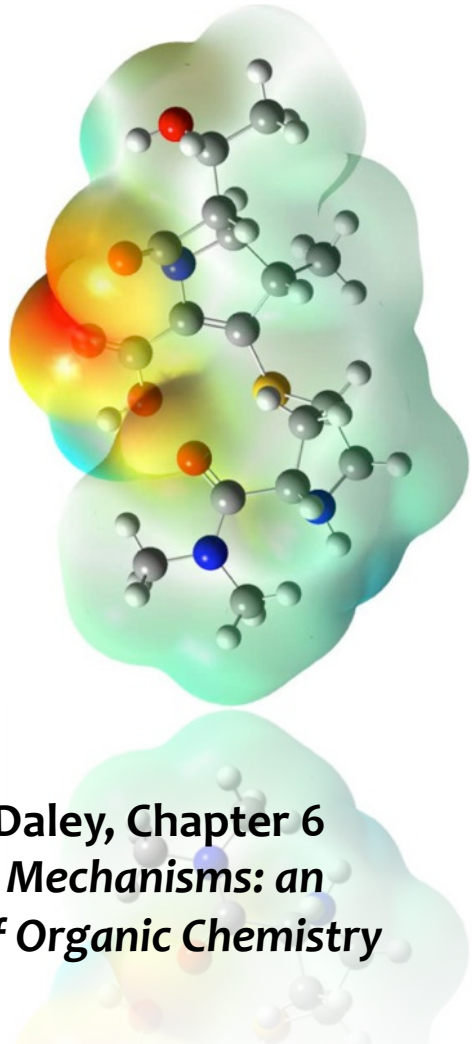
7.4 Substitution reactions

7.5 Addition reactions

7.6 Elimination reactions

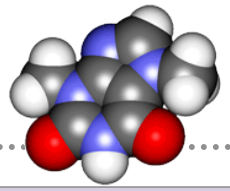
7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions



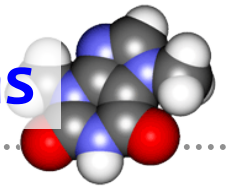
Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry

Diagnostic chart for S, A, E reactions



	Substitutions			Additions		Eliminations	
	SN1	**SN2**	**electro-philic**	**nucleo-philic**	**electro-philic**	**E1**	**E2**
substrate	alkane 2°/3°	alkane 1°	arene (Nu:)	carbonyl (E+)	alkene (Nu:)	alkane (E+)	alkane (E+)
reactant	weak Nu:	strong Nu:-	E+ (can be X2)	strong Nu:-	strong E+	H_3O^{+1}	very strong Nu:-
steps	2	1	2	1	2	2	1
inter-mediate	carbo +	5-bond C	stable σ carbo +	none	carbo +	carbo +	none
product	alkane	alkane (inversion)	arene	alkane	alkane	alkene	alkene

CHE2060 Lecture 7: Brief Overview of Reactions



7.1 Reaction energies & transition states

7.2 Review of acid-base reaction mechanisms

7.3 Writing reactions as transformations

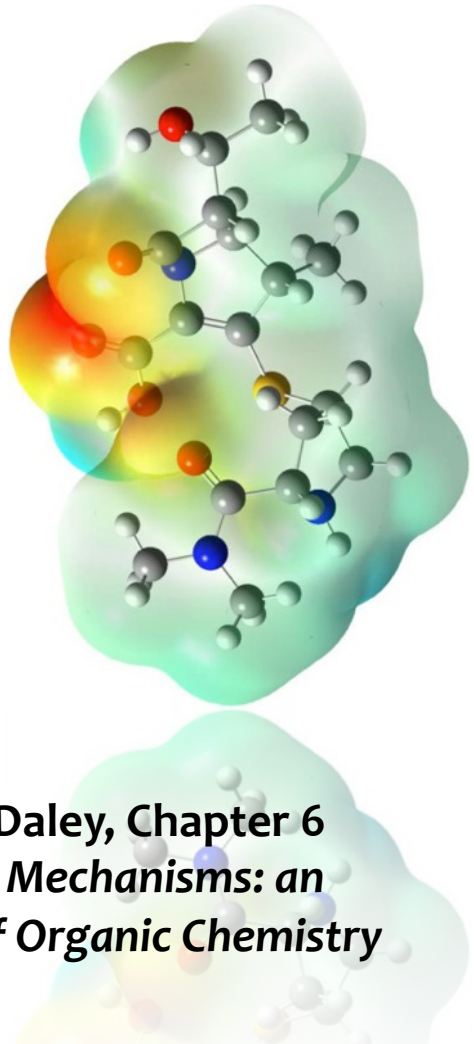
7.4 Substitution reactions

7.5 Addition reactions

7.6 Elimination reactions

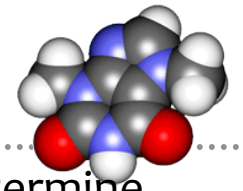
7.7 Competition between substitution, addition & elimination reactions

7.8 Diagnostic chart to identify reactions



Daley & Daley, Chapter 6
Reaction Mechanisms: an Overview of Organic Chemistry

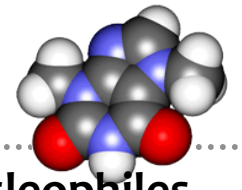
Key Concepts for Lecture 7 (1)



- The **relative free energies** of the molecules involved in a reaction determine their positions in the chemical equilibrium. The equilibrium moves toward the most stable molecule.
- Reactants often form products via unstable species called **transition states**. Among reactions, the smaller the differences in the energy levels between reactants and transition states the faster the reaction rate.
- The **slowest step** of a multistep reaction mechanism governs the rate of that reaction. The transition state is involved in the step with **the highest energy of activation**.
- A **curved arrow symbolizes the electron movement** in a reaction. This curved arrow shows the formal flow of electrons as the bonds form or break. A double barb arrow shows the movement of an electron pair. A single barb arrow shows the movement of a single electron.
- A chemical reaction involves the **substrate, other reagents, product, and by-products**.
- Organic chemists often do not write a balanced equation for a chemical reaction; instead they write a **transformation**. A transformation shows only what changes occur in the substrate as it reacts with the reagent to form the product.

D&D, p.286

Key Concepts for Lecture 7 (2)



- Most organic reagents fall into two categories: **electrophiles and nucleophiles.** An electrophile is a Lewis acid. A nucleophile is a Lewis base.
- All organic reactions can be classified as **substitution, addition, or elimination** reactions. Each of these categories has a number of different reaction mechanisms.
- In a **substitution** reaction, an incoming atom or group of atoms replaces a leaving atom or group of atoms.
- In an **addition** reaction, pairs of atoms or groups of atoms add to a multiple bond.
- In an **elimination** reaction, a pair of atoms or group of atoms leaves the substrate. The substrate then forms a multiple bond or forms a cyclic structure.
- Addition, elimination, and substitution reactions may proceed through a **nucleophilic or electrophilic mechanism**.

D&D, p.286