Intro to Organic Reactions

Nov 18-22

Concept Video 30
Overview of Organic Reactions

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Reaction Mechanisms

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Substitution and Elimination Reactions

Concept Video 33
Additions to Alkenes

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Overview of Organic Reactions

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WHEN YOU BREAK IT DOWN...

... THERE ARE REALLY ONLY
FOUR TYPES OF ORGANIC REACTIONS

Simplifying Organic Reactions

1. Substitution

2. Addition

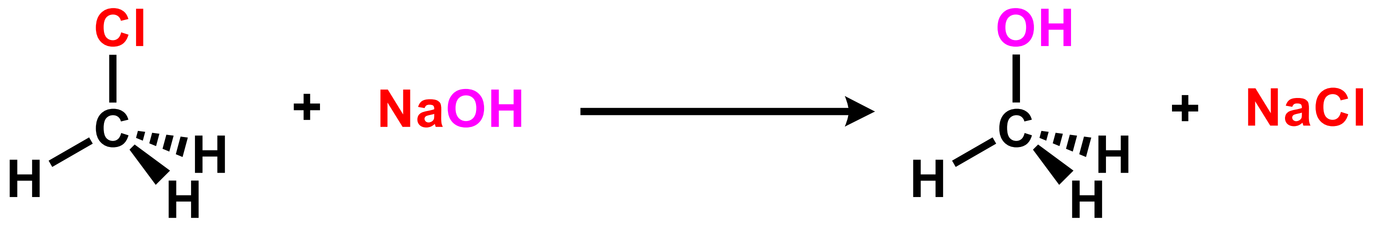
3. Elimination

4. Rearrangement

Organic Reactions: Four main types

1. Substitution

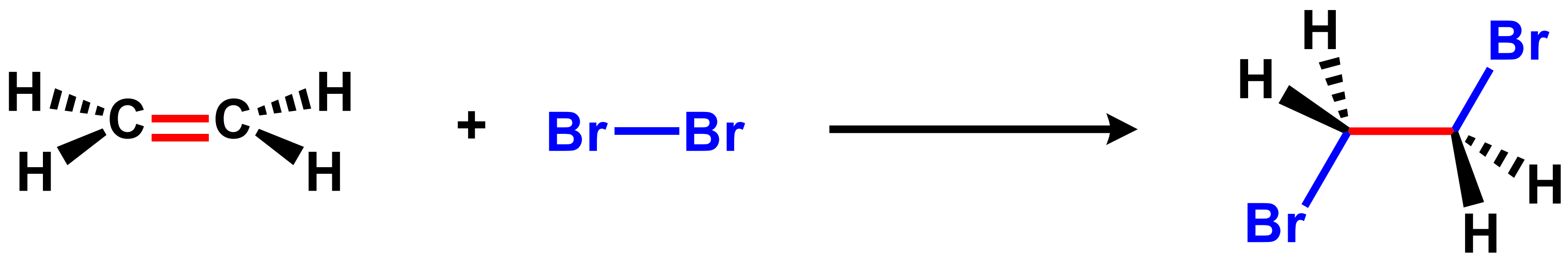
One group *replaces* another – characteristic of saturated compounds and aromatic compounds



Organic Reactions: Four main types

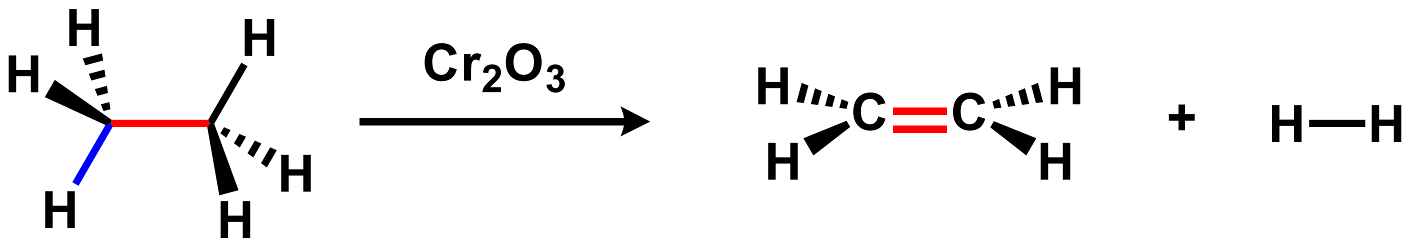
2. Addition

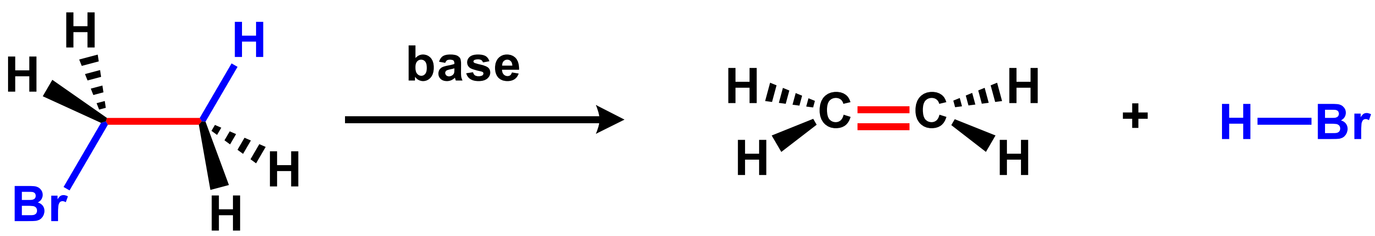
Reagent adds to substrate (two molecules become one!)
– characteristic of π bonds/unsaturated compounds



3. Elimination

In simple terms: One molecule becomes two or more. Main reaction in preparation of π bonds/unsaturated compounds

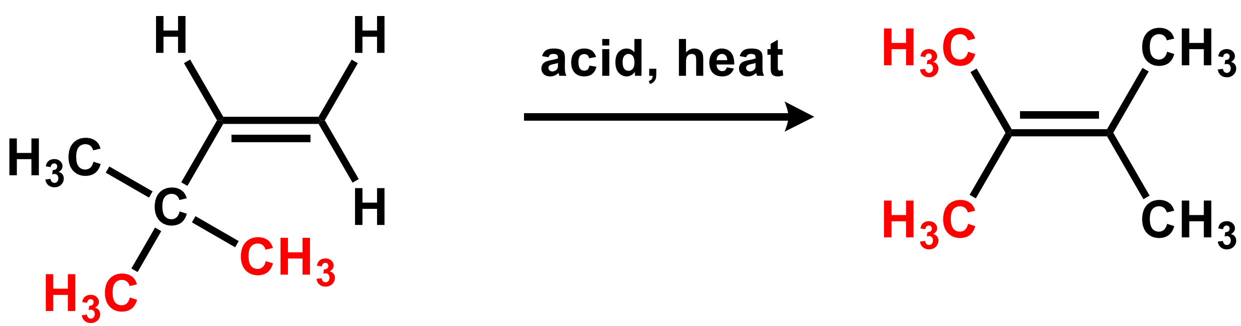




Organic Reactions: Four main types

4. Rearrangement

Reorganization of a molecule – Characteristic of reactive intermediates



Formal Charge: Review and Practice

What is the formal charge?

1. Draw Lewis Structure
2. Determine neutral valence of atom
3. Assign to each atom ½ for each bonding electrons + 1 for each lone pairs
4. FC = Neutral Valence – Assigned electrons

Formal Charge: Review and Practice

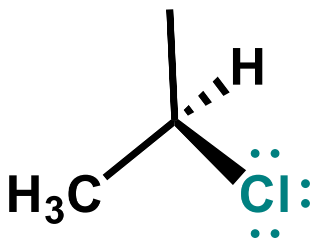
What is the formal charge?

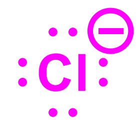
1. Draw Lewis Structure ✓
2. Determine neutral valence of atom **7**
3. Assign to each atom ½ for each bonding electrons + 1 for each lone pairs **(1 bond with 2 electrons; 6 lone pairs)**
4. FC = Neutral Valence – Assigned electrons **= 7-7**

   = 0

Formal Charge: Review and Practice

What is the formal charge?





1. Draw Lewis Structure
2. Determine neutral valence of atom **7**
3. Assign to each atom ½ for each bonding electrons + 1 for each lone pairs **(8 lone pairs)**
4. FC = Neutral Valence – Assigned electrons **= 7-8**

   = -1

Reaction **Pathway**

In simple terms: The potential energy pathway from the reactants to the products

1: Reactants converted directly to products – one-step

2: Reactants converted to products *via* intermediates – multi-step

Reaction Pathway:Concerted Reaction

Reactants converted directly to products – one-step

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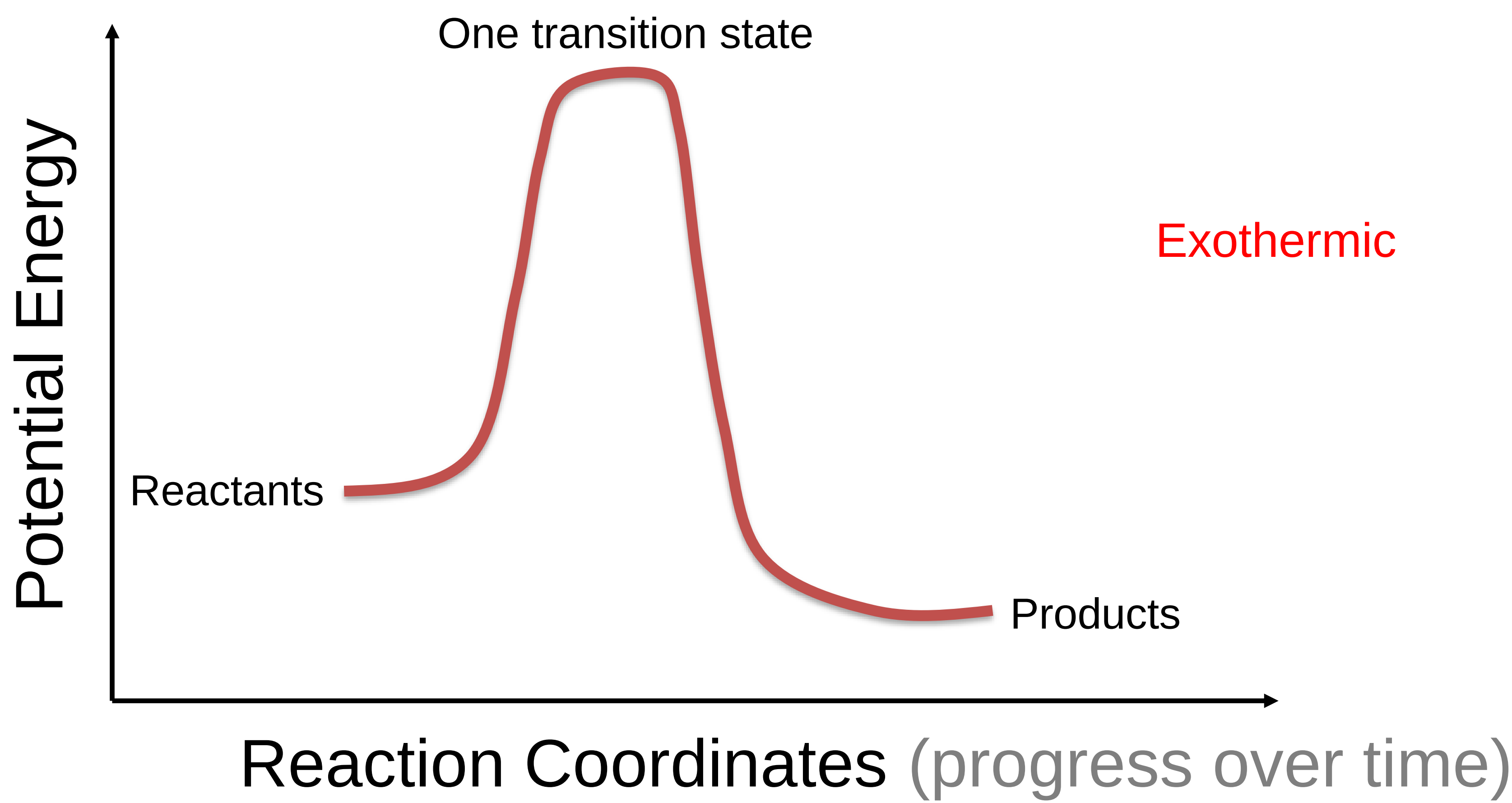
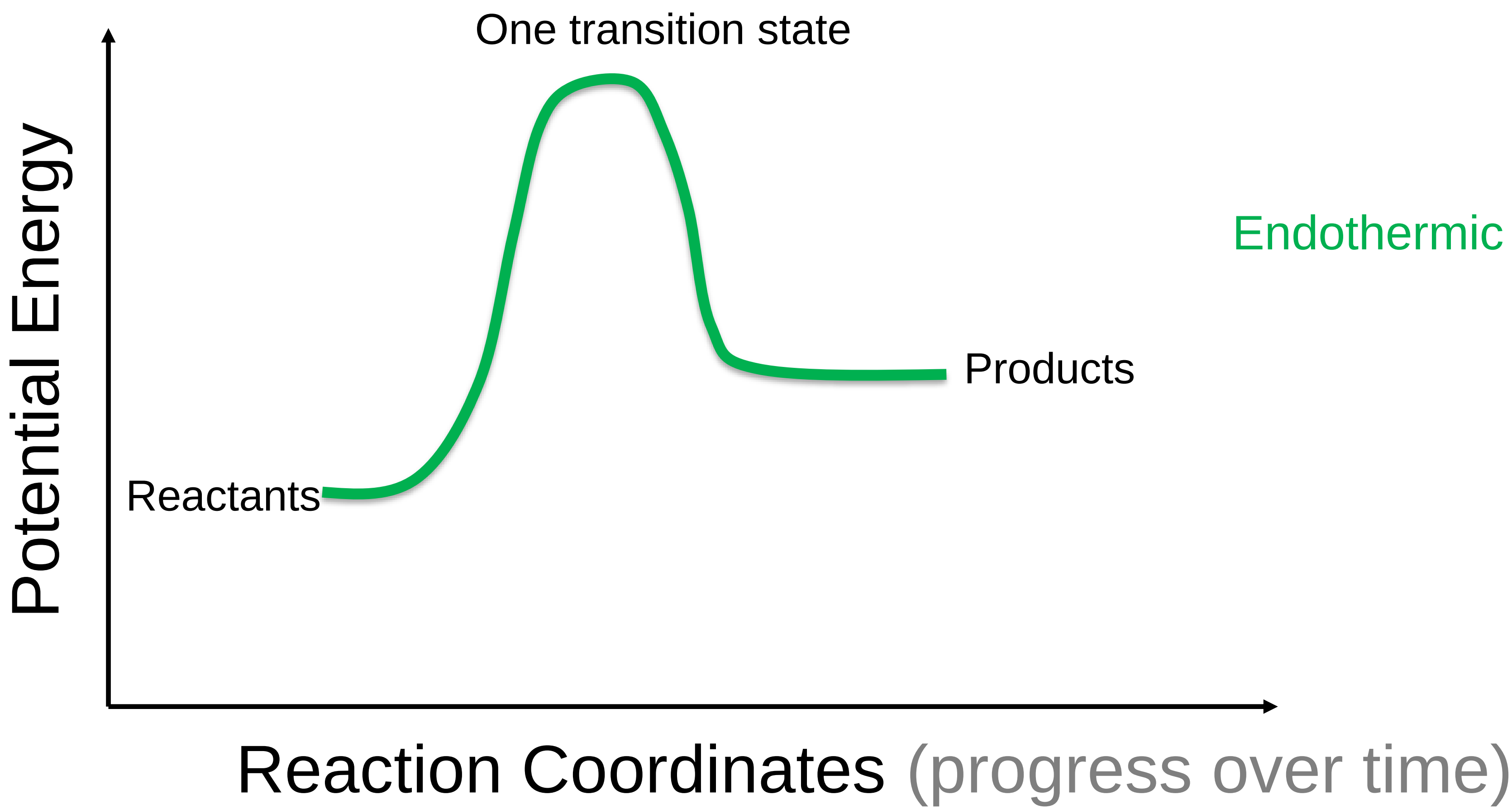


Reaction Pathway:Concerted Reaction

Reactants converted directly to products – one-step

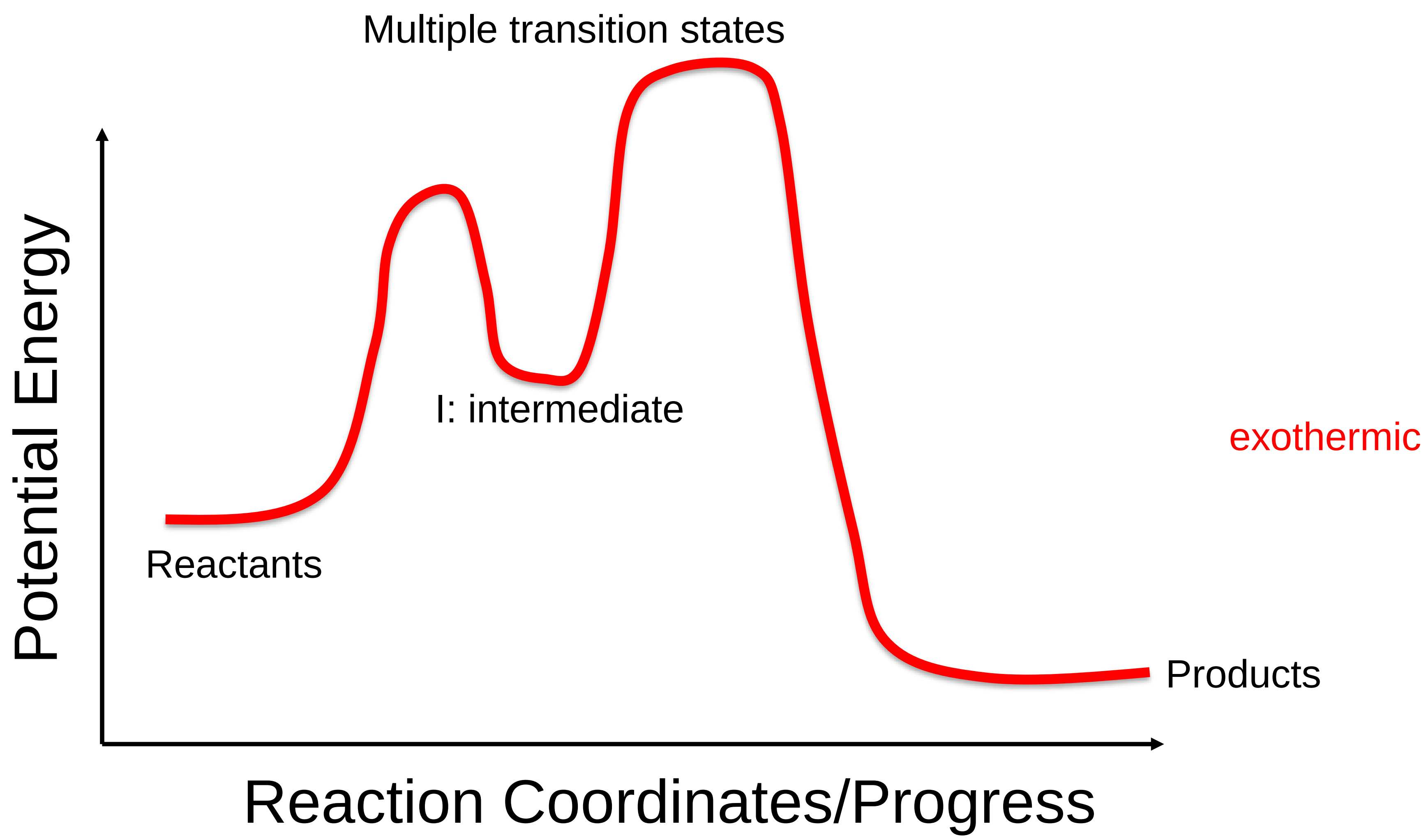


Reaction Pathway:Stepwise Reaction

2: Reactants converted to products *via* intermediates – multi-step

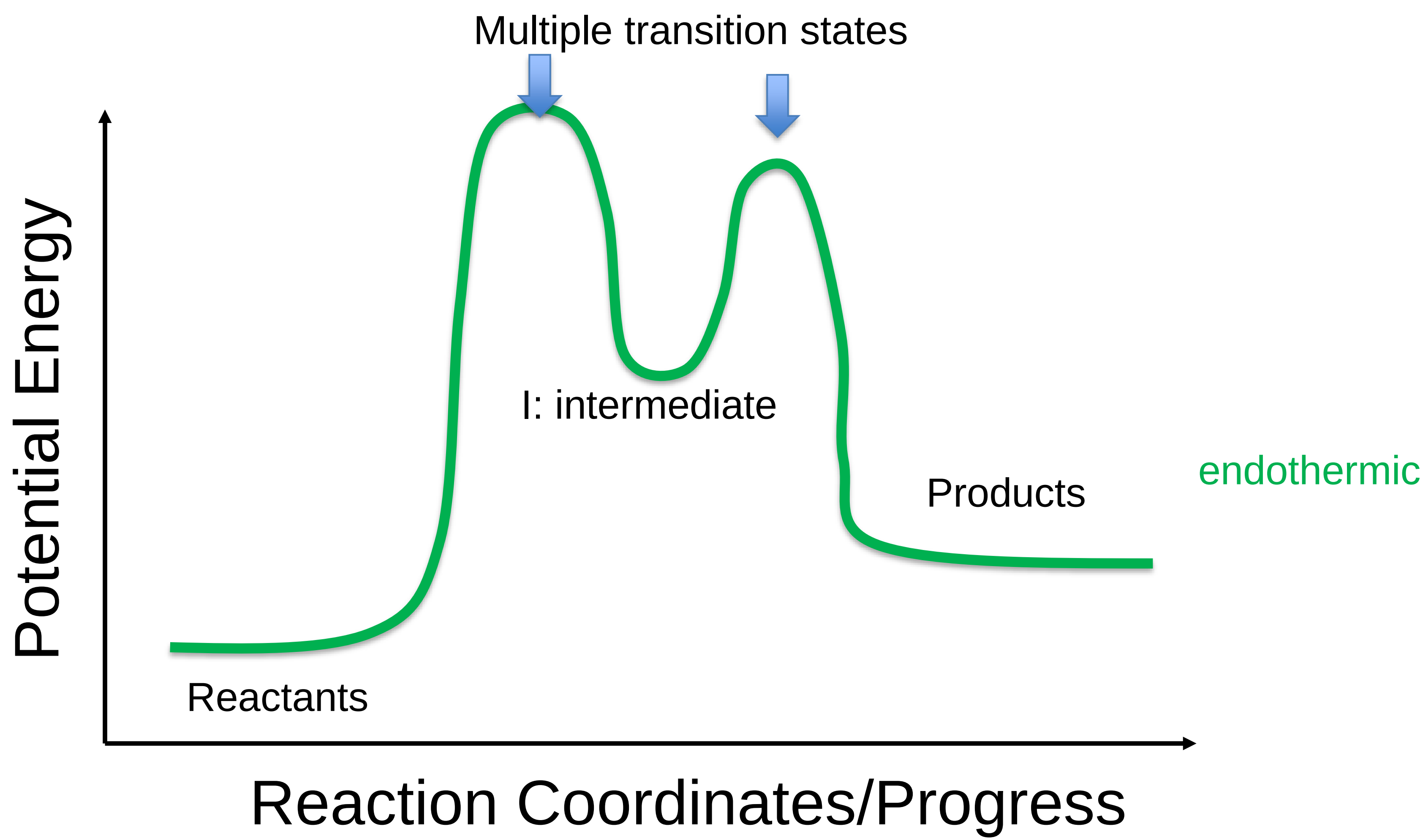
Reaction PathwayStepwise Reaction

Reactants converted to products *via* intermediates (multi-step)



Reaction PathwayStepwise Reaction

Reactants converted to products *via* intermediates (multi-step)



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Nov 20-24

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Reaction Mechanisms

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The two ways to break bonds

Homolysis (Homolytic cleavage/breaking)

Heterolysis (Heterolytic cleavage/breaking)

The two ways to break bonds

Homolysis (Homolytic cleavage/breaking)

Formation of radicals. Radicals are neutral species that carry an unpaired electron

$$A\cdot\cdot B \longrightarrow A\cdot + \cdot B$$

Heterolysis (Heterolytic cleavage/breaking)

Formation of ions. Complete transfer of electrons to one atom

$$^{\delta+}A\cdot\cdot B^{\delta-} \longrightarrow A^{\oplus} + :B^{\ominus}$$

The two ways to break bonds

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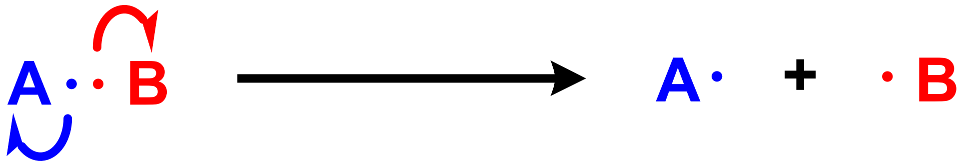
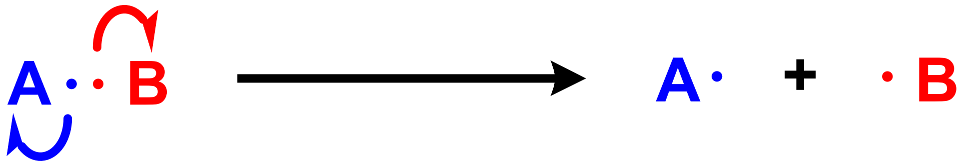


Single arrowhead (because there is only 1 electron in each move)

The two ways to break bonds

Homolysis (Homolytic cleavage/breaking)

Formation of radicals. Radicals are neutral species that carry an unpaired electron



Heterolysis (Heterolytic cleavage/breaking)

Formation of ions. Complete transfer of electrons to one atom

Note the **double** headed arrow! (2 electrons move)

Heterolytic cleavage of carbon compounds (for all reactions we will learn about from this point on!)

AND SINCE CARBON IS KEY...

... LET’S FOCUS ON BREAKING/MAKING BONDS AT CARBON!

Breaking Bonds to Carbon

<u>CARBOCATION</u> – electron deficient carbon (positive charge)
<u>CARBANION</u> – electron rich carbon (negative charge)

$$\overset{\delta+}{H_3C}-\overset{\delta-}{Z} \longrightarrow$$

$$\overset{\delta-}{H_3C}-\overset{\delta+}{Z} \longrightarrow$$

*** <u>heterolysis</u> of "C-Z" bond makes a carbocation or carbanion ***
depending on the bond polarity (dipole moment)

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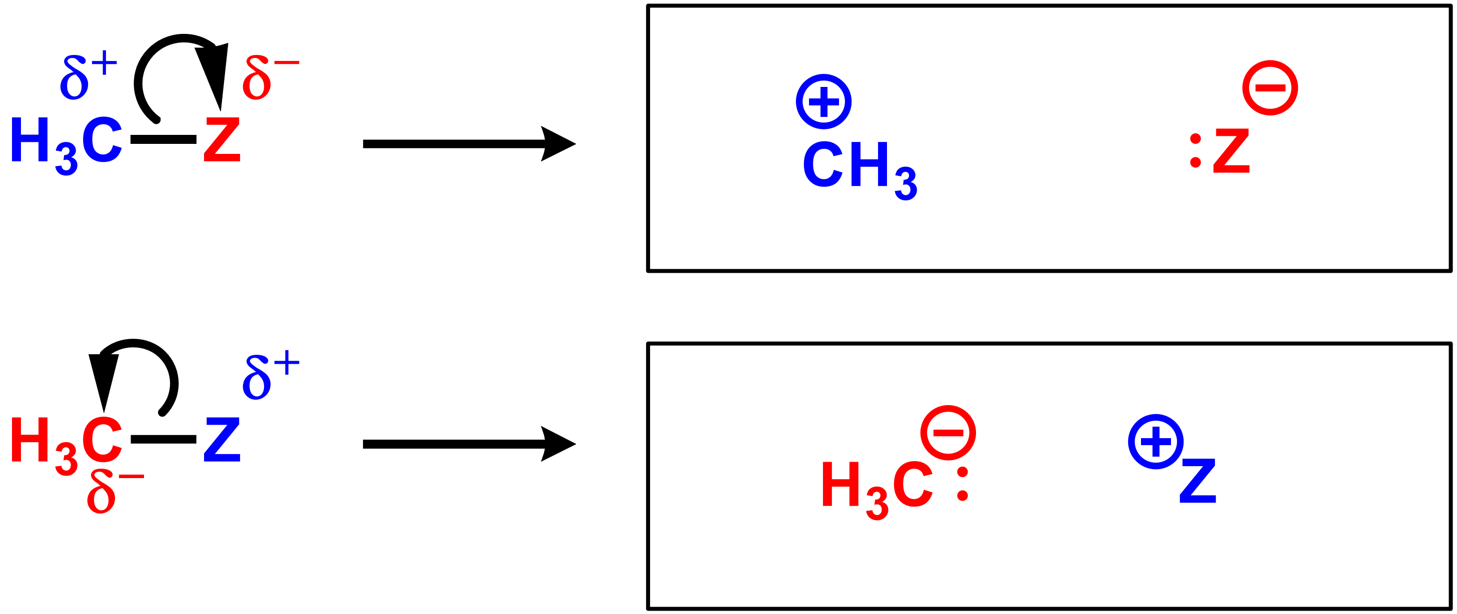


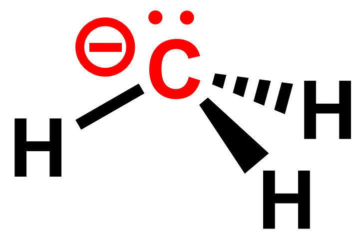
* **<u>heterolysis</u> of "C-Z" bond makes a carbocation or carbanion** *
depending on the bond polarity (dipole moment)

How do reactions happen?

- Need different reaction “partners”
- We call these “partners” *species*
- One species does the attacking, one gets attacked!
- The species with more electrons does the attacking.

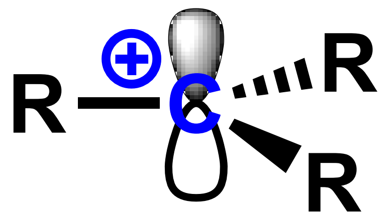
Reactive carbon species: What are these “species”?

Nucleophiles: Electron rich species (seeking a positive center – nucleus)



Carbanion

Electrophiles: Electron deficient species (they like/want electrons to complete octet)



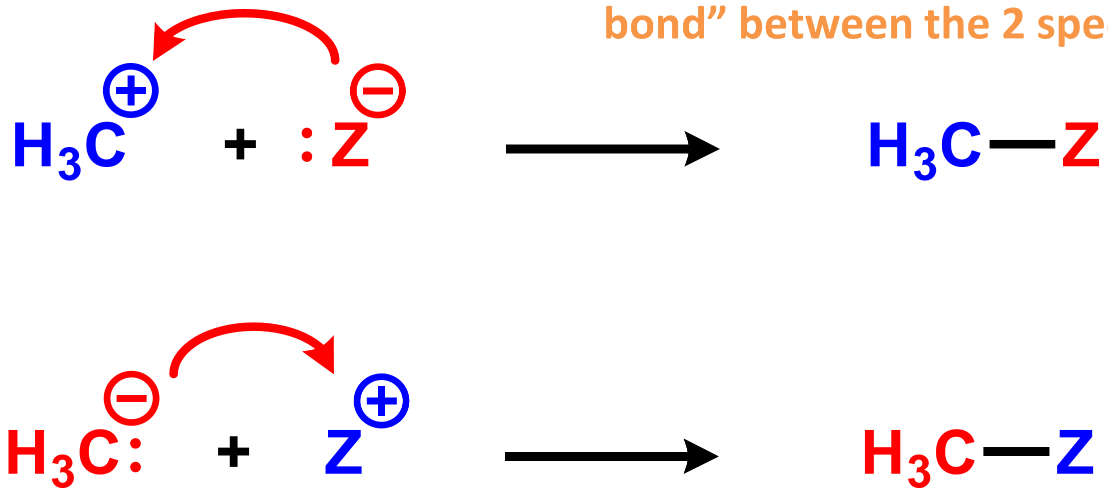
Carbocations

*** organic reactions = <u>nucleophile “attacks” electrophile</u> ***

Making bonds to carbon

NUCLEOPHILE – electron rich species (seeks a positive center)
ELECTROPHILE – electron deficient species (seeks e^- to fill octet)

Think of this arrow as drawing a "new bond" between the 2 species



- **organic reactions = <u>nucleophile "attacks" electrophile</u> ***

ALWAYS draw arrow in direction of attack!

The electrons are what moves!

Reactions

Use **<u>curved arrows</u>** to show the <u>movement on the electrons</u> – only electrons can move!!!

WE SHOW "NUCLEOPHILIC ATTACK"
BY DRAWING CURVED ARROWS...

...this is the <u>REACTION MECHANISM</u>

Will all nucleophiles be able to attack?

Nucleophiles: Electron rich species (seeking a positive center – nucleus): may or may not be –vely charged
Must have a lone pair or a π bond

Nucleophiles can be:
1) An anion (like OH^- or CN^-)
2) A neutral molecule with a lone pair of electrons ($:NH_3$)
3) Molecules with π bonding electrons

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Nucleophiles: Electron rich species (seeking a positive center – nucleus): may or may not be –vely charged
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Strength of nucleophiles: The more basic a compound is the better it is as a nucleophile

A negatively charged (anionic) nucleophile is stronger than it's conjugate acid (i.e. add H)

Examples:
OH^- is a stronger nucleophile than H_2O
NH_2^- is a stronger nucleophile than NH_3

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Polarizability: more polarizable ions are better nucleophiles
(*i.e*. more willing to give up its electrons)

- In a group: larger ions = better nucleophiles
- Within a row: less electronegative = better nucleophile

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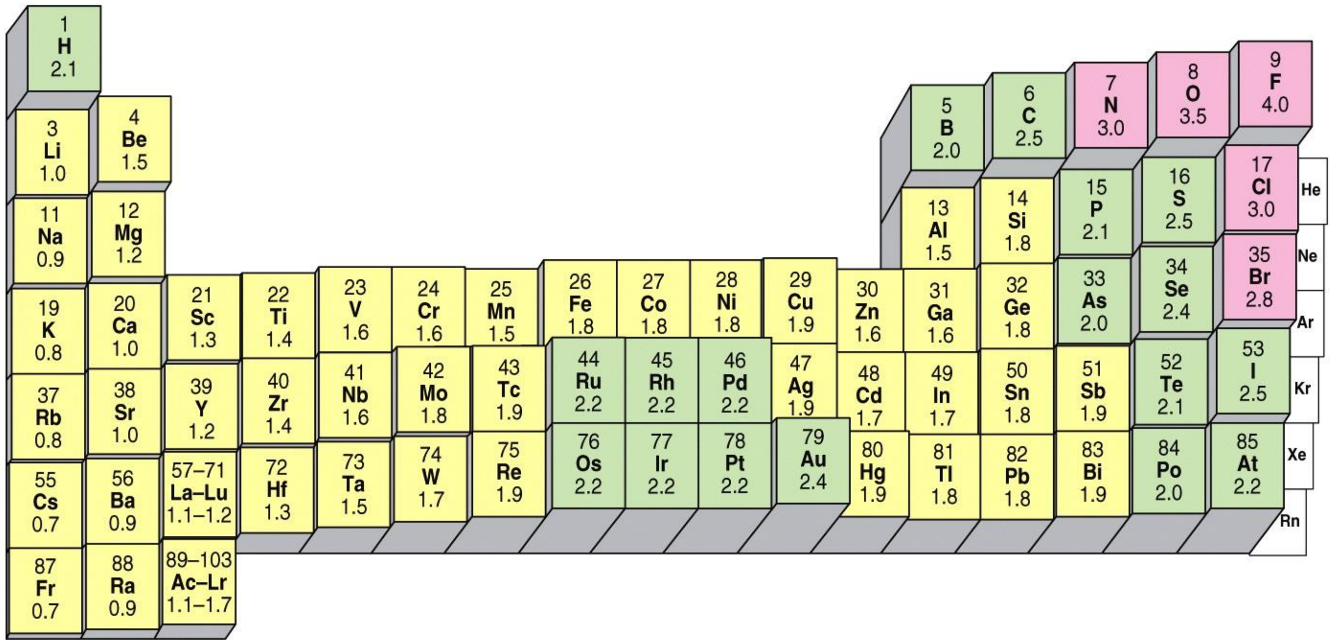

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- Within a row: less electronegative = better nucleophile

Examples:
I^- is a stronger nucleophile than F^-
CH_3^- is a better nucleophile than OH^-

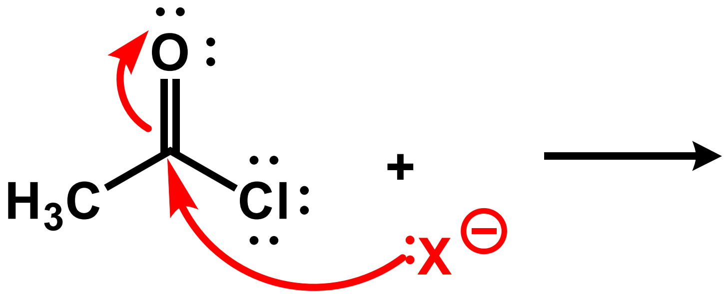
A chemical reaction: breaking and making bonds

Making a bond

Breaking a bond

Reactions: Practice

Write the product of the following reactions:



Reactions: Practice

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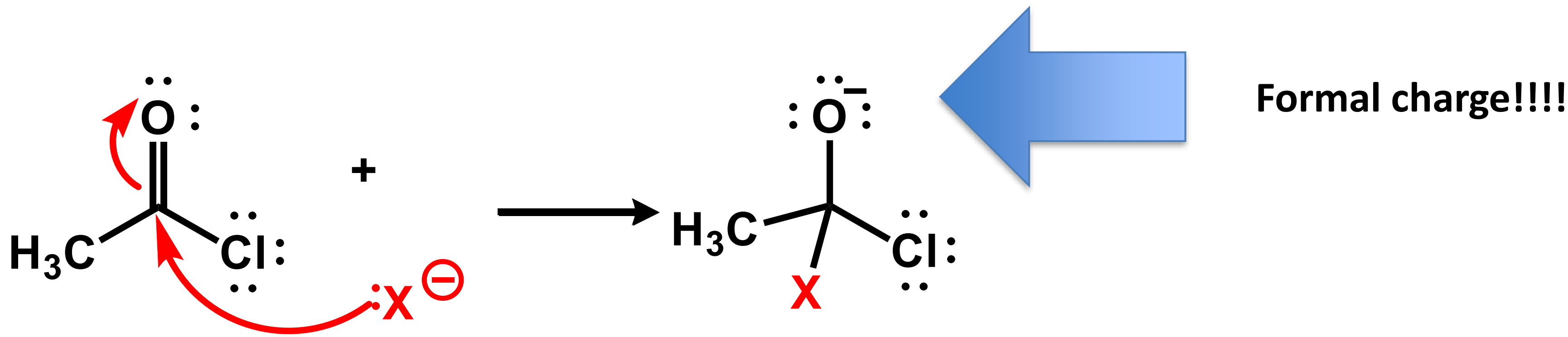

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Reactions: Practice

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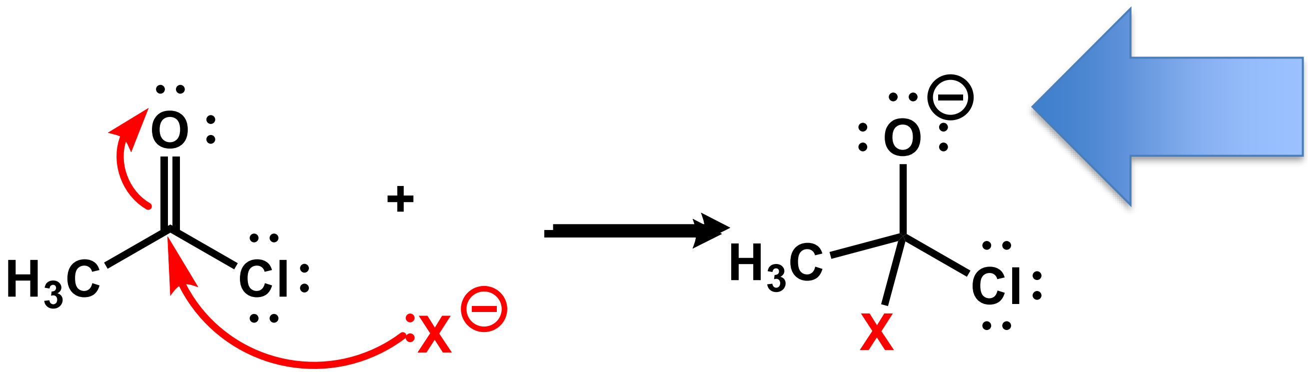

Formal charge!!!!

1. Draw Lewis Structure ✓
2. Determine neutral valence of atom **6**
3. Assign to each atom ½ for each bonding electrons + 1 for each lone pairs **(1 bond with 2 electrons; 6 lone pairs)**
4. FC = Neutral Valence – Assigned electrons **= 6-7**

   = -1

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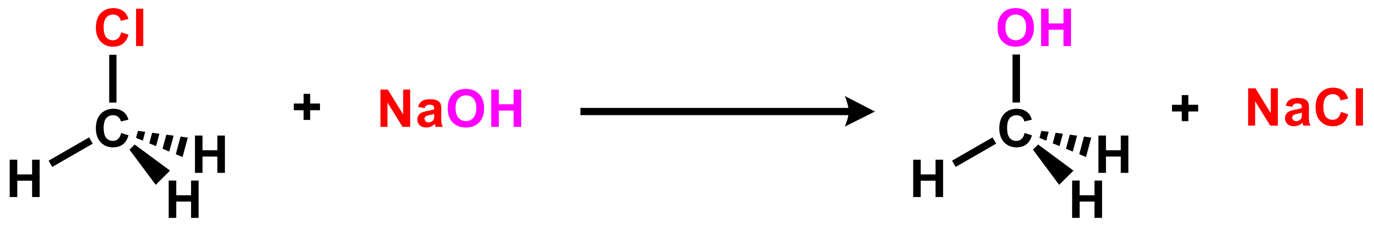
Substitution and Elimination Reactions

Organic Reactions: Four main types (review)

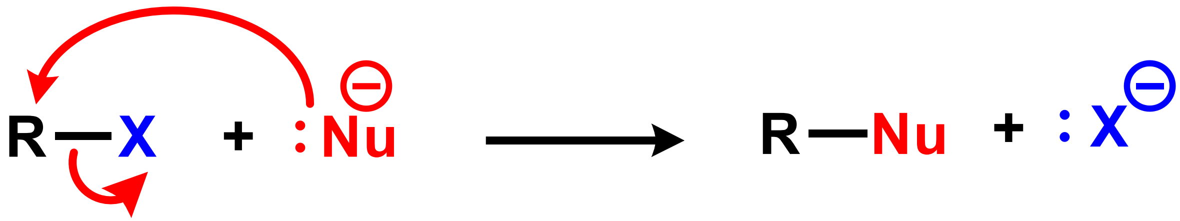
1. Substitution

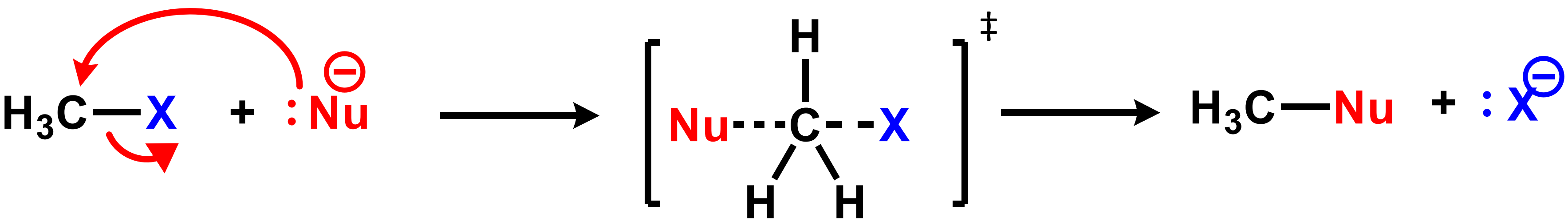
One group *replaces* another – characteristic of saturated compounds and aromatic compounds



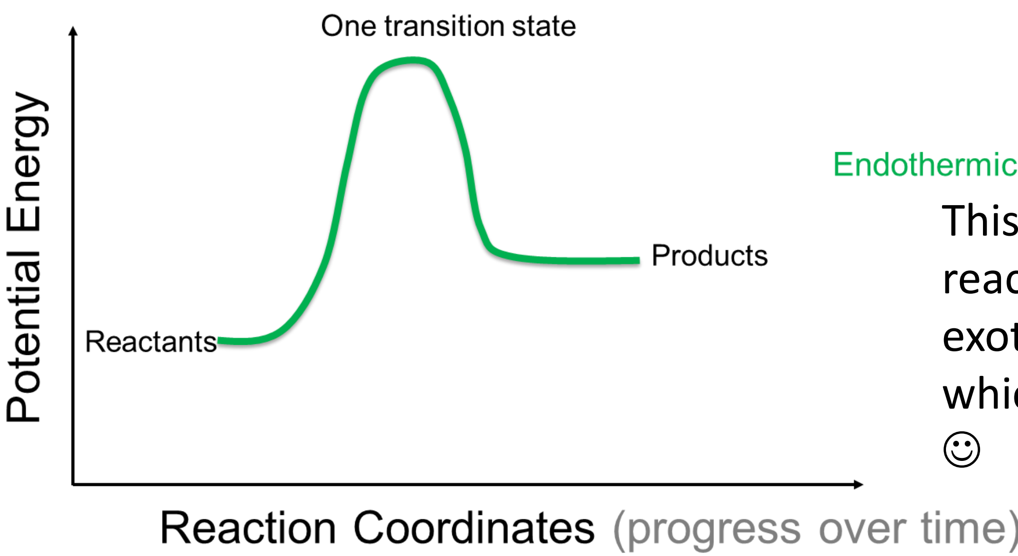
Nucleophilic Substitution Reactions

Nucleophile substitutes a “leaving group”





transition state



Endothermic

This is just an example, the reaction can be endothermic OR exothermic, I would specify which reaction pathway to draw ☺

Nucleophilic Substitution Reactions

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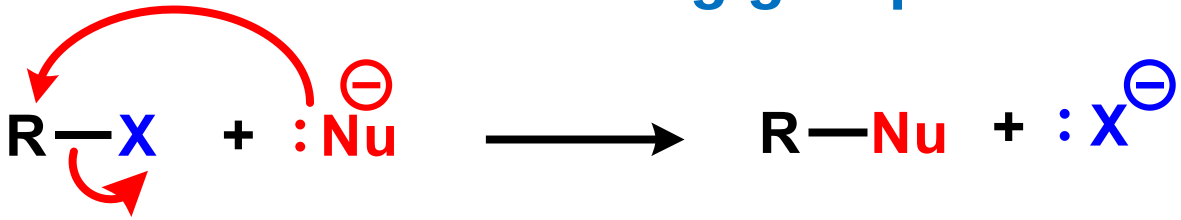
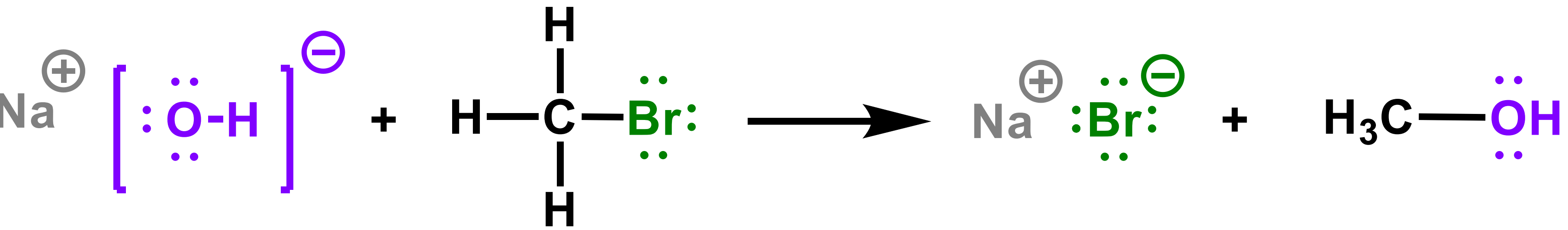


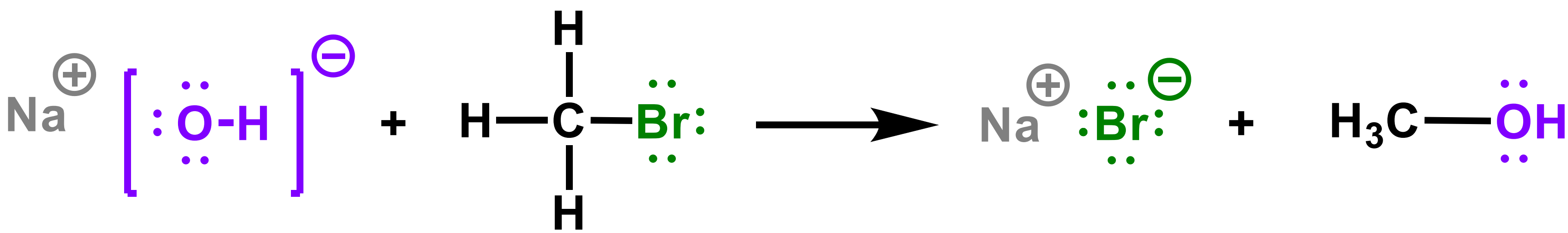
Heterolytic cleavage: Leaving group departs with a pair of electrons

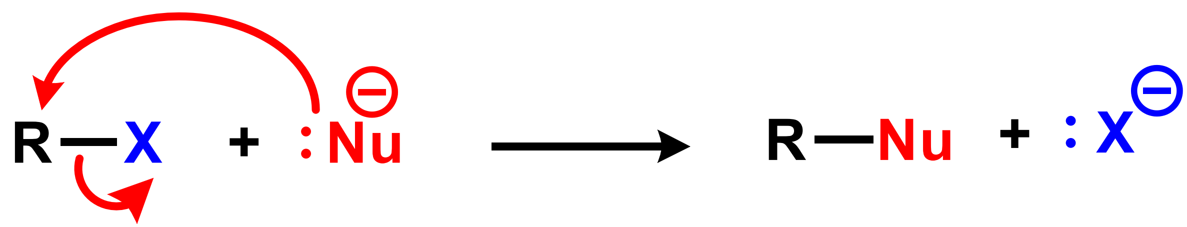
Nucleophilic Substitution Reactions Example



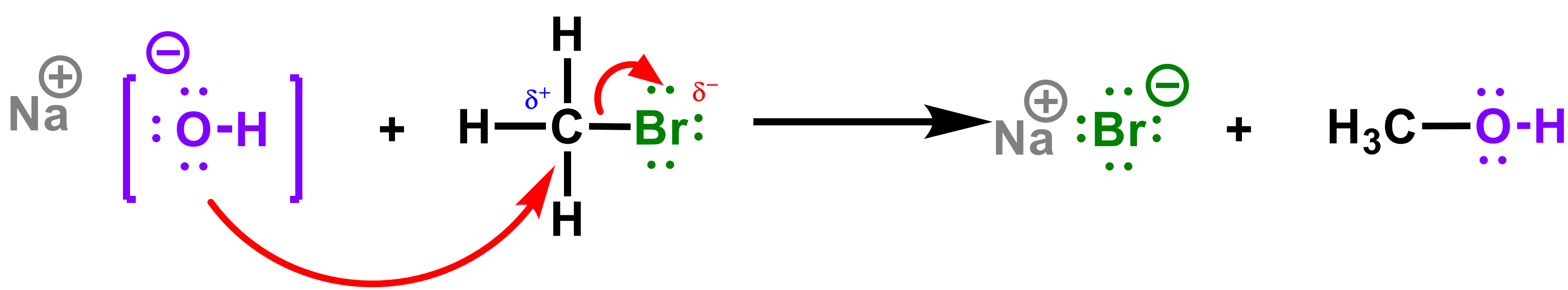
Need to draw the transition state ONLY if asked (but usually I will)!

Nucleophilic Substitution Reactions Example





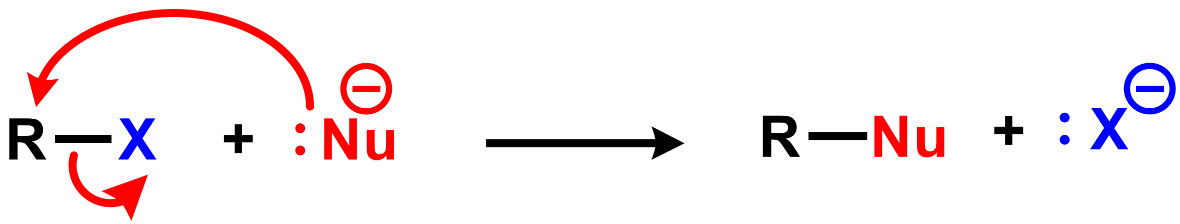
there is usually a counter cation here; just include it along the reaction
if I wrote it in :), for example Na^+



Nucleophilic Substitution Reactions

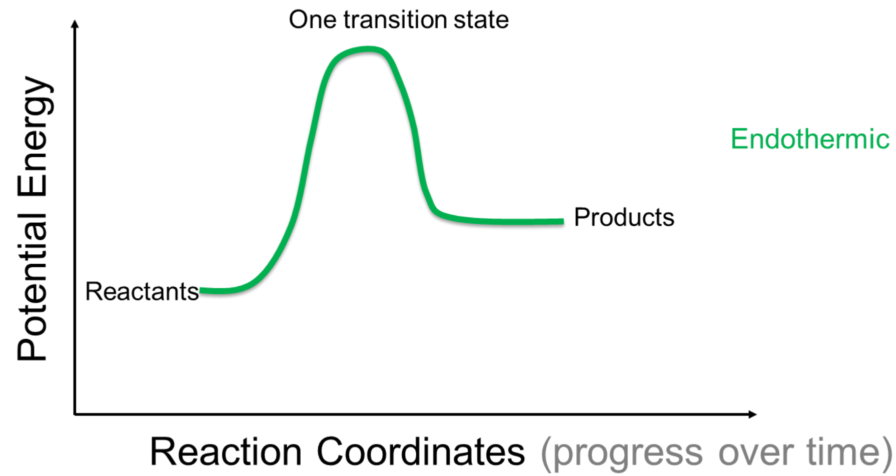
Two nucleophilic substitution (SN) reaction mechanisms

A: The nucleophilic attack and the leaving group departure occurs in one-step: Concerted: S_N**2**



S_N2: 2 (bimolecular) = 2 "species" are involved to get the reaction started (rate limiting step)

This is just an example, the reaction can be endothermic OR exothermic, I would specificity which reaction pathway to draw ☺



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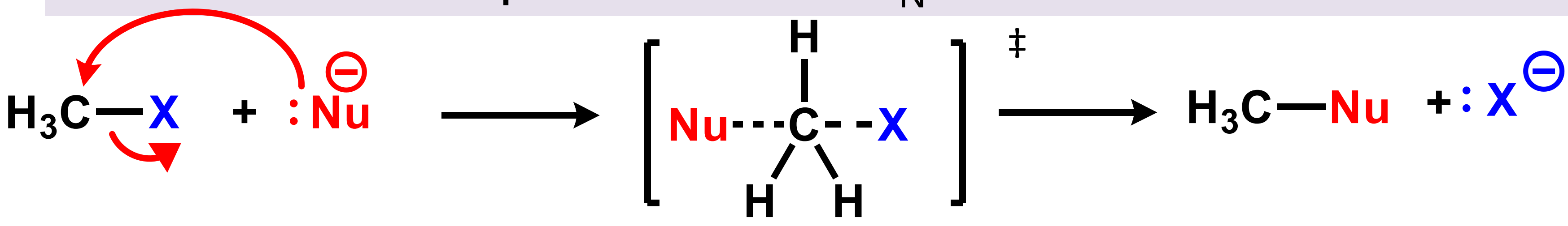

transition state

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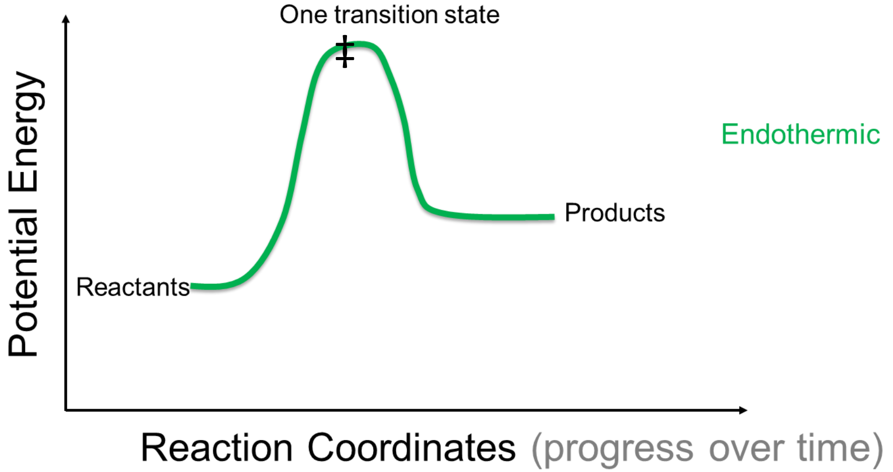
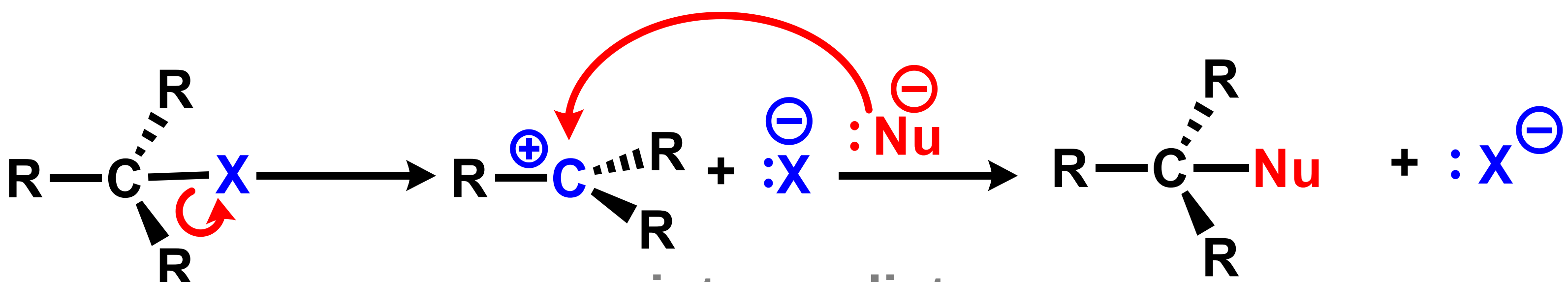


Nucleophilic Substitution Reactions

Two nucleophilic substitution (SN) reaction mechanisms

S_N1: 1 (unimolecular) = only 1 “species” is involved to get the reaction started (rate limiting step)

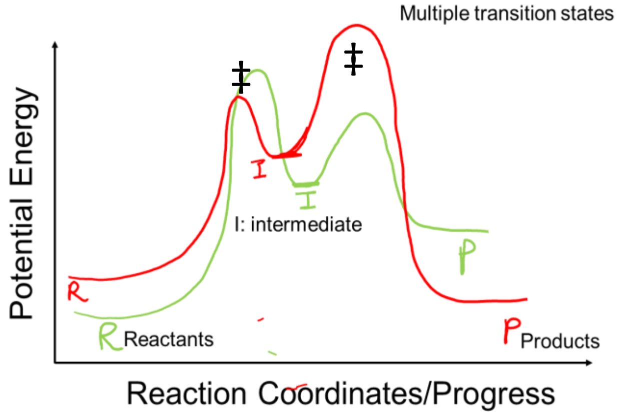
B: Reactants converted to products via more than one step: S_N1
Step 1: Heterolytic **cleavage** of C-X bond – carbocation formed
Step 2: Then nucleophile attacks the electrophile



Nucleophilic Substitution Reactions

Two nucleophilic substitution (SN) reaction mechanisms

Many "steps" in the reaction



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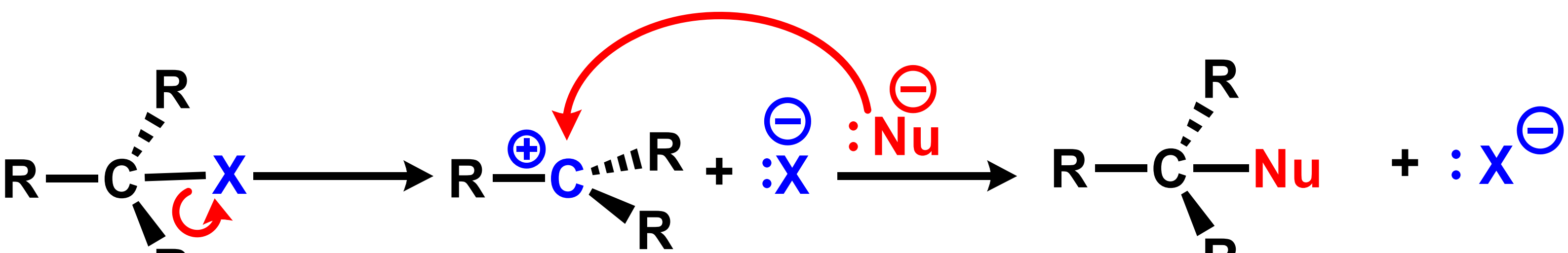
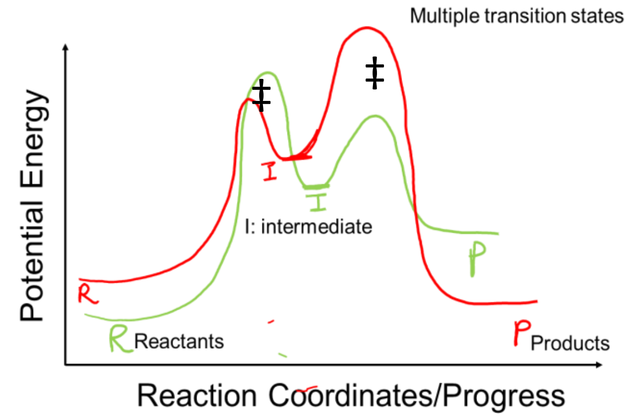
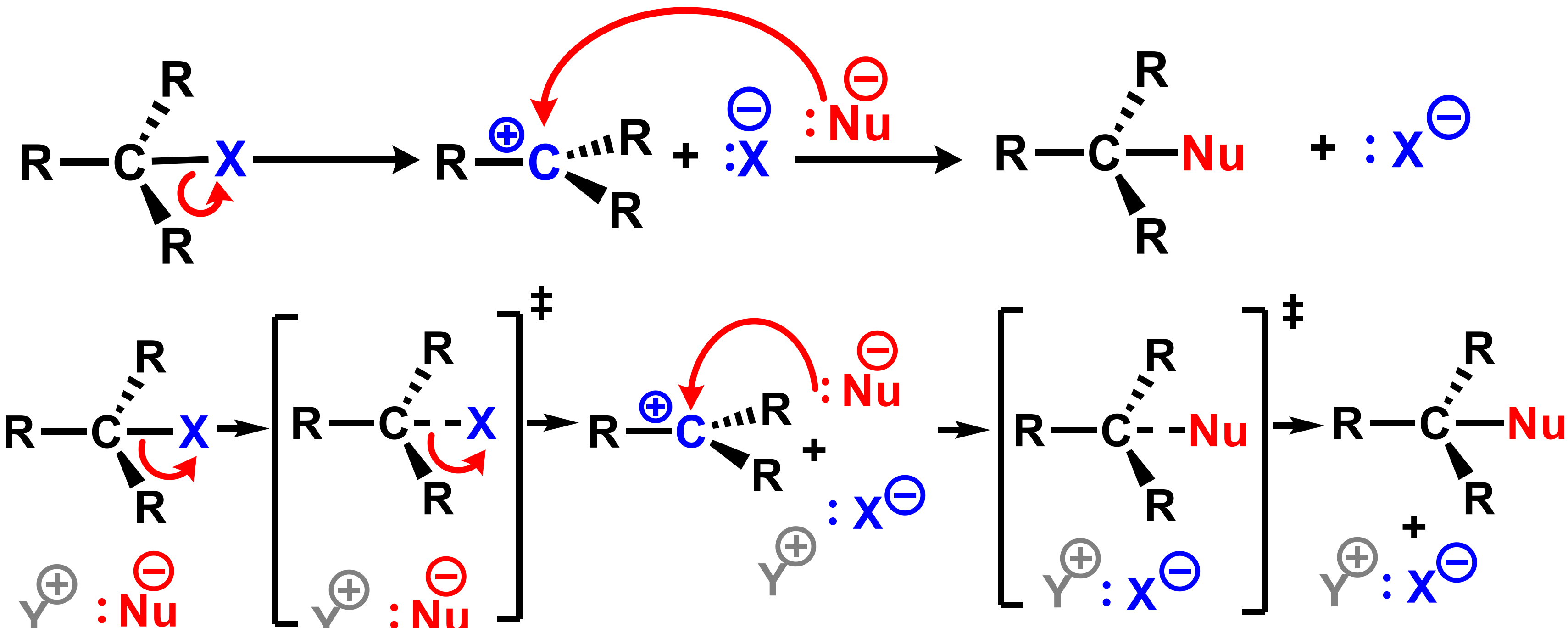


intermediate

Nucleophilic Substitution Reactions

Two nucleophilic substitution (SN) reaction mechanisms





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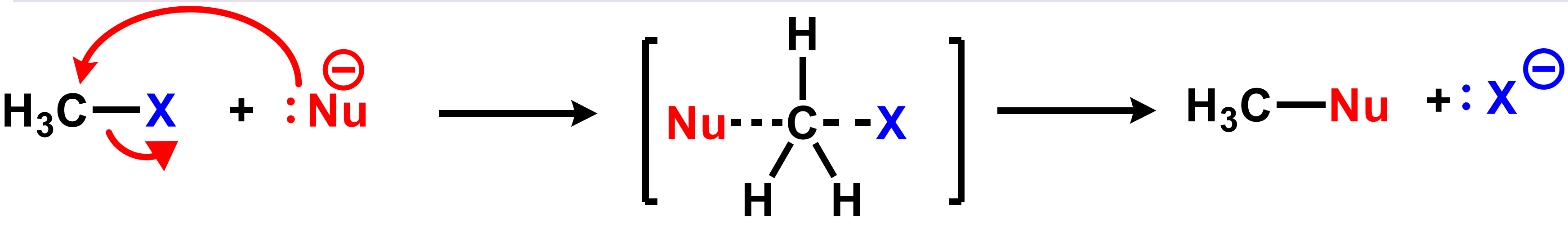

transition state

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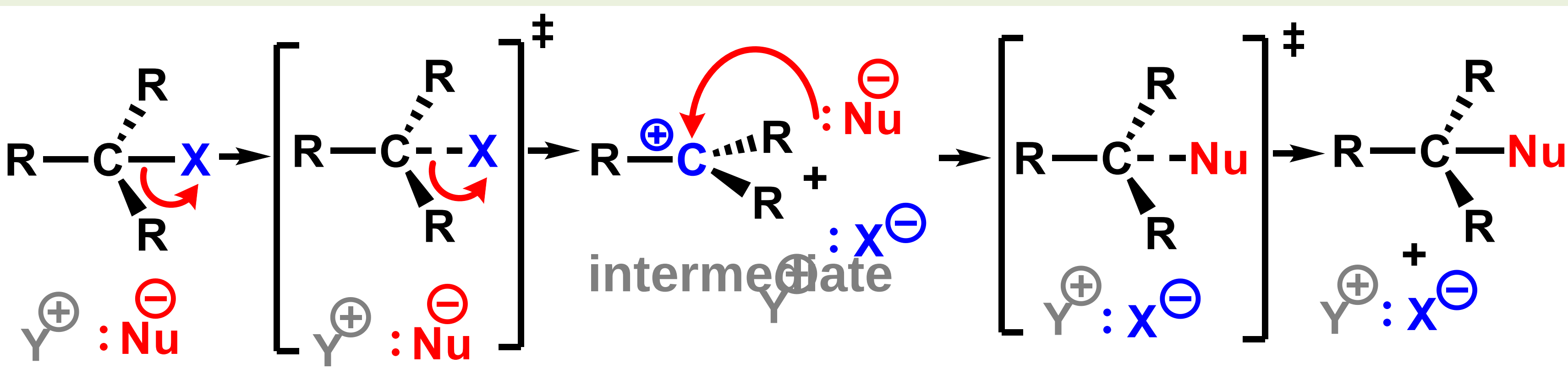
Step 1: Heterolytic **cleavage** of C-X bond – carbocation formed
Step 2: Then nucleophile attacks the electrophile



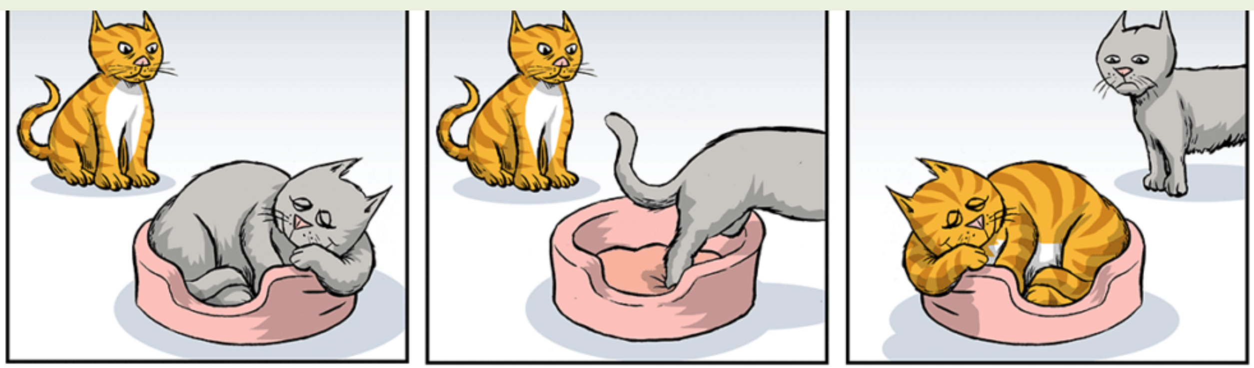
Nucleophilic Substitution Reactions

Two nucleophilic substitution (SN) reaction mechanisms

S_N2

[Transition state]

S_N1

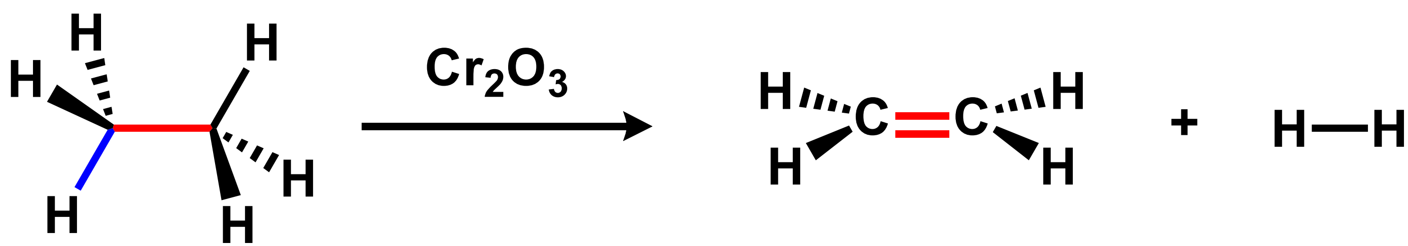


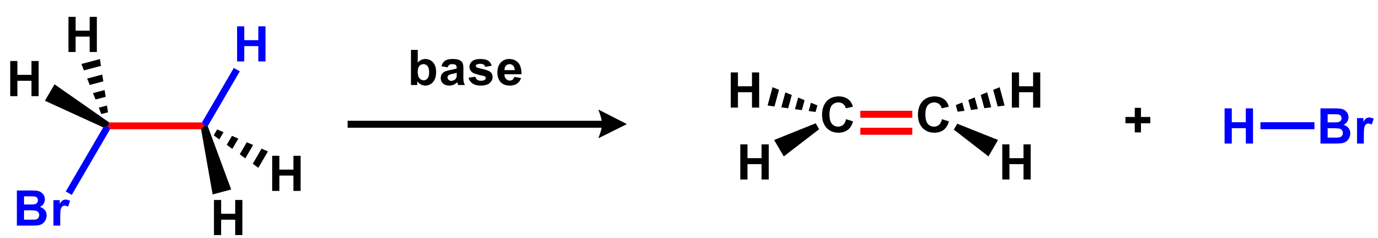
intermediate

Organic Reactions: Four main types (review)

3. Elimination

In simple terms: One molecule becomes two or more. Main reaction in preparation of π bonds/unsaturated compounds

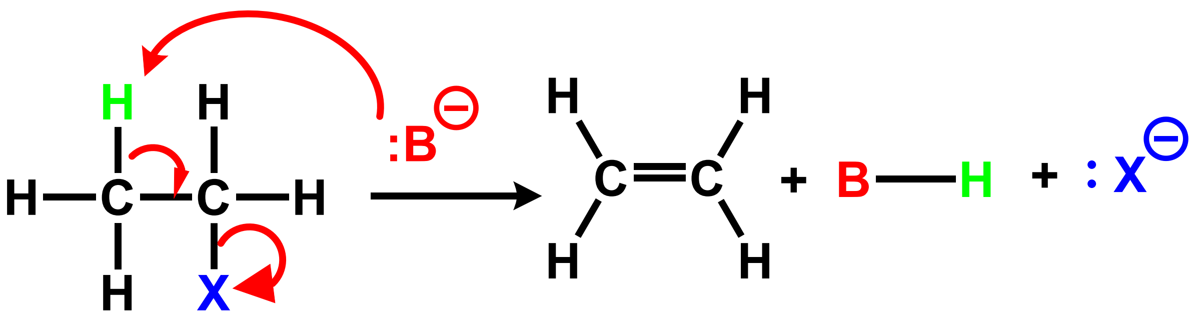




Elimination Reactions

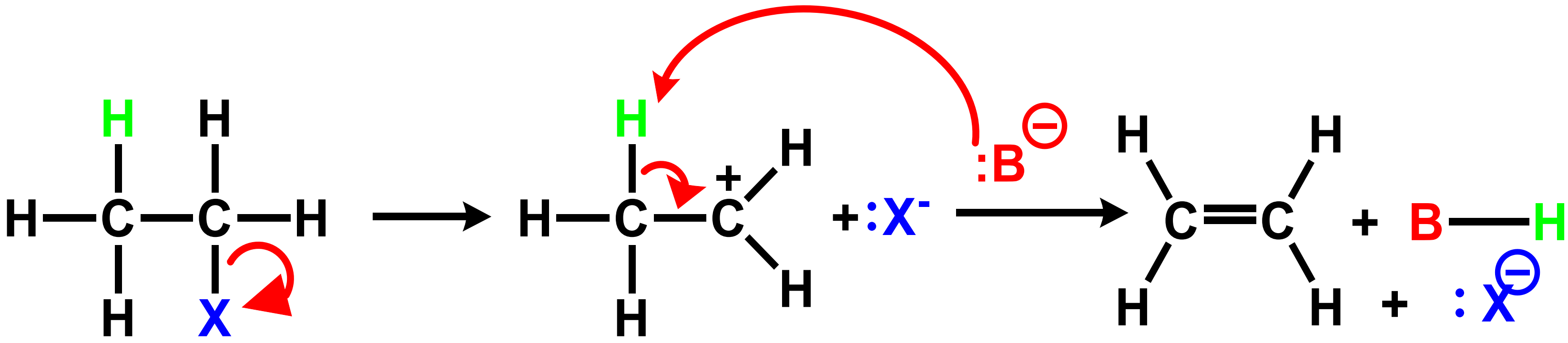
Two elimination (E) reaction mechanisms

1: Bond breaking and bond formation occur one-step: E2



Two elimination (E) reaction mechanisms

2: Reactants converted to products via more than one step: E1
Step 1: Heterolytic cleavage of C-X bond – carbocation formed
Step 2: Nucleophile attacks the electrophile



Elimination Reactions

Two elimination (E) reaction mechanisms

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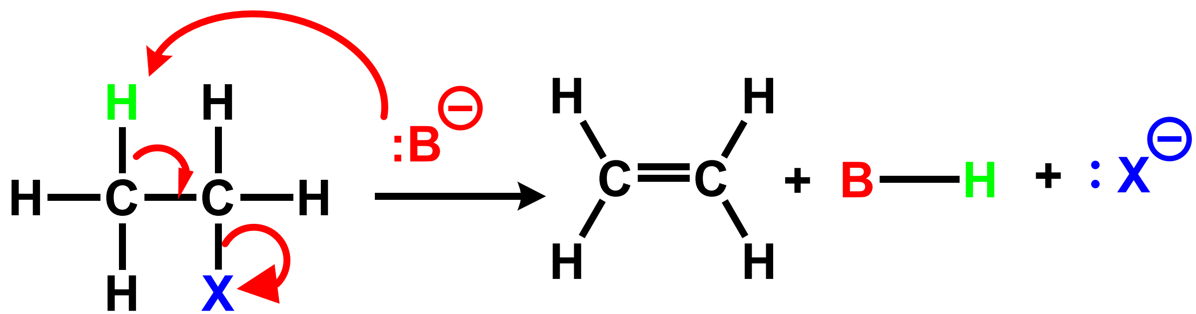

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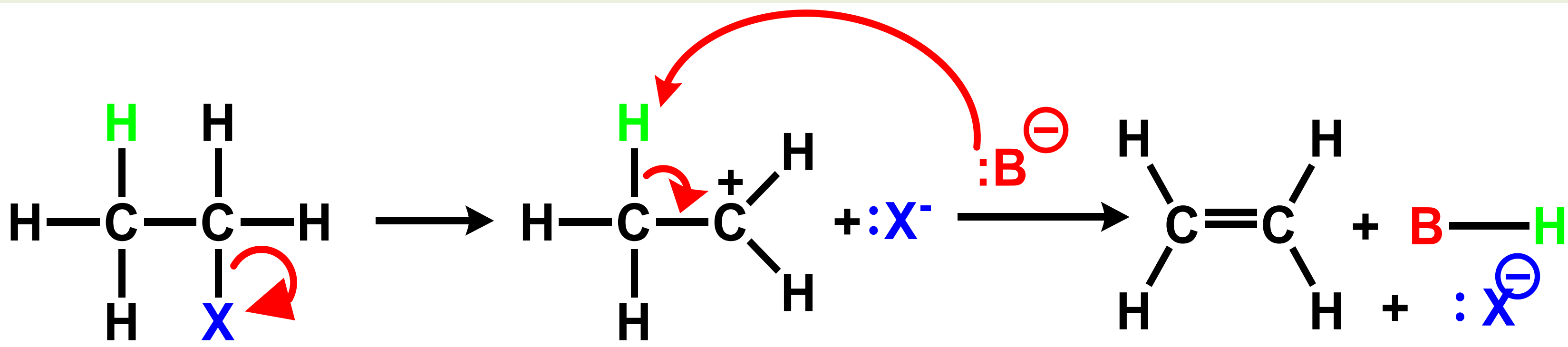


Intro to Organic Reactions

Nov 18-22

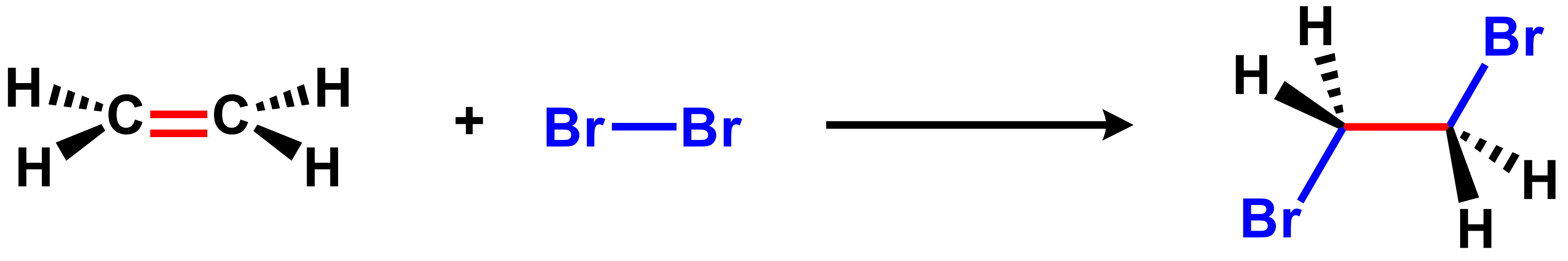
Concept Video 33

Additions to Alkenes

Organic Reactions: Four main types (review)

2. Addition

Reagent adds to substrate (two molecules become one!)
– characteristic of π bonds/unsaturated compounds



How is it made? Hydrogenation in fats/oils

Hydrogenation: Addition of molecular hydrogen (usually in the presence of a catalyst)

Hydrogenation

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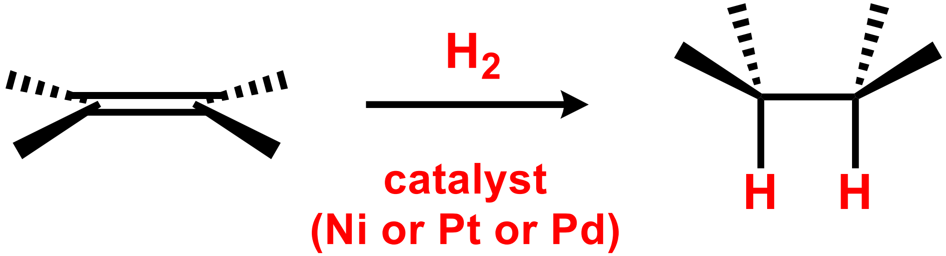
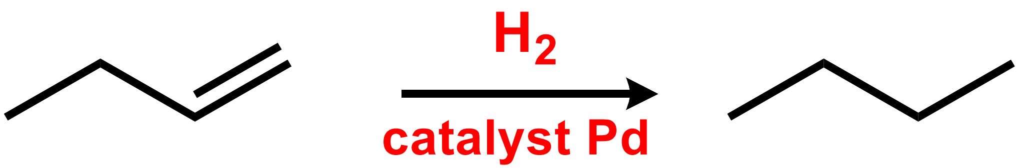
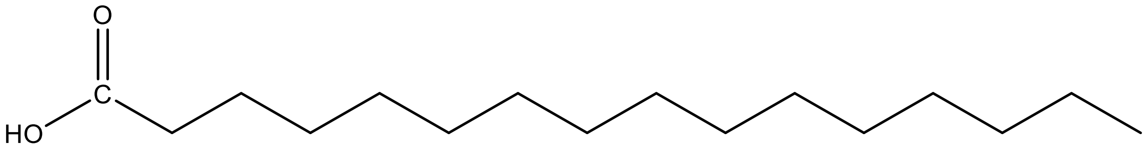


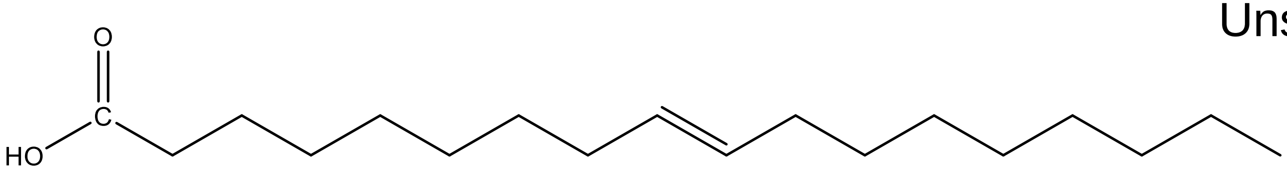


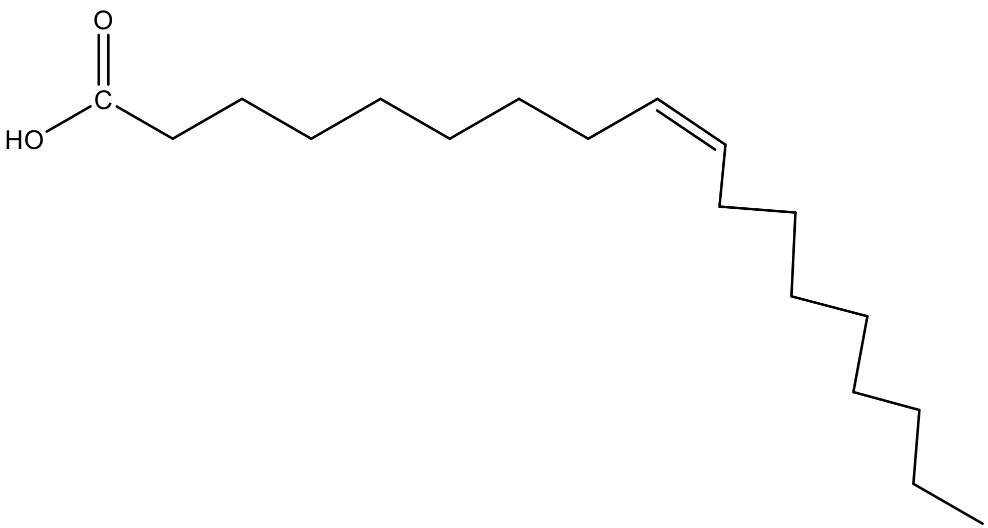
Hydrogenation in fats/oils



Saturated Fatty Acid

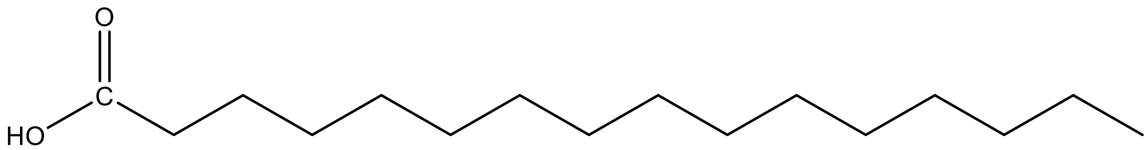
Unsaturated Fatty Acid





Look at the geometric isomers!
Are they cis or trans?

Hydrogenation in fats/oils



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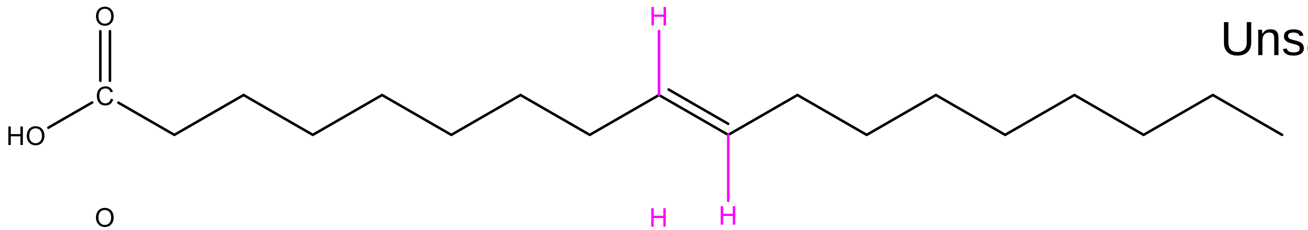
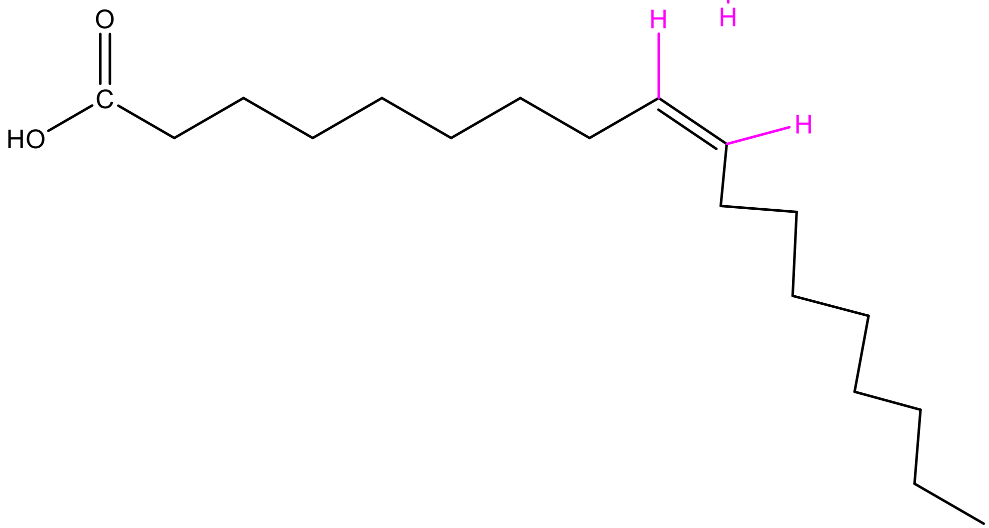


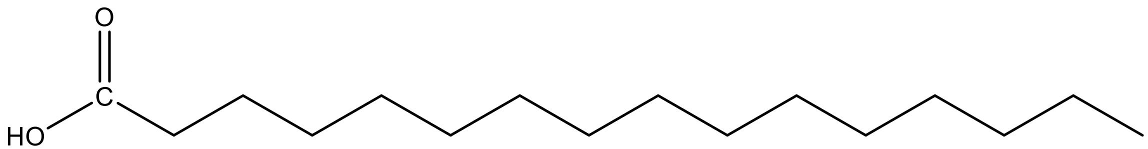
Unsaturated Fatty Acid

Trans

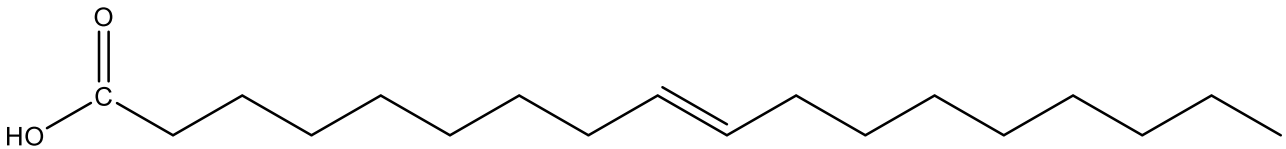


Cis

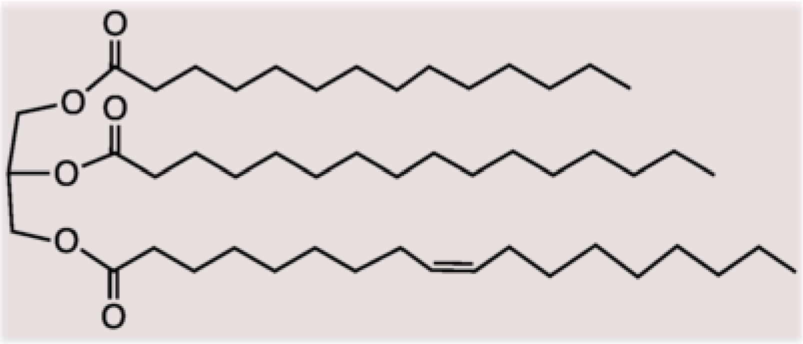
Hydrogenation in fats/oils



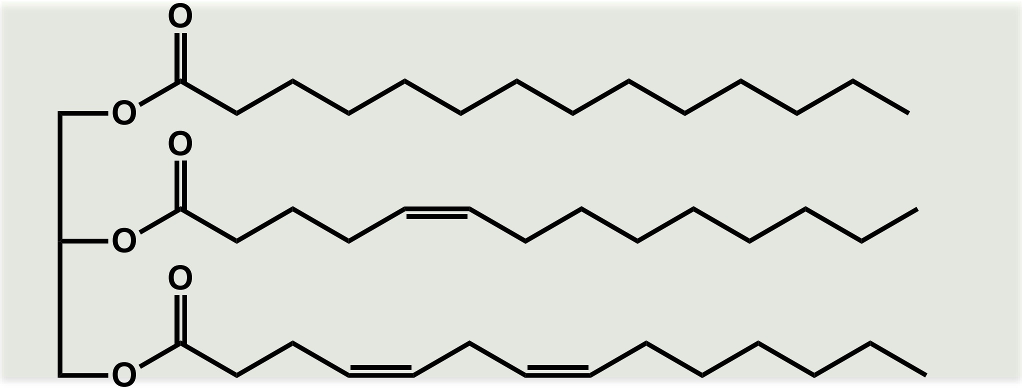
Saturated Fatty Acid



Unsaturated Fatty Acid



Monounsaturated

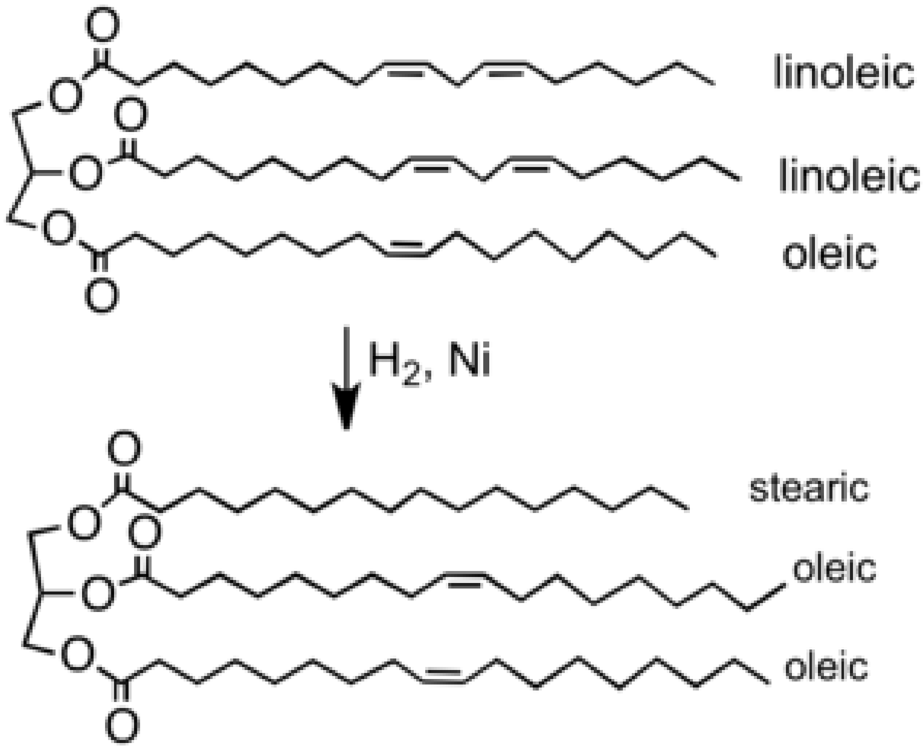


Oils

Polyunsaturated

Hydrogenation in fats/oils

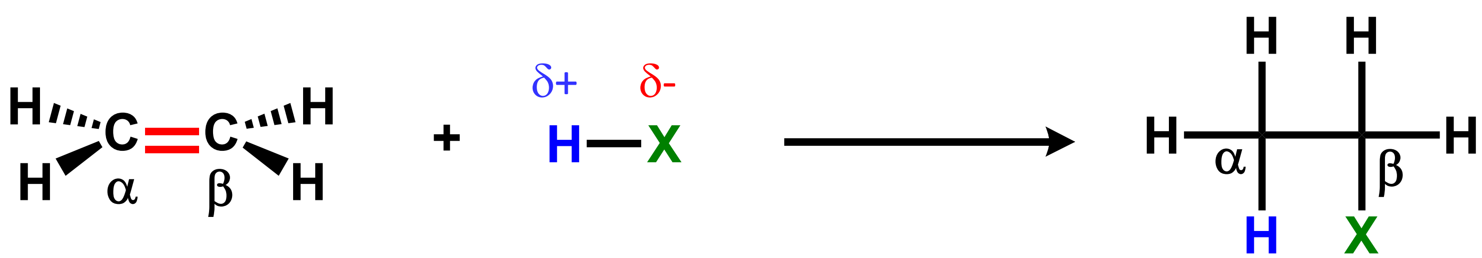
Hydrogenation: Addition of molecular hydrogen (usually in the presence of a catalyst)



ELECTROPHILE – hydrogen of H-X (or other δ+ of x-X reagent)

NUCLEOPHILE – "attacking" π bond

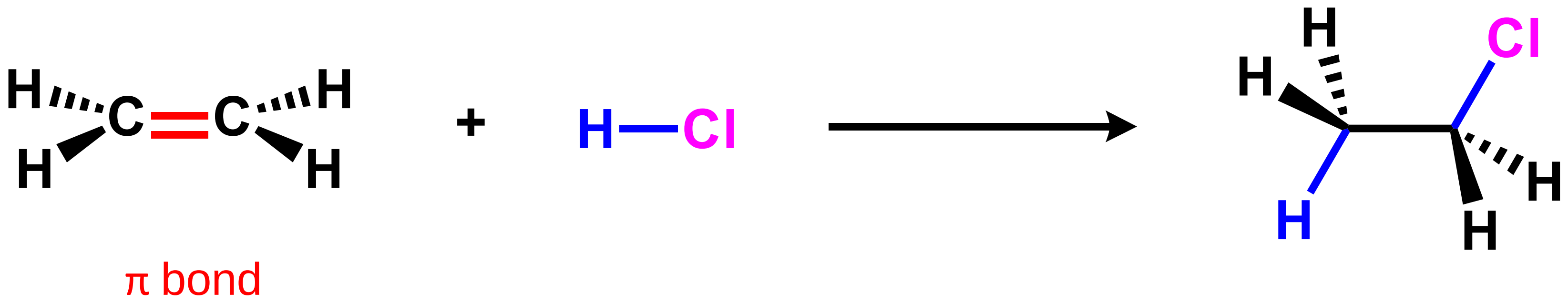
ADDITION OF STRONG ACIDS: addition of **HX**



*** *addition* reactions = nucleophile "attacks" electrophile ***

Electrophilic Addition to Alkenes

Addition Reaction of strong acids: **Symmetric alkenes**



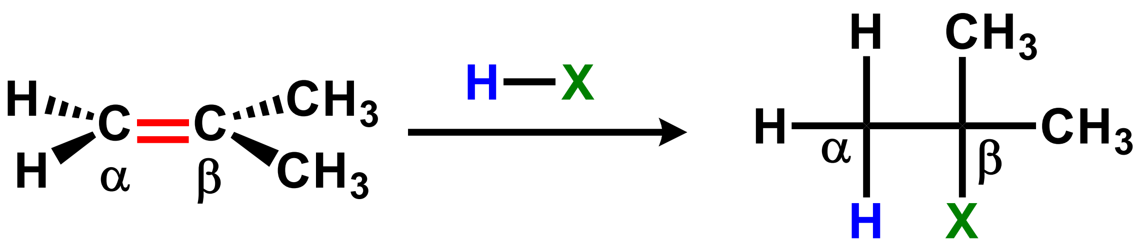
What if you have an asymmetric alkene??

- **WHERE DO YOU ADD THE "H" & "X"?**

  ...USE MARKOVNIKOV'S RULE, OF COURSE!

Electrophilic Addition to Alkenes

Addition Reaction of strong acids: Asymmetric alkenes



Markovnikov's rule: **hydrogen adds to the carbon in the double bond that has more hydrogen atoms**, and **the halogen adds to the carbon with fewer hydrogen atoms**

"the rich get richer"