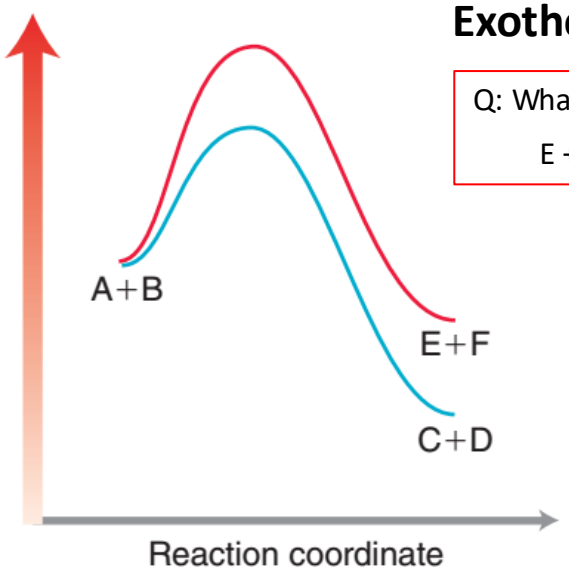


Nucleophiles, Electrophiles & Arrow Pushing

Exothermic vs. Endothermic

Q: What type of reaction is:

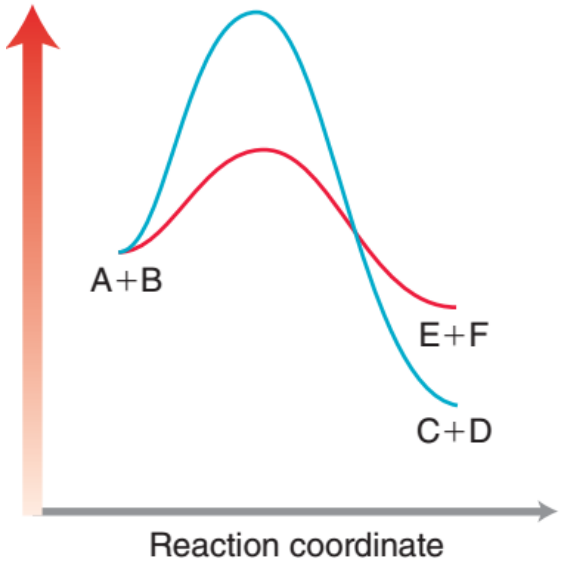
E + F ——> A + B



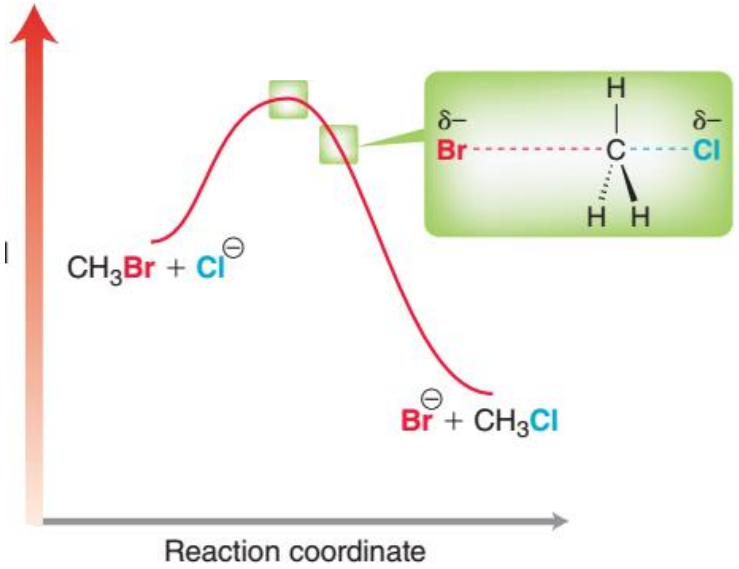
Kinetic vs. Thermodynamic

Q: What type of reaction is:

A + B ——> C + D

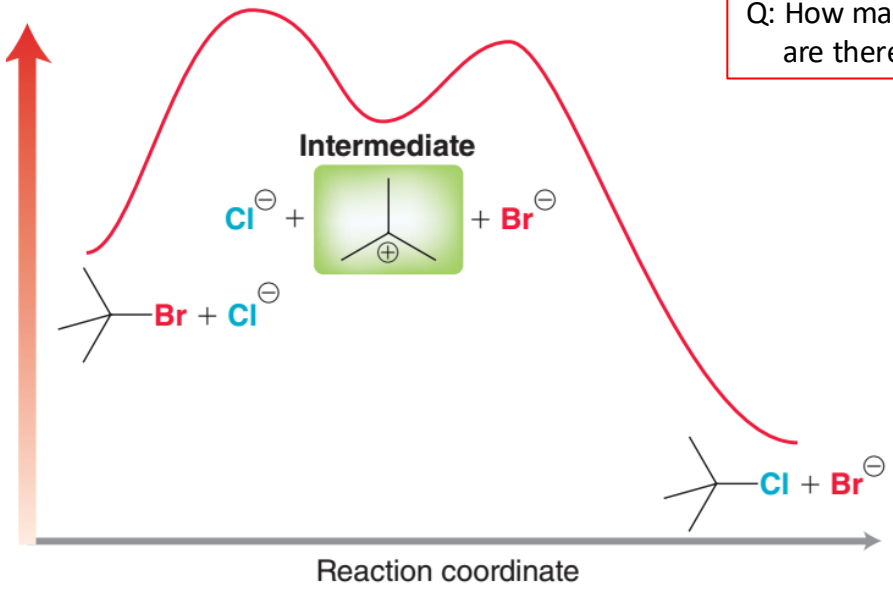


The Hammond Postulate



Intermediates vs. Transition States

Q: How many transition states are there in this reaction?



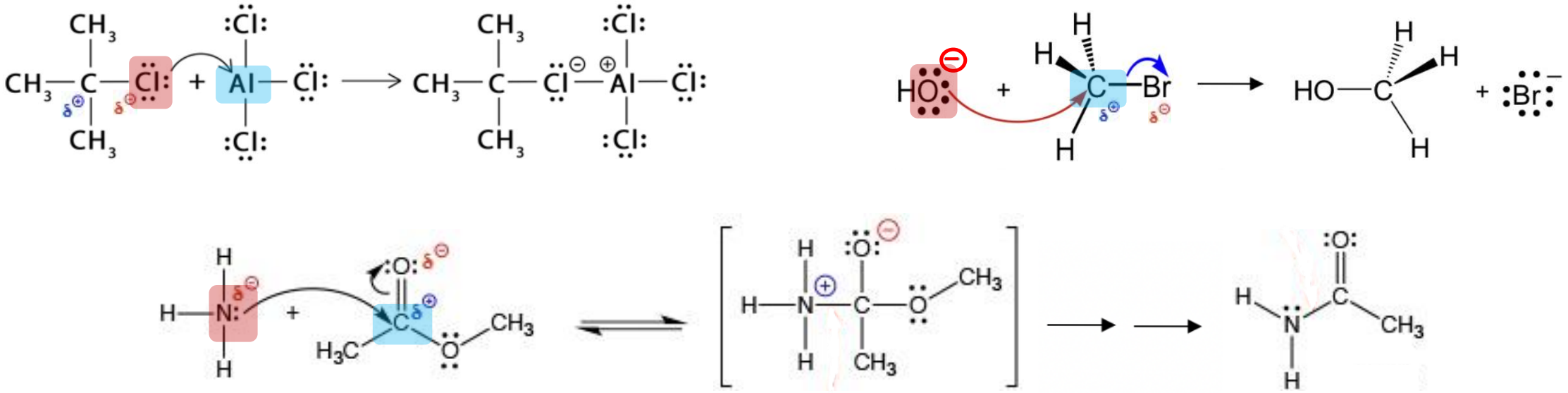
Nucleophiles & Electrophiles: How do we identify each class of compounds?

A **Nucleophile** is electron-_____ atom & reacts with a _____ charge

- Nuc^- form new bonds by attacking exposed $Elec^+$ centers and give away Nuc^- *electrons*.
- Nuc^- can make new bonds by holding a strong negative charge and being streamlined.

An **Electrophile** is electron- _____ atom & reacts with a _____ charge.

- $Elec^+$ form new bonds by being attacked by Nuc^- and receiving Nuc^- *electrons*.
- $Elec^+$ can make new bonds by either: (a) **having** space in their "octet" or an empty *p* orbital.
  (b) **making** space by opening a π bond or "



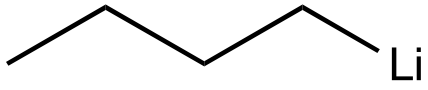
Nucleophiles & Electrophiles: What are some easy ways to spot them within compounds?

Nucleophilic Identifiers	Electrophilic Identifiers
1.	1.
2.	2.
3.	3.

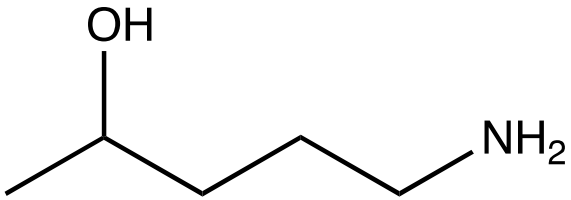
2

Indicate the **electrophilic** and **nucleophilic** centers.

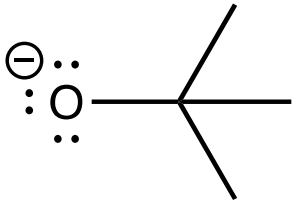
a)



b)



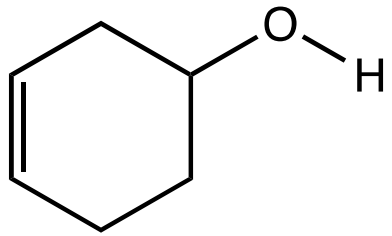
c)



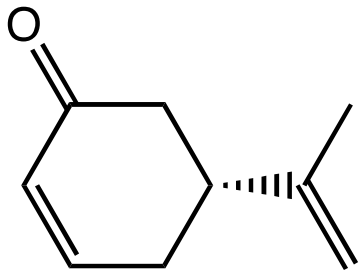
d)



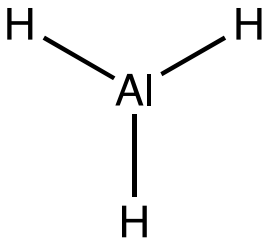
e)



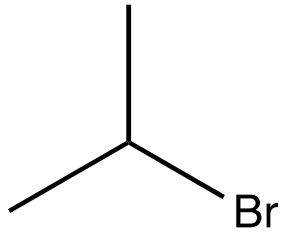
f)



g)



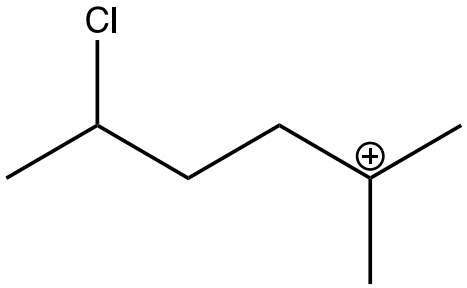
h)



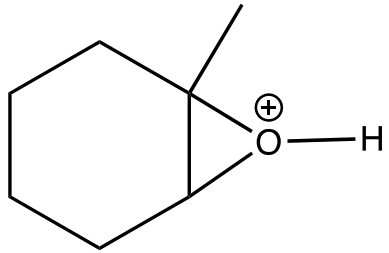
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Indicate the **electrophilic** and **nucleophilic** centers.

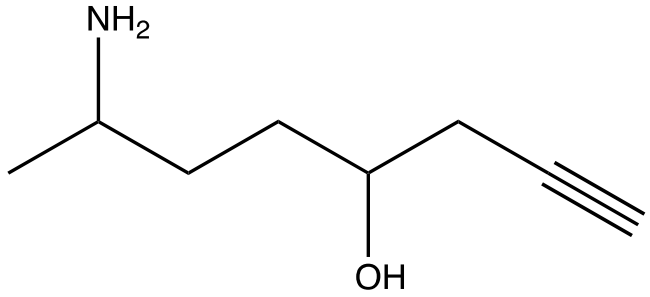
a)



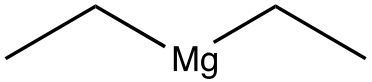
b)



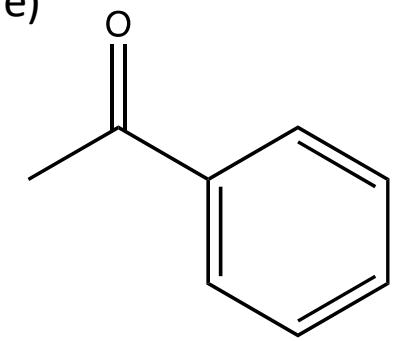
c)



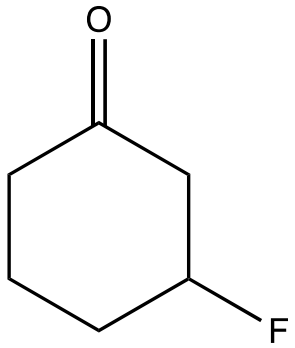
d)



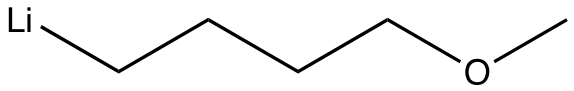
e)



f)



g)



h)



4

What are the four types of **arrow pushing mechanisms**?

1.

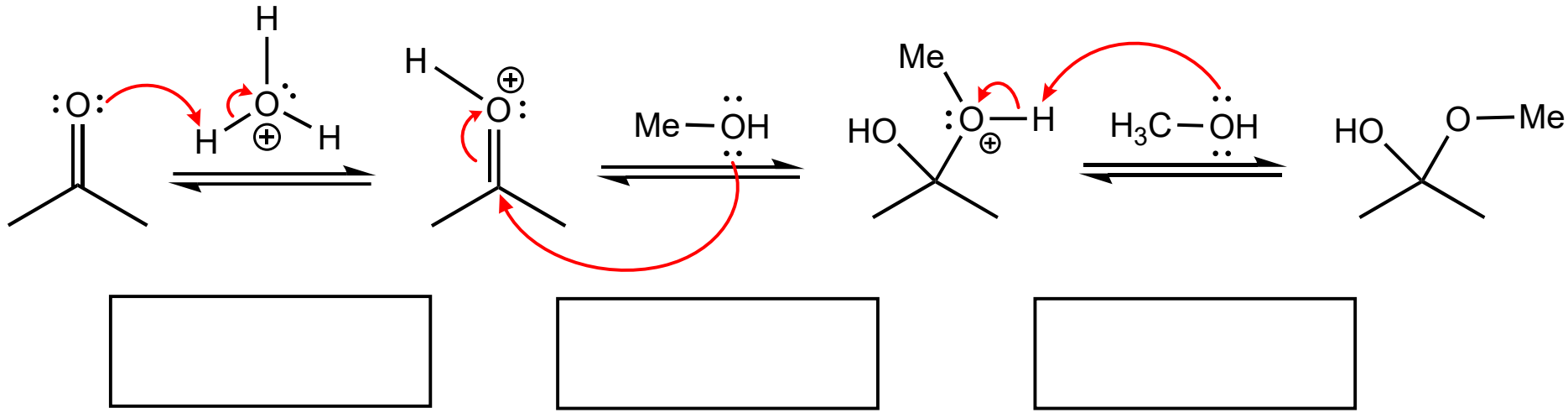
2.

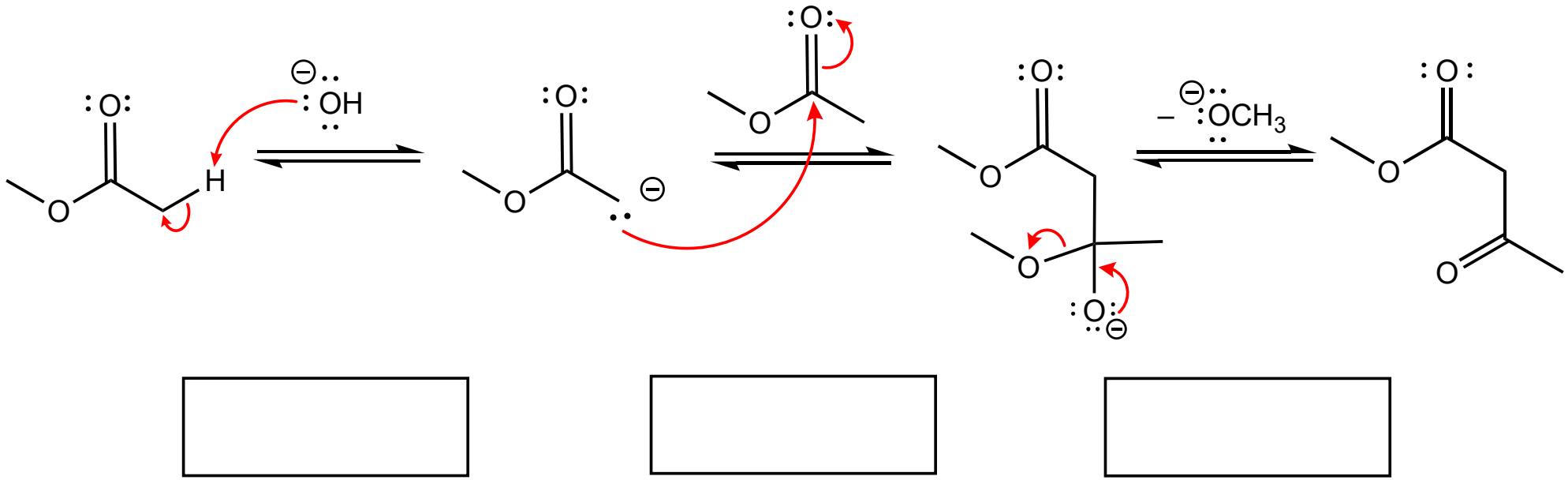
3.

4.

5

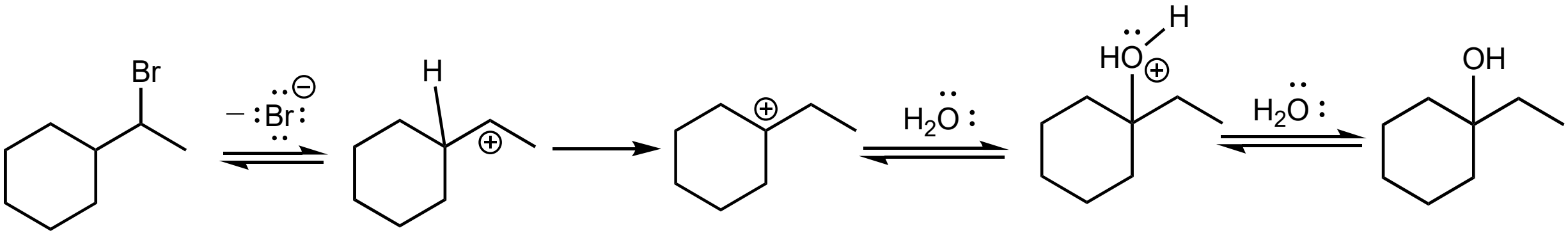
Identify the sequence of curved arrows (electron movement) in the steps of the following reactions:





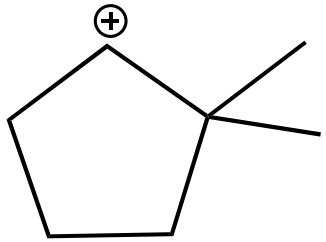
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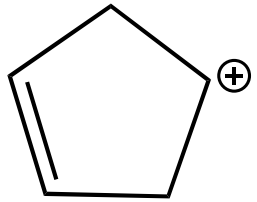
Draw the electron pushing arrows and identify the arrow pushing mechanism in the following:

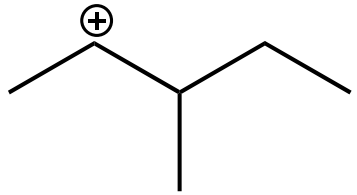


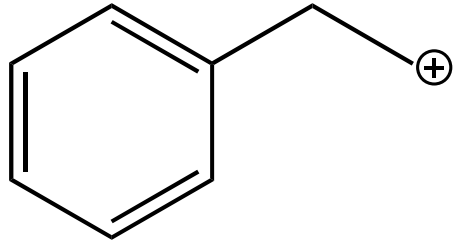
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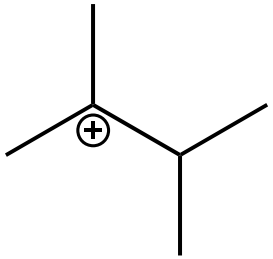
Predict which of the following carbocations will rearrange. If so, draw the expected arrangement using curved arrows.

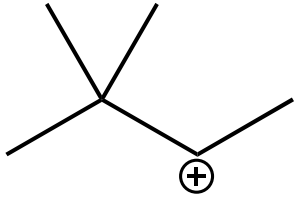


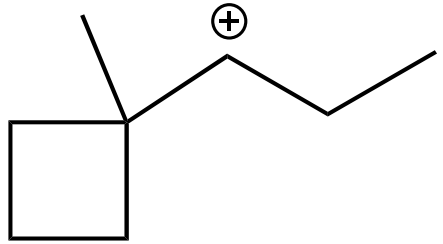


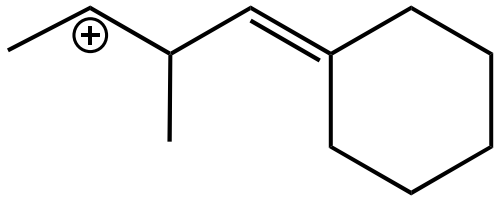






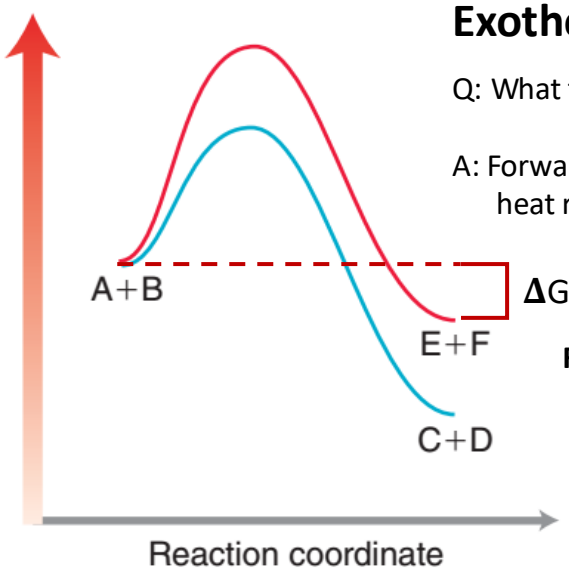






ANSWER KEY

Exothermic vs. Endothermic



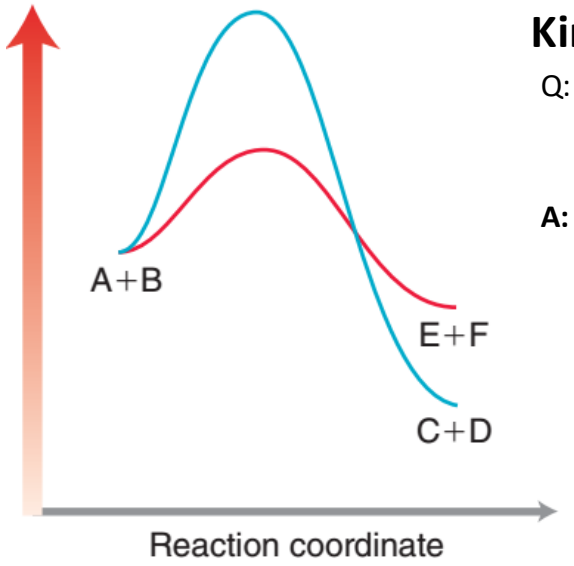
Q: What type of reaction is: E + F ——> A + B

A: Forward reaction (A + B → E + F) is exothermic, heat released.

ΔG = (–)

Reverse reaction (E + F → A + B) is endothermic, heat absorbed.

Kinetic vs. Thermodynamic



Q: What type of reaction is:

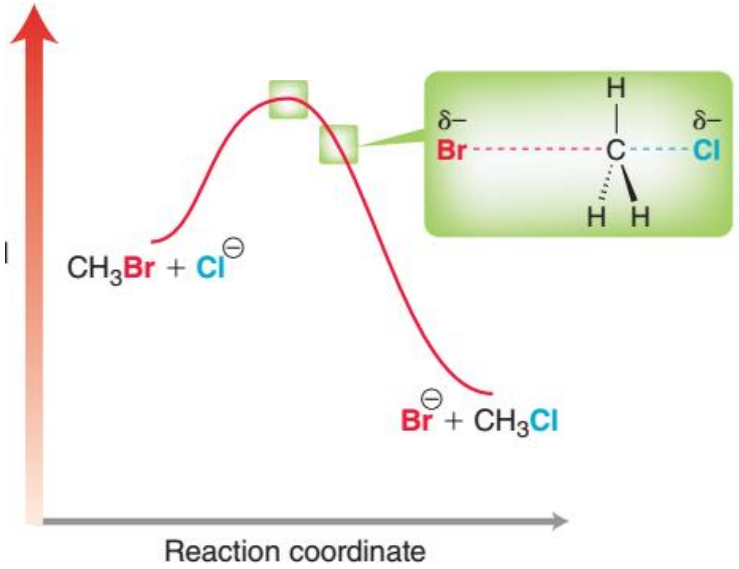
A + B ——> C + D

A: Thermodynamic

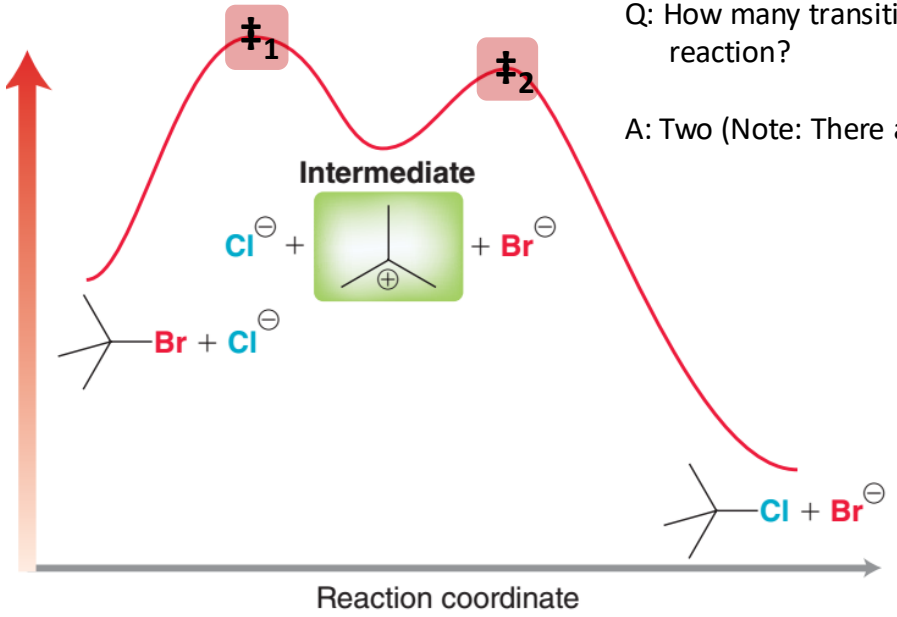
Formation of E + F is faster due to lower energy transition state (lower E_A).

Formation of C + D is slower (due to higher energy E_A) but results in lower energy (more stable) product.

The Hammond Postulate



Intermediates vs. Transition States



Q: How many transition states are there in this reaction?

A: Two (Note: There are 2 peaks).

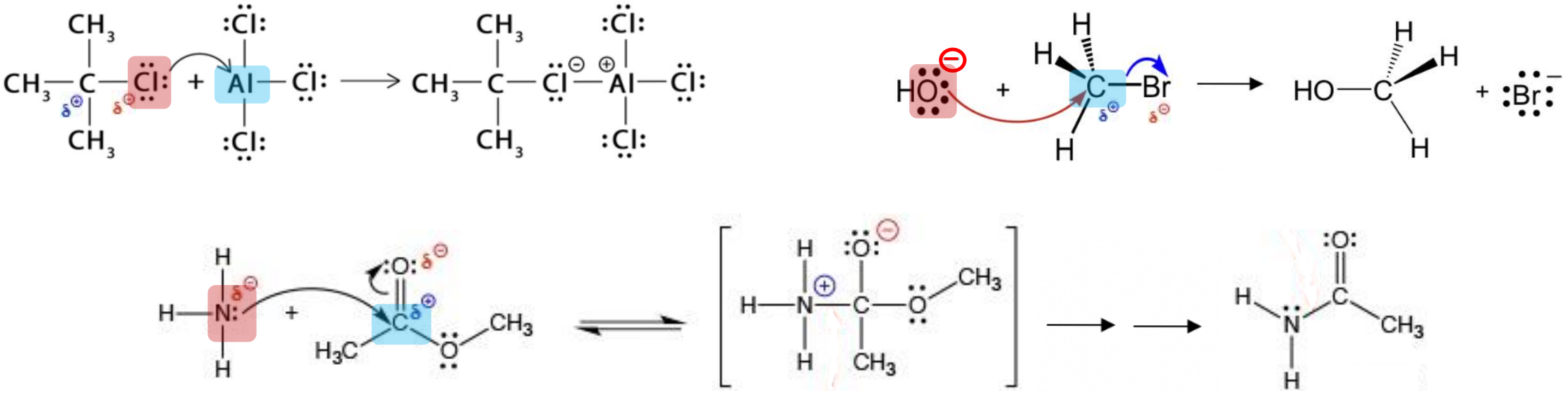
Nucleophiles & Electrophiles: How do we identify each class of compounds?

A **Nucleophile** is an electron-rich atom capable of reacting with a (+) *or* δ(+) charge

- Nuc^- form new bonds by attacking exposed $Elec^+$ centers and give away Nuc^- *electrons*.
- Nuc^- can make new bonds by holding a strong negative charge and being streamlined.

An **Electrophile** is an electron-poor atom capable of reacting with a (–) *or* δ(–) charge.

- $Elec^+$ form new bonds by being attacked by Nuc^- and receiving Nuc^- *electrons*.
- $Elec^+$ can make new bonds by either: (a) **having** space in their "octet" or an empty *p* orbital.
  (b) **making** space by opening a π bond or "

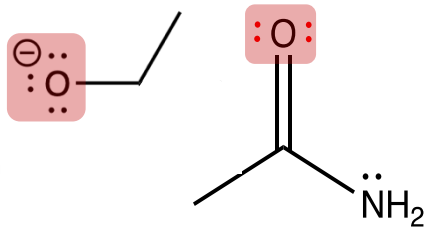


Nucleophiles & Electrophiles: What are some easy ways to spot them within compounds?

Nucleophilic Identifiers

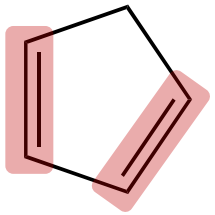
1. ⊖ Charge on Lone Pairs

Neutral LPs are still nucleophiles, though they are weaker ("neutral") compared to their (–) counterparts.

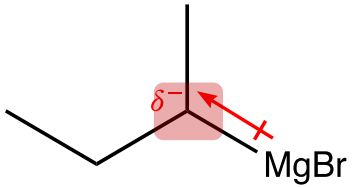


2. π Bond Electrons

Pi bonds are sources of e^- density with *or* without explicit δ^-

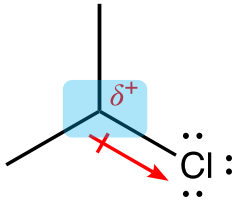


3. Polar Bonds with δ^-



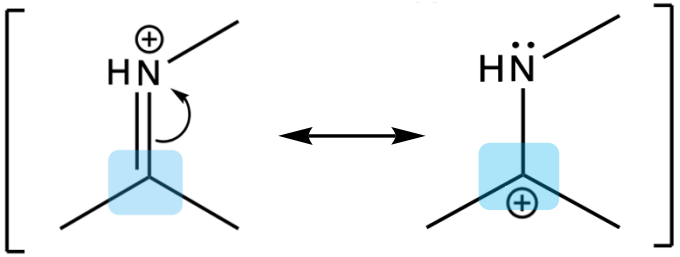
Electrophilic Identifiers

1. Polar Bonds with δ^-



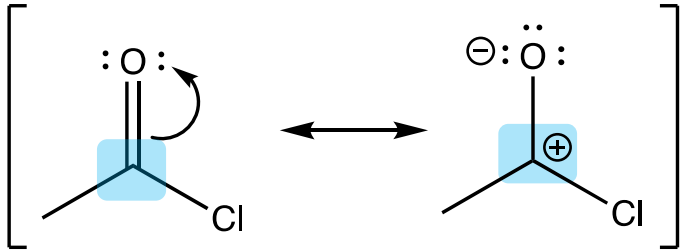
2. π Bonds with δ^+

Pi bonds can open to reveal δ^+ charge in the hybrid structure.



3. Empty *p* Orbitals

- carbocations
- Lewis acids (BH_3)



2

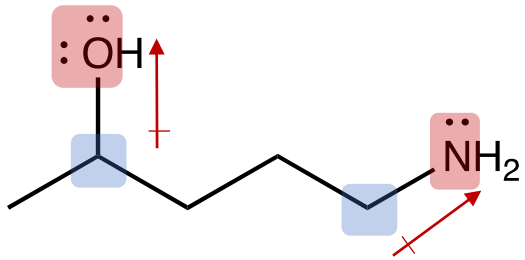
Indicate the **electrophilic** and **nucleophilic** centers.

a)

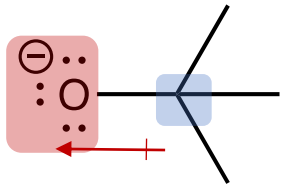


Groups 1-2 cannot be Elec⁺

b)

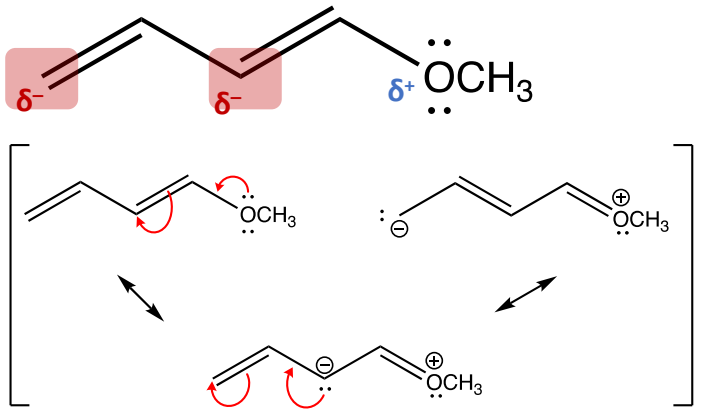


c)

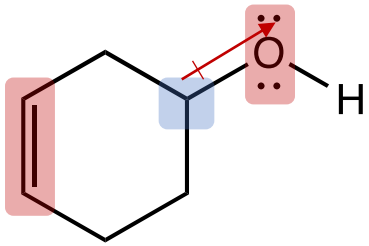


d)

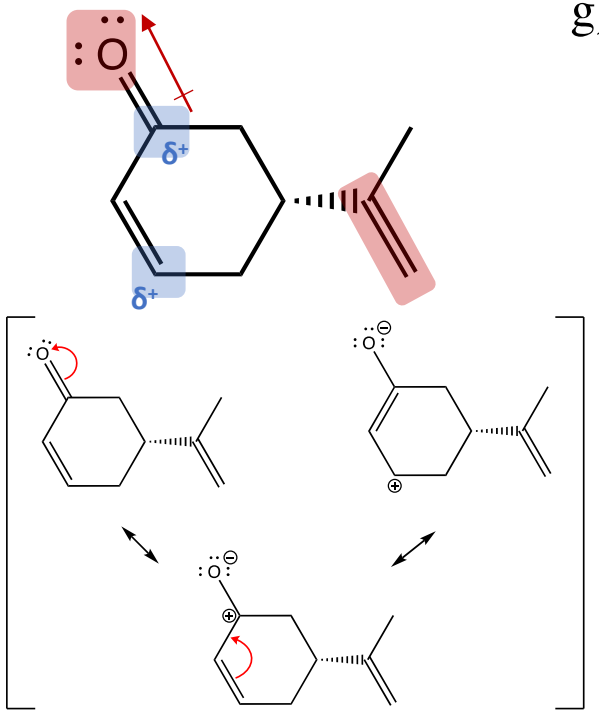
The O's LPs are **not** nucleophilic the O is (+) according to resonance. The O's LPs are also in resonance, making them even less nucleophilic, even without considering O's resultant charge.



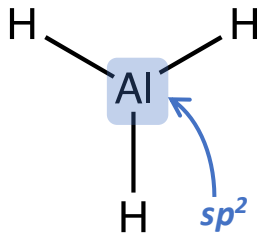
e)

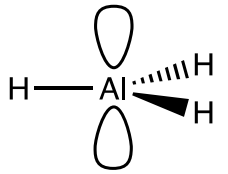


f)



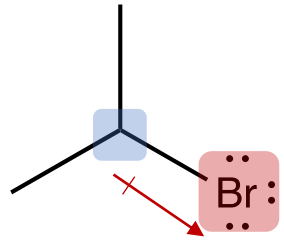
g)





Group 3 metals have an empty p orbital that is electrophilic.

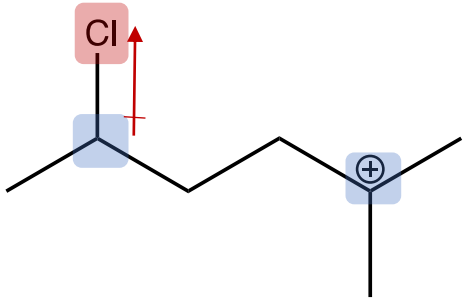
h)



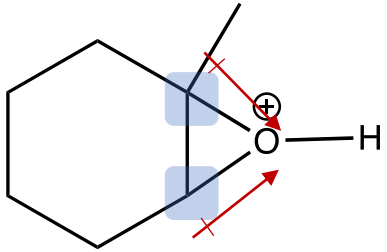
3

Indicate the **electrophilic** and **nucleophilic** centers.

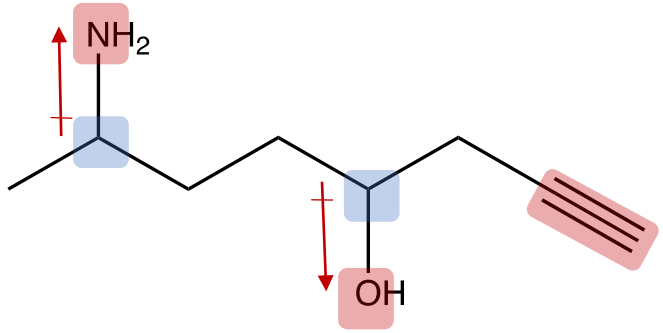
a)



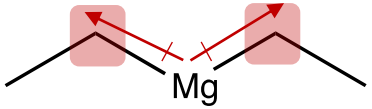
b)



c)

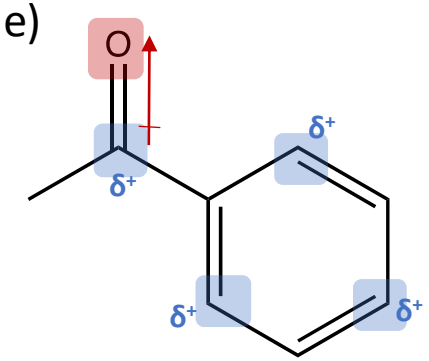


d)

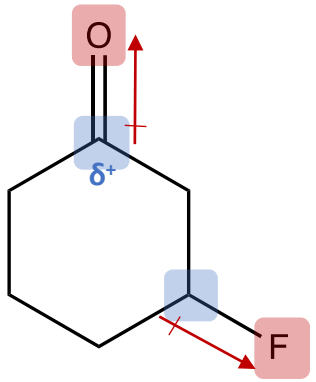


Group 1 and 2 metals cannot be electrophiles

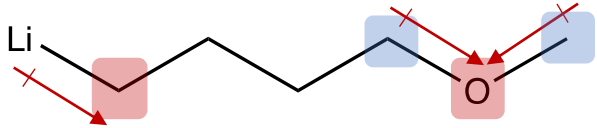
e)



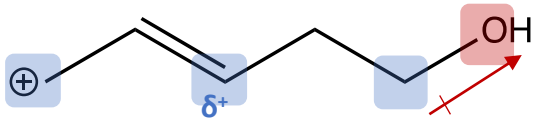
f)



g)



h)



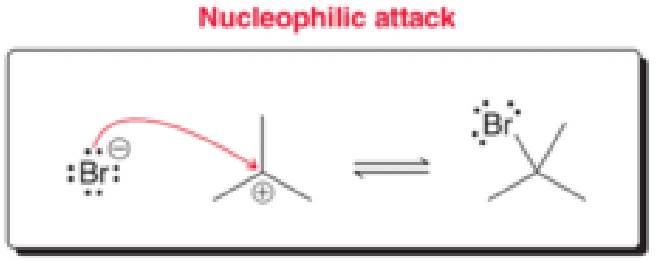
What are the four types of **arrow pushing mechanisms**?

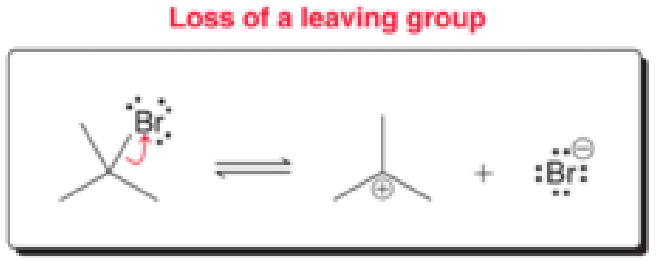
1. **Nucleophilic Attack**
   - nucleophile shares e^- with electrophile
   - can be *inter-* or *intra*-molecular

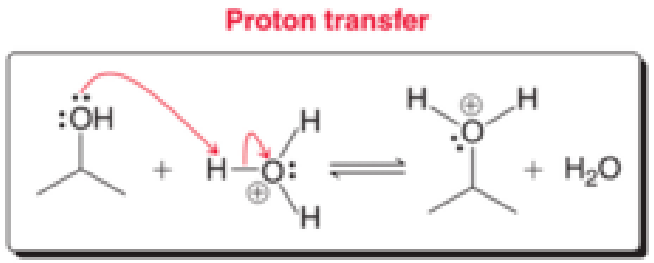
2. **Loss of Leaving Group (LG)**
   - LG takes pair of e^- and goes on vacation
     - maybe it comes back if it can't find something better to do

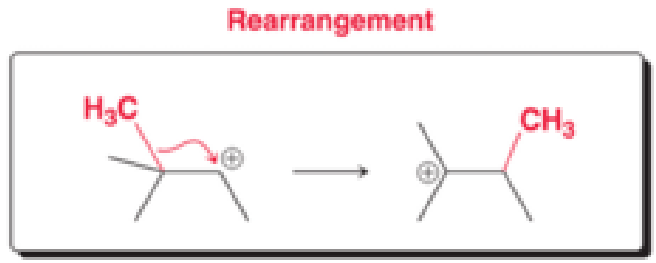
3. **Proton Transfer**
   - acid-base step
   - can be *inter-* or *intra*-molecular

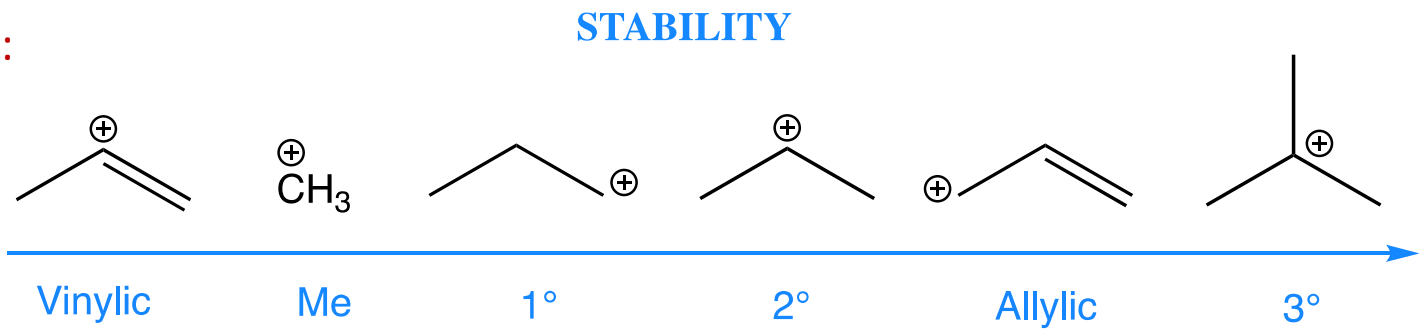
4. **Rearrangement**
   - occurs to form more stable carbocation:
     - Hydride Shift – shift of $H:^-$
     - Methyl Shift – shift of $^-:CH_3$





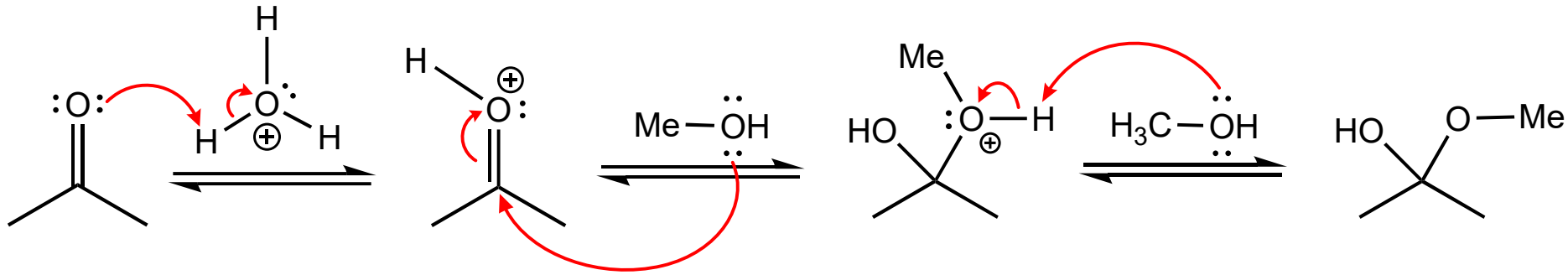




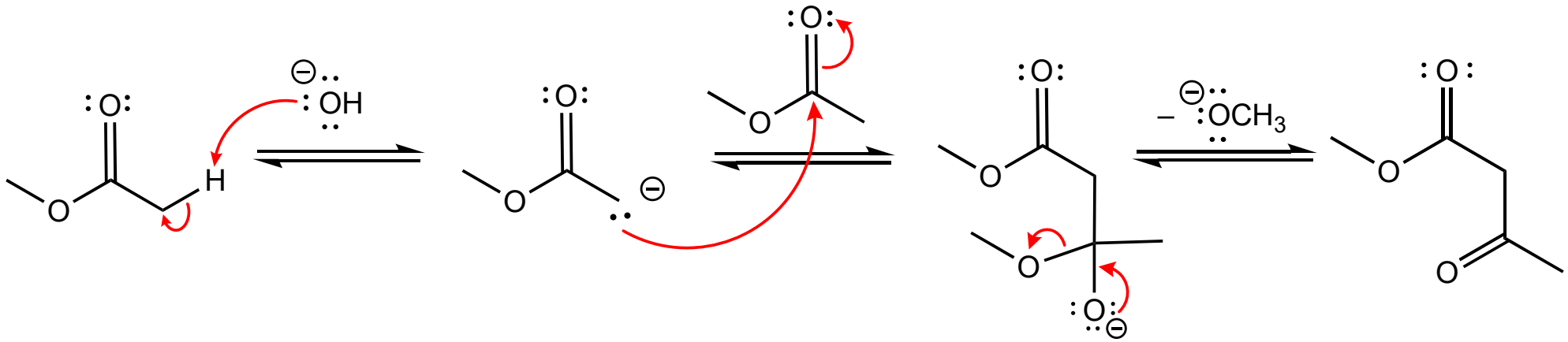


5

Identify the sequence of curved arrows (electron movement) in the steps of the following reactions:



Proton Transfer | **Nuc⁻ Attack** | **Proton Transfer**



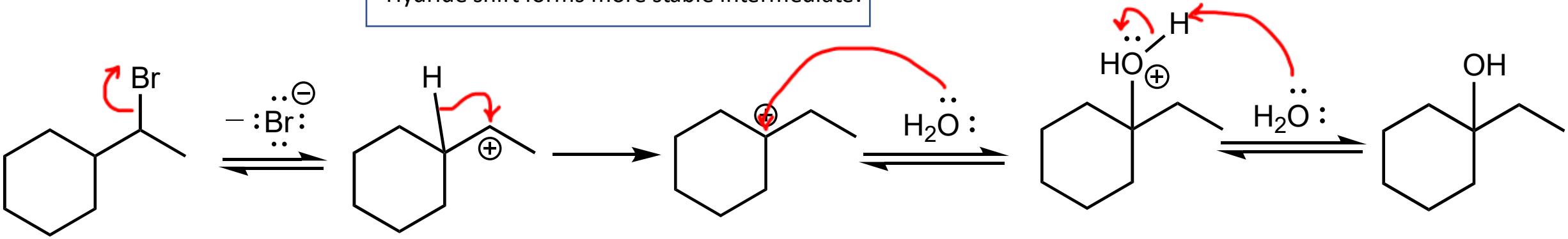
Proton Transfer | **Nuc⁻ Attack** | **Loss of LG**

6

Draw the electron pushing arrows and identify the arrow pushing mechanism in the following:

2° carbocation < **3° carbocation**

Hydride shift forms more stable intermediate.

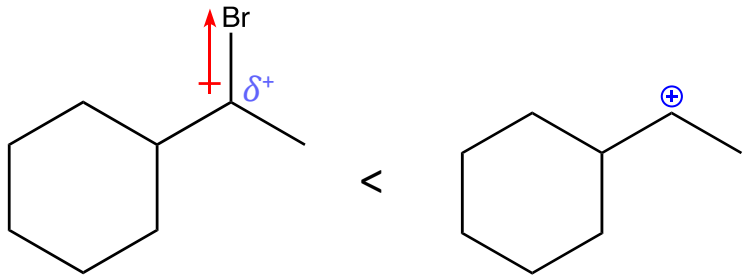


Loss of LG

Hydride Shift

Nucleophilic Attack

Proton Transfer



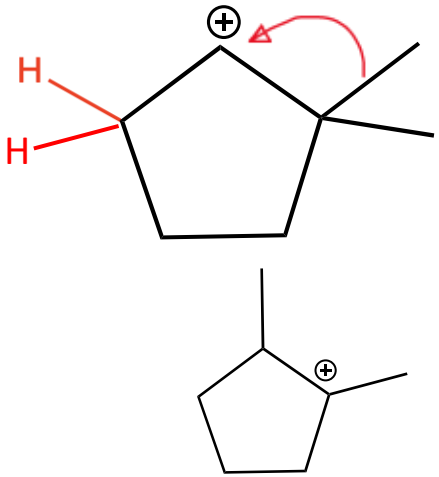
Bromide leaves to form a stronger electrophile.

A strong (i.e. charged) electrophile is required because H_2O is a weak (i.e. neutral, non-charged) nucleophile.

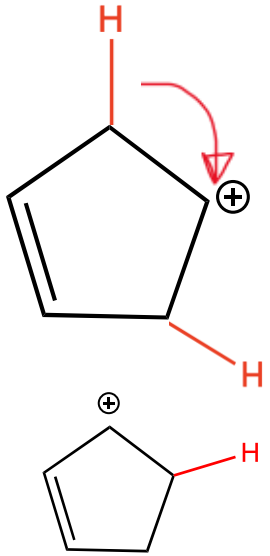
A proton transfer forms a more stable (i.e. neutral) product.

7

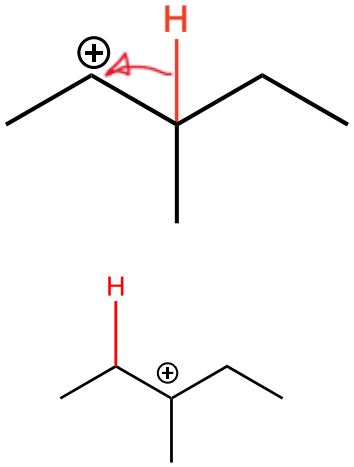
Predict which of the following carbocations will rearrange. If so, draw the expected arrangement using curved arrows.



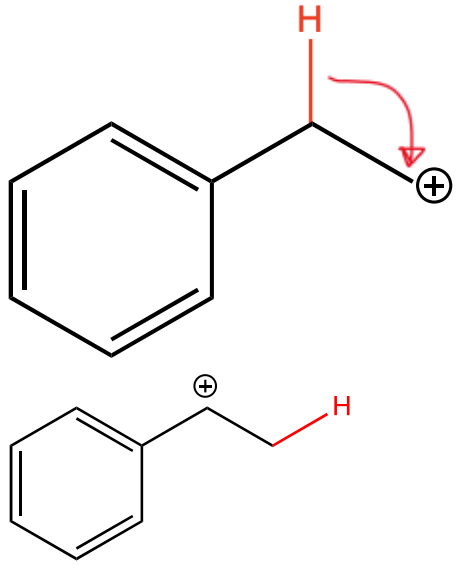
From **2°** to **3°** with Me shift.



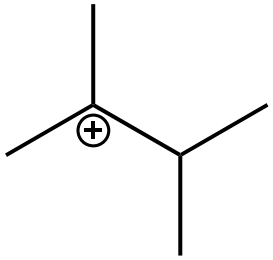
From **2°** to **2° allylic** with hydride shift.



From **2°** to **3°** with hydride shift.

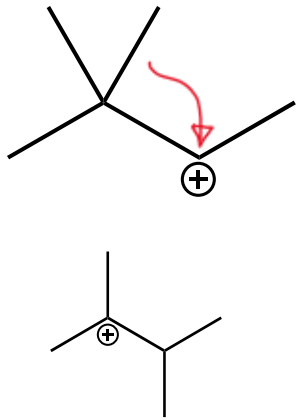


From **1°** to **2° benzylic** with hydride shift.

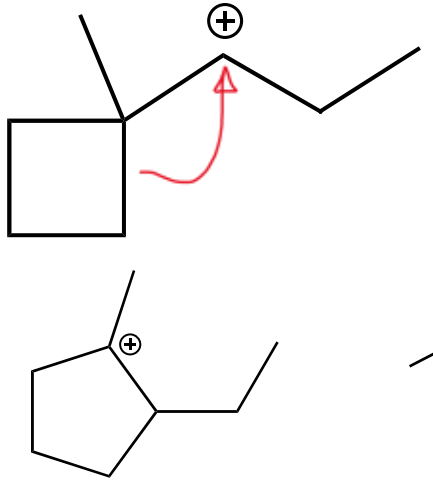


No Rearrangement

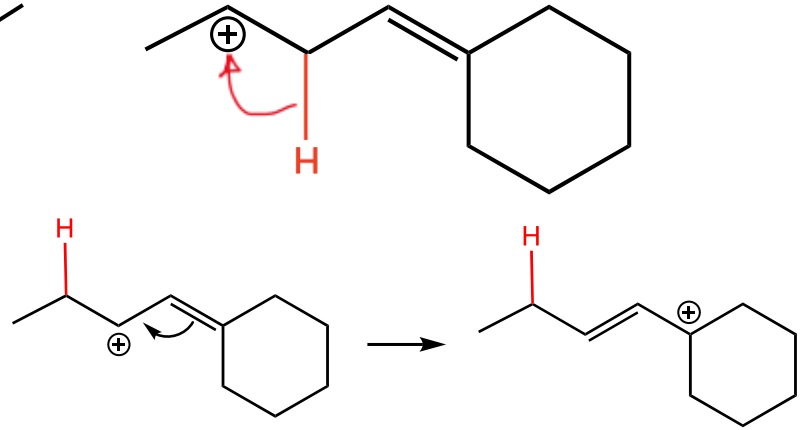
3° carbocation is the most stable possible, regardless of rearrangement



From **2°** to **3°** with Me shift.



From **2°** to **3°** with Me shift. (via ring opening).



From **2°** to **2° allylic** with hydride shift.