Cornell University

Cycloalkanes, Chair Conformation, and Curved Arrow Formalism

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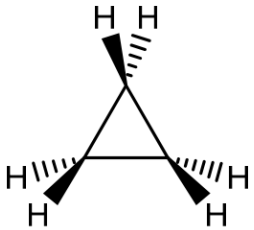
OCSP Lecture #3

Lecture 3 Learning Objectives

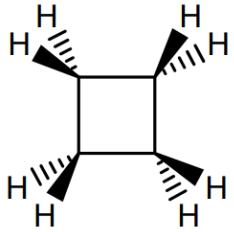
- General Introduction to Cycloalkanes
  - Ring Strain (angle, torsional/eclipsing, and steric)
  - Cyclopropane
  - Cyclobutane
  - Cyclopentane
  - Cyclohexane
    - Mechanistic Approach of Chair Flips (axial and equatorial substituents)
    - Ranking Conformer Stability via 1,3-Diaxial Interactions
- Curved Arrow Formalism
    - Using Curved Arrows for Resonance Structures
    - Carbocation Formation
    - Acid and Base Reactions (Bronsted and Lewis Definitions) using Curved Arrows
    - Identifying Nucleophilic and Electrophilic Centers

What are cycloalkanes?



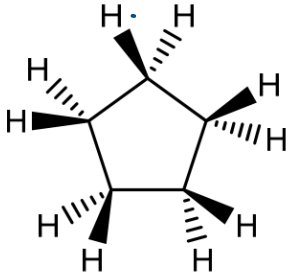
cyclopropane

C_3H_6



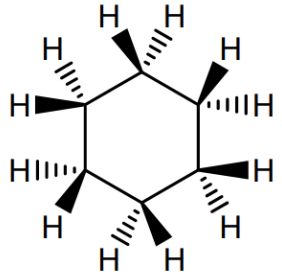
cyclobutane

C_4H_8



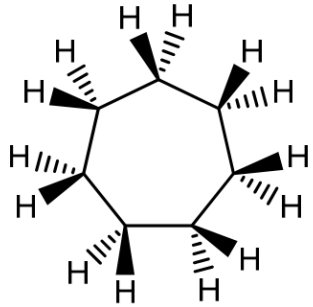
cyclopentane

C_5H_{10}



cyclohexane

C_6H_{12}

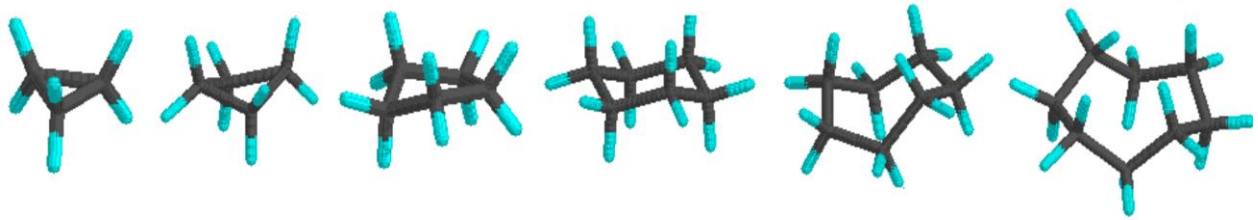


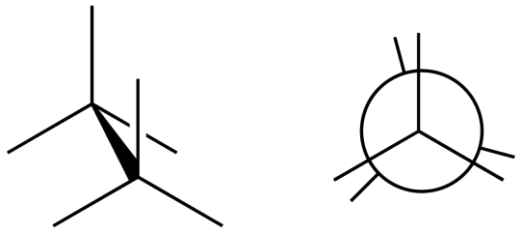
cycloheptane

C_7H_{14}

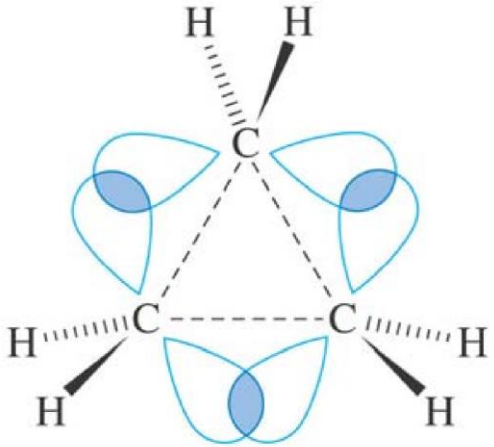
https://www.masterorganicchemistry.com/2014/06/06/the-cyclohexane-chair-flip-energy-diagram/

Ring Strain: what is it?

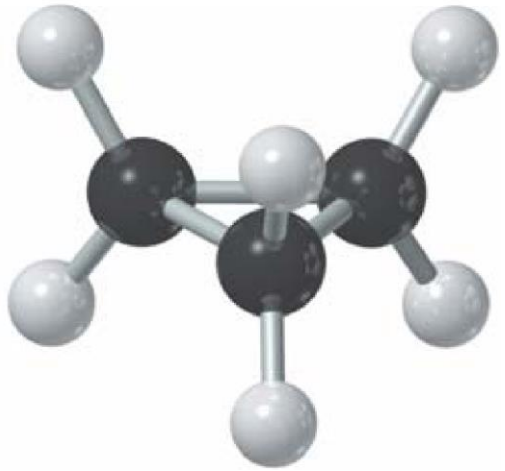




Cyclopropane



"bent bonds"
nonlinear overlap

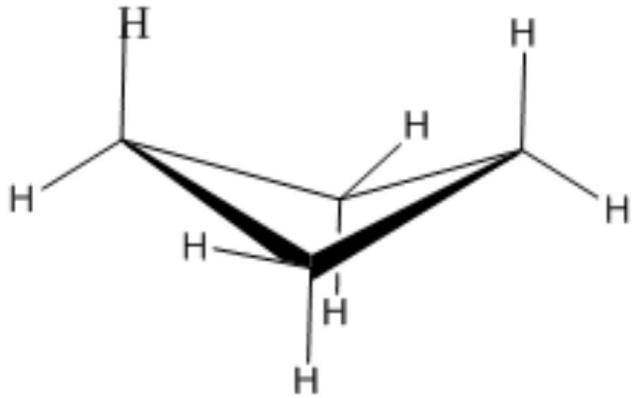


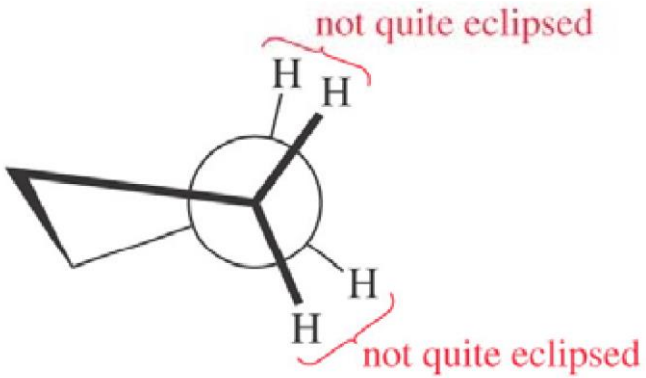
Example Problem

Cyclopropane is a highly strained molecule. Why? Select all that apply.

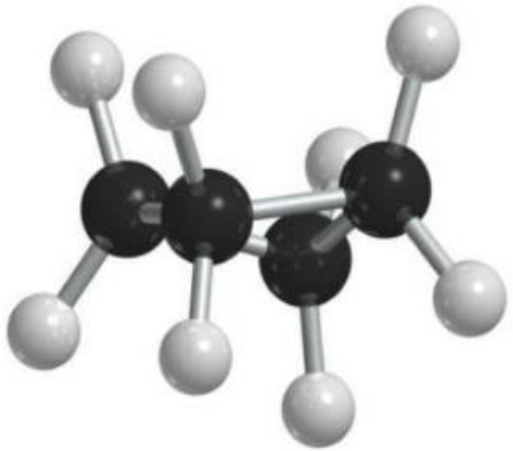
- ❑ The cyclopropane CH2 groups are eclipsed with each other leading to torsional strain.
- ❑ The cyclopropane ring is unable to pucker and relieve some angle strain.
- ❑ The cyclopropane CH2 groups are staggered with each other leading to torsional strain.
- ❑ The bond angles of cyclopropane are 120 degrees, leading to angle strain.
- ❑ The bond angles of cyclopropane are 60 degrees, leading to angle strain.

Cyclobutane

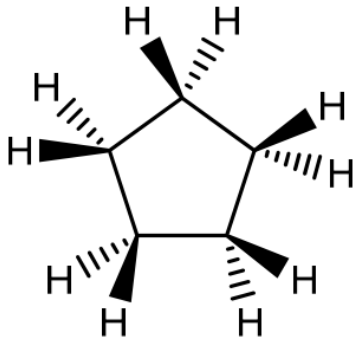


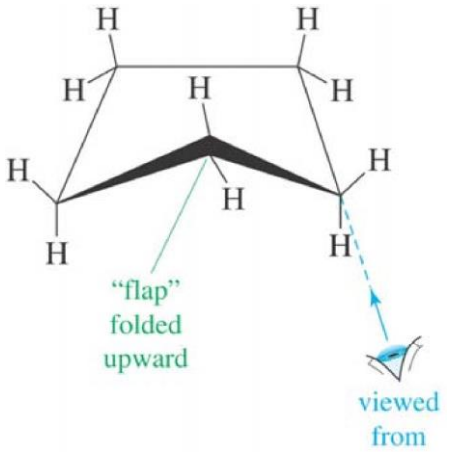


Newman projection of one bond

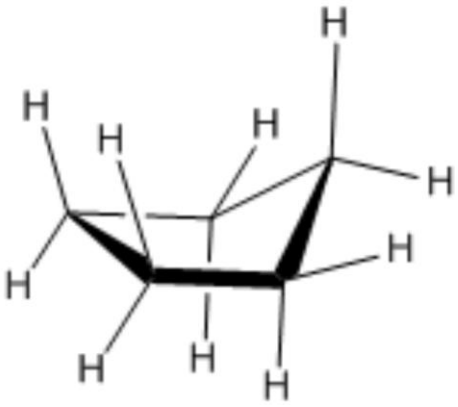


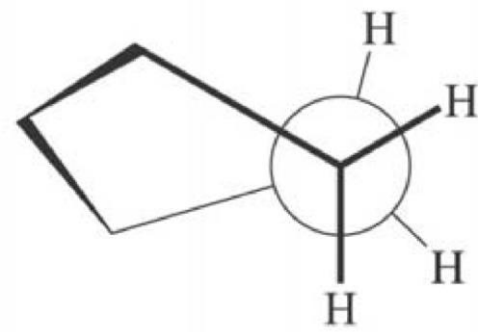
Cyclopentane





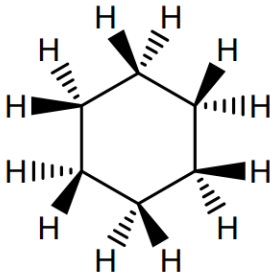
Decreased torsional strain (only found in base Hydrogens)





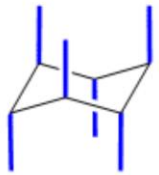
Newman projection showing relief of eclipsing of bonds

Cyclohexane



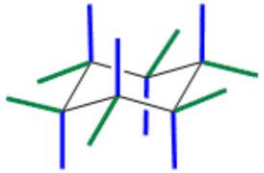
cyclohexane

C_6H_{12}



axial positions

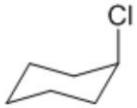
equatorial positions



axial & **equatorial** positions

typical drawing showing all the axial and equatorial positions. Each C looks tetrahedral

equatorial substituent

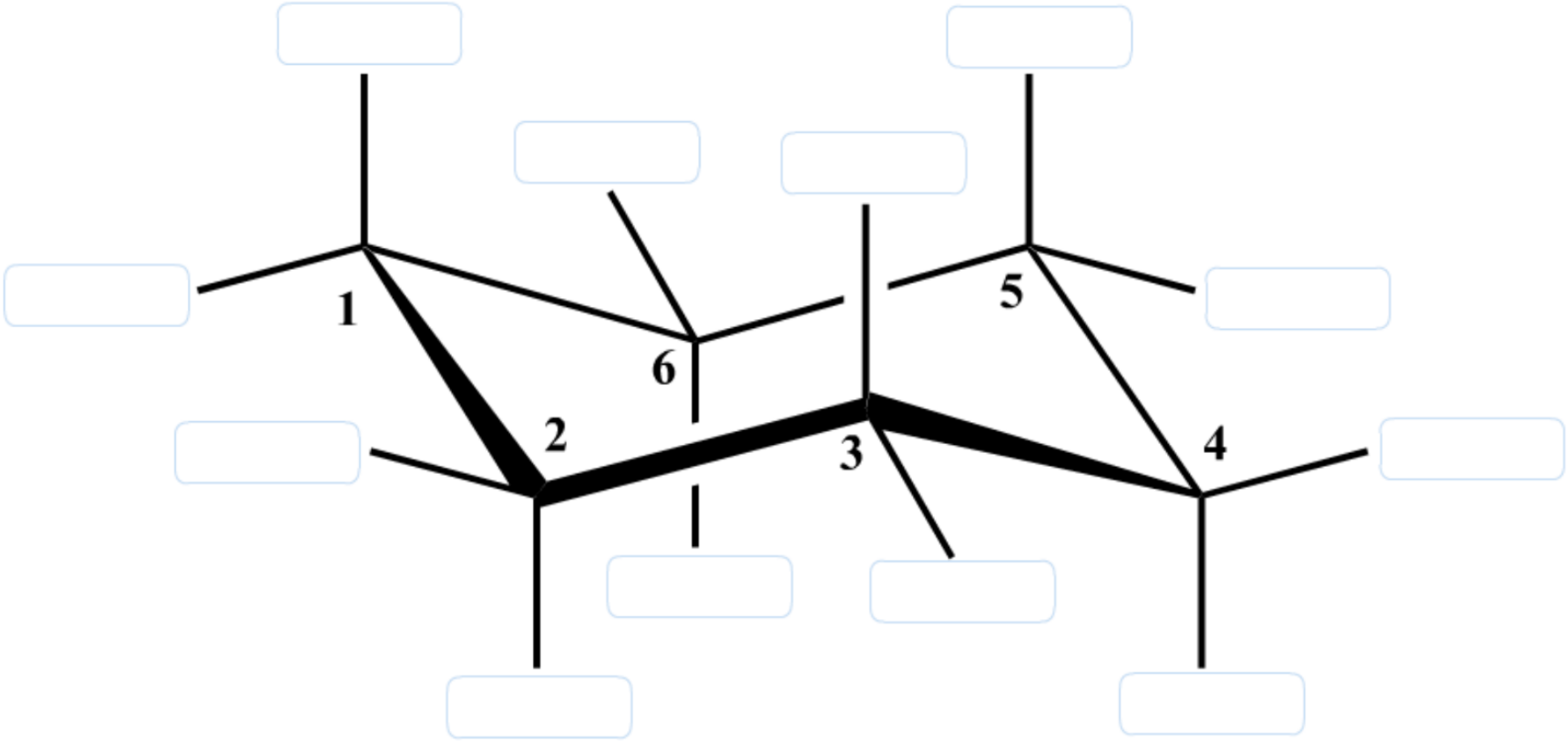


axial substituent

poorly drawn substituent, fails to accurately show position

Example Problem

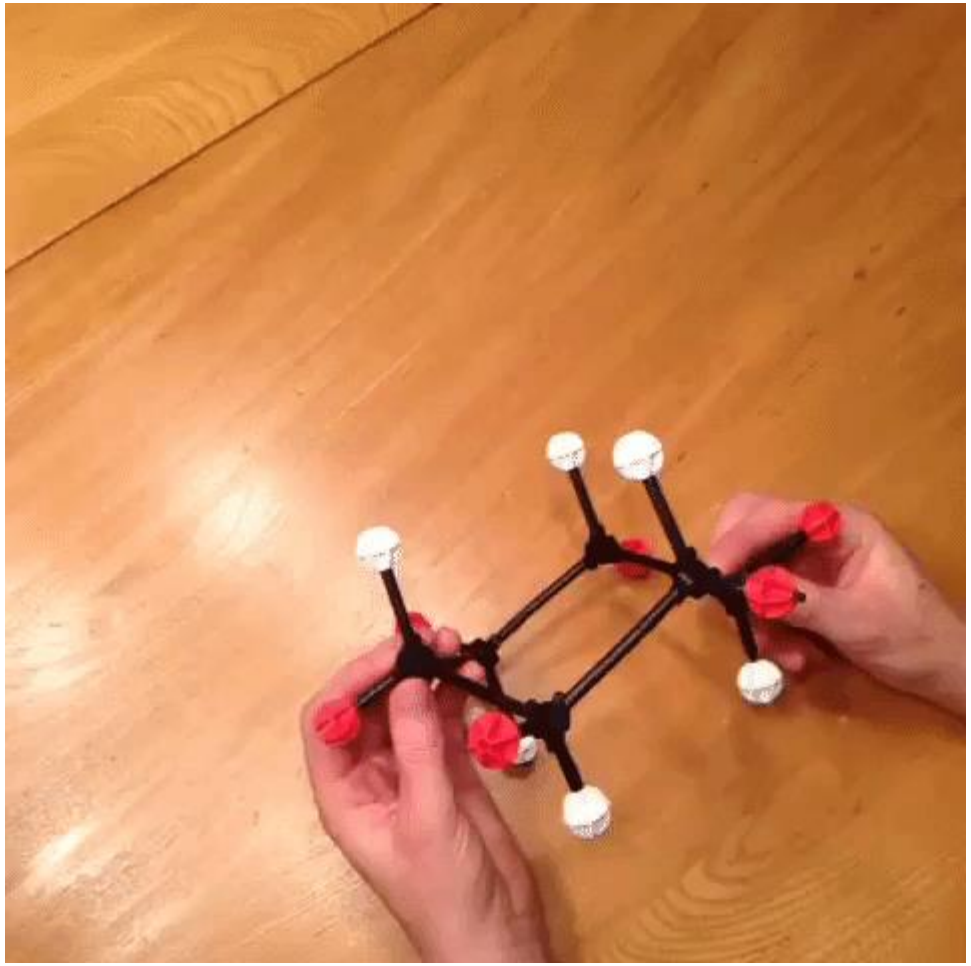
Given the cyclohexane framework in the chair conformation, label each position as axial or equatorial.

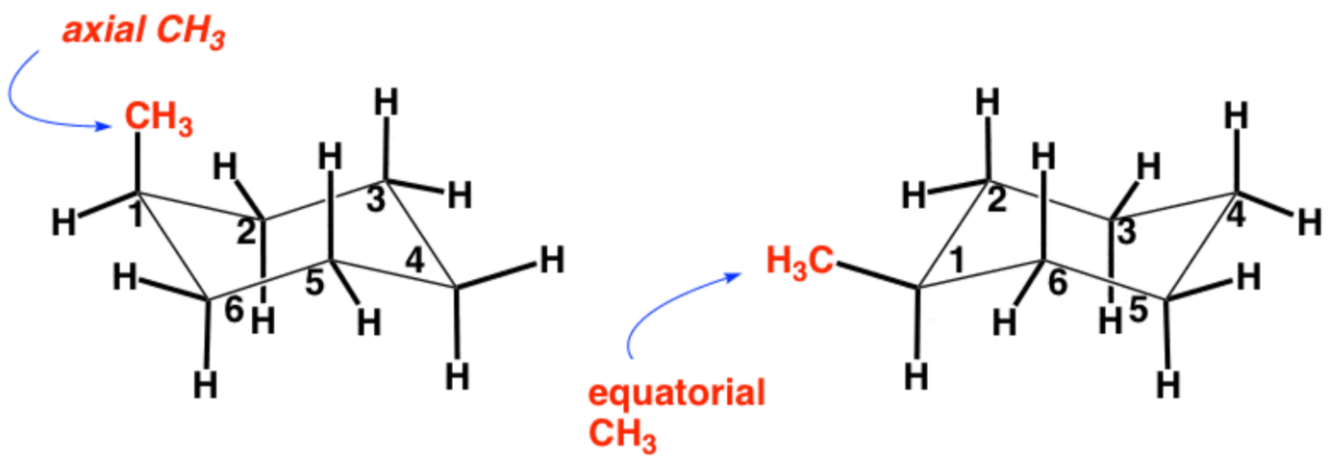


Drawing Chairs: An Artistic Approach

Drawing Chairs: An Artistic Approach (cont.)

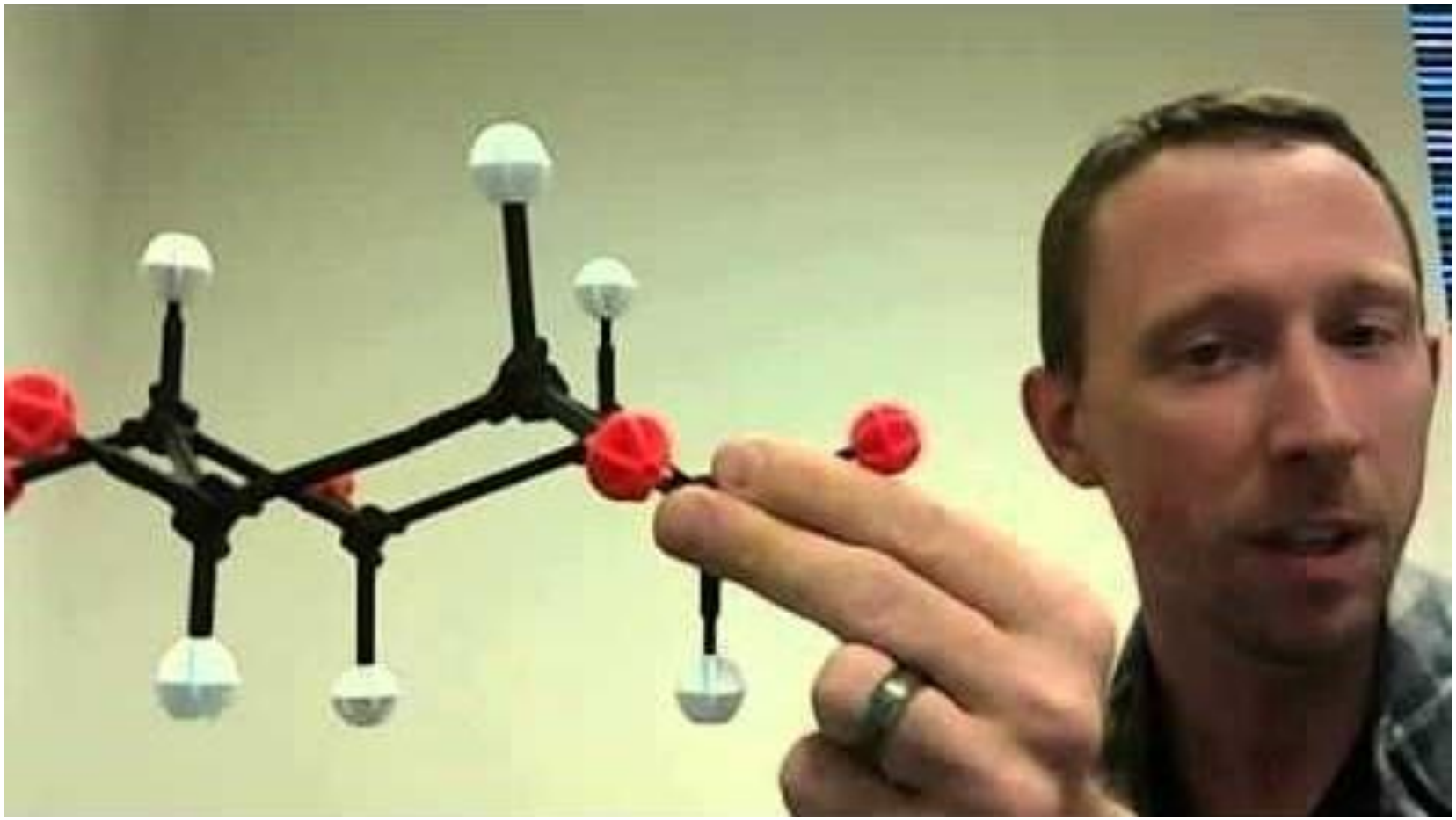
The Chair Flip





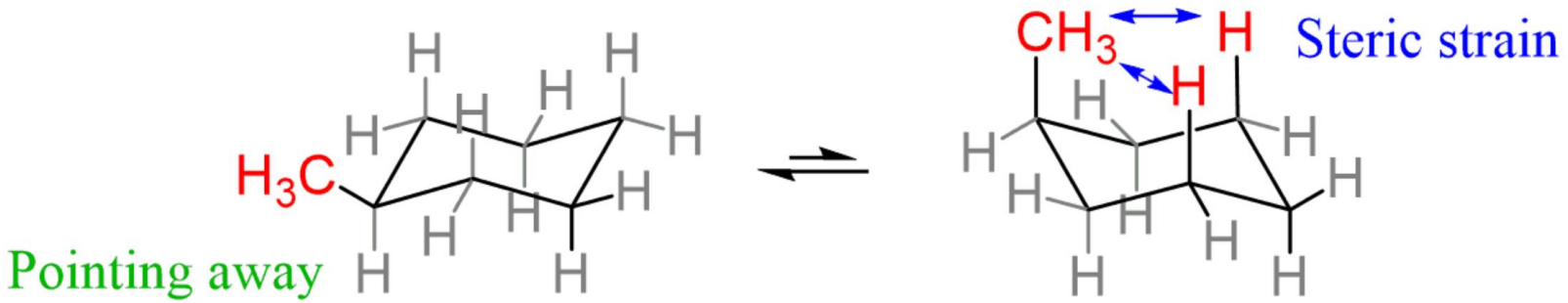
https://www.masterorganicchemistry.com/2014/05/30/the-cyclohexane-chair-flip/

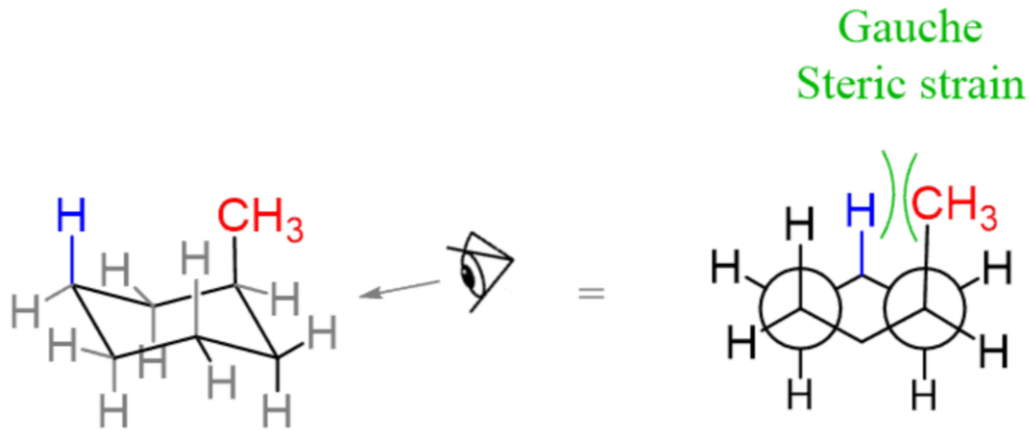
The Chair-Chair Flip



https://youtu.be/6VUU-_JExMs

Limiting 1,3-Diaxial Interactions





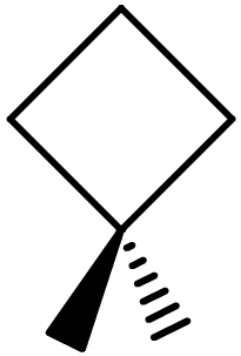
Cyclohexane

https://www.chemistrysteps.com/13-diaxial-interactions-and-a-value-for-cyclohexanes/

Example Problem

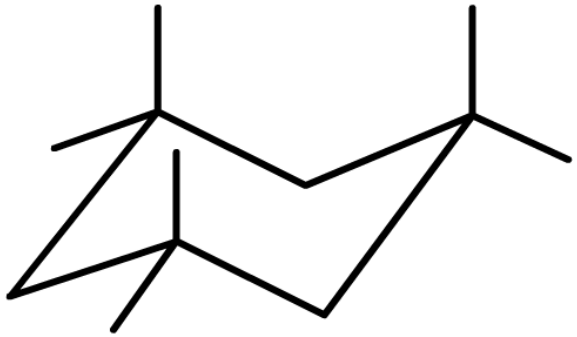
- Which structure has the most angle strain?
- Which structure has the most steric strain?
- Which structure has the most torsional (eclipsing) strain?

1,1-dimethylcyclobutane



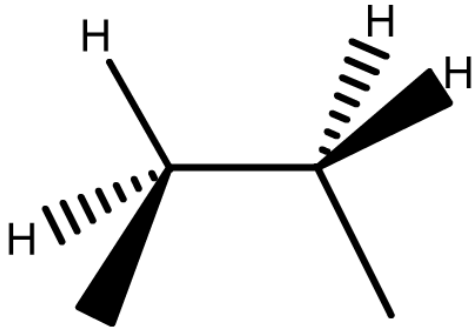
A

1,1,3,3,5,5-hexamethylcyclohexane



B

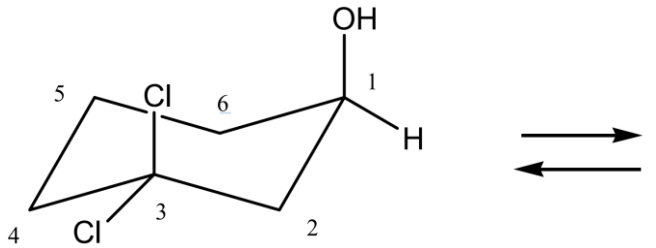
staggered butane

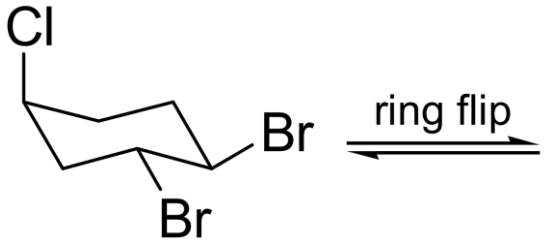


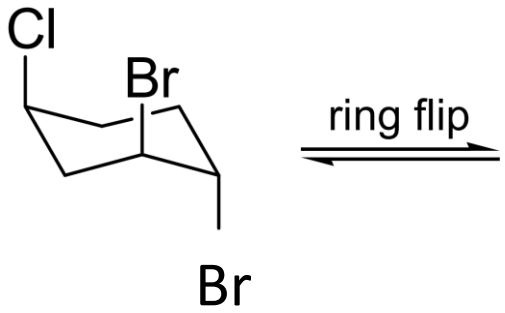
C

Example Problem

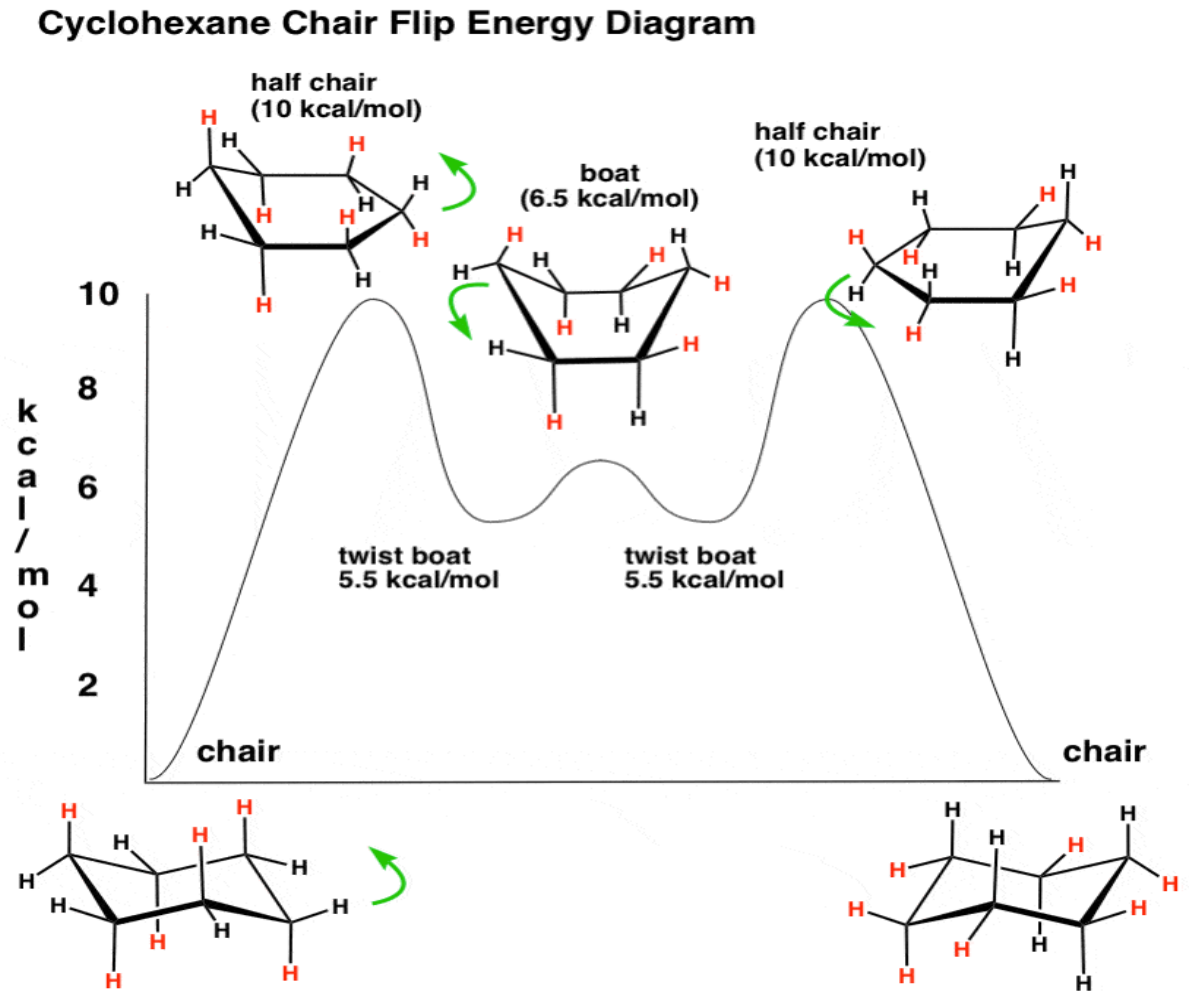
Draw the product of the following cyclohexanes after undergoing a ring flip. Be sure to clearly indicate axial and equatorial substituents.







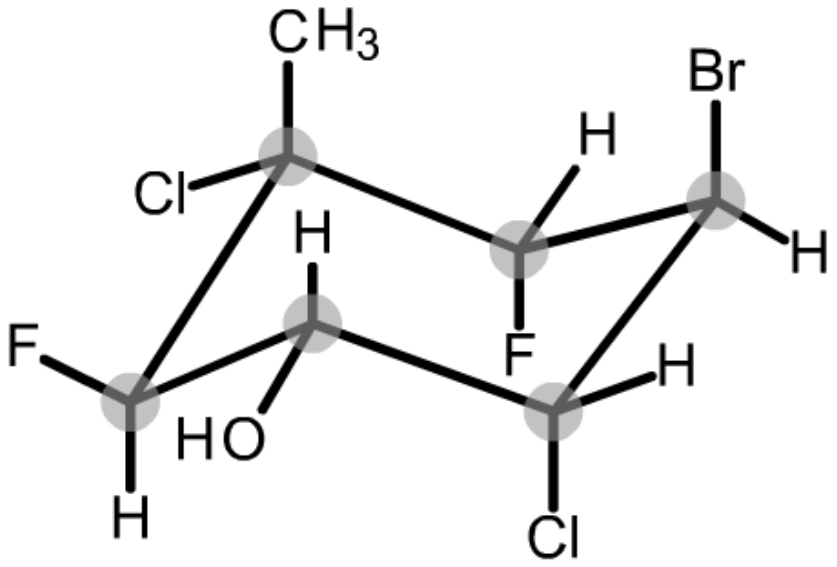
Mechanistic Approach of Chair Flipping



https://www.masterorganicchemistry.com/2014/06/06/the-cyclohexane-chair-flip-energy-diagram/

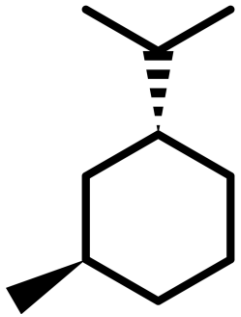
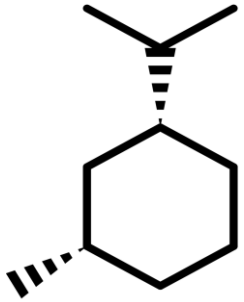
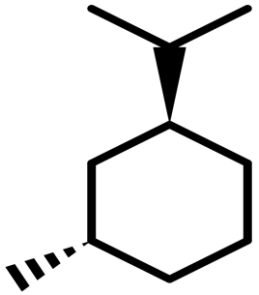
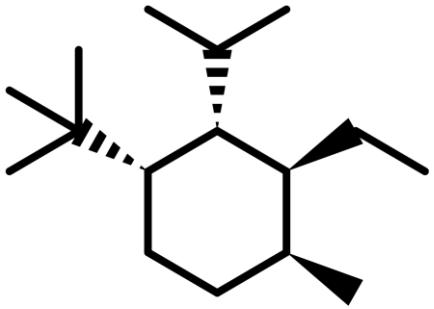
Example Problem

- For the substituted cyclohexane compound given below, which groups will sterically interact with the methyl group in a 1,3-diaxial fashion.



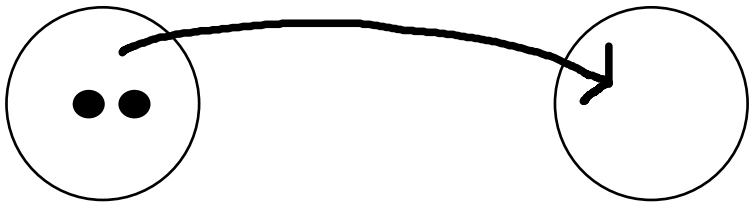
Example Problem

- Convert the cyclohexanes into the most stable chair conformation. Then, rank each chair from 1 (highest stability) to 4 (lowest stability).

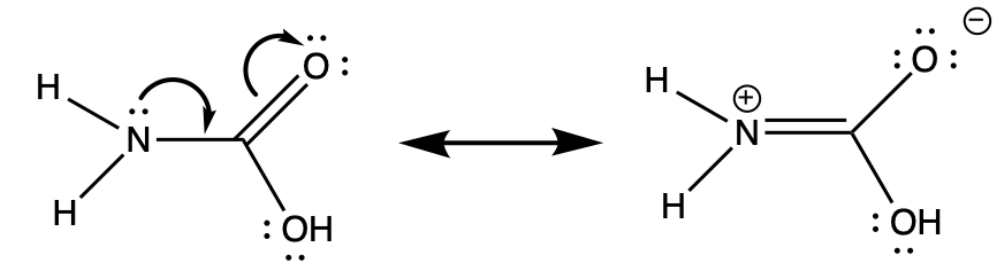





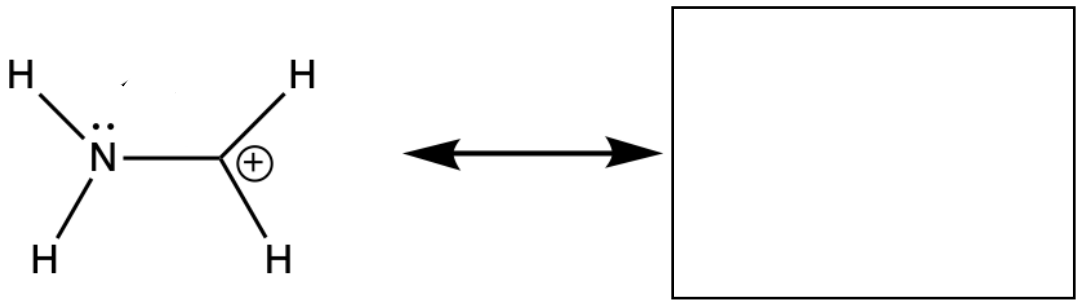
Curved Arrow Formalism

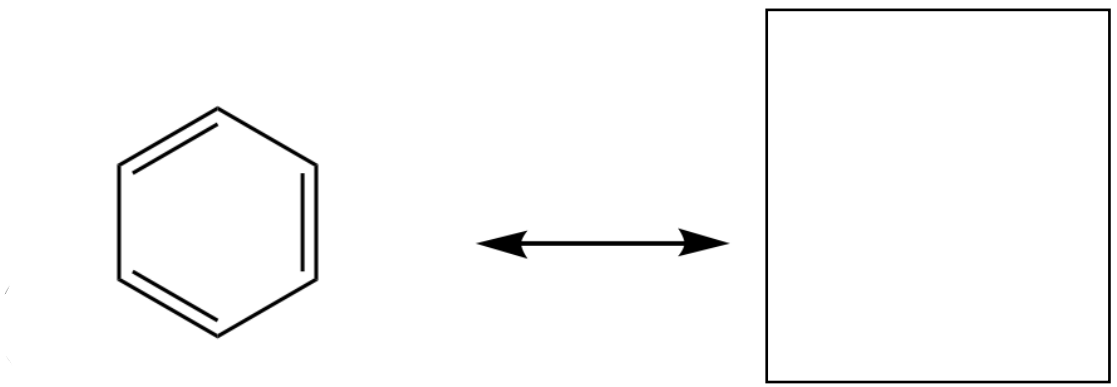
- General principle: Arrow points from the electron source to the electron acceptor.

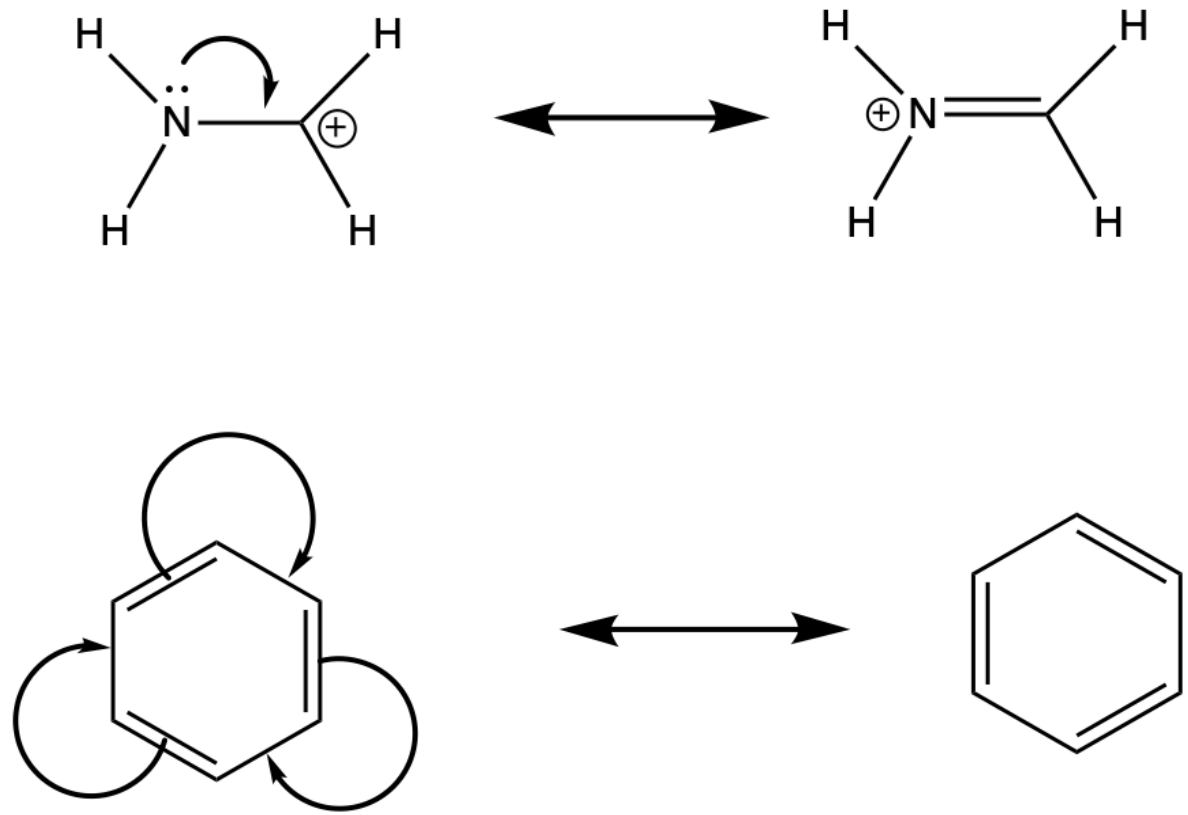


Resonance

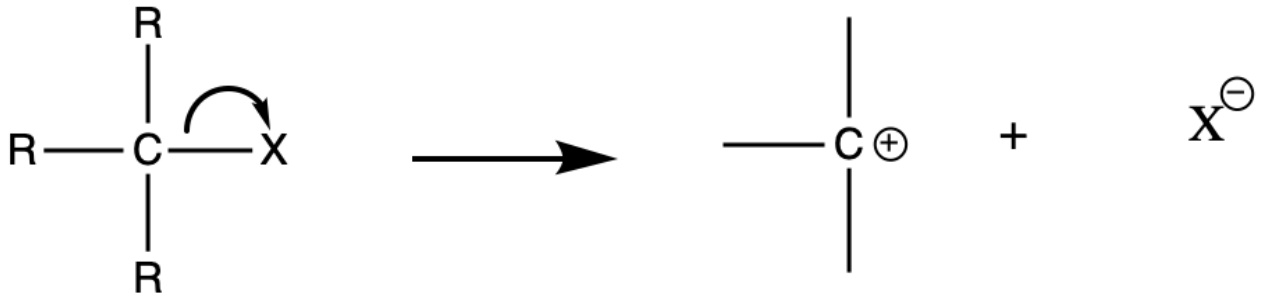







H
H
N
H
H
H
N
H
H
H
H

Carbocation Formation

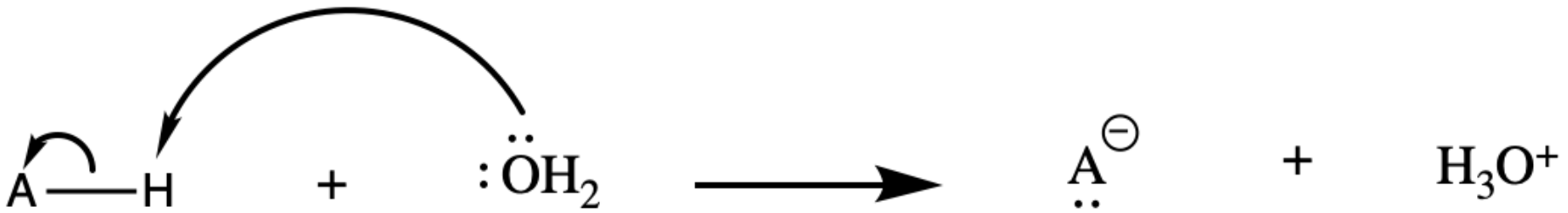


X = Cl, Br, I

Carbocation

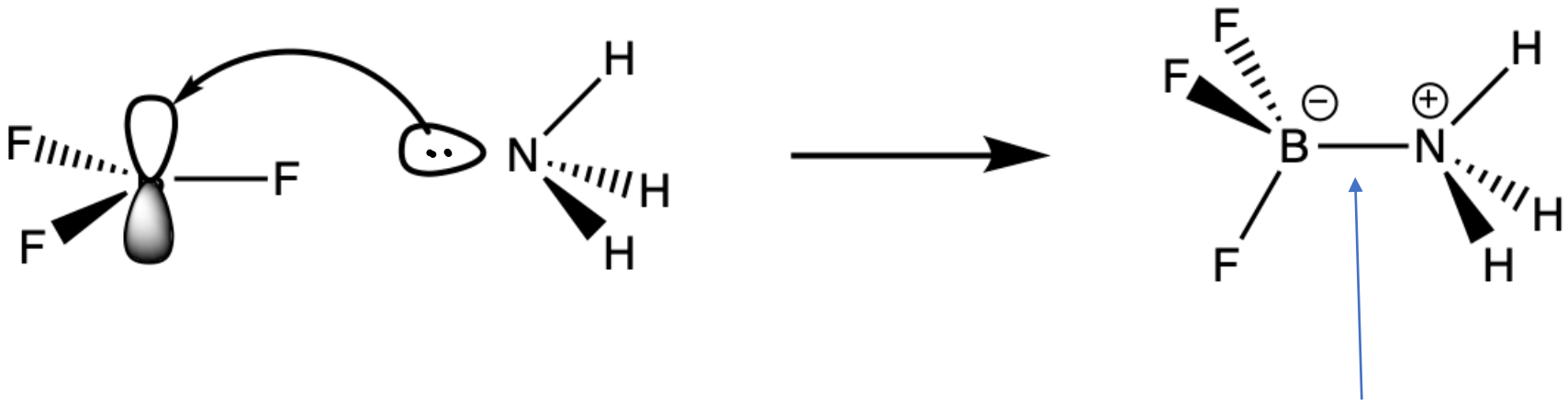
Bronsted Acids and Bases

- Bronsted Acid = H+ donor
- Bronsted Base = H+ acceptor



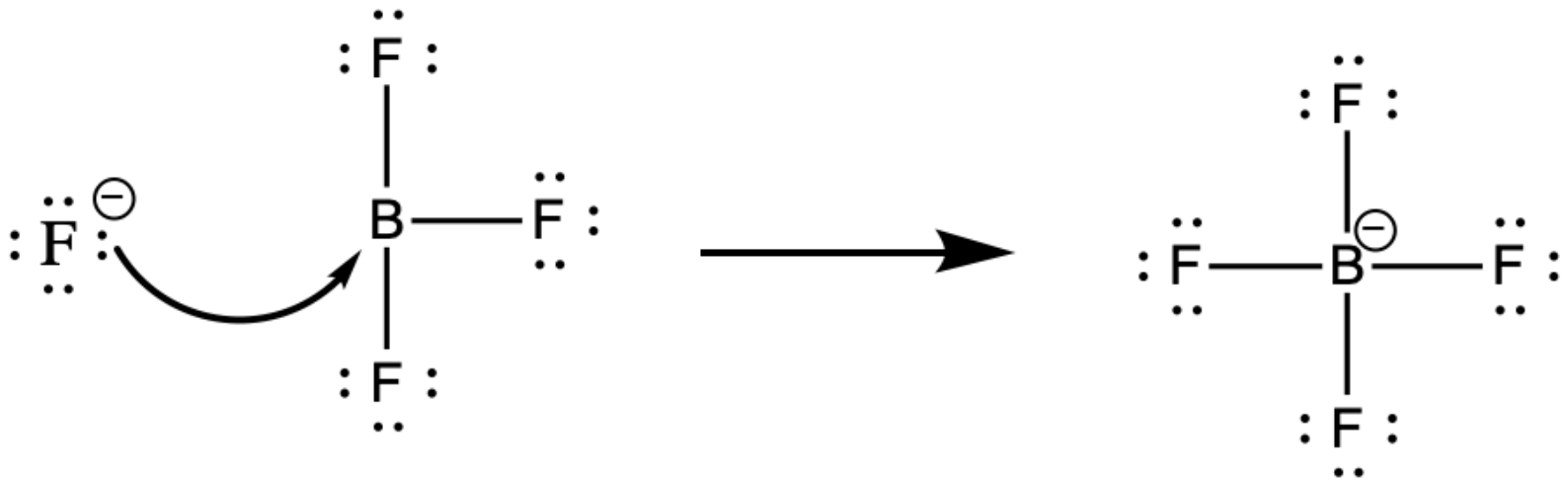
Lewis Acids and Bases

- Lewis Acid = accepts an electron pair…to form a new covalent bond
- Lewis Base = donates an electron pair…to form a new covalent bond



Example 1

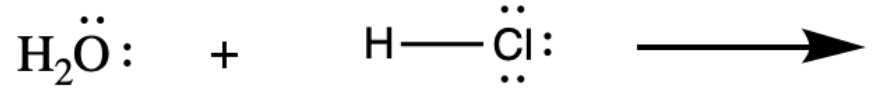
Lewis Acids and Bases Continued

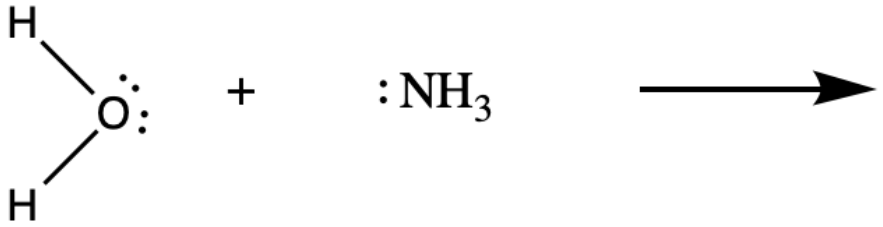


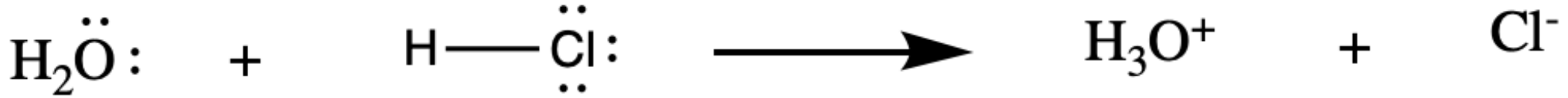
Example 2

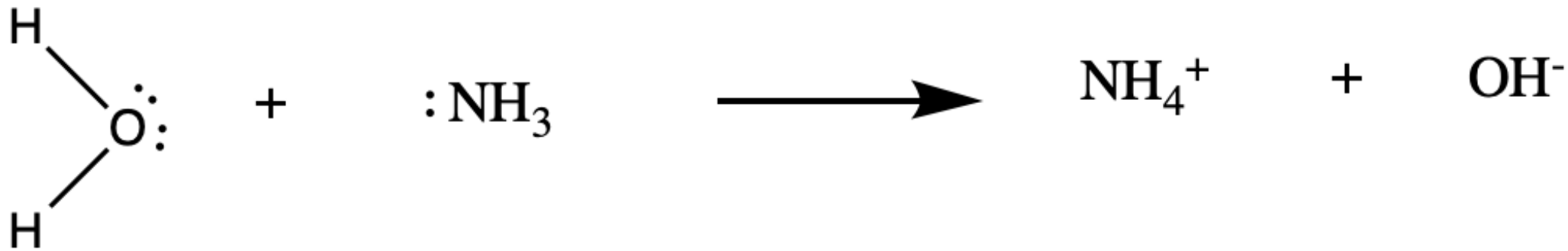
Practice

Use curved arrows to show the flow of electrons in the following reactions or resonance structures. If it is a reaction, give the products.



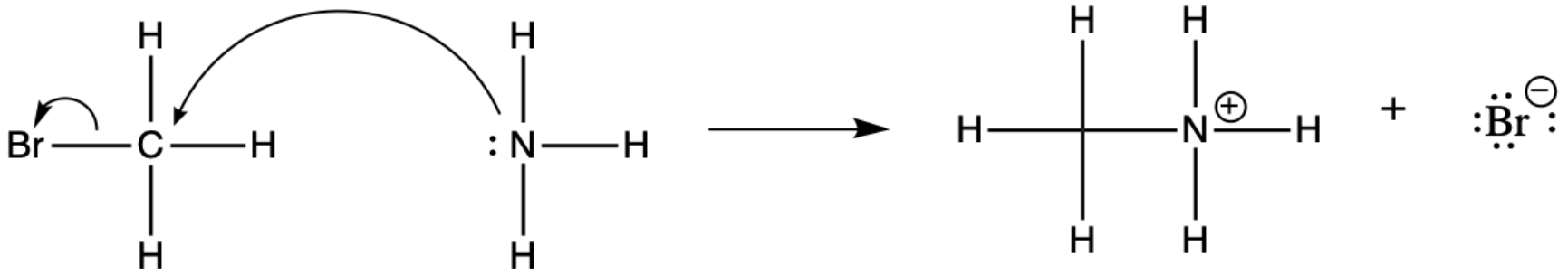



H_2O : + H—Cl : → H_3O^+ + Cl^-


H
O :
H
+ : NH_3 → NH_4^+ + OH^-

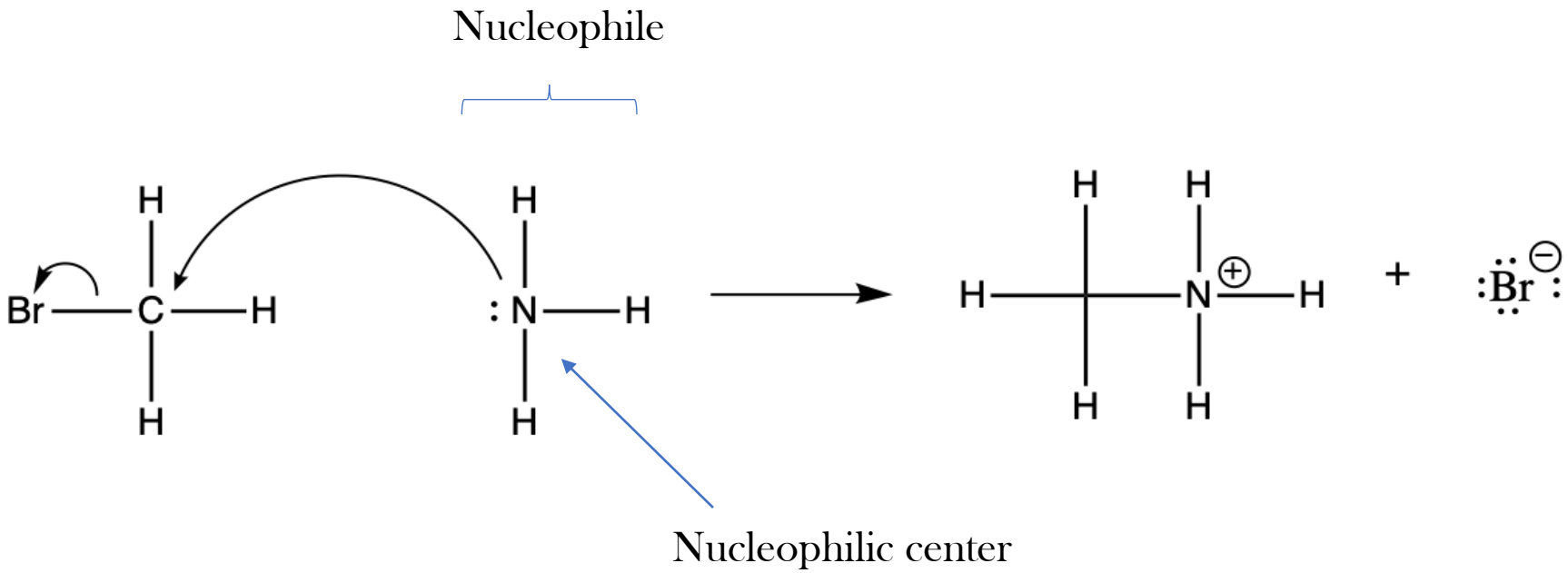

⊖ : O —≡ N :
↔
O = C = N ⊖ :

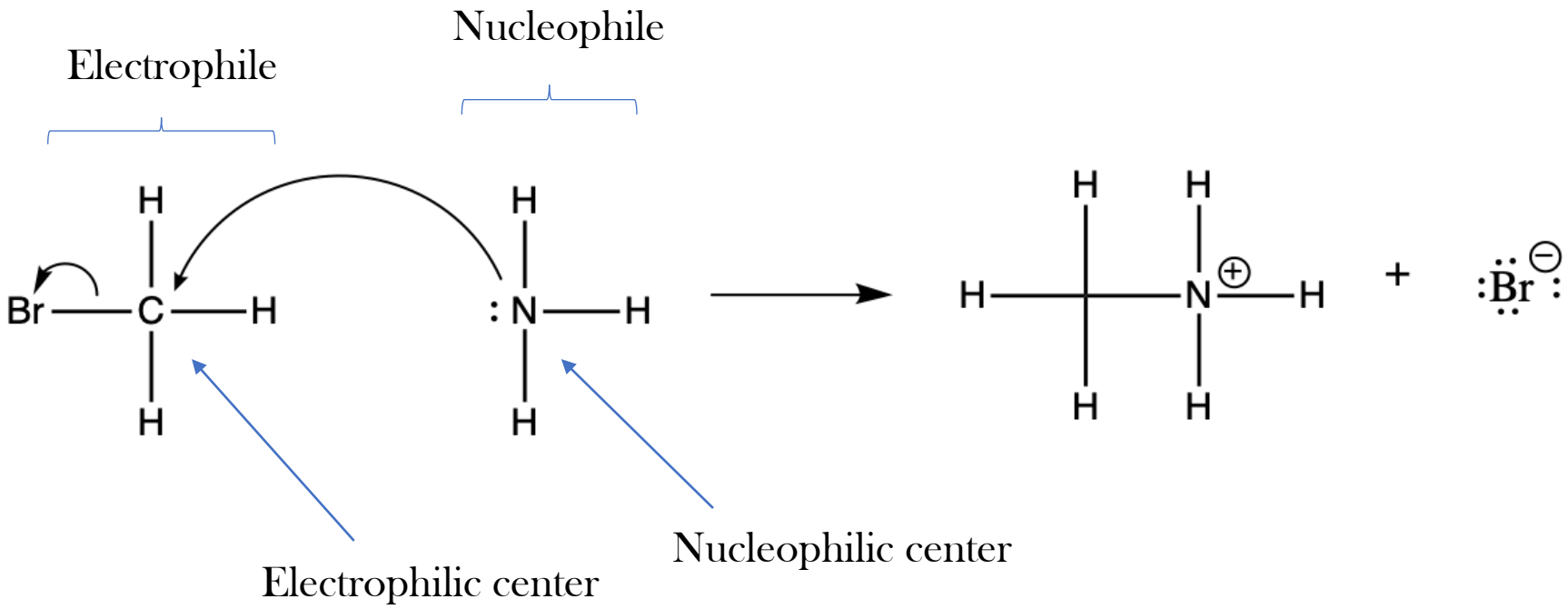
Nucleophiles and Electrophiles

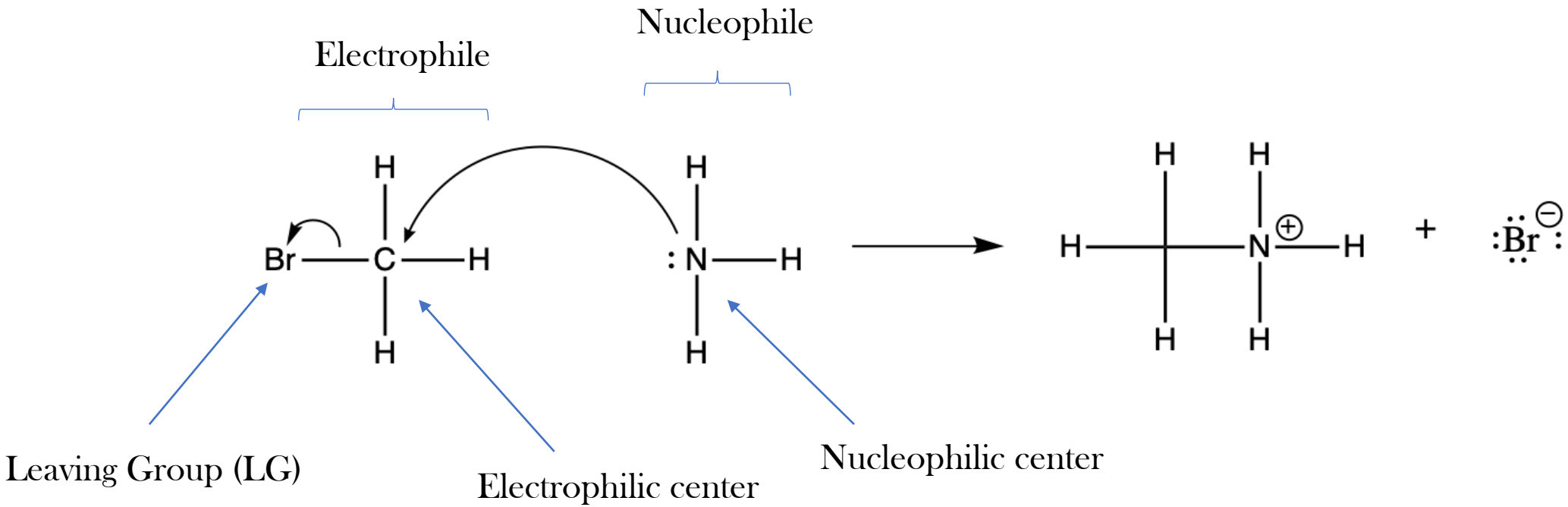


Definitions

Nucleophile: "nucleus loving", a species that donates an electron pair to form a new bond.
Nucleophilic atom/center: the atom that actually donates the electrons.
Electrophile: "electron loving", a species that accepts an electron pair to form a new bond.
Electrophilic atom/center: the atom that actually accepts the electron pair
Leaving group: atom or group that is expelled when it accepts electrons from the breaking bond.


Nucleophile
H
Br
C
H
H
H
: N
H
H
H
H
H
N
H
H
H
+
:Br:
Nucleophilic center

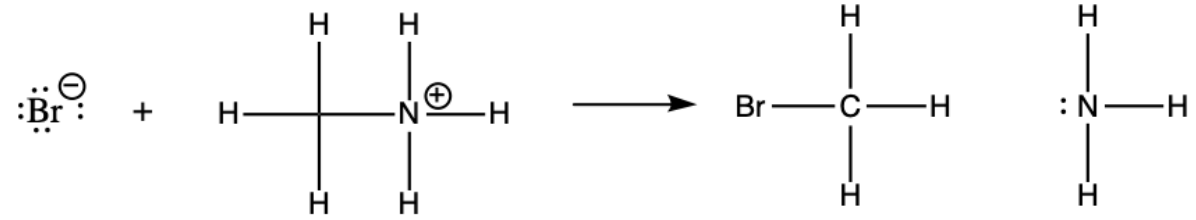

Electrophile
Nucleophile
H
Br
C
H
H
H
: N
H
H
H
H
H
N
H
H
H
+
:Br:
Electrophilic center
Nucleophilic center


Electrophile
Nucleophile
H
Br
C
H
H
H
: N
H
H
H
H
H
N
H
H
H
+
:Br:
Leaving Group (LG)
Electrophilic center
Nucleophilic center

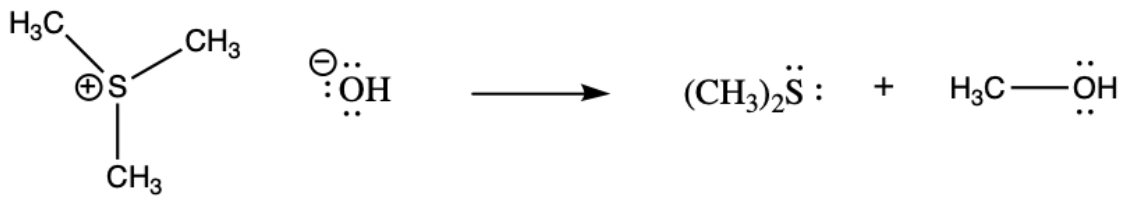
Practice

Identify the nucleophilic center, electrophilic center, and the leaving group

a)

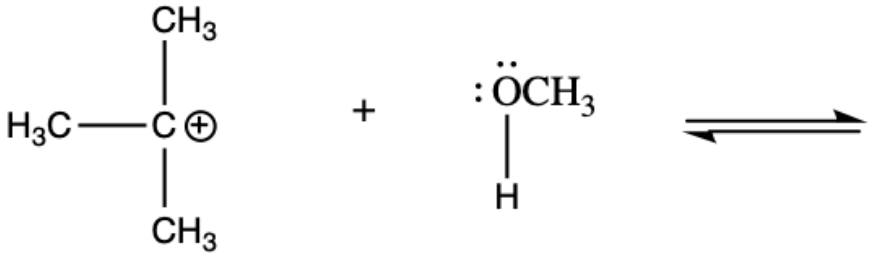


b)

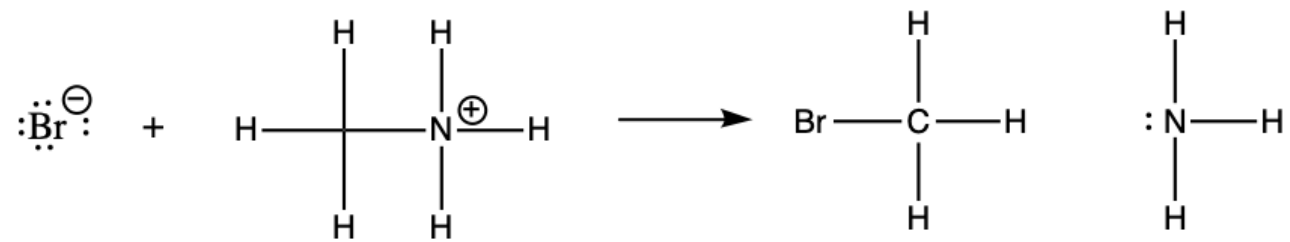


Using curved arrow notation to guide you, complete the following Lewis acid-base association reaction

c)



a)



b)

c)