CH 209 – Basic Organic Chemistry

Reaction mechanisms: Curved arrow representations

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Why do molecules react?

- Bottles of acetone, or chloroform can be stored for years without any change in the chemical composition of the molecules inside.
- Yet when we add chemical reagents, say, sodium cyanide (NaCN) to acetone, or sodium hydroxide to methyl iodide, chemical reactions occur.

Why they don't and why they do react?

- Molecules move continuously in space (bond stretching, bending), collide each other, into the walls of the vessel they are in, and into the solvent if they are in solution.
- When one bond in a single molecule stretches too much it may break, interact with another molecule and a chemical reaction occurs.

Why do molecules react?

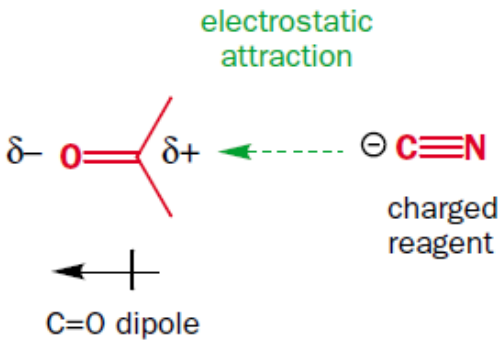
- Not all collisions between molecules lead to chemical change

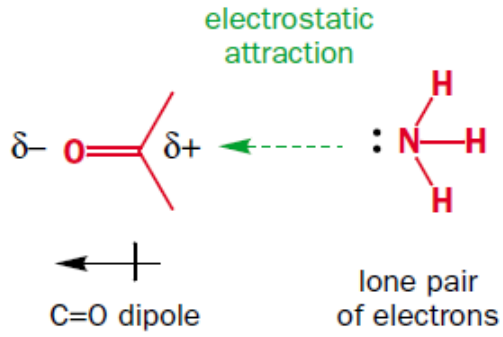
-charge–charge repulsion between the electrons in bonding and nonbonding orbitals ensures that all molecules repel each other.
-Activation energy must be provided for such molecules to react

- Charge attraction brings molecules together – Bond polarity

- Electron flow is the key to reactivity
- Cations (+) and anions (–) attract each other electrostatically and this may be enough for reaction to occur.

- Attraction between a charged reagent (cation or anion) and an organic compound that has a dipole.





Electron flow is the key to reactivity

- Majority of organic reactions are polar in nature
- Electrons flow from one molecule to another as the reaction proceeds.
- *The electron donor is called a nucleophile (nucleus loving) while the electron acceptor is called the electrophile (electron-loving).*

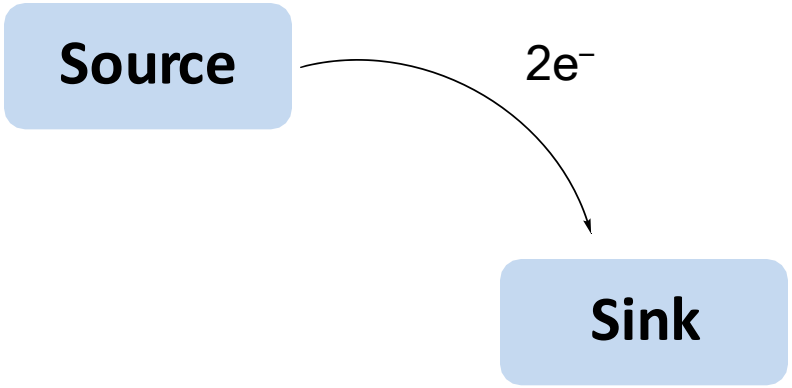
Polar Mechanism

- **Nucleophiles donate electrons**
- **Electrophiles accept electrons**

Arrow pushing

Arrow pushing or electron pushing

Used by chemists to pictorially represent movement of bonds, electrons or electron pairs



Double headed arrow shows movement of two electrons

How do we know which direction probably the electrons would flow in a reaction?

Unequal Electron Distribution across a Bond

- Inductive effect
- Resonance effect

Inductive Effect

The phenomenon of withdrawing electrons through σ bonds to the more electronegative atom

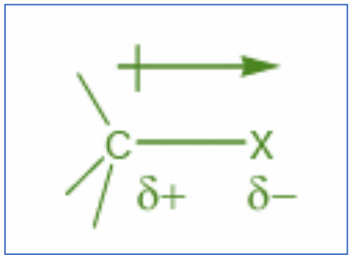
Atom	Pauling Scale
H	2.1
B	2.0
C	2.5
N	3.0
O	3.5
F	4.0
Cl	3.0

Understanding relative electronegativity is very important

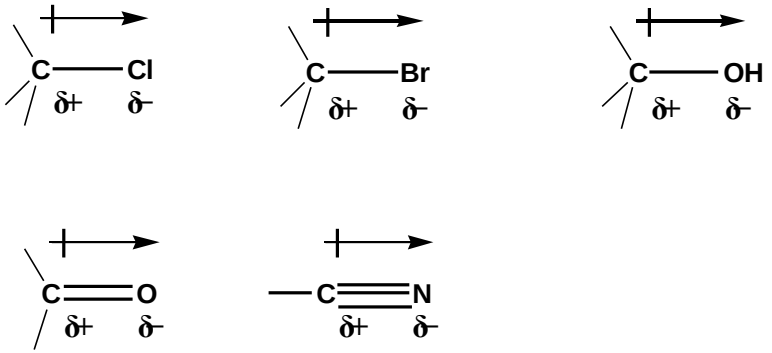
Bond polarity

- Most heteroatoms (X) are more electronegative than carbon and C-X bonds are polarized so that there is a partial positive charge on the carbon atom.

The polarity is illustrated thus:

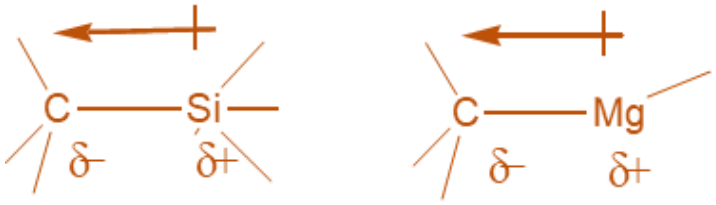


Examples of covalent bonds which contain a dipole:



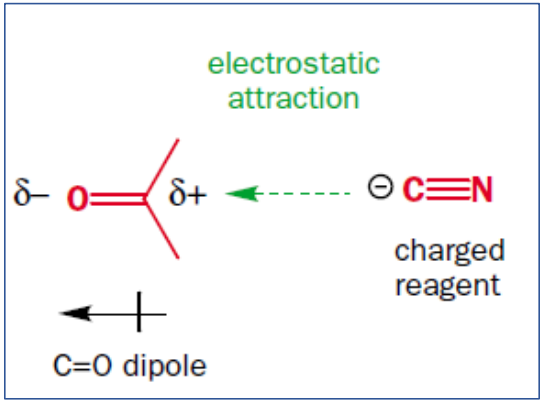
Note: in the case of double and triple bonds, resonance (delocalisation) effects also contribute to the polarity.

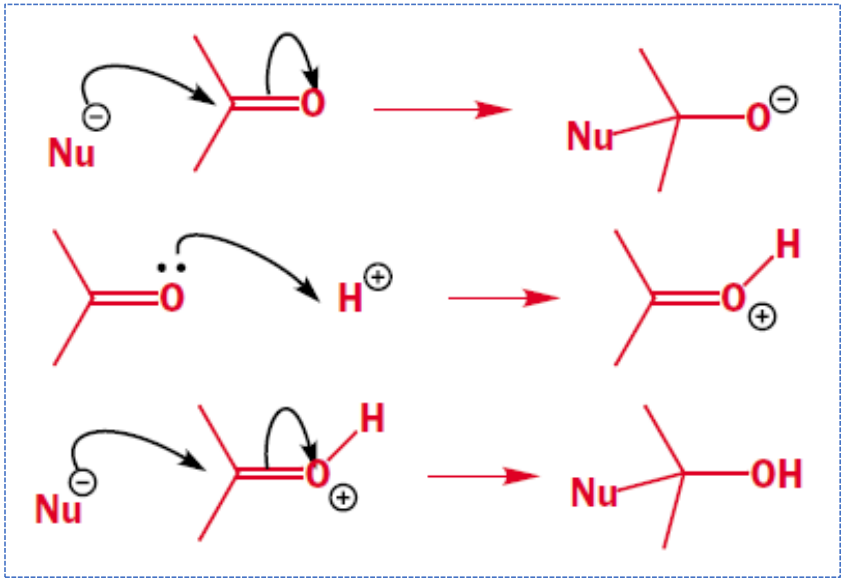
- A few elements (notably metals) are less electronegative than C. As a result the dipole is reversed:



Bond polarity

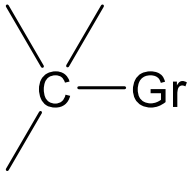
- Bond polarity allows us to predict where reactions will take place.





Group Electronegativity

Withdrawing electrons through σ bond

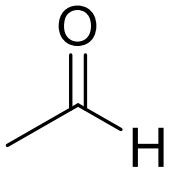


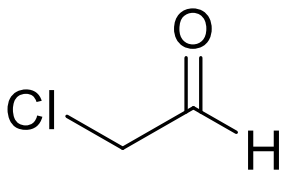
Group	Pauling Scale
CH_3	2.3
CH_2Cl	2.8
$CHCl_2$	3.0
CF_3	3.4
Ph	3.0
$CH{=}CH_2$	3.0
$C{\equiv}CH$	3.4
NH_3^+	3.8
NO_2	3.4
OH	3.7

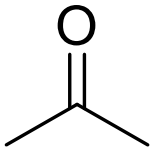
Let us try to figure out the relative group electronegativity

- With varied substituents, the reaction progress would be significantly different.

Predict the reactivity of the following towards nucleophilic addition reaction



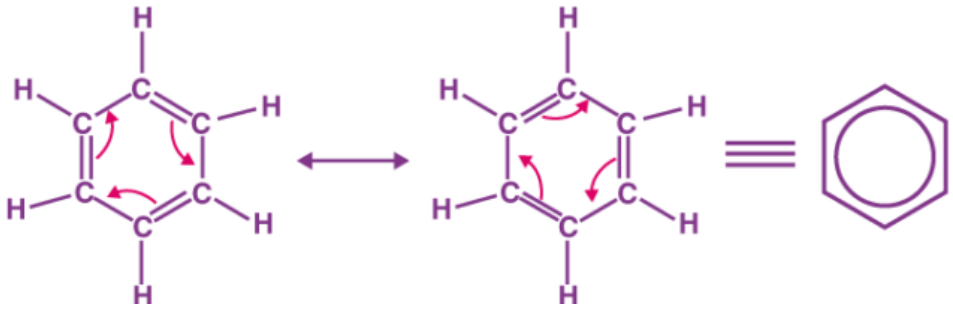




Resonance Effect

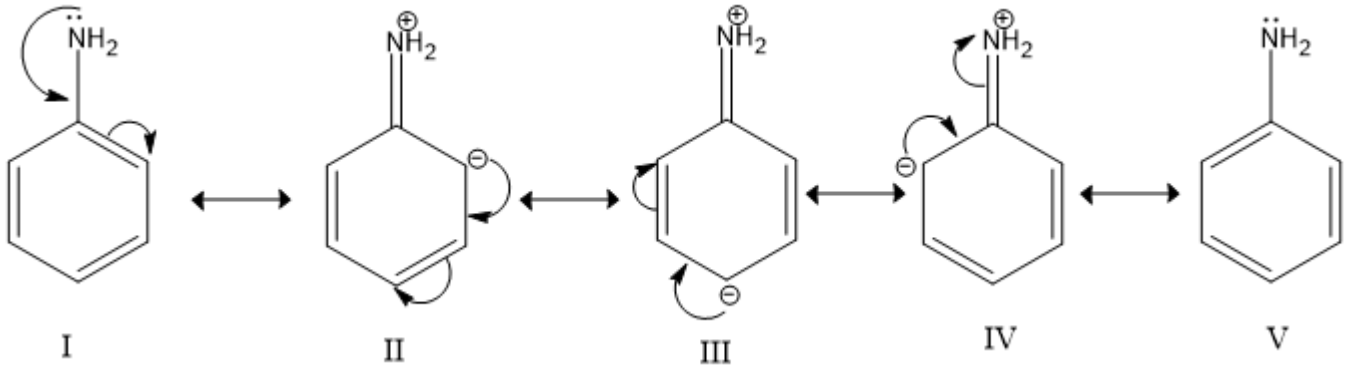
Multiple Lewis structure possible for same molecule

- Useful for conjugated systems and intermediates
- Involves involvement of p orbitals
- Helps in predicting mechanism of a reaction



Actual structure is the hybrid of resonance structures. Depending on stability some may contribute more

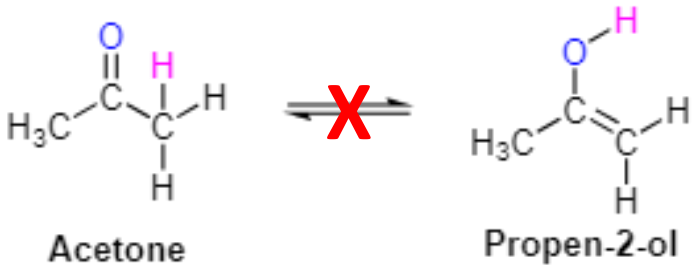
Movement of electrons from source to sink

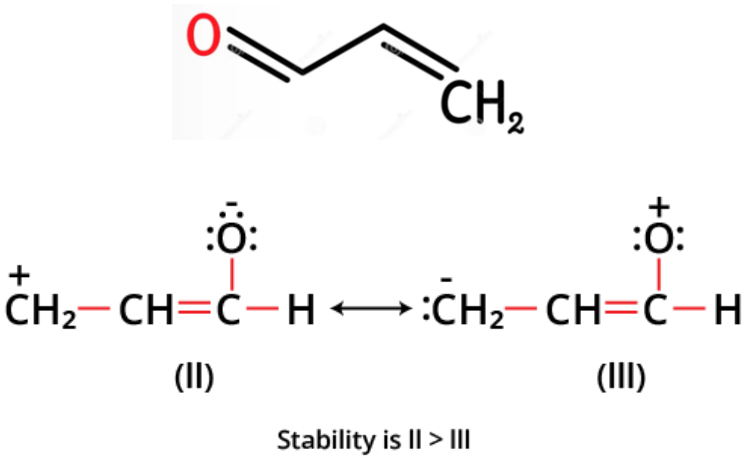


Resonance Effect

Rules for Resonance

- Only electrons move around. **All** nuclei in the same position
- Some structures are more favorable and contribute more
- Remember the octet rule while writing the structure
- Charge remains same



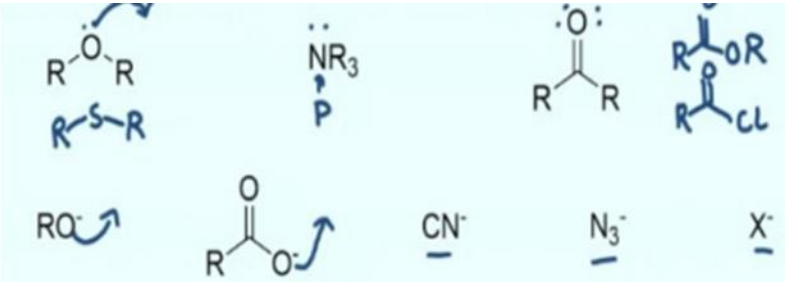


- Resonance structures often times will guide us predict mechanism of a reaction.

Electron Sources

- Non-bonding electrons

- Neutral, charged



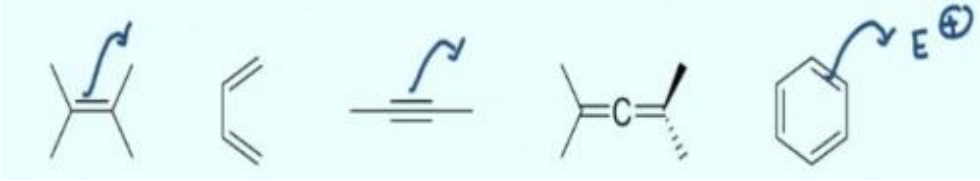
- Electron rich σ bonds

-Organometallics, Hydride reagents

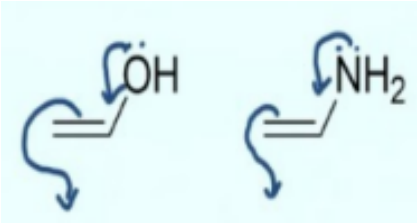
RMgX, RLi, R_2CuLi, R_2Zn

$LiAlH_4$, $NaBH_4$, NaH, BH_3

- π-Bonds



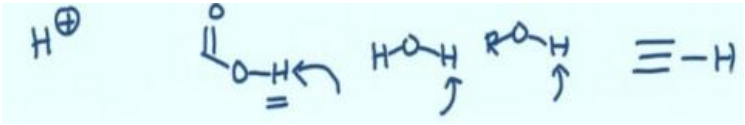
- Electron rich π-bonds



Electron Sinks (Destination)

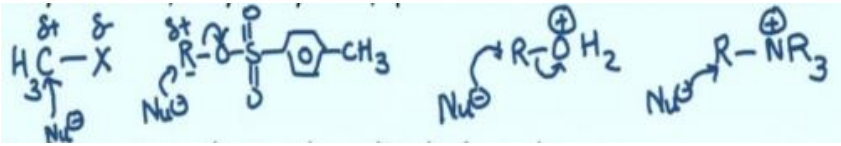
- Species with empty orbitals

- Carbocation, Lewis acids



- Acidic hydrogens

-mineral acids, carboxylic acids, water, alcohol, terminal alkynes

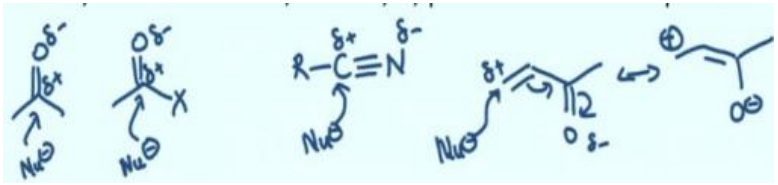


- Carbons in polarized σ-bonds

-Alkyl halides, protonated alcohols and amines

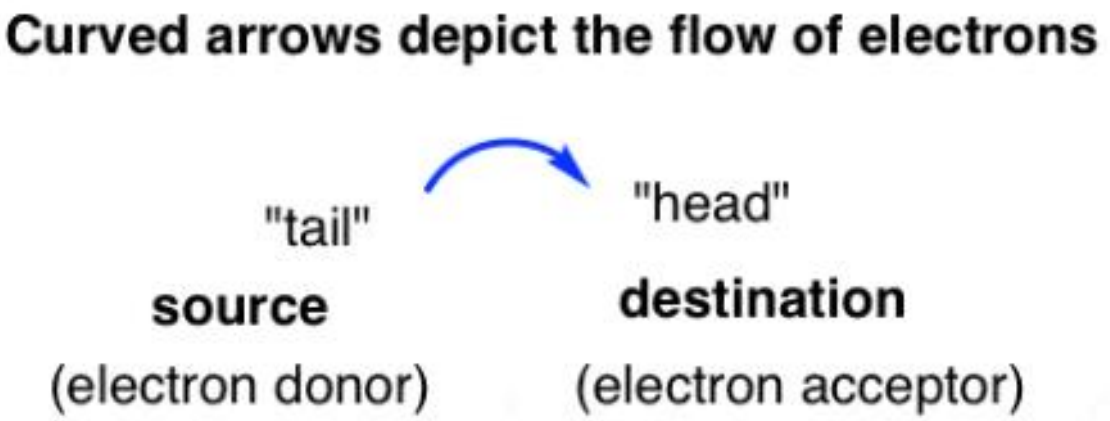
- Carbons in polarized multiple bonds

-Ketones, acid derivatives, nitriles, unsaturated carbonyl compounds



Mechanism and arrow pushing

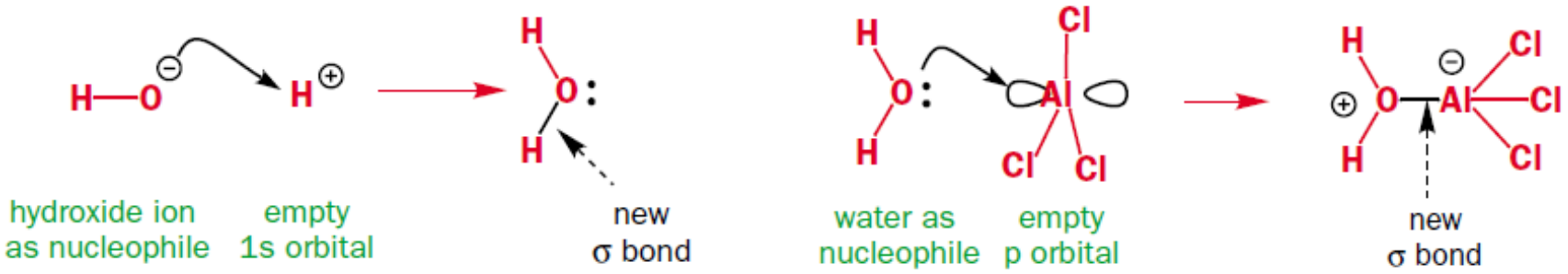
- A **curly arrow** represents the *actual movement of a pair of electrons* from a filled orbital into an empty orbital.
- 'Arrow pushing' is employed to illustrate mechanisms in organic chemistry
- Used by chemists to pictorially represent movement of bonds, electrons or electron pairs
- Double headed arrow shows movement of two electrons



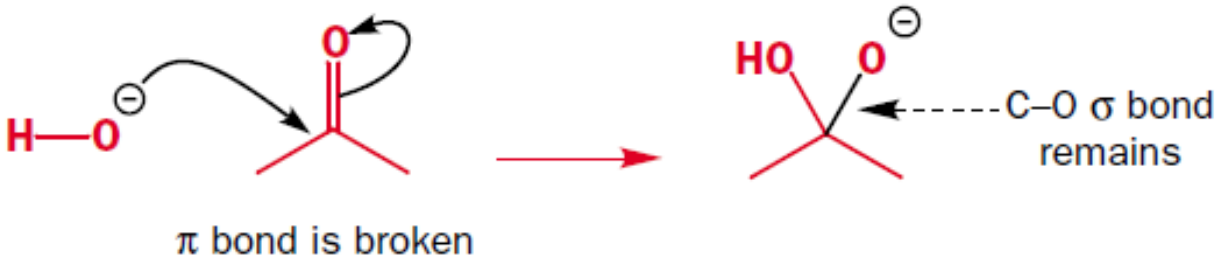
Curved Arrow Notation

- The arrow always starts with its tail on the source of the moving electrons, representing the filled orbital involved in the reaction

- The head of the arrow indicates the final destination of the pair of electrons—the new bond between oxygen and hydrogen or oxygen and aluminum



- Charge is conserved in each step of a reaction



The starting materials had an overall negative charge and this is preserved as the oxyanion in the product

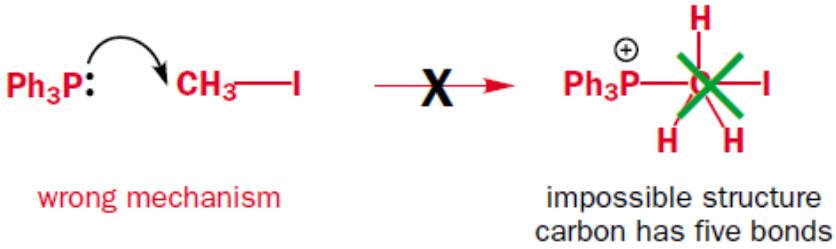
Drawing your own mechanisms with curly arrows

- First observe what has happened: new bond has been formed between the phosphorus atom and the methyl group and the carbon–iodine bond has been broken.
- Arrows represent movement of electron pairs *not* atoms so the reactants must be drawn within bonding distance before the mechanism can be drawn.
- First draw the two molecules so that the atoms that form the new bond (P and C) are near each other and draw out the bonds that are involved

- Now ask: which is the electrophile and which the nucleophile (and why)?

Drawing your own mechanisms with curly arrows

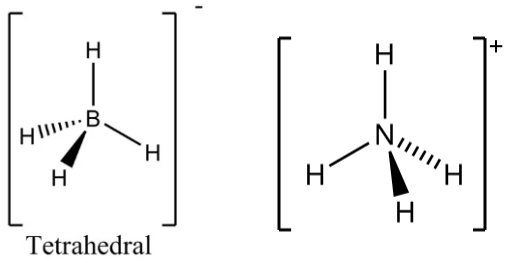
- Eight electrons is the maximum for B, C, N, or O
- If you make a new bond to uncharged H, C, N, or O you must also break one of the existing bonds in the same step.



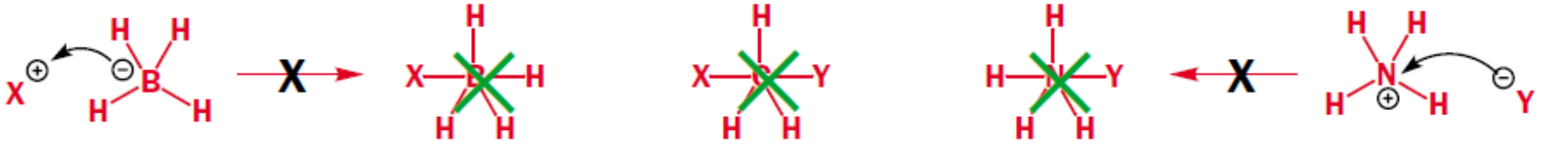
wrong mechanism

impossible structure
carbon has five bonds

- What happens if you have charged species like BH_4^- or NH_4^+



Tetrahedral



impossible reaction

impossible structure
boron has five bonds

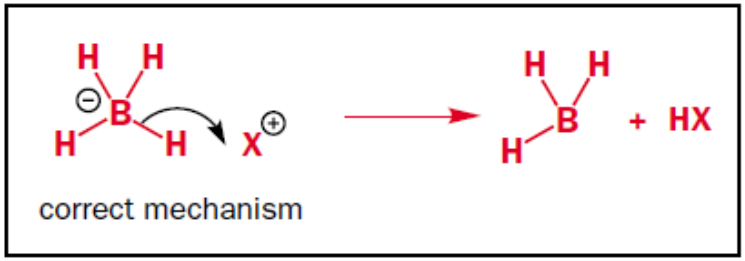
impossible structure
carbon has five bonds

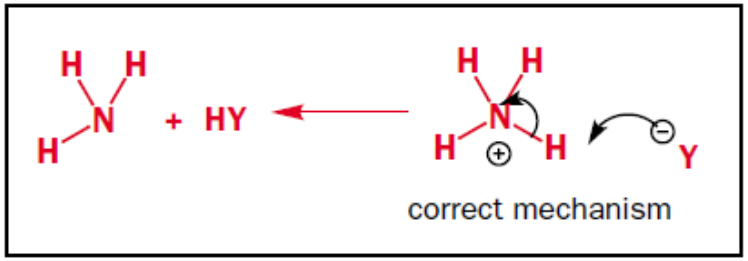
impossible structure
nitrogen has five bonds

impossible reaction

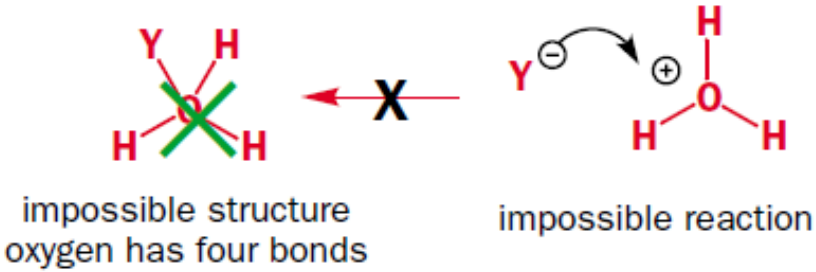
Drawing your own mechanisms with curly arrows

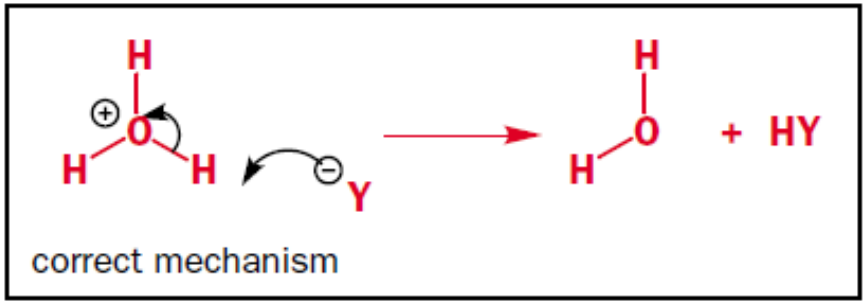
- Reactions with BH_4^- always involve the loss of H and a pair of electrons using the BH bond as nucleophile and reactions with NH_4^+ always involve the loss of H without a pair of electrons using the NH bond as electrophile





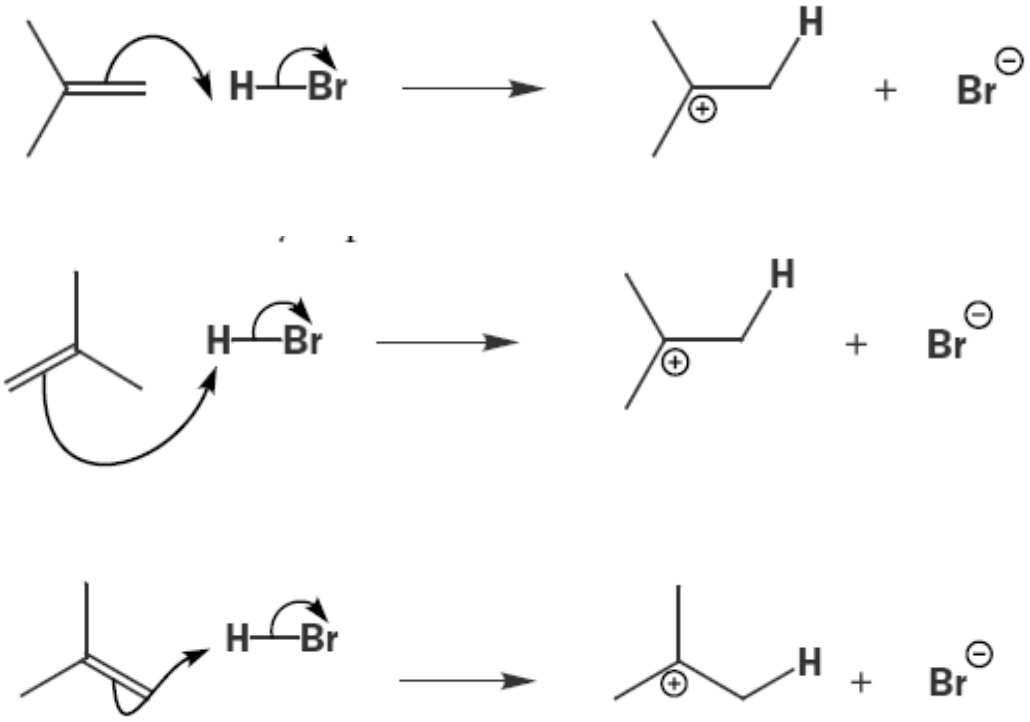
Similarly,





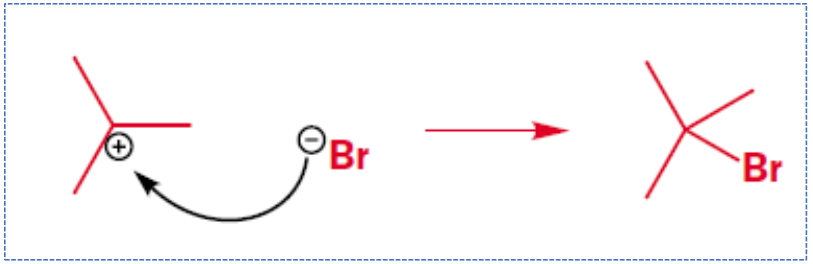
Mechanism & Curved Arrow Notation

- Electrons can be donated from π bonds and from σ bonds too

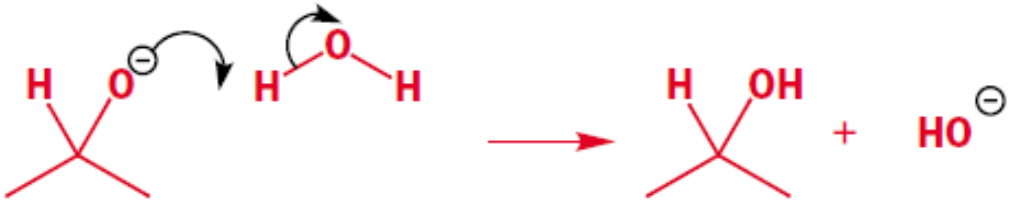


Two step reaction *via* an unstable intermediate

This reaction does not stop here as the two ions produced now react with each other to form the product of the reaction.



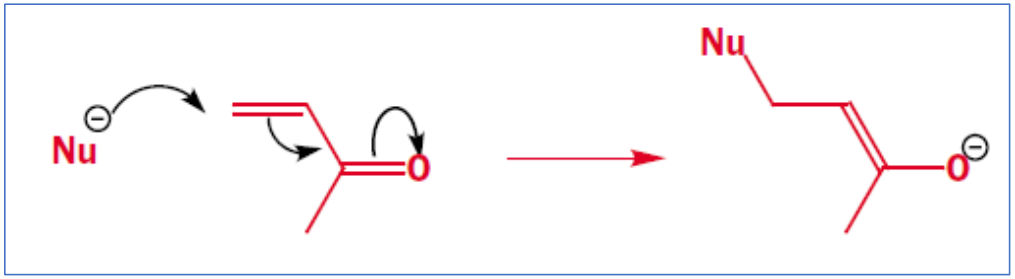
Mechanism and arrow pushing



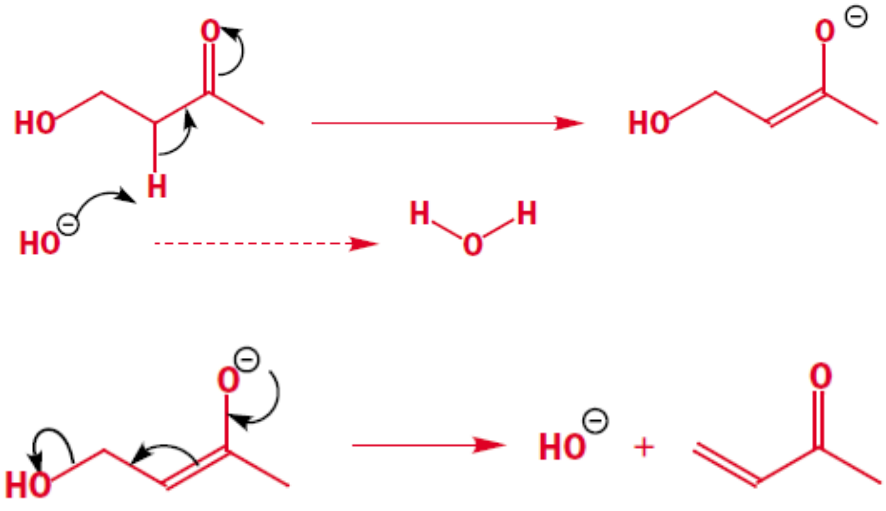
In this example, one of the atoms (the hydrogen atom) moves away from the rest of the BH_4 anion and becomes bonded to the carbonyl compound.

Mechanism and arrow pushing

- **Curly arrows also show movement of electrons within molecules**



The first arrow from the nucleophile makes a new σ bond and the last breaks the carbonyl π bond. The middle arrow just moves the C–C π bond along the molecule.

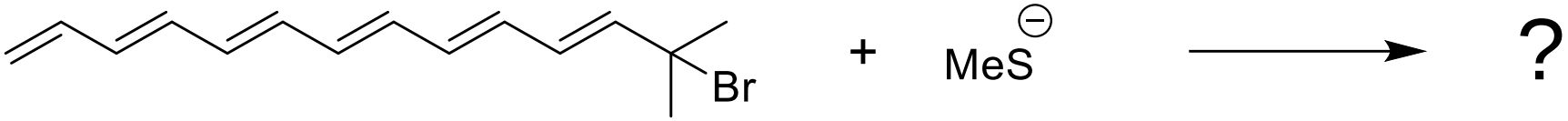


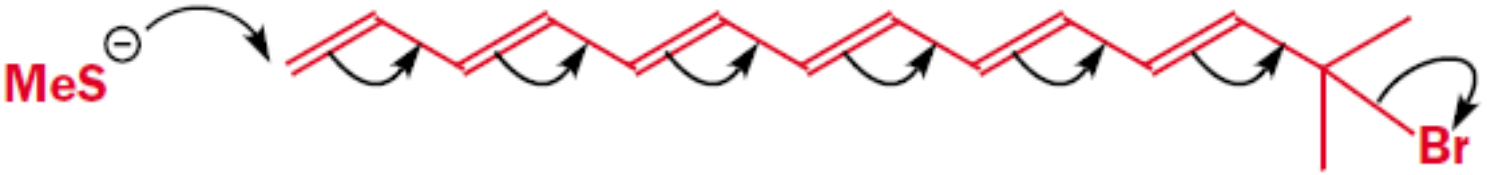
The arrow from the hydroxide ion removes a proton from the molecule making a new O–H bond in a molecule of water.

The middle arrow moves the electrons of a C–H bond into a C–C bond making it into a π bond and the third arrow polarizes the carbonyl π bond leaving an oxyanion as the product.

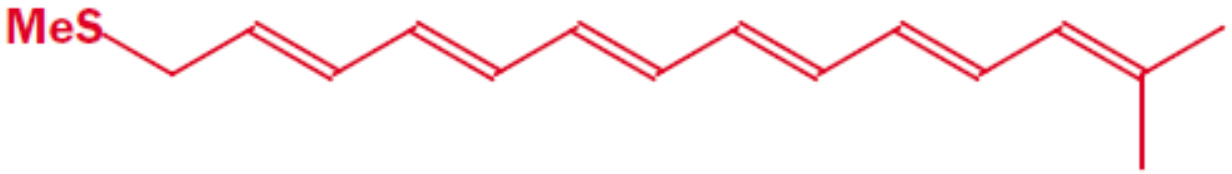
Charge is conserved—an anion gives an anion

Mechanism and arrow pushing

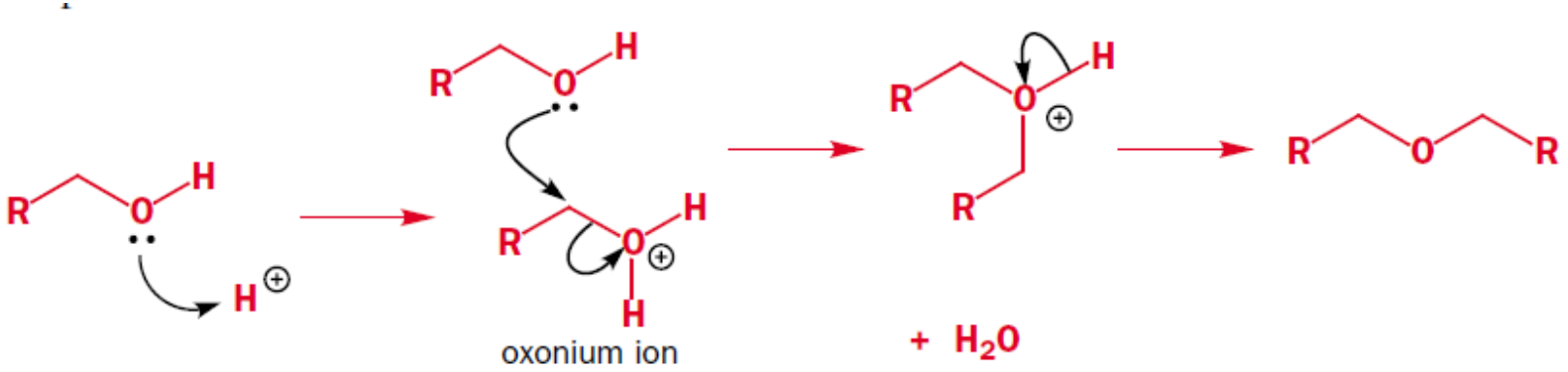




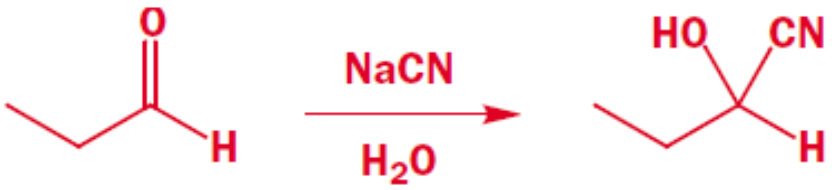
- The first arrow forms a new C–S σ bond and the last arrow breaks a C–Br σ bond but all the rest just move π bonds along the molecule.



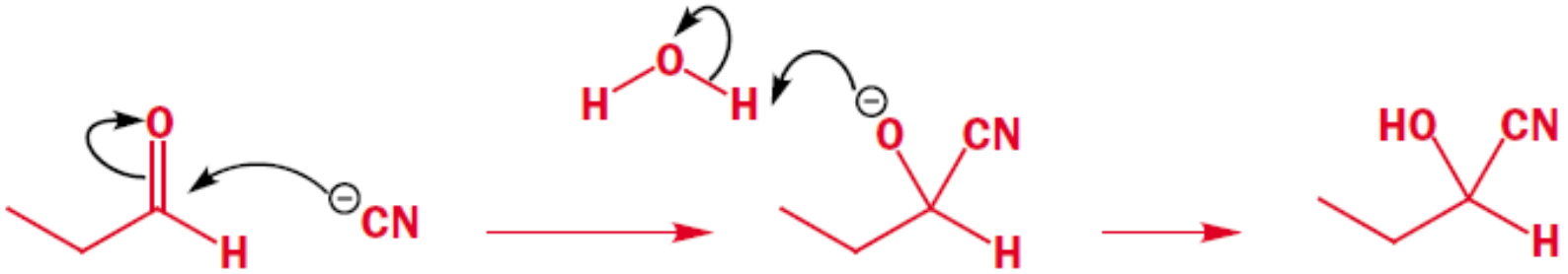
Suggest a mechanism for this acid-catalysed conversion of one functional group into another.



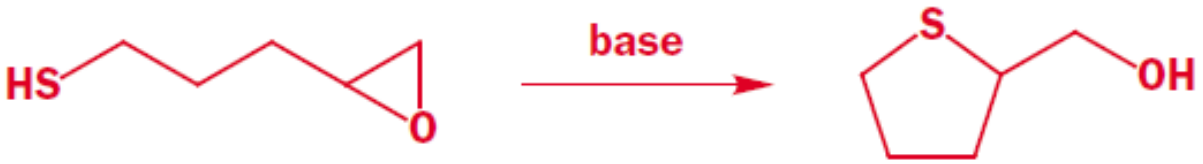
Drawing a two-step mechanism: cyanohydrin formation

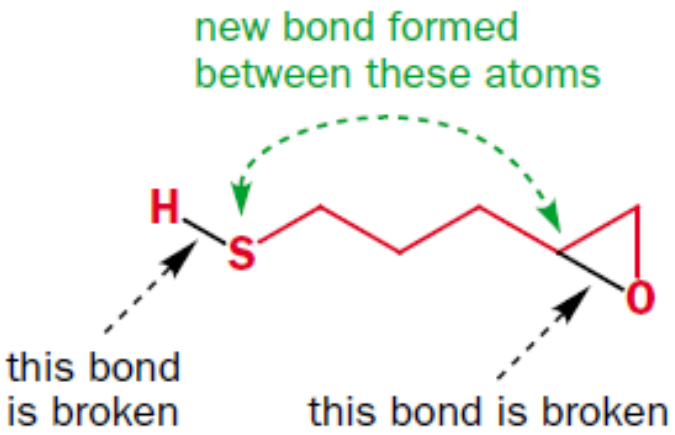


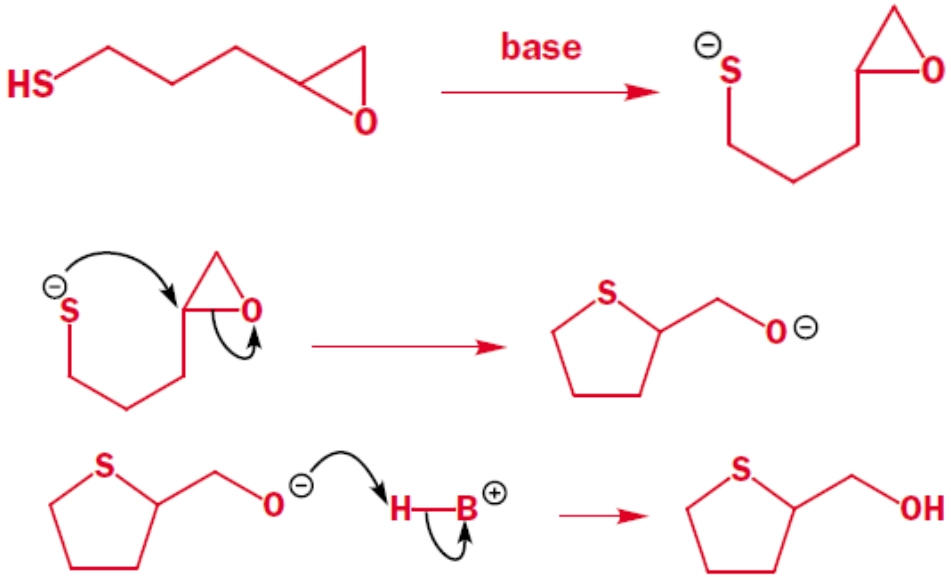
Suggest a mechanism!



Suggest a mechanism!





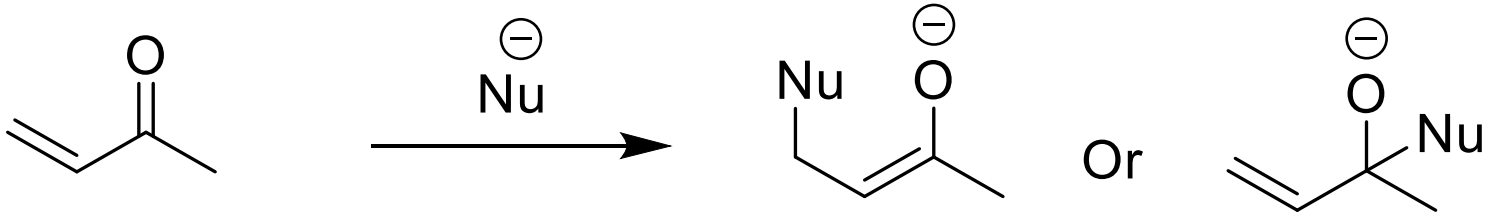


- This is a three-step mechanism involving chemistry unknown to you and yet you could draw a mechanism for it.

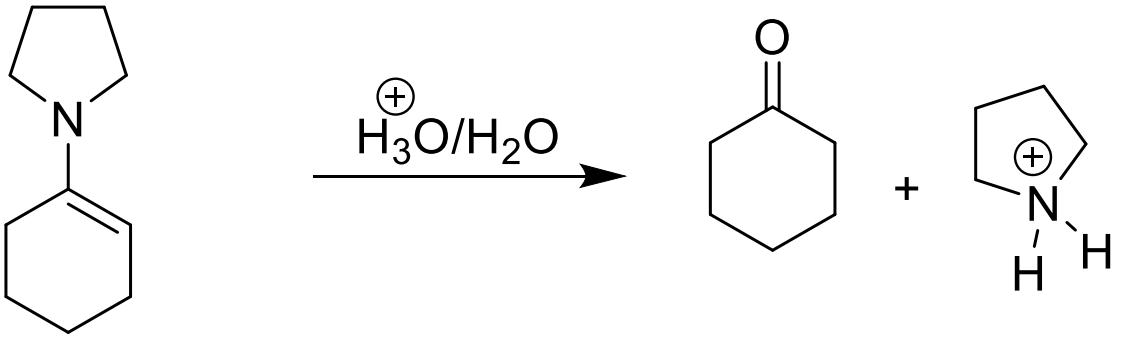
Points to Remember when drawing a mechanism

- Charge should be maintained for each step of mechanism
- Do not forget octet rule
- Learn to distinguish between formal charge and electron deficiency/rich
- Do not write multiple steps together
- Make sure the arrow always begins at the source & ends at sink/destination

Identify the product and write the plausible mechanism



Write the plausible mechanism



Reference:

Chapter 5; J. Clayden, N. Greeves and S. Warren, *Organic Chemistry*, 2nd Ed., Oxford University Press, 2012