

Chapter 5: Reactions of Alkenes and Alkynes

5.1. Characteristic Reactions of Alkenes

Hydrochlorination (Hydrohalogenation):

Hydration:

Bromination (Halogenation):

Hydroboration:

Hydrogenation (Reduction):

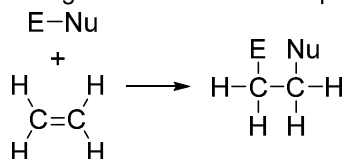
5.1

5.2 Reaction Mechanisms

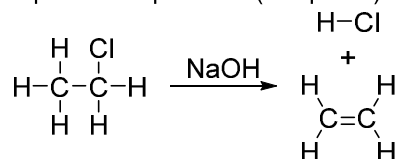
Reaction mechanisms describe in detail exactly what happens at each stage of a chemical transformation including which bonds are broken, which bonds are formed, which sequence of reactions leads to the observed product(s), what the reaction order is, and why we observe a given reaction rate

a) Types of Reactions

Addition Reactions: 2 reactants come together to form one compound

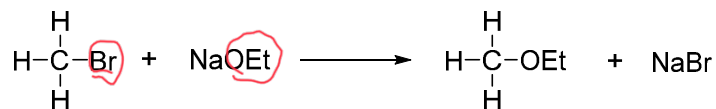


Elimination Reactions: 1 reactant splits into 2 products (Chapter 7)

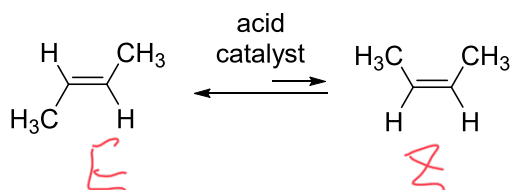


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Substitution Reactions: 2 reactants exchange parts to make 2 new products (Chapter 7)



Rearrangement Reactions: 1 reactant undergoes a reorganization of bonds and atoms to give a single isomeric product



5.3

b) Bond Cleavage and Formation

Ionic Reactions: Heterolytic Cleavage and Heterogenic Formation

Only species with paired electrons in valence shell are involved in ionic reactions (e.g. nucleophiles and electrophiles, Lewis acids and bases).

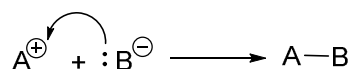
Ionic reactions generally involve the formation or cleavage of strong, polar bonds.

Heterolytic Cleavage



Polar: Unequal breaking of a bond

Heterogenic Formation

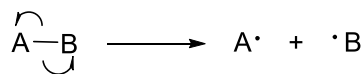


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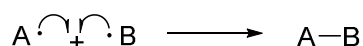
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Radical Reactions: Homolytic Cleavage and Homogenic Formation

Radical species contain unpaired electrons in the valence shell (most often they have an uneven number of electrons) and can be formed by homolytic cleavage of weak (often apolar) bonds.

Homolytic Cleavage**Homogenic Formation**

Two radicals can recombine to form a bond:

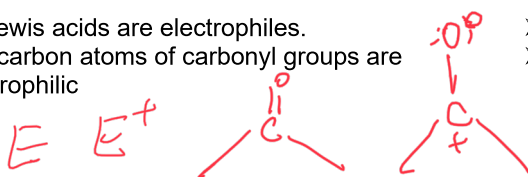


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c) Electrophiles and Nucleophiles

Electrophile = A species with an empty orbital it would like to fill.

- All Lewis acids are electrophiles.
- The carbon atoms of carbonyl groups are electrophilic

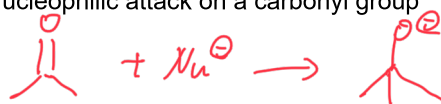


Nucleophile = A species with a pair of electrons it would like to donate/share.

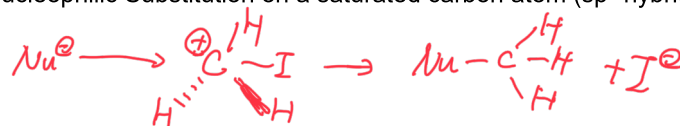
- All Lewis bases can act as nucleophiles
- Electron-rich π -bonds (e.g. ~~double bonds~~) can act as nucleophile.



Example 1: Nucleophilic attack on a carbonyl group



Example 2: Nucleophilic Substitution on a saturated carbon atom (sp^3 hybridized)



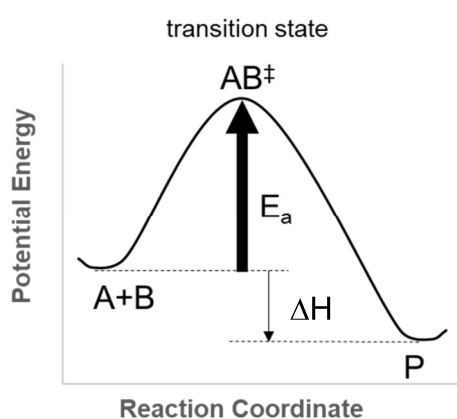
Example 3: Reaction of a nucleophile with a carbocation

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d) Energy Diagrams and Reaction Mechanisms

Energy diagrams show the energy changes that occur during a reaction.

Example of an energy diagram for a one-step reaction:



Transition state:

Activation Energy:

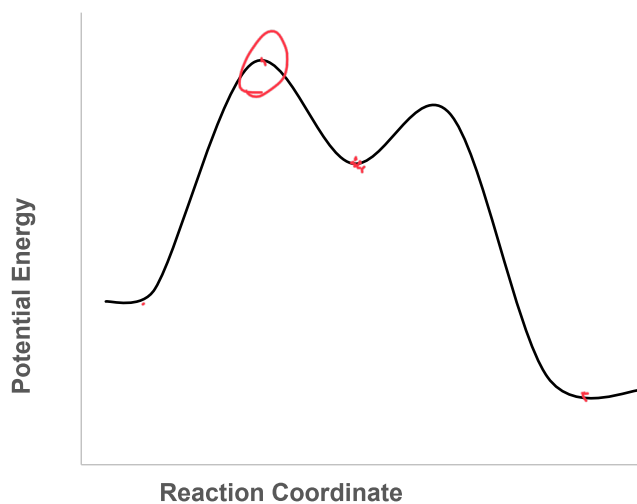
Heat of Reaction:

Exothermic:

Endothermic:

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Example of an energy diagram for a reaction involving intermediates:



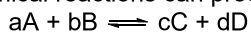
Reaction Intermediate:

Rate-determining step:

5.8

e) Review of Thermodynamics and Kinetics**Reaction Equilibrium: Thermodynamics**

Chemical reactions can proceed in both directions (are reversible)



$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The equilibrium constant, K_{eq} , tells us which direction is favored $K_{eq} > 1$ – products (C & D) are favored $K_{eq} < 1$ – reactants (A & B) are favored

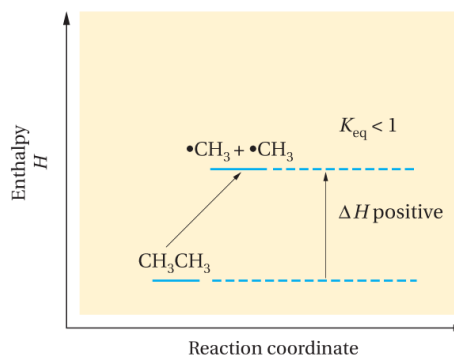
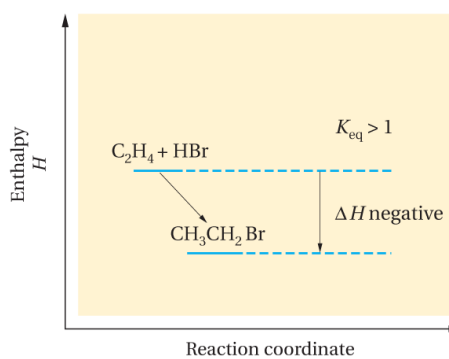
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Reactions occur when the products are more stable than reactants

Reactions want to go from high energy to low energy

Heat is released in these *exothermic* reactions ΔH (change in enthalpy) = energy difference between reactants and products

- negative ΔH indicates a favored, *exothermic* reaction
- If heat or energy is required for the reaction to proceed, the reaction is *endothermic* and unfavored

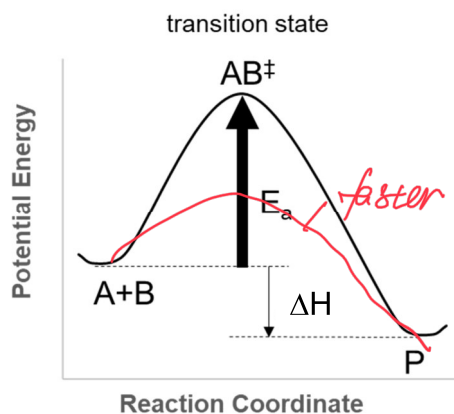


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Reaction Rates: How fast are reactions? (Kinetics)

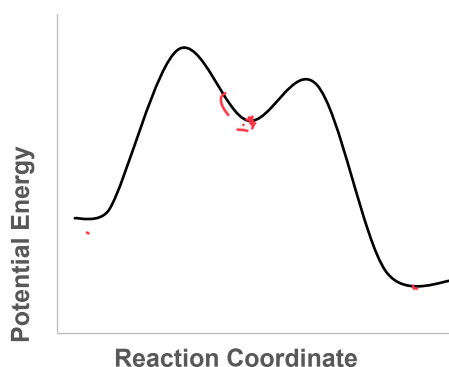
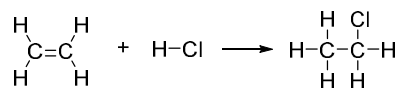
Molecules must collide with enough energy and in the right orientation so bonds can be made and broken

The higher the energy barrier the slower the reaction
Rates also affected by temperature and catalysts



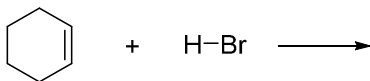
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Review: Answer the questions below regarding the reaction profile which belongs to the following reaction:



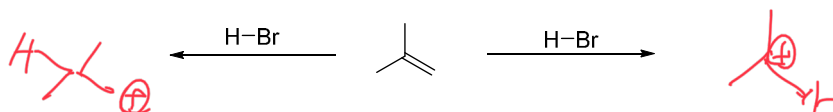
1. Is the first step exothermic or endothermic? Why?
2. Is the second step exothermic or endothermic? Why?
3. Which is the rate-determining step? Why?

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5.3 Electrophilic Addition of H-X to Alkenes and Alkynes**a) Electrophilic addition of H-Br across the double bond****Electrophilic addition of H-Br across the double bond of a symmetrical alkene:**

Points to note regarding the mechanism:

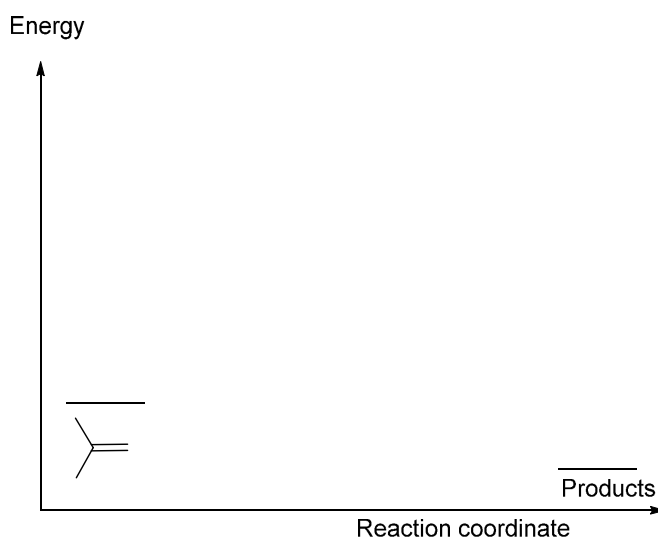
1. Draw the arrow beginning from the *middle* of the double bond with the electrons moving out *through the carbon* that is picking up the proton in the first step.
2. Because the substrate is symmetrical, either carbon could pick up the proton. Important is, that the carbocation is on the other carbon.

Electrophilic addition of H-Br across the double bond of an unsymmetrical alkene:

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The addition of HBr is *regioselective* for the more substituted alkyl bromide being formed when unsymmetrical alkenes are used. Why?

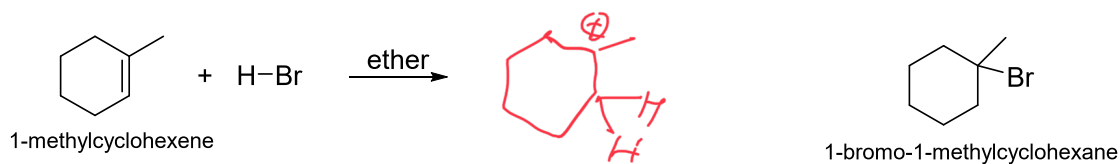
Reaction Profiles of the Two Possible Pathways:



- The *higher energy reactive carbocation intermediate* has a *higher energy transition state*.
- Formation of *more stabilized carbocation intermediate* during RDS is **faster** due to its lower energy pathway via the *lower energy transition state*.

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The more substituted product is often called **Markovnikov product**, and the addition reaction leading to it can be called a **Markovnikov addition**.



5.15

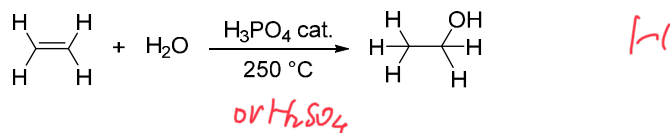
b) Addition of Hydrogen Halides to Alkynes

The electrophilic addition of hydrogen halides to triple bonds can be stopped after addition of one equivalent of HX (HCl, HBr, HI) if added stoichiometrically.

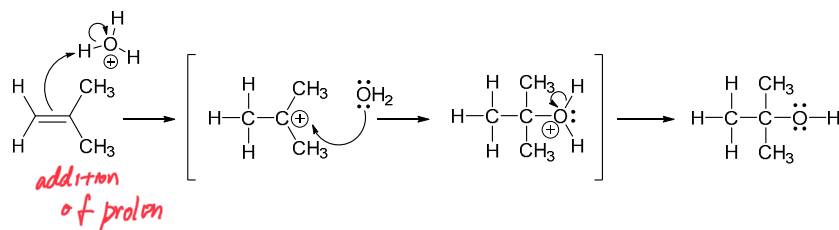
As with double bonds, this reaction results in the more substituted halide (follows Markovnikov's rule):



5.16

5.4 Acid catalyzed hydration: Addition of water across an unsaturated C,C bond

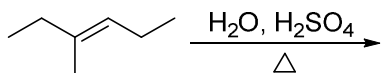
Mechanism:



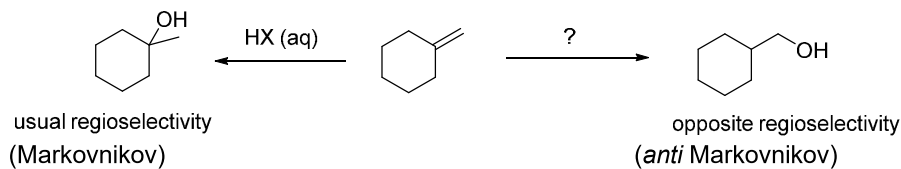
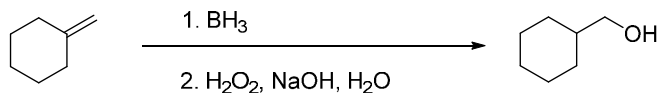
Important points:

- The acid is only needed in catalytic quantities
- The catalytic acid must have a conjugate base which is a worse nucleophile than water. Good choices are: phosphoric acid (H₃PO₄) and sulfuric acid (H₂SO₄)

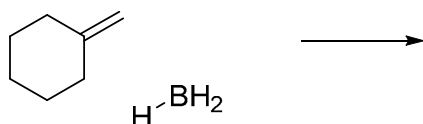
With unsymmetrically substituted alkenes, the more substituted alcohol is obtained (Markovnikov product).



5.17

5.5 Hydroboration-Oxidation: anti-Markovnikov Syn Addition of water across an unsaturated C,C bond**Hydroboration-Oxidation: Addition of water with opposite regioselectivity:**

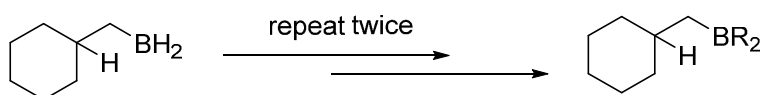
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Step 1: Borane Addition

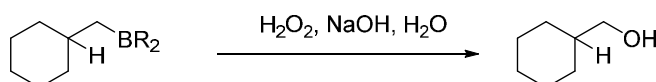
Reasons for the observed *regioselectivity*:

- **Electronics:** the π -bond electrons are being donated into the empty p-orbital of the boron atom (which is sp^2 hybridized). The partial positive charge this generates needs to go onto the carbon atom best able to stabilize this positive charge.
- **Sterics:** BH_2 is larger than H so it ends up where there is less steric hindrance.

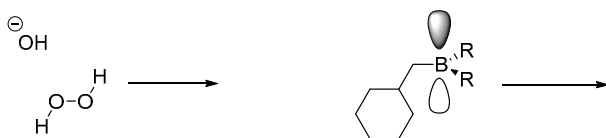
With BH_3 , this process can occur three times, giving the trialkylated borane:



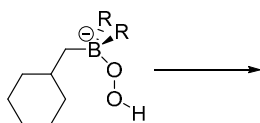
5.19

Step 2. Oxidation using an aqueous mixture of NaOH and H_2O_2 **Mechanism:**

In a first step, hydrogen peroxide is deprotonated by hydroxide and then forms the Lewis Acid-Base adduct with borane:



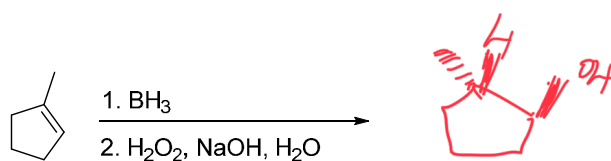
The O-O bond is weak and can break, losing OH^- at the same time as forming a strong C-O bond:



5.20

Stereochemical Outcome of the Hydroboration-Oxidation Reaction:

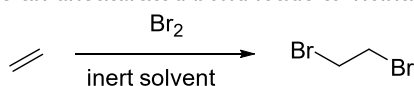
Syn addition of H and OH to the double bond



5.21

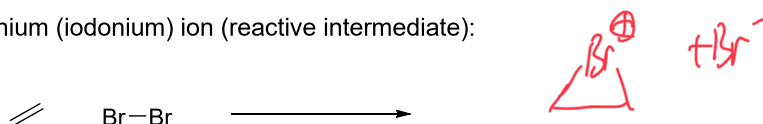
5.6 Electrophilic Addition of X_2 to Alkenes and Alkynes**a) Electrophilic Addition of X_2 to Alkenes**

Electrophilic addition of Br_2 across an unsaturated bond leads to vicinal dibromides:

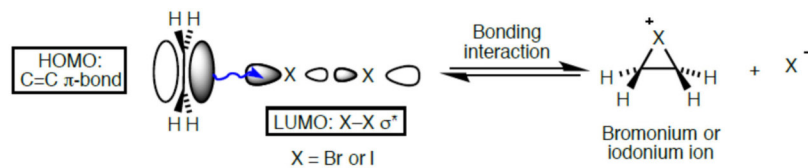


Mechanism: The addition of halogens to the double bond occurs in two steps.

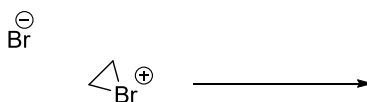
1. Formation of bromonium (iodonium) ion (reactive intermediate):



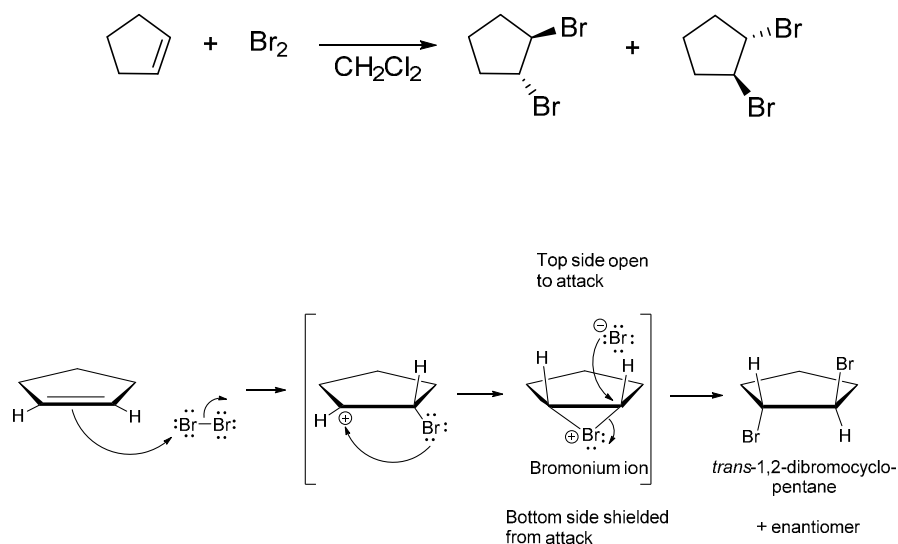
Orbital picture:



2. The bromonium (iodonium) is attacked by the bromide/iodide ion formed in the first step via a $\text{S}_{\text{N}}2$ reaction:

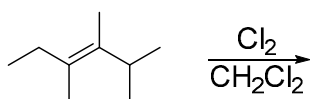
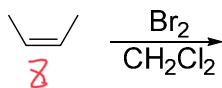
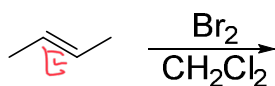


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Stereochemical Outcome of Bromination of Cyclopentene:

- *Anti addition*
- *Stereospecific reaction*
- Multiple products: bromonium ion can form on both sides of the double bond & the bromide can attack either of the carbons in the second step

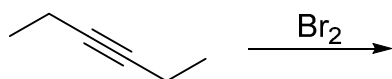
5.23

What are the products of these reactions?

5.24

b) Electrophilic Addition of Bromine to Alkynes

Anti stereochemistry

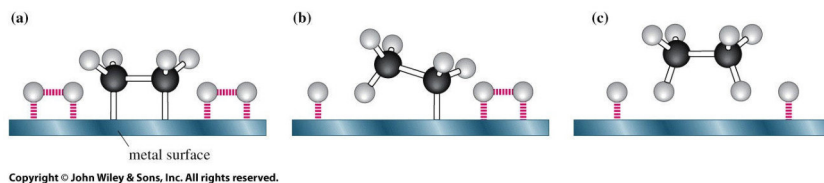


5.25

5.7 Hydrogenation of Alkenes and Alkynes*Reduction:* Addition of H₂ (or removal of O).

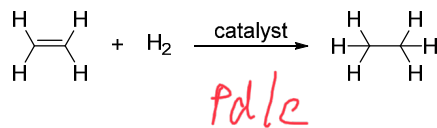
Hydrogenation of alkenes:

Hydrogenation of alkynes:

The role of the catalyst: Activation of hydrogen and lowering the transition state energy

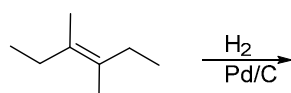
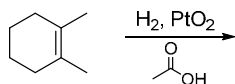
Energy diagram

5.26

a) Hydrogenation of Alkenes

Catalysts = Pd, PtO₂, or Ni

Hydrogenation of alkenes occurs with syn stereochemistry and is another example of a *stereospecific* reaction.

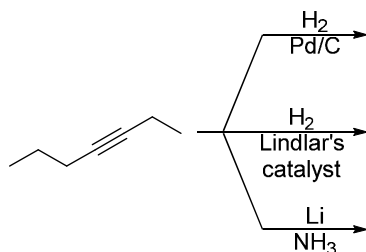


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b) Hydrogenation of Alkynes

Three possibilities:

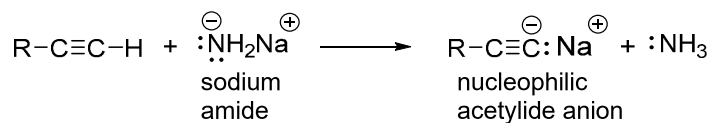
1. Full reduction to alkane
2. Reduction to *cis*-alkene (**Syn addition of hydrogen with Lindlar's catalyst**)
3. Reduction to *trans*-alkene (**Anti addition of hydrogen by dissolving metal reduction**)



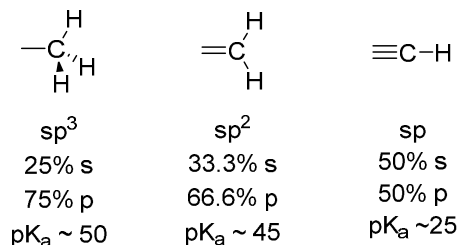
5.28

5.8 Formation and Use of Acetylide Anions

Terminal $\text{C}\equiv\text{C}-\text{H}$ are weakly acidic ($\text{pK}_a \approx 25$) and can be deprotonated by strong bases such as amides.



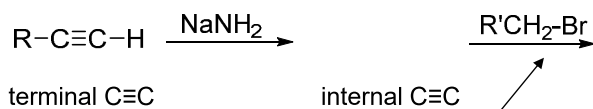
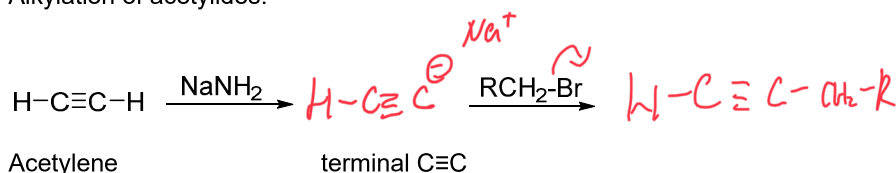
Acidity of terminal H is due to hybridization



- As hybridization of C becomes more s-like the acidity of the attached H increases
- Though acidic, terminal alkynes are far less acidic than H_2O
- In the presence of H_2O , acetylides react to give alkynes
- Internal alkynes have no exceptionally acidic Hs

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Alkylation of acetylides:



Only 1° alkyl halides can be used

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