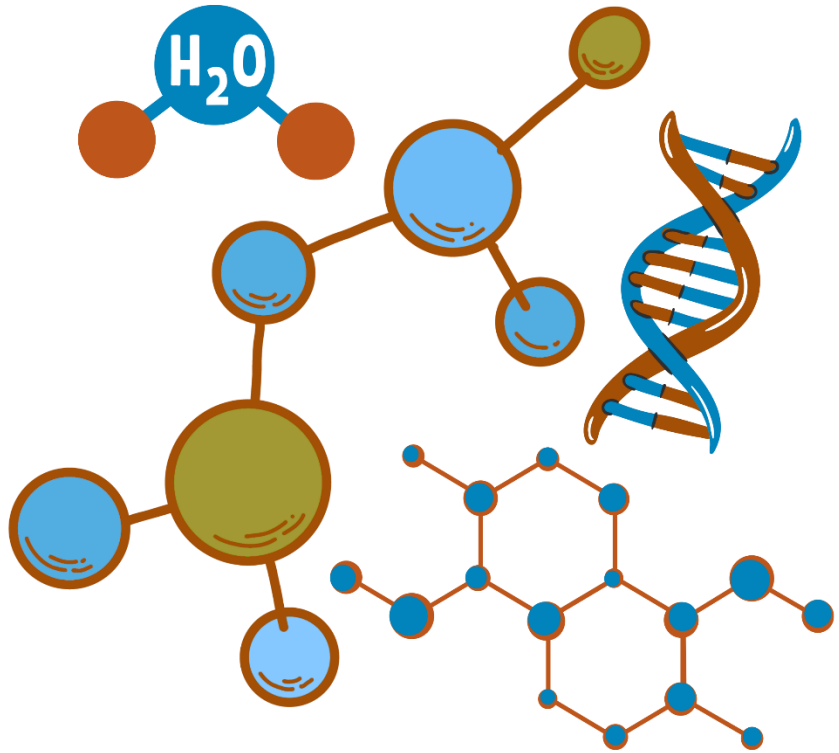
Principles of Organic Chemistry I
CHEM 244

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Chapter 5: Organic Reactions



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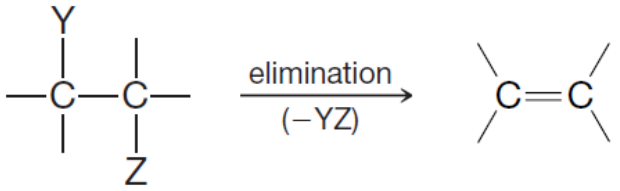
Elimination Reactions

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1. Elimination Reactions

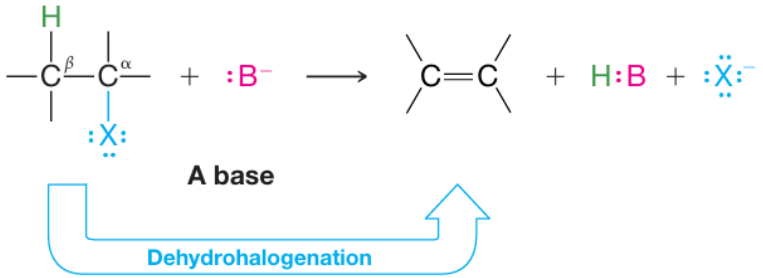
1.1. Synthesis of Alkenes

- Elimination reactions are the most important means for synthesizing alkenes.

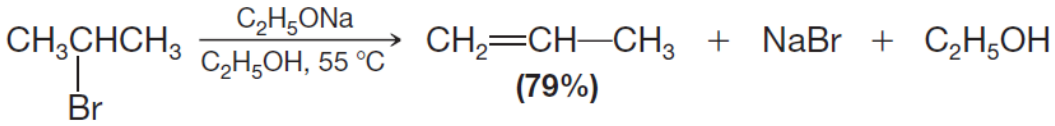


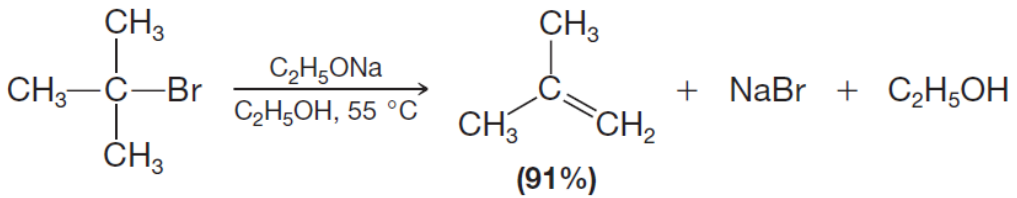
1.1.1. Dehydrohalogenation (Elimination of Hydrogen Halide) of Alkyl Halides

- Heating the alkyl halide with a strong base causes the reaction to take place.



- **Examples;**





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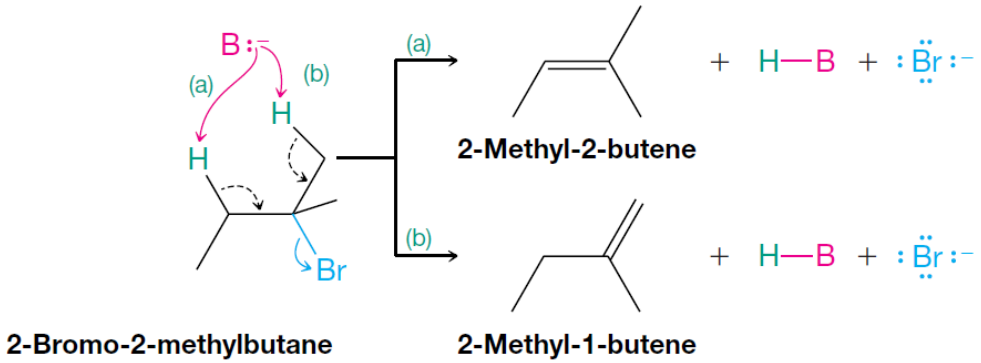
1. Elimination Reactions

1.1. Synthesis of Alkenes

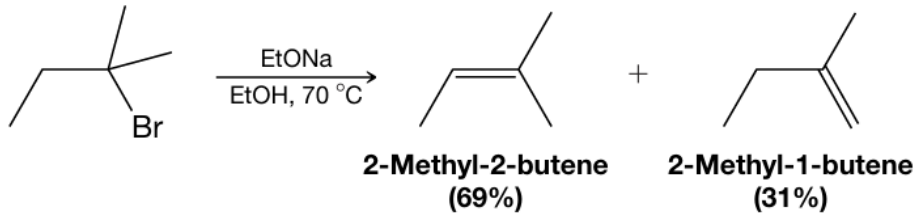
1.1.1. Dehydrohalogenation (Elimination of Hydrogen Halide) of Alkyl Halides

- **Zaitsev's Rule:** Formation of the more substituted alkene (more stable) is favored with a small base.

  Dehydrohalogenation of Hydrogen halides, can often yield more than one product.



- **Example;** Dehydrohalogenation of 2-bromo-2-methylbutane**:**



Trisubstituted: more stable

Disubstituted: less stable

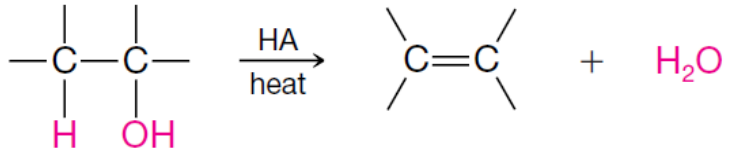
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1. Elimination Reactions

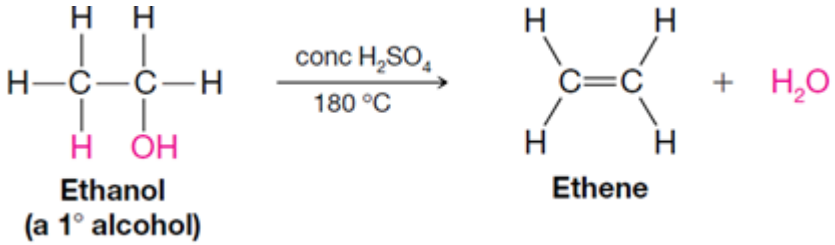
1.1. Synthesis of Alkenes

1.1.2. Acid-catalyzed Dehydration (Elimination of Water) of Alcohols

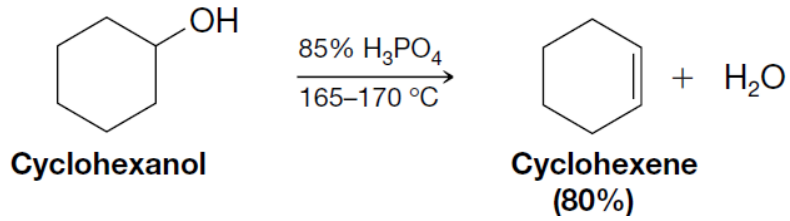
- Most alcohols undergo dehydration (*lose a molecule of water*) to form an alkene when heated with a strong acid as sulfuric acid, H_2S0_4, and phosphoric acid, H_3P0_4.



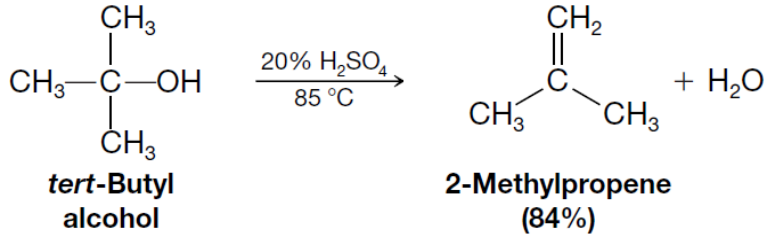
  - Primary alcohol; Ethanol dehydrates in concentrated sulfuric acid and a temperature of 180 °C.



  - Secondary alcohol; Cyclohexanol dehydrates in 85% phosphoric acid at 165–170 °C.



  - Tertiary alcohol; *tert*-Butyl alcohol dehydrates in 20% aqueous sulfuric acid at a temperature of 85 °C.



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1. Elimination Reactions

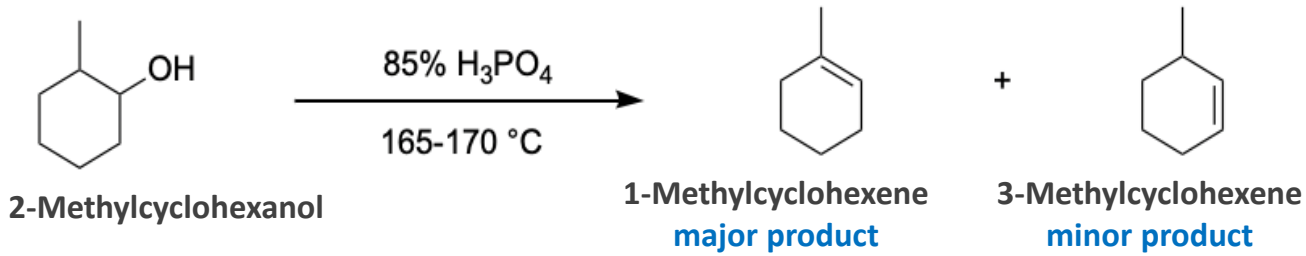
1.1. Synthesis of Alkenes

1.1.2. Acid-catalyzed Dehydration (Elimination of Water) of Alcohols

- Sometimes, a single alcohol can yield two or more different alkenes.

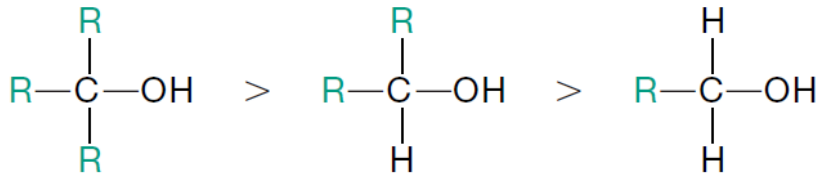
  Example; 2-methylcyclhexanol can give two alkenes.

  - In these cases, the alkene with the most substituted double bond usually predominates.
  - By "most substituted," we mean the alkene with the greatest number of alkyl groups on the doubly bonded carbons.



2-Methylcyclohexanol → 1-Methylcyclohexene (major product) + 3-Methylcyclohexene (minor product)

- The relative ease with which alcohols undergo dehydration is 3° > 2° > 1°.



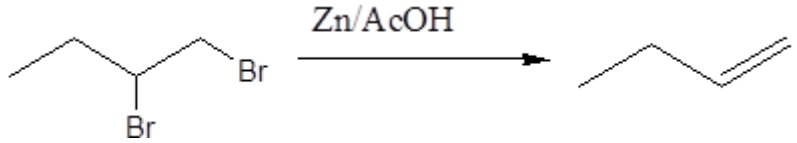
3° Alcohol > 2° Alcohol > 1° Alcohol

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1. Elimination Reactions

1.1. Synthesis of Alkenes

1.1.3. Dehalogenation of Vicinal Dibromides



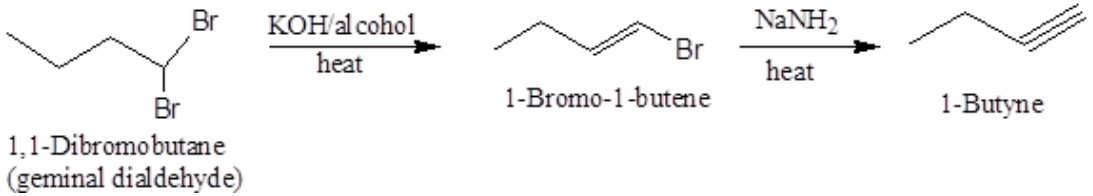
1.2. Synthesis of Alkynes

1.2.1. Dehydrohalogenation (Elimination of Hydrogen Halide) of Alkyl dihalides

- Alkynes can be prepared under alkaline conditions via dehydrohalogenation of alkyl dihalides
  - Dehydrohalogenation of *vicinal* dibromide



  - Dehydrohalogenation of *geminal* dibromide



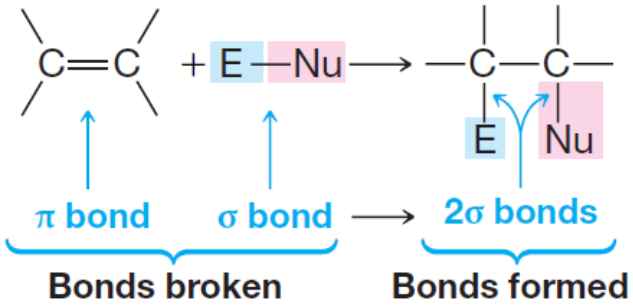
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Electrophilic Addition Reactions

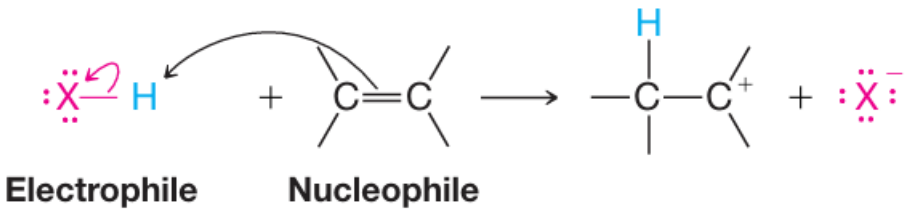
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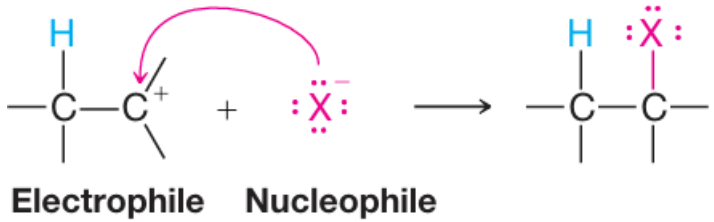
2. Electrophilic Addition Reactions

- Generally, the reaction is exothermic because one π and one σ bond are converted to two σ bonds.



- In addition reactions, the alkene changes from a nucleophile in the first step to an electrophile in the second.





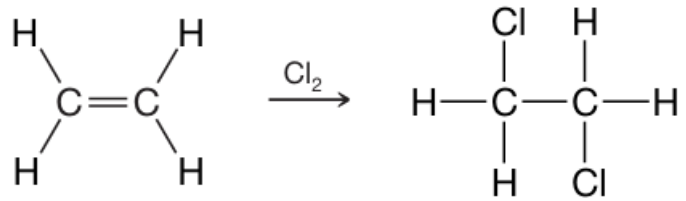
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2. Electrophilic Addition Reactions

2.1. Halogenation (Addition of Halogen)

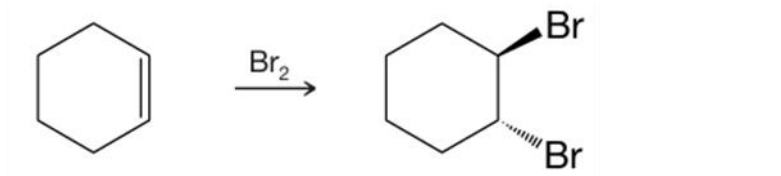
2.1.1. *Halogenation of Alkenes and Cycloalkenes*

- Alkenes react rapidly with bromine and chlorine to form *vicinal* dihalides.
- The addition of halogens is an anti addition to the double bond.



Ethene **1,2-Dichloroethane**

- Example; Addition of bromine to cyclohexene to yield *trans*-1,2-dibromocyclohexane.



Cyclohexene ***trans*-1,2-Dibromocyclohexane**

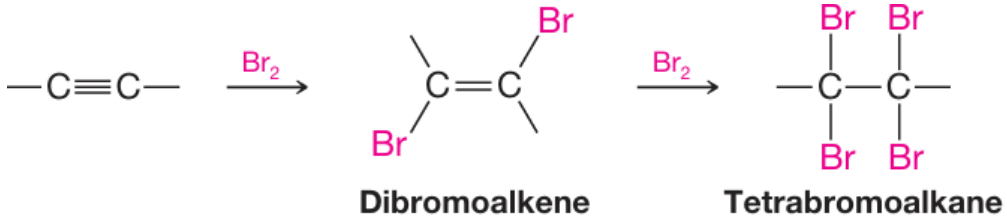
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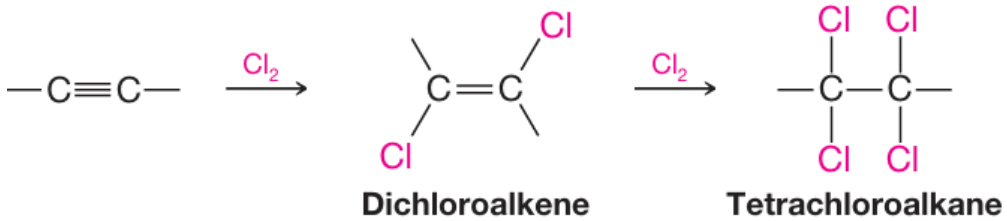
2. Electrophilic Addition Reactions

2.1. Halogenation (Addition of Halogen)

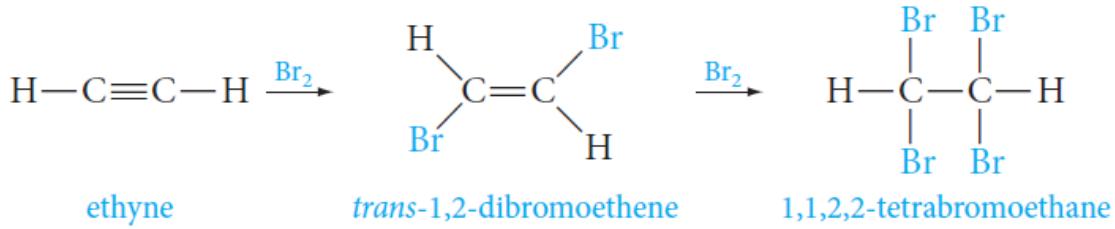
2.1.2. Halogenation of Alkynes

- Alkynes show the same kind of addition reactions with chlorine and bromine that alkenes do.
- With alkynes, the addition may occur once or twice, depending on the number of molar equivalents of halogen added.





- Example; Addition of bromine to ethyne gives the *trans* isomer.



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2. Electrophilic Addition Reactions

2.1. Halogenation (Addition of Halogen)

2.1.2. Halogenation of Alkynes

- Addition of one molar equivalent of chlorine o bromine to an alkyne generally results in anti addition and yields a *trans*-dihaloalkene.
- **Example;** Addition of bromine to 2-pentyne gives the *trans* isomer.



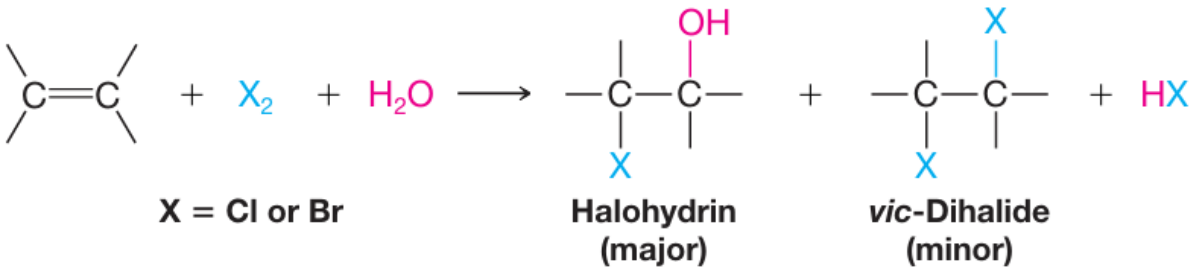
2-Pentyne **_trans_-2,3-Dibromo-2-pentene**

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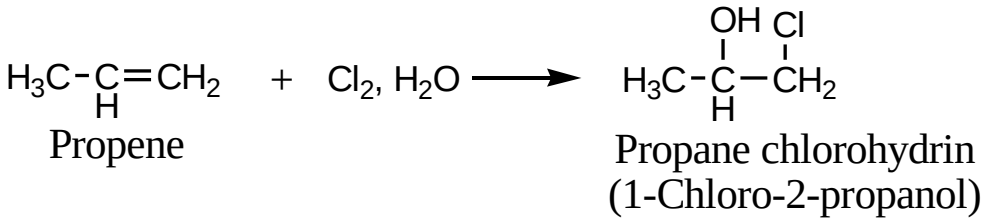
2. Electrophilic Addition Reactions

2.2. Addition of Hypohalous Acid (X_2/H_2O) to Alkenes; Halohydrin Formation

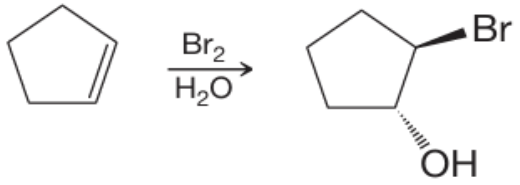
- Halogenation of an alkene in aqueous solution, the major product is a halohydrin (halo alcohol)
- The reaction proceeds as if hypochlorous acid, HO—Cl, or hypobromous acid, HO—Br, were the adding reagent.



- Addition of HOX also follows Markovnikov's rule.



- Example; Addition of bromine to cyclopentene to yield *trans*-2-bromocyclopentanol.



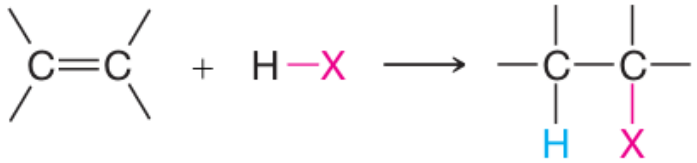
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2. Electrophilic Addition Reactions

2.3. Hydrohalogenation (Addition of Hydrogen Halide); Markovnikov's Rule

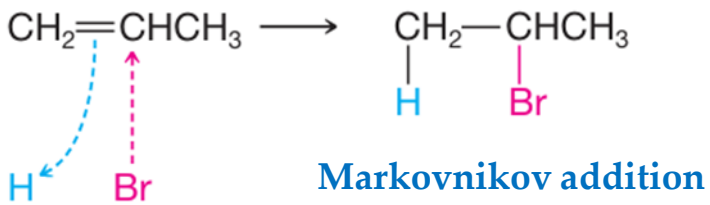
2.3.1. *Hydrohalogenation of Alkenes*

- Hydrogen halides (HI, HBr, HCl, and HF) add to the double bond of alkenes to form alkyl halide:



- The order of reactivity of the hydrogen halides in alkene addition is HI > HBr > HCl > HF
- The addition of HX to an unsymmetrical alkene could occur in two ways.

The alkene carbon atom with the greater number of hydrogen atoms receives the hydrogen.



Markovnikov addition product

- Markovnikov's rule is to say that in the addition of HX to an alkene, the hydrogen atom adds to the carbon atom of the double bond that already has the greater number of hydrogen atoms.

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2. Electrophilic Addition Reactions

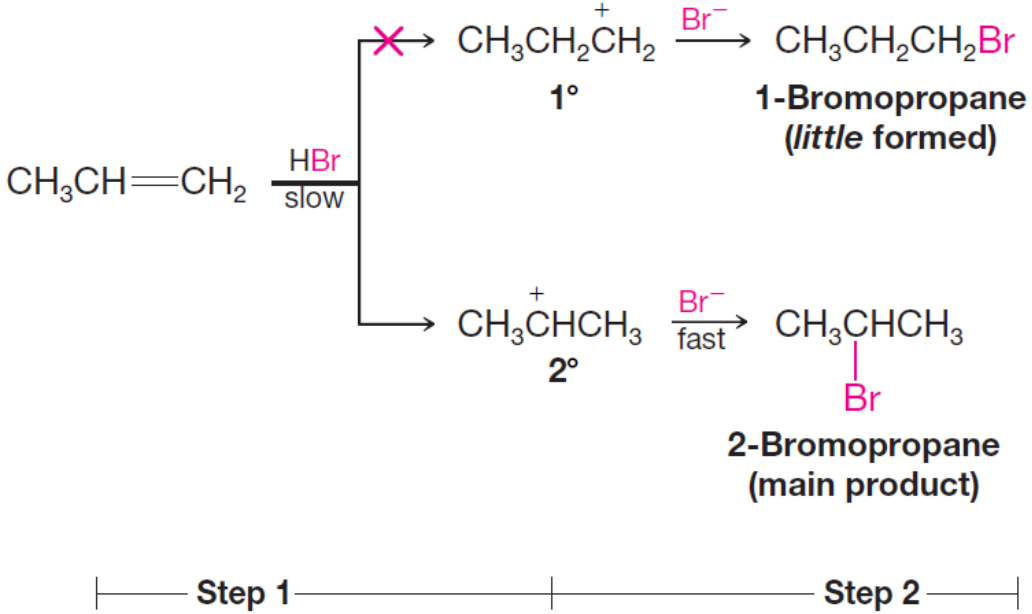
2.3. Hydrohalogenation (Addition of Hydrogen Halide); Markovnikov's Rule

2.3.1. *Hydrohalogenation of Alkenes*

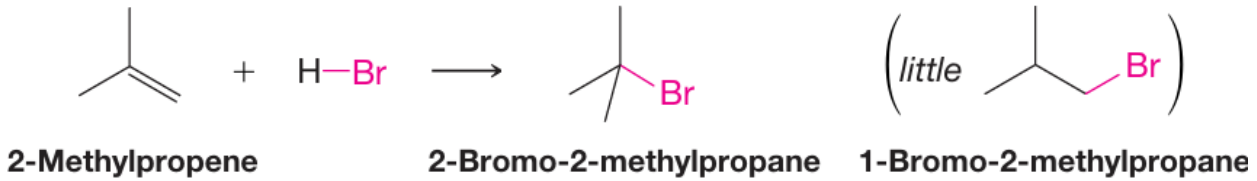
- Theoretical Explanation of Markovnikov's Rule
  - These two carbocations are not of equal stability.
  - **Example;**

    Addition of HBr to 2-methylpropene;

    The main product is 2-bromo-2-methylpropane, not 1-bromo-2-methylpropane.



- Anti-Markovnikov addition of HBr occurs in the Presence of Peroxides (see Section 3.4).



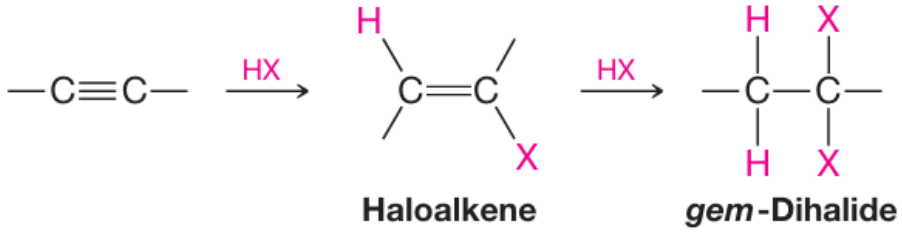
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2. Electrophilic Addition Reactions

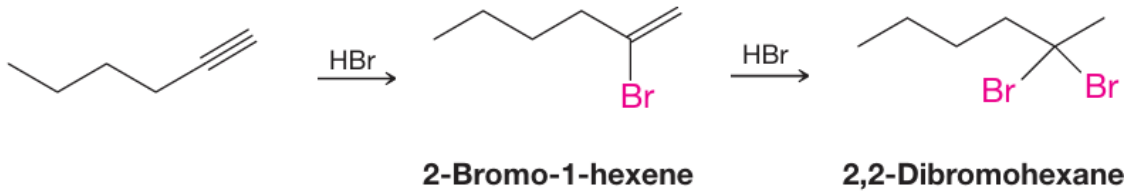
2.3. Hydrohalogenation (Addition of Hydrogen Halide); Markovnikov's Rule

2.3.2. *Hydrohalogenation of Alkynes*

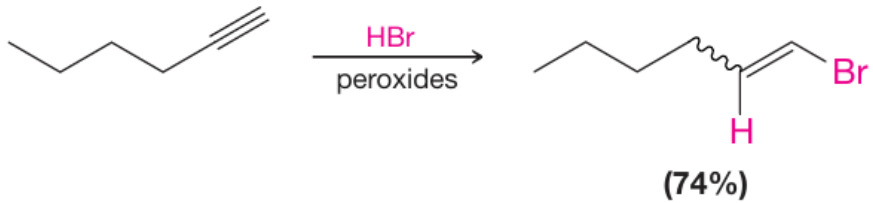
- Alkynes react with one molar equivalent of hydrogen chloride or hydrogen bromide to form haloalkenes, and with two molar equivalents to form *geminal* dihalides and follow Markovnikov's rule.



- Example; Addition of HBr to 1-hexyne.



- Anti-Markovnikov addition of HBr occurs in the presence of peroxide (see Section 3.4) .



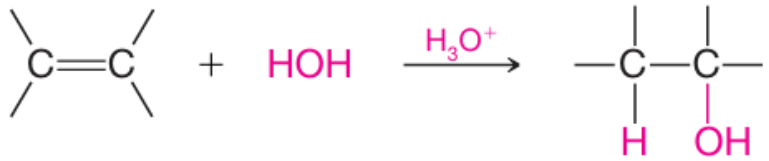
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2. Electrophilic Addition Reactions

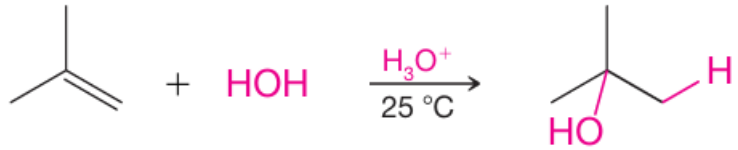
2.4. Hydration (Addition of Water)

2.4.1. Acid-Catalyzed Hydration of Alkenes; Markovnikov's Rule

- The reaction of alkenes with dilute aqueous acid leads to Markovnikov addition of water.



- Example; The hydration of 2-methylpropene.



2-Methylpropene (isobutylene) → **2-Methyl-2-propanol (*tert*-butyl alcohol)**

- Because the reactions follow Markovnikov's rule, acid-catalyzed hydrations of alkenes do not yield primary alcohols except in the special case of the hydration of ethene.

$$CH_2{=}CH_2 + HOH \xrightarrow[300\ ^\circ C]{H_3PO_4} CH_3CH_2OH$$

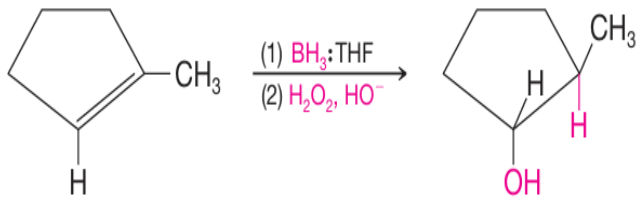
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2. Electrophilic Addition Reactions

2.4. Hydration (Addition of Water)

2.4.2. *Hydroboration–Oxidation of Alkenes: Anti-Markovnikov Syn Hydration*

- Hydroboration–oxidation takes place as anti-Markovnikov.
- Example; The hydroboration of 1-methylcyclopentene.



1-Methylcyclopentene **2-Methylcyclopentanol**

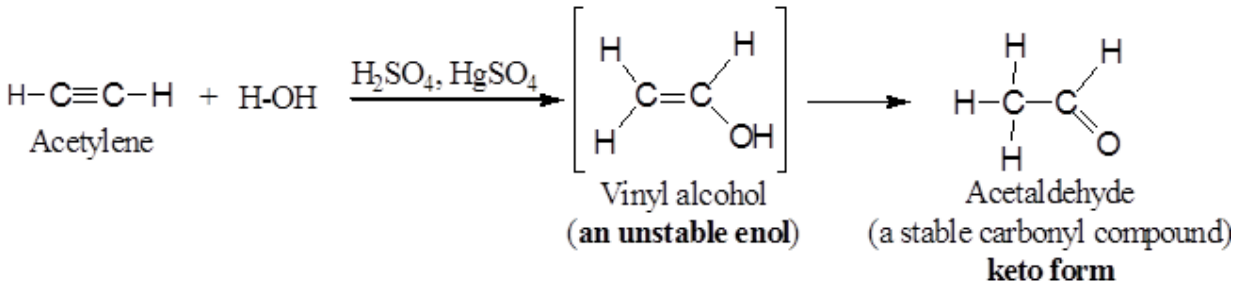
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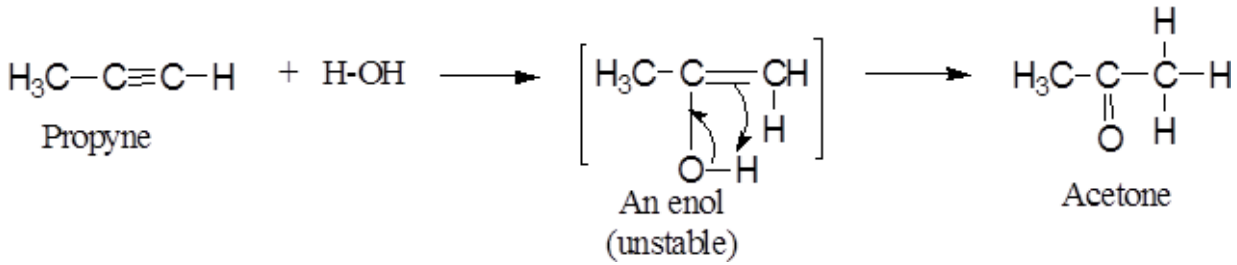
2. Electrophilic Addition Reactions

2.4. Hydration (Addition of Water)

2.4.3. Hydration of Alkynes: Markovnikov's Rule

- Addition of water to alkynes requires an *acid catalyst* and *mercuric ion* as well.
- The mercuric ion forms a complex with the triple bond and activates it for addition.
- Although the reaction is similar to that of alkenes, the initial product - *a vinyl alcohol or enol* - rearranges to a *carbonyl compound (keto form)*.





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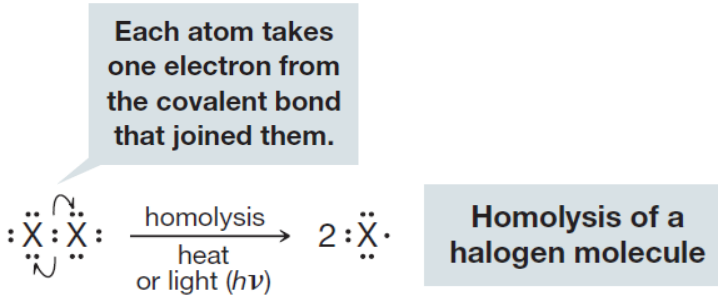
Free Radical Reactions

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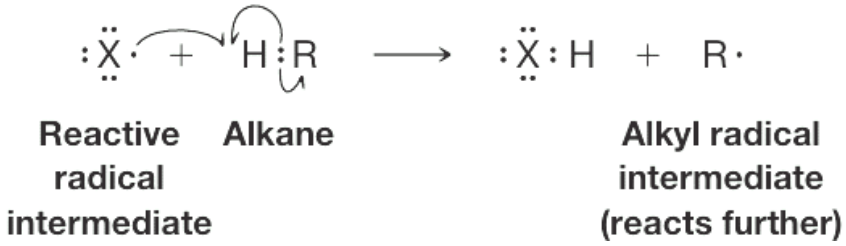
3. Radical Reactions

3.1. Formation of Free Radicals

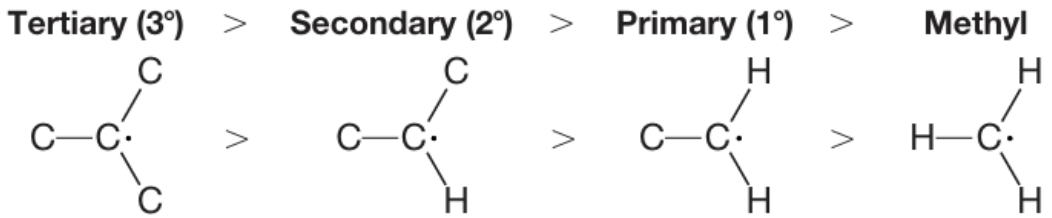
- Homolytic bond cleavage leads to the formation of free radicals, which are highly reactive, and short-lived species.



- Hydrogen abstraction is one way a halogen radical can react to pair its unshared electron.



- The relative stabilities of radicals are 3° > 2° > 1° > methyl, follows the same trend as for carbocations.
- Radicals are electron deficient, as are carbocations, and the most substituted radical is most stable.

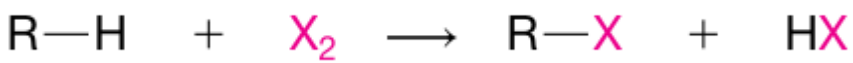


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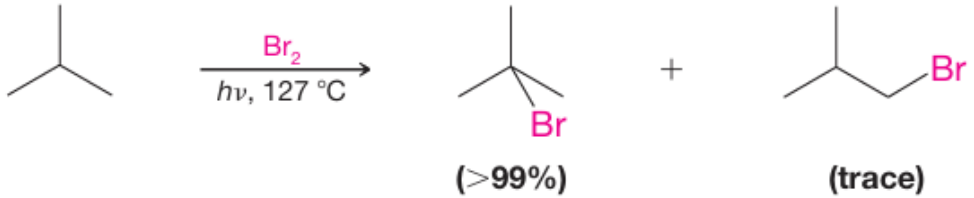
3. Radical Reactions

3.2. Halogenation of Alkanes

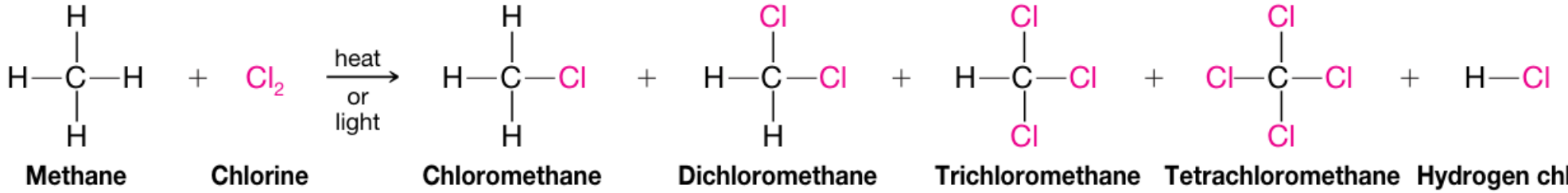
- A halogen atom replaces one or more of the hydrogen atoms of the alkane to produce alkyl halides by a *free radical substitution reaction*.
- Alkanes undergo substitution reactions with halogens, fluorine, bromine and chlorine, in the presence of heat or light.
- Fluorine reacts explosively whereas iodine is unreactive.



- Tertiary hydrogens are more reactive than secondary hydrogens which are more reactive than primary hydrogens.



- Free Radical halogenation can yield a mixture of halogenated compounds by substitution of all hydrogen atoms in alkane.

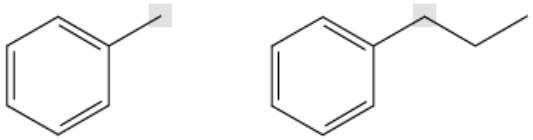


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3. Radical Reactions

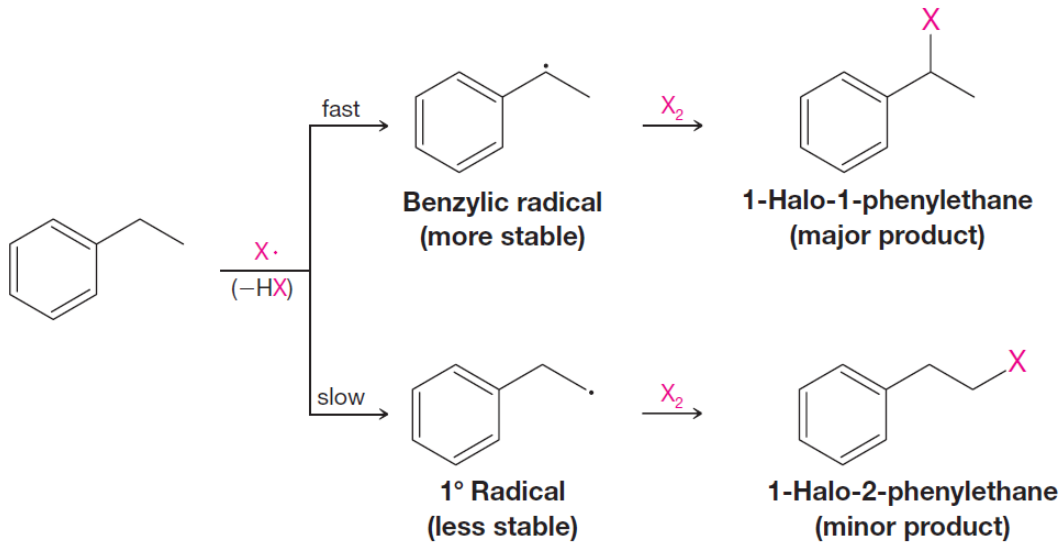
3.3. Benzylic Substitution and Benzylic Radicals

- An atom or group bonded to a sp^3-hybridized carbon adjacent to a benzene ring is called a benzylic group.



The hydrogen atoms bonded at the highlighted carbons are benzylic hydrogens

- Example; Halogenation of ethylbenzene.
  - The major product is the 1-halo-1-phenylethane.
  - The benzylic radical is formed much faster than the 1° radical due to the greater stability of benzylic radicals.

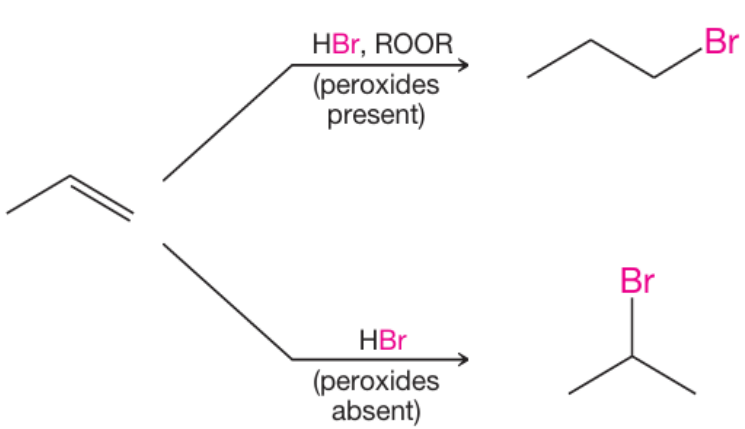


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3. Radical Reactions

3.4. Free Radical Addition of Hydrogen Halide to Alkenes: *Anti-Markovnikov's Rule*

- Ionic Addition; The result is Markovnikov addition
- Free Radical Addition; in the presence of peroxides (R-O-O-R), The result is anti-Markovnikov addition.
  - Hydrogen bromide is the only hydrogen halide that gives anti-Markovnikov addition when peroxides are present.
  - Hydrogen fluoride, hydrogen chloride, and hydrogen iodide do not give anti-Markovnikov addition even with peroxides.



Anti-Markovnikov addition **Free Radical Addition**

Markovnikov addition **Ionic Addition**

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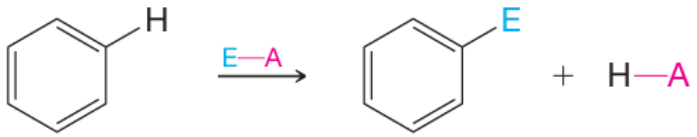
Electrophilic Aromatic Substitution Reactions

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4. Electrophilic Aromatic Substitution Reactions

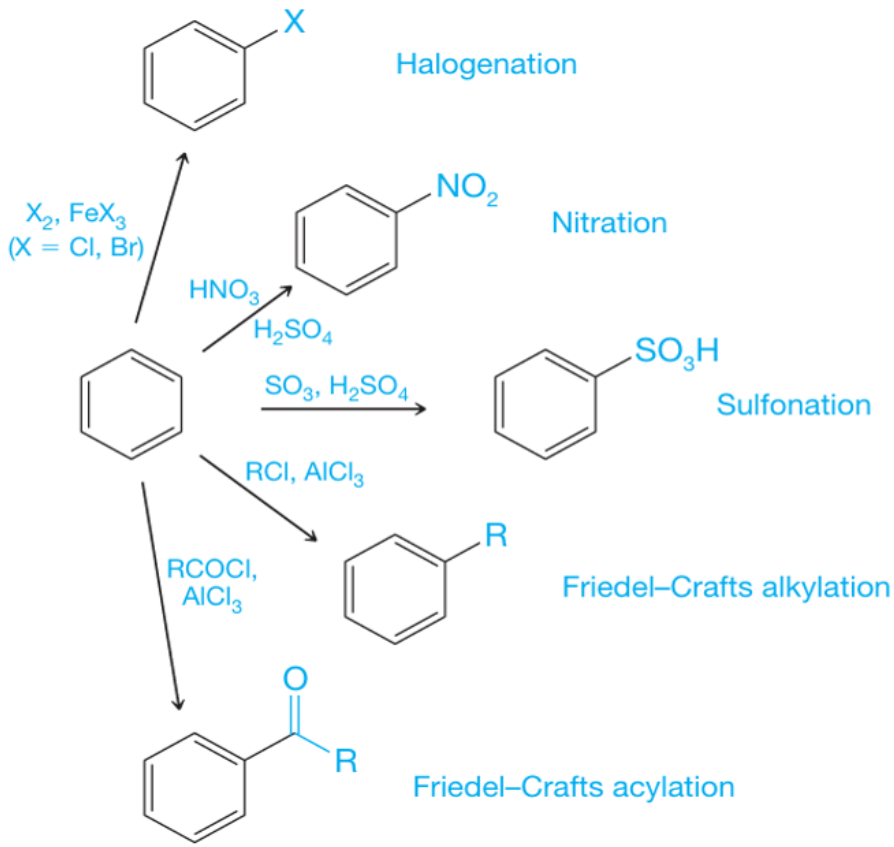
4.1. Reactions of Benzene

- Electrophilic aromatic substitutions (EAS) are the most important reactions of aromatic compounds, in which an electrophile replaces one of the hydrogen atoms of the ring.



(E—A is an electrophilic reactant)

- Five different types of electrophilic aromatic substitutions including;
  - Halogenation of Benzene
  - Nitration of Benzene
  - Sulfonation of Benzene
  - Friedel–Crafts Alkylation
  - Friedel–Crafts Acylation



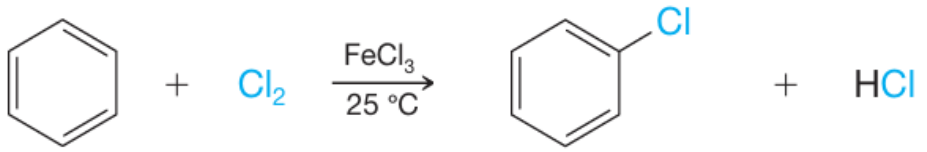
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4. Electrophilic Aromatic Substitution Reactions

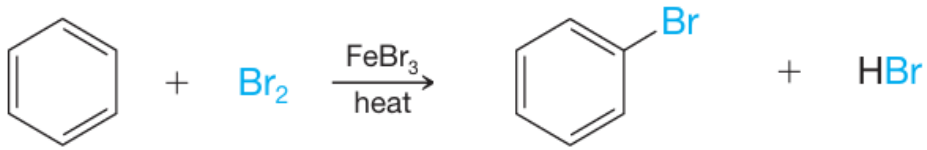
4.1. Reactions of Benzene

4.1.1. Halogenation of Benzene

- Benzene reacts with bromine and chlorine in the presence of Lewis acids to give halogenated substitution products.

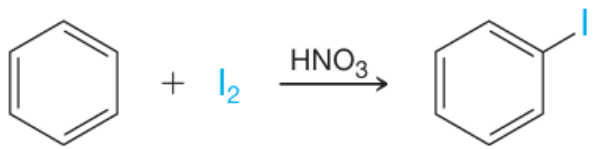


Chlorobenzene (90%)



Bromobenzene (75%)

- Fluorine reacts so rapidly with benzene, and it is difficult to limit the reaction to monofluorination.
- Iodine is so unreactive; the reaction must be carried out in the presence of an oxidizing agent such as nitric acid.



Iodobenzene (86%)

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4. Electrophilic Aromatic Substitution Reactions

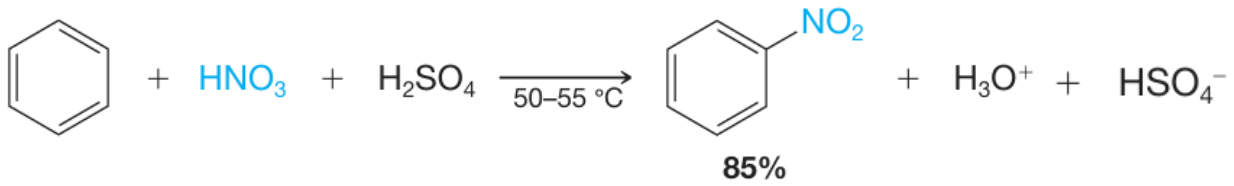
4.1. Reactions of Benzene

4.1.2. Nitration of Benzene

- Benzene undergoes nitration on reaction with a mixture of concentrated nitric acid and concentrated sulfuric acid.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

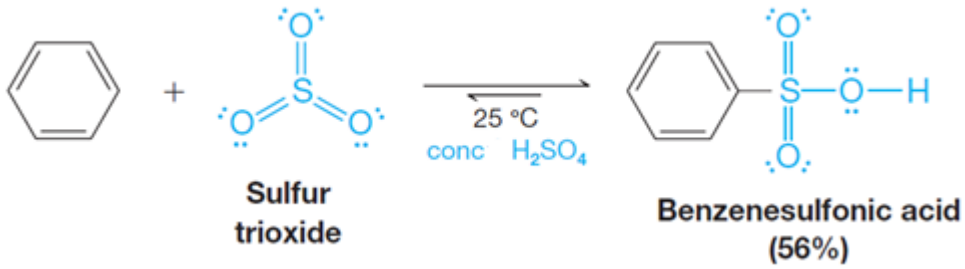
- The electrophile for the reaction is the nitronium ion (NO_2^+).



4.1.3. Sulfonation of Benzene

- Benzene reacts with fuming sulfuric acid (sulfuric acid contains added sulfur trioxide (SO_3)) at room temperature to produce benzenesulfonic acid.

$$SO_3 + H_2SO_4 \longrightarrow SO_3H^+ + HSO_4^-$$



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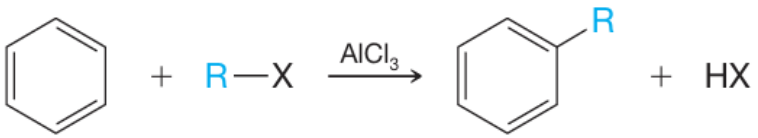
4. Electrophilic Aromatic Substitution Reactions

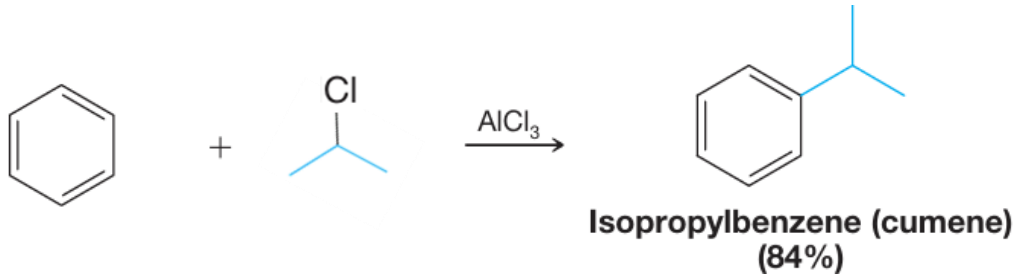
4.1. Reactions of Benzene

4.1.4. Friedel–Crafts Alkylation

- An aromatic ring can be alkylated by an alkyl halide in the presence of a Lewis acid.
- The Lewis acid serves to generate a carbocation electrophile.

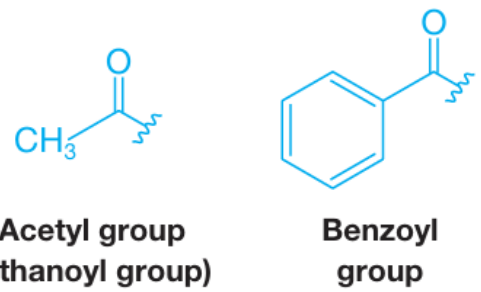
$$RCl + AlCl_3 \longrightarrow R^+ + AlCl_4^-$$

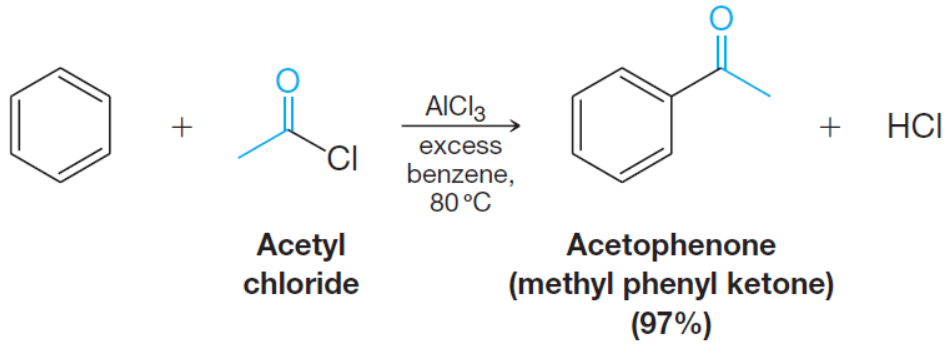




4.1.5. Friedel–Crafts Acylation

- An acyl group has a carbonyl attached to some R group
- Friedel-Crafts acylation requires reaction of an acid chloride with a Lewis acid such as aluminum chloride.





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4. Electrophilic Aromatic Substitution Reactions

4.1. Reactions of Benzene

4.1.6. Effects of Substituents on Reactivity and Orientation

- The nature of groups on an aromatic ring affect both;
  - **Reactivity of benzene ring towards EAS reactions.**
    - Activating groups; Substituents that release electrons to the ring will activate the ring toward electrophilic substitution to be more reactive than benzene.
    - Deactivating groups; Substituents that withdraw electrons from the ring will deactivate the ring toward electrophilic substitution to be less reactive than benzene.
  - **Orientation on benzene ring for future substitution.**
    - *Ortho-para* directors direct future substitution to the *ortho* and *para* positions.
    - *Meta* directors direct future substitution to the *meta* position.

	Substituent group	Name of group	
Ortho,Para-Directing	$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$	amino	Activating
	$-\ddot{O}H$, $-\ddot{O}CH_3$, $-\ddot{O}R$	hydroxy, alkoxy	
	$-\ddot{N}HC(=O)-R$	acylamino	
	$-CH_3$, $-CH_2CH_3$, $-R$	alkyl	
	$-\ddot{F}:$, $-\ddot{Cl}:$, $-\ddot{Br}:$, $-\ddot{I}:$	halo	Deactivating
Meta-Directing	$-C(=O)-R$, $-C(=O)-\ddot{O}H$	acyl, carboxy	
	$-C(=O)-\ddot{N}H_2$, $-C(=O)-\ddot{O}R$	carboxamido, carboalkoxy	
	$-S(=O)(=O)-\ddot{O}H$	sulfonic acid	
	$-C\equiv N:$	cyano	
	$-N^{+}(=O)-\ddot{O}:^{-}$	nitro	

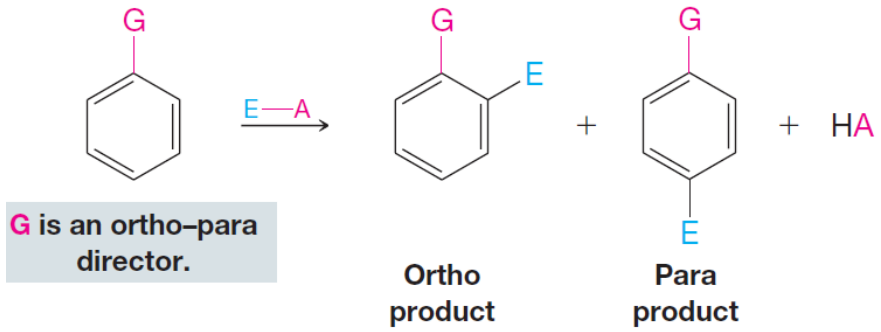
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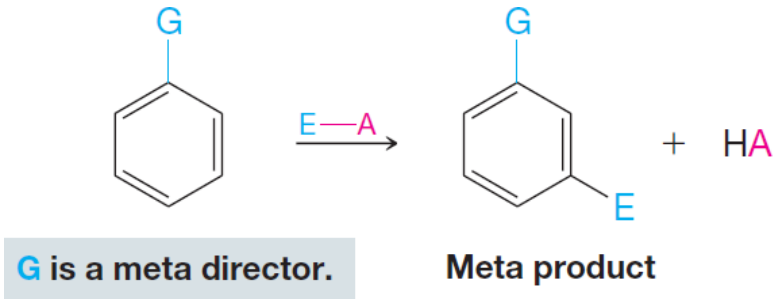
4. Electrophilic Aromatic Substitution Reactions

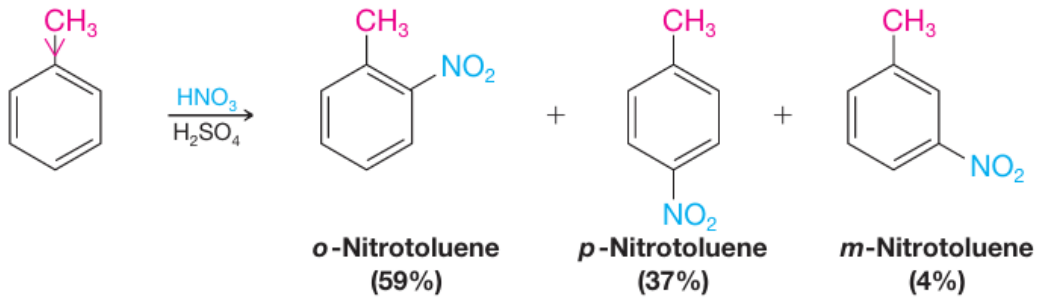
4.1. Reactions of Benzene

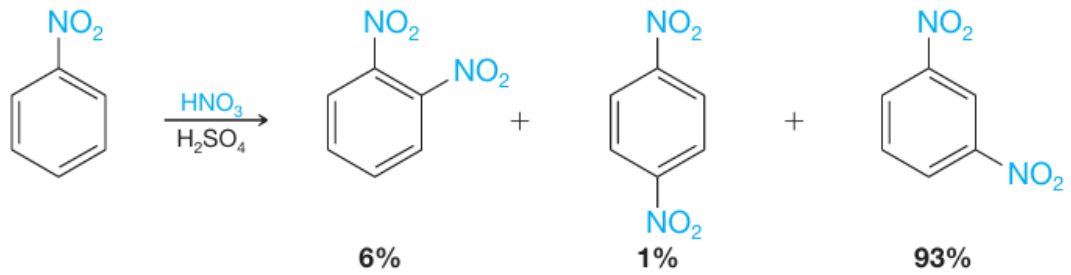
4.1.6. Effects of Substituents on Reactivity and Orientation

- **Example;**









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Nucleophilic Reactions

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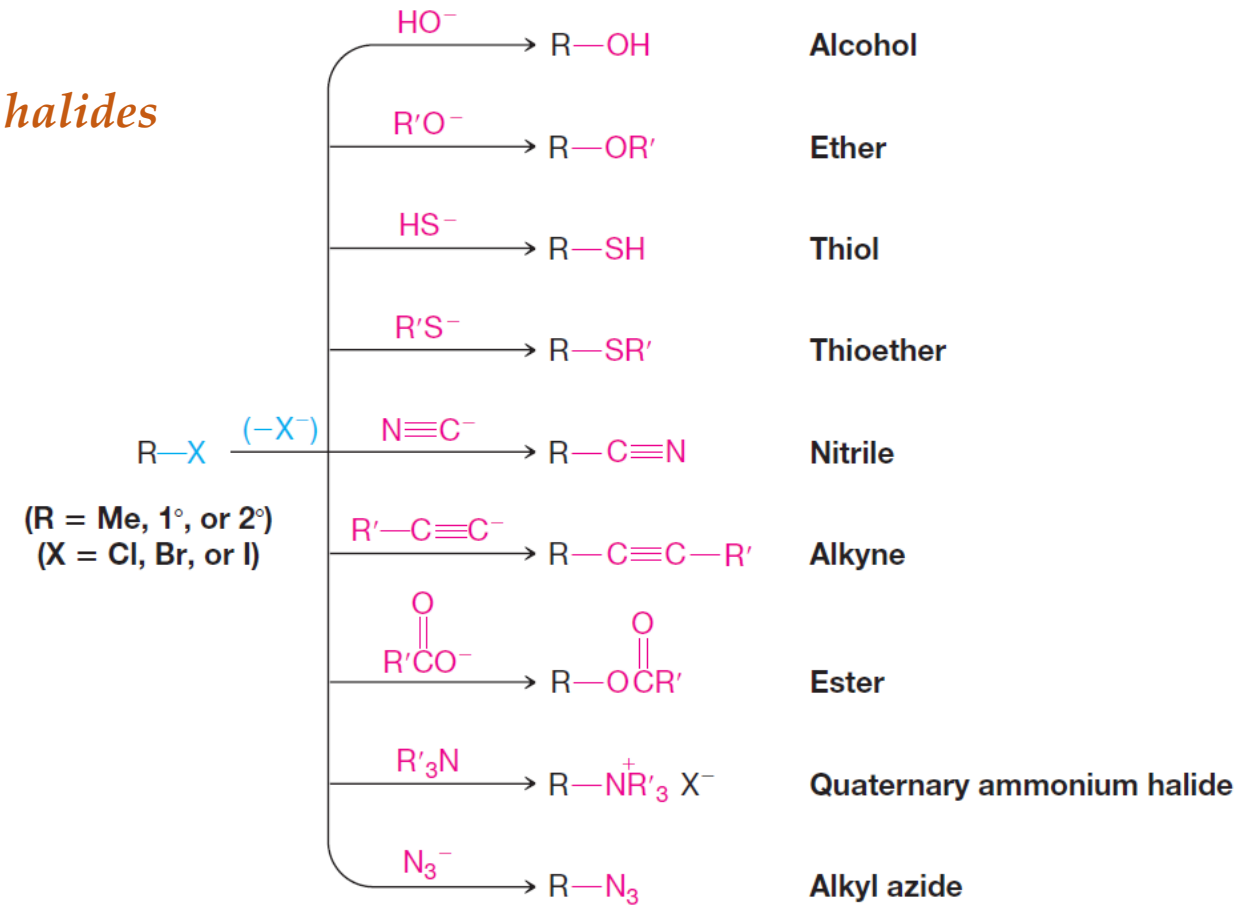
5. Nucleophilic Reactions

5.1. Nucleophilic Substitution Reactions

- In a nucleophilic substitution reaction, a nucleophile (Nu:) displaces a leaving group (LG) in the molecule that undergoes the substitution.



5.1.1. Nucleophilic Substitution Reactions of Alkyl halides



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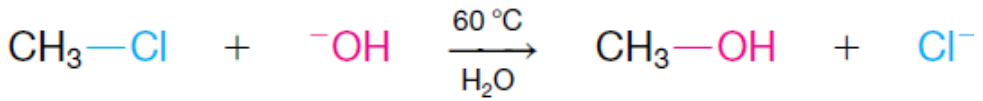
5. Nucleophilic Reactions

5.1. Nucleophilic Substitution Reactions

5.1.1. Nucleophilic Substitution Reactions of Alkyl halides

5.1.1.1. Synthesis of Alcohols

- The reaction that takes place between primary alkyl halide and hydroxide ion in aqueous solution.

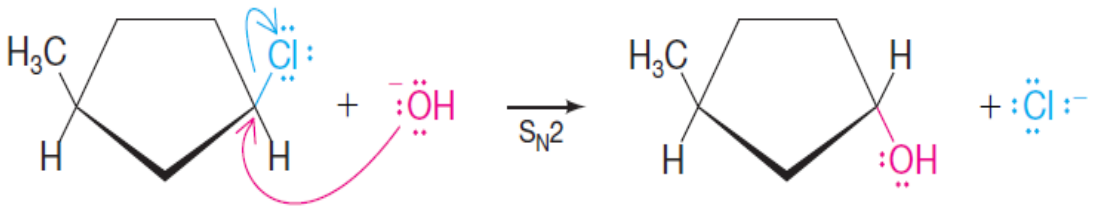


- The reaction of *tert*-butyl chloride with water yields *tert*-butyl alcohol.



***tert*-Butyl chloride** ***tert*-Butyl alcohol**

- The hydroxyl group ends up bonded on the *opposite side of the ring* from the chlorine it replaces:



***cis*-1-Chloro-3-methylcyclopentane** ***trans*-3-Methylcyclopentanol**

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5. Nucleophilic Reactions

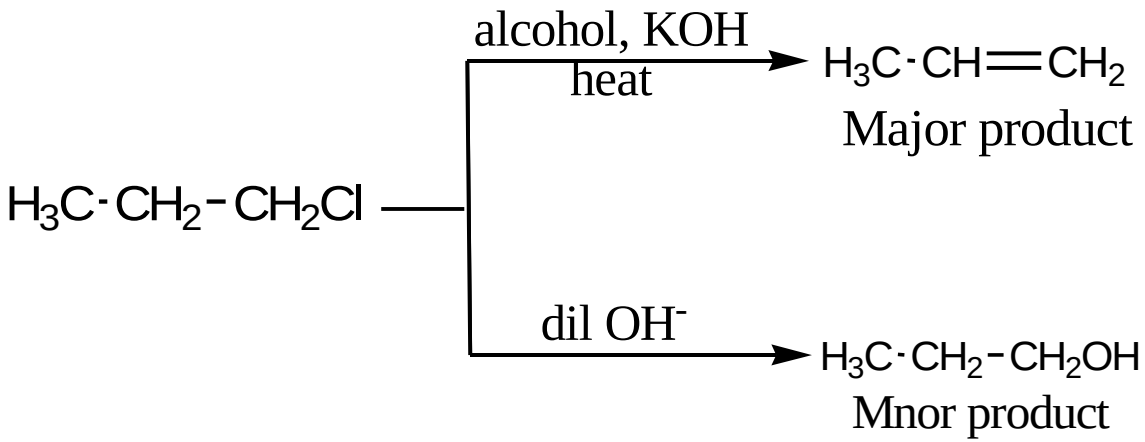
5.1. Nucleophilic Substitution Reactions

5.1.1. Nucleophilic Substitution Reactions of Alkyl halides

5.1.1.1. Synthesis of Alcohols

- **Elimination versus Substitution**

Elimination is favored over substitution when strongly basic solutions and high temperatures are used.



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5. Nucleophilic Reactions

5.1. Nucleophilic Substitution Reactions

5.1.1. Nucleophilic Substitution Reactions of Alkyl halides

5.1.1.2. Synthesis of Higher Alkynes

- Alkynide anions can be formed from the reaction of the acetylenic proton of ethyne or any terminal alkyne with a strong base such as sodium amide ($NaNH_2$) .

$$H{-}C{\equiv}C{-}H + NaNH_2 \xrightarrow[\text{liq. } NH_3]{} H{-}C{\equiv}C{:}^{-}\ Na^{+} + NH_3$$

$$CH_3C{\equiv}C{-}H + NaNH_2 \xrightarrow[\text{liq. } NH_3]{} CH_3C{\equiv}C{:}^{-}\ Na^{+} + NH_3$$

- Alkyl halides can be reacted with alkynide anions to yield higher alkynes.

$$R{-}C{\equiv}C{:}^{-}\ Na^{+} + R'CH_2{-}Br \longrightarrow R{-}C{\equiv}C{-}CH_2R' + NaBr$$

Sodium alkynide — Primary alkyl halide — Mono- or disubstituted acetylene

(R or R′ or both may be hydrogen.)

$$CH_3CH_2C{\equiv}C{:}^{-}\ Na^{+} + CH_3CH_2{-}Br \xrightarrow[6\text{ h}]{\text{liq. } NH_3} CH_3CH_2C{\equiv}CCH_2CH_3 + NaBr$$

3-Hexyne (75%)

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5. Nucleophilic Reactions

5.1. Nucleophilic Substitution Reactions

5.1.1. Nucleophilic Substitution Reactions of Alkyl halides

5.1.1.3. Synthesis of Nitriles

- Alkyl bromides are converted to alkyl cyanide (Nitriles) by nucleophilic substitution reactions

$$CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$$

5.1.1.4. Halogen Exchange

- Alkyl chlorides and bromides are also easily converted to alkyl iodides by nucleophilic substitution reactions.

$$\begin{matrix} R{-}Cl \\ \text{or} \\ R{-}Br \end{matrix} \xrightarrow{I^-} R{-}I\ (+\ Cl^-\ \text{or}\ Br^-)$$

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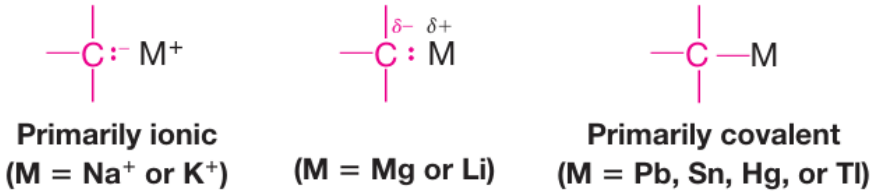
5. Nucleophilic Reactions

5.2. Nucleophilic Addition Reactions

5.2.1. Nucleophilic Addition of Grignard Reagents

5.2.1.1. Formation of Grignard Reagents from Halogen Compounds

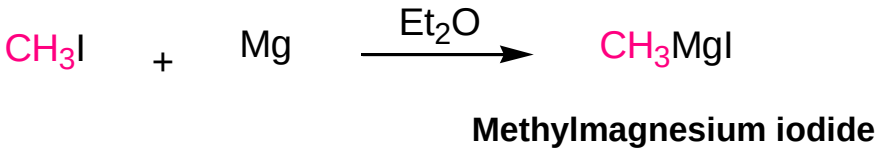
- Compounds that contain carbon–metal bonds are called organometallic compounds.



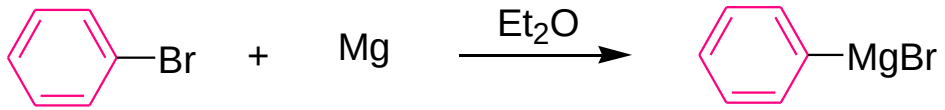
Primarily ionic (M = Na^+ or K^+) | **(M = Mg or Li)** | **Primarily covalent (M = Pb, Sn, Hg, or Tl)**

- Grignard reagents are prepared by the reaction of an organic halide with magnesium metal in anhydrous ether solvent.





Methylmagnesium iodide



Phenylmagnesium bromide

- The order of reactivity of halides with magnesium is also; RI > RBr > RCl.

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5. Nucleophilic Reactions

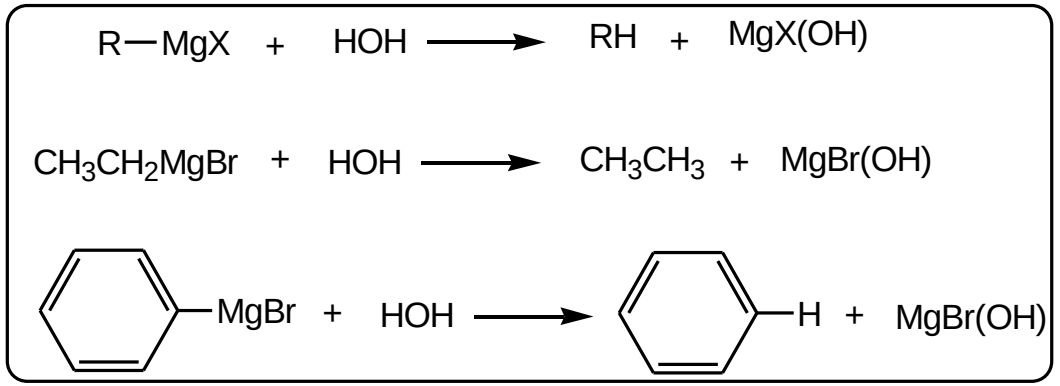
5.2. Nucleophilic Addition Reactions

5.2.1. Nucleophilic Addition of Grignard Reagents

5.2.1.2. Hydrolysis of Grignard Reagents

- Grignard reagents are very strong bases and can react with acidic hydrogen atoms that attached to an electronegative atom such as oxygen, nitrogen, or sulfur.





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Oxidation and Reduction Reactions

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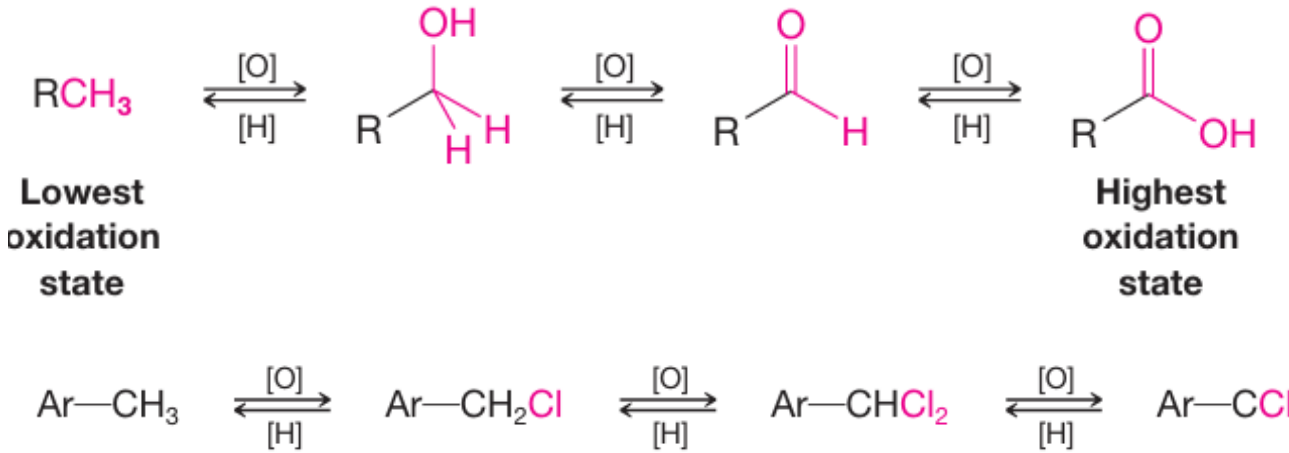
6. Oxidation and Reduction Reactions

- Reduction; increasing the hydrogen content or decreasing the oxygen content of an organic molecule.

  A general symbol for reduction is [H].

- Oxidation; increasing the oxygen content (or the content of any element more electronegative than carbon) of an organic molecule or decreasing its hydrogen content.

  A general symbol for oxidation is [O].



- When an organic compound is reduced, the reducing agent is oxidized.
- When an organic compound is oxidized, the oxidizing agent is reduced.
- These oxidizing and reducing agents are often inorganic compounds.

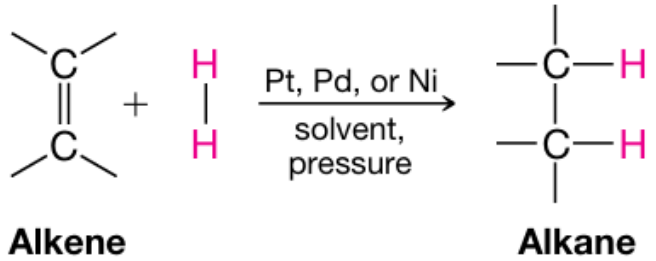
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6. Oxidation and Reduction Reactions

6.1. Reduction Reactions

6.1.1. Hydrogenation of Unsaturated Aliphatic Hydrocarbons

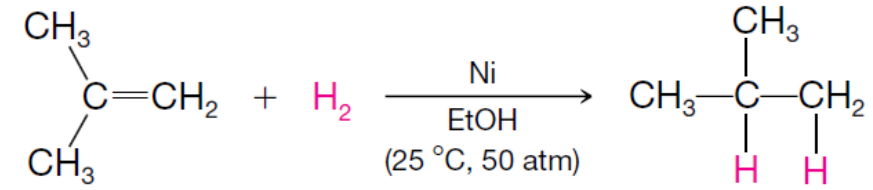
- Heterogeneous catalysts: Insoluble platinum, palladium, or nickel catalysts, which are not soluble in the reaction mixture.
- Homogeneous catalysts: Soluble catalysts, including rhodium or ruthenium complexes; tris(triphenylphosphine)rhodium chloride ($Rh[(C_6H_5)_3P]_3Cl$).



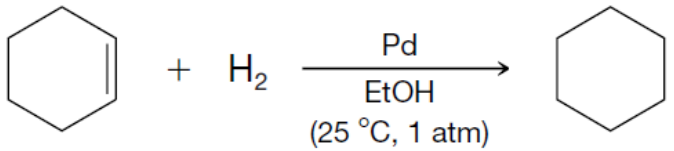
Alkene **Alkane**

A) Hydrogenation of Alkenes and Cycloalkenes: Synthesis of Alkanes and Cycloalkanes

- An unsaturated compound becomes a saturated compound upon the addition of hydrogen.



2-Methylpropene **Isobutane**



Cyclohexene **Cyclohexane**

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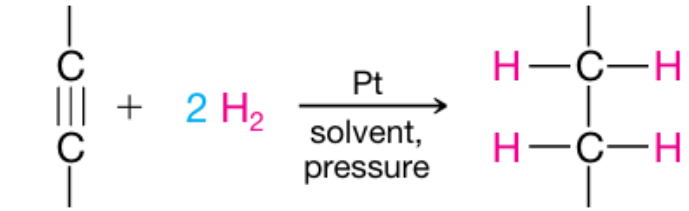
6. Oxidation and Reduction Reactions

6.1. Reduction Reactions

6.1.1. Hydrogenation of Unsaturated Aliphatic Hydrocarbons

B) Hydrogenation of Alkynes: Synthesis of Alkanes and Alkenes

- When a platinum catalyst is used, an alkyne reacts with two molar equivalents of hydrogen to give an alkane.



Alkyne **Alkane**

$$CH_3C{\equiv}CCH_3 \xrightarrow{Pt,\ H_2} [CH_3CH{=}CHCH_3] \xrightarrow{Pt,\ H_2} CH_3CH_2CH_2CH_3$$

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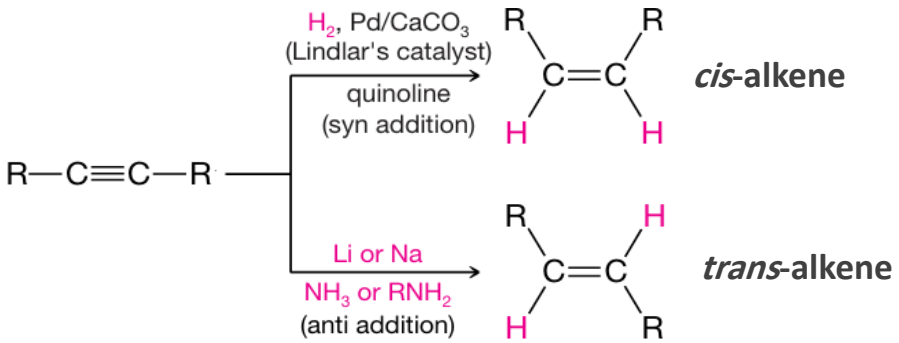
6. Oxidation and Reduction Reactions

6.1. Reduction Reactions

6.1.1. Hydrogenation of Unsaturated Aliphatic Hydrocarbons

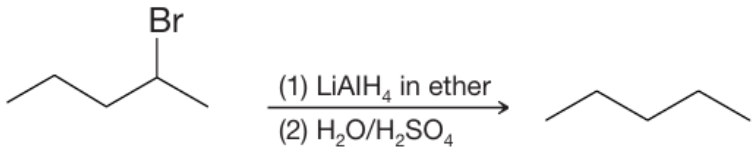
B) Hydrogenation of Alkynes: Synthesis of Alkanes and Alkenes

- *Syn* Addition of Hydrogen: Synthesis of *cis*-Alkenes
  Metallic palladium deposited on calcium carbonate (Lindlar's catalyst) can be used to prepare *cis*-alkenes.
- *Anti* Addition of Hydrogen: Synthesis of *trans*-Alkenes
  Treatment of alkynes with lithium or sodium metal in ammonia or ethylamine at low temperatures prepare *trans*-alkene.



6.1.2. Reduction of Alkyl Halides to Hydrocarbons: RX to RH

- Replacement of the halogen atom of an alkyl halide by hydrogen can be accomplished by treating the alkyl halide with lithium aluminum hydride.



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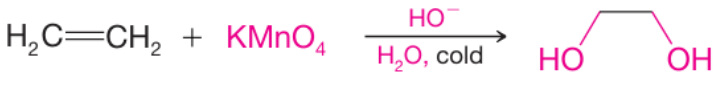
6. Oxidation and Reduction Reactions

6.2. Oxidation Reactions

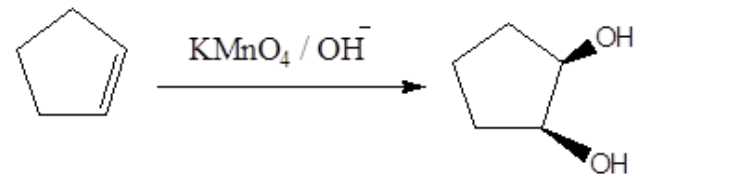
6.2.1. Oxidation of Alkenes and Cycloalkenes

A) Oxidation with Cold Basic Potassium Permanganate

Alkenes react with alkaline potassium permanganate under basic conditions to form cis-diol (glycol) (compounds with two adjacent hydroxyl groups).



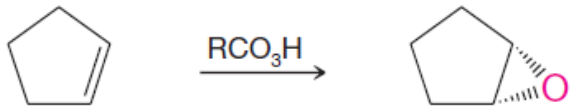
Ethene **1,2-Ethanediol (ethylene glycol)**



Cyclopentene *cis*-Cyclopentane-1,2-diol

B) Oxidation with a Peroxycarboxylic Acid

Epoxidation of cyclopentene with a peroxycarboxylic acid produces 1,2-epoxycyclopentane.



Cyclopentene **1,2-Epoxycyclopentane**

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6. Oxidation and Reduction Reactions

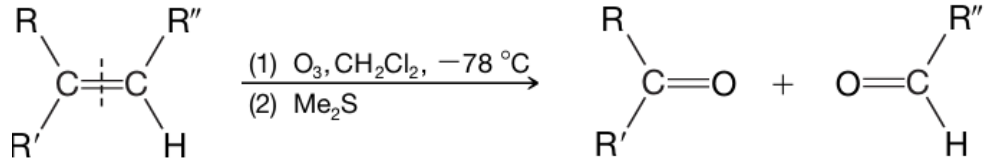
6.2. Oxidation Reactions

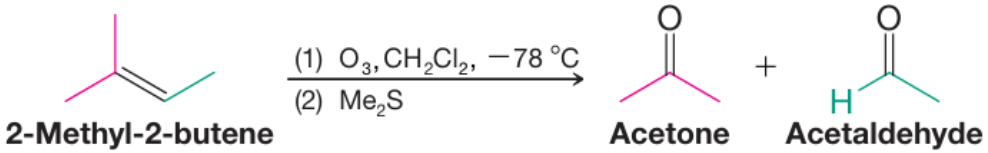
6.2.1. Oxidation of Alkenes and Cycloalkenes

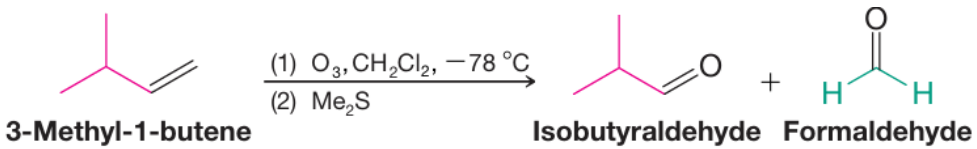
C) Oxidative Cleavage of Alkenes: Cleavage with Ozone (Ozonolysis)

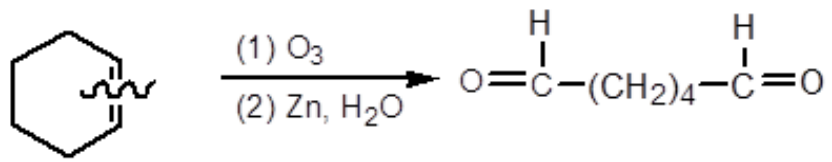
The most useful method for cleaving alkenes is to use ozone (O_3).

- Unsubstituted carbons are oxidized to formaldehyde,
- Monosubstituted carbons are oxidized to aldehydes and
- Disubstituted carbons are oxidized to ketones.









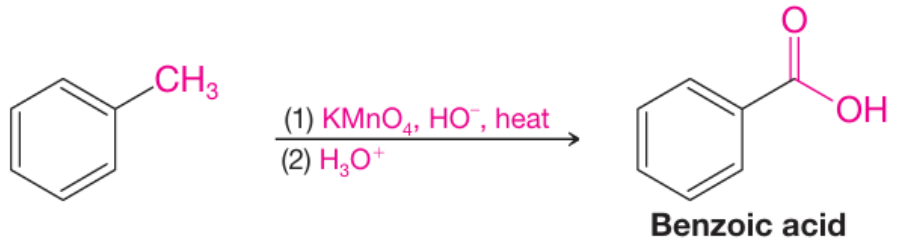
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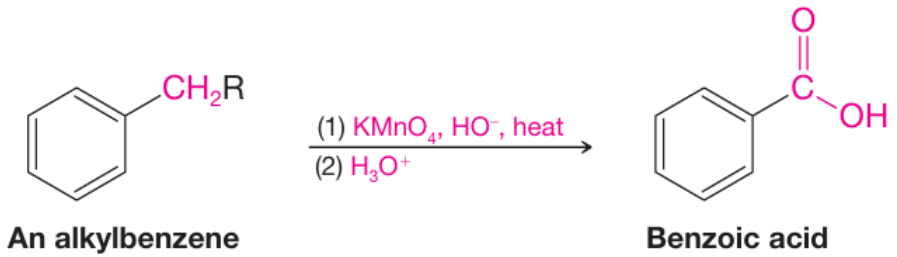
6. Oxidation and Reduction Reactions

6.2. Oxidation Reactions

6.2.2. Oxidation of the Side Chain of Aromatic Compounds

- Saturated alkyl groups on aromatic rings are oxidized by hot $KMnO_4$ to yield aromatic carboxylic acids.
- This reaction requires at least one hydrogen atom on the carbon directly attached to the ring, known as a benzylic hydrogen.





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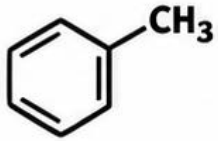
7. Practice Problems

1 Predict the major product(s) for the following reactions.

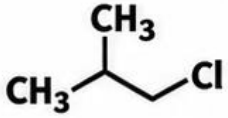
a)  $\xrightarrow[Pd/C]{H_2}$?

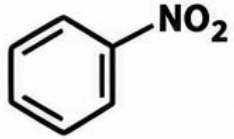
b) $CH_3CH_2CH_2Br \xrightarrow{KOH\ (alc.),\ \Delta}$?

c) $CH_3CH{=}CHCH_3 \xrightarrow[CCl_4]{Br_2}$?

d)  $\xrightarrow[FeBr_3]{Br_2}$?

e) $HC{\equiv}CCH_3 \xrightarrow[(1\ equiv)]{HBr}$?

f)  $\xrightarrow{KOH\ (aq)}$?

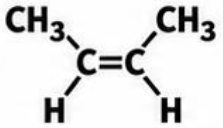
g)  $\xrightarrow{H_2,\ Pd/C}$?

h) $CH_3CH_2CH{=}CH_2 \xrightarrow[(no\ peroxides)]{HBr}$?

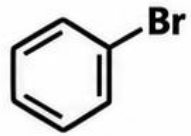
2 Identify the required reactant(s) to obtain the given product(s).

a) ? + $\xrightarrow[h\nu]{Cl_2}$ $CH_3CHClCH_3$

b) ? + $\xrightarrow[CCl_4]{Br_2\ (1\ equiv)}$ $CH_3CBr{=}CBrCH_3$

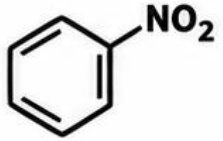
c) ? + $\xrightarrow[Lindlar\ catalyst]{H_2}$ 

d) ? + $\xrightarrow{H_2SO_4\ (conc.),\ \Delta}$ $CH_2{=}CH_2$

e) ? + $\xrightarrow[FeBr_3]{Br_2}$ 

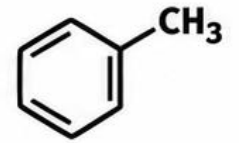
f) ? + $\xrightarrow{KOH\ (alc.),\ \Delta}$ $CH_3CH{=}CHCH_3$

g) ? + $\xrightarrow[(2\ equiv)]{NaNH_2}$ $HC{\equiv}CH$

h) ? + $\xrightarrow[H_2SO_4]{HNO_3}$ 

3 Provide the appropriate reagent(s) or conditions for the following transformations.

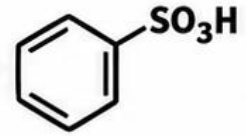
a) $CH_3CH_2CH_3 \xrightarrow{?} CH_3CH{=}CH_2$

b)  $\xrightarrow{?}$ 

c) $CH_3CH{=}CH_2 \xrightarrow{?} CH_3CH_2CH_2Br$

d) $CH_3CH_2OH \xrightarrow{?} CH_3CH_2Br$

e) $CH_3CH_2C{\equiv}CH \xrightarrow{?} CH_3CH_2CH{=}CH_2$

f)  $\xrightarrow{?}$ 

g) $CH_3CH_2Br \xrightarrow{?} CH_3CH_2CH_2CH_3$

h)  $\xrightarrow{?}$ 