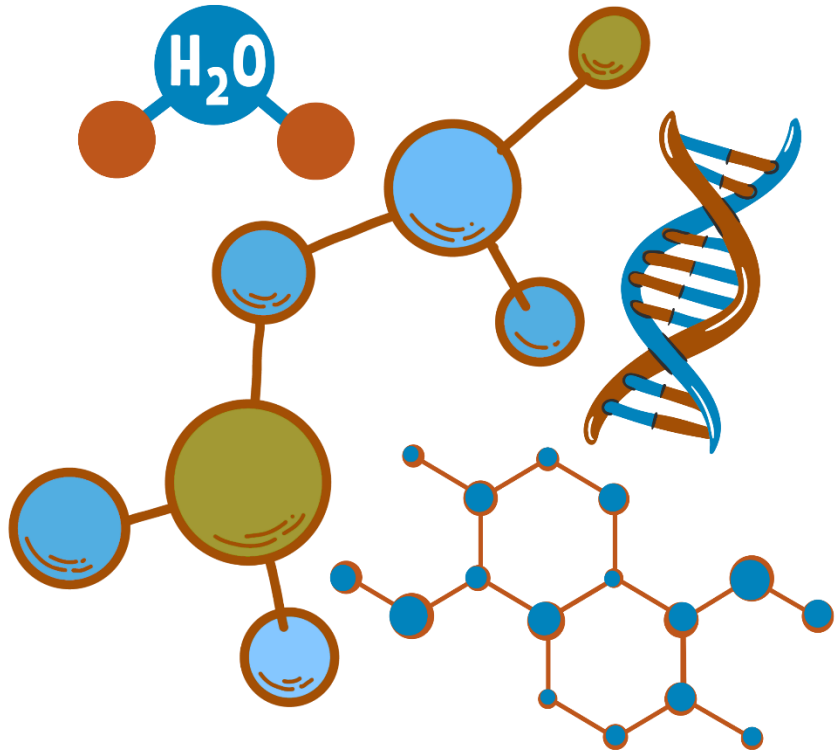
Introduction to Organic Chemistry
CHEM 109

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Chapter 5: Organic Reactions



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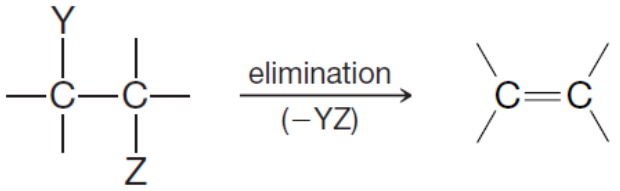
Elimination Reactions

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1. Elimination Reactions

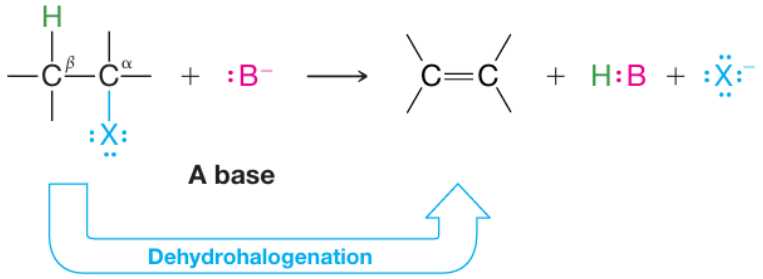
1.1. Synthesis of Alkenes

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

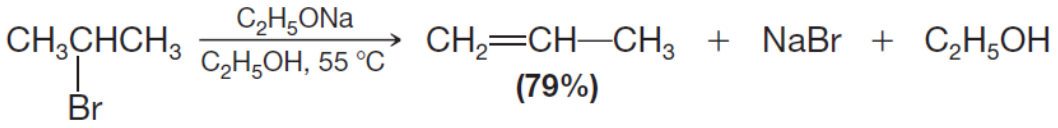


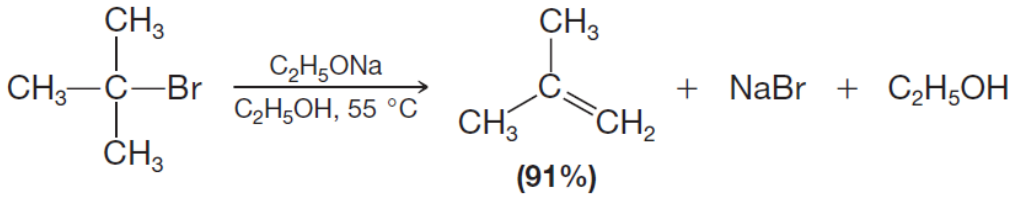
1.1.1. *Dehydrohalogenation (Elimination of Hydrogen Halide) of Alkyl Halides*

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



- **Examples;**





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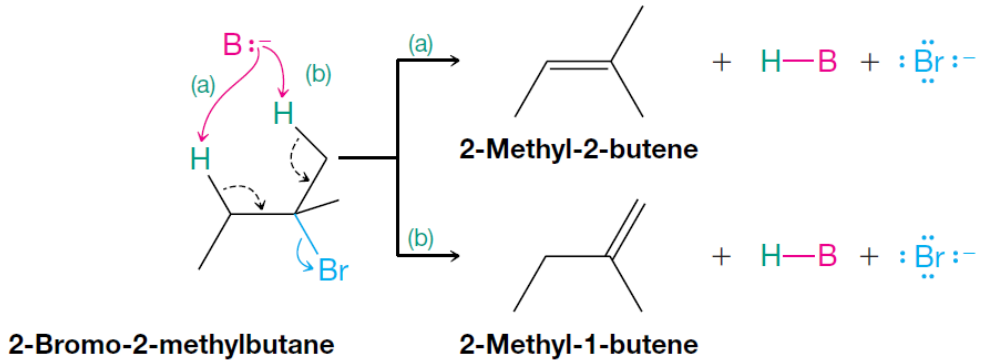
1. Elimination Reactions

1.1. Synthesis of Alkenes

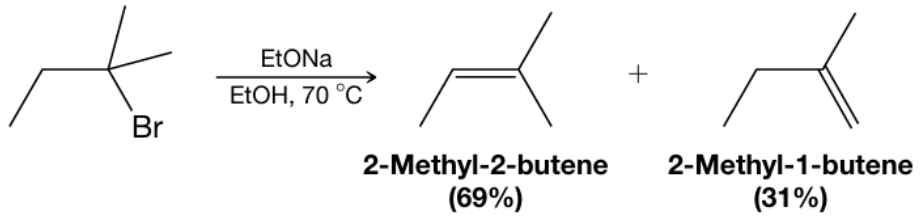
1.1.1. *Dehydrohalogenation (Elimination of Hydrogen Halide) of Alkyl Halides*

- **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

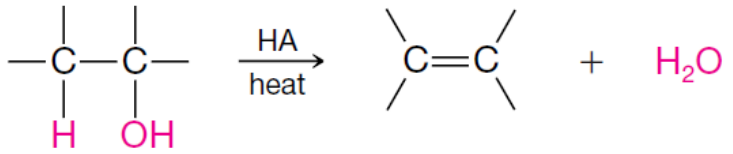
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1. Elimination Reactions

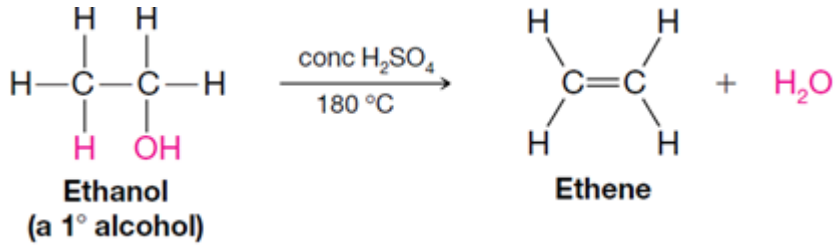
1.1. Synthesis of Alkenes

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

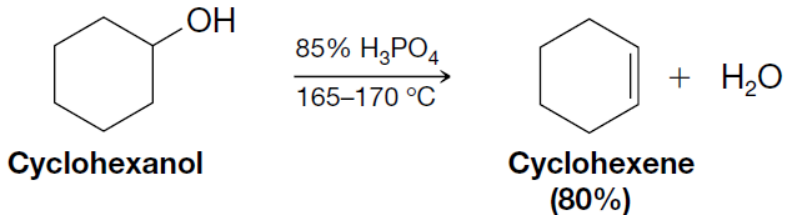
- **Most alcohols undergo dehydration (*lose a molecule of water*) to form an alkene when heated with a strong acid as sulfuric acid, H_2S0_4, and phosphoric acid, H_3P0_4.**



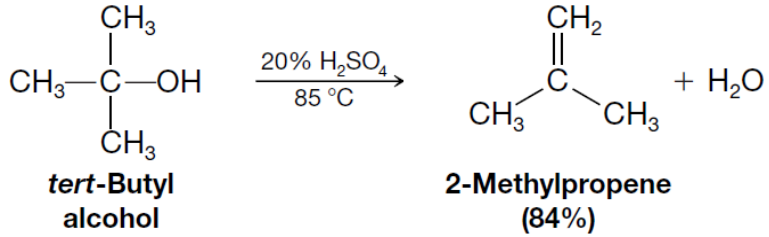
  - **Primary alcohol; Ethanol dehydrates in concentrated sulfuric acid and a temperature of 180 °C.**



  - **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

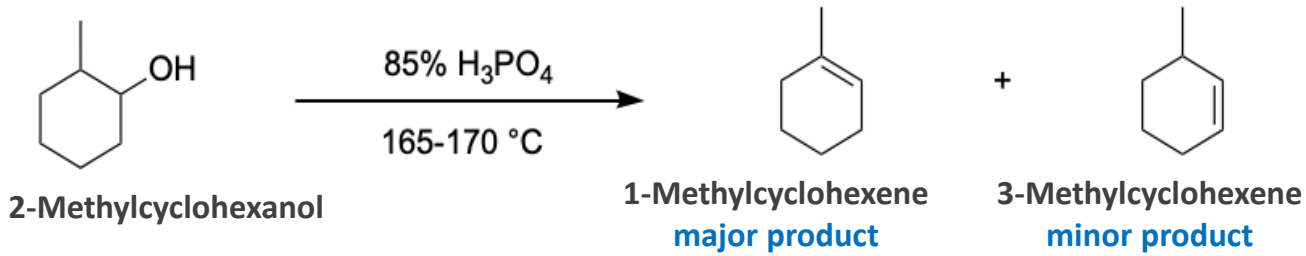
1.1. Synthesis of Alkenes

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.

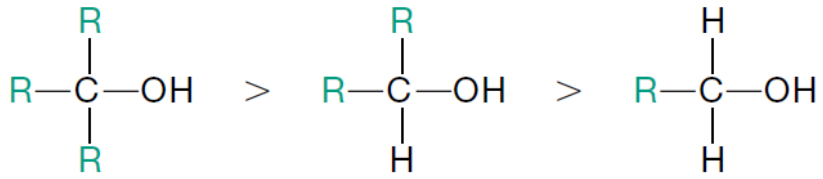


2-Methylcyclohexanol

1-Methylcyclohexene
major product

3-Methylcyclohexene
minor product

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



3° Alcohol

2° Alcohol

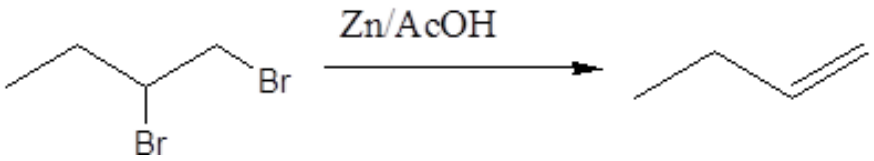
1° Alcohol

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1. Elimination Reactions

1.1. Synthesis of Alkenes

1.1.3. Dehalogenation of Vicinal Dibromides



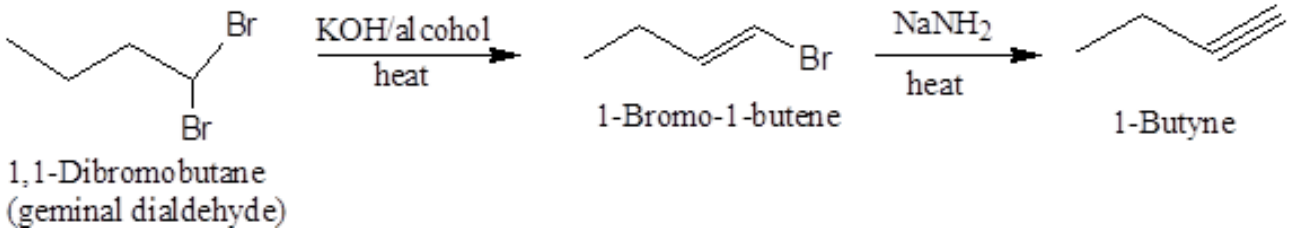
1.2. Synthesis of Alkynes

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**



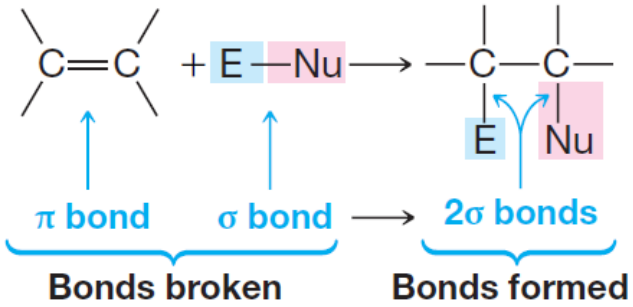
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Electrophilic Addition Reactions

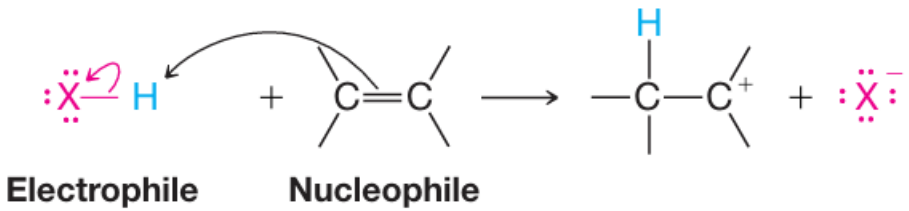
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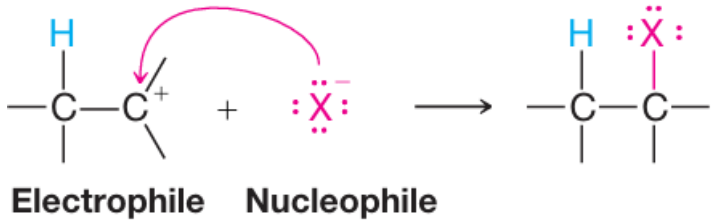
2. Electrophilic Addition Reactions

- **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.**





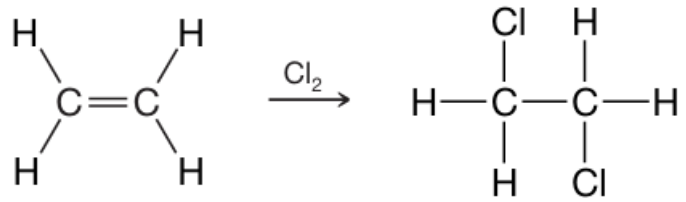
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2. Electrophilic Addition Reactions

2.1. Halogenation (Addition of Halogen)

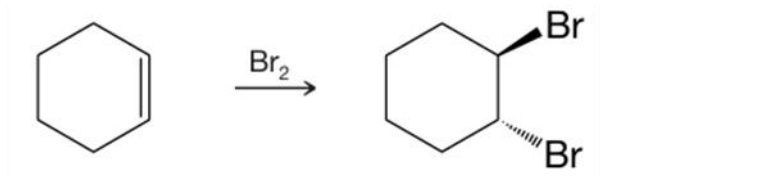
2.1.1. Halogenation of Alkenes and Cycloalkenes

- **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**

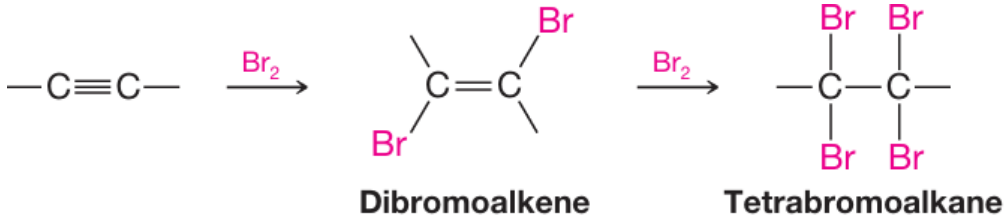
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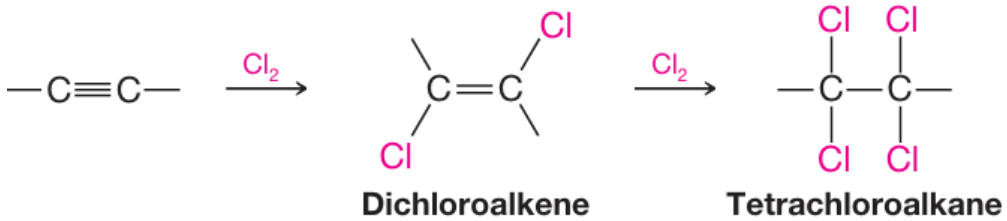
2. Electrophilic Addition Reactions

2.1. Halogenation (Addition of Halogen)

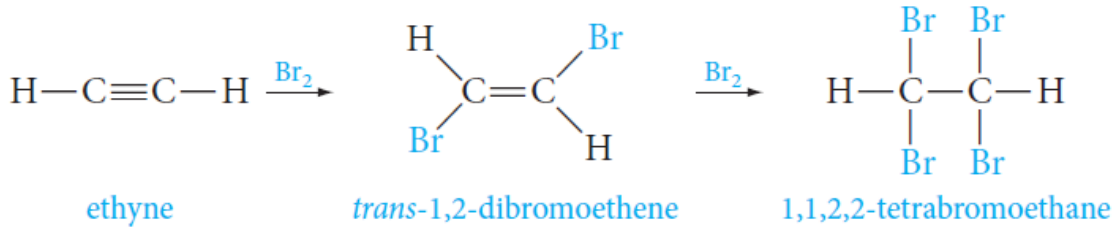
2.1.2. Halogenation of Alkynes

- **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.**



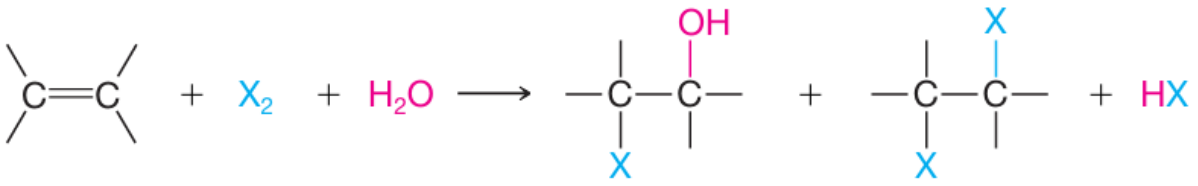
2-Pentyne **_trans_-2,3-Dibromo-2-pentene**

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2. Electrophilic Addition Reactions

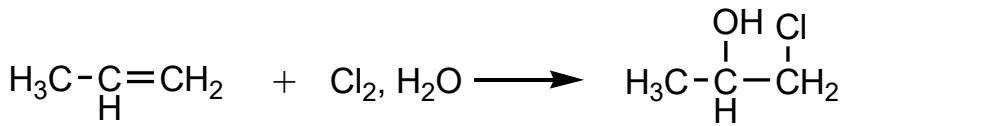
2.2. Addition of Hypohalous Acid (X_2/H_2O) to Alkenes; Halohydrin Formation

- 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.



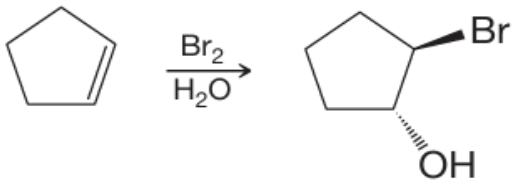
X = Cl or Br — Halohydrin (major) — *vic*-Dihalide (minor)

- Addition of HOX also follows Markovnikov's rule.



Propene — Propane chlorohydrin (1-Chloro-2-propanol)

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



Cyclopentene **2-Bromocyclopentanol**

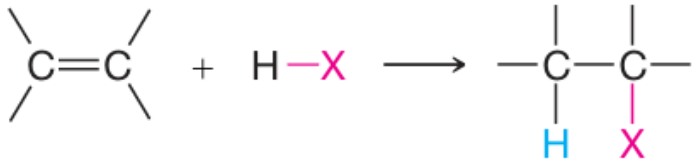
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2. Electrophilic Addition Reactions

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

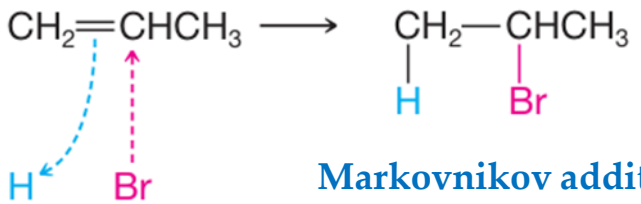
2.3.1. *Hydrohalogenation of Alkenes*

- 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

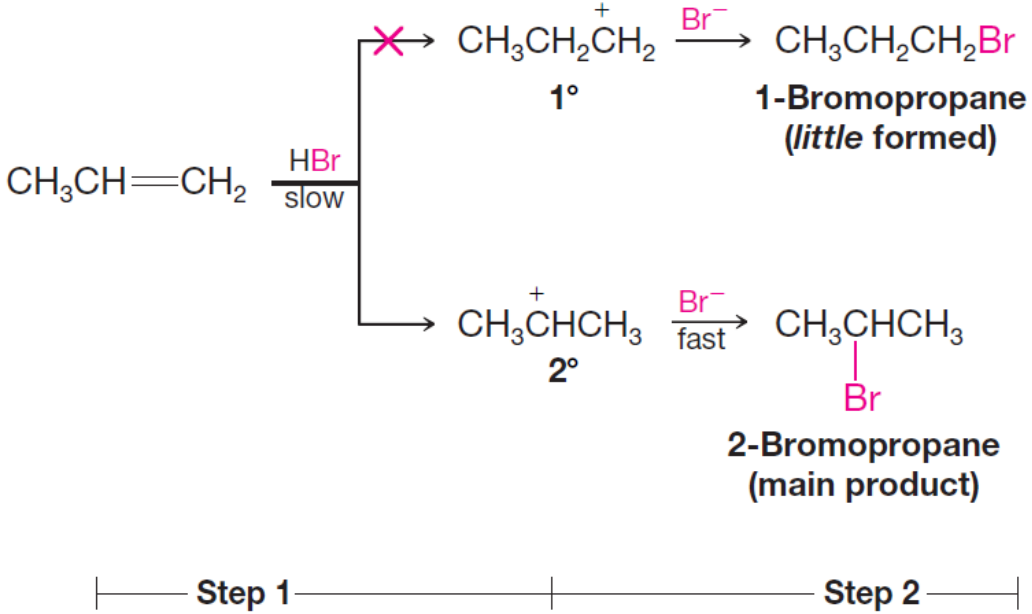
2.3. Hydrohalogenation (Addition of Hydrogen Halide); Markovnikov's Rule

2.3.1. *Hydrohalogenation of Alkenes*

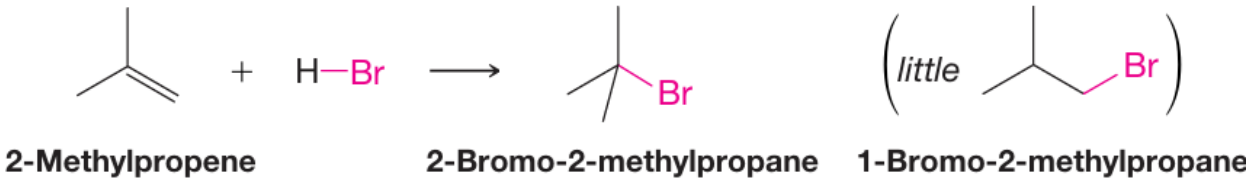
- Theoretical Explanation of Markovnikov's Rule
  - These two carbocations are not of equal stability.
  - **Example;**

    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).



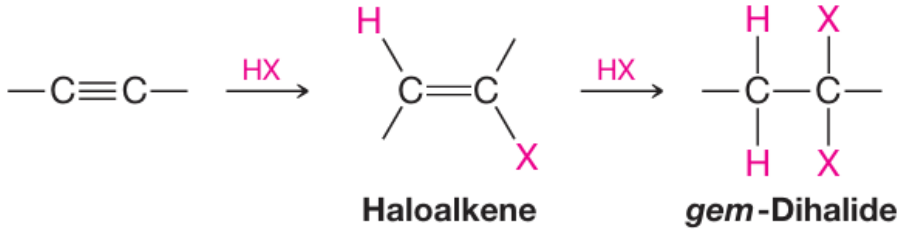
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2. Electrophilic Addition Reactions

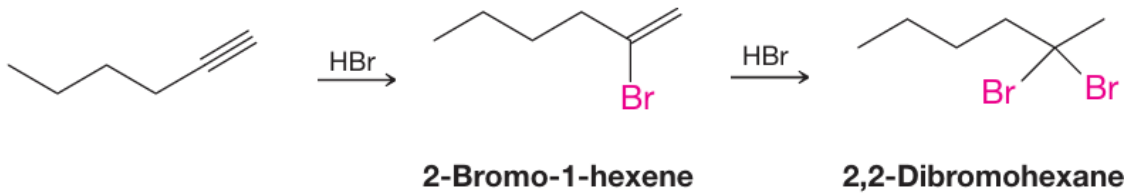
2.3. Hydrohalogenation (Addition of Hydrogen Halide); Markovnikov's Rule

2.3.2. *Hydrohalogenation of Alkynes*

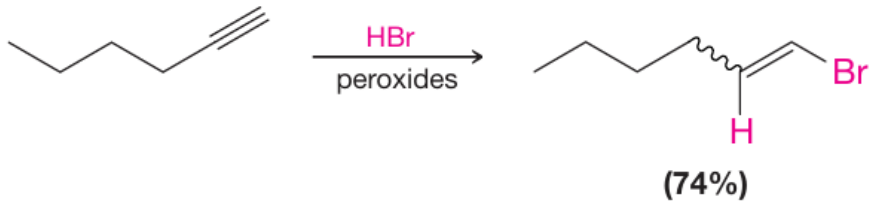
- Alkynes react with one molar equivalent of hydrogen chloride or hydrogen bromide to form haloalkenes, and with two molar equivalents to form *geminal* dihalides and follow Markovnikov's rule.



- **Example;** Addition of HBr to 1-hexyne.



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



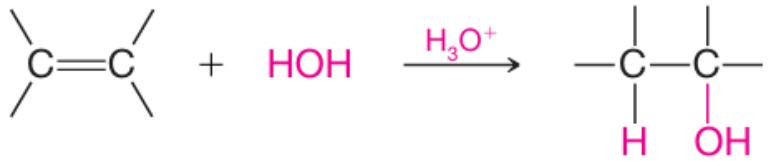
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2. Electrophilic Addition Reactions

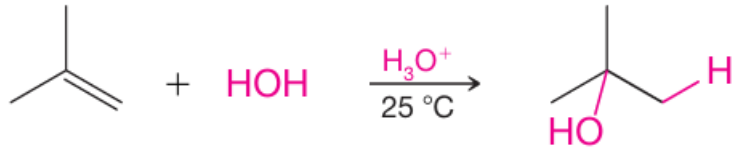
2.4. Hydration (Addition of Water)

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.

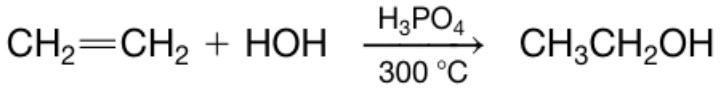


- Example; The hydration of 2-methylpropene.



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.



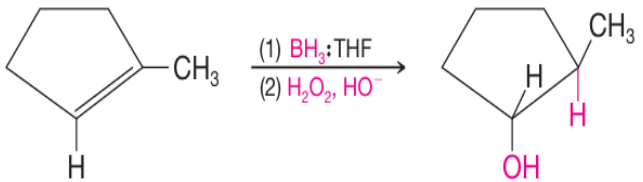
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2. Electrophilic Addition Reactions

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**

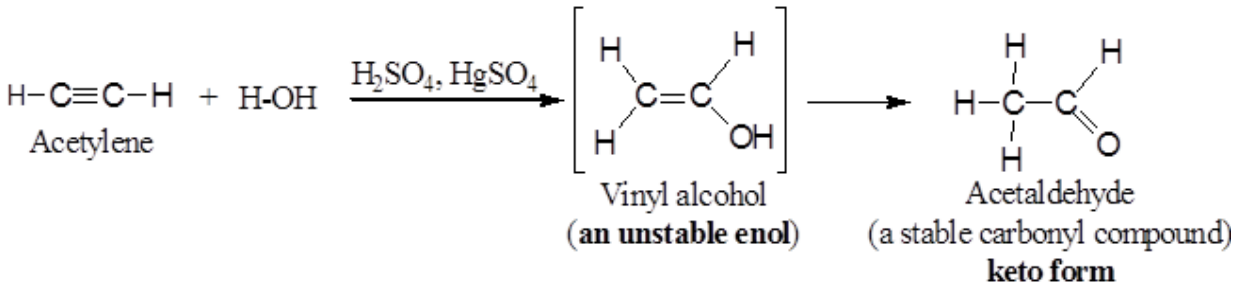
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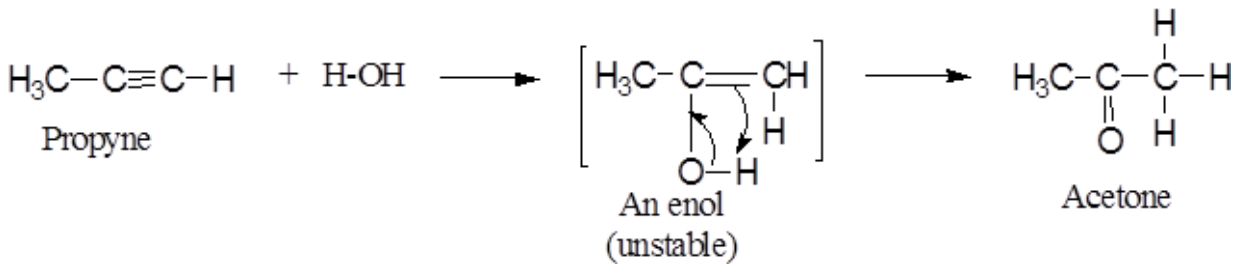
2. Electrophilic Addition Reactions

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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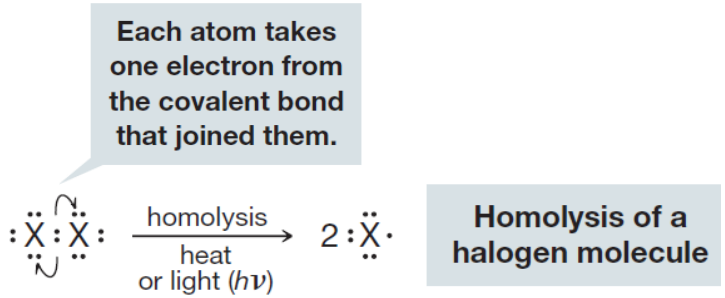
Free Radical Reactions

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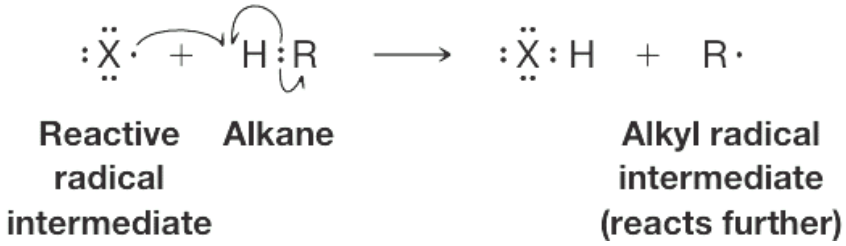
3. Radical Reactions

3.1. Formation of Free Radicals

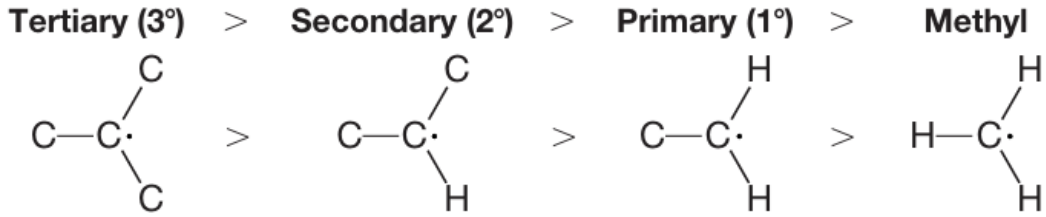
- Homolytic bond cleavage leads to the formation of free radicals, which are highly reactive, and short-lived species.



- 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.

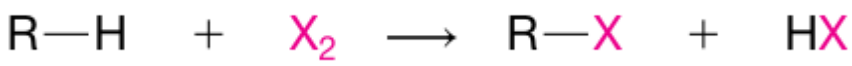


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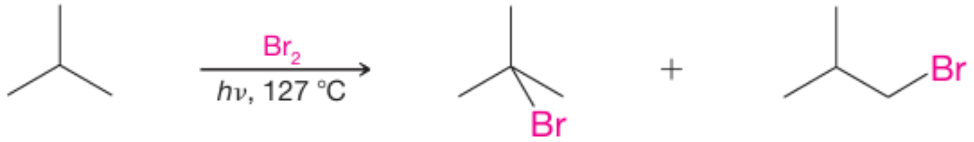
3. Radical Reactions

3.2. Halogenation of Alkanes

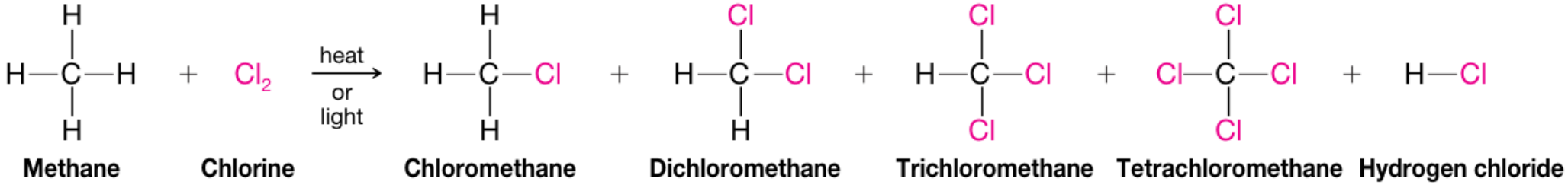
- A halogen atom replaces one or more of the hydrogen atoms of the alkane to produce alkyl halides by a *free radical substitution reaction*.
- Alkanes undergo substitution reactions with halogens, fluorine, bromine and chlorine, in the presence of heat or light.
- Fluorine reacts explosively whereas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

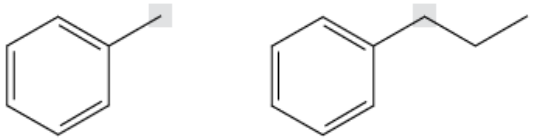


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3. Radical Reactions

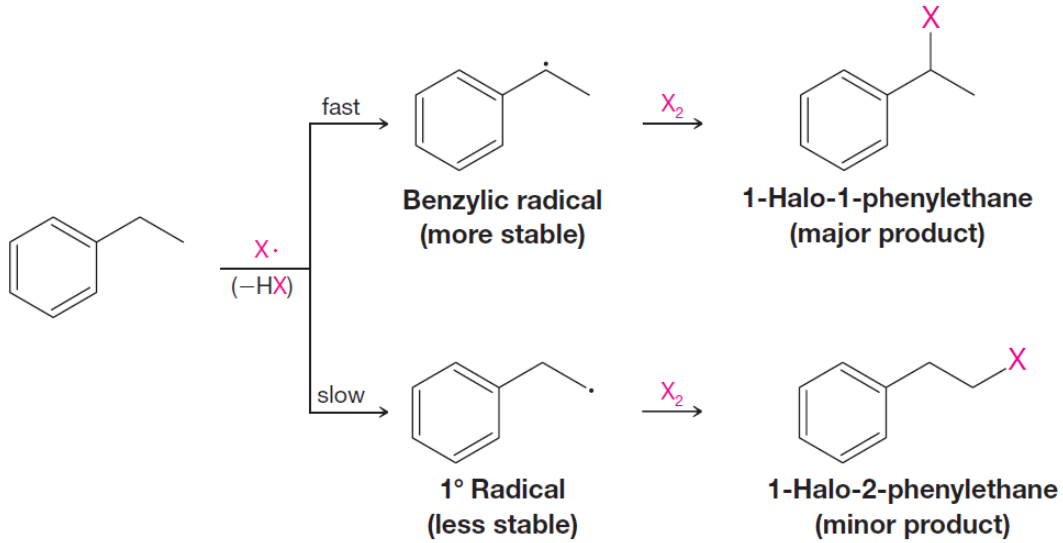
3.3. Benzylic Substitution and Benzylic Radicals

- 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.

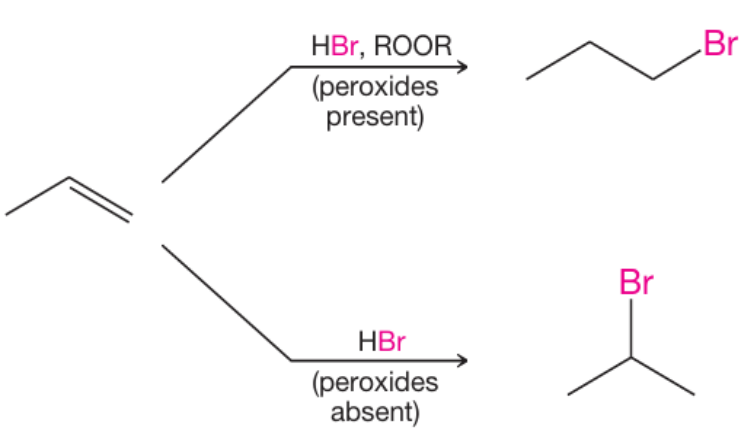


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3. Radical Reactions

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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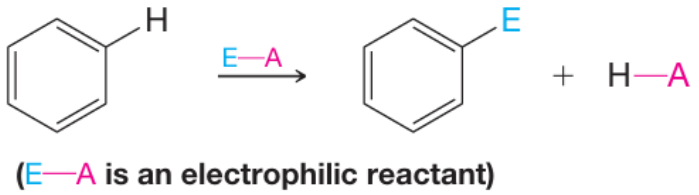
Electrophilic Aromatic Substitution Reactions

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4. Electrophilic Aromatic Substitution Reactions

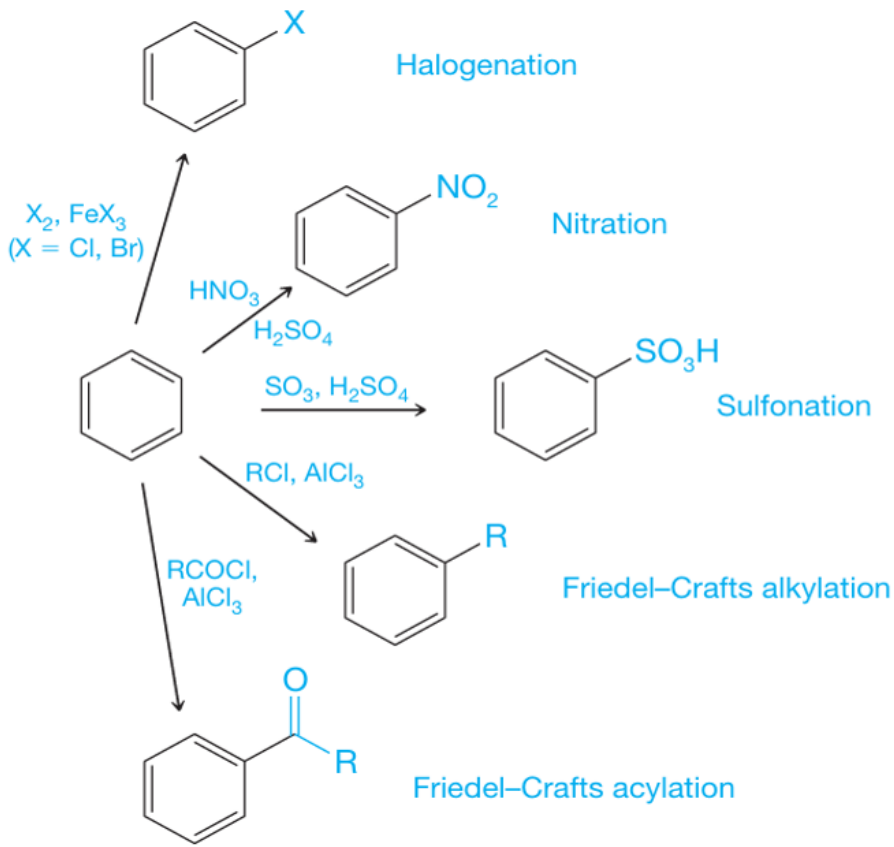
4.1. Reactions of Benzene

- 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



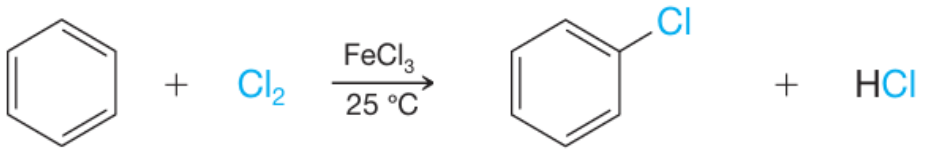
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4. Electrophilic Aromatic Substitution Reactions

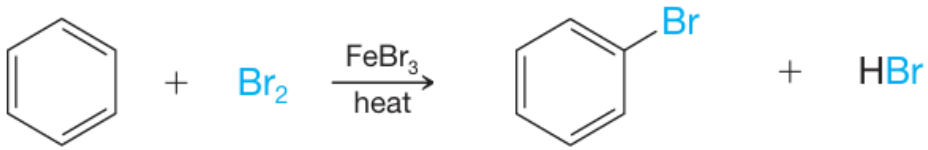
4.1. Reactions of Benzene

4.1.1. Halogenation of Benzene

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

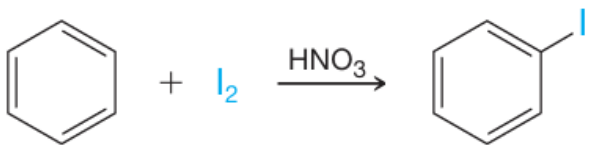


Chlorobenzene (90%)



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

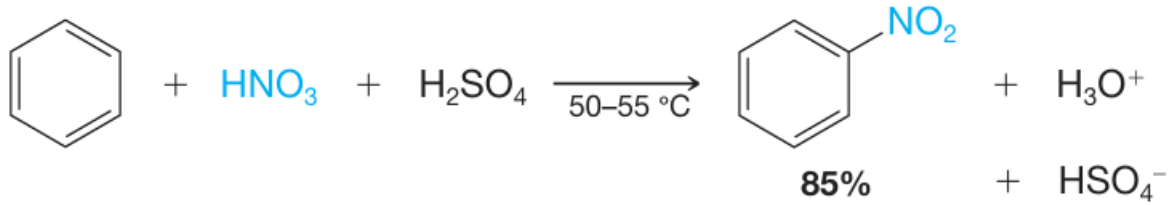
4.1. Reactions of Benzene

4.1.2. Nitration of Benzene

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

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

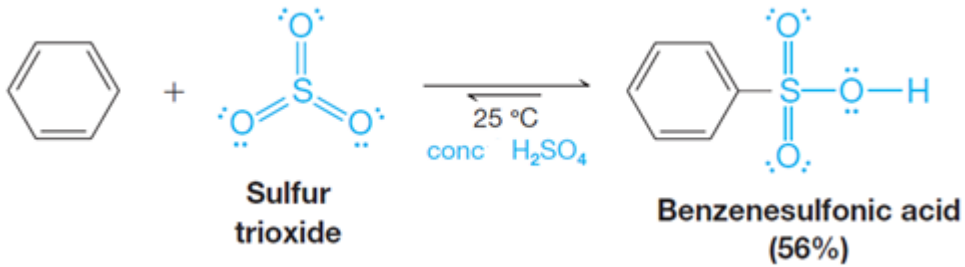
- The electrophile for the reaction is the nitronium ion (NO_2^+).



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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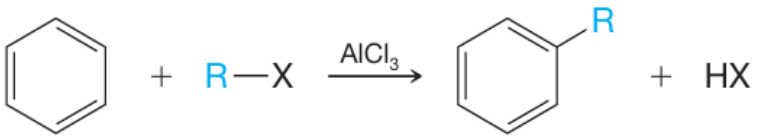
4. Electrophilic Aromatic Substitution Reactions

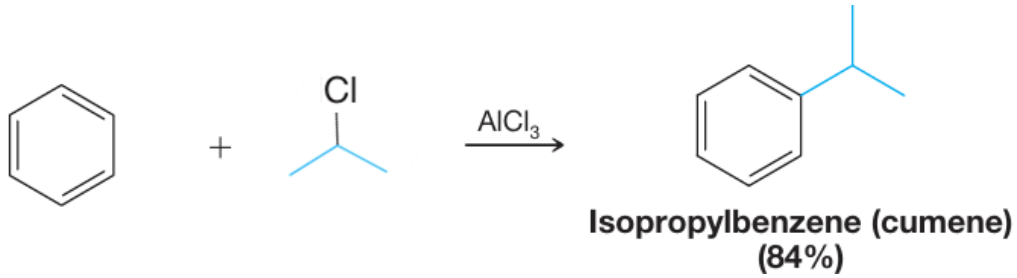
4.1. Reactions of Benzene

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.

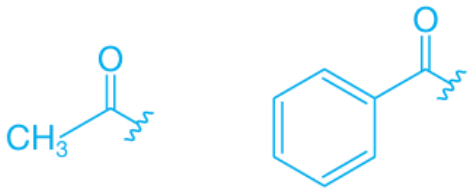
$$RCl + AlCl_3 \longrightarrow R^+ + AlCl_4^-$$

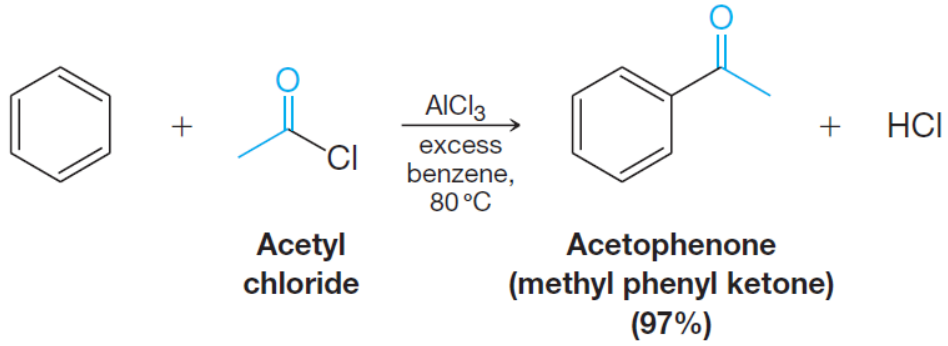




4.1.5. Friedel–Crafts Acylation

- 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	$-C(=O)-R$	acyl, carboxy	
	$-C(=O)-\ddot{O}H$		
	$-C(=O)-\ddot{N}H_2$	carboxamido, carboalkoxy	
	$-C(=O)-\ddot{O}R$		
	$-S(=O)(=O)-\ddot{O}H$	sulfonic acid	
	$-C\equiv N:$	cyano	
	$-N^{+}(=O:)\ddot{O}:^{-}$	nitro	

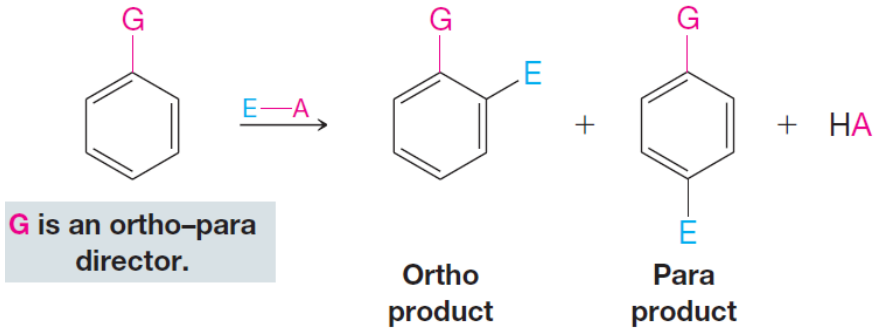
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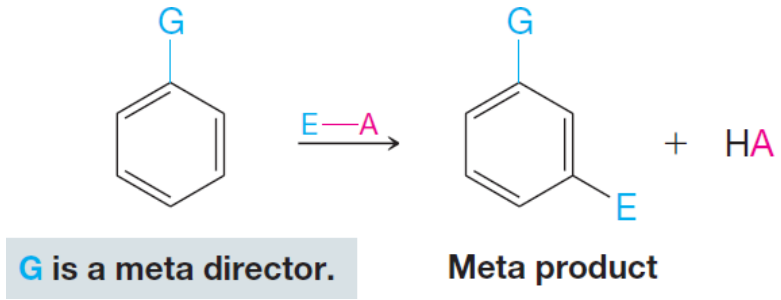
4. Electrophilic Aromatic Substitution Reactions

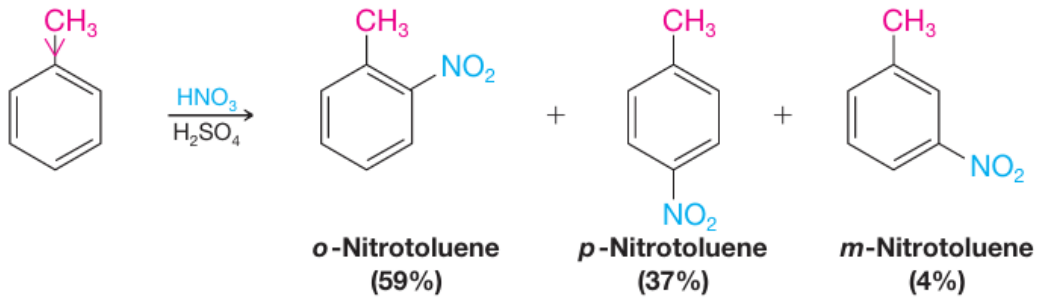
4.1. Reactions of Benzene

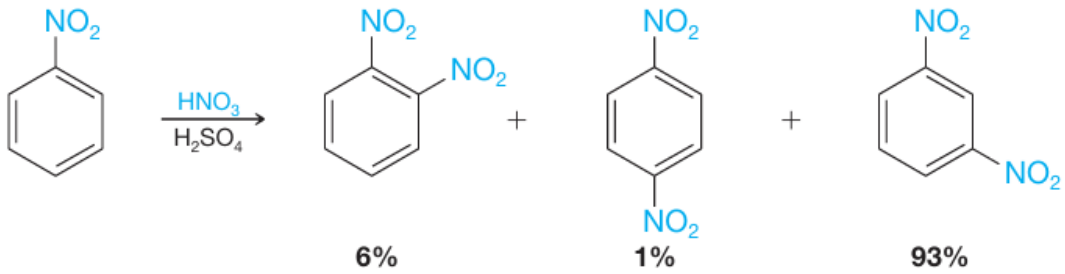
4.1.6. Effects of Substituents on Reactivity and Orientation

- **Example;**









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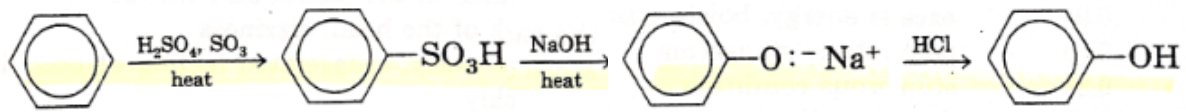
4. Electrophilic Aromatic Substitution Reactions

4.2. Reactions of Phenols

4.2.1. Synthesis of Phenols; The Alkali Fusion of Sulfonates

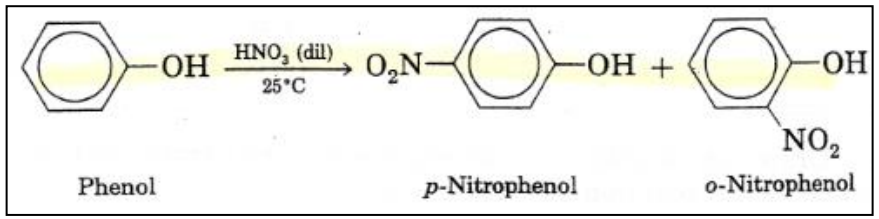
- Phenol can be prepared by the alkali fusion of sulfonates *via* the following steps;

1. Sulfonation of an aromatic ring.
2. Melting (fusion) of the aromatic sulfonic acid with sodium hydroxide to give a phenoxide salt.
3. Acidification of the phenoxide with HCl to produce the phenol.



4.2.2. Reactions of Phenols

- Nitration of phenol goes so rapidly that dilute nitric acid at room temperature must be used.



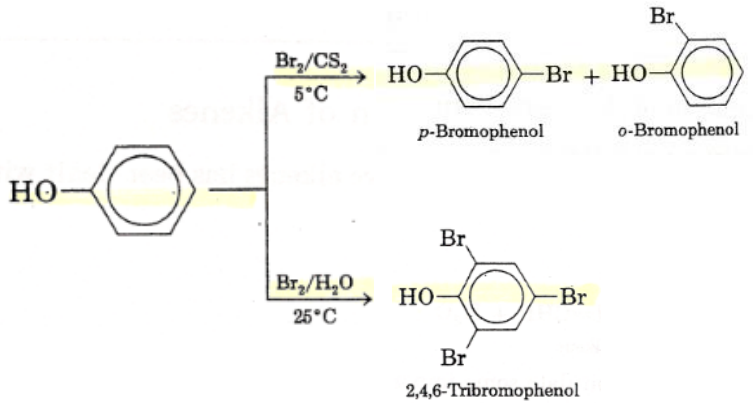
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4. Electrophilic Aromatic Substitution Reactions

4.2. Reactions of Phenols

4.2.2. Reactions of Phenols

- **Halogenation** takes place without catalyst.



  - The products depend on the solvent used.
    - In aprotic solvents (solvents that do not release protons) (CCl_4, CS_2)-bromination gives a mixture of *o*- and *p*-bromophenol.
    - In protic solvents (solvents that can release protons) (H_2O)-halogenation gives a trisubstituted phenol is produced.

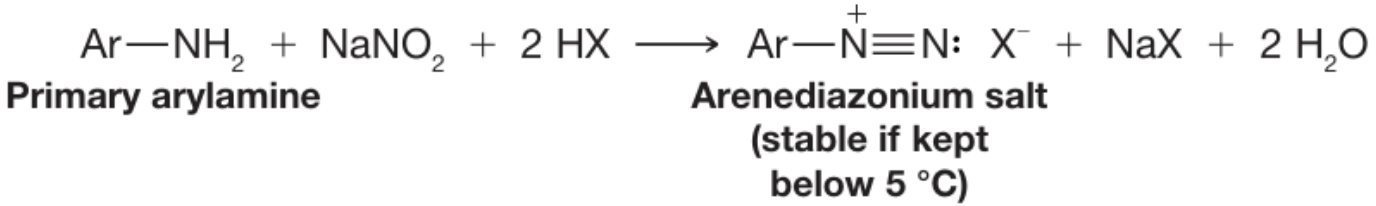
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4. Electrophilic Aromatic Substitution Reactions

4.3. Reactions of Aromatic Amines

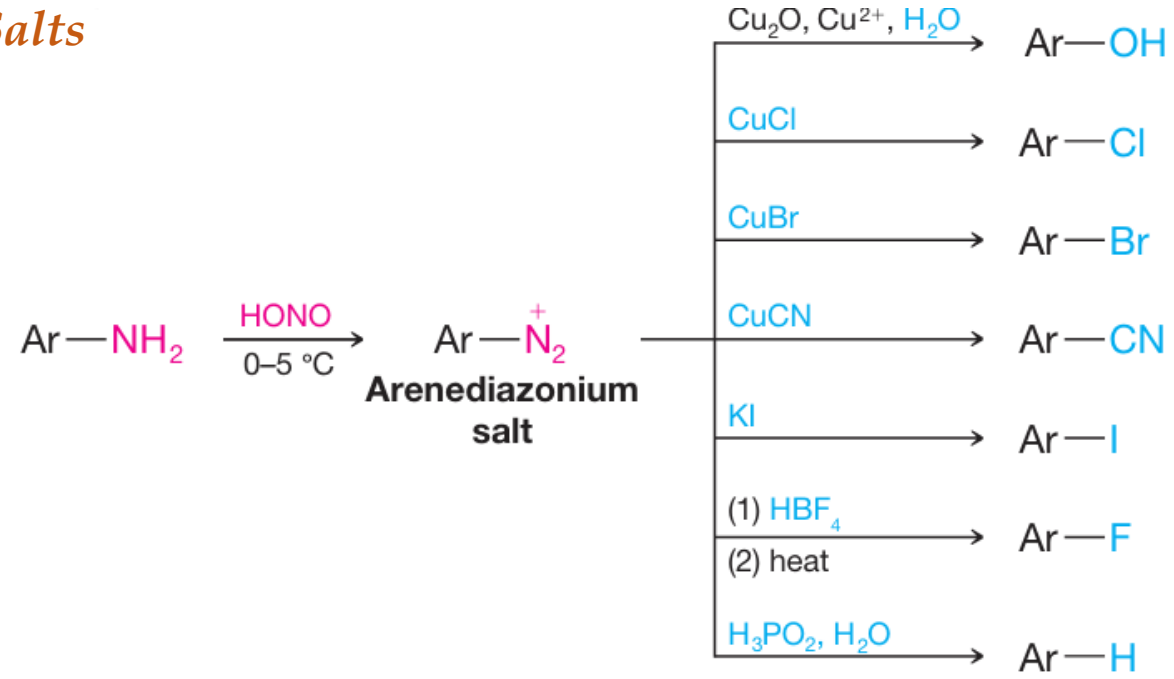
4.3.1. Reactions of Primary Arylamines with Nitrous Acid

- Reaction of primary arylamines with nitrous acid results in the formation of relatively stable arenediazonium salts.



4.3.2. Replacement Reactions of Arenediazonium Salts

- Arenediazonium salts are highly useful intermediates in the synthesis of aromatic compounds, because the diazonium group can be replaced by any one of a number of other atoms or groups, including –F, –Cl, –Br, –I, –CN, –OH, and –H.



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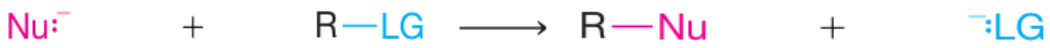
Nucleophilic Reactions

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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.

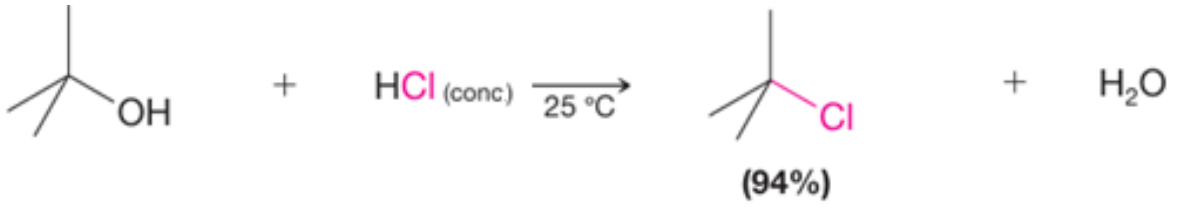


5.1.1. Nucleophilic Substitution Reactions of Alcohols: Synthesis of Alkyl halides

A) Alcohols react with a hydrogen halide (HCl, HBr, HI), to yield alkyl halide and water.

- The order of reactivity of alcohols is 3° > 2° > 1°.
- The order of reactivity of the hydrogen halides is HI > HBr > HCl (HF is generally unreactive).





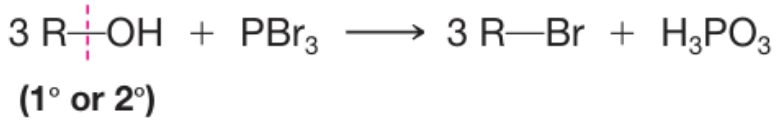
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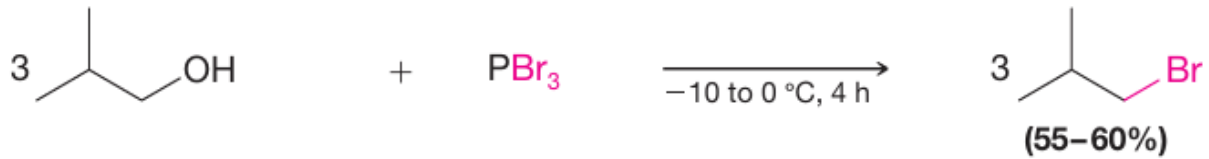
5. Nucleophilic Reactions

5.1. Nucleophilic Substitution Reactions

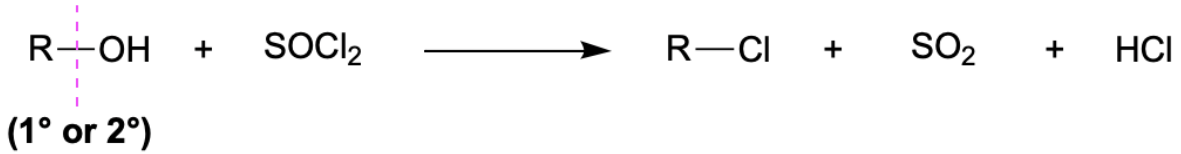
5.1.1. Nucleophilic Substitution Reactions of Alcohols: Synthesis of Alkyl halides

B) Primary and secondary alcohols react with phosphorus tribromide (PBr3) to yield alkyl bromides.





C) Thionyl chloride (SOCl2) converts primary and secondary alcohols to alkyl chlorides.





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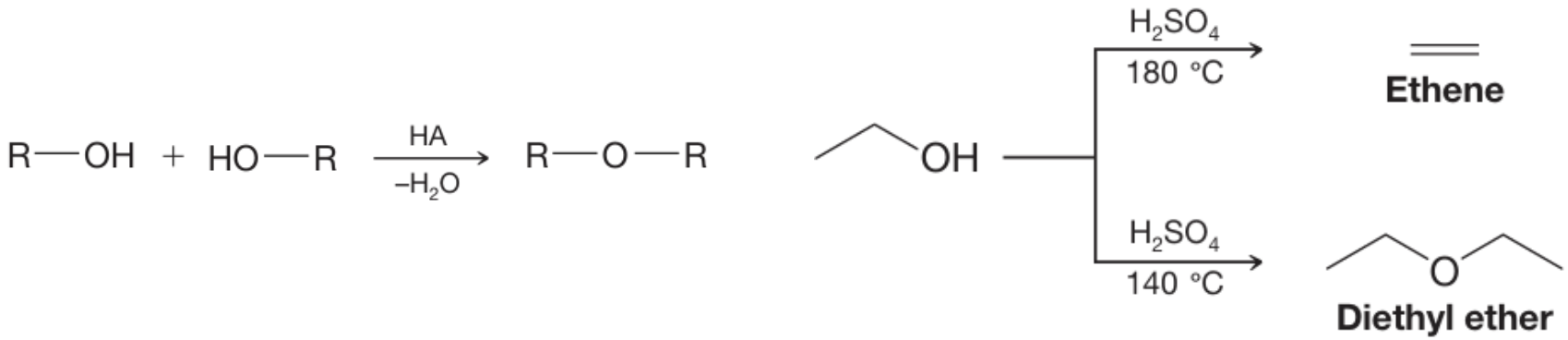
5. Nucleophilic Reactions

5.1. Nucleophilic Substitution Reactions

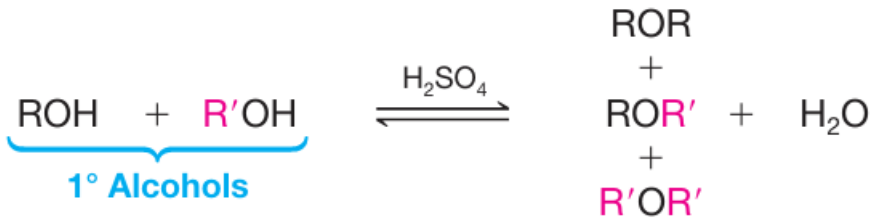
5.1.2. Synthesis of Ethers

A) Ethers by Intermolecular Dehydration of Alcohols

- Acid-catalyzed substitution reaction between two alcohol molecules can form an ether by loss of water.
- This reaction occurs at lower temperature than the competing dehydration to an alkene at high temperature.



- Intermolecular dehydration is not useful for the preparation of unsymmetrical ethers from primary alcohols because the reaction leads to a mixture of products.



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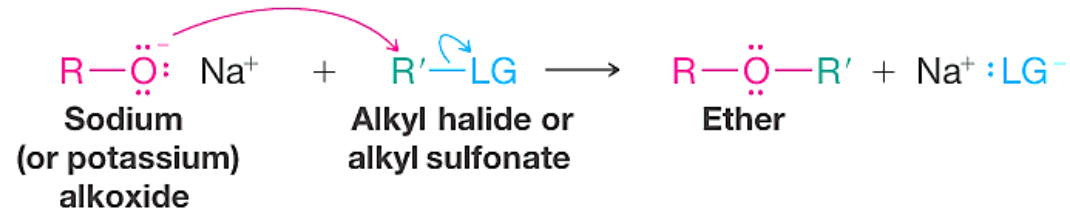
5. Nucleophilic Reactions

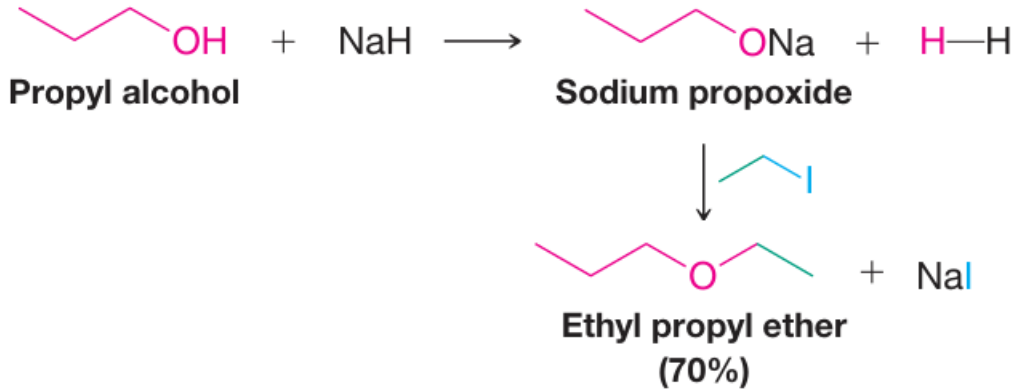
5.1. Nucleophilic Substitution Reactions

5.1.2. Synthesis of Ethers

B) The Williamson Ether Synthesis

- This is a good route for synthesis of unsymmetrical ethers.
- Best results are obtained when the alkyl halide is primary (or methyl).
- Substitution is also favored over elimination at lower temperatures.





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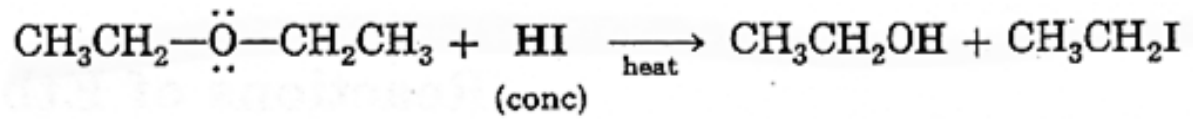
5. Nucleophilic Reactions

5.1. Nucleophilic Substitution Reactions

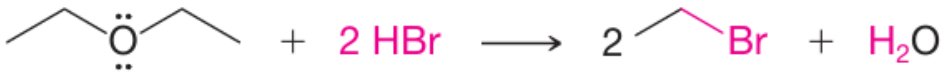
5.1.3. Cleavage of Ethers

A) Cleavage of Dialkyl Ethers

- Heating dialkyl ethers with very strong acids (HI, HBr, and H_2SO_4) causes them to undergo reactions in which the carbon–oxygen bond breaks.

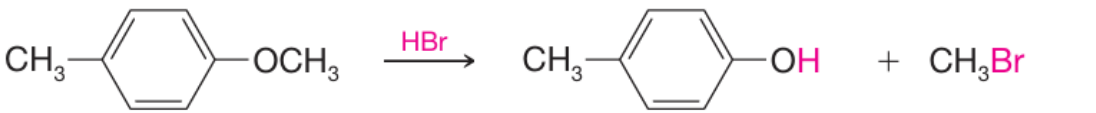


- If an excess of acid is present, the alcohol initially produced is converted into an alkyl halide by the reaction.



B) Cleavage of Alkyl Aryl Ethers

- When alkyl aryl ethers react with strong acids such as HI and HBr, the reaction produces an alkyl halide and a phenol.



p-Methylanisole — 4-Methylphenol — Bromomethane

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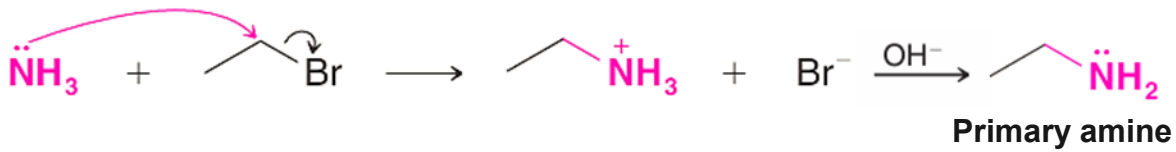
5. Nucleophilic Reactions

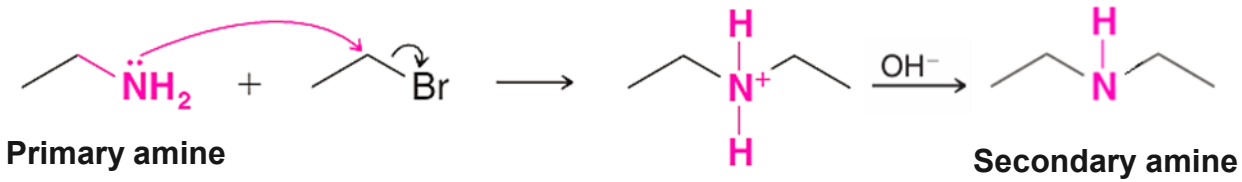
5.1. Nucleophilic Substitution Reactions

5.1.4. Preparation of Amines

- **Alkylation of Ammonia:**
  - Reaction of ammonia with an alkyl halide leads to an ammonium salt.
  - Subsequent treatment of the resulting ammonium salts with a base gives primary amines.
- Primary, secondary, and tertiary amines can be similarly alkylated.



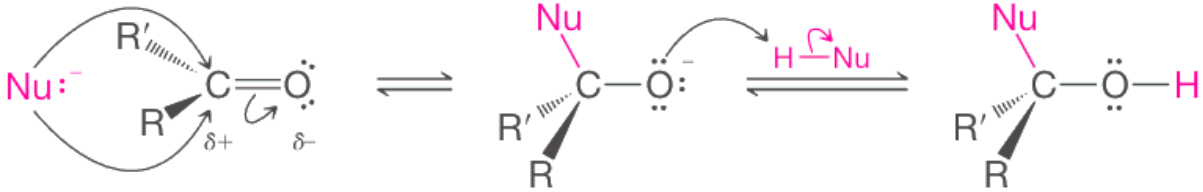




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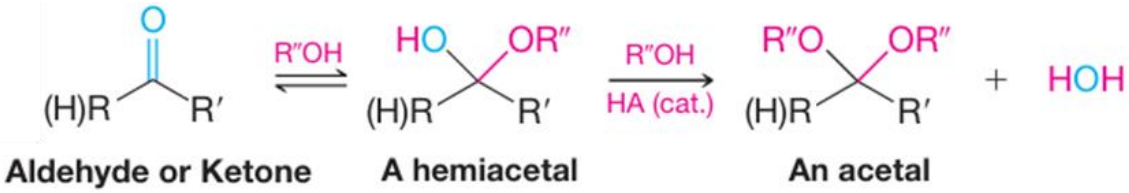
5. Nucleophilic Reactions

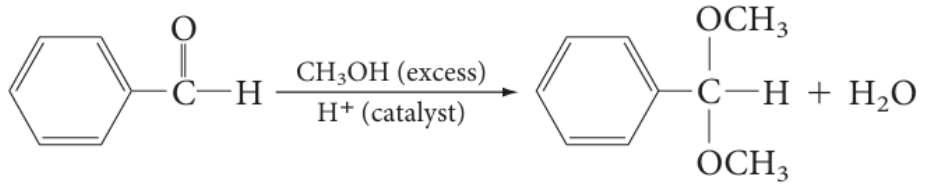
5.2. Nucleophilic Addition Reactions



5.2.1. *Addition of Alcohols to Aldehyde or Ketone: Hemiacetals and Acetals Formation*

- Hemiacetals; an –OH and an –OR group attached to the same carbon atom.
- Acetals; has two –OR groups attached to the same carbon atom.
- An acetal forms when an aldehyde or ketone is treated with an excess of alcohol in the presence of an acid catalyst.





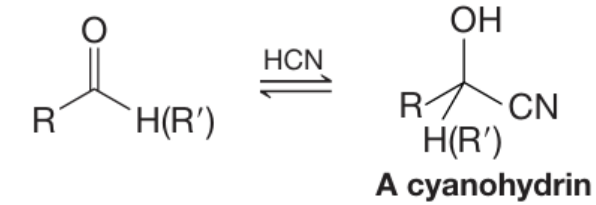
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5. Nucleophilic Reactions

5.2. Nucleophilic Addition Reactions

5.2.2. Addition of Hydrogen Cyanide to Aldehyde or Ketone: Cyanohydrins Formation

- Hydrogen cyanide adds to the carbonyl groups of aldehydes and most ketones to form compounds called cyanohydrins.

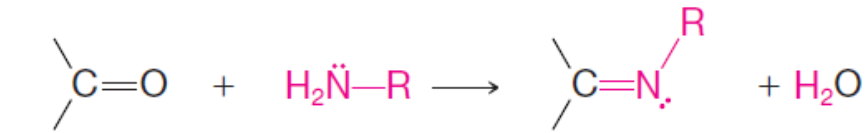


A cyanohydrin



5.2.3. Addition of Primary Amines to Aldehyde or Ketone: Imine Formation

- Imine formation is acid catalyzed, and the product can form from a primary amine and an aldehyde or ketone.



Aldehyde or ketone | **A 1° amine** | **An imine [(*E*) and (*Z*) isomers]**

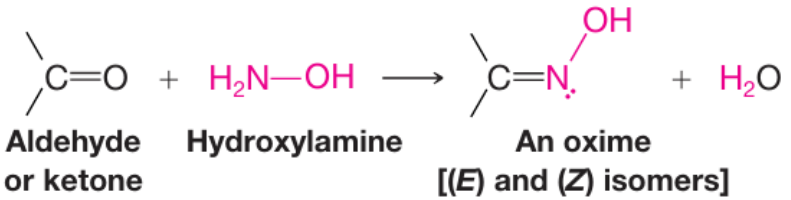
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5. Nucleophilic Reactions

5.2. Nucleophilic Addition Reactions

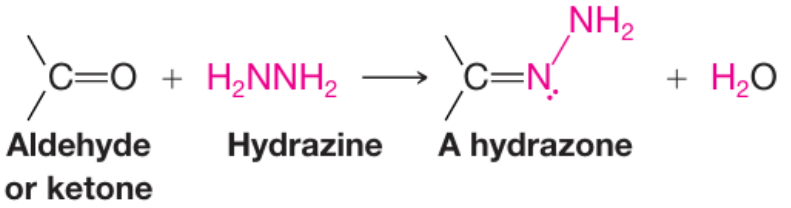
5.2.4. Addition of Hydroxylamine to Aldehyde or Ketone: Oxime Formation

- Oximes are formed when aldehydes or ketones react with hydroxylamine (H_2N-OH).



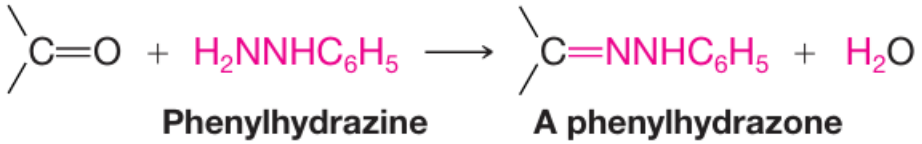
5.2.5. Addition of Hydrazine to Aldehyde or Ketone: Hydrazone Formation

- Hydrazone can be formed when aldehydes or ketones react with hydrazine (H_2N-NH_2).



5.2.6. Addition of Phenylhydrazine to Aldehyde or Ketone: Phenylhydrazone Formation

- Phenylhydrazine can be formed when aldehydes or ketones react with phenylhydrazone (H_2N-NHC_6H_5).



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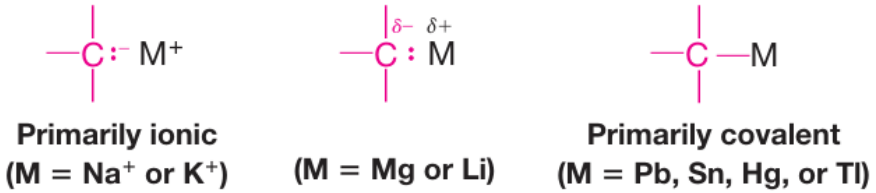
5. Nucleophilic Reactions

5.2. Nucleophilic Addition Reactions

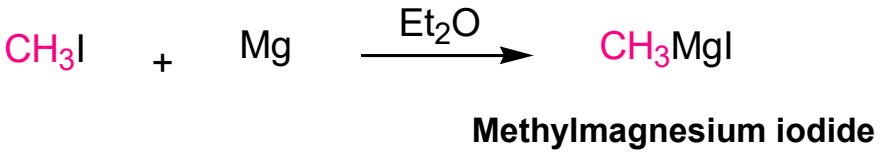
5.2.7. Nucleophilic Addition of Grignard Reagents

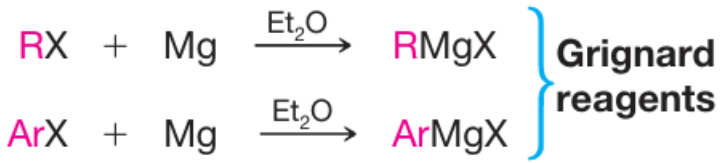
5.2.7.1. Formation of Grignard Reagents from Halogen Compounds

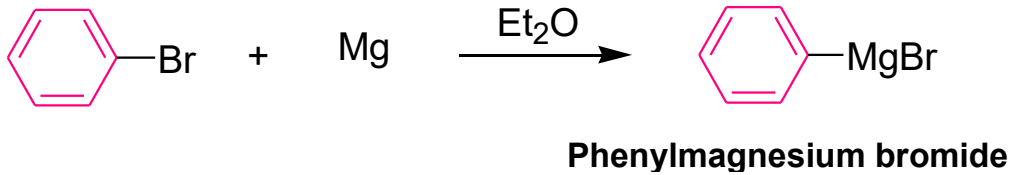
- Compounds that contain carbon–metal bonds are called organometallic compounds.



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







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

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5. Nucleophilic Reactions

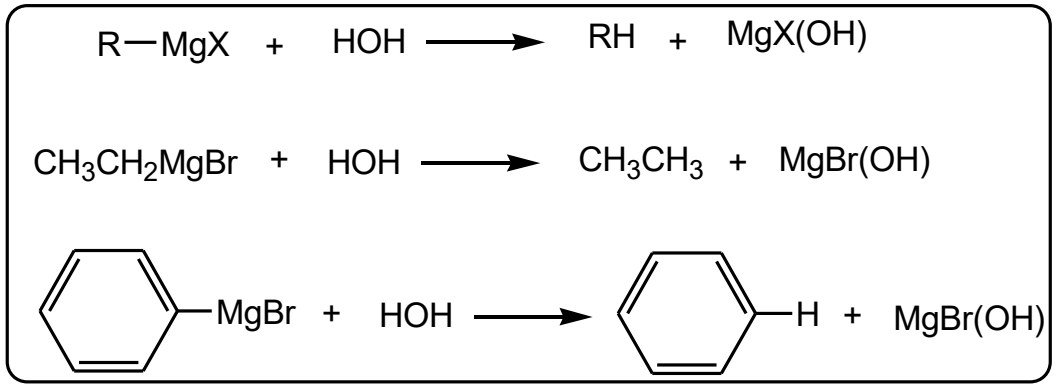
5.2. Nucleophilic Addition Reactions

5.2.7. Nucleophilic Addition of Grignard Reagents

5.2.7.2. 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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5. Nucleophilic Reactions

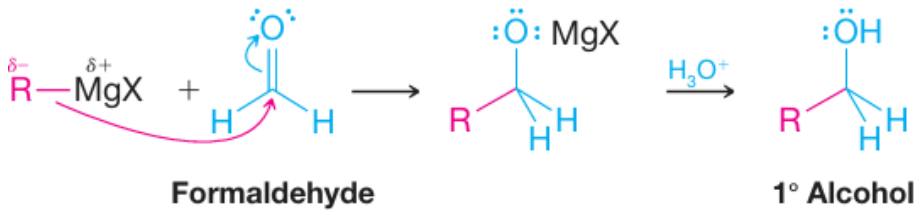
5.2. Nucleophilic Addition Reactions

5.2.7. Nucleophilic Addition of Grignard Reagents

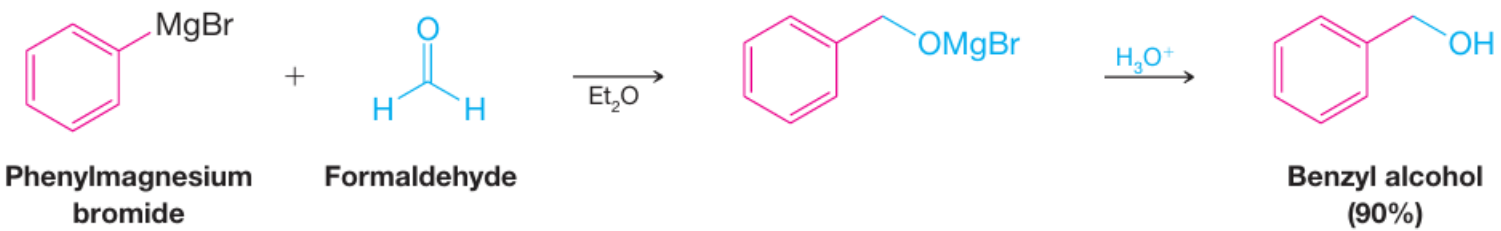
5.2.7.3. Addition of Grignard Reagents to Aldehydes and Ketones

- Grignard reagents react as nucleophiles and attack an unsaturated carbon—the carbon of a carbonyl group (aldehyde and ketone) to prepare primary, secondary, or tertiary alcohols.

A) Addition of Grignard reagents to Formaldehyde yields a Primary Alcohol.



- **Examples,**



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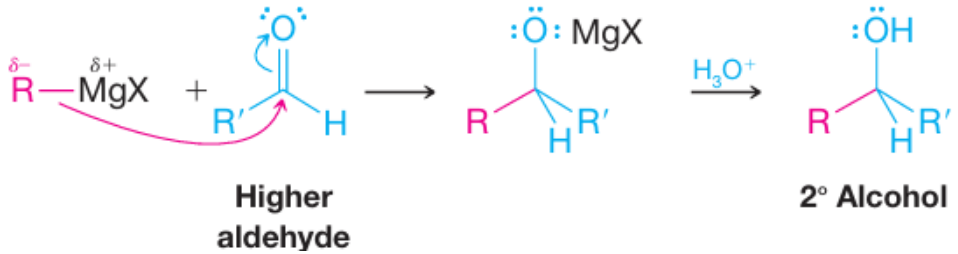
5. Nucleophilic Reactions

5.2. Nucleophilic Addition Reactions

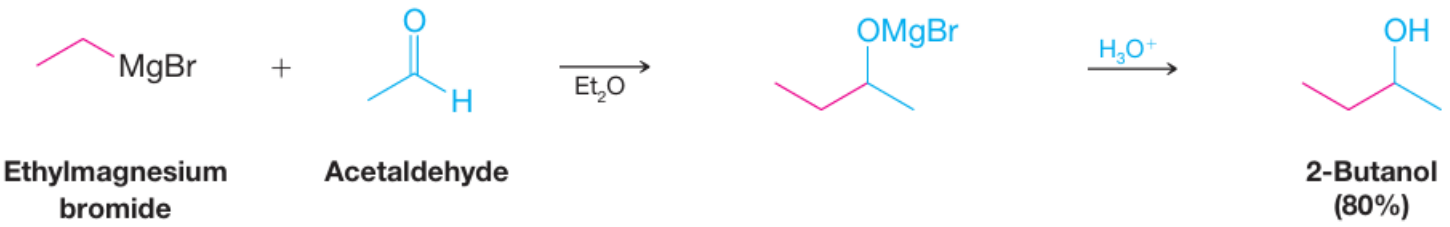
5.2.7. Nucleophilic Addition of Grignard Reagents

5.2.7.3. Addition of Grignard Reagents to Aldehydes and Ketones

B) Addition of Grignard reagents to all other Aldehydes yields Secondary Alcohols.



- **Examples,**



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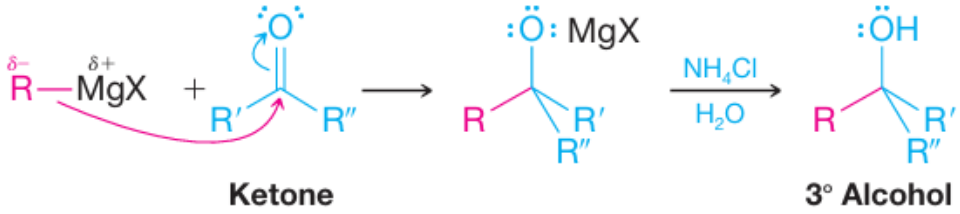
5. Nucleophilic Reactions

5.2. Nucleophilic Addition Reactions

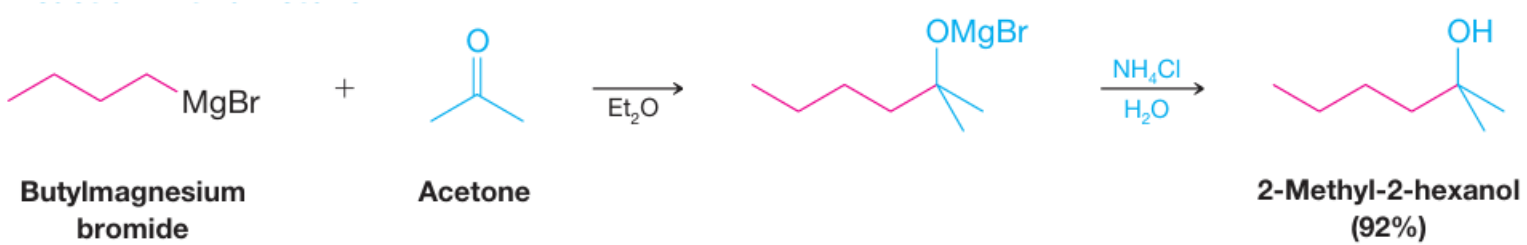
5.2.7. Nucleophilic Addition of Grignard Reagents

5.2.7.3. Addition of Grignard Reagents to Aldehydes and Ketones

C) Addition of Grignard reagents to Ketones yields Tertiary Alcohols.



- **Examples,**



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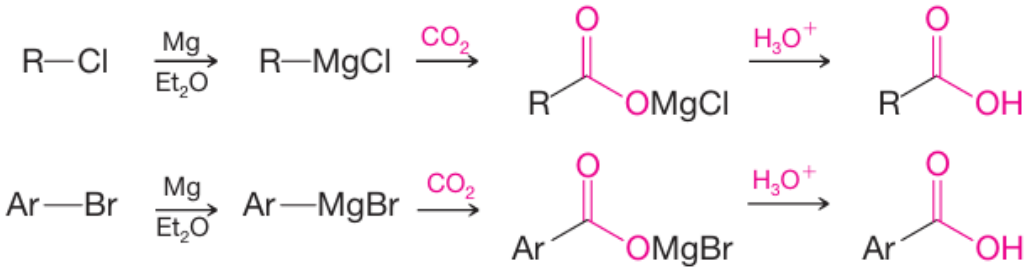
5. Nucleophilic Reactions

5.2. Nucleophilic Addition Reactions

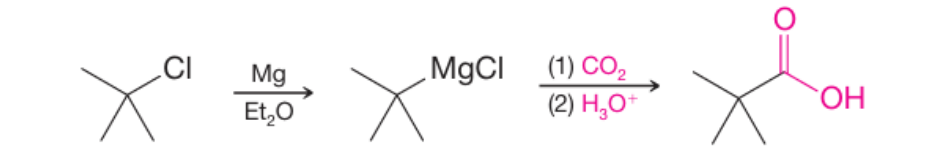
5.2.7. Nucleophilic Addition of Grignard Reagents

5.2.7.4. Carbonation of Grignard Reagents: Preparation of carboxylic acids

- Grignard reagents react with carbon dioxide to yield magnesium carboxylates. Acidification produces carboxylic acids.

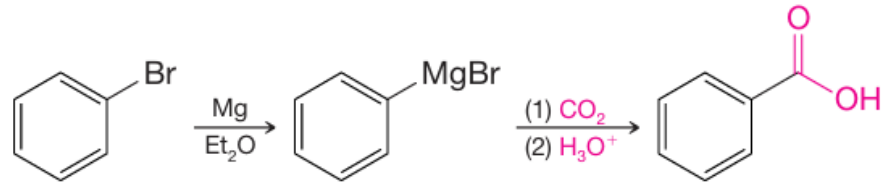


- This synthesis of carboxylic acids is applicable to primary, secondary, tertiary, allyl, benzyl, and aryl halides.



tert-Butyl chloride

2,2-Dimethylpropanoic acid
(79–80% overall)



Bromobenzene

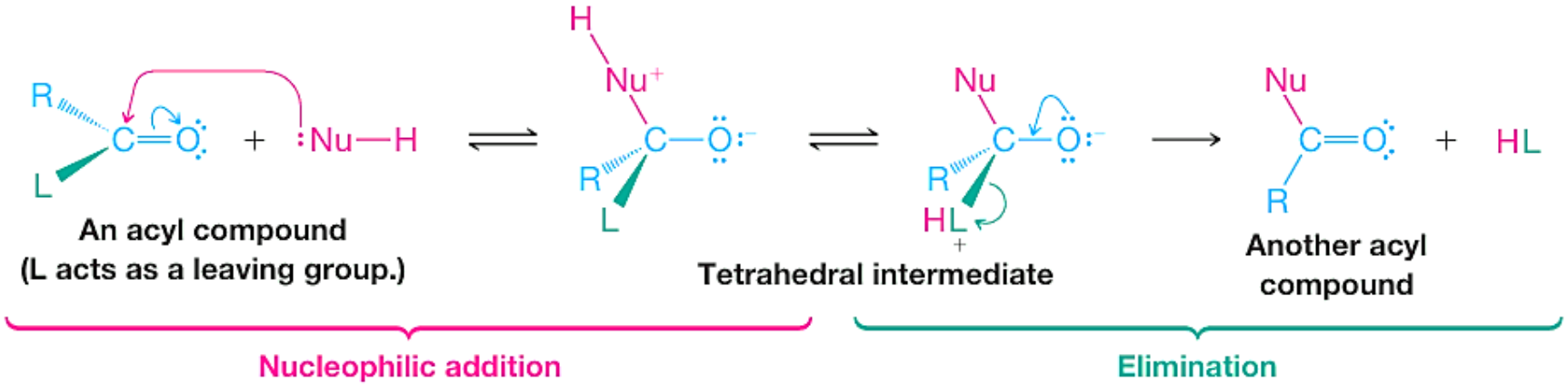
Benzoic acid
(85%)

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5. Nucleophilic Reactions

5.3. Substitution by Nucleophilic Addition-Elimination Reaction

- The reactions of carboxylic acids and their derivatives are characterized by nucleophilic addition–elimination at their acyl (carbonyl) carbon atoms. The result is a substitution at the acyl carbon.



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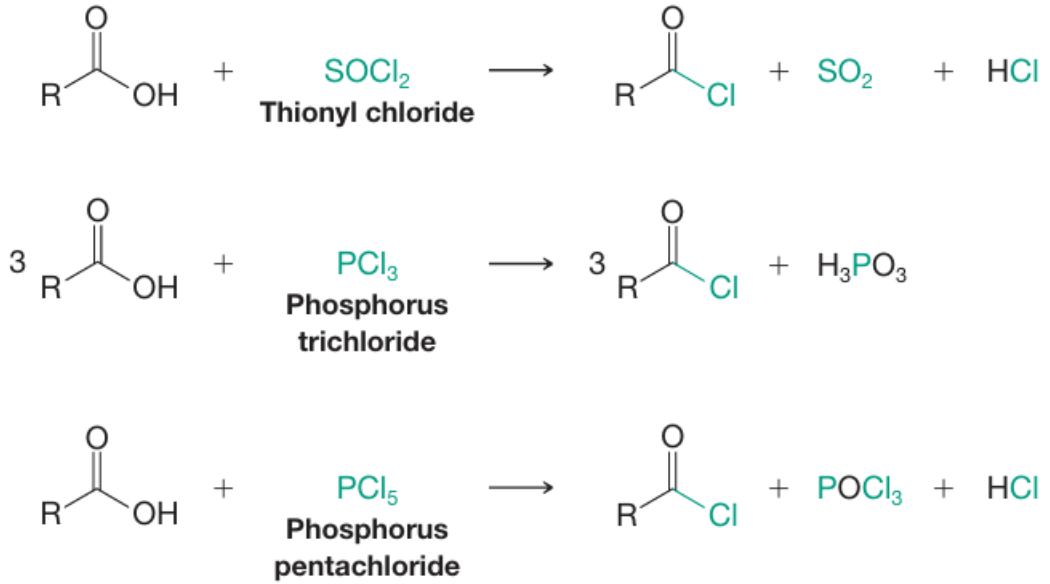
5. Nucleophilic Reactions

5.3. Substitution by Nucleophilic Addition-Elimination Reaction

5.3.1. Acyl Chlorides

5.3.1.1. Synthesis of Acyl Chlorides

- Acid chlorides are prepared from the reaction of carboxylic acids with *thionyl chloride*, *phosphorus trichloride* or *phosphorus pentachloride*.



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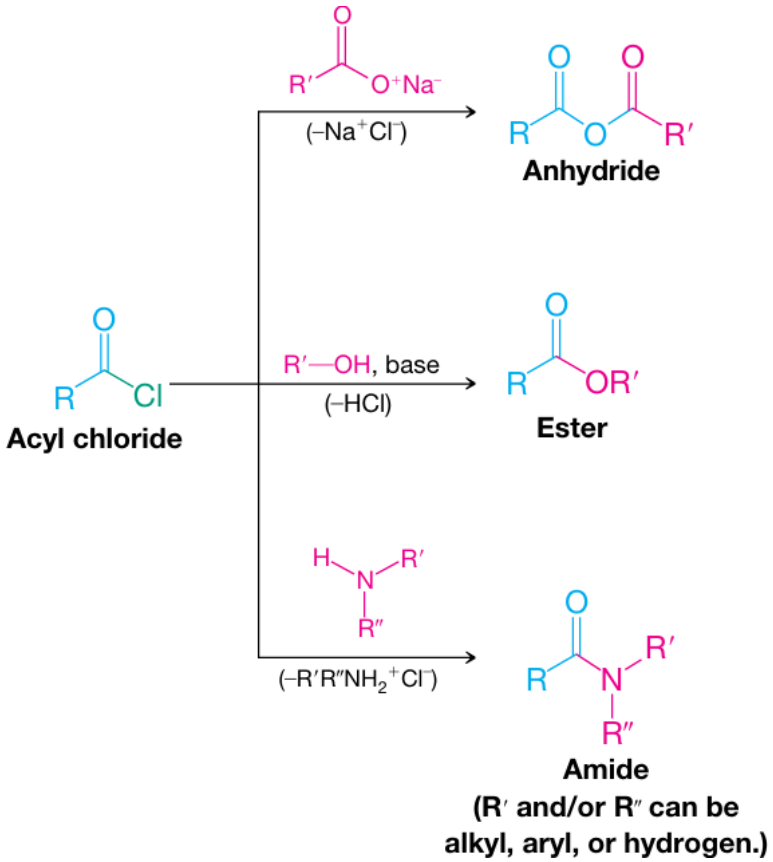
5. Nucleophilic Reactions

5.3. Substitution by Nucleophilic Addition-Elimination Reaction

5.3.1. Acyl Chlorides

5.3.1.2. Reactions of Acyl Chlorides

- Acyl chlorides are very reactive and can be used to synthesize anhydrides, esters and amides.



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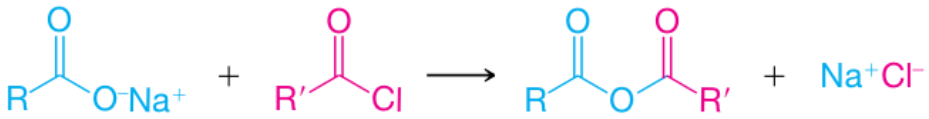
5. Nucleophilic Reactions

5.3. Substitution by Nucleophilic Addition-Elimination Reaction

5.3.2. Carboxylic Acid Anhydrides

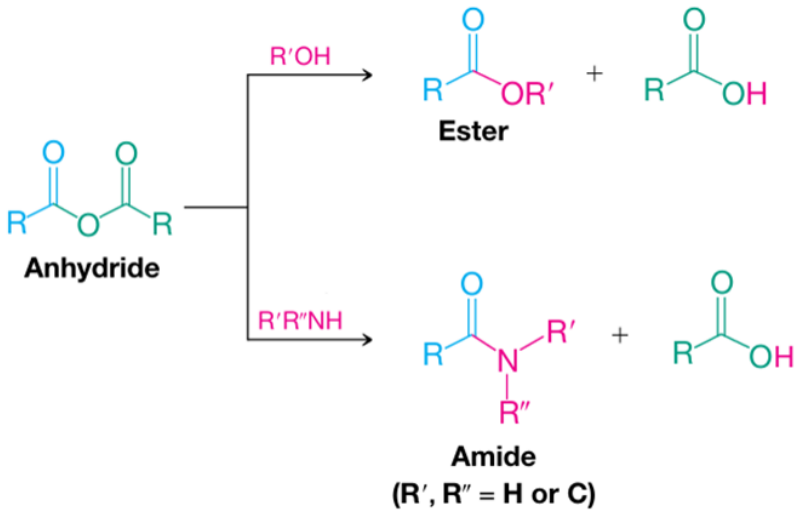
5.3.2.1. Synthesis of Carboxylic Acid Anhydrides

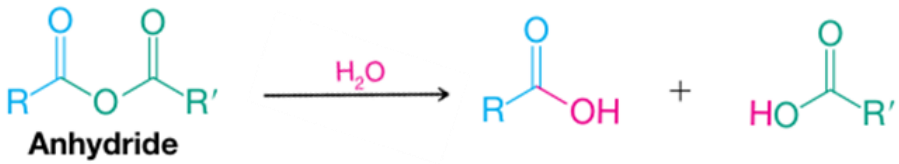
- Sodium salts of carboxylic acids react with acyl chlorides to give anhydrides.



5.3.2.2. Reactions of Carboxylic Acid Anhydrides

- Carboxylic acid anhydrides are very reactive and can be used to synthesize esters and amides.
- Hydrolysis of an anhydride yields the corresponding carboxylic acids.





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5. Nucleophilic Reactions

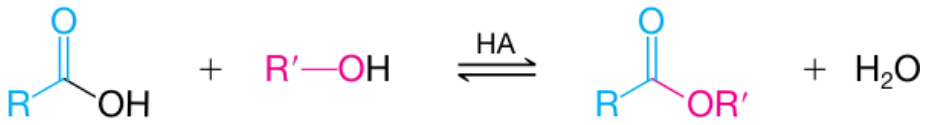
5.3. Substitution by Nucleophilic Addition-Elimination Reaction

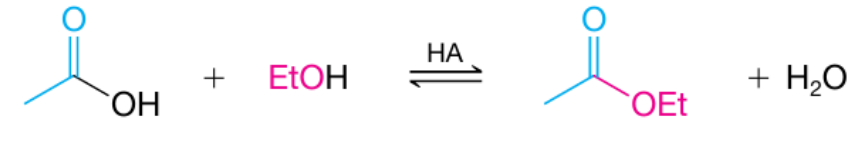
5.3.3. Esters

5.3.3.1. Synthesis of Esters: Esterification

A) Acid-Catalyzed Esterification: Fischer esterification

Esters can be prepared by the reaction of a carboxylic acid with an alcohol or phenol in the presence of an acid catalyst.



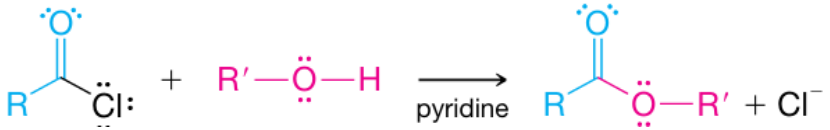


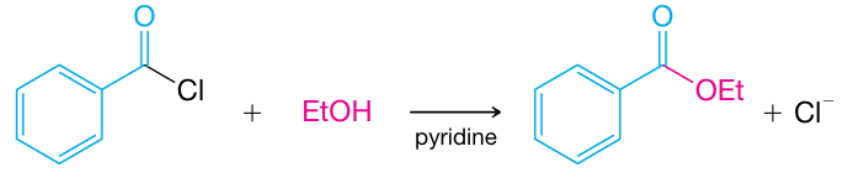
Acetic acid **Ethanol** **Ethyl acetate**

B) Esters from Acyl Chlorides:

Esters can be prepared by the reaction of acyl chlorides with alcohols or phenols.

This method is fast and efficient compared to Fischer esterification.





Benzoyl chloride **Ethyl benzoate (80%)**

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5. Nucleophilic Reactions

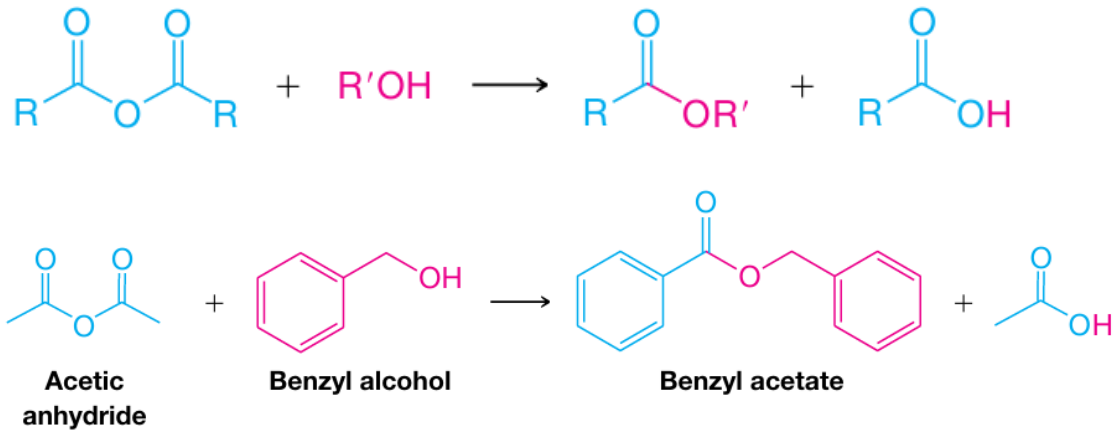
5.3. Substitution by Nucleophilic Addition-Elimination Reaction

5.3.3. Esters

5.3.3.1. Synthesis of Esters: Esterification

C) Esters from Carboxylic Acid Anhydrides

Carboxylic acid anhydrides react with alcohols and phenols to form esters in the absence of acid catalyst.



Acetic anhydride | Benzyl alcohol | Benzyl acetate

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5. Nucleophilic Reactions

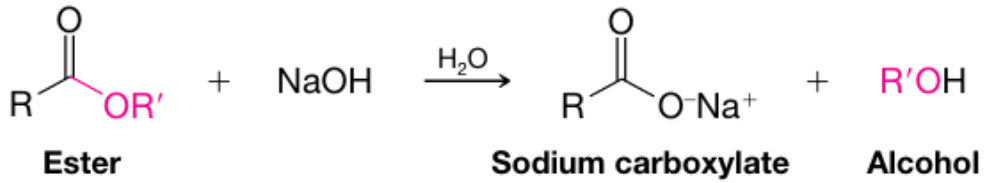
5.3. Substitution by Nucleophilic Addition-Elimination Reaction

5.3.3. Esters

5.3.3.2. Reactions of Esters

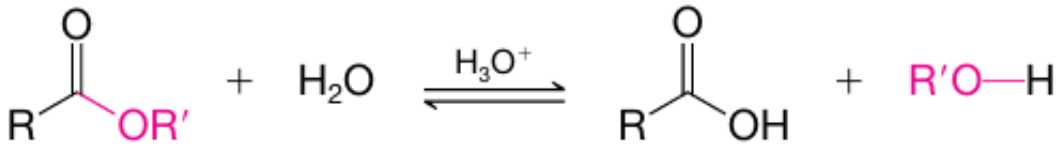
A) Base-Promoted Hydrolysis of Esters: Saponification

Reaction of an ester with sodium hydroxide results in the formation of a sodium carboxylate and an alcohol.



B) Acid-Catalyzed Ester Hydrolysis

Reaction of an ester with a large excess of water and dilute aqueous HCl or dilute aqueous H_2SO_4 results in the formation of a carboxylic acid and an alcohol.



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5. Nucleophilic Reactions

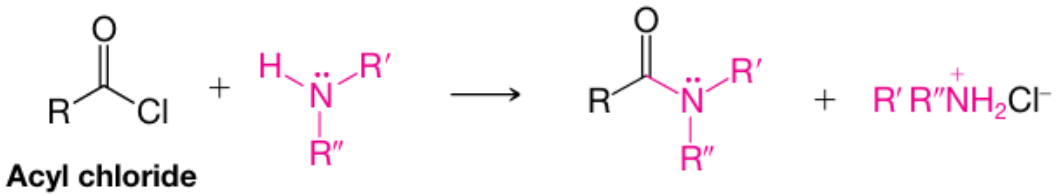
5.3. Substitution by Nucleophilic Addition-Elimination Reaction

5.3.4. Amides

5.3.4.1. Synthesis of Amides

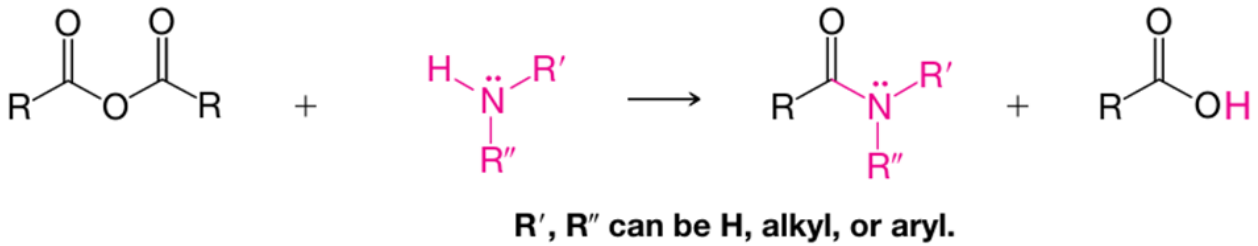
A) From Acyl Chlorides

Ammonia, primary or secondary amines react with acid chlorides to form amides.



B) From Carboxylic Anhydrides

Acid anhydrides react with amine to produce an amide and carboxylic acid.



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5. Nucleophilic Reactions

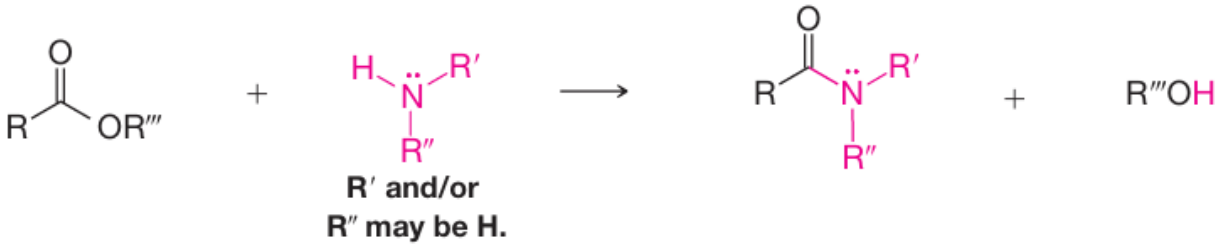
5.3. Substitution by Nucleophilic Addition-Elimination Reaction

5.3.4. Amides

5.3.4.1. Synthesis of Amides

C) Amides from Esters

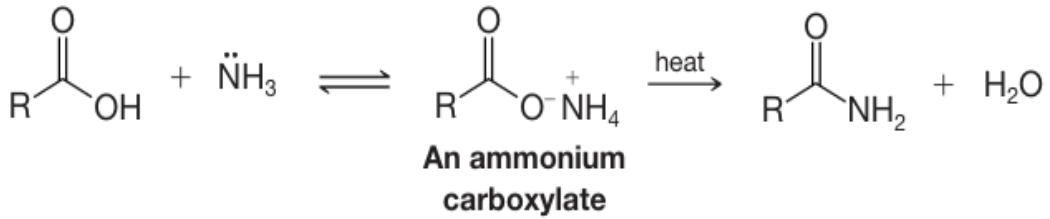
Esters react with ammonia (a process called ammonolysis) or with primary and secondary amines to produce an amide and an alcohol.



D) From Carboxylic Acids and Ammonium Carboxylates

Carboxylic acids react with aqueous ammonia to form ammonium salts.

Some ammonium salts of carboxylic acids can be dehydrated to the amide at high temperatures



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5. Nucleophilic Reactions

5.3. Substitution by Nucleophilic Addition-Elimination Reaction

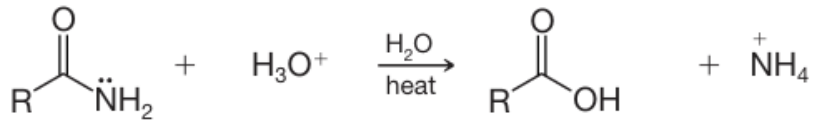
5.3.4. Amides

5.3.4.2. Reactions of Amides

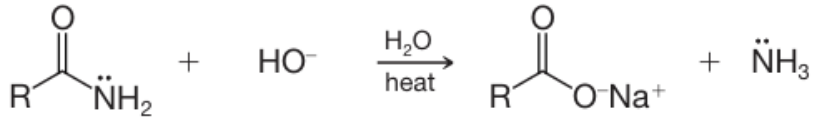
A) Hydrolysis of Amides

Amides undergo hydrolysis when they are heated with aqueous acid or aqueous base.

Acidic Hydrolysis

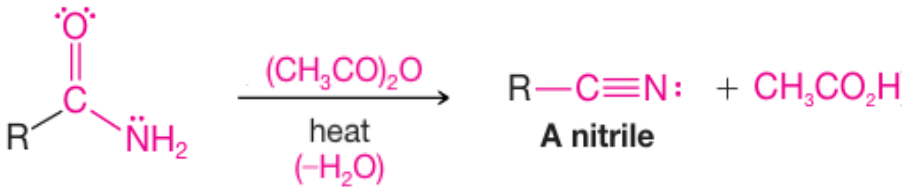


Basic Hydrolysis



B) Dehydration of Amides

Amides react with boiling acetic anhydride to form nitriles.



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Oxidation and Reduction Reactions

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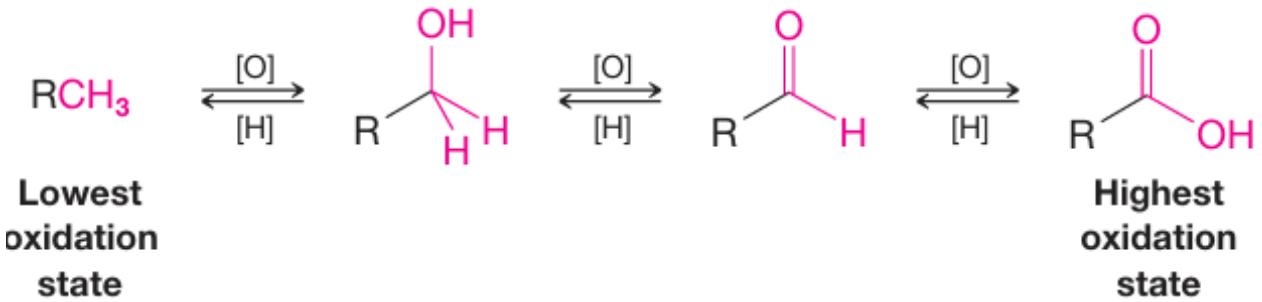
6. Oxidation and Reduction Reactions

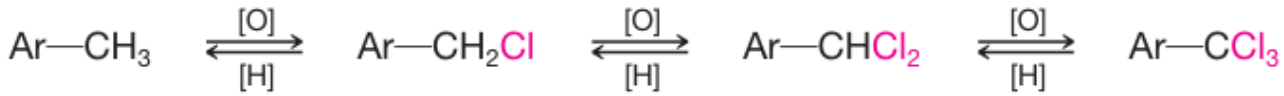
- Reduction; increasing the hydrogen content or decreasing the oxygen content of an organic molecule.

  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.

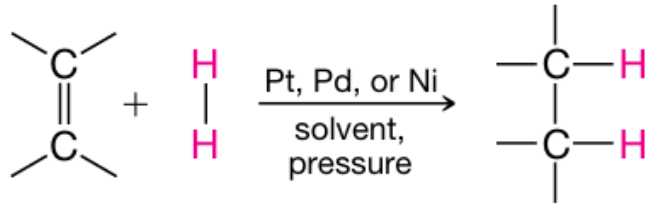
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6. Oxidation and Reduction Reactions

6.1. Reduction Reactions

6.1.1. Hydrogenation of Unsaturated Aliphatic Hydrocarbons

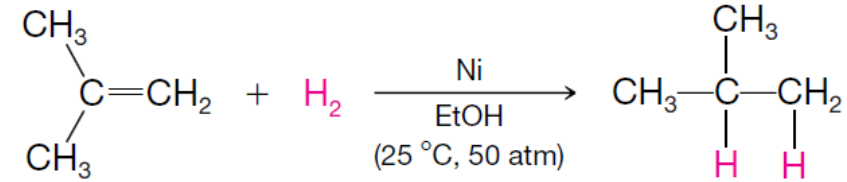
- Heterogeneous catalysts: Insoluble platinum, palladium, or nickel catalysts, which are not soluble in the reaction mixture.
- Homogeneous catalysts: Soluble catalysts, including rhodium or ruthenium complexes; tris(triphenylphosphine)rhodium chloride ($Rh[(C_6H_5)_3P]_3Cl$).



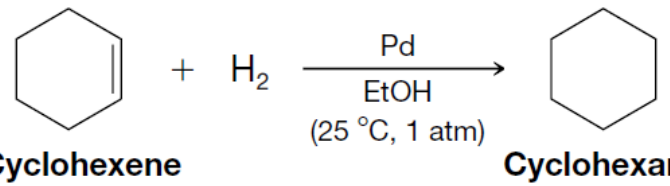
Alkene **Alkane**

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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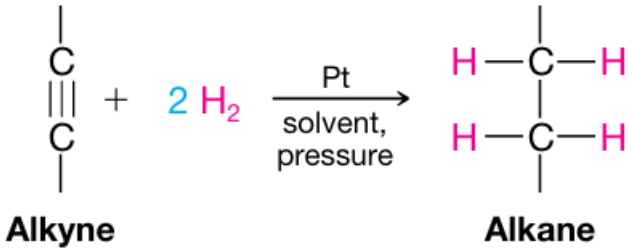
6. Oxidation and Reduction Reactions

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**

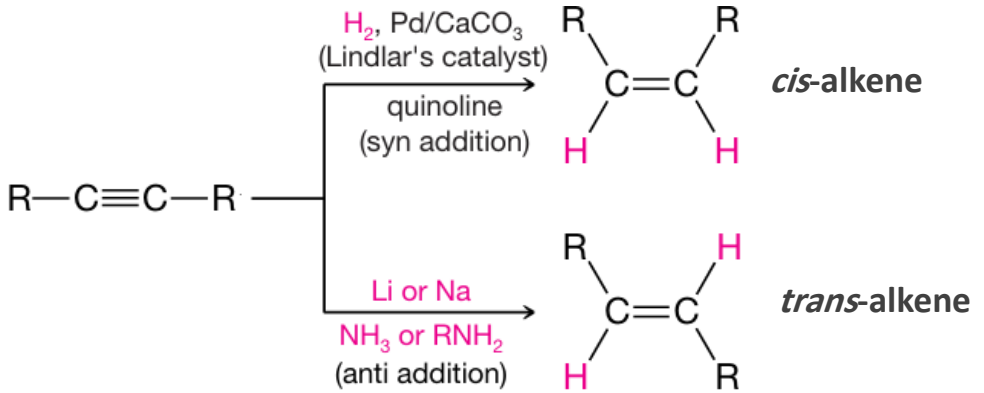
$$CH_3C{\equiv}CCH_3 \xrightarrow{Pt,\ H_2} [CH_3CH{=}CHCH_3] \xrightarrow{Pt,\ H_2} CH_3CH_2CH_2CH_3$$

- *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.



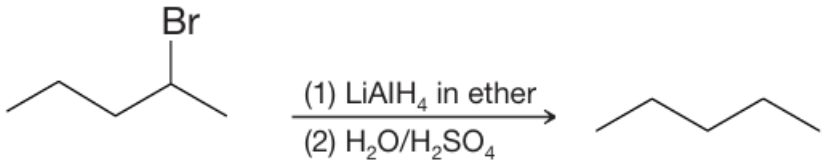
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6. Oxidation and Reduction Reactions

6.1. Reduction Reactions

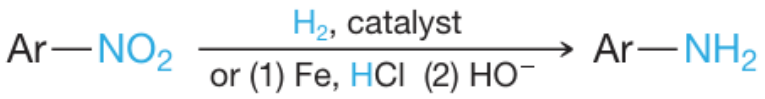
6.1.2. Reduction of Alkyl Halides to Hydrocarbons: RX to RH

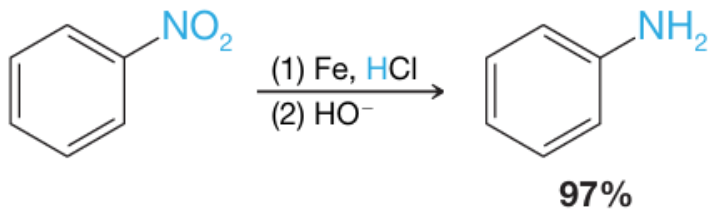
- Replacement of the halogen atom of an alkyl halide by hydrogen can be accomplished by treating the alkyl halide with lithium aluminum hydride.



6.1.3. Reduction of Nitro Compounds: Preparation of Aromatic Amines

- Aromatic amines can be synthesized by reduction of the corresponding nitro compound.





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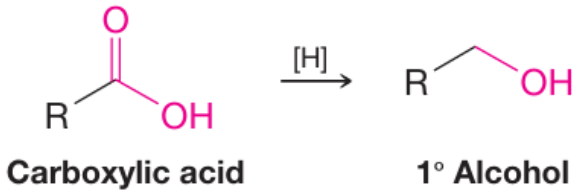
6. Oxidation and Reduction Reactions

6.1. Reduction Reactions

6.1.4. Reduction of Carbonyl Compounds

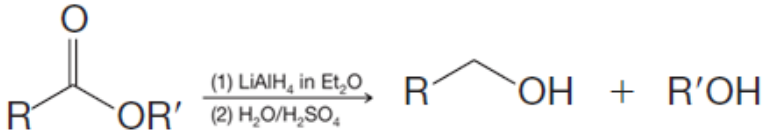
A) Reduction of Carboxylic acids

- Carboxylic acids can be reduced to primary alcohols, with Lithium Aluminum Hydride ($LiAlH_4$)

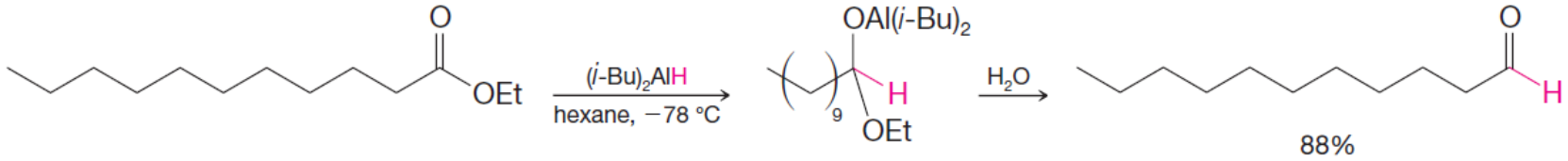


B) Reduction of Ester

- Esters can be reduced to primary alcohols. with Lithium Aluminum Hydride ($LiAlH_4$)



- Esters can be reduced to aldehydes, with DIBAL-H at low temperatures by the addition of a hydride ion to the carbonyl carbon of the ester , followed by hydrolysis for the formed intermediate.



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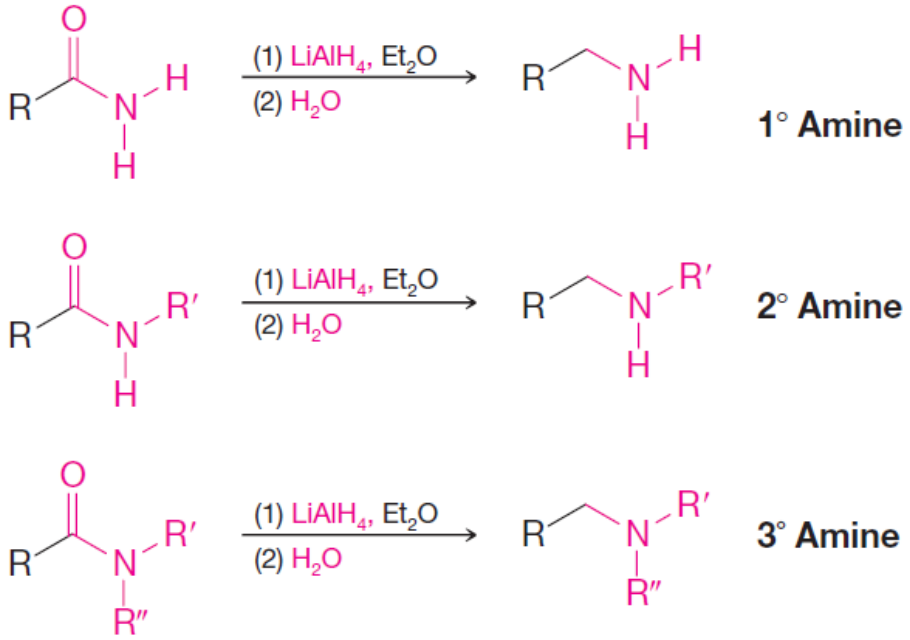
6. Oxidation and Reduction Reactions

6.1. Reduction Reactions

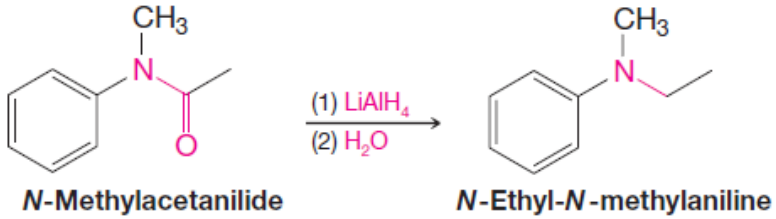
6.1.4. Reduction of Carbonyl Compounds

C) Reduction of Amides

- Reduction of an amide can yield a primary, secondary, or tertiary amine:

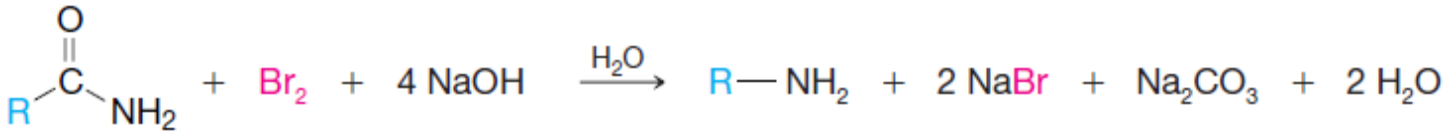


  - Example:



N-Methylacetanilide → *N*-Ethyl-*N*-methylaniline

- Hofmann degradation: Amides with no substituent on the nitrogen react with solutions of bromine or chlorine in sodium hydroxide to yield amines through loss of their carbonyl carbon.



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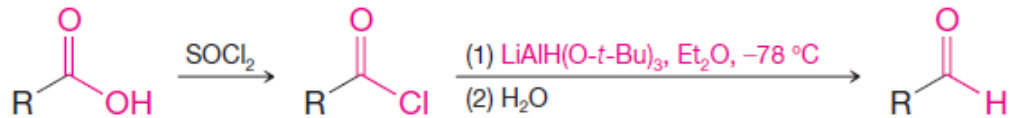
6. Oxidation and Reduction Reactions

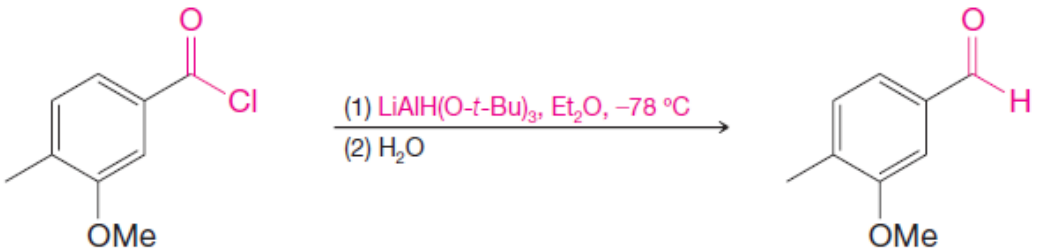
6.1. Reduction Reactions

6.1.4. Reduction of Carbonyl Compounds

D) Reduction of Acyl Chloride

- Acyl chlorides can be reduced to aldehydes by treating them with lithium tri-*tert*-butoxyaluminum hydride, $LiAlH[OC(CH_3)_3]_3$, at −78 °C.





3-Methoxy-4-methylbenzoyl chloride

3-Methoxy-4-methylbenzaldehyde

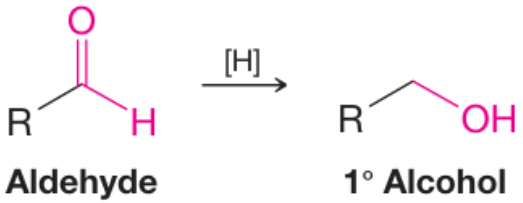
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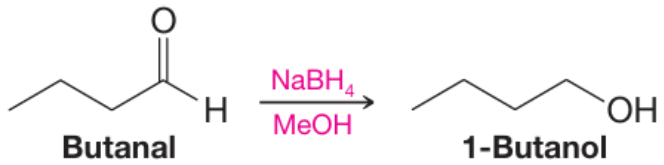
6. Oxidation and Reduction Reactions

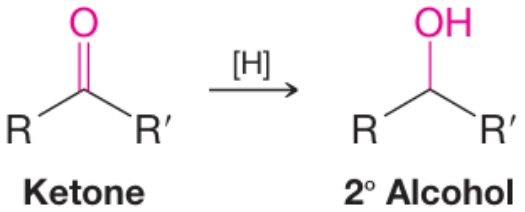
6.1. Reduction Reactions

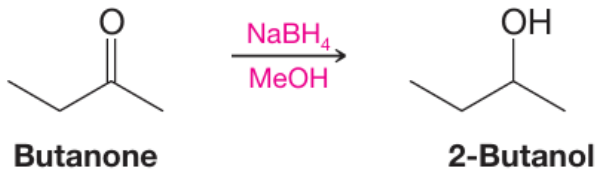
6.1.5. Reduction of Aldehydes and Ketones to Alcohols

Aldehydes and ketones are reduced by mild reducing agent sodium borohydride ($NaBH_4$) to 1° and 2° alcohols, respectively.









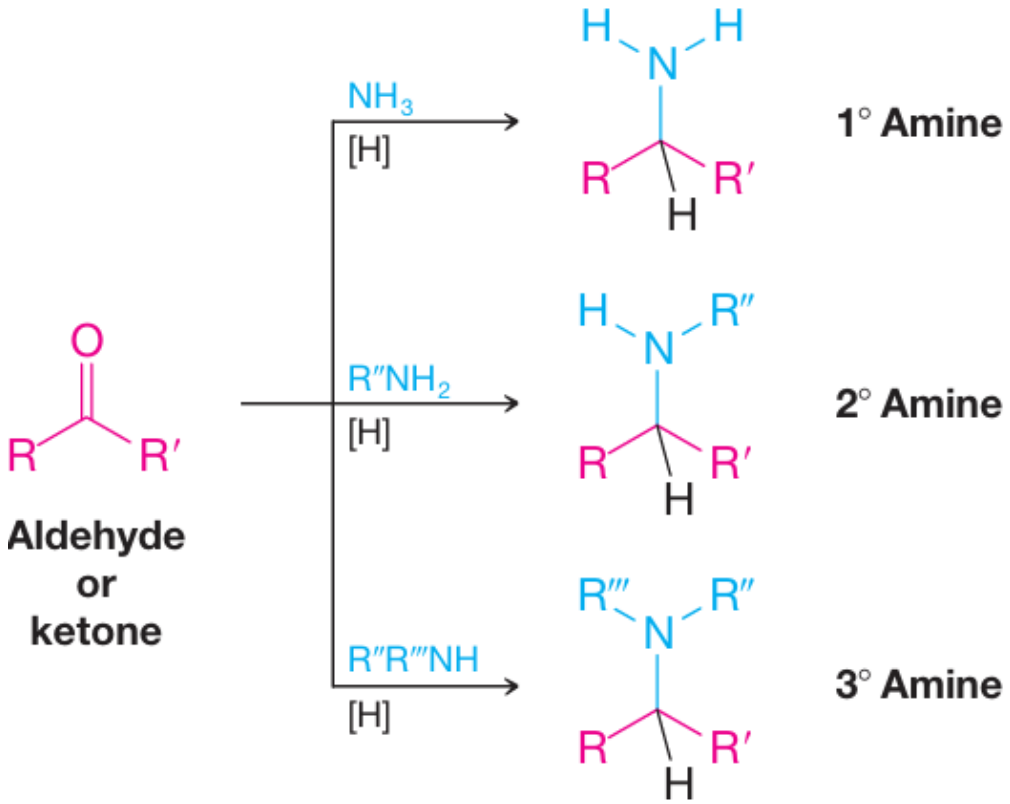
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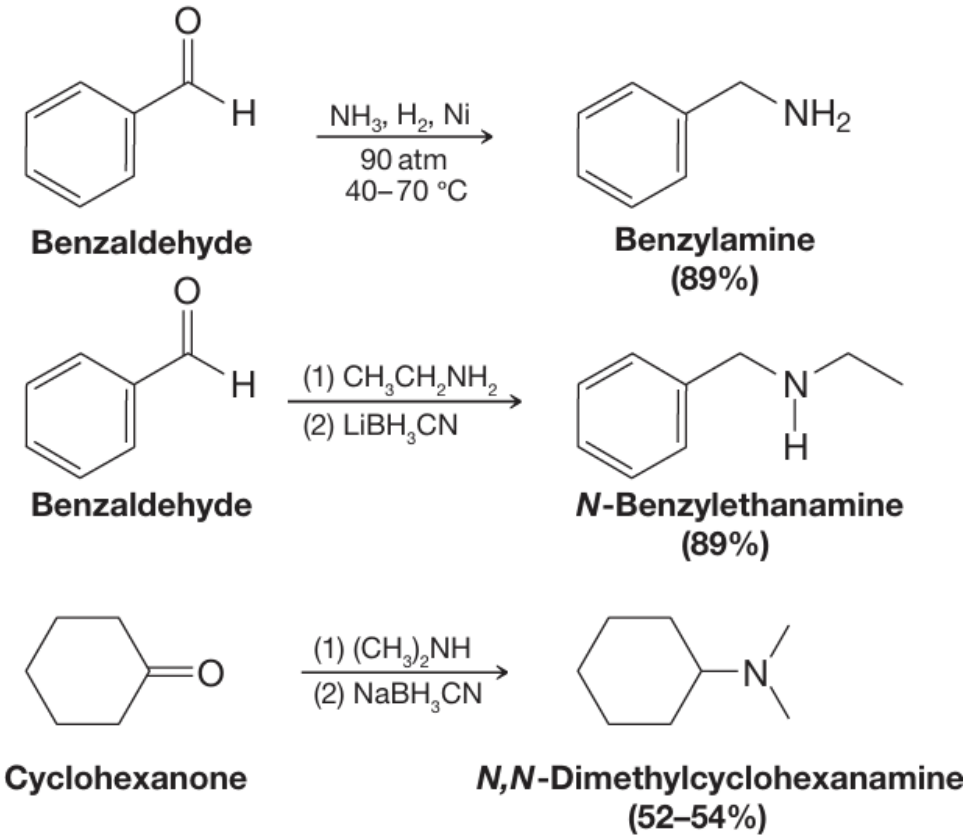
6. Oxidation and Reduction Reactions

6.1. Reduction Reactions

6.1.6. Reductive Amination of Aldehyde or Ketone: Preparation of Primary, Secondary, and Tertiary Amines

- Aldehydes and ketones can be converted to amines through catalytic or chemical reduction in the presence of ammonia or an amine.





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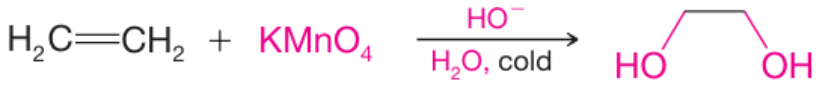
6. Oxidation and Reduction Reactions

6.2. Oxidation Reactions

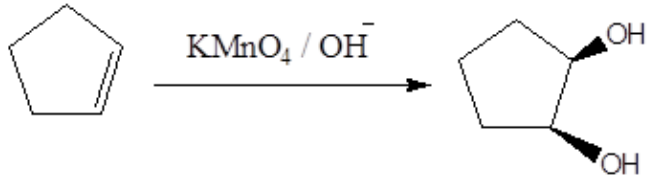
6.2.1. Oxidation of Alkenes and Cycloalkenes

A) Oxidation of Alkenes: *Syn* 1,2-Dihydroxylation 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).*



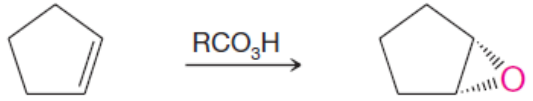
Ethene **1,2-Ethanediol (ethylene glycol)**



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

B) Oxidation of Alkenes: with 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

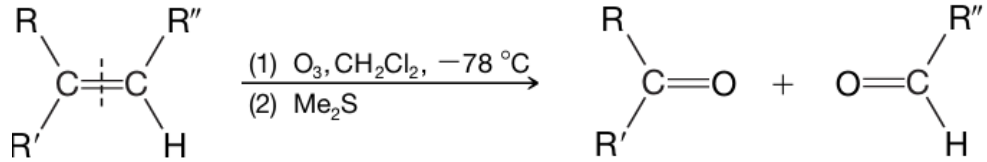
6.2. Oxidation Reactions

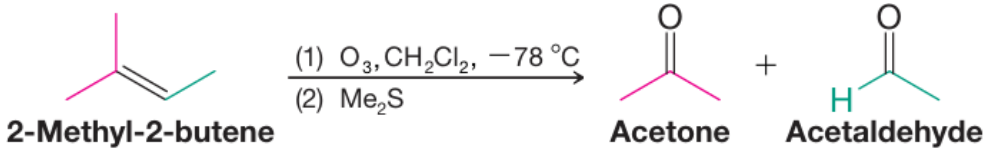
6.2.1. Oxidation of Alkenes and Cycloalkenes

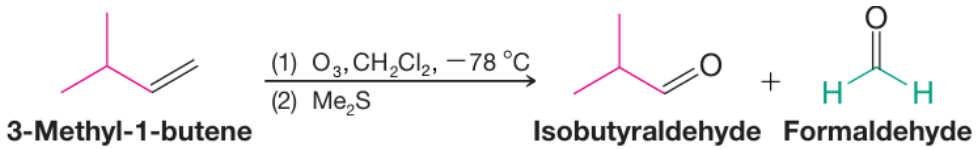
C) Oxidative Cleavage of Alkenes: Cleavage with Ozone (Ozonolysis)

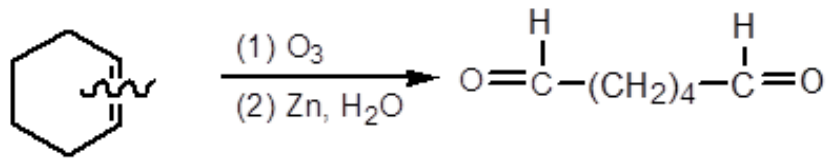
The most useful method for cleaving alkenes is to use ozone (O_3).

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









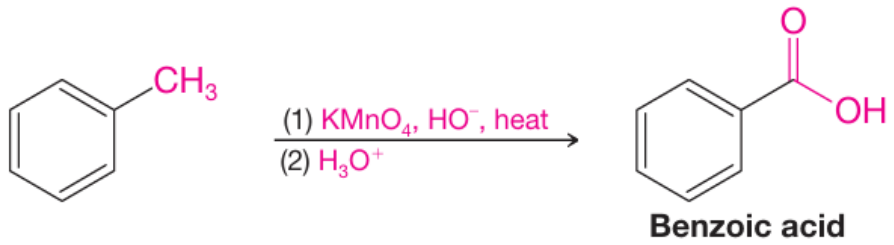
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6. Oxidation and Reduction Reactions

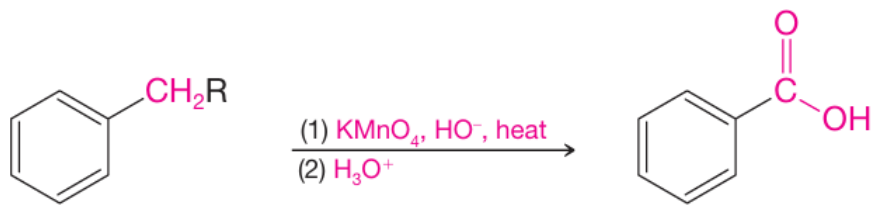
6.2. Oxidation Reactions

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.



Benzoic acid



An alkylbenzene **Benzoic acid**

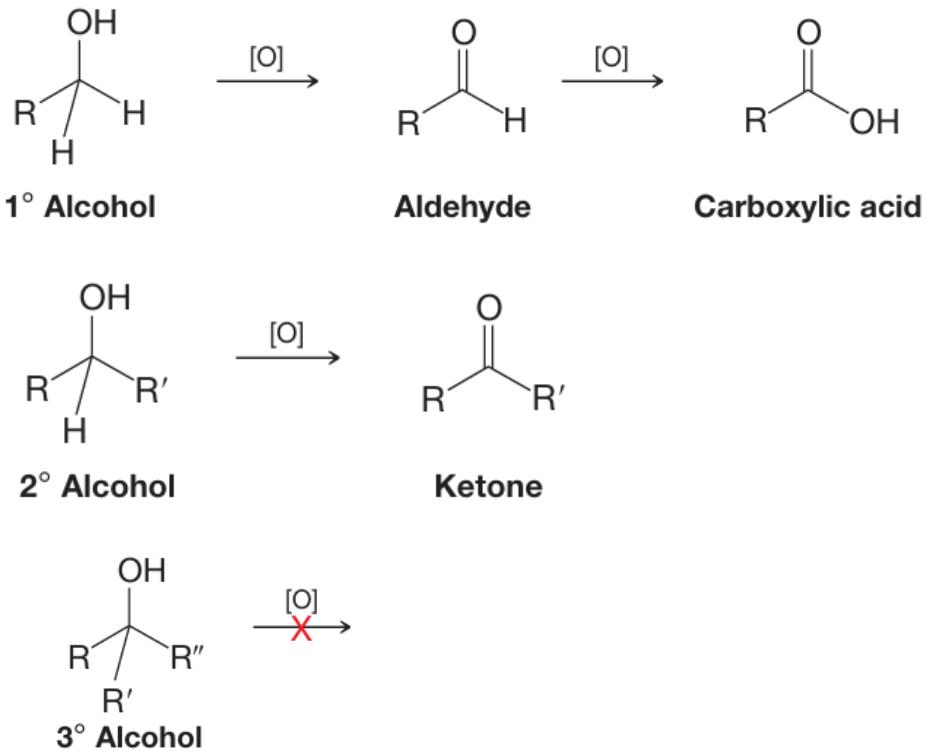
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6. Oxidation and Reduction Reactions

6.2. Oxidation Reactions

6.2.3. Oxidation of Alcohols: Preparation of Aldehydes, Ketones, and Carboxylic Acids

- Primary alcohols can be oxidized to aldehydes, and aldehydes can be oxidized to carboxylic acids.
- Secondary alcohols can be oxidized to ketones.
- Tertiary alcohols cannot be oxidized to carbonyl compounds.



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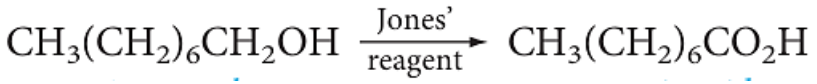
6. Oxidation and Reduction Reactions

6.2. Oxidation Reactions

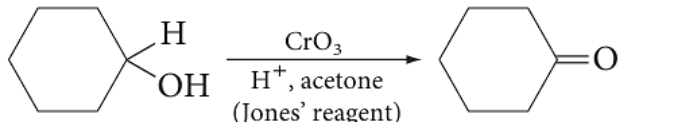
6.2.3. Oxidation of Alcohols: Preparation of Aldehydes, Ketones, and Carboxylic Acids

A) Oxidation by Chromic acid (H_2CrO_4)

- Oxidations involving chromium (VI) reagents such as Jones reagent H_2CrO_4 (CrO_3 in H_2SO_4).
- Primary alcohols are oxidized to carboxylic acids.
- Secondary alcohols are oxidized to ketones.



1-Octanol **Octanoic acid**



Cyclohexanol **Cyclohexanone**

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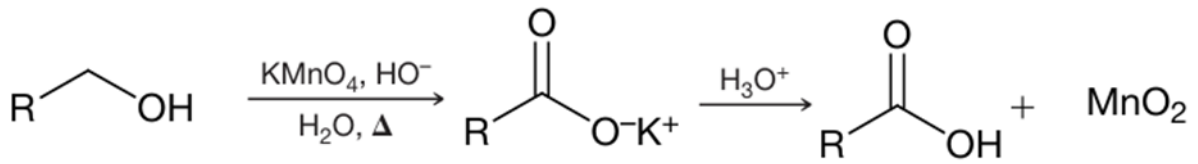
6. Oxidation and Reduction Reactions

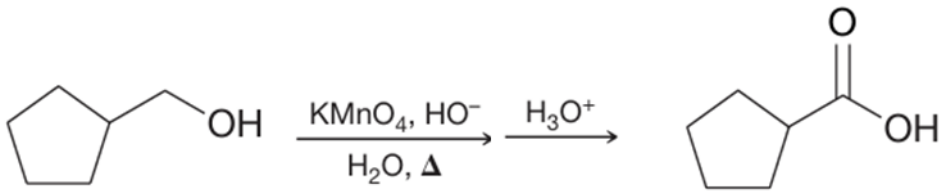
6.2. Oxidation Reactions

6.2.3. Oxidation of Alcohols: Preparation of Aldehydes, Ketones, and Carboxylic Acids

B) Oxidation by Potassium Permanganate ($KMnO_4$)

- Primary alcohols and aldehydes can be oxidized by potassium permanganate ($KMnO_4$) to the corresponding carboxylic acids.
- Secondary alcohols can be oxidized to ketones.
- The reaction is usually carried out in basic aqueous solution.





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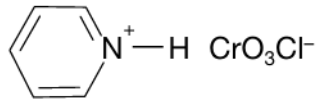
6. Oxidation and Reduction Reactions

6.2. Oxidation Reactions

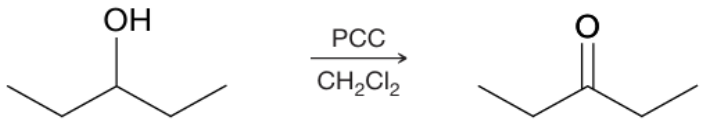
6.2.3. Oxidation of Alcohols: Preparation of Aldehydes, Ketones, and Carboxylic Acids

C) Oxidation by Pyridinium Chlorochromate (PCC)

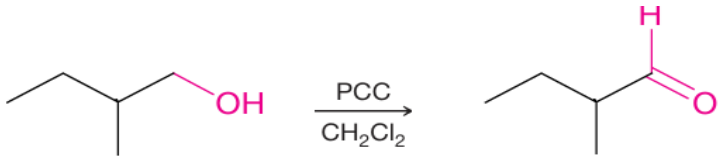
PCC (moderate oxidizing agent) is soluble in dichloromethane and can be used under conditions that exclude water, allowing for the selective oxidation of primary alcohols to aldehydes and secondary alcohols to ketones.



Pyridinium chlorochromate (PCC)



3-Pentanol **3-Pentanone**

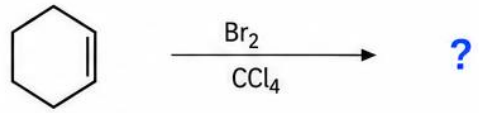


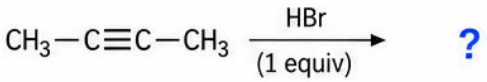
2-Methylbutanol **2-Methylbutanal**

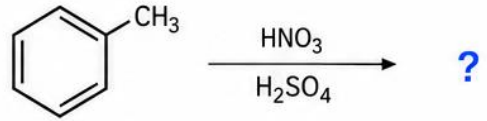
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7. Practice Problems

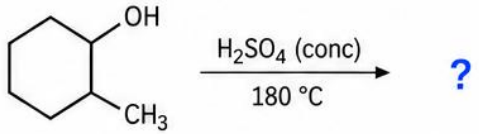
1 Complete the following reactions by giving the organic product(s).

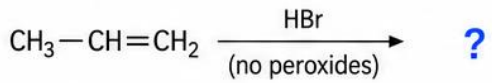
a) 

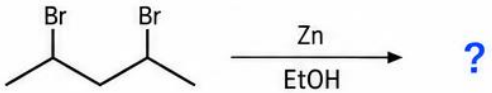
b) 

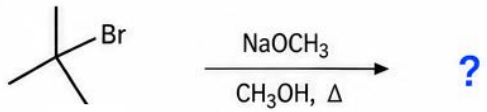
c) 

d) 

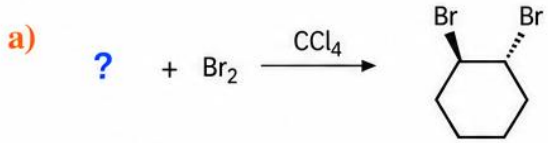
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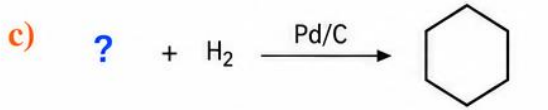
g) 

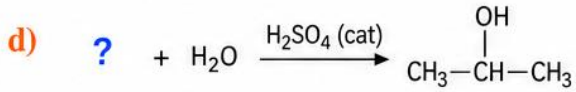
h) 

2 Complete the following reactions by giving the missing reactant(s).

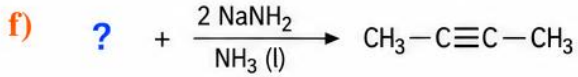
a) 

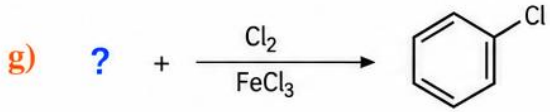
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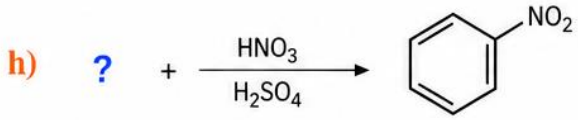
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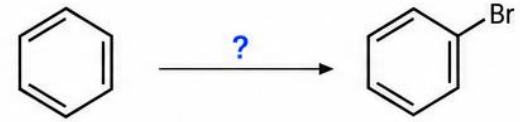
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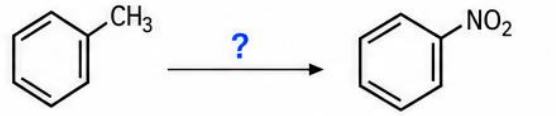
3 Complete the following reactions by giving the required reagent(s) or conditions.

a) 

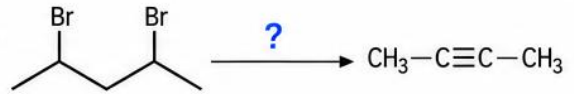
b) 

c) 

d) 

e) 

f) 

g) 

h) 