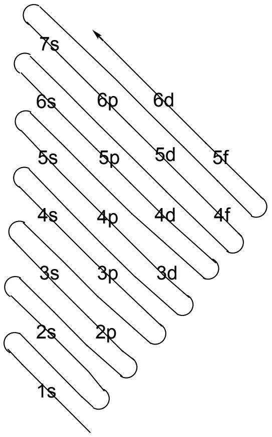
Organic Chemistry, 1 of 6

01: General Chemistry Review

- **Electron configuration**: Using the number of electrons, follow the arrow from the bottom.



s = 2

p = 6

d = 10

f = 14

- **Hybridization:** Determined by sigma bonds and nonbonding electron pairs around one atom.
  - 2 sigma bonds and 0 nonbonding electron pairs = sp, linear, 180°.
  - 3 sigma bonds and 0 nonbonding electron pairs = sp^2, trigonal planar, 120°.
  - 4 sigma bonds and 0 nonbonding electron pairs = sp^3, tetrahedral, 109.5°.
  - 3 sigma bonds and 1 nonbonding electron pairs = sp^3, trigonal pyramidal, 107°.
  - 2 sigma bonds and 2 nonbonding electron pairs = sp^3, bent, 105°.

02: Introduction to Organic Chemistry

- **Alkane:** Contains a carbon-carbon single bond.
- **Alkene:** Contains a carbon-carbon double bond.
- **Alkyne:** Contains a carbon-carbon triple bond.
- **Aromatic:** Contains a six-membered ring, with alternating double and single bonds.
- **Alkyl Halide:** Contains an alkyl and a halogen, RX.
- **Alcohol**: Contains a ROH.
- **Ether**: Contains a ROR.
- **Thiol**: Contains RSH.
- **Sulfide**: Contains a RSR.
- **Aldehyde**: Contains a H bonded to a C on one side of a C=O and a R or H bonded to a C on the other side.
- **Ketone**: Contains 2 R groups attached to the C on either side of a C=O.
- **Acid Halide:** Contains a C=O, with an X attached to the C on one side and an R or H attached on the other side.
- **Carboxylic Acid**: Contains a COOH, with an R or H attached to the C of the COOH.
- **Ester**: Contains a COO, with an R attached to the O and a H or R attached to the C.
- **Anhydride**: Contains an OCOCO, with an R or H attached on either side of the O.
- **Amine:** Contains an N, with R and / or H attached to N.
- **Amide**: Contains a N attached to the C of a C=O, with H or R on the other positions.
- **Nitrile**: Contains a carbon nitrogen triple bond.
- **Arrhenius Acid**: Dissociates to give H_3O^+.
- **Arrhenius Base:** Dissociates to give ^-OH.
- **Bronsted-Lowry Acid:** Donates an H^+.
- **Bronsted-Lowry Base:** Accepts an H^+.
- **Lewis Acid**: Accepts electron pairs to form new bonds.
- **Lewis Base**: Donates electron pairs to form new bonds.

03: Organic Nomenclature I

IUPAC for Alkanes, Alkenes, Alkynes, and Alkyl Halides

1. The longest continuous carbon chain is the parent compound.
2. Use "ane" for alkane, "ene" for alkene, and "yne" for alkyne.
3. Circle the carbon chain to aid in identifying the parent compound.
4. Number the carbon chain in alkenes and alkynes so that the multiple bonds have the lowest number, then number the substituents.
5. For alkanes, number from whichever end that gives the substituents the lowest possible combination of numbers.
6. Give the location of each substituent with a number.
7. Use numerical prefixes for more than one identical group.
8. Use "yl" on alkyl prefixes and "o" on halogen prefixes.
9. Alphabetize the groups, ignoring all numerical prefixes.
10. For alkenes, use cis if same groups are on the same side or trans if the same groups are on different sides.

Common for Alkanes and Alkyl Halides

- **n Prefix:** The structure is a straight chain, with the halogen on the end.
- **iso Prefix**: The structure contains two methyls attached to CH, with functional group on the other end.
- **sec Prefix**: The halogen is attached to secondary carbon; use only if total number of carbons is four.
- **tert Prefix**: The halogen is attached to tertiary carbon; use only if total number of carbons is four or five.
- **neo Prefix**: The halogen is attached to a carbon and that carbon is attached to tert-butyl group.

04: Organic Nomenclature II

IUPAC Nomenclature Rules for Alcohols, Ethers, Aldehydes, Ketones, Carboxylic Acids, and Amines

1. The longest continuous carbon chain is the parent compound.
2. Circle the carbon chain.
3. Number the chain so that the C-O bond has the lowest possible number.
4. From the alkyl prefixes, use "anol" for alcohols and "ane" for ethers.
5. For ethers, the longest carbon chain is the parent compound and use "oxy" for the substituent group.
6. Give the location of the C-O bond with a number.
7. From the alkyl prefixes, use "anal" for aldehydes, and "anone" for ketones.
8. From the alkyl prefixes, use "anoic acid" for carboxylic acids and "anamine" for amines.
9. For amines, give the location of the attachment of the N to the parent amine and number the groups attached to N.
10. Give the location of each substituent with a number.
11. Use numerical prefixes if more than one identical group is present
12. Alphabetize the groups, ignoring all prefixes.

IUPAC Nomenclature for Carboxylic Acids and Derivatives

1. An ester is named as an alkyl alkanoate.
2. An anhydride is named as an alkanoic alkanoic anhydride.
3. An acid halide is named as alkanoyl halide.
4. An amide is named as an alkanamide. Any group attached to the N is numbered as "N."

Common Nomenclature Rules for Alcohols, Ethers, Ketones, and Amines

1. Use common prefixes, if needed.
2. An alcohol is named as an alkyl alcohol.
3. An ether is named as an alkyl alkyl ether.
4. A ketone is named as an alkyl alkyl ketone.
5. An amine is named with the alkyl groups, then "amine."

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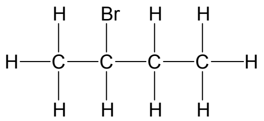
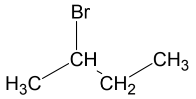
05: Drawing Organic Structures

Types of Structures

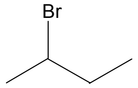
- **Lewis Structure:** All individual bonds are shown.



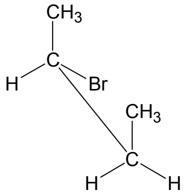
- **Condensed Structure:** Atoms are bonded to a central atom are listed after the atom.



- **Skeletal Structure:** Carbon atoms are assumed to be where two lines meet or at the end of the line. Hydrogens are not shown.



- **Sawhorse Structure:** The drawing is looking down a carbon-carbon bond.



06: Alkanes and Cycloalkanes

Reactions of Alkanes

- Combustion converts alkanes to carbon dioxide and water. The formula is based on n, the number of carbons.

$$C_nH_{(2n+2)} + \frac{3n+1}{2} O_2 \longrightarrow nCO_2 + (n+1)\,H_2O$$

- Cracking of hydrocarbons at high temperatures yield a mixture of smaller alkanes and alkenes.

$$\text{large alkane} \xrightarrow[\text{catalyst}]{\text{heat}} \text{smaller alkanes + alkenes}$$

- Halogenation of alkanes occurs with halogen in the presence of heat or light and through a radical mechanism.

$$R\text{-}H + X_2 \xrightarrow[\text{light}]{\text{heat or}} R\text{-}X + H\text{-}X$$

  - In initiation, radicals are formed.

$$Cl_2 \xrightarrow[\text{light}]{\text{heat or}} 2\ :\!\ddot{\underset{..}{Cl}}\cdot$$

  - In propagation, radicals are consumed and radicals are formed.

$$CH_3CH_3 + :\!\ddot{\underset{..}{Cl}}\cdot \longrightarrow CH_3CH_2\cdot + HCl$$

$$CH_3CH_2\cdot + Cl_2 \longrightarrow CH_3CH_2Cl + :\!\ddot{\underset{..}{Cl}}\cdot$$

  - In termination, the radical are consumed.

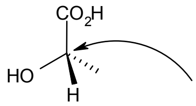
$$CH_3CH_2\cdot + CH_3CH_2\cdot \longrightarrow CH_3CH_2CH_2CH_3$$

$$:\!\ddot{\underset{..}{Cl}}\cdot + :\!\ddot{\underset{..}{Cl}}\cdot \longrightarrow Cl_2$$

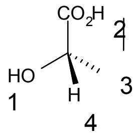
$$CH_3CH_2\cdot + :\!\ddot{\underset{..}{Cl}}\cdot \longrightarrow CH_3CH_2Cl$$

07: Stereochemistry

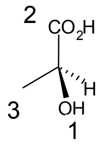
Assigning Configuration for a Chiral Center



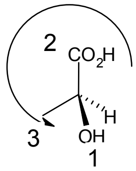
1. Find the chiral center
4 different groups on carbon



2. Assign priority to the groups
OH>CO$_2$H>CH$_3$>H



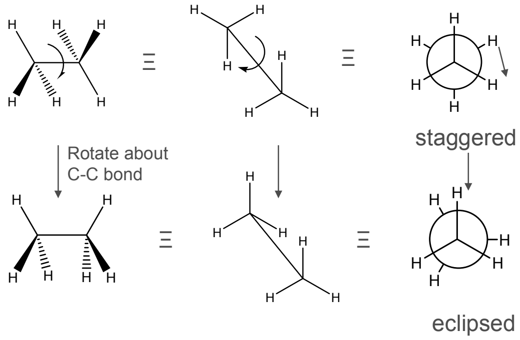
3. Orient lowest priority in back
H in this case



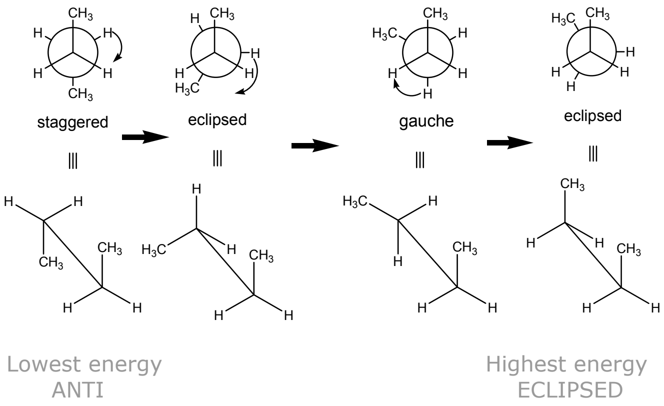
4. Trace from high to low
Clockwise, assign **R**
Counterclockwise, **S**

08: Conformational Analysis

Conformations for Ethane



Conformations for Butane



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09: Alkyl Halides: Nucleophilic Substitution and Elimination

Substitution Unimolecular Unimolecular, SN1

- Slow step = bromide takes the electron pair and departs as leaving group.
- Carbocation is formed.
- Faster step = rearrangement, if present.
- Fast step = weak nucleophile attacks the carbocation from both sides.
- Nucleophile abstracts the extra proton from the product and the electron pairs move from O-H bond to O.

Substitution Bimolecular, SN2

- Nucleophile attacks on the carbon, but on the opposite side of the halogen.
- Bromide takes its electron pair and leaves.
- In the intermediate, the nucleophile and leaving group are drawn 180° apart.

Elimination Unimolecular, E1

- Bromide takes the electron pair and departs as the leaving group, a carbocation is formed.
- Slow step = formation of carbocation.
- Weak base abstracts hydrogen on carbon next to carbocation, then electron pair goes from C-H bond to C-C bond to form double bond.

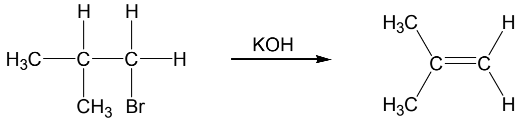
Elimination Bimolecular, E2

- Strong nucleophile abstracts proton from carbon adjacent to carbon with X, but on opposite side from X = anti elimination.
- C-H electrons go to C-C bond to form double bond.
- C-Br bond electrons go to Br.
- Br leaves with electron pair.

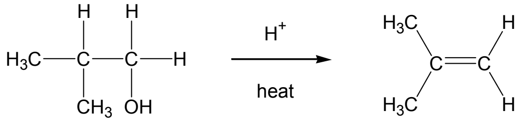
10: Alkenes, Alkynes, and Dienes

Synthesis of Alkenes

- Dehydrohalogenation of Alkyl Halides

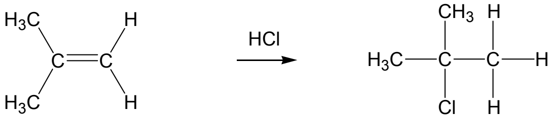


- Dehydration of Alcohols

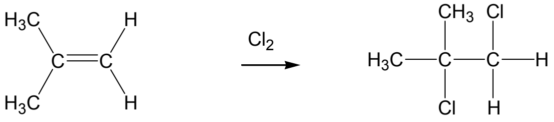


Reactions of Alkenes

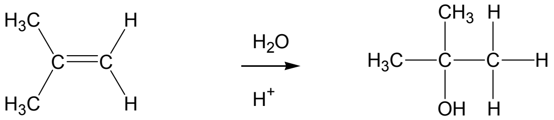
- Addition of hydrogen halide. Product = alkyl halides.



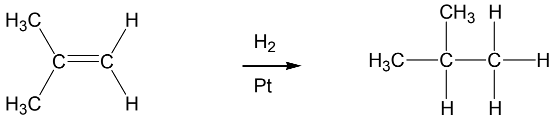
- Halogenation. Product = dihaloalkanes.



- Hydration. Product = alcohols.



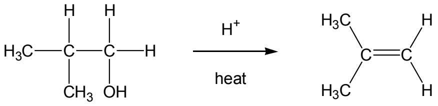
- Hydrogenation. Product = alkanes.



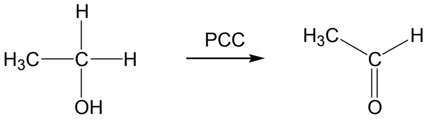
11: Alcohols and Ethers

Reactions of Alcohols

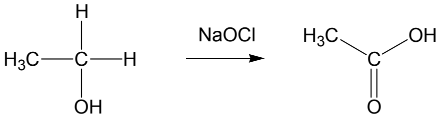
- Reaction with metal. Product = alkoxide.
- Reaction with HX, PCl_3, or PCl_5. Product = alkyl halide.
- Dehydration.



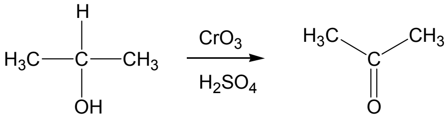
- Oxidation of 0° and 1° alcohols with PCC.



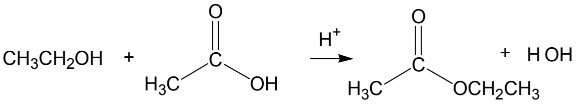
- Oxidation of 0° and 1° alcohols with $Na_2Cr_2O_7$, $K_2Cr_2O_7$, $KMnO_4$, NaOCl, HNO_3, or CrO_3.



- Oxidation of 2° alcohols with $Na_2Cr_2O_7$, $K_2Cr_2O_7$, $KMnO_4$, NaOCl, HNO_3, CrO_3, or PCC.



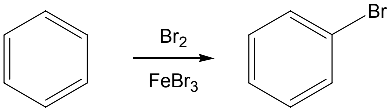
- Esterification.



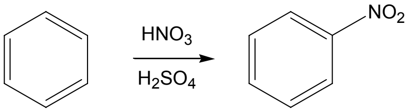
12: Aromatic Compounds, Aromaticity and Reactions

Reactions of Benzene

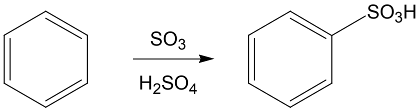
- Reaction with Br_2, $FeBr_3$; Cl_2, $AlCl_3$; or I_2, HNO_3. Product = halobenzenes.



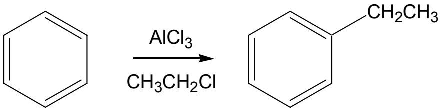
- Reaction with HNO_3 + H_2SO_4. Product = nitrobenzenes.



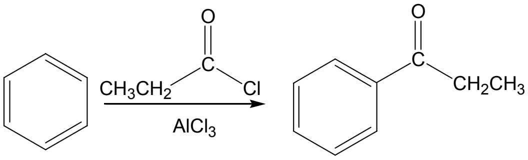
- Reaction with with SO_3 + H_2SO_4. Product = benzenesulfonic acids.



- Reaction with $AlCl_3$ and RX. Product = alkylbenzenes.



- Reaction with $AlCl_3$ and an acid halide. Product = ketones.



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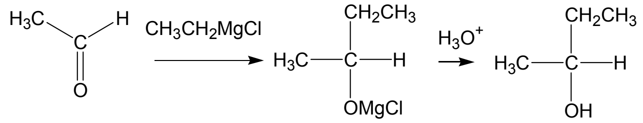
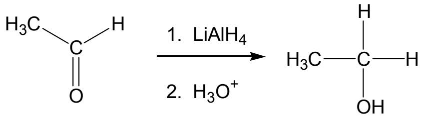
13: Aldehydes and Ketones

Reactions of Aldehydes and Ketones

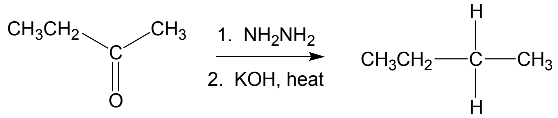
- With RLi or RMgX, followed by acid. Product = alcohols.



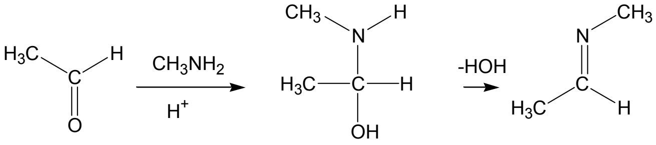
- With H_2 and Ni; $LiAlH_4$; or $NaBH_4$. Product = alcohols.



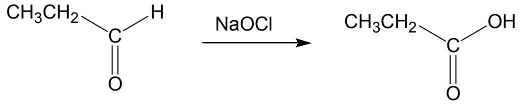
- With Zn(Hg) + HCl or NH_2NH_2 + KOH. Product = alkanes.



- With ammonia derivatives and acid. Product = imines.

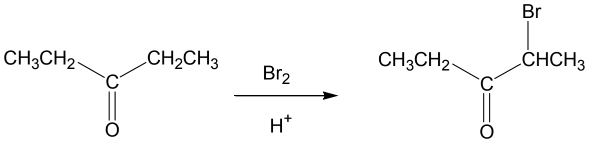


- Aldehydes with $Na_2Cr_2O_7$, $K_2Cr_2O_7$, $KMnO_4$, NaOCl, HNO_3, or CrO_3. Product = carboxylic acids.

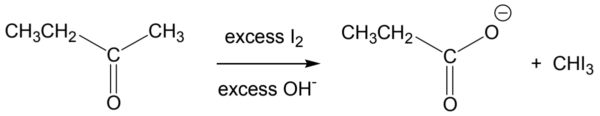


14: Enols and Enolates

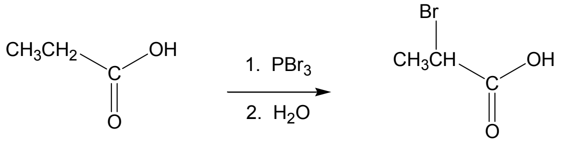
- Ketones or aldehydes + X_2 + H^+ or ketones or aldehydes + X_2 + OH^-. Product = α-halo ketones or aldehydes.



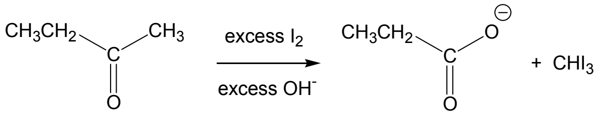
- Haloform reaction: Methyl ketones + excess OH^- + excess X_2. Product = carboxylate anions + haloforms.



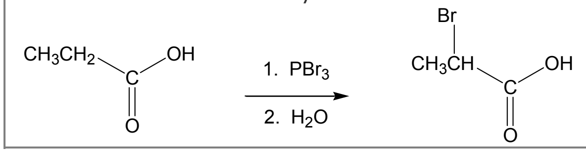
- Hell-Volhard-Zelinsky reaction: Carboxylic acids + PX_3. Product = α-halo carboxylic acids.



- Haloform reaction: Methyl ketones + excess OH^- + excess X_2. Product = carboxylate anions + haloforms.



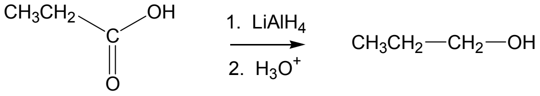
- Hell-Volhard-Zelinsky reaction: Carboxylic acids + PX_3. Product = α-halo carboxylic acids.



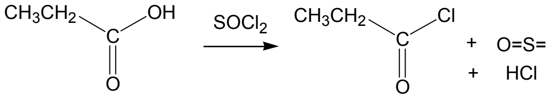
15: Carboxylic Acids and Derivatives

Reactions of Carboxylic Acids

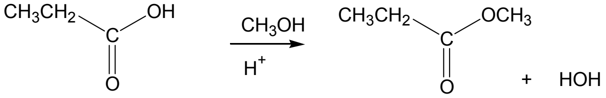
- Carboxylic acids + $LiAlH_4$, then H_3O^+. Product = alcohols.



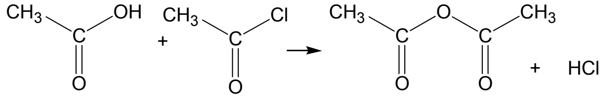
- Carboxylic acids + $SOCl_2$. Product = acid halides.



- Carboxylic acids + ROH + H^+. Product = esters.

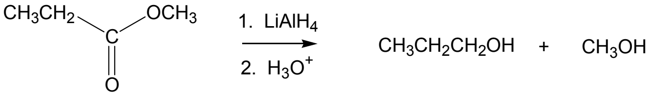


- Carboxylic acids + acid halides. Product = anhydrides.

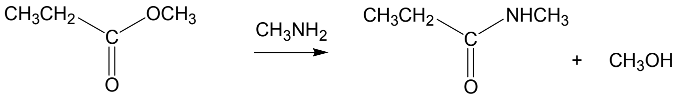


Reactions of Esters

- Esters + $LiAlH_4$, then H_3O^+. Products = alcohols.



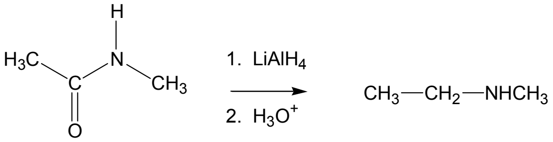
- Esters + amines. Products = amides + alcohols.



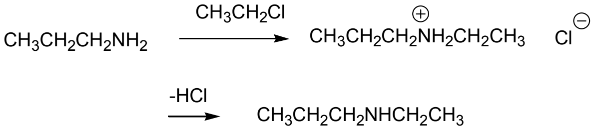
16: Amines

Synthesis of Amines

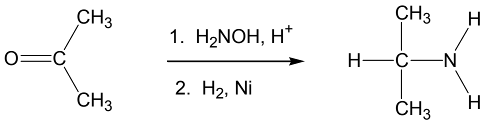
- Amides + $LiAlH_4$, then H_3O^+. Product = amines.



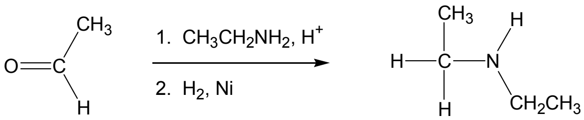
- Alkyl halides + amines, then loss of HX. Product = amines.



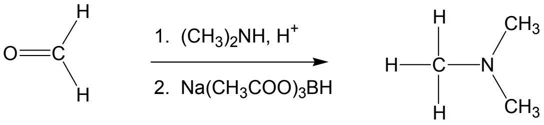
- Aldehydes or ketones + (1) H_2NOH + H^+, (2) H_2 + Ni; **or** $LiAlH_4$, then H_3O^+; **or** Zn + HCl. Product = 1° amines.



- Aldehydes or ketones + (1) 1° amines + H^+, (2) H_2 + Ni; **or** $LiAlH_4$, then H_3O^+. Product = 2° amines.



- Aldehydes or ketones + (1) 2° amines + H^+, (2) $Na(CH_3COO)_3BH$. Product = 3° amines.



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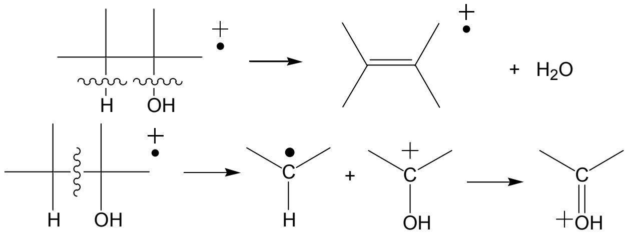
17: IR and Mass Spectrometry

IR Problem Solving

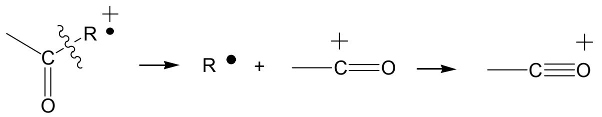
- Calculate the unsaturation number and give interpretation.
- Using the formula and interpretation of the unsaturation number, predict possible functional groups present.
- Look for frequencies for the functional groups in the table.
- Once all of the frequencies have been identified, draw the structure.

Cleavage Reactions in a Mass Spectrum

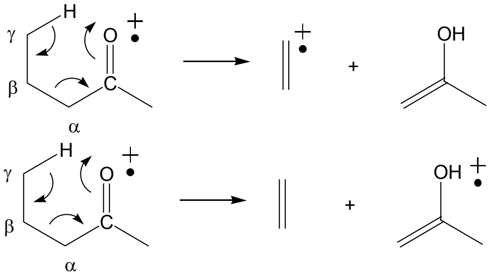
- Alcohols dehydrate to yield alkenes and undergo α cleavage of the C-C bond to form cations.



- Amines undergo N-C cleavage and α cleavage of the C-C bond to form iminium ions.
- Ethers undergo O-C cleavage and α cleavage of the C-C bond to form cations.
- Aldehydes and ketones undergo C-C cleavage to form acylium ions.



- Carbonyl compounds undergo McLafferty rearrangement to form alkenes and enols.



18: NMR and Problem Solving

^1H NMR Problem Solving

1. Calculate unsaturation number and give interpretation.
2. List the chemical shifts.
3. Compare to Proton Magnetic Resonance tables.
4. List splitting.
5. Measure vertical distance of integration with ruler.
6. Add up integrations.
7. Determine multiplication factor by dividing H by sum of integrations.
8. Multiply each integration by multiplication factor to get H per signal.
9. For interpretation, use calculated H that are adjacent to splitting minus 1.
10. Put the structure together, following the formula.

^{13}C NMR Problem Solving

1. Calculate unsaturation number and give interpretation.
2. List the chemical shifts.
3. List the splitting.
4. Give the interpretation of the splitting.
5. Give the interpretation by chemical shift.
6. Put the structure together.

19: Understanding Organic Reactions

Reactions

- Alkyl Halides
- Alkenes
- Alkynes
- Benzene
- Amines
- Alcohols
- Aldehydes and Ketones
- Carboxylic Acids
- Acid Halides
- Esters
- Anhydrides
- Amides

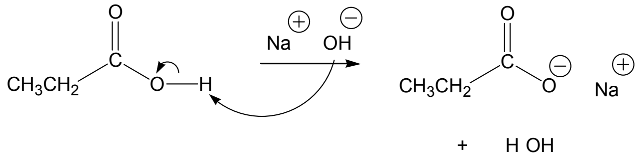
20: Mechanisms of Organic Reactions

Addition to Carbonyl Compounds

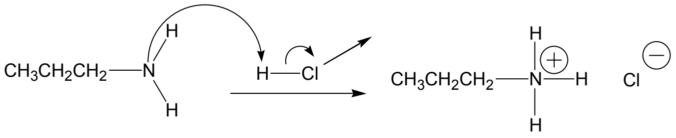
- Reaction of Grignard reagents with aldehydes and ketones.
- Reaction of aldehydes and ketones with primary amines.

Mechanisms of Acid-Base Reactions

- Reaction of carboxylic acids with sodium hydroxide.

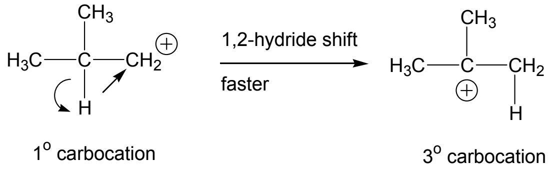


- Reaction of amines with hydrogen chloride.

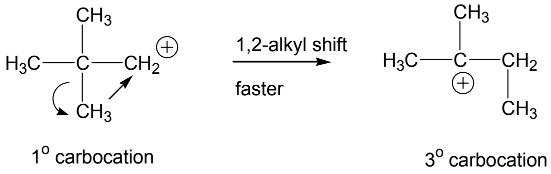


Carbocation Rearrangements

- 1,2-Hydride shift.

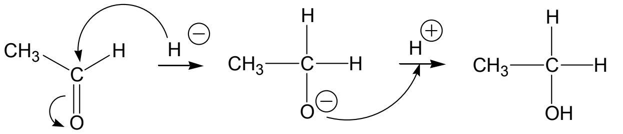


- 1,2-Alkyl shift.



Anion Mechanisms

- Mechanism of carbonyl compounds with LDA.
- Mechanism for addition of hydride ion.



Radical Mechanisms

- Halogenation of alkanes.

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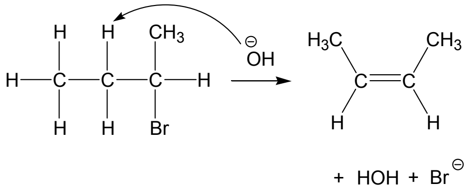
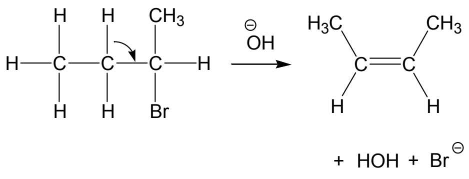
21: Writing Reaction Mechanisms

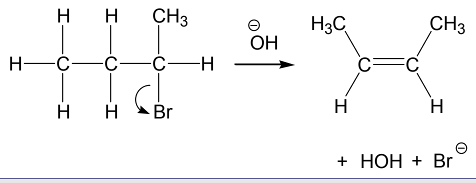
- Unshared pair to shared pair.



- Shared pair to shared pair.

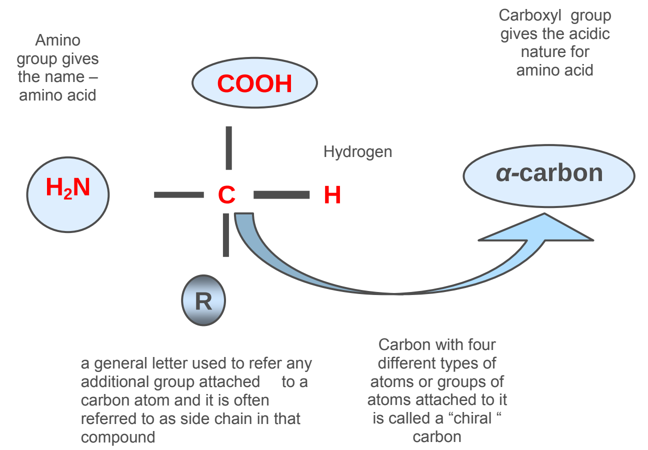


- Shared pair to unshared pair.



22: Amino Acids, Peptides, and Proteins

Structure of Amino Acids



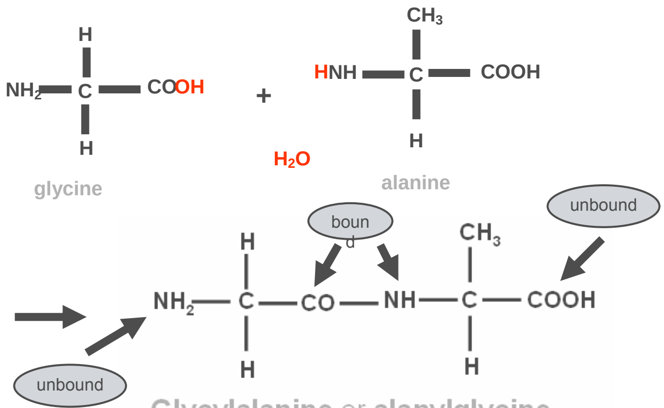
Amino group gives the name – amino acid

Carboxyl group gives the acidic nature for amino acid

a general letter used to refer any additional group attached to a carbon atom and it is often referred to as side chain in that compound

Carbon with four different types of atoms or groups of atoms attached to it is called a “chiral “ carbon

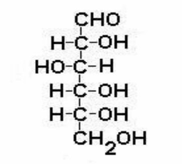
Peptide Bonds



Glycylalanine or alanylglycine

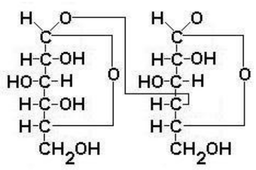
23: Carbohydrates

Monosaccharides



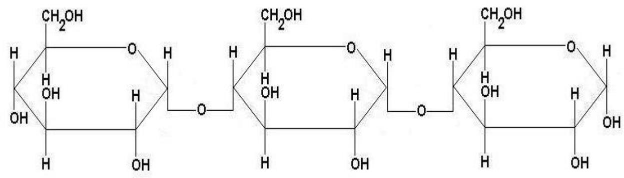
Glucose

Disaccharides



Maltose

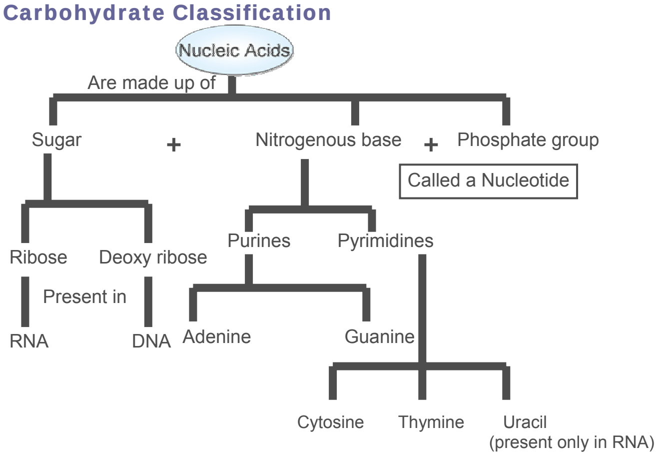
Oligosaccharides



Maltotriose

24: Nucleic Acids

Carbohydrate Classification



Nucleic Acids

Are made up of

Sugar + Nitrogenous base + Phosphate group

Called a Nucleotide

Sugar: Ribose, Deoxy ribose

Present in: RNA, DNA

Nitrogenous base: Purines, Pyrimidines

Purines: Adenine, Guanine

Pyrimidines: Cytosine, Thymine, Uracil (present only in RNA)

Types of Nucleotides

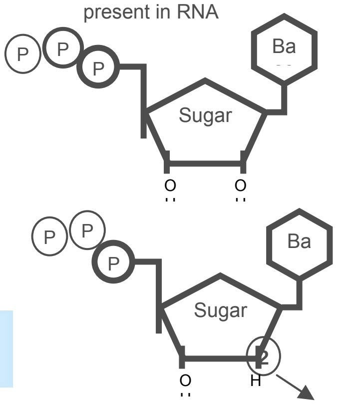
There are two types of nucleotides present in nucleic acids. They are deoxy- ribonucleotide & ribonucleotide

Nucleotide monophosphate e.g. AMP,GMP

Nucleotide di phosphate e.g. ADP,GDP

Nucleotide triphosphate e.g. ATP,GTP

Ribonucleotide, present in RNA



Deoxyribonucleotide, present in DNA