Organic Chemistry

Ms. Peace

Lesson 1

10.1 Fundamentals of Organic Chemistry

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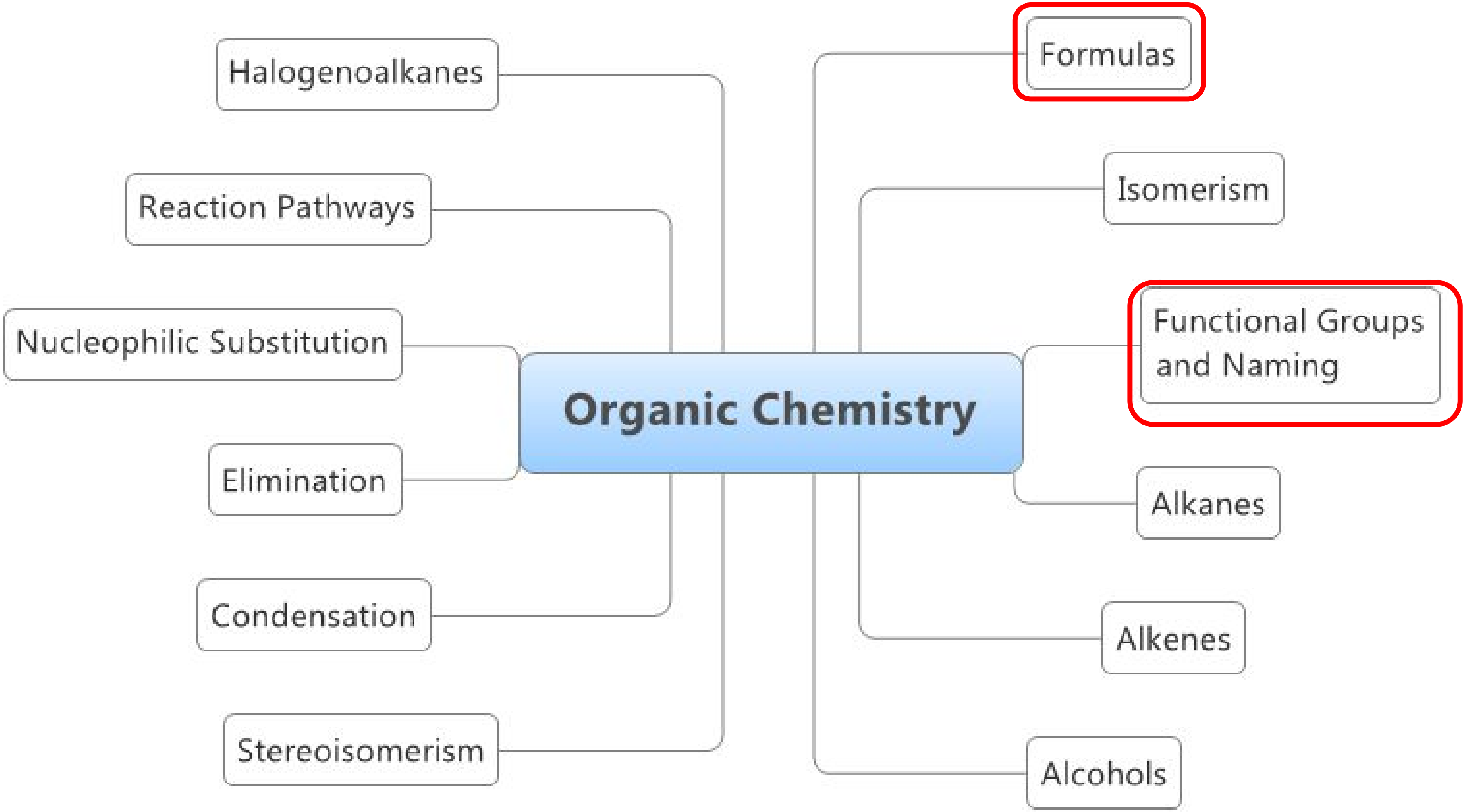

Organic Chemistry

Halogenoalkanes

Reaction Pathways

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Elimination

Condensation

Stereoisomerism

Formulas

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Functional Groups and Naming

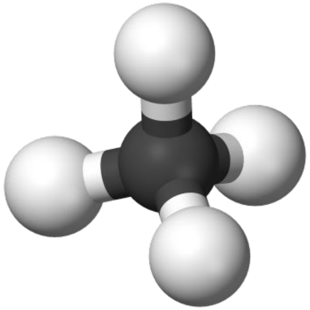
Alkanes

Alkenes

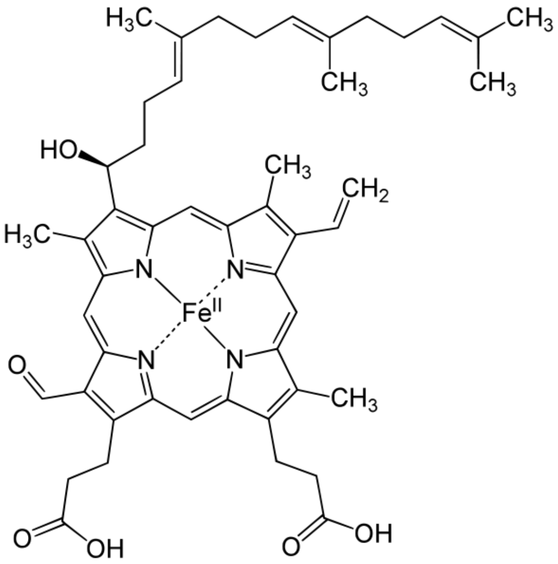
Alcohols

Organic Chemistry

- Organic chemistry is the chemistry of carbon containing compounds.
- From the very simple: methane



- To the very complex: Haem B



Main

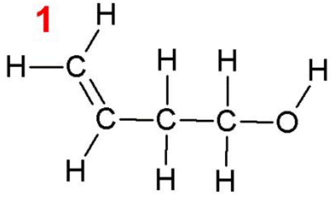
Types of Formula

- Empirical Formula C_4H_8O C_4H_8O

- Molecular Formula C_4H_8O C_4H_8O

- Full Structural Formula
  - Displayed formula

1



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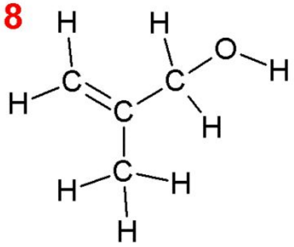

- Condensed Structural Formula
  - Note the '=' used for the C=C double bond

CH_2=$CHCH_2CH_2OH$ CH_2=$C(CH_3)CH_2OH$

- Skeletal formula
  - Not required but v. useful

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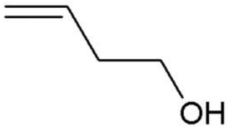

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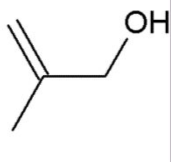

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Empirical and Molecular Formulas

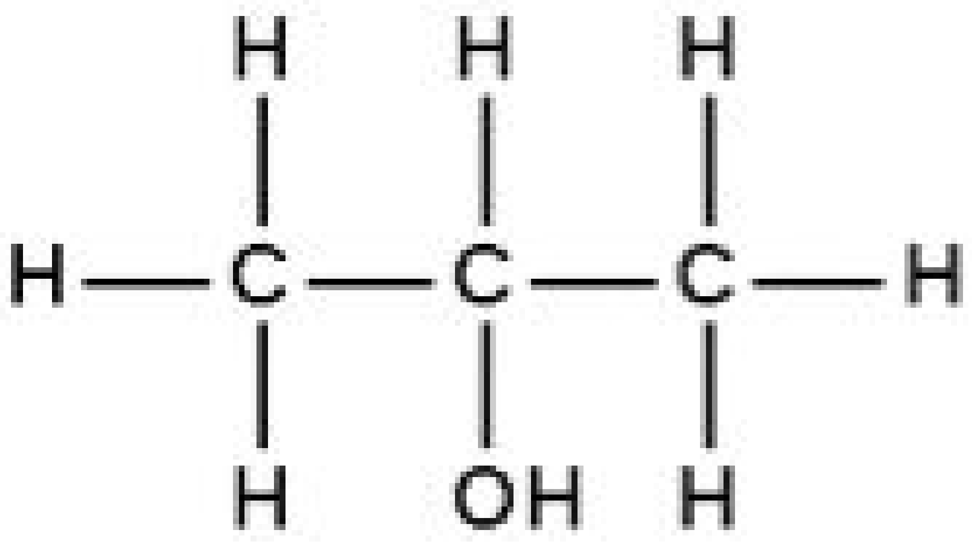
- Empirical formulas represent the simplest ratio of atoms present in a molecule
  - CH_2O

- Molecular formulas describe the actual number of atoms present in the molecule
  - $C_6H_{12}O_6$

- Both of these offer little information about the possible structure of complex molecules

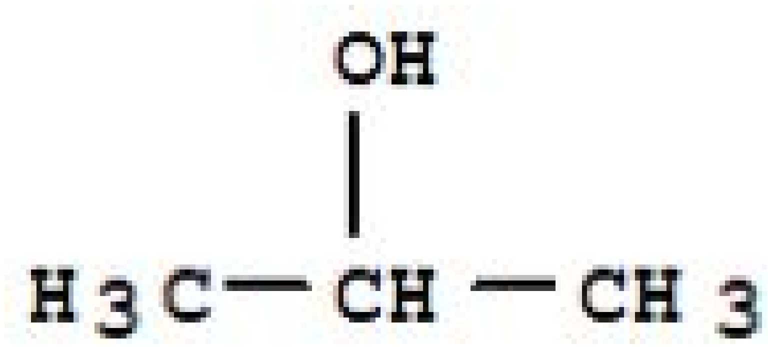
Structural Formulas

- Full structural formula – graphic formula showing every bond and atom. Usually 90° and 180° angles are used to show the bonds because this is the clearest representation on a 2-dimensional page, although it is not the true geometry of the molecule. *(MUST DRAW H's!)*



Condensed Structural Formulas

- Condensed structural formula – often omits bonds where they can be assumed, and groups atoms together. It contains the minimum information needed to describe the molecule unambiguously.



$$\mathrm{H_3C-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3}$$

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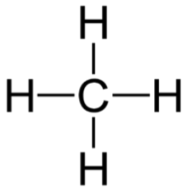
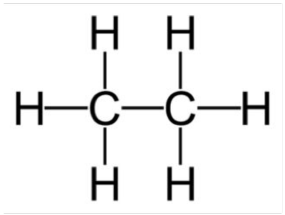
Homologous Series

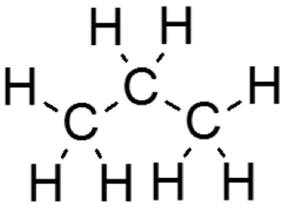
- A homologous series is a series of compounds of the same family, with the same general formula, which differ from each other by a common structural unit
- Structural isomers are compounds with the same molecular formula but different arrangements of atoms



Methane



Ethane



Propane

Main

Homologous Series

- Alkanes
  - General formula C_nH_{2n+2}
  - Hydrocarbons-contain only hydrogens and carbons
- Alkenes
  - Hydrocarbon homologous series that contain carbon-carbon double bonds
- Alkynes
  - Hydrocarbon homologous series that contain carbon-carbon triple bonds

- Saturated compounds contain single bonds only and unsaturated compounds contain double or triple bonds

Main

Physical Properties of Homologous Series

- The physical properties of homologous series changes gradually as the length of the carbon chain increases

- Boiling point/melting point rises with an increasing number of carbon atoms (molar mass)

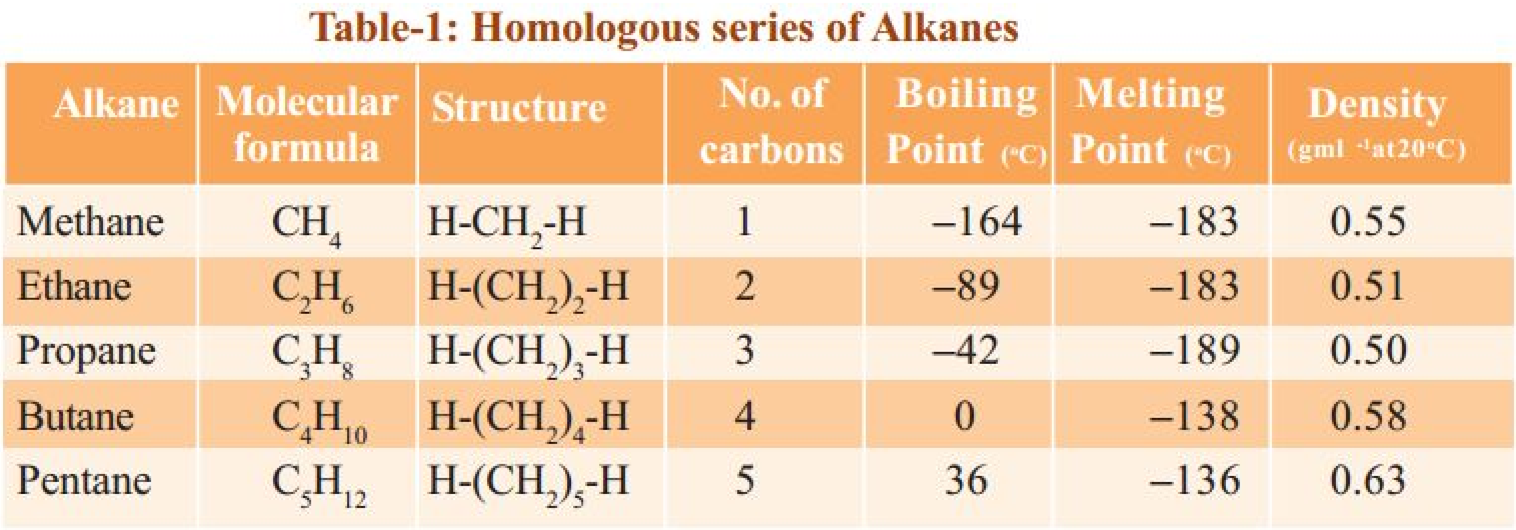


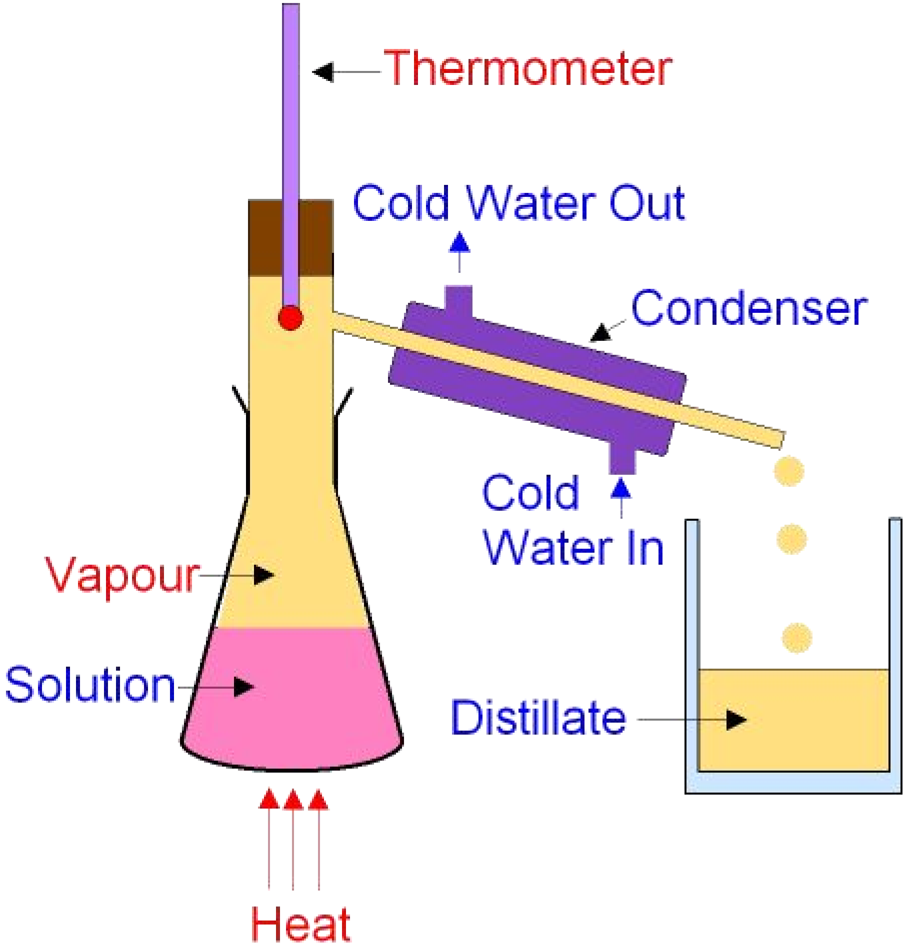
Table-1: Homologous series of Alkanes

Alkane	Molecular formula	Structure	No. of carbons	Boiling Point (°C)	Melting Point (°C)	Density (gml $^{-1}$at20°C)
Methane	CH_4	$H\text{-}CH_2\text{-}H$	1	–164	–183	0.55
Ethane	C_2H_6	$H\text{-}(CH_2)_2\text{-}H$	2	–89	–183	0.51
Propane	C_3H_8	$H\text{-}(CH_2)_3\text{-}H$	3	–42	–189	0.50
Butane	C_4H_{10}	$H\text{-}(CH_2)_4\text{-}H$	4	0	–138	0.58
Pentane	C_5H_{12}	$H\text{-}(CH_2)_5\text{-}H$	5	36	–136	0.63

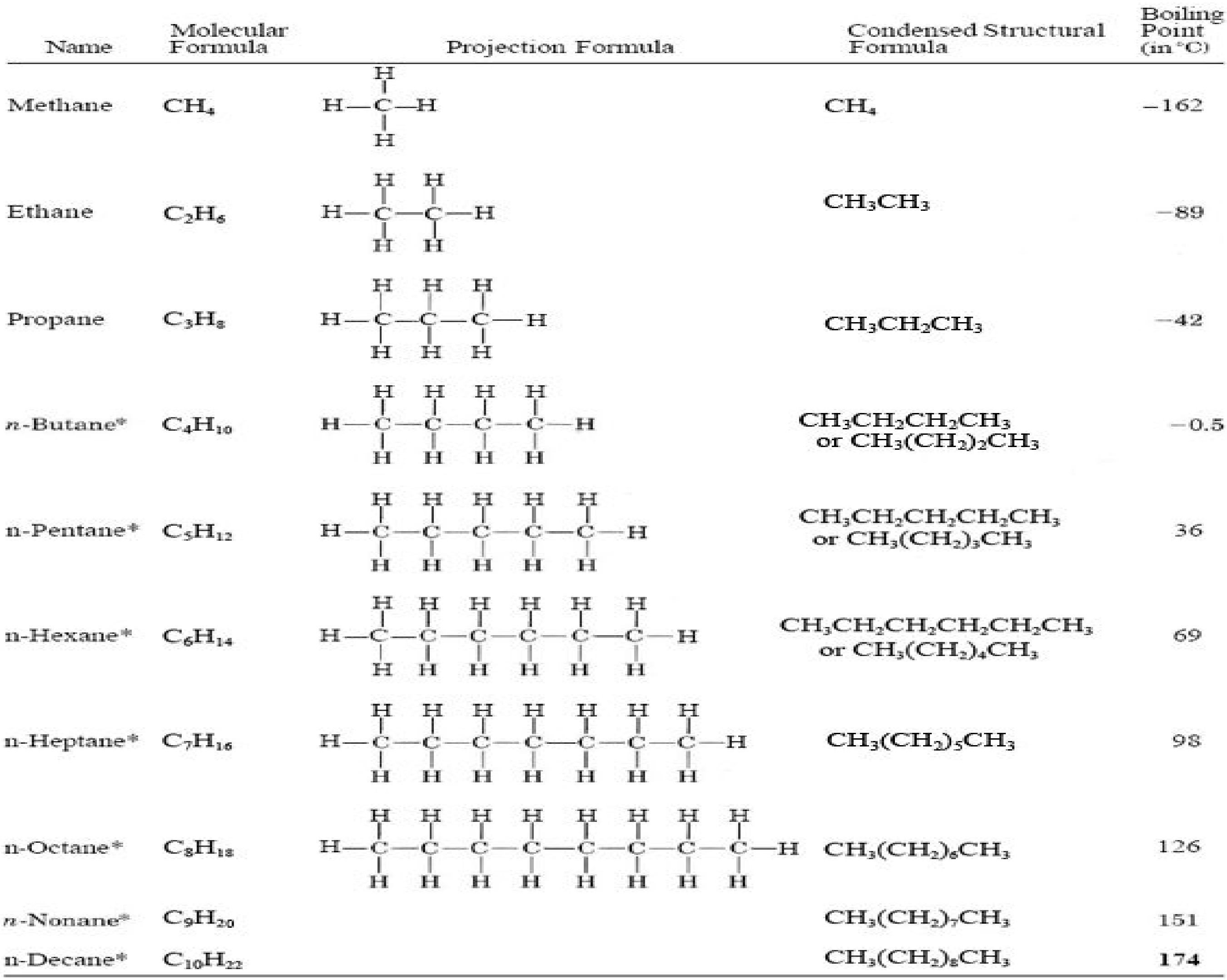
Main

Boiling Point

- The increase in boiling point is due to the increasingly strong intermolecular forces as the carbon chain becomes longer
- Fractional distillation is a physical separation process that uses differences in boiling points to separate the mixture into fractions of similar boiling point.



Carbon Chains



Name	Molecular Formula	Projection Formula	Condensed Structural Formula	Boiling Point (in °C)
Methane	CH_4		CH_4	−162
Ethane	C_2H_6		CH_3CH_3	−89
Propane	C_3H_8		$CH_3CH_2CH_3$	−42
n-Butane*	C_4H_{10}		$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$	−0.5
n-Pentane*	C_5H_{12}		$CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$	36
n-Hexane*	C_6H_{14}		$CH_3CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_4CH_3$	69
n-Heptane*	C_7H_{16}		$CH_3(CH_2)_5CH_3$	98
n-Octane*	C_8H_{18}		$CH_3(CH_2)_6CH_3$	126
n-Nonane*	C_9H_{20}		$CH_3(CH_2)_7CH_3$	151
n-Decane*	$C_{10}H_{22}$		$CH_3(CH_2)_8CH_3$	174

Nomenclature of Organic Compounds

- International Union of Pure and Applied Chemistry (IUPAC) is the world authority of chemical nomenclature

- The name of a chemical substance needs to provide enough information to signify the class of the compound from which the chemical is derived, including substituents and functional groups

Main

IUPAC Nomenclature

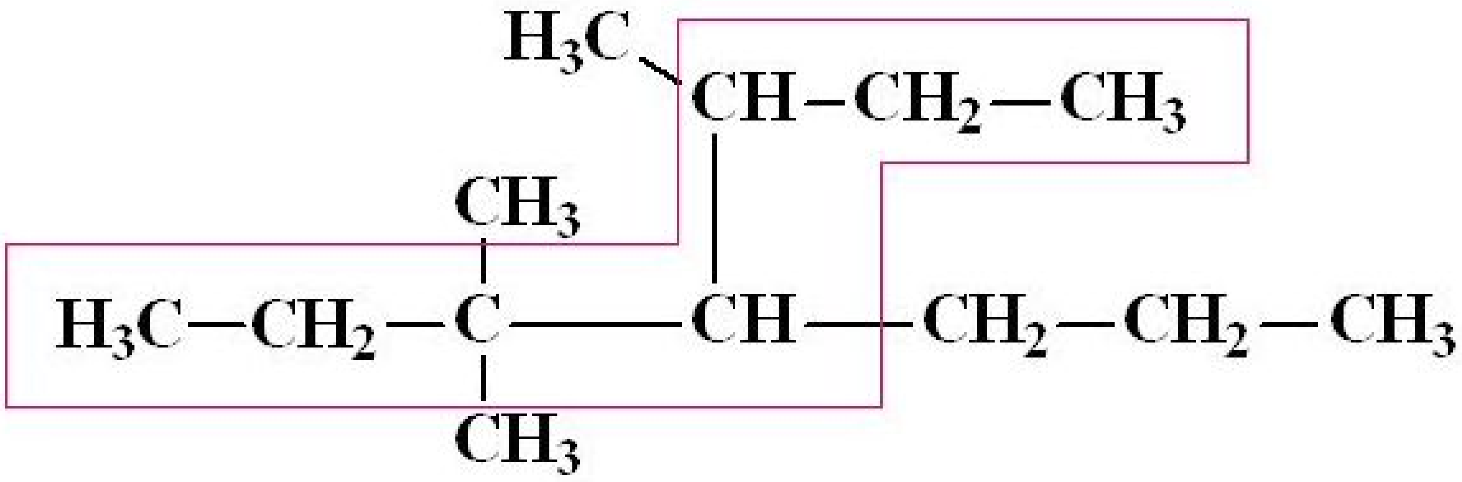
Length of Carbon Chain	Root Name
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-

Substituent Name	Condensed Formula
Methyl	$-CH_3$
Ethyl	$-CH_2CH_3$
Propyl	$-CH_2CH_2CH_3$
Butyl	$-CH_2CH_2CH_2CH_3$

Nomenclature of Alkanes

Step 1:

Determine the longest continuous carbon chain. This will be the root name for the alkane



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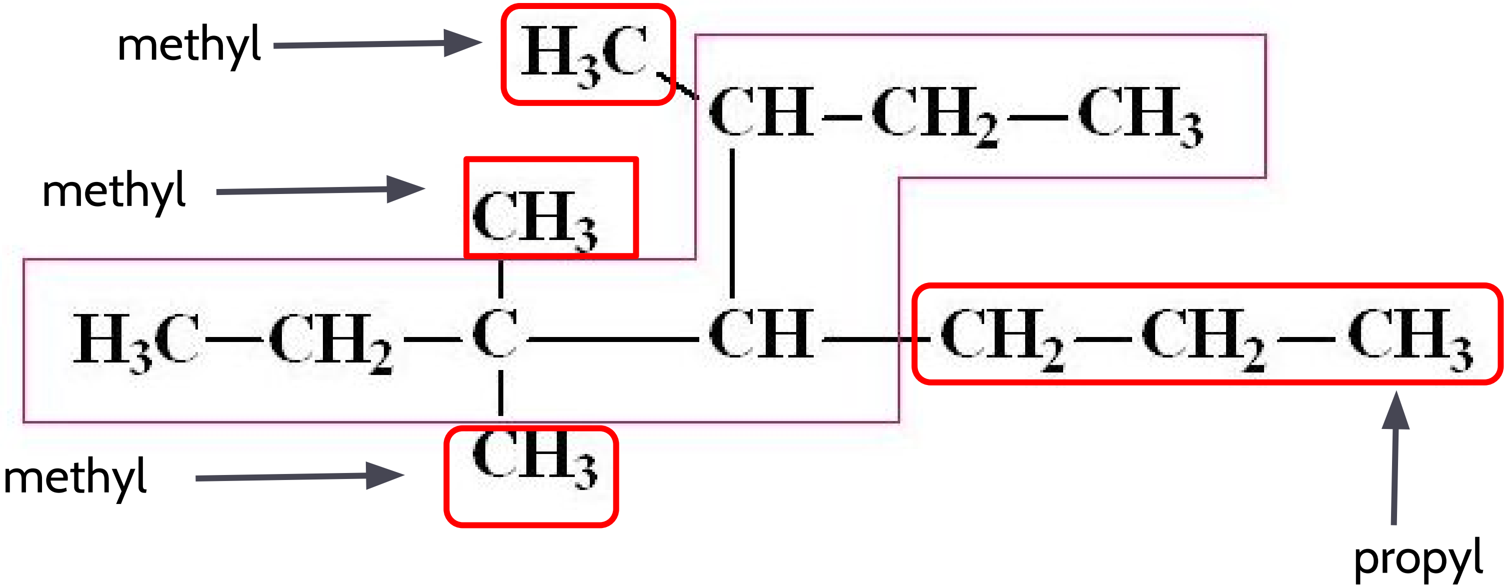
Nomenclature of Alkanes

Step 2:

If substituents are present, creating branched chains, the name of the branch will be determined by the number of carbons



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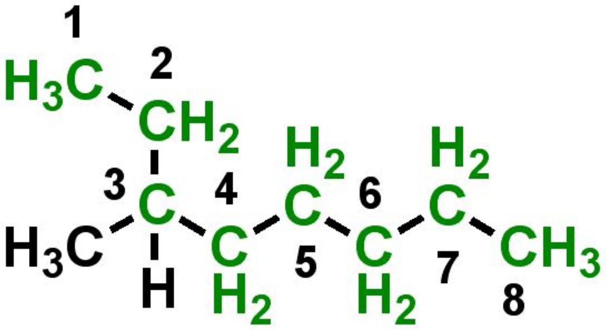
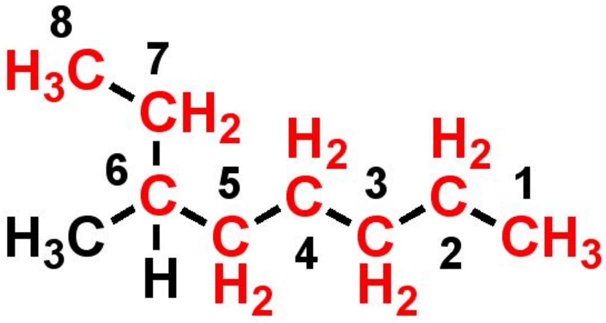
Nomenclature of Alkanes

Step 3:

When numbering the longest carbon chain, the position of any substituent must be the lowest numbered carbon.



Right !



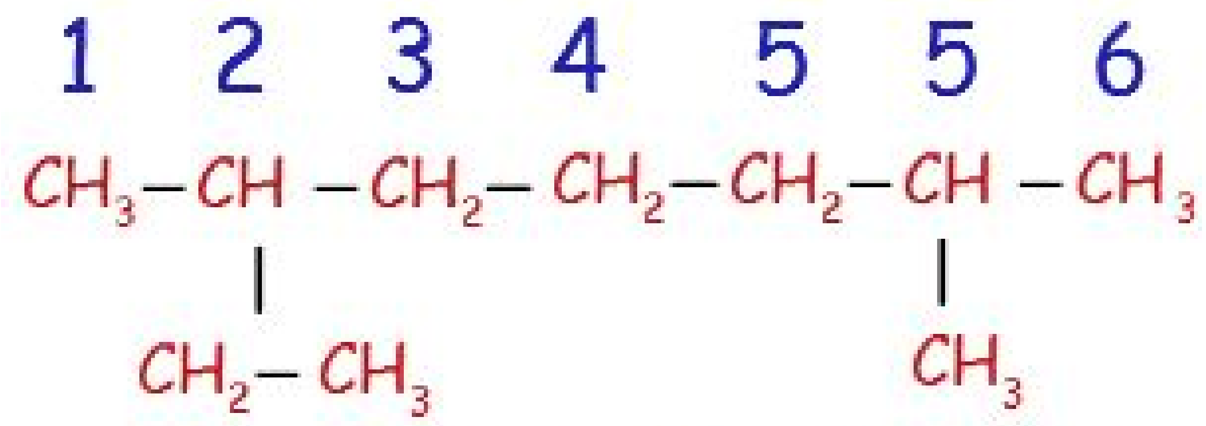
Wrong !

Main

Nomenclature of Alkanes

Step 4:

When there are several different substituents, arrange them in alphabetical order prior to the root name



$CH_3-CH(CH_2-CH_3)-CH_2-CH_2-CH_2-CH(CH_3)-CH_3$

2 - ETHYL - 1 - METHYL HEXANE

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Nomenclature of Alkanes

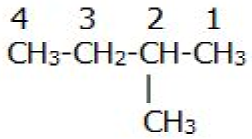
Step 5:

Use a comma to separate numbers

Step 6:

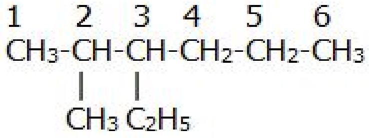
Use a hyphen to separate numbers and letters

E.g.



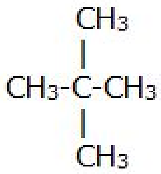
$$\begin{array}{cccc} 4 & 3 & 2 & 1 \\ CH_3- & CH_2- & CH- & CH_3 \\ & & | & \\ & & CH_3 & \end{array}$$

2-methylbutane



$$\begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \\ CH_3- & CH- & CH- & CH_2- & CH_2- & CH_3 \\ & | & | & & & \\ & CH_3 & C_2H_5 & & & \end{array}$$

3-ethyl-2-methylhexane



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3- & C & -CH_3 \\ & | & \\ & CH_3 & \end{array}$$

2,2-dimethylpropane

Main

Nomenclature of Alkanes

Step 7:

The number of multiple substituents of the same type is indicated by prefixes

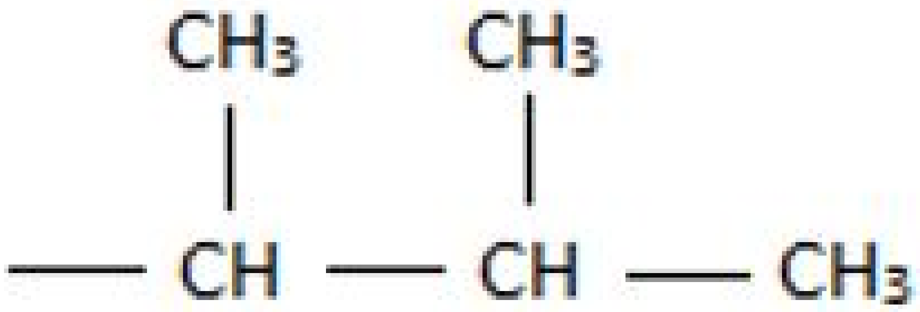
1	mono
2	di
3	tri
4	tetra
5	penta

Main

Nomenclature of Alkanes

Step 8:

Successive words are merged into one word



$$-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_3}$$

1, 2 - Dimethylpropyl

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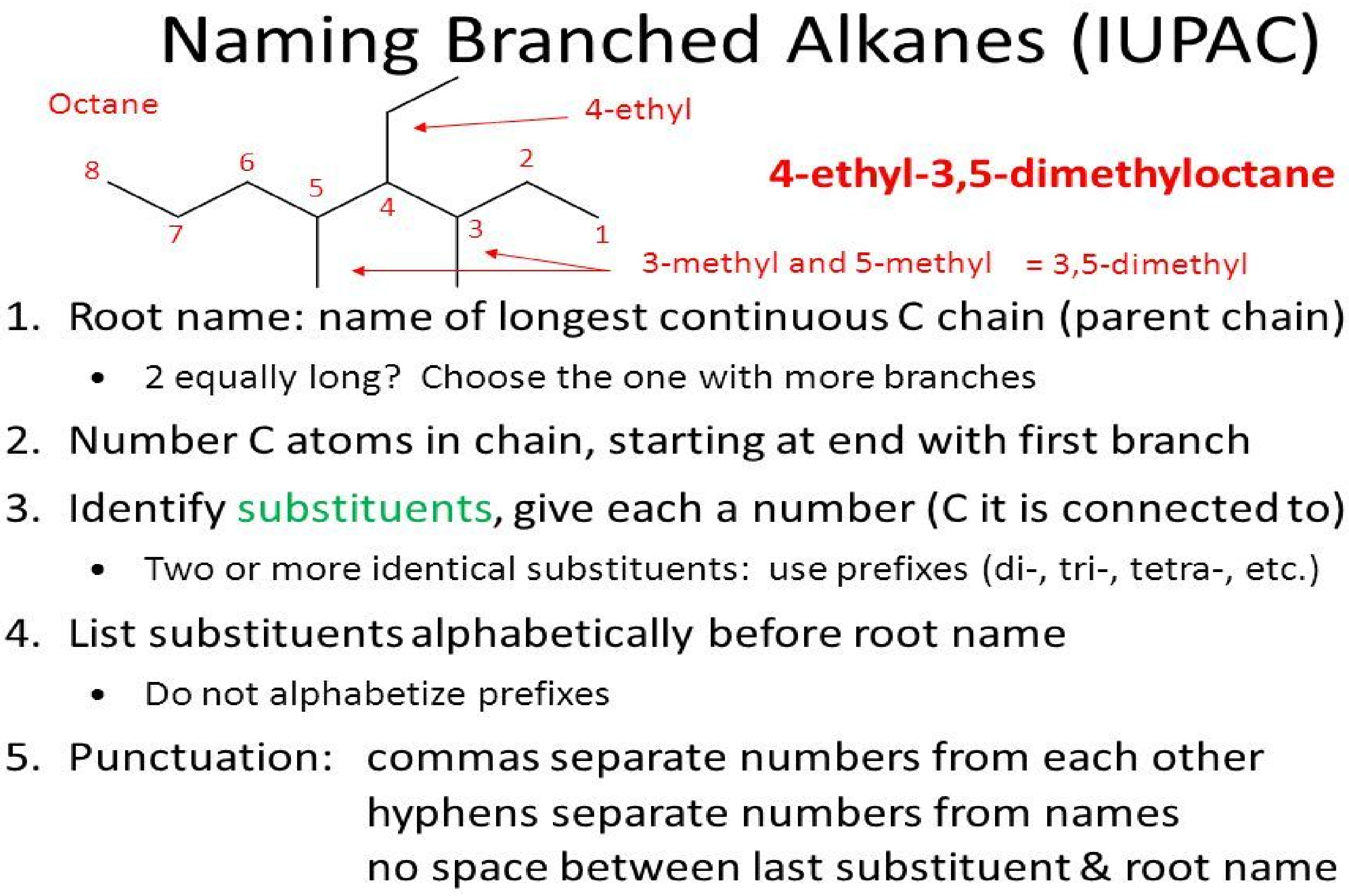
IUPAC Nomenclature



Naming Branched Alkanes (IUPAC)

4-ethyl-3,5-dimethyloctane

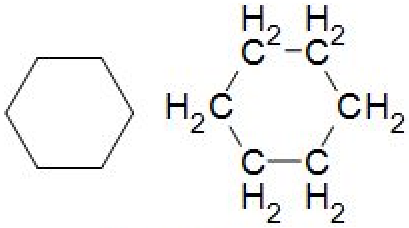
1. Root name: name of longest continuous C chain (parent chain)
    - 2 equally long? Choose the one with more branches
2. Number C atoms in chain, starting at end with first branch
3. Identify substituents, give each a number (C it is connected to)
    - Two or more identical substituents: use prefixes (di-, tri-, tetra-, etc.)
4. List substituents alphabetically before root name
    - Do not alphabetize prefixes
5. Punctuation: commas separate numbers from each other
   hyphens separate numbers from names
   no space between last substituent & root name

Hydrocarbons

- Alkanes are aliphatic-straight-chain compounds
- The majority of naturally occurring hydrocarbons come from crude oil
- The mixture is extracted from beneath the Earth's surface, refined, and separated by fractional distillation into useful substances such as petroleum, butane, and kerosene

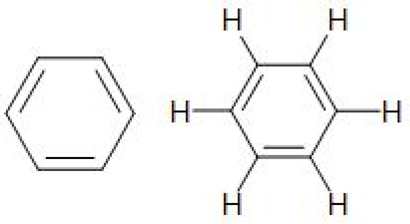
Hydrocarbons

- The mixture that makes up crude oil is a combination of mainly alkanes, cycloalkanes, and aromatic hydrocarbons
- Cycloalkanes are ring structures that contain single carbon-carbon bonds
- Aromatic hydrocarbons or arenes are ring structures containing of alternating single and double bond carbon-carbon bonds



Cyclohexane

v.s.



Benzene

Main

Isomers

- Compounds with the same molecular formula but different structural formula
- The 20 different C_4H_8O compounds are isomers of each other
- These are all **structural isomers**
  - Same number of each atom, but bonded in a different order
- Isomers have unique physical and chemical properties

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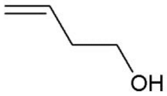
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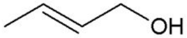
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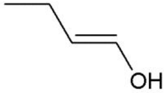
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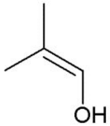
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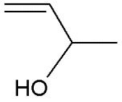
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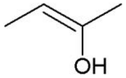
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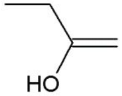
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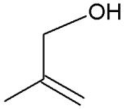
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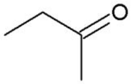
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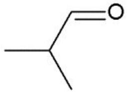
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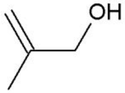
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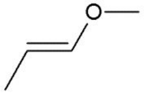
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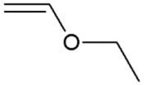
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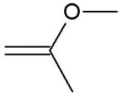
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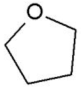
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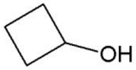
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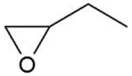
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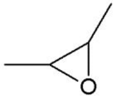
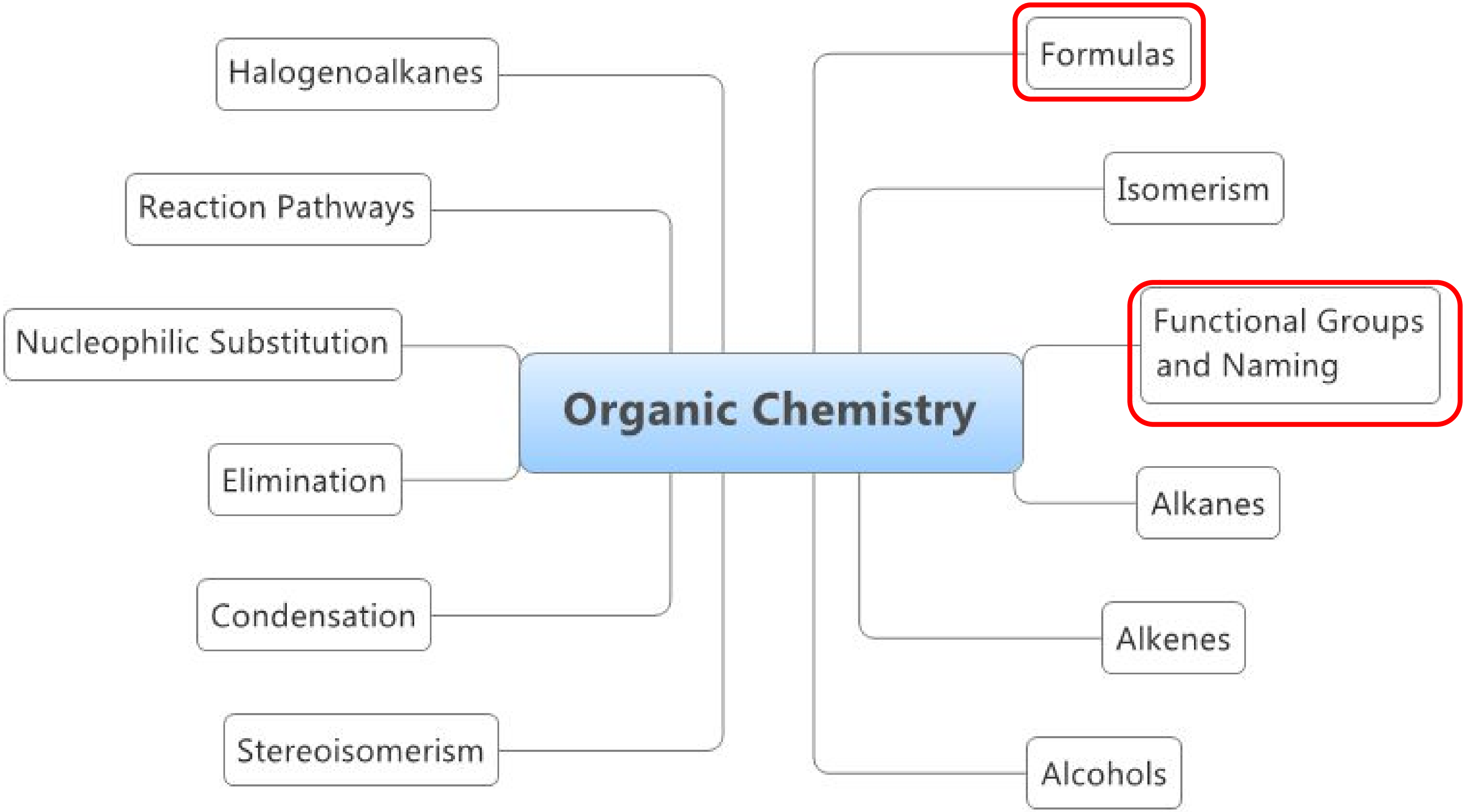


Main

Lesson 2

10.1 Fundamentals of Organic Chemistry

Main Menu



Organic Chemistry

Halogenoalkanes

Reaction Pathways

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Functional Groups and Naming

Alkanes

Alkenes

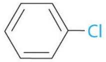
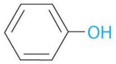
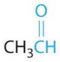
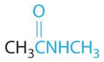
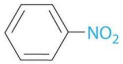
Alcohols

Functional Groups

- Functional groups are the reactive parts of molecules
- Identification of different classes: alkanes, alkenes, alkynes, halogenoalkanes, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, amines, amides, nitriles and arenes
- Identification of typical functional groups in molecules: phenyl, hydroxyl, carbonyl, carboxyl, carboxamide, aldehyde, ester, ether, amine, nitrile, alkyl, alkenyl and alkyny

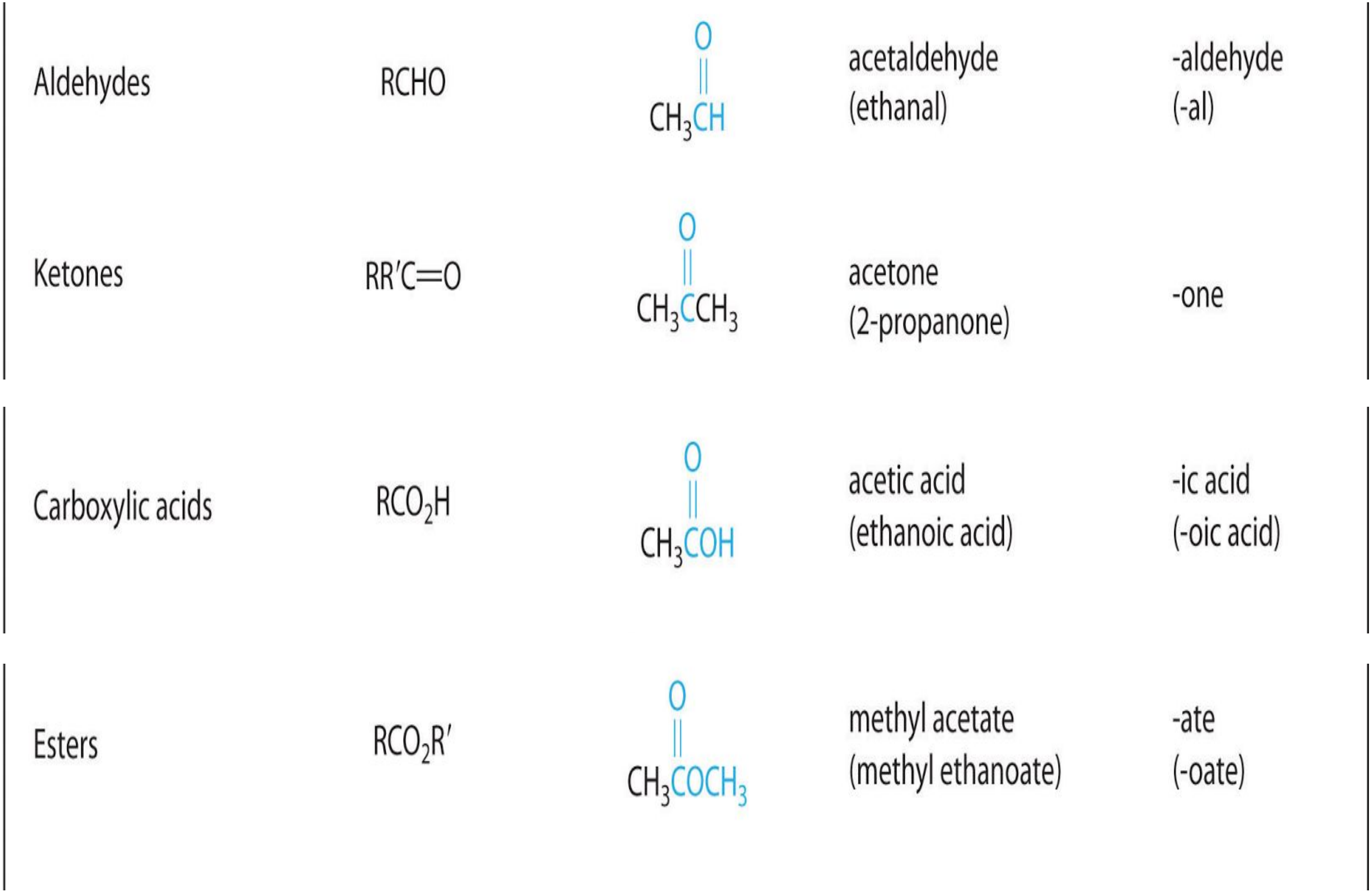
Main

Class	Functional Group	Prefix/Suffix
alkanes	alkyl	-ane
alkenes	alkenyl	-ene
alkynes	alkyny	-yne
halogenoalkanes		halo-
alcohols	hydroxyl	-ol
ethers	ether	-oxy-
aldehydes	aldehyde	-al
ketones	carbonyl	-one
esters	ester	-oate -
carboxylic acids	carboxyl	-oic acid
amines	amino	-amine
amides	amido	-amide
nitriles	cyano	-nitrile
arenes	phenyl	-yl benzene

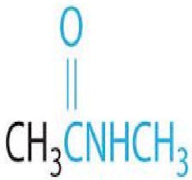
Class	General Formula	Example	(Systematic Name)	Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH[a]		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX[a]		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	ArOH[b]		phenol	-ol
Ethers	ROR′	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO	 $CH_3\overset{\overset{\displaystyle O}{\parallel}}{C}H$	acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	$RR'C{=}O$	 $CH_3\overset{\overset{\displaystyle O}{\parallel}}{C}CH_3$	acetone (2-propanone)	-one
Carboxylic acids	RCO_2H	 $CH_3\overset{\overset{\displaystyle O}{\parallel}}{C}OH$	acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'	 $CH_3\overset{\overset{\displaystyle O}{\parallel}}{C}OCH_3$	methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	RCONHR′	 $CH_3\overset{\overset{\displaystyle O}{\parallel}}{C}NHCH_3$	*N*-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, RNHR′, RNR′R″	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC{\equiv}N$	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2$[a]		nitrobenzene	nitro-

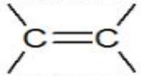
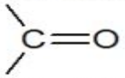
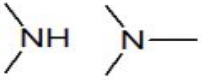
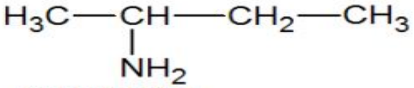
[a] R indicates an alkyl group [b] Ar indicates an *aryl* group.

Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH[a]		benzene	-ene
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol



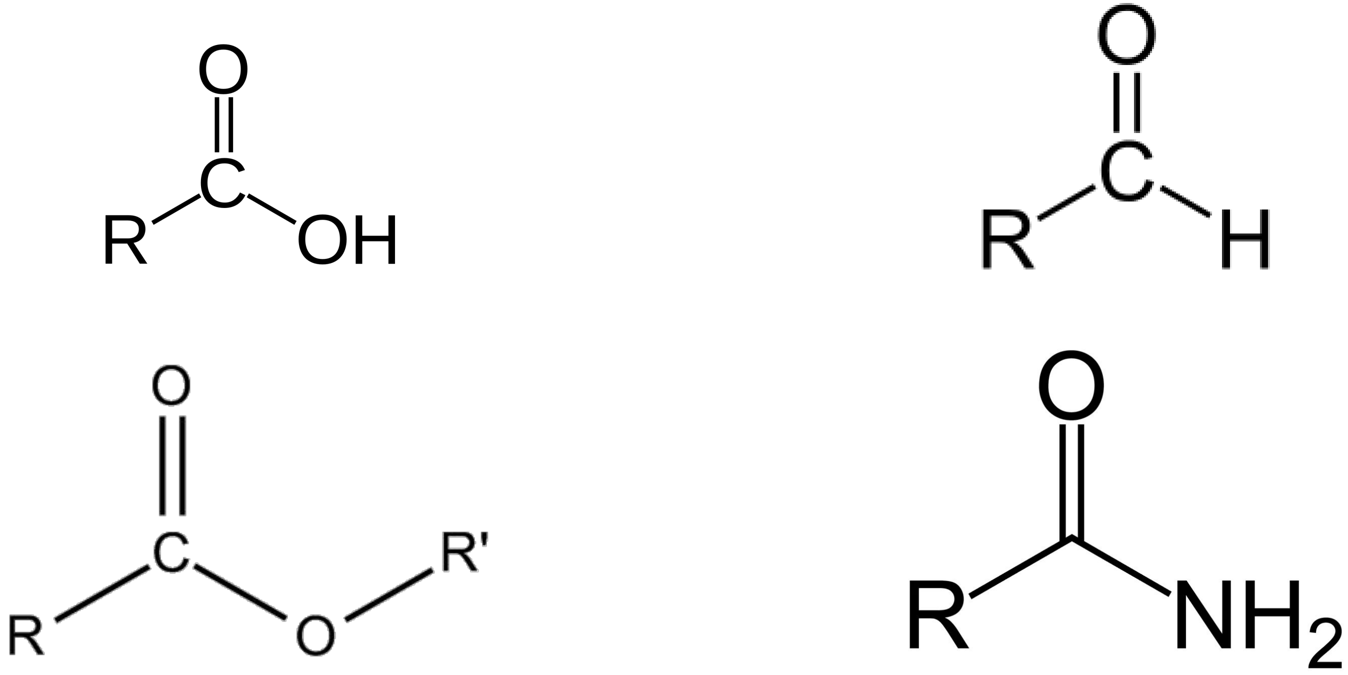
Aldehydes	RCHO	$CH_3\overset{O}{\overset{\|}{C}}H$	acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	$RR'C{=}O$	$CH_3\overset{O}{\overset{\|}{C}}CH_3$	acetone (2-propanone)	-one
Carboxylic acids	RCO_2H	$CH_3\overset{O}{\overset{\|}{C}}OH$	acetic acid (ethanoic acid)	-ic acid (-oic acid)
Esters	RCO_2R'	$CH_3\overset{O}{\overset{\|}{C}}OCH_3$	methyl acetate (methyl ethanoate)	-ate (-oate)

Ethers	ROR'	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Amines	RNH_2, $RNHR'$, $RNR'R''$	$CH_3CH_2NH_2$	ethylamine	-amine
Amides	$RCONHR'$	 $CH_3\overset{O}{\overset{\parallel}{C}}NHCH_3$	*N*-methylacetamide	-amide
Nitriles	$RC\equiv N$	$H_3CC\equiv N$	acetonitrile	-nitrile

CLASS OF ORGANIC COMPOUND	STRUCTURE OF THE FUNCTIONAL GROUP	IUPAC GROUP PREFIX	IUPAC GROUP SUFFIX	EXAMPLES
Alkanes	—	—	– ane	**propane**
Alkenes		—	– ene	$H_3C-CH_2-CH=CH_2$ **but-1-ene**
Alkynes	$-C\equiv C-$	—	– yne	$H_3C-CH_2-C\equiv CH$ **but-1-yne**
Arenes	—	—	—	**benzene**
Halides	$-X$ (X = F, Cl, Br, I)	**halo-**	—	$H_3C-CH_2-CH_2-CH_2-Br$ **1-bromobutane**
Alcohols	$-OH$	**hydroxy-**	– ol	$H_3C-CH_2-CH_2-OH$ **propan-1-ol**
Aldehydes	$-CHO$	**formyl or oxo**	– al	$H_3C-CH_2-CH_2-CHO$ **butanal**
Ketones		**oxo-**	– one	$H_3C-CO-CH_2-CH_3$ **butan-2-one**
Nitriles	$-C\equiv N$	**cyano**	**nitrile**	$H_3C-CH_2-CH_2-CH_2-CH_2CN$ **pentanenitrile**
Ethers	$R-O-R$	**alkoxy-**	—	$H_5C_2-O-C_2H_5$ **ethoxyethane**
Carboxylic acids	$-COOH$	**carboxy**	– oic acid	$H_3C-CH_2-CH_2-COOH$ **butanoic acid**
Carboxylate ions	$-COO^-$	—	– oate	$CH_3(CH_2)_2COO^-Na^+$ **sodium butanoate**
Esters	$-COOR$	**alkoxy carbonyl**	– oate	$H_3C-CH_2-COO-CH_3$ **methyl propanoate**
Acyl halides	$-COX$ (X = F, Cl, Br, I)	**halo carbonyl**	– oyl halide	$CH_3(CH_2)_2COCl$ **butanoyl chloride**
Amines	$-NH_2$ 	**amino-**	–amine	 $H_3C-CH(NH_2)-CH_2-CH_3$ **butan-2-amine**
Amides	$-CONH_2$ $-CONHR$ $-CONR_2$	-carbamoyl	–amide	$CH_3(CH_2)_2CONH_2$ **butanamide**
Nitro	$-NO_2$	**nitro**	—	$CH_3(CH_2)_3NO_2$ **1-nitrobutane**

Aliphatic Compounds

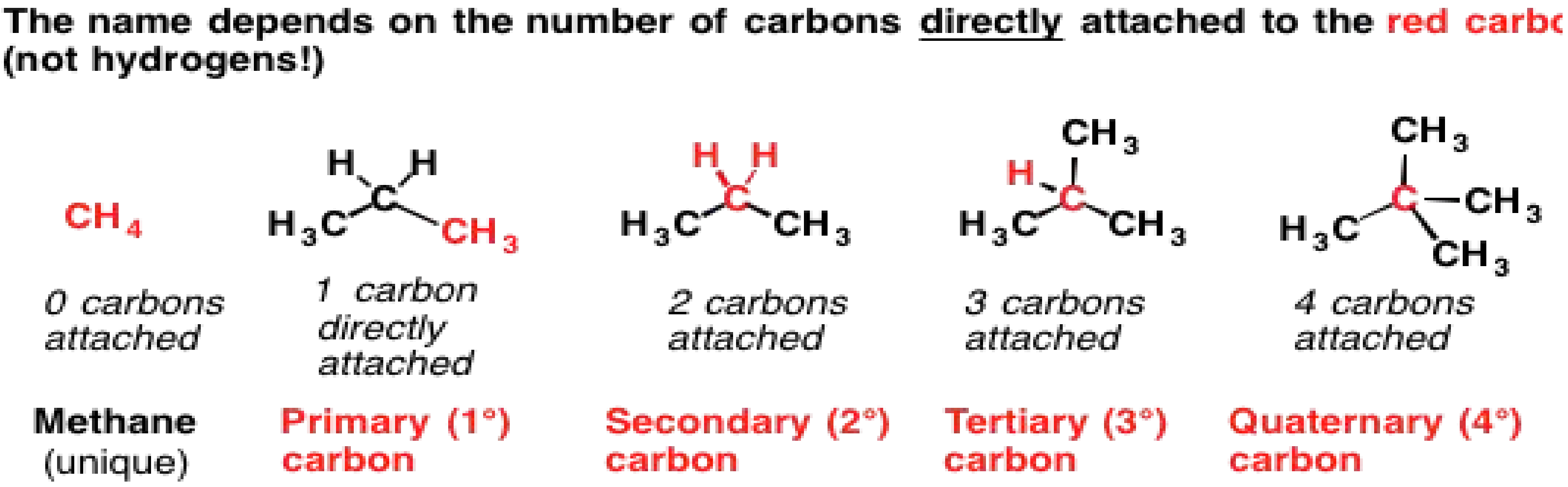
- By convention, the functional group of the carboxylic acids, aldehydes, esters, and amides are positioned at the right-hand end of the structural formula of organic compounds.



Main

Classifying Molecules

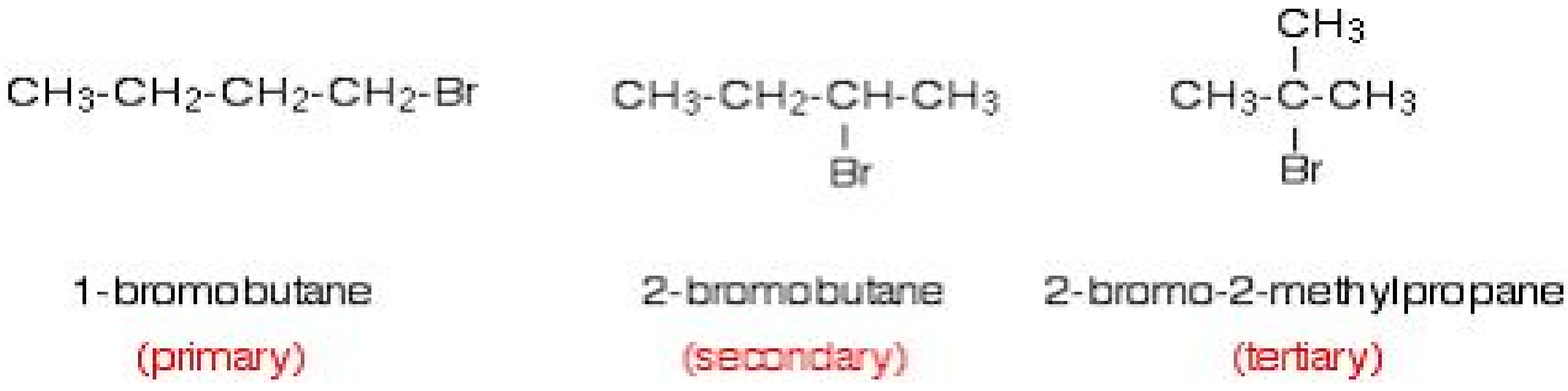
- Primary Carbon: carbon atom is bonded to one other carbon atom
- Secondary Carbon: carbon atom is bonded to two other carbon atoms
- Tertiary Carbon: carbon atom is bonded to three other carbon atoms



The name depends on the number of carbons <u>directly</u> attached to the red carb (not hydrogens!)

Main

Classifying Molecules



$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br$

1-bromobutane

(primary)

$CH_3\text{-}CH_2\text{-}\underset{\displaystyle Br}{\underset{|}{CH}}\text{-}CH_3$

2-bromobutane

(secondary)

$CH_3\text{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}\text{-}CH_3$

2-bromo-2-methylpropane

(tertiary)

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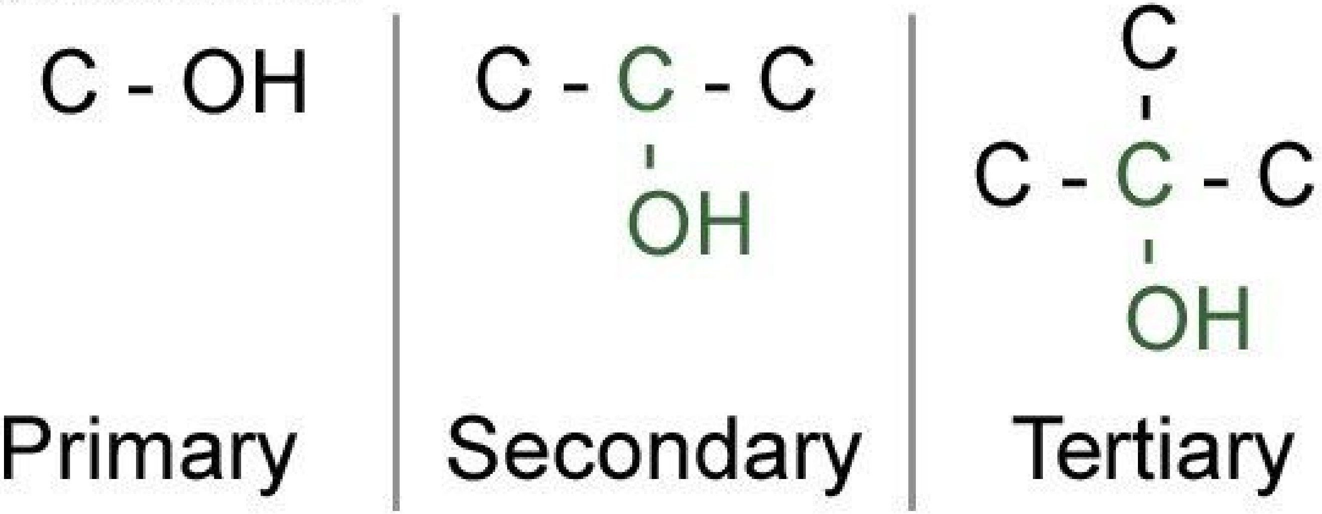


$C - OH$

$C - \underset{\displaystyle OH}{\underset{|}{C}} - C$

$C - \overset{\displaystyle C}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}} - C$

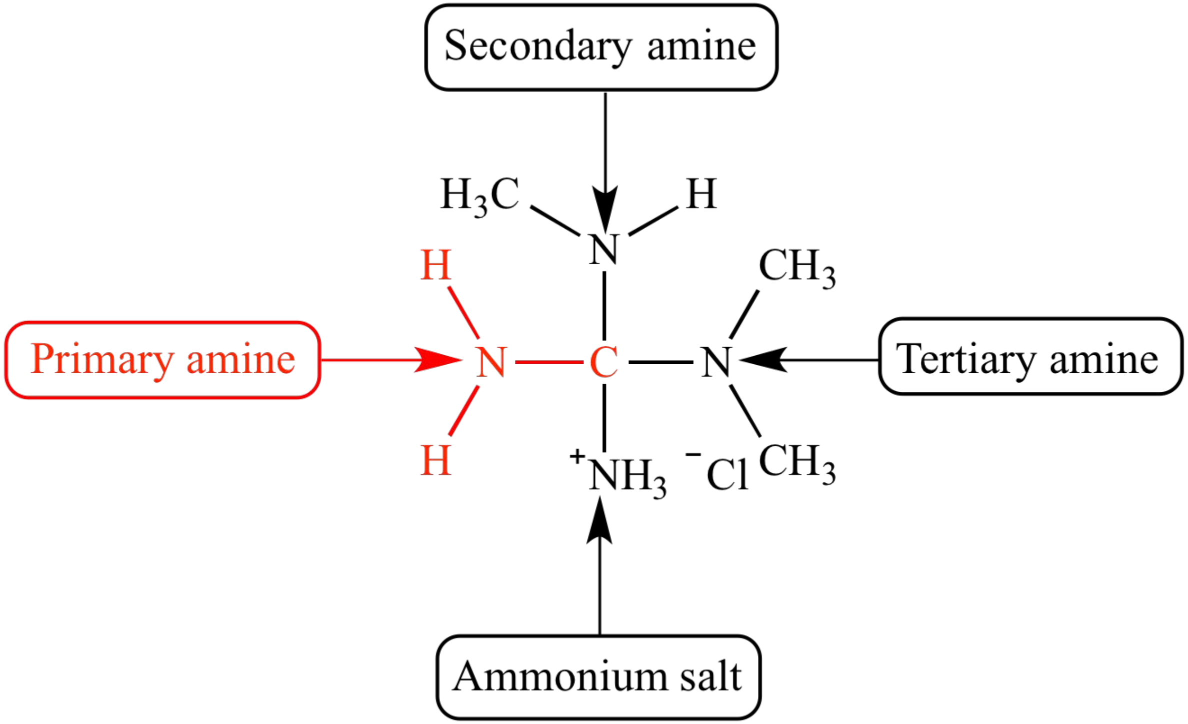
Primary

Secondary

Tertiary

Classifying Molecules

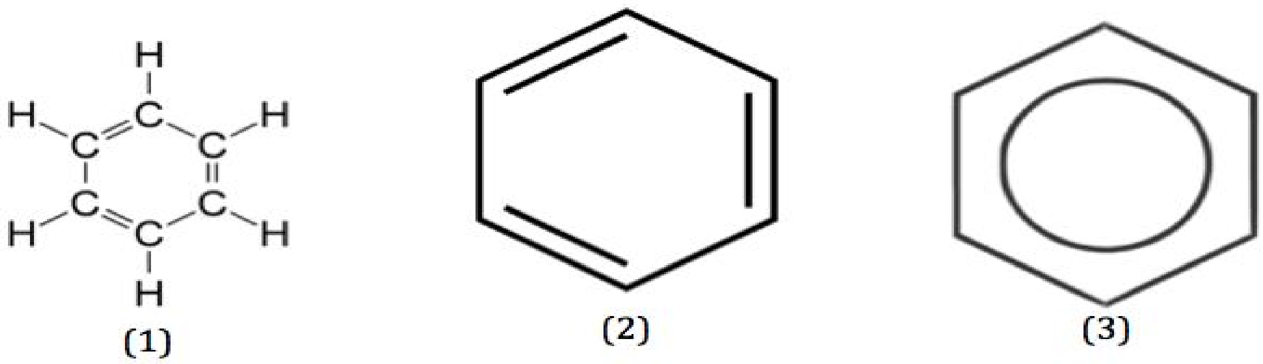
- An amine is classified as primary, secondary, or tertiary based on the number of alkyl groups bonded to the nitrogen atom of the functional group



Aromatic Hydrocarbons

- Aromatic hydrocarbons are characterized by the presence of the benzene ring.
- August Kekule proposed a structure for benzene C6H6 composed of six carbons bonded together by alternating double and single bonds.
- The structure results in an molecule with carbon-carbon bonds of different bond lengths.

Benzene: C_6H_6



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Aromatic Hydrocarbons

- X-ray diffraction patterns from the crystalline structure of benzene show that all carbon-carbon bonds in the molecule have identical bond lengths of 140pm

- It is now understood that the carbon-carbon bonds are intermediate in length between single (154pm) and double (136pm) carbon-carbon bonds.

- Electrostatic potential mapping confirms that all the carbon atoms have equal electron density so the molecule is symmetrical.

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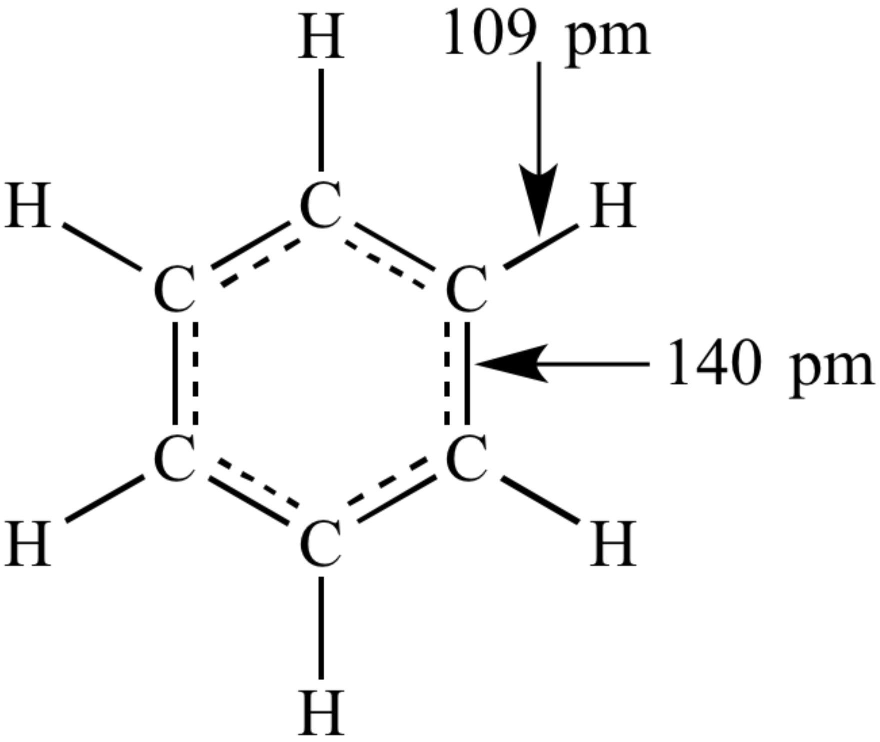
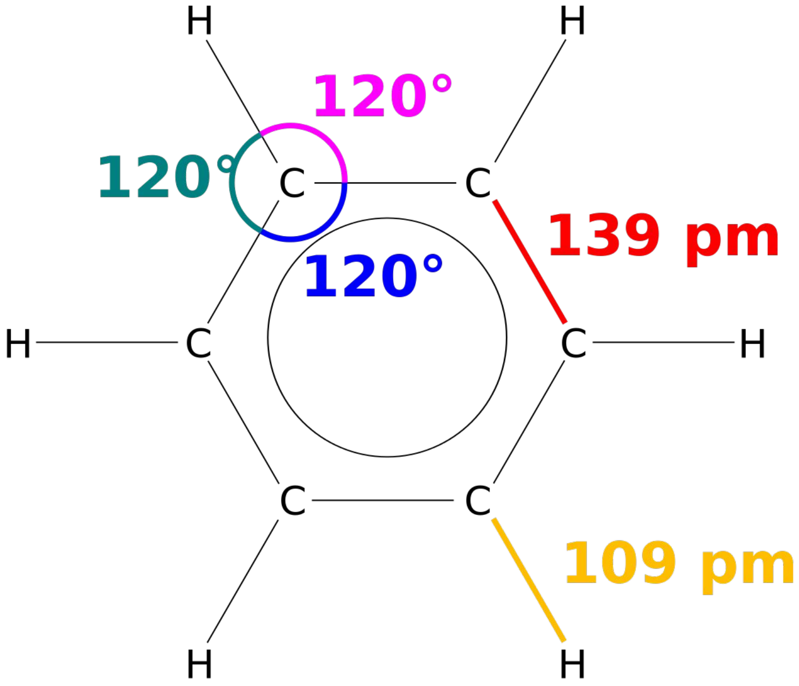
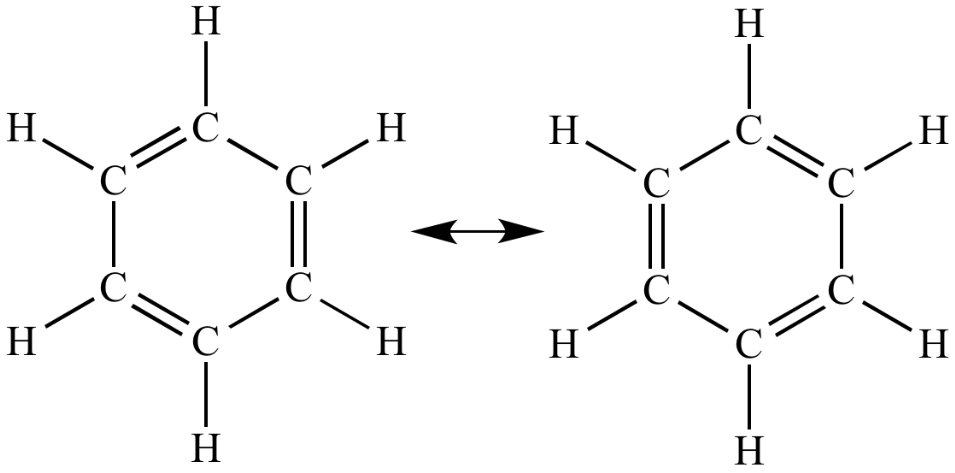
Aromatic Hydrocarbons





Aromatic Hydrocarbons

- Benzene contains six sp^2 hybridized carbon atoms bonded to one another and each carbon is bonded to a single hydrogen atom by sigma bonds.
- The p orbitals of the six sp^2 hybridized carbon atoms overlap one another, forming a continuous π bond that lies above and below the plane of the six carbon atoms.



Main

International Mindedness

- A small proportion of nations have control over the world's oil resources. The interdependence of the countries that are net importers and those that are net exporters is an important factor in shaping global policies and economic developments.

- The octane rating (octane number) can be described as a standard measure of the performance of the fuel used in cars and aircraft. Octane ratings often vary quite widely regionally throughout the globe, and are complicated by the fact that different countries use different means of expressing the values.

Main

Lesson 3

10.2 Functional Group Chemistry

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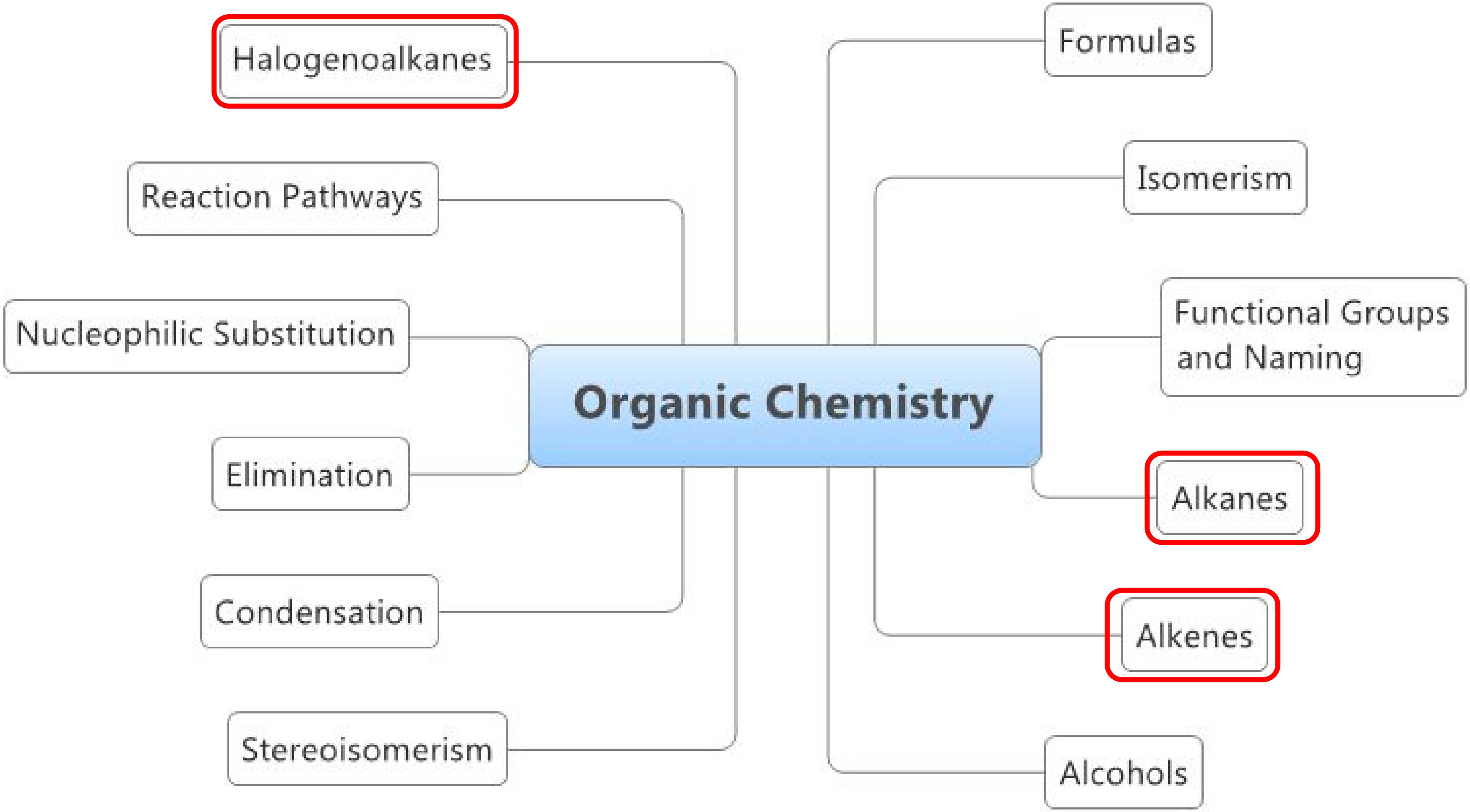

Organic Chemistry

Halogenoalkanes

Reaction Pathways

Nucleophilic Substitution

Elimination

Condensation

Stereoisomerism

Formulas

Isomerism

Functional Groups and Naming

Alkanes

Alkenes

Alcohols

Alkanes

- Alkanes have low bond polarity and strong covalent carbon-carbon bonds and carbon-hydrogen bonds.
- Alkanes are relatively inert
- Alkanes are commonly used as fuels, releasing large amounts of energy in combustion reactions.
- Volatility decreases as the length of the carbon chain increases.
- Alkanes used as fuels tend to be short-chain molecules such as butane and octane.

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Combustion of Alkanes

- Complete combustion:
  - alkane + oxygen → carbon dioxide + water
  - Highly exothermic
  - Clean flame
  - CO_2 produced has a significant environmental impact, contributing to global warming

- Incomplete combustion:
  - Alkane + oxygen → carbon + carbon monoxide + water
  - Insufficient O_2 is present
  - The amounts of C, CO and H_2O will vary depending on conditions
  - Smoky flame
  - Poisonous CO gas is produced

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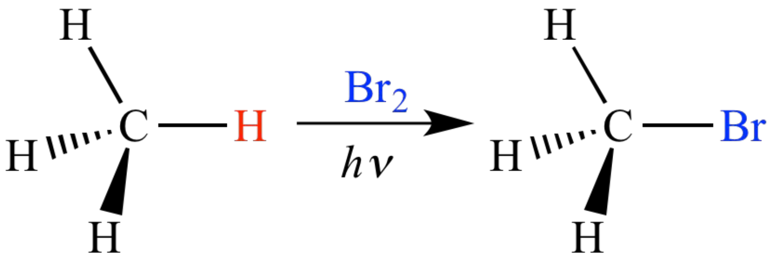
Unreactivity of Alkanes

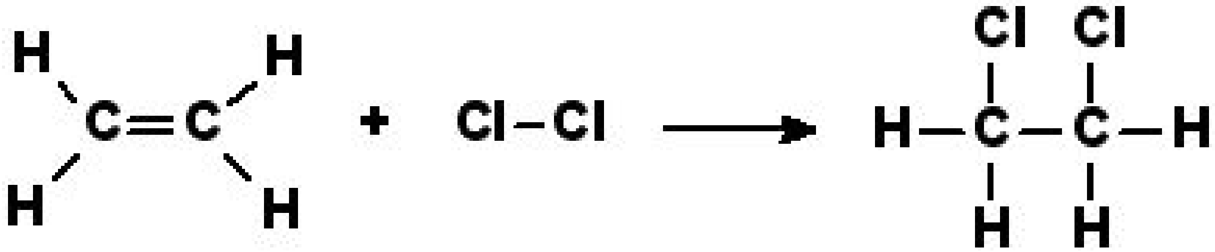
- There are at least two reasons why alkanes are so unreactive:
  - High strength of C-C and C-H bonds that is generally unfavorable to break
  - C-C and C-H bonds are essentially non-polar and are unlikely to attract polar molecules or ions

Common Reactions of Alkanes

- Substitution: replacement of individual atoms with other single atoms or with a small group of atoms



- Addition: two molecules are added together to produce a single molecule



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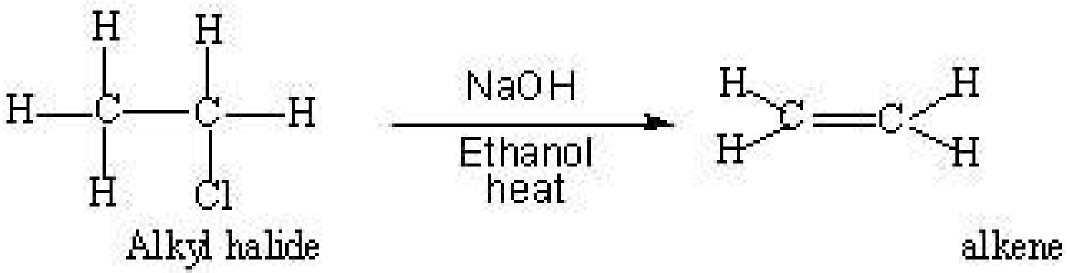
Common Reactions of Alkanes

- Elimination: the removal of two substituents from the molecule



- Alkanes can undergo free-radical substitution and elimination to form unsaturated alkenes and alkynes.

- Alkenes and alkynes can undergo all three types of reactions listed.

Halogenation

- Chemists work to “activate” alkanes to increase their reactivity.

- Alkanes will undergo halogenation if reacted with a halide in the presence of u.v. light.

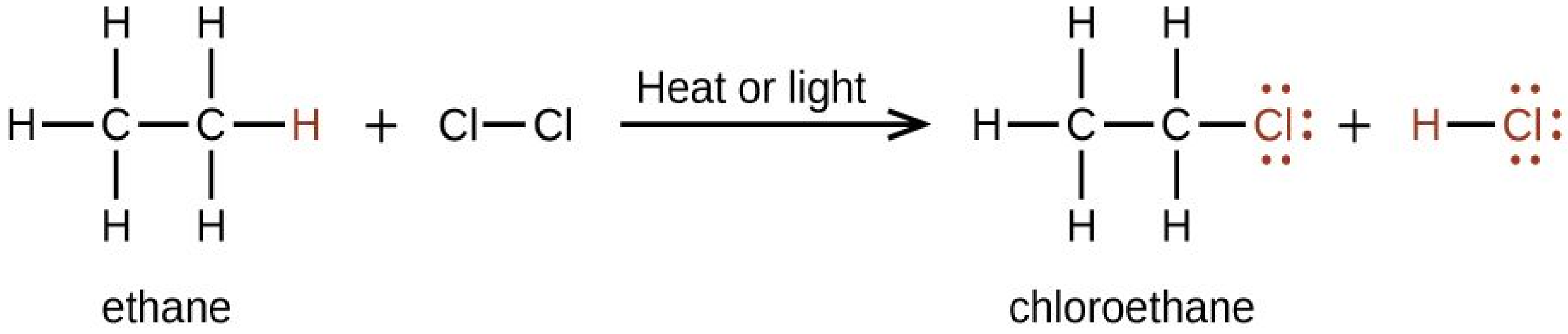
- For example:
  - $C_2H_6(g) + Cl_2(g) \xrightarrow{\text{u.v.}} CH_3CH_2Cl(g) + HCl(g)$

    ethane → chloroethane

- This reaction is an example of **free radical substitution**

Halogenation

- An atom or group is replaced by a different group or atom
- The replacement of one hydrogen atom in the molecule by one halogen atom
- The reaction can be difficult to control and a number of products, some involving multiple steps, can be formed



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Radical

- Radicals are species with unpaired electrons
  - They are extremely reactive

- Halogens form radicals when hit by uv light of the right frequency:
  - $Cl_2 \xrightarrow{u.v} Cl\bullet + Cl\bullet$
  - The dot after the Cl represents the unpaired electron and tells us we have a radical
  - This process is called **homolytic fission** – the bond breaks equally with one electron going to each chlorine resulting in two free-radicals

- Heterolytic fission-bond creates a cation and an anion, as the electrons involved in the bond are unequally split between the two atoms
  - $Cl_2 \xrightarrow{u.v.} Cl^+ + \bullet\bullet Cl^-$

Main

Reaction Mechanism: Free Radical Substitution

- $Cl_2 \xrightarrow[.]{u.v} 2\,Cl\bullet$

- $Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$
- $CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

- $Cl\bullet + Cl\bullet \rightarrow Cl_2$
- $Cl\bullet + CH_3\bullet \rightarrow CH_3Cl$
- $CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$

- **Initiation**
  - Radicals formed by homolytic fission

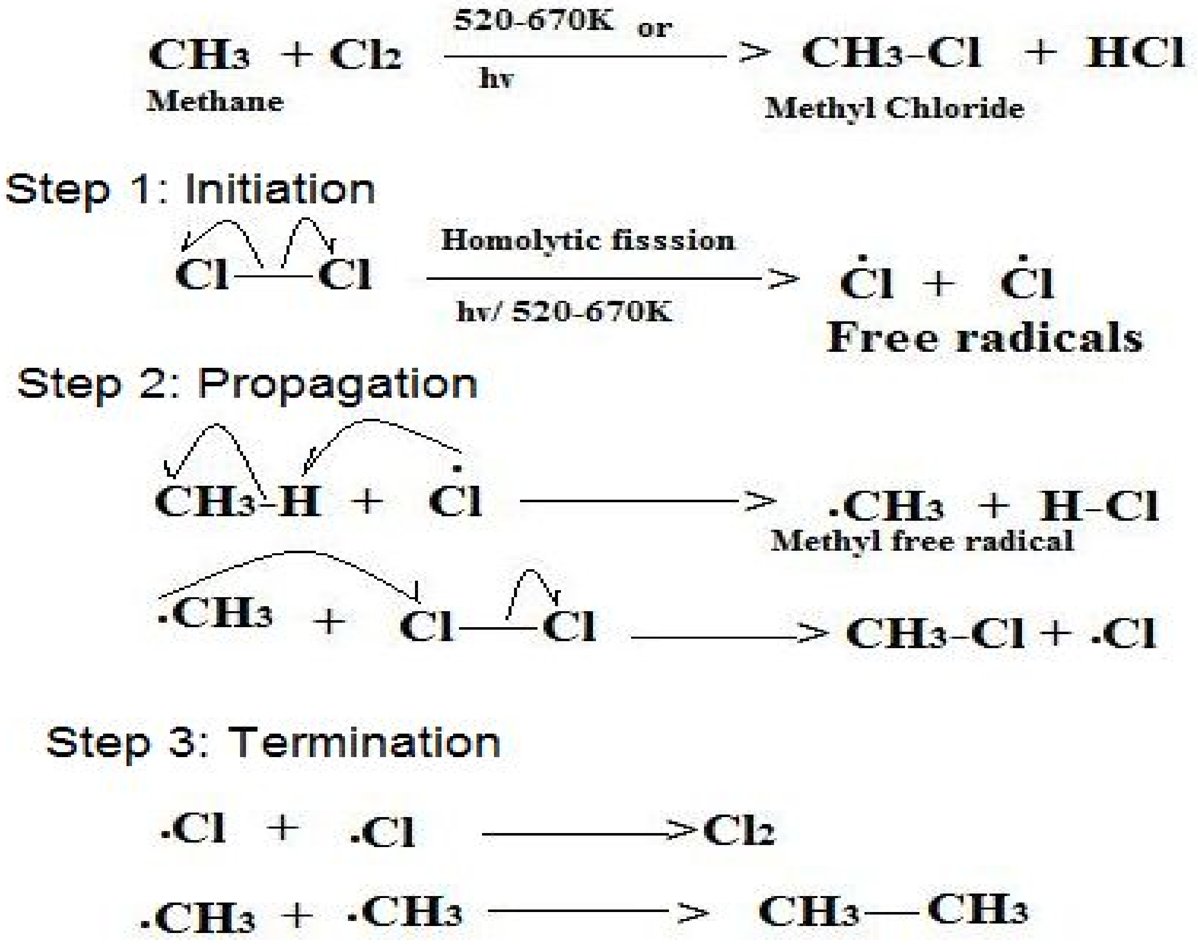
- **Propagation**
  - These steps feed each other the radicals needed to continue

- **Termination**
  - Any two radicals can combine to terminate the reaction
  - Concentration of radicals is low so this is a rare event

- A single radical can cause thousands of cycles of the propagation stage before it reaches termination
- This same mechanism applies to all of the halogens
- The alkane can be substituted multiple times, until every H has been replaced

Main

Reaction Mechanism: Free Radical Substitution



$$CH_3 + Cl_2 \xrightarrow[hv]{520\text{-}670K\ \ or} CH_3\text{-}Cl + HCl$$

Methane

Methyl Chloride

Step 1: Initiation

$$Cl\text{—}Cl \xrightarrow[hv/\ 520\text{-}670K]{\text{Homolytic fisssion}} \dot{C}l + \dot{C}l$$

Free radicals

Step 2: Propagation

$$CH_3\text{-}H + \dot{C}l \longrightarrow \cdot CH_3 + H\text{-}Cl$$

Methyl free radical

$$\cdot CH_3 + Cl\text{—}Cl \longrightarrow CH_3\text{-}Cl + \cdot Cl$$

Step 3: Termination

$$\cdot Cl + \cdot Cl \longrightarrow Cl_2$$

$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3\text{—}CH_3$$

Free Radical Substitution

https://www.youtube.com/watch?v=XAWWf86TJOc

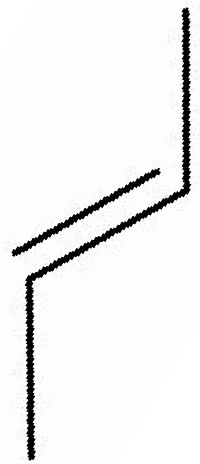
Main

Reactivity of Alkenes

- Alkenes are considerably more reactive than alkanes and are a major industrial feedstock

- The reactivity is due to the double bond:
  - The double bond contains 4 electrons
  - This is a significant amount of charge which:
    - Makes it attractive to electrophiles
    - Enables it to polarise approaching molecules

- Most reactions of alkenes are **addition reactions** where two molecules come together to make one new one



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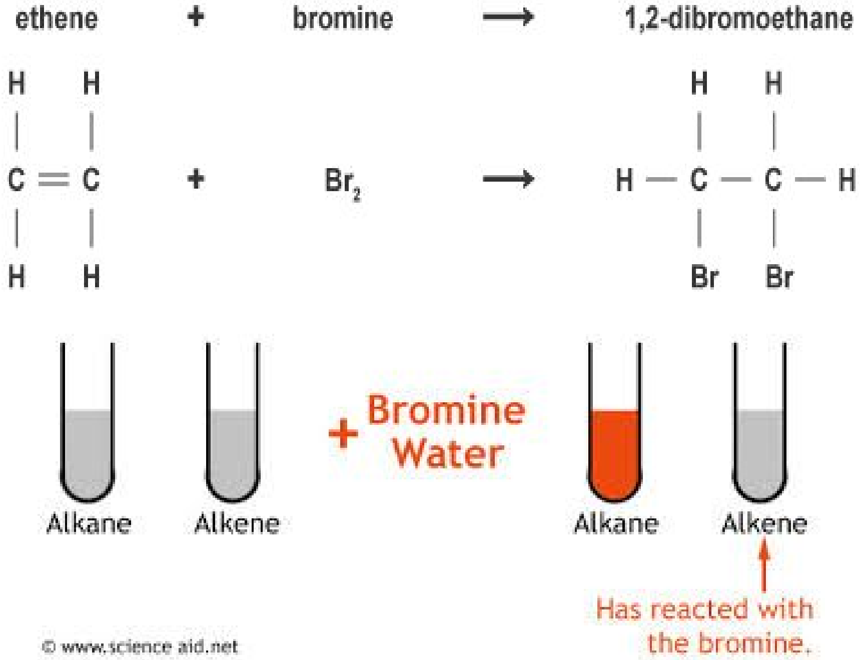
Test for Unsaturation

- The presence of a double bond in a hydrocarbon can be determined using the addition of bromine water, $Br_2(aq)$
- A mixture of the alkene and bromine water will undergo a color change from brown to colorless



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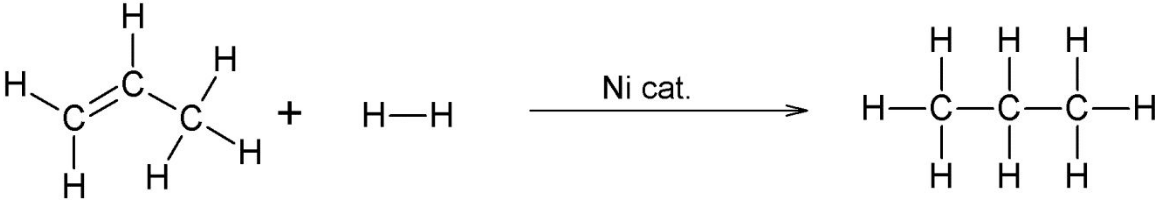
Addition of Hydrogen: Hydrogenation

- Alkene + hydrogen → alkane



- Reaction conditions:
  - Hot
  - Ni catalyst

- This is an addition reaction, in which the hydrogen adds across the double bond

Addition of Hydrogen: Hydrogenation

- The addition of hydrogen to unsaturated fats and oils occurs in the manufacture of margarine.

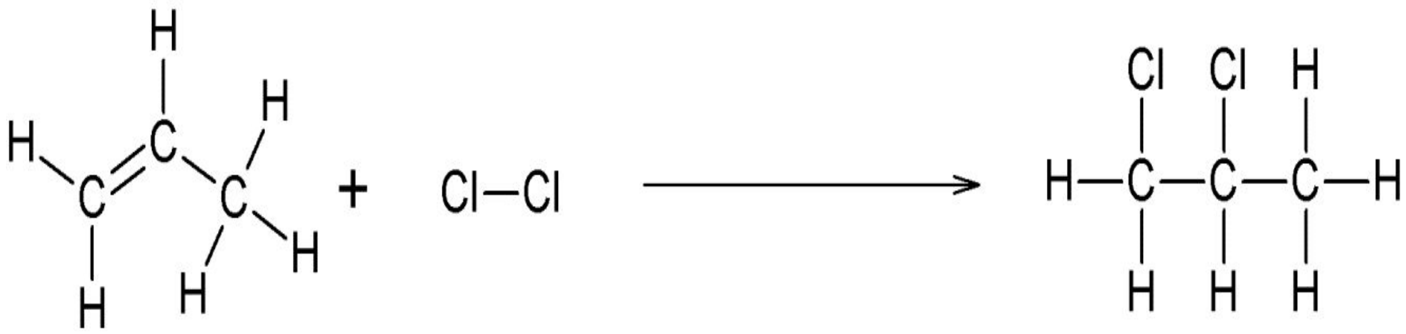
- Removing the carbon-carbon double bonds increases the melting point, making a substance that is solid rather than liquid at room temperature.

- The food industry uses partially hydrogenated oils as they have a prolonged shelf life, the length of time a product can be stored in a supermarket and remain fit for consumption.

Main

Halogenation of Alkenes

- Alkene + halogen → dihalogenoalkane



- Reaction conditions:
  - This reaction occurs very readily and needs no special conditions

Halogenation of Alkenes

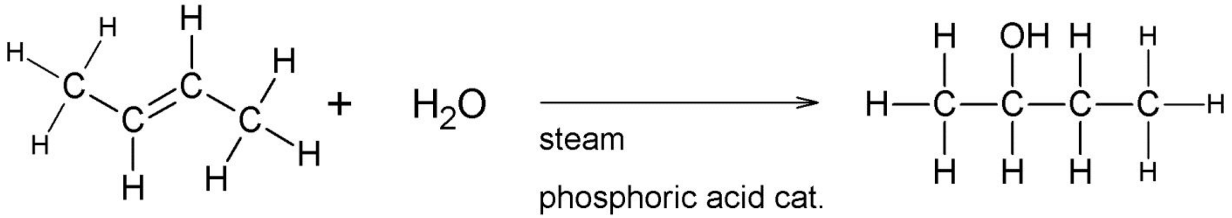
- Alkene + hydrogen halide → halogenoalkane

- Reaction conditions:
  - This reaction occurs very readily and needs no special conditions

- This is an addition reaction, in which the hydrogen halide adds across the double bond

Alkenes and water

- Alkene + water → alcohol



- Reaction conditions:
  - Water must be steam
  - Phosphoric or sulfuric acid catalyst
  - Pressure of 6-7MPa

- This is the process used to make industrial ethanol which has a variety of uses including an additive to gasoline or petrol, creating a biofuel.

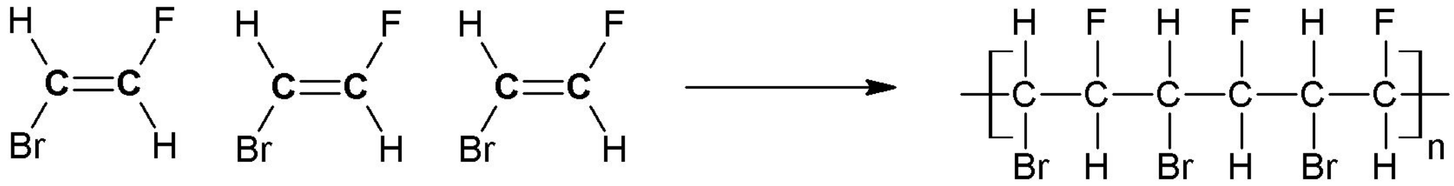
Polymerization of Alkenes

- The plastics industry is one of the largest manufacturing bodies in the world.
- Polymers improve the quality of our lives although they can have a negative impact on the environment.
- Addition polymerization is the reaction of many small monomers that contain a carbon-carbon double bond, linking together to form a polymer.
- Any monomer that contains a carbon-carbon double bond can undergo polymerization.

Main

Polymerization of Alkenes

- Under the right conditions, alkene molecules will add to each other creating a polymer



- Conditions vary from alkene to alkene but often include high pressure, temperature and a catalyst
- The carbons in the C=C double bonds form the carbon chain, everything else hangs off this chain
- The basis of the plastics industry!

Lesson 4

10.2 Functional Group Chemistry

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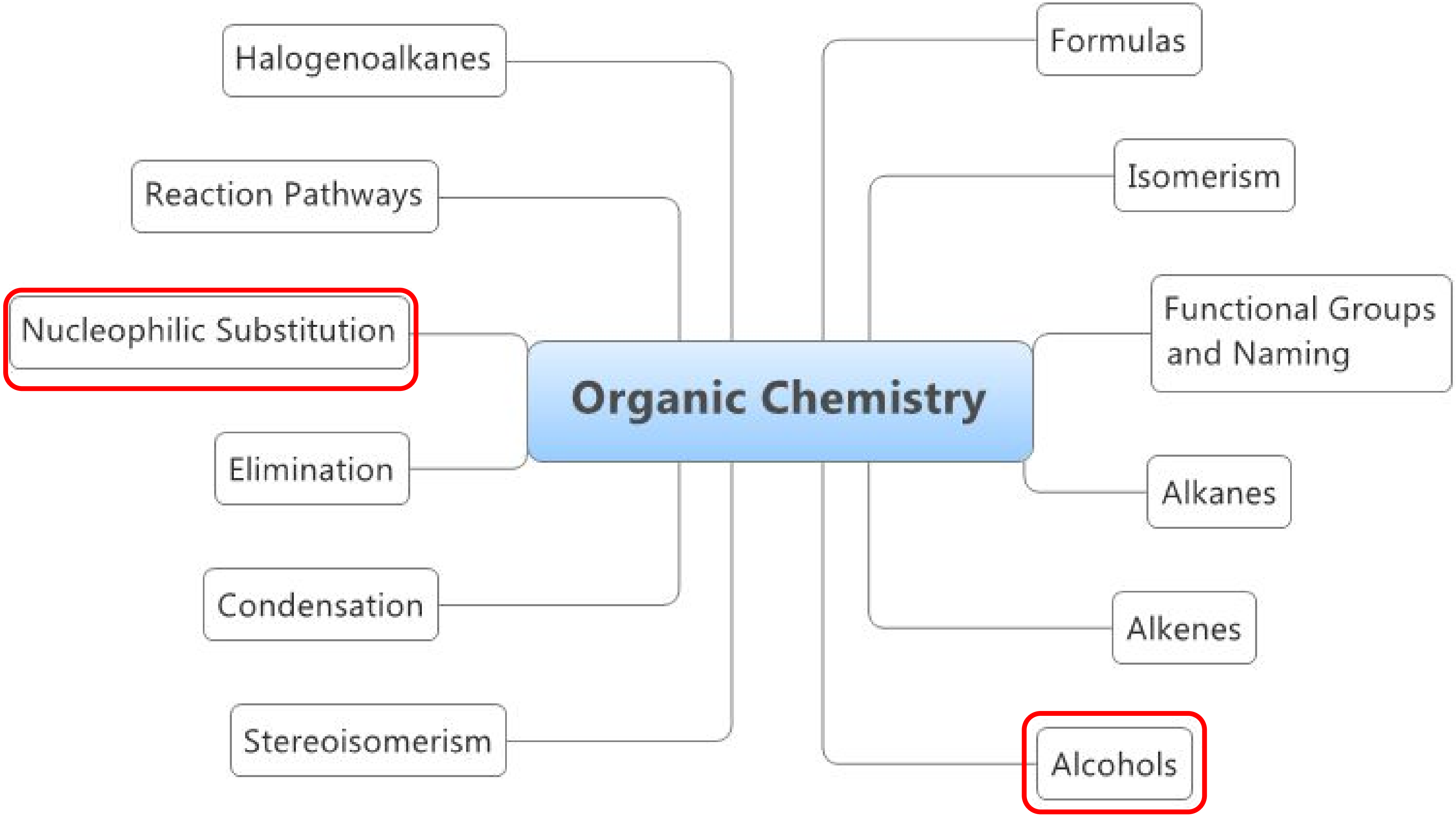
We Are Here



Organic Chemistry

- Halogenoalkanes
- Reaction Pathways
- Nucleophilic Substitution
- Elimination
- Condensation
- Stereoisomerism
- Formulas
- Isomerism
- Functional Groups and Naming
- Alkanes
- Alkenes
- Alcohols

Main

Alcohols as Fuels

- Alcohols combust more readily than equivalent alkanes but release less energy since they are already partially oxidized

  Alcohol + oxygen → carbon dioxide + water

- Exothermic reactions

- Alcohols are used as fuels:
  - As a fuel for cars – either pure or blended with petrol
  - Methanol as fuel for competitive motorsports including dragsters and monster trucks

Oxidation of Alcohols

- Acidified potassium dichromate (VI) or potassium manganate (VII) can be used for the oxidation of alcohols.
  - When using $KCr_2O_7^{2-}$, orange Cr (VI) is reduced to green Cr (III)
- A range of compounds will oxidize them so the oxidizer is often represented as [O]

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

- The oxidation products of alcohols depend on the types of alcohols involved.

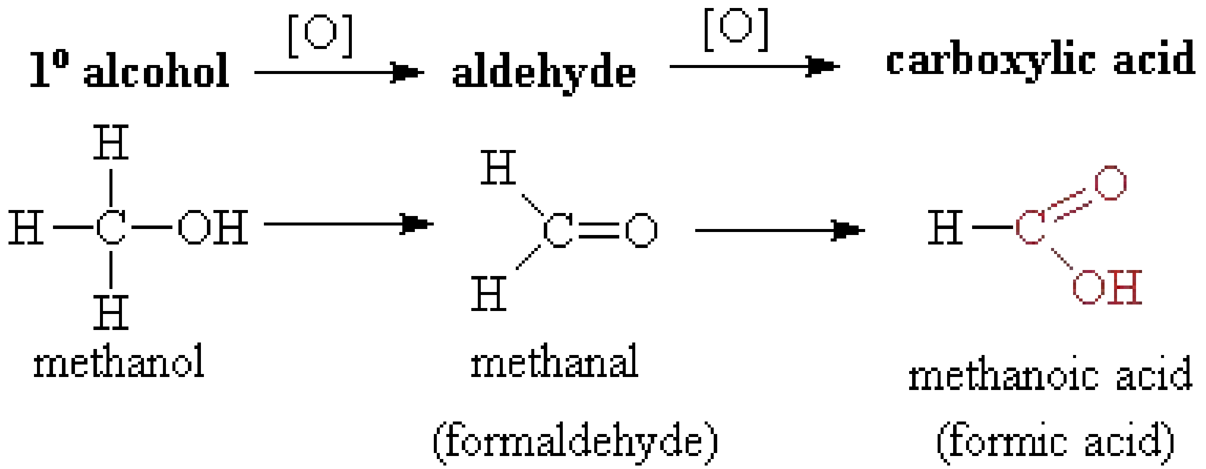
Main

Utilization

- Breathalyzer test: blow into bag through tube of acidified $K_2Cr_2O_7$ crystals. If orange crystals turn green, this indicates presence of a lot of ethanol (high BAC).

Oxidation of Primary Alcohols

- The oxidation of a primary alcohol is a two-stage process that first produces an aldehyde followed by a carboxylic acid.
- Potassium dichromate is a milder oxidizing agent than potassium manganate.
- When a primary alcohol is heated with acidified $K_2Cr_2O_7$ the aldehyde is produced



Main

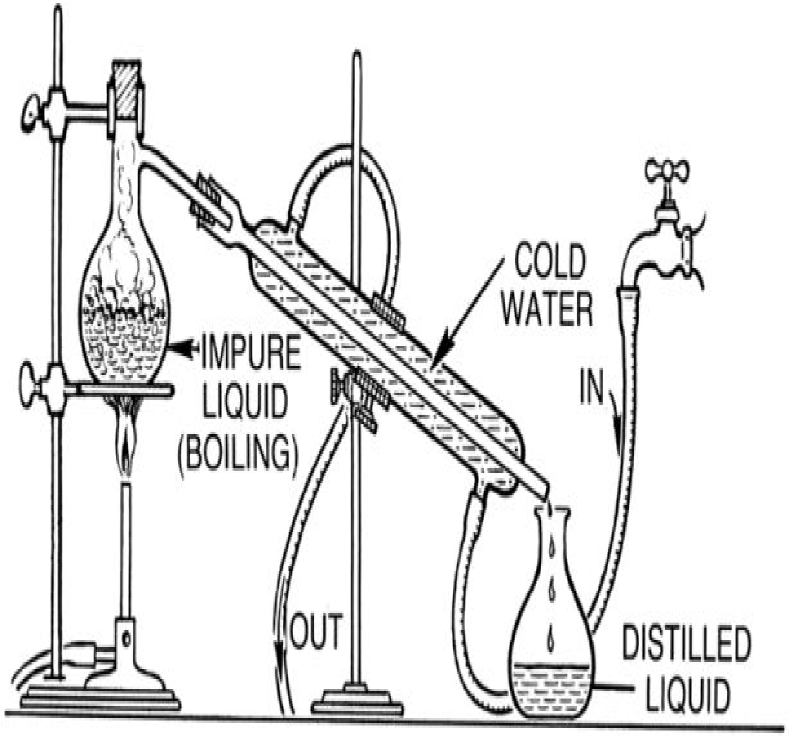
Oxidation of Primary Alcohols

- To stop rxn at aldehyde stage, distill aldehyde from the rxn mixture as soon as it is formed.
  - The aldehyde has a lower boiling point than carboxylic acid due to differences in IMF
  - Aldehydes: weak dipole-dipole
  - Carboxylic acids: hydrogen bonding

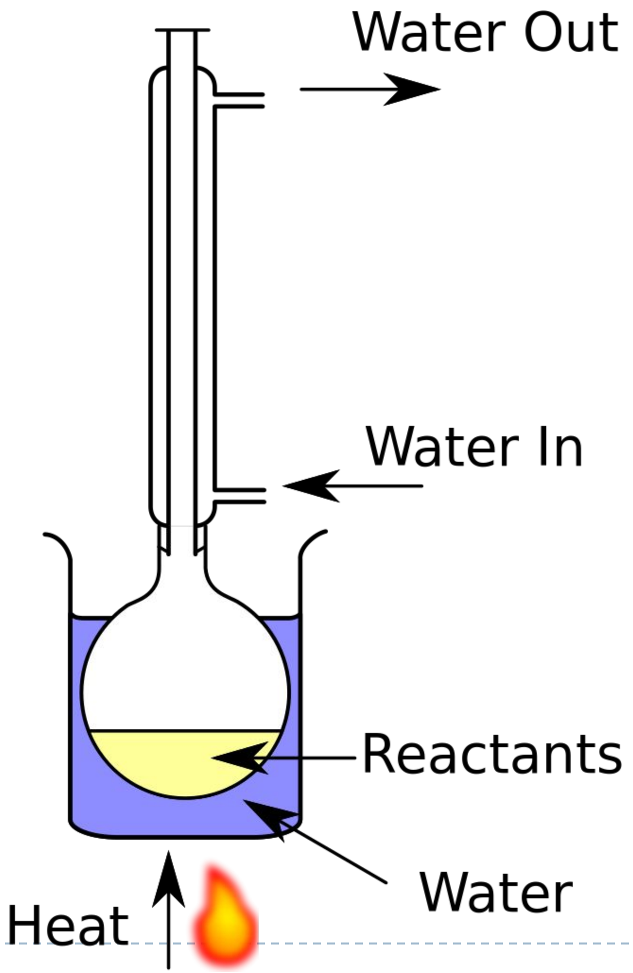
- If complete oxidation to carboxylic acid is desired, heat the mixture under reflux so that none of the carboxylic acid can escape.
  - Refluxing is a technique that involves the cyclic evaporation and condensation of a volatile reaction mixture, preserving the solvent as it does no evaporate

Oxidation

Distillation



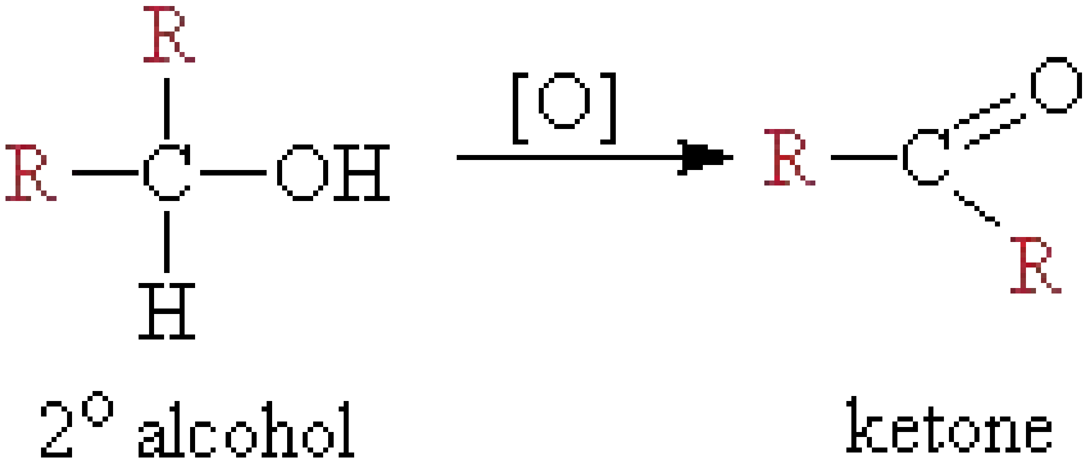
Reflux



Oxidation of Secondary Alcohols

- The oxidation of a secondary alcohol forms a ketone.

- No further oxidation is possible as the carbon atom of the functional group has no hydrogens attached to it.



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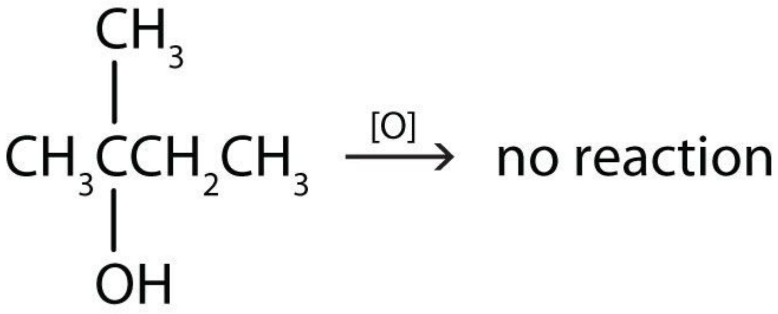
Oxidation of Tertiary Alcohols

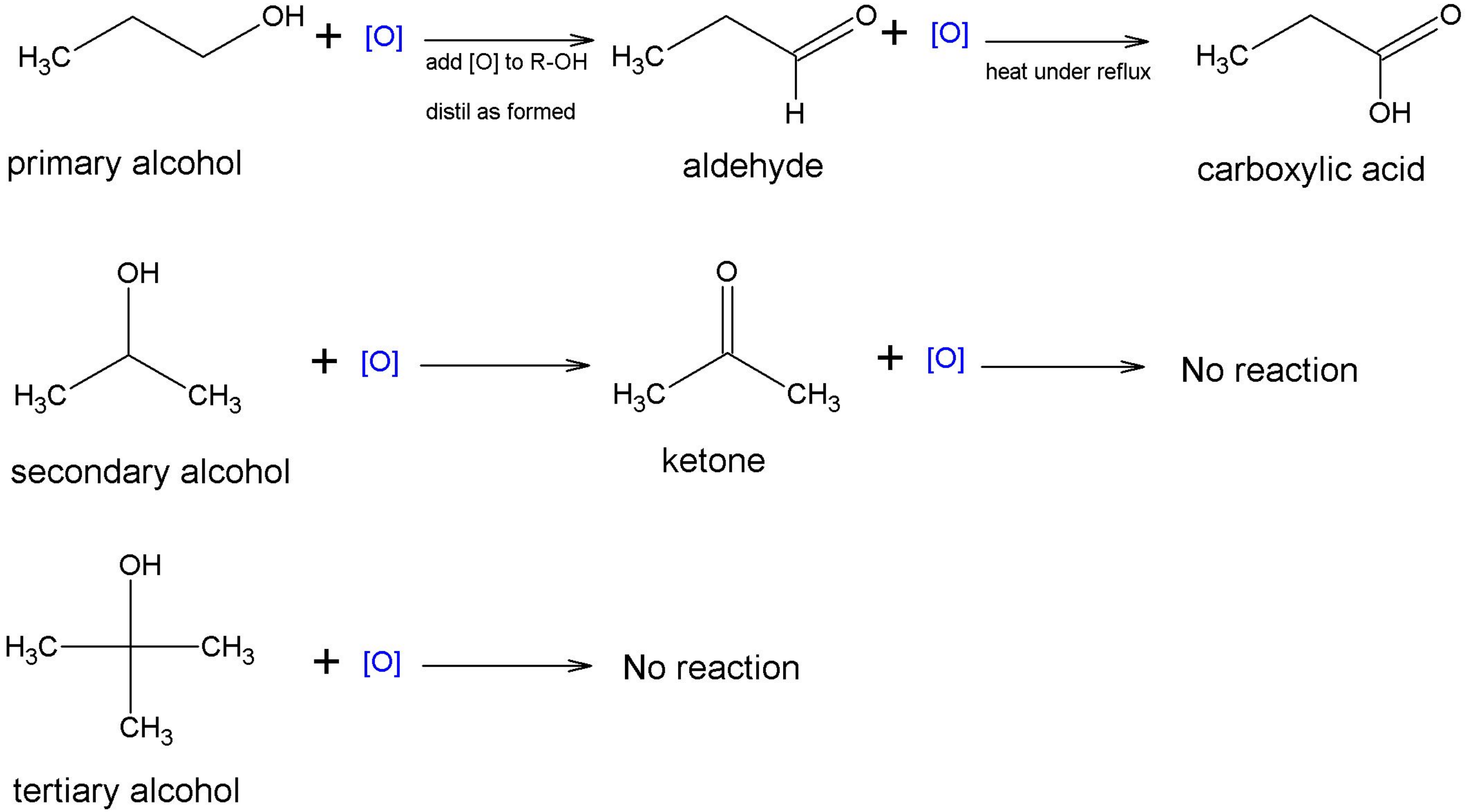
- Tertiary do not oxidize due to the 3 strong C-C bonds surrounding the –OH carbon



$$\mathrm{CH_3}\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\mathrm{CH_2CH_3} \xrightarrow{[\mathrm{O}]} \text{no reaction}$$

Main

Oxidation reaction scheme



Main

Esterification

- Esters are derived from carboxylic acids and have a variety of applications ranging from flavoring agents and medications to solvents and explosives

- Esterification is a reversible reaction that occurs when a carboxylic acid and an alcohol are heated in the presence of a catalyst, normally concentrated sulfuric acid.

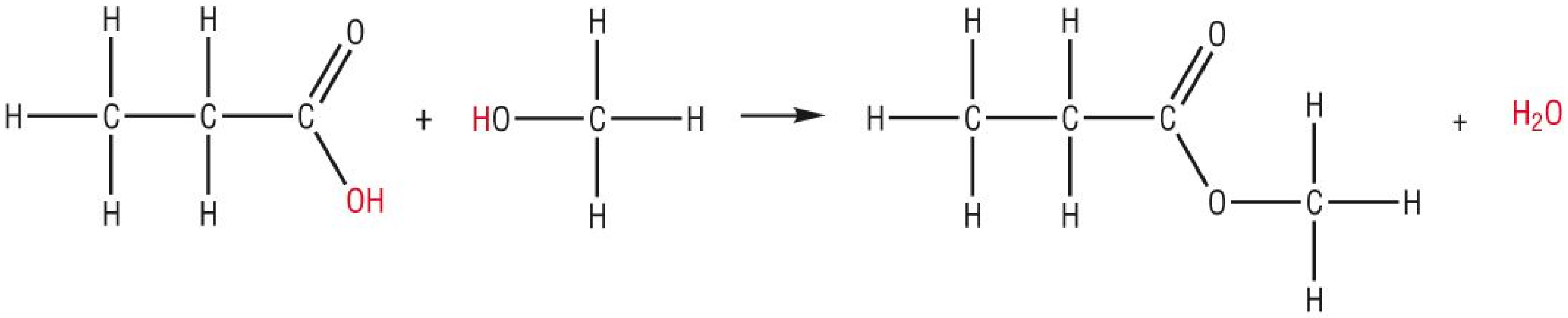
Main

Esterification

$$\text{Alcohol + carboxylic acid} \xrightarrow[\text{heat}]{\text{Conc } H_2SO_4} \text{ester + water}$$

$$CH_3CH_2COOH + CH_3OH \longrightarrow CH_3CH_2COOCH_3 + H_2O$$

Propanoic acid Methanol Methyl propanoate



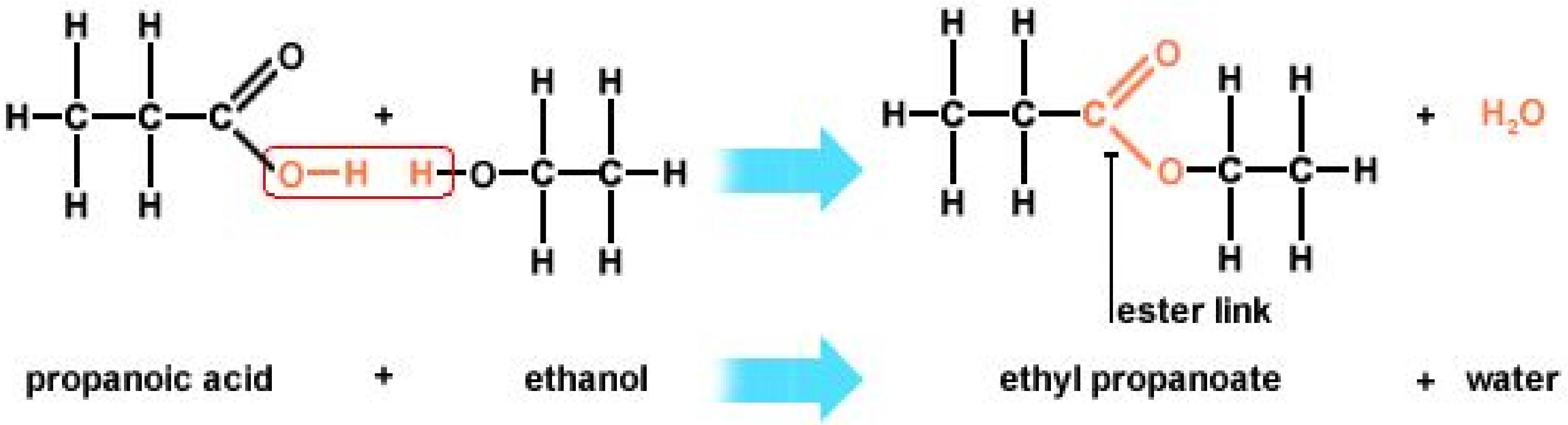
methylproponoate

-anoate is the suffix for esters

Methyl is derived from alcohol, methanol

-prop-signifies three carbons present in the carboxylic acid parent molecule

Main



- This reaction is described as a nucleophilic substitution
  - The alcohol acts as a nucleophile-substitutes (replaces) the OH group of the carboxylic acid
- The esterification reaction can be classified as a condensation reaction-two molecules join together

Main

Nucleophilic Substitution

- Halogenoalkanes are more reactive than alkanes. They can undergo (nucleophilic) substitution reactions.

- A nucleophile is an electron-rich species containing a lone pair that it donates to an electron-deficient carbon

- An aqueous solution of sodium hydroxide, NaOH(aq), contains the nucleophile ••OH^-

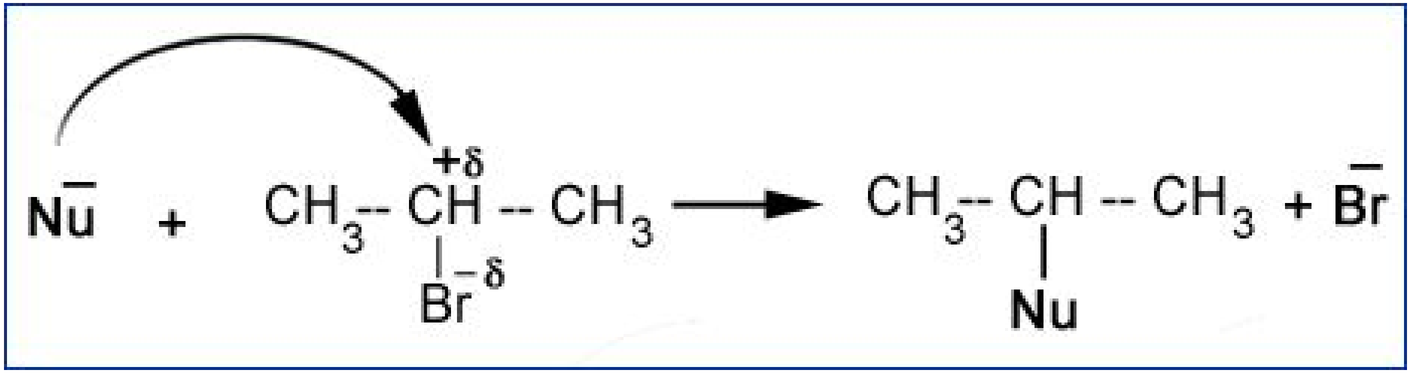
- The partial positive charge on the carbon atom in the C-X bond makes it susceptible to attack by the hydroxide ion.

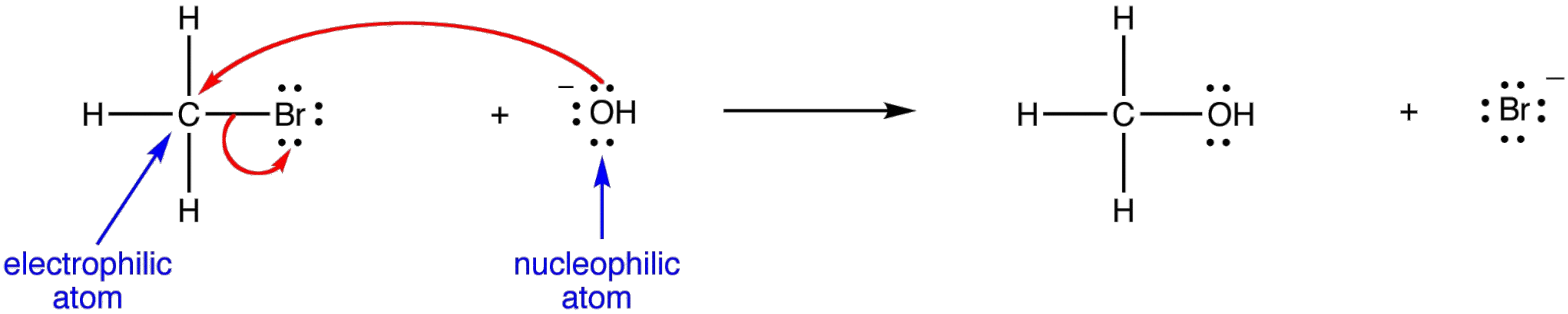
- The substitution of the halogen atom by the nucleophile will result in an alcohol being formed.

Main

Nucleophilic Substitution

- The mechanism that occurs depends on the class of halogenoalkane present

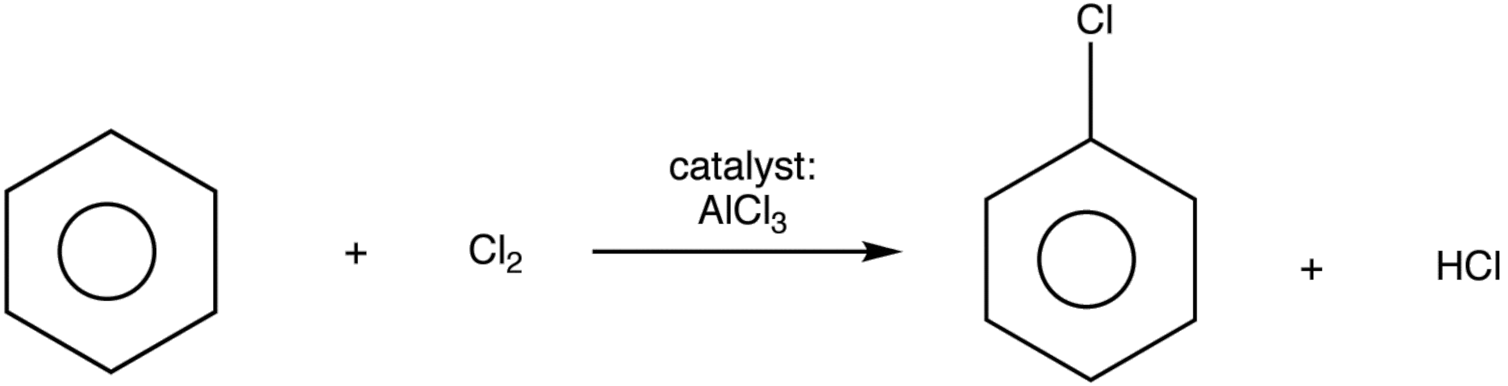




Main

Electrophilic Substitution

- Benzene does not readily undergo addition reactions, but will undergo electrophilic substitution reactions
- An electrophile is an electron-poor species capable of accepting an electron pair.
- While electron-poor electrophiles are attracted to the π electrons in the aromatic benzene ring, the stability of the ring leads to substitution rather than addition.



TOK

- The label “organic chemistry” originates from a misconception that a vital force was needed to explain the chemistry of life. Can you think of examples where vocabulary has developed from similar misunderstandings? Can and should language ever be controlled to eliminate such problems?

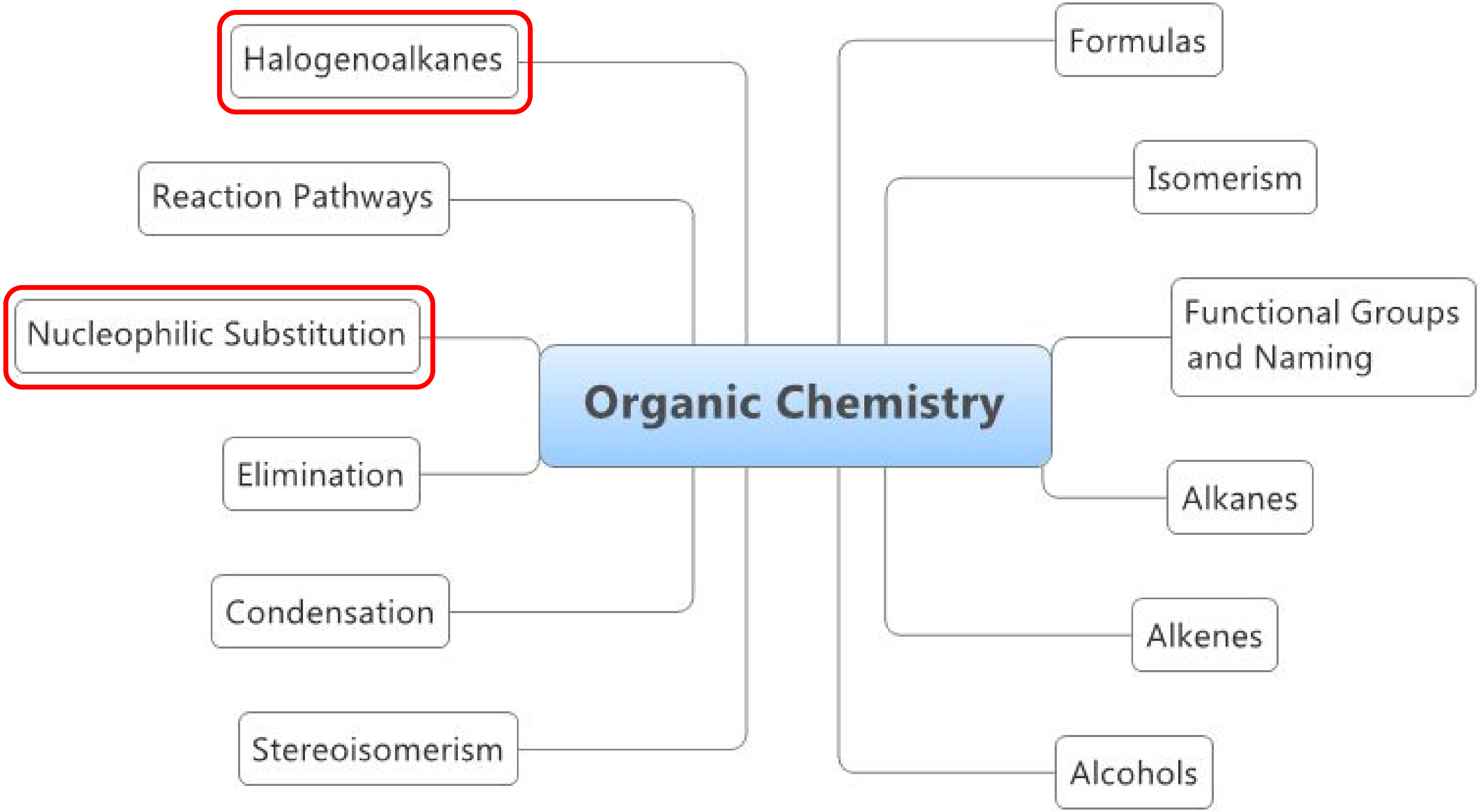
Main

Lesson 5

20.1 Types of Organic Reactions

Main Menu

We Are Here



Main

Nucleophilic Substitution

- One of the most important reactions undergone by halogenoalkanes is nucleophilic substitution

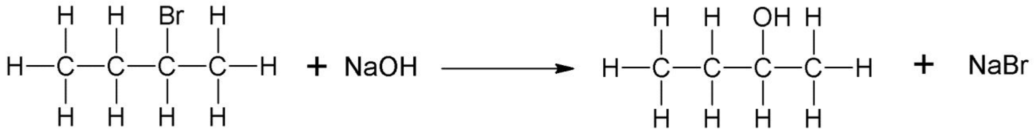
- A nucleophile is a ‘nucleus-loving’ species that is attracted to positive charges.
  - Nucleophiles have either full negative charges or delta-negative charges
  - Water and hydroxide are both nucleophiles
    - In this case we can also call the reaction ‘hydrolysis’

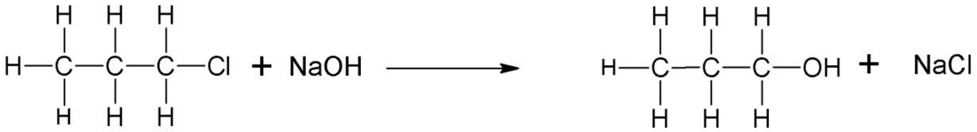
- The carbon in the carbon-halogen bond has a δ+ charge due to the greater electronegativity of the halogen
  - This makes it susceptible to attack by nucleophiles

Halogenoalkanes and strong bases

- A substitution reaction takes place, where the halogen atom is displaced by the hydroxide ion

halogenoalkane + sodium hydroxide → alcohol + sodium chloride

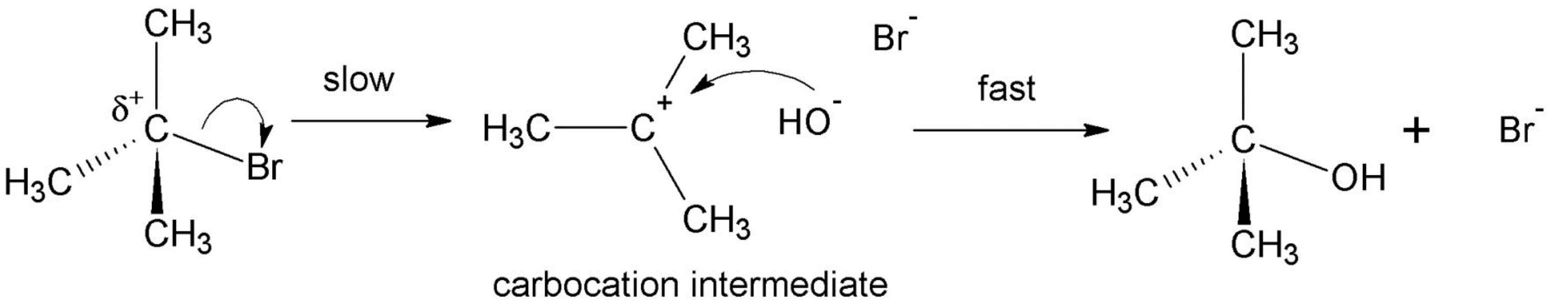




- Conditions:
  - Aqueous base
  - Gently warmed (can occur at room temperature, but may be quite slow)

- This is a nucleophilic substitution. (Also called a condensation reaction)
  - The C attached to the halogen is δ^+ due to the high electronegativity of the halogen
  - The OH^- ion (our nucleophile) is attracted to the δ^+ carbon
    - A nucleophile is a species with a negative charge or a lone pair that is attracted to positive/delta-positive atoms

S_N1 – Unimolecular nucleophilic substitution



- Unimolecular because only one molecule is involved in the rate determining step

- The rate determining step involves the spontaneous breaking of the carbon-halogen bond and is a **heterolytic fission**, forming a halide ion and a carbocation intermediate
  - The stability of the carbocation intermediate is a key factor in S_N1

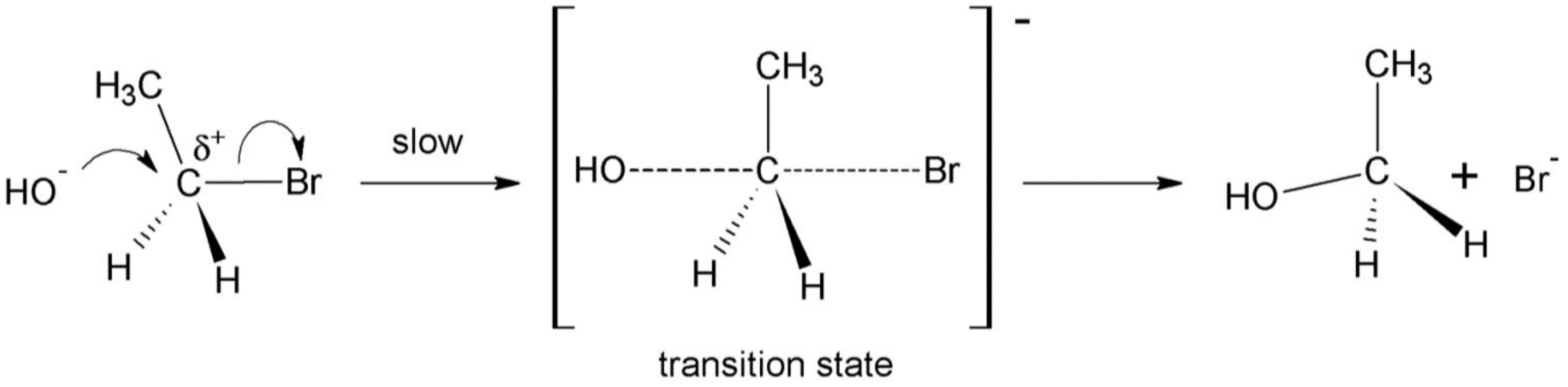
Note: the curly arrows show the movement of pairs of electrons

S_N1 – Unimolecular nucleophilic substitution

- The attack by the nucleophile (OH$^-$) is very fast, but does need the carbocation to be formed first
- The rate is only dependent on the concentration of the halogenoalkane:
  - Rate = k[halogenoalkane]
- Leaving group strength: **F^{-1} < Cl^{-1} < Br^{-1} < I^{-1}**
- S_N1 reactions are best conducted using protic, polar solvents.
  - Have H joing to N or O and can participate in hydrogen bonding. Able to solvate both negative ions and positive ions in solution.
  - Ex: Water, ethanol, and ammonia

Main

S_N2 – Bimolecular nucleophilic substitution



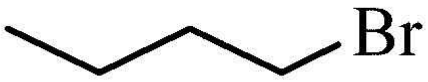
- Bimolecular because two molecules are involved in the rate determining step
- In the rate determining step, the nucleophile (OH^-) attacks at the same time as the carbon-halogen bond breaks.

S_N2 – Bimolecular nucleophilic substitution

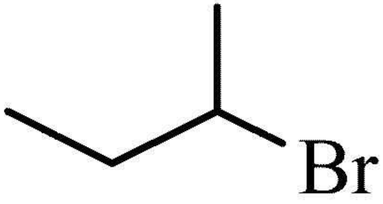
- The reaction passes through a negative transition state where the carbon has a 'half-bond' to both the –OH and the –Br with an overall negative charge
- The rate is dependent on both the concentration of the halogenoalkane and the nucleophile
  - Rate = k[halogenoalkane][nucleophile]
- S_N2 reactions are best conducted using aprotic, non-polar solvents
  - Do not have H atom joined to N or O and cannot participate in hydrogen bonding. Good at solvating positive ions but not negative ions
  - Ex: DMSO (dimehtyl sulfoxide), propanone
  - Act as proton donors

S_N1 or S_N2?

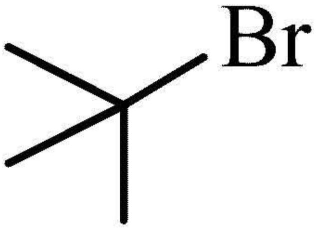
- 1° halogenoalkanes predominantly undergo S_N2



- 2° halogenoalkanes undergo a mix of S_N1 and S_N2



- 3° halogenoalkanes predominantly undergo S_N1



Main

Things to Remember

- OH^- is a better nucleophile than H_2O due to the negative charge on the hydroxide making it more ready to attack positive ions

Main

Understanding Check

- Write balanced equations, using condensed structural formulas, and name the products of the reactions of the following with dilute sodium hydroxide:
  - Bromoethane
  - 1-chloro-2-iodopropane
  - 3-chloro-3-ethylhexane

- Name and draw the mechanism for all 3.

Main

Refresh

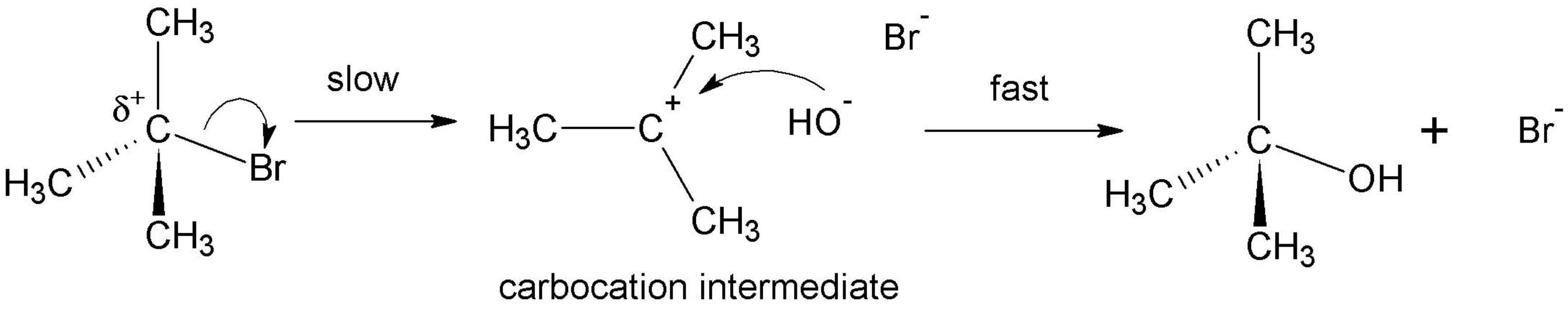
- Halogenoalkanes undergo substitution with strong bases to form alcohols

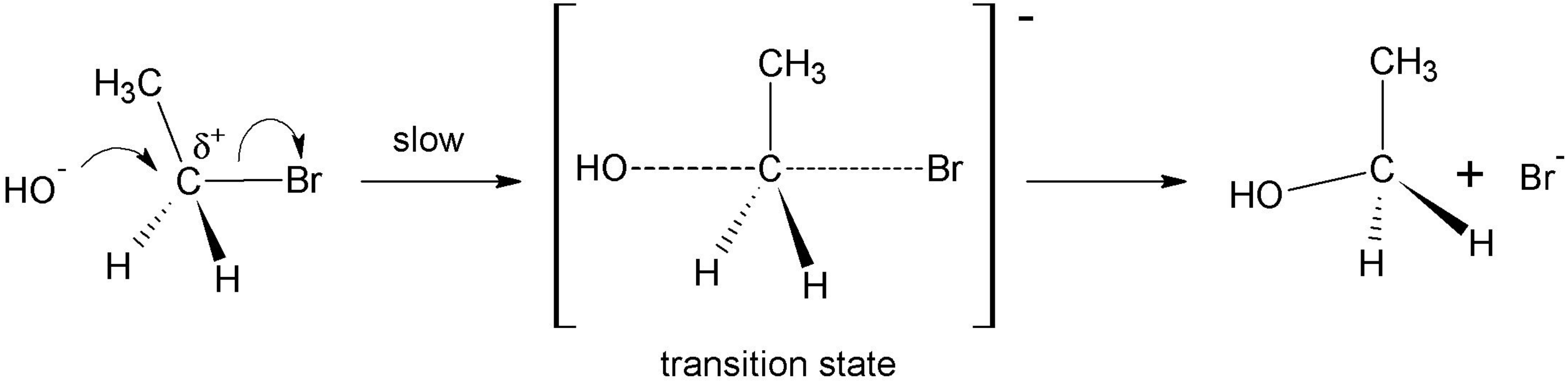
- The reaction has two possible mechanisms:
  - **S_N1**: the C-X bond breaks and then the nucleophile attacks
  - **S_N2**: the nucleophile attacks at the same time as the C-X bond breaks

- The mechanism depends on the halogenoalkane:
  - 1° - S_N2
  - 2° - S_N1 and S_N2
  - 3° - S_N1

Main

S_N1 and S_N2 Recap



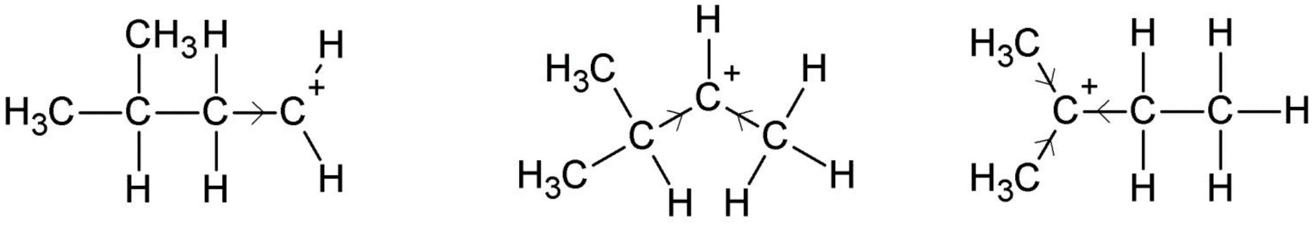


Main

S_N1 and the carbocation

- The carbocation is an unstable species, and will often immediately attract the halide ion straight back

- Alkyl groups surrounding the carbocation donate electron charge to it and stabilise it



primary secondary tertiary

- In thi ge donated by the surrounding alkyl groups

- 3° carbocations have most surrounding alkyl groups and therefore are most stable, thus S_N1 is preferred for 3° halogenoalkanes

Main

Mechanism and rate

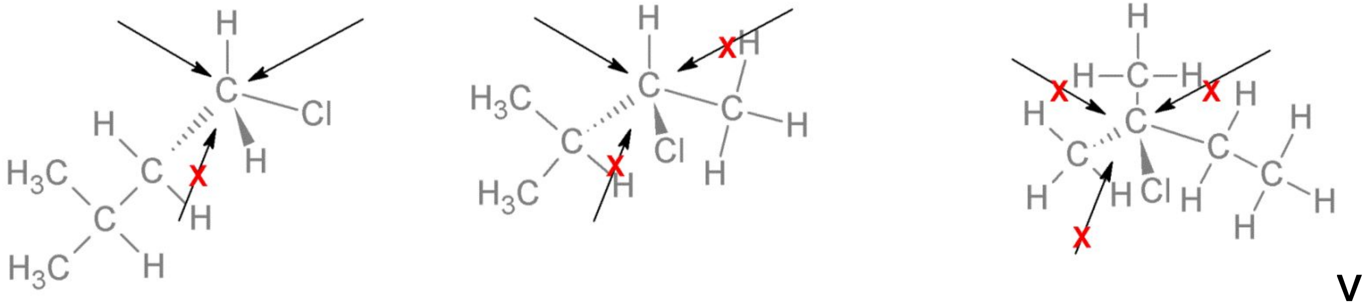
- For S_N1: rate = k[halogenoalkane]
- For S_N2: rate = k[halogenoalkane][nucleophile]
- Since S_N1 only depends on one reactant, it tends to be faster (all else being equal) than S_N2
- Therefore, if we consider the rates of hydrolysis / substitution, as a rule of thumb:

Tertiary > Secondary > Primary

Main

S_N2 and steric hindrance

- Alkyl groups are physically bulky, and make it difficult for a nucleophile to attack the carbon: this is called steric hindrance
- 1° halogenoalkanes only have one surrounding alkyl group so steric hindrance is low and SN2 is favourable
- 3° halogenoalkanes have three surrounding alkyl groups so steric hindrance is high and SN2 is unfavourable



primary secondary tertiary

- The l venues of ap blocked

Changing the Nucleophile

- Water can act as our nucleophile:
  - Halogenoalkane + water → alcohol + hydrogen halide

- However, hydroxide is much better. Why?

  - Explain why using ideas from the bonding unit

Changing the Halogen

- The rate of substitution / hydrolysis varies greatly depending on the halogen atom

- As a rule, with all else being equal, the rate changes as follows:

Iodine > Bromine > Chlorine

- Explain why using ideas from the bonding unit

Key Points

- The substitution mechanism followed depends on:
    - Stabilisation of the carbocation by surrounding alkyl groups
    - Steric hindrance of the carbocation by surrounding alkyl groups

- Hydroxide ions are better nucleophiles than water due to their strong negative charge

- Iodoalkanes react faster than chloroalkanes due to the C-I bond being weaker than the C-Cl bond

Main

Lesson 6

20.1 Types of Organic Reactions

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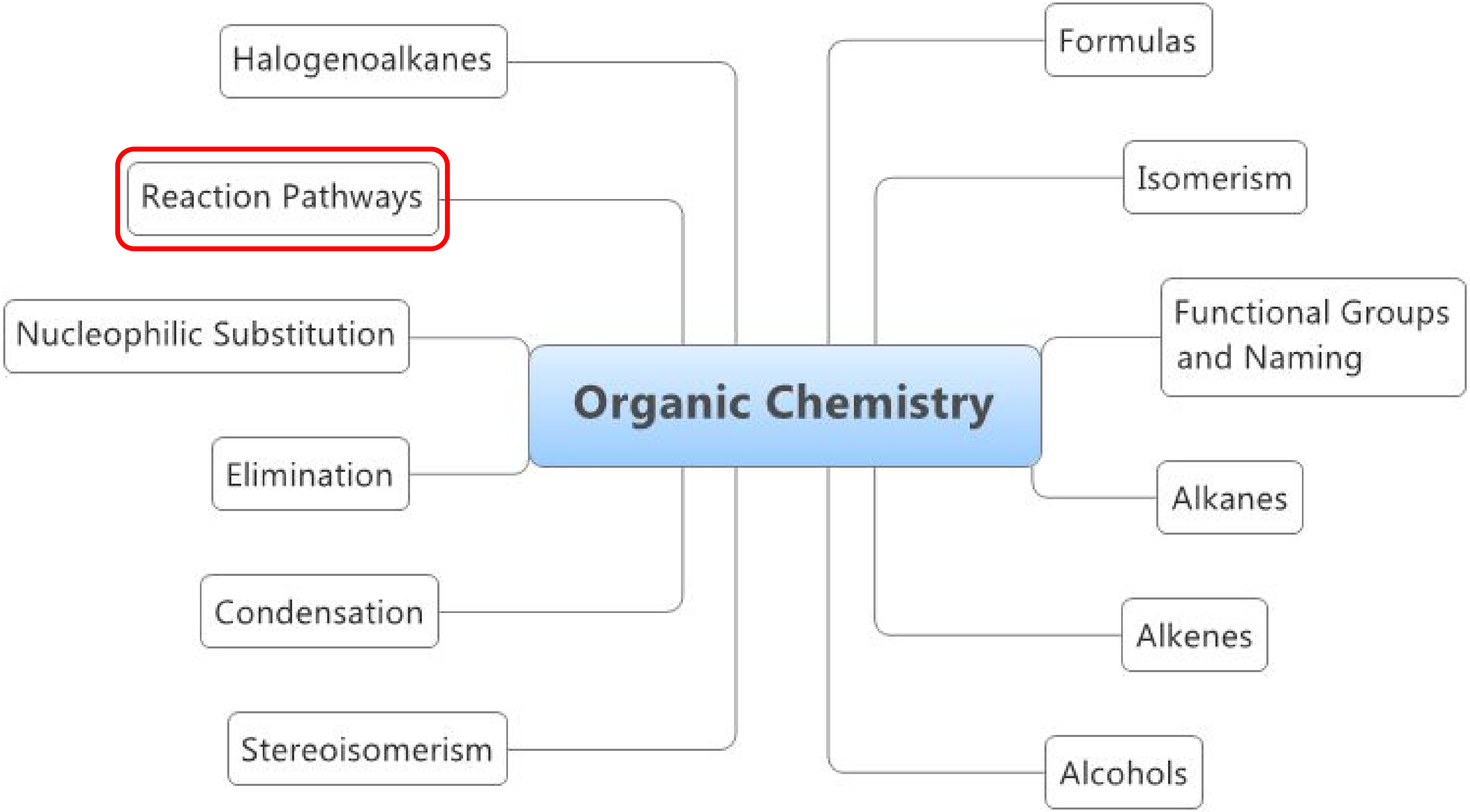


Organic Chemistry

Halogenoalkanes

Reaction Pathways

Nucleophilic Substitution

Elimination

Condensation

Stereoisomerism

Formulas

Isomerism

Functional Groups and Naming

Alkanes

Alkenes

Alcohols

Main

Electrophilic Addition Reactions

- An electrophile is an electron-deficient species that can accept electron pairs from a nucleophile. Electrophiles are Lewis acids.

- Markovnikov’s rule can be applied to predict the major product in electrophilic addition reactions of unsymmetrical alkenes with hydrogen halides and interhalogens. The formation of the major product can be explained in terms of the relative stability of possible carbocations in the reaction mechanism.

Main

Electrophilic Substitution Reactions

- Benzene is the simplest aromatic hydrocarbon compound (or arene) and has a delocalized structure of bonds around its ring. Each carbon to carbon bond has a bond order of 1.5. Benzene is susceptible to attack by electrophiles

Reduction Reactions

- Carboxylic acids can be reduced to primary alcohols (via the aldehyde). Ketones can be reduced to secondary alcohols. Typical reducing agents are lithium aluminium hydride (used to reduce carboxylic acids) and sodium borohydride.

Main

The Story of Benzene

A new hydrocarbon isolated by Michael Faraday in 1825

Carbon = 92% Carbon (Atomic mass = 12)

Hydrogen = ? % (Atomic mass = 1)

Relative molecular mass = 78.

Empirical Formula	**C**	**H**
%	92	100-92 = 8
% divided by RAM	92 / 12 = 7.67	8 / 1 = 8
Divide by smallest	7.67 / 7.67 = 1	8 / 7.67 = 1.04
Ratio	1	1

Main

Benzene

Molecular formula

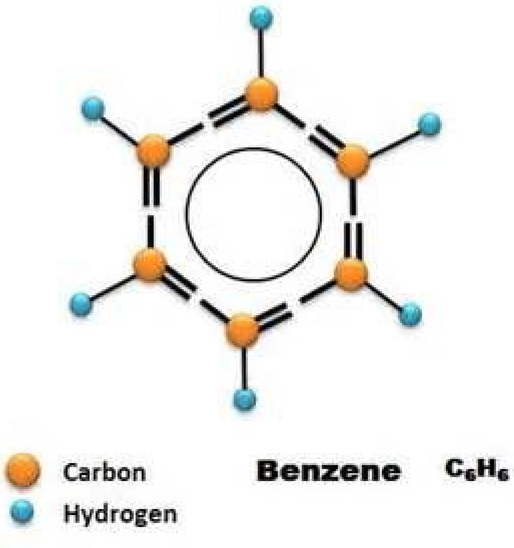
Known RAM / RMM of empirical formula

78 / (12 + 1) = 6

The empirical formula is CH and the molecular formula is C_6H_6 suggesting that the molecule contained a large number of double bonds.

Main

In 1865 after a dream about a snake biting its own tail, Kekulé suggested the following structure for benzene.



Main

Lack of Reactivity

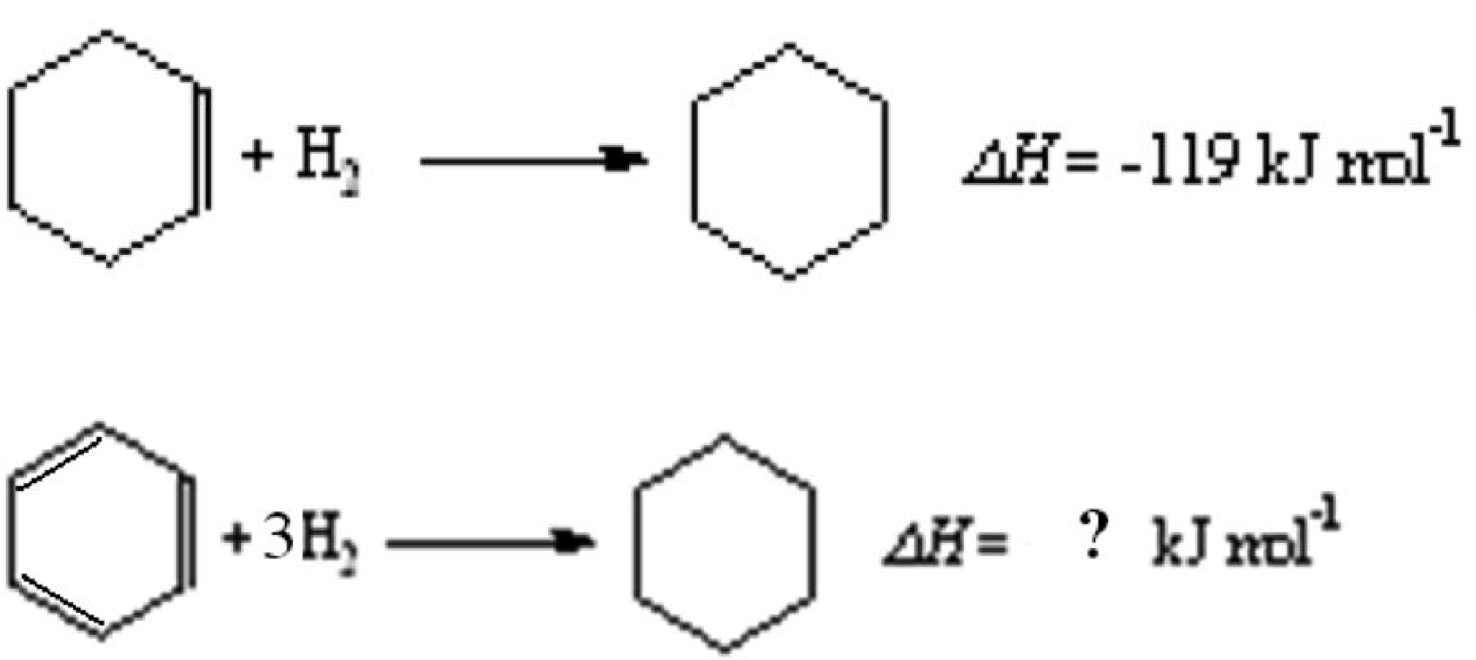
Chemists at the time were convinced that benzene (like other alkenes) should react with bromine in the dark at room temperature.

Observation: This did NOT happen with benzene.
Conclusion: Benzene more stable than a normal alkene

Main

Thermodynamic Stability

Enthalpy of **hydrogenation** (addition of hydrogen) to cyclohexene was found to be -119kJmol^{-1}



Main

Since three double bonds are present in benzene, then the comparable reaction should liberate 3 times the energy of cyclohexene

$= -(3 \times 119) = -357$ kJ mol^{-1}

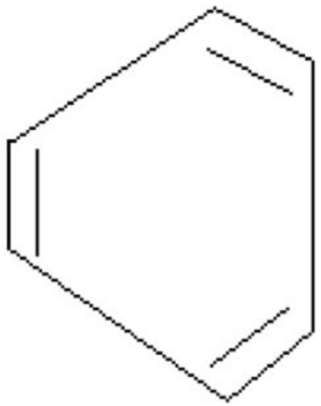
Experimentally determined value for the hydrogenation of benzene ΔH (hydrogenation) = -208kJ mol^{-1}

Benzene is more stable than predicted

Bond Lengths of Benzene

What benzene should look like

Bond lengths in single and double bonds should be different.



In benzene

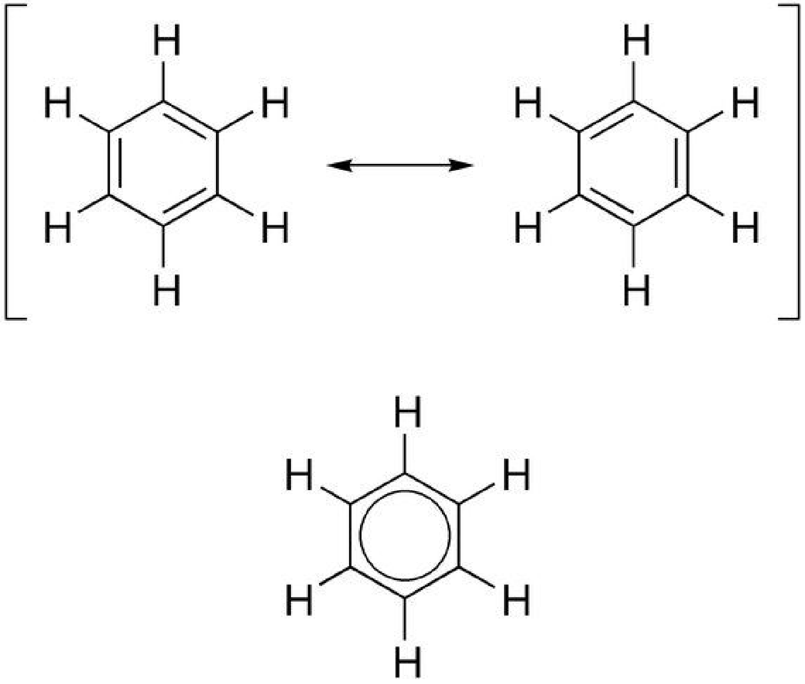
1. All bonds are of equal length

2. The bond length is between a double bond and a single bond.

Main

The bonds can’t be fixed

Resonance suggests the two structures rapidly alternate between the two forms.



Main

The resonance explanation suggests that Benzene is in such rapid equilibrium between the two forms; we detect a ‘blurred’ combination of the two forms.

The electrons from the double bonds are therefore drawn as a circle shared equally between the carbon atoms.

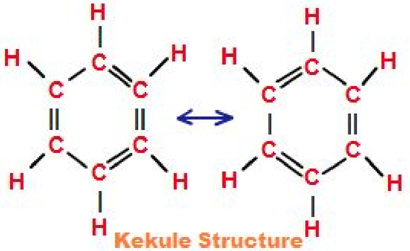
Main

***Valence bond theory** explains the bonding in benzene as a series of unhybridized p-orbitals which overlap forming a cloud of electron density above and below the molecule.*

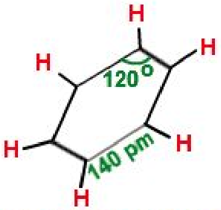
The spreading of electrons **STABILIZES** the molecule.

C_6H_6

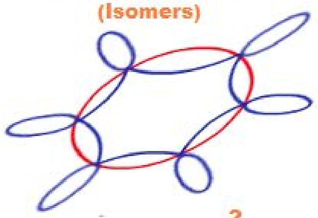
Benzene Moleculer formula



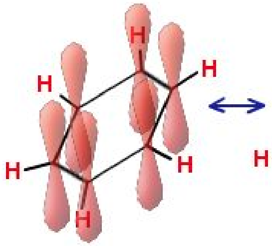
Kekule Structure (Isomers)



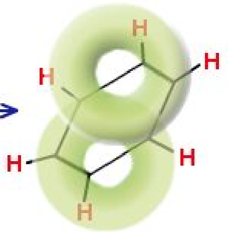
Planar Hexagon Bond Length 140 pm



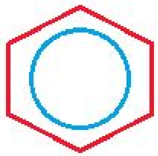
Sigma Bonds SP^2 Hybridized or orbitals



6p $_z$ Orbitals



delocaized pi system

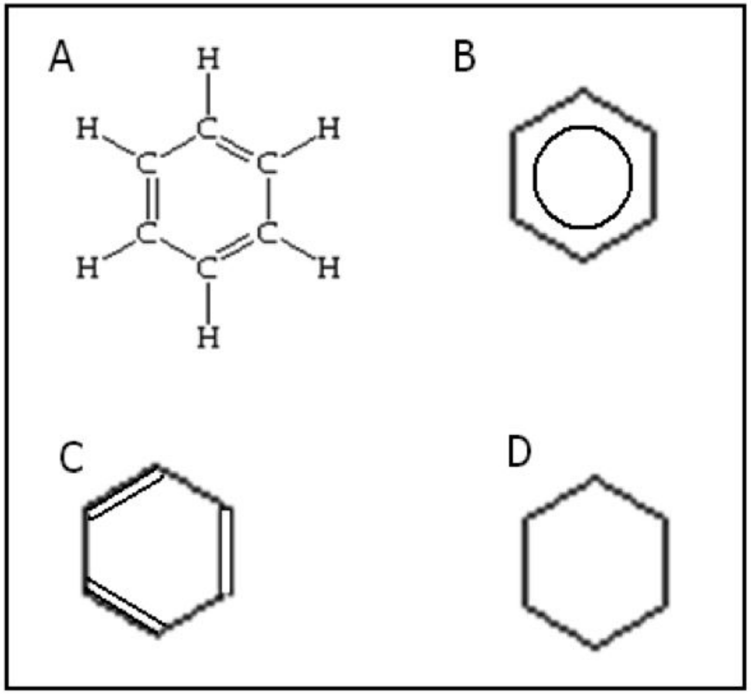


Benzene ring Simplified depiction

Main

Which drawing most accurately represents the structure and bonding in Benzene? Explain

Are any of the pictures completely incorrect? (i.e. not Benzene) if so which and why?

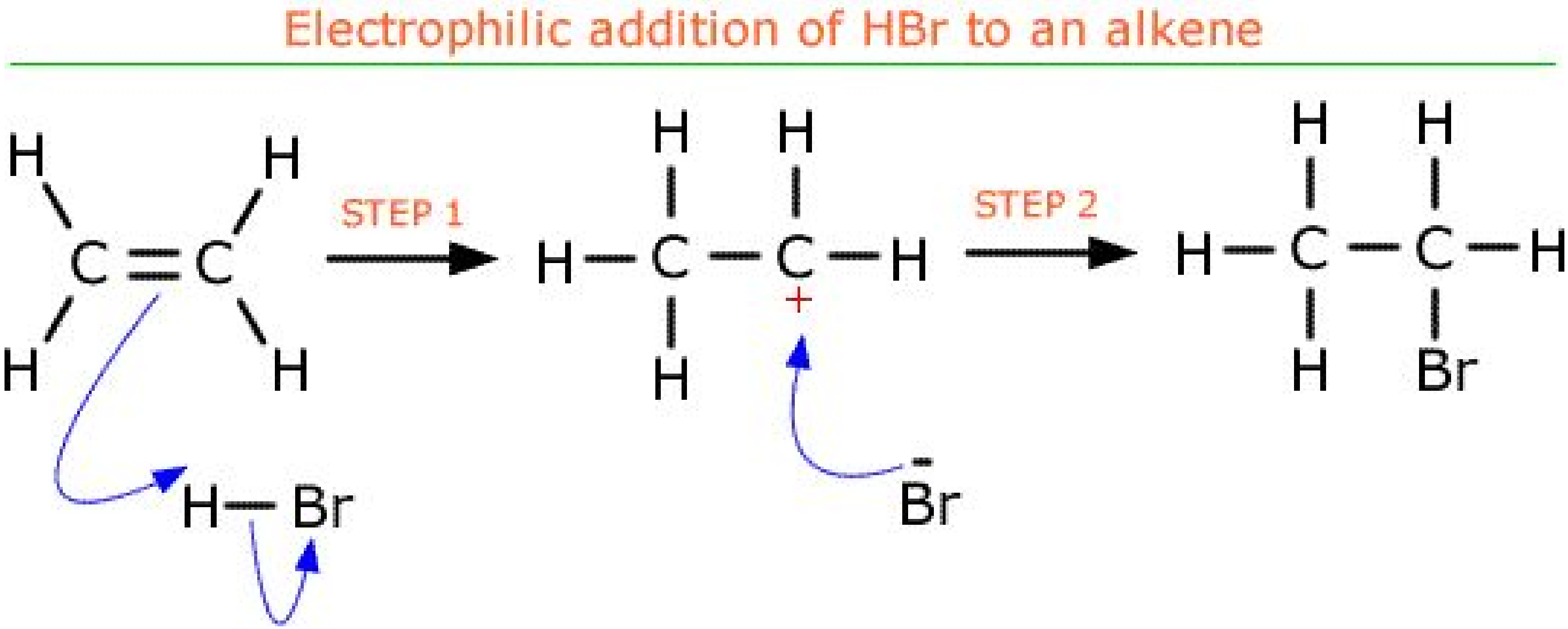


- ***D is incorrect (cyclohexane not benzene!)***
- ***A doesn't show delocalized electrons***
- ***Organic chemists tend to use B or C if they want to draw mechanisms***

Main

Electrophilic Addition Reaction of Alkene

- Deduction of the mechanism of the electrophilic addition reactions of alkenes with halogens/interhalogens and hydrogen halides.



Main

Electrophilic Addition Reaction of Alkene

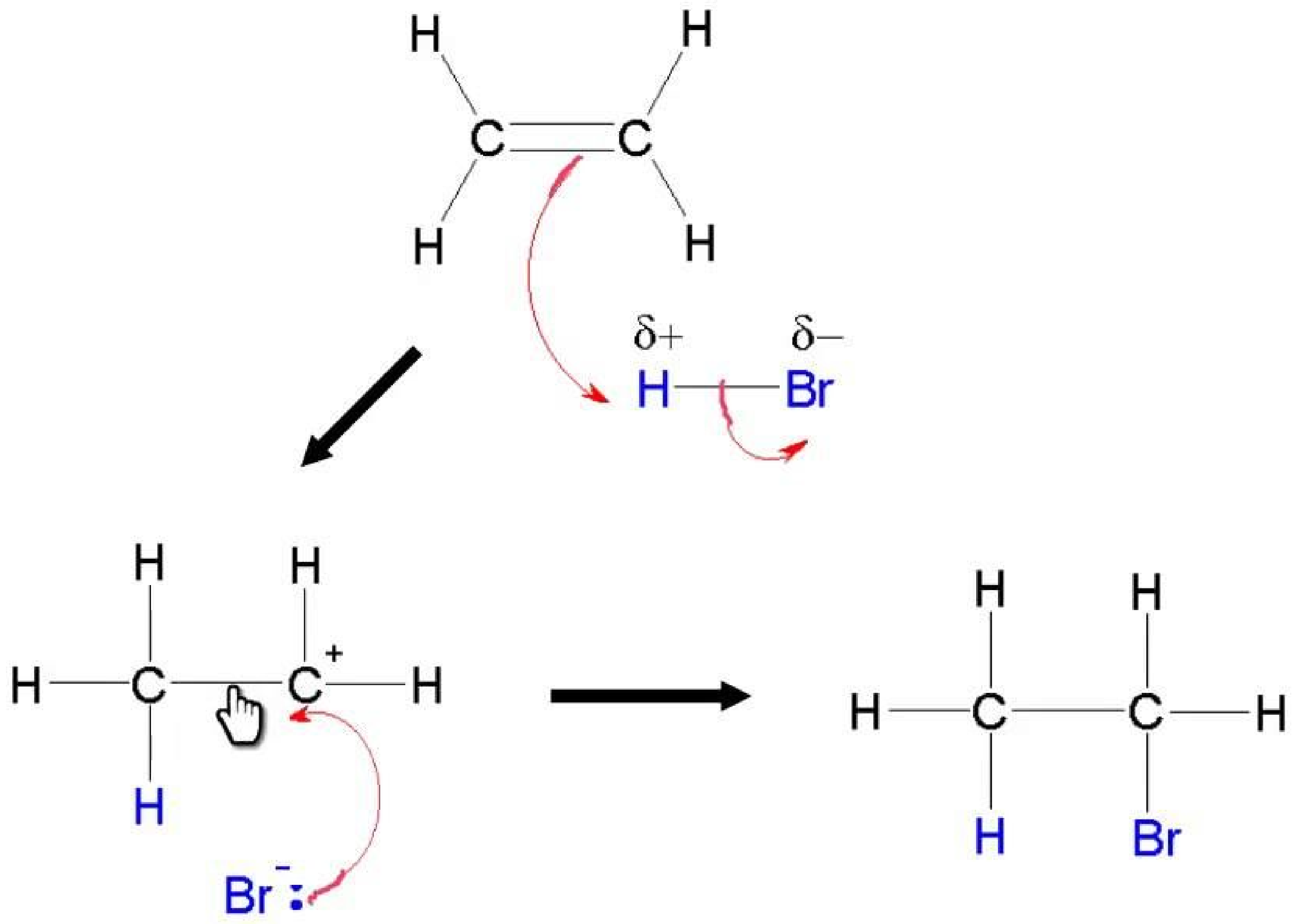
First Stage

- The positive charge of the electrophile is attracted to the electron density of the double bond.
- As the electrophile approaches the double bond electrons in the H-X are repelled towards the the X(halogen).
- The pi bond breaks, forming a carbocation-an ion with a positively charged carbon atom, while the H attaches and the halogen is left to form an ion
- The initial breaking of the H-X is called heterolytic fission

Electrophilic Addition Reaction of Alkene

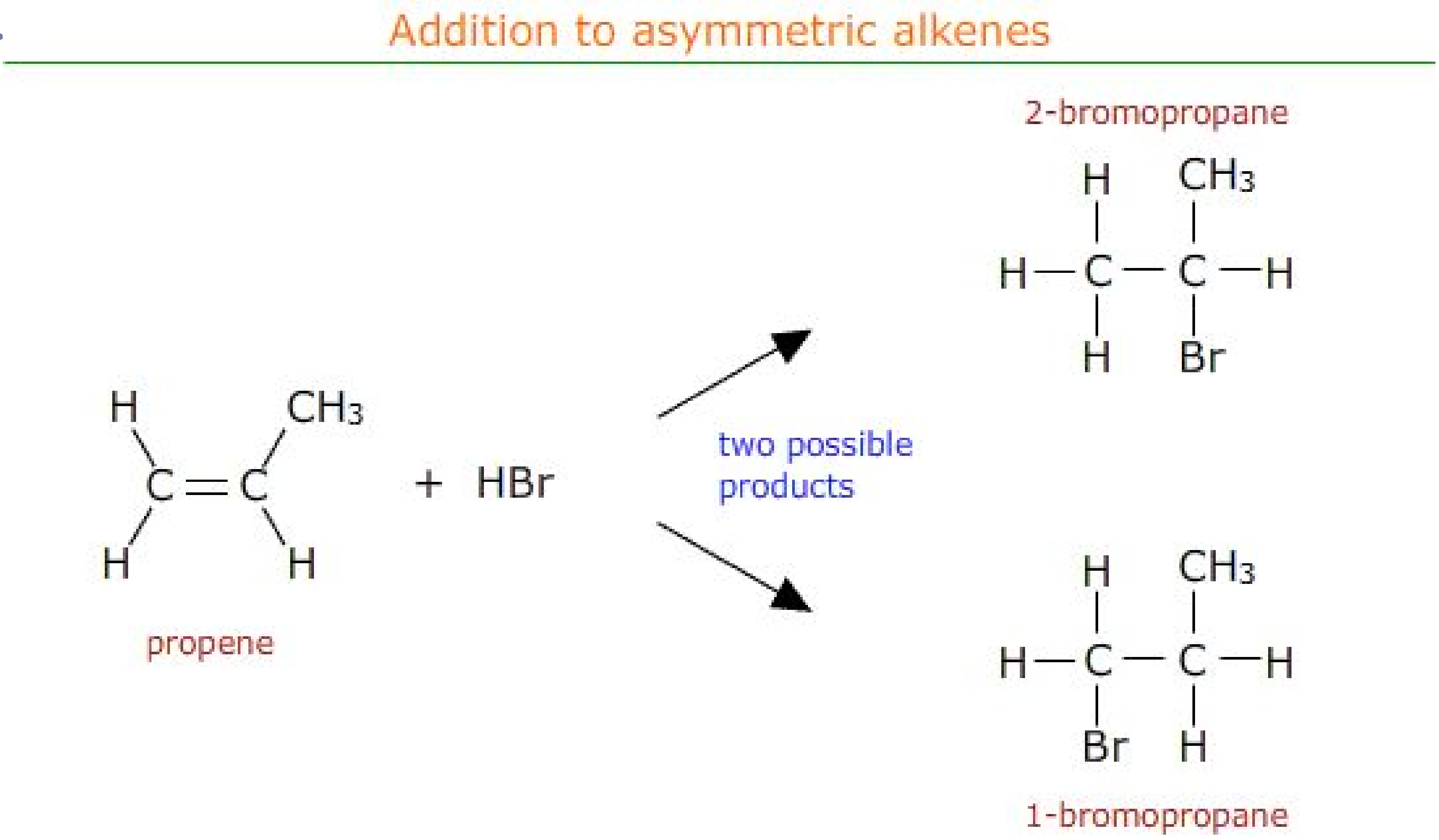
Second Stage

- The halogen act as a nucelophile and attacks the carbocation



Main

Asymmetric Alkenes



Addition to asymmetric alkenes

Main

Markovnikov's Rule

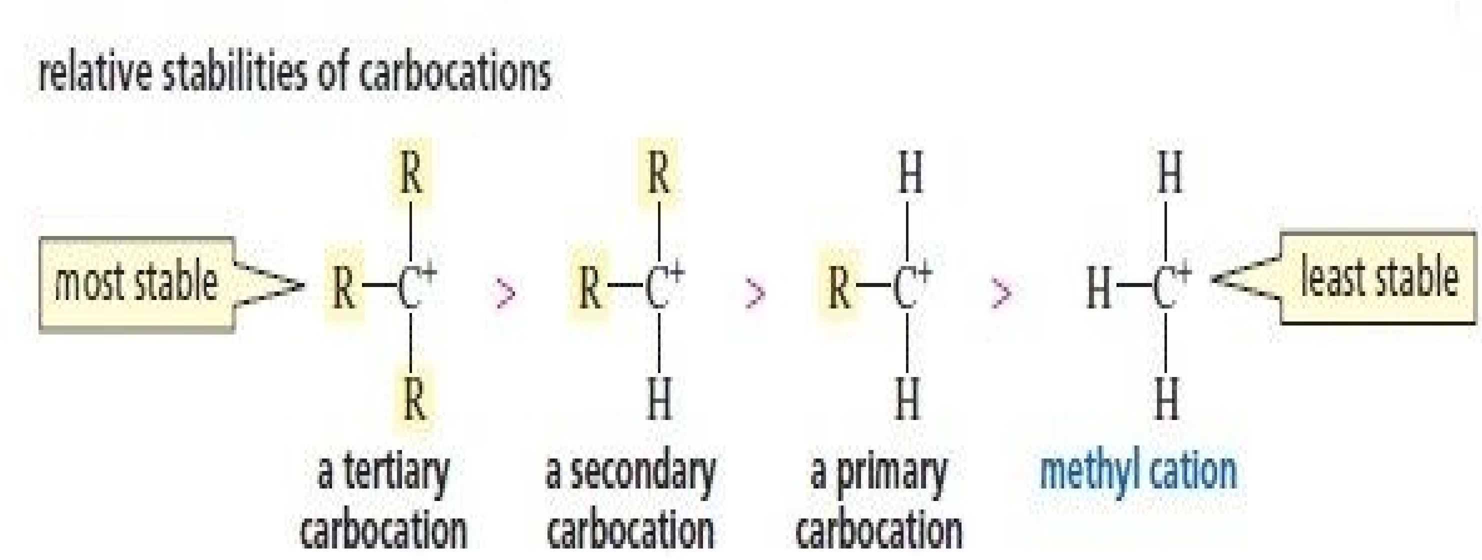
- The formation of the major product can be explained in terms of the relative stability of possible carbocations in the reaction mechanism.

- When H-X adds across the double bond of an alkene, the H atom becomes attached to the C atom that has the larger number of H atoms already attached

Main

Stability of Carbocations

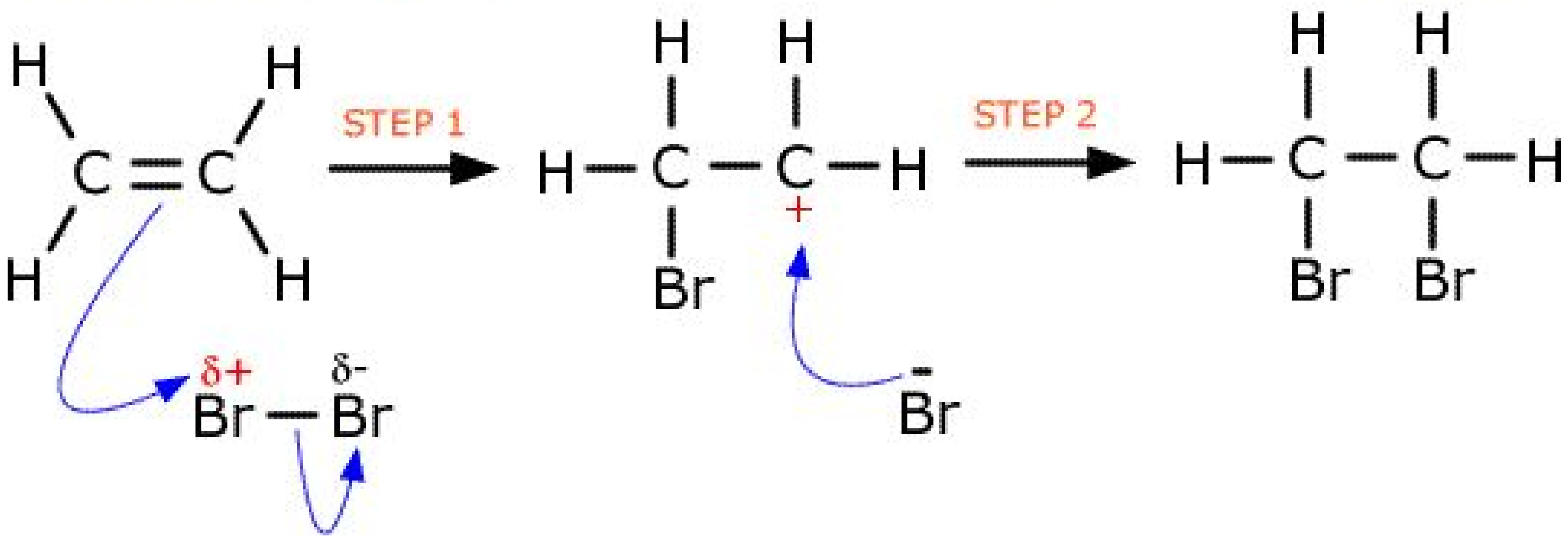
There are more electron releasing alkyl groups around the positively charged carbon



Main

Ethene with Br_2

Electrophilic addition of bromine to an alkene

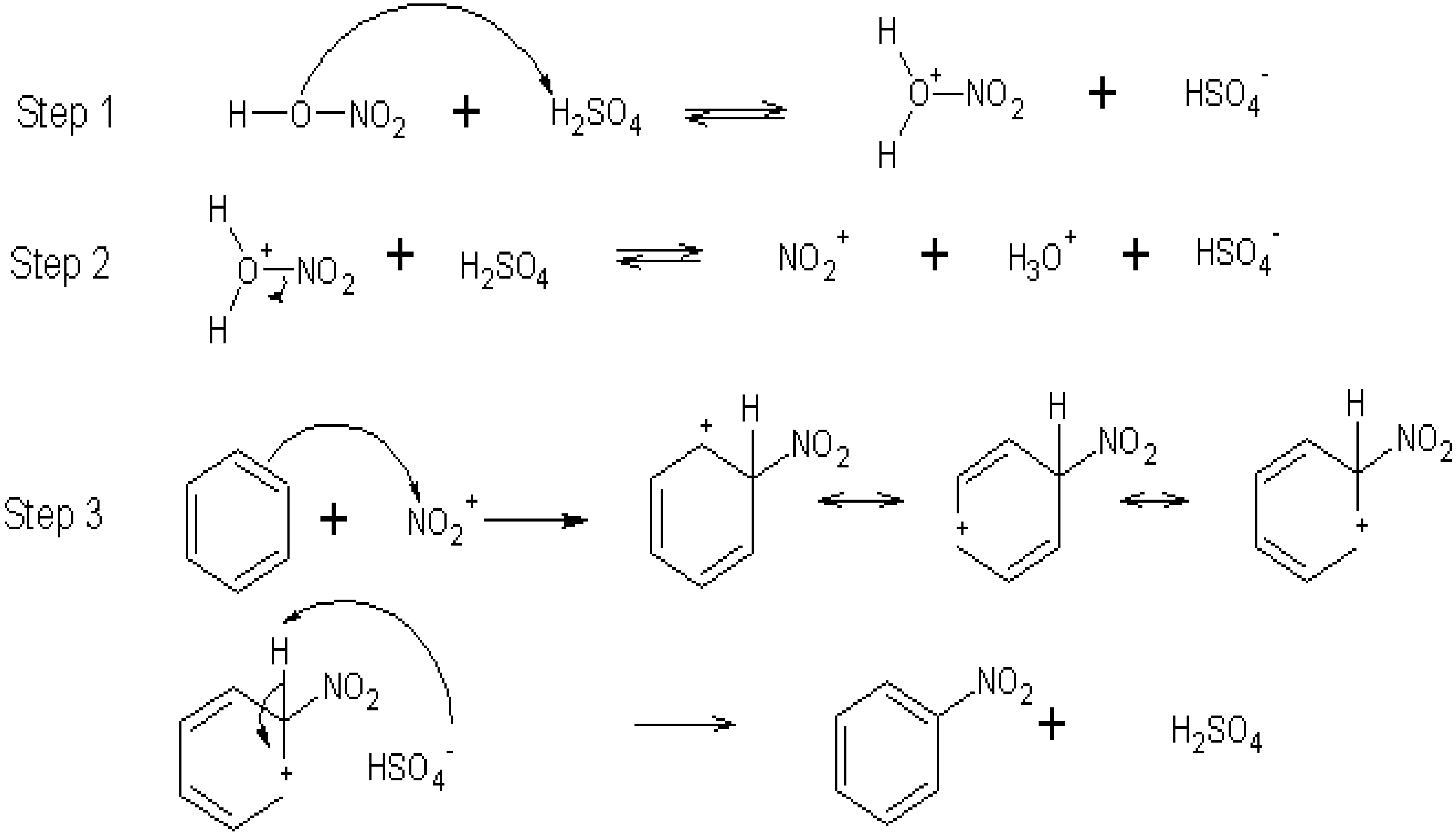


Main

Nitration of Benzene

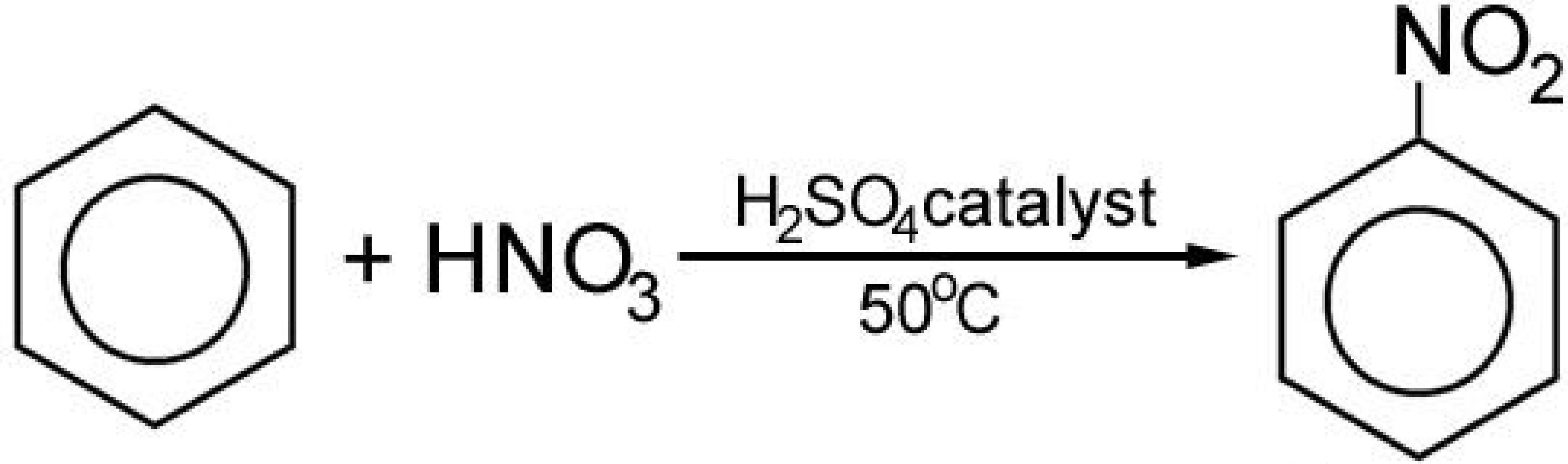
- Step 1: The formation of the electrophile-NO_2^+, which is formed when concentrated sulfuric acid reacts with concentrated nitric acid
  - a pair of electrons from the benzene π delocalized system is used to form a bond to the NO_2^+ electrophile
- Step 2: The collision between the benzene molcule and the electrophile
  - Releases a pair of electrons to restore the π delocalized system

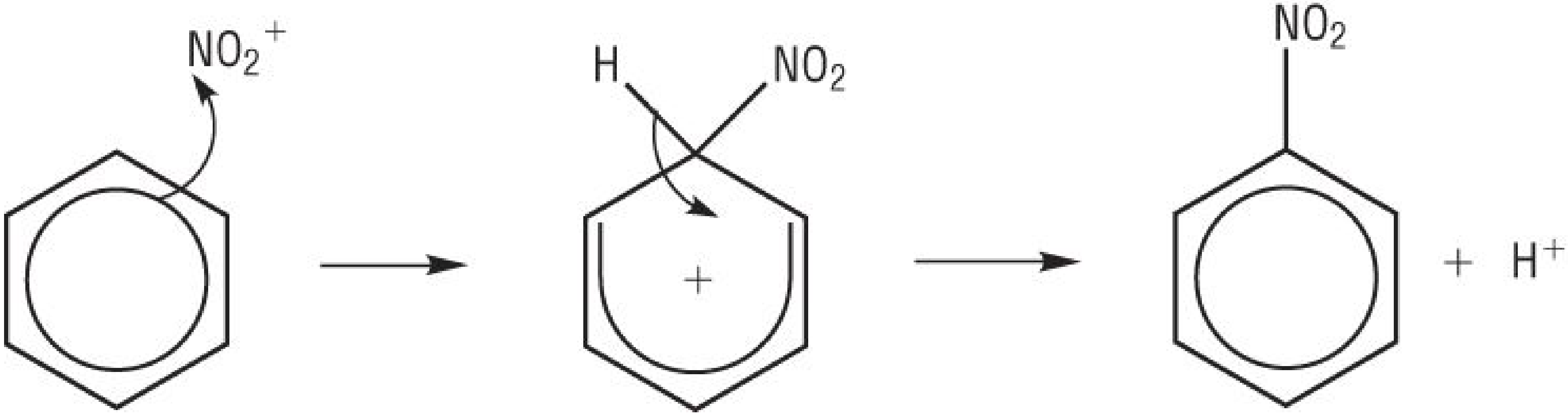
Main


Step 1
H—O—NO2 + H2SO4
H, O+—NO2, H + HSO4-
Step 2
H, O+—NO2, H + H2SO4
NO2+ + H3O+ + HSO4-
Step 3
+ NO2+
H, NO2, +
HSO4-
NO2 + H2SO4

Main

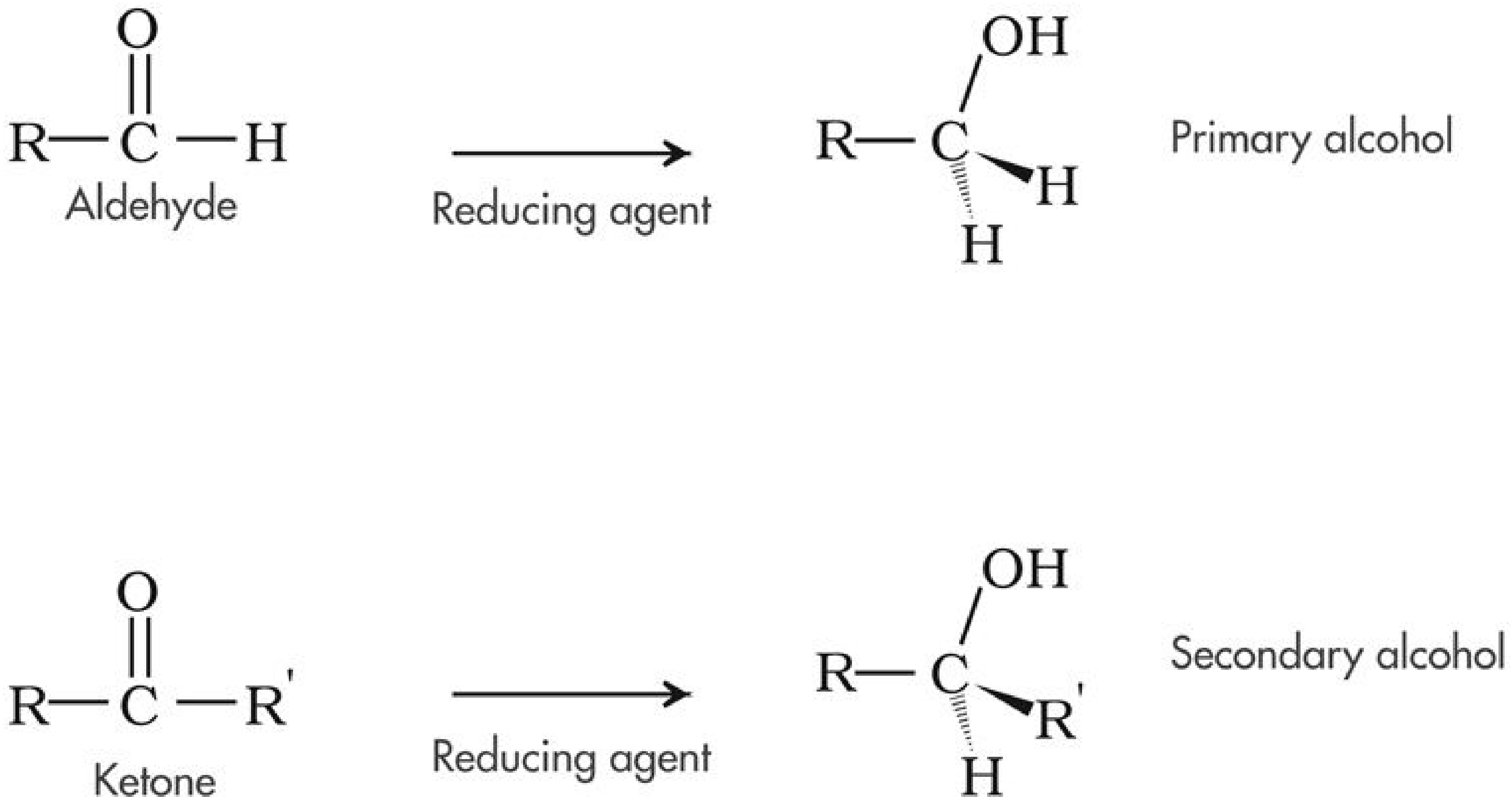
Nitration of Benzene





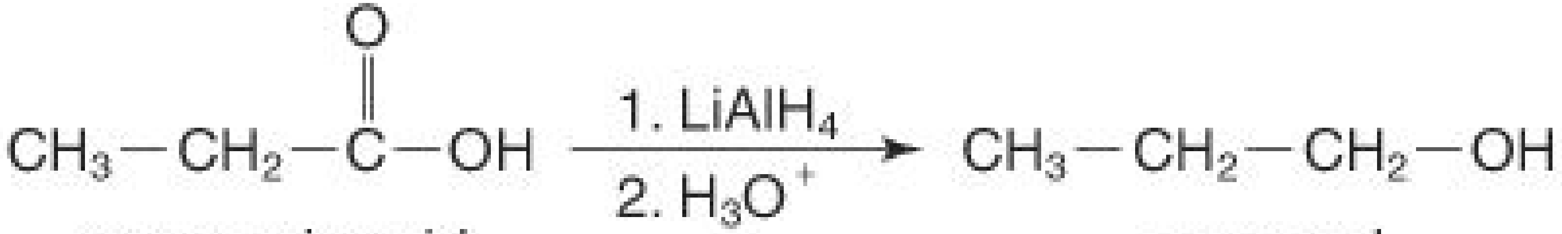
Main

Reduction Reactions



Main

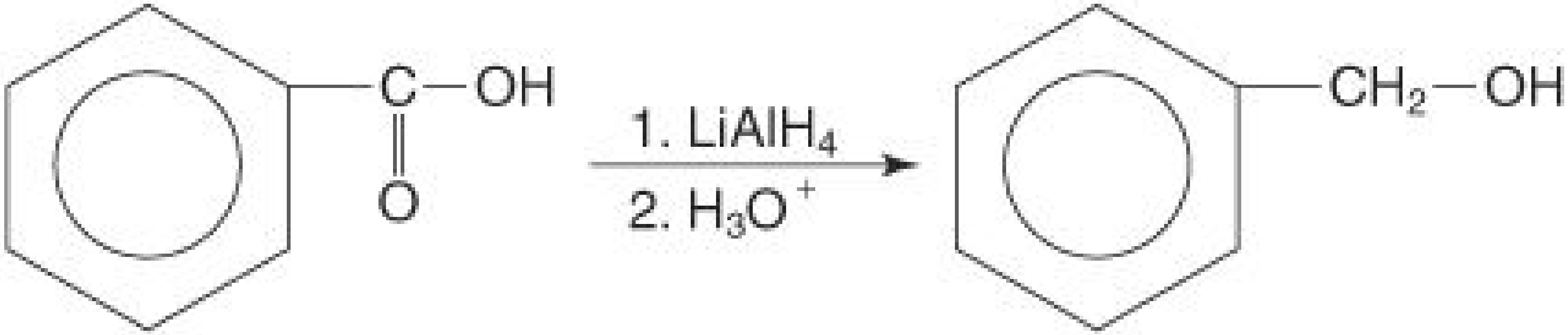
Reduction Reactions



$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} CH_3-CH_2-CH_2-OH$$

propanoic acid

propanol

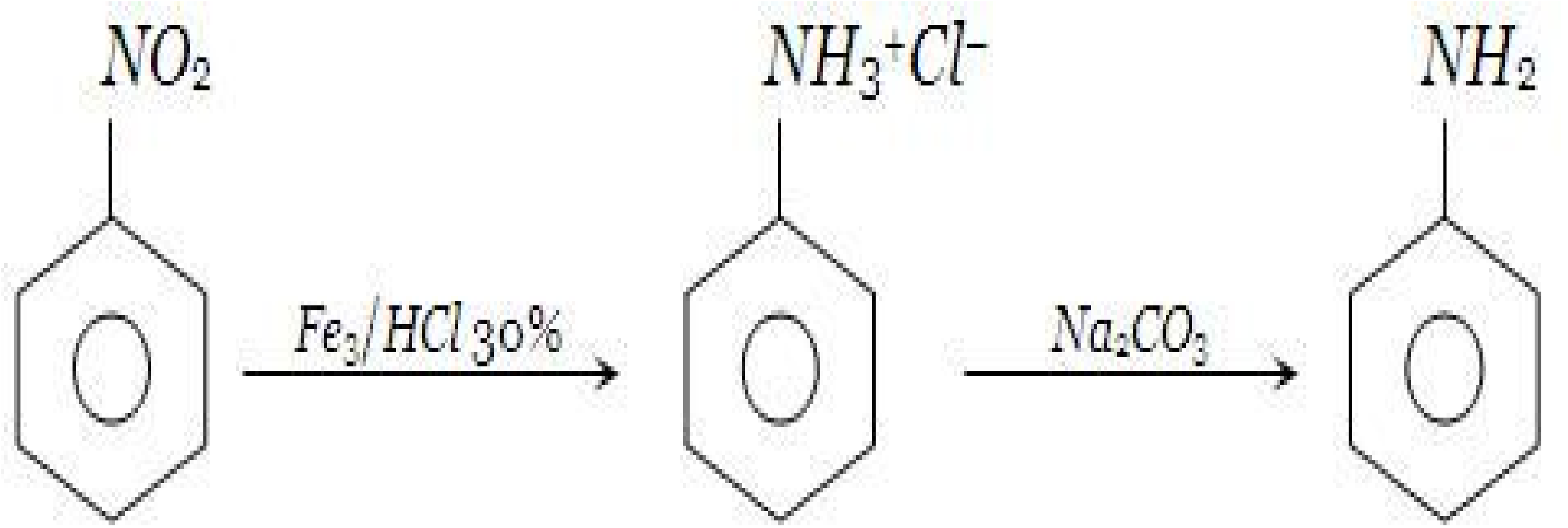


benzoic acid

benzyl alcohol

Main

Reduction Reactions



Main

Reduction Reaction Equations

When writing the equations for reduction reactions

$$\text{Reactant} + [\text{H}] \longrightarrow \text{Product}$$

The [H] represents the hydrogen from the reducing agent

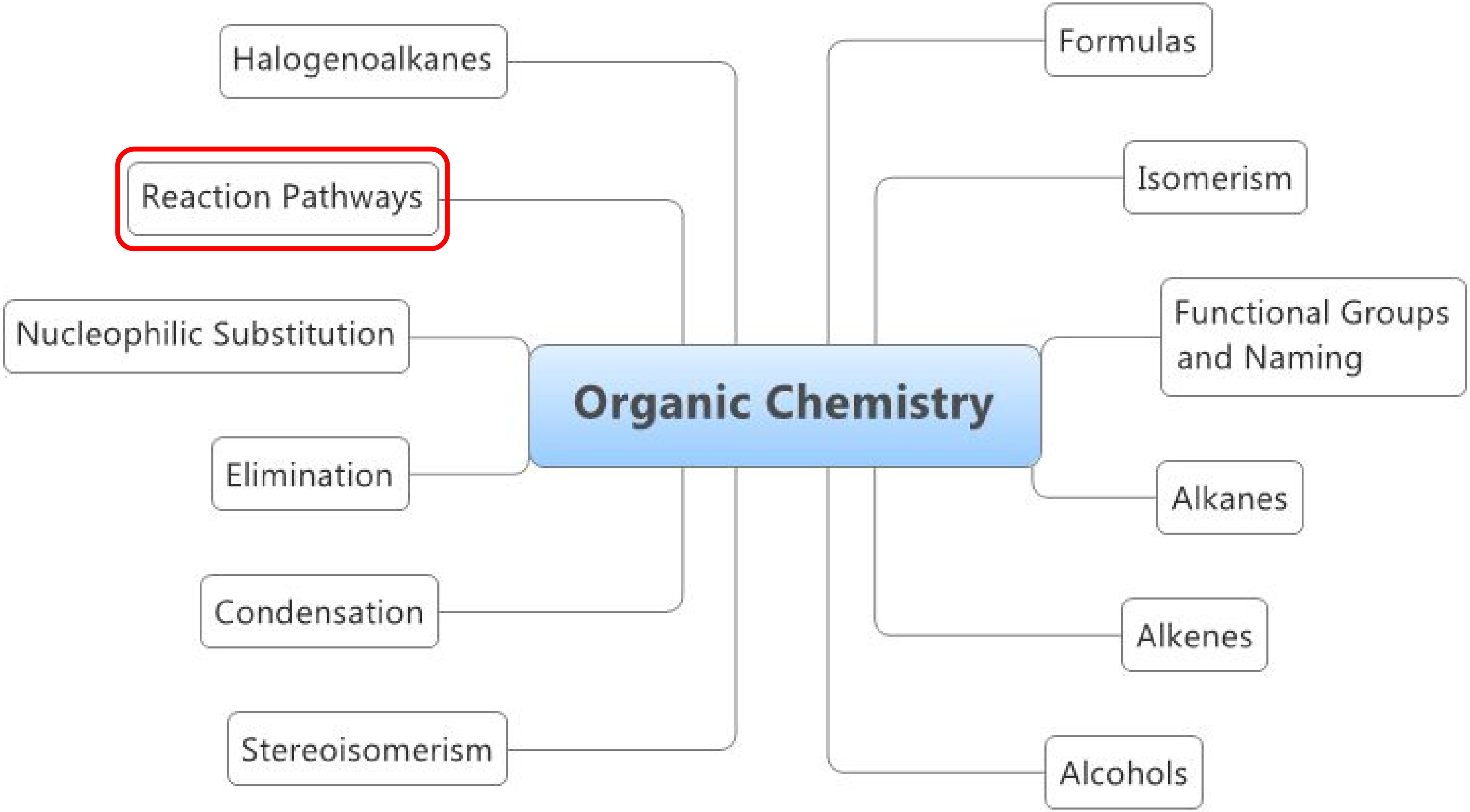
Balance as needed

Lesson 7

20.2 Synthetic Routes

Main
Menu

We Are Here



Organic Chemistry

Halogenoalkanes

Reaction Pathways

Nucleophilic Substitution

Elimination

Condensation

Stereoisomerism

Formulas

Isomerism

Functional Groups and Naming

Alkanes

Alkenes

Alcohols

Main

Synthetic Routes

- The synthesis of an organic compound stems from a readily available starting material via a series of discrete steps. Functional group interconversions are the basis of such synthetic routes

- A retro-synthetic approach is often used in the design of synthetic routes
  - Start with the target molecule and work backwards, using known reactions to get an appropriate and readily available starting material

- Conversions with more than four stages will not be assessed in synthetic routes

Main

Retro-Synthesis

Step 1:

- Draw the structural formula of both the starting compound and the desired product(s)
- Identify the functional group(s) present in the product

Step 2:

- List the possible reactions that would produce the desired functional group(s)

Retro-Synthesis

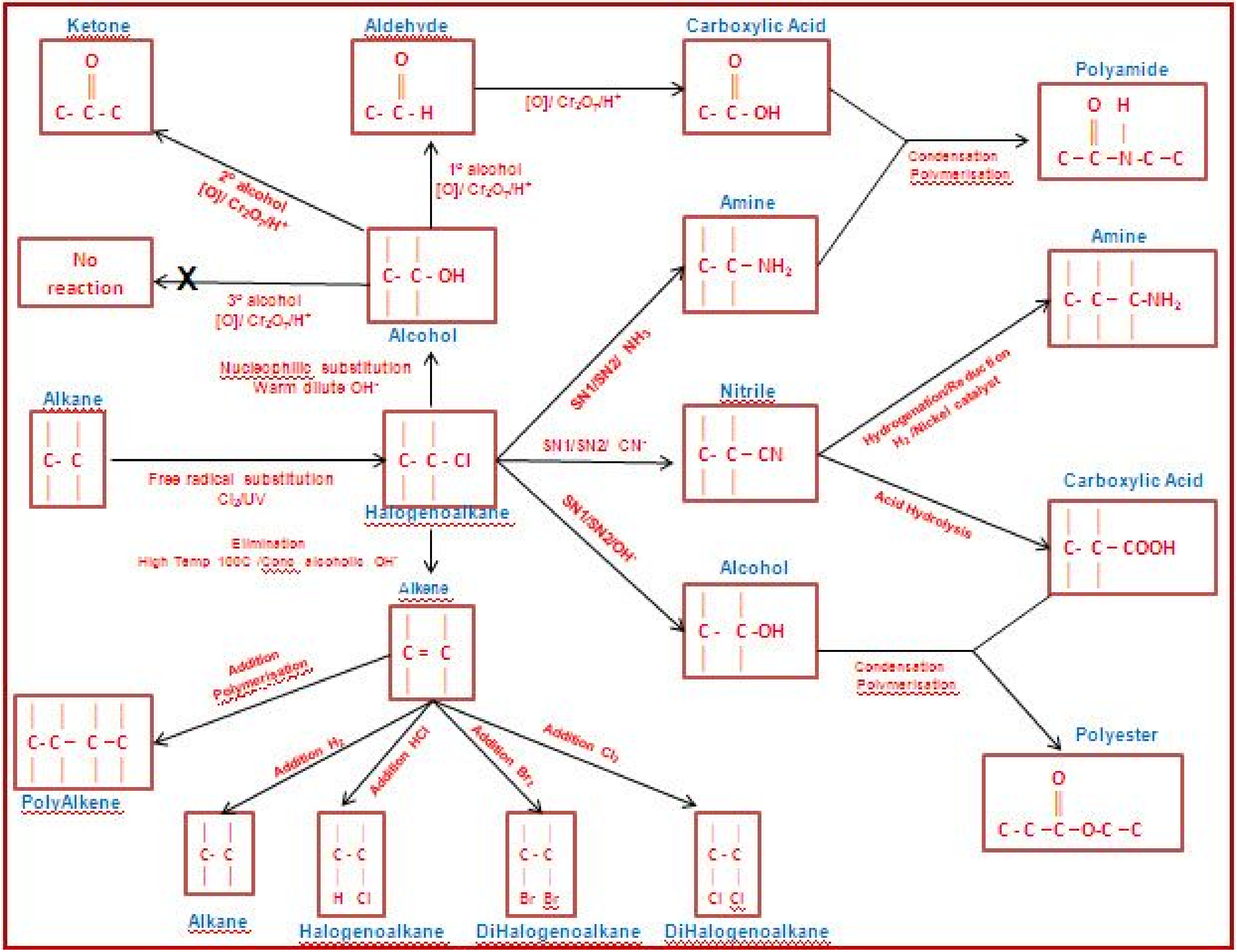
Step 3:

- Identify the functional group(s) present in the starting material and identify any relationship between the starting reagents and any intermediate compounds you have listed in step 2

Step 4:

- Design a reaction pathway that has the minimum number of steps. Include all the reaction conditions and reagents required.

Main



Ketone

C- C - C

Aldehyde

C- C - H

$[O]/ Cr_2O_7/H^+$

Carboxylic Acid

C- C - OH

Condensation Polymerisation

Polyamide

C – C –N -C –C

2° alcohol $[O]/ Cr_2O_7/H^+$

1° alcohol $[O]/ Cr_2O_7/H^+$

No reaction

X

3° alcohol $[O]/ Cr_2O_7/H^+$

C- C - OH

Alcohol

Amine

$C- C – NH_2$

Amine

$C- C – C-NH_2$

Nucleophilic substitution Warm dilute OH^-

Alkane

C- C

Free radical substitution Cl_2/UV

C- C - Cl

Halogenoalkane

$SN1/SN2/ NH_3$

$SN1/SN2/ CN^-$

$SN1/SN2/OH^-$

Nitrile

C- C – CN

Hydrogenation/Reduction H_2 /Nickel catalyst

Acid Hydrolysis

Carboxylic Acid

C- C – COOH

Elimination High Temp 100C /Conc alcoholic OH^-

Alkene

C = C

Alcohol

C - C -OH

Condensation Polymerisation

Addition Polymerisation

C- C – C –C

PolyAlkene

Addition H_2

Addition HCl

Addition Br_2

Addition Cl_2

Polyester

C - C –C –O-C –C

C- C

Alkane

C - C

H Cl

Halogenoalkane

C - C

Br Br

DiHalogenoalkane

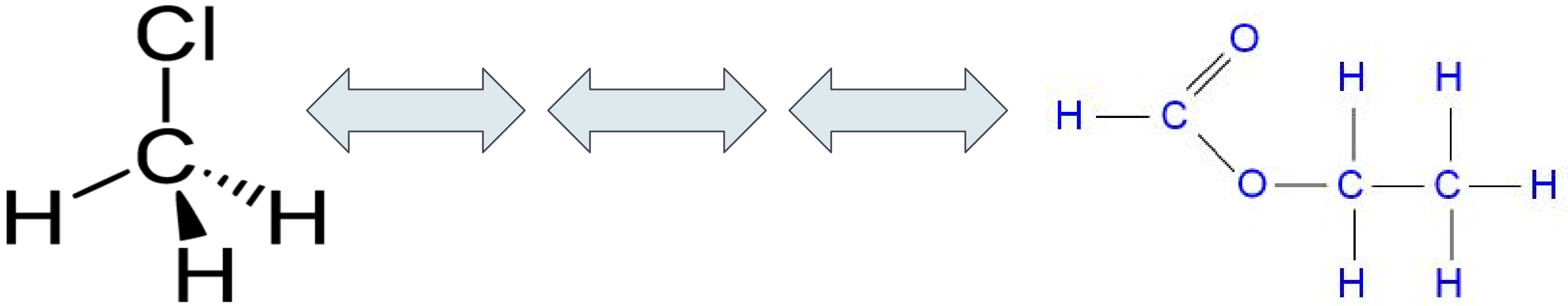
C - C

Cl Cl

DiHalogenoalkane

Design a synthetic route to produce ethyl methanoate from chloromethane

Step 1:



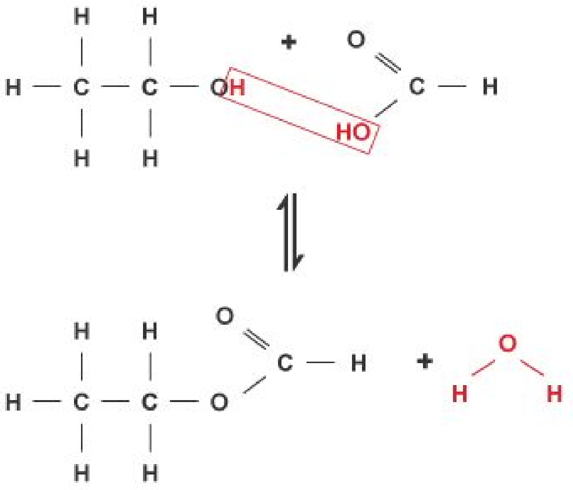
- Chloromethane is a halogenoalkane.
- Ethyl methanoate is an ester

Main

Design a synthetic route to produce ethyl methanoate from chloromethane

Step 2:

- Ethyl methanoate is the product of a condensation (esterification) reaction between a carboxylic acid (methanoic acid) and an alcohol (ethanol)
- The condensation reaction is achieved by heating the carboxylic acid and alcohol in the presence of concentrated sulfuric acid , creating an ester and water



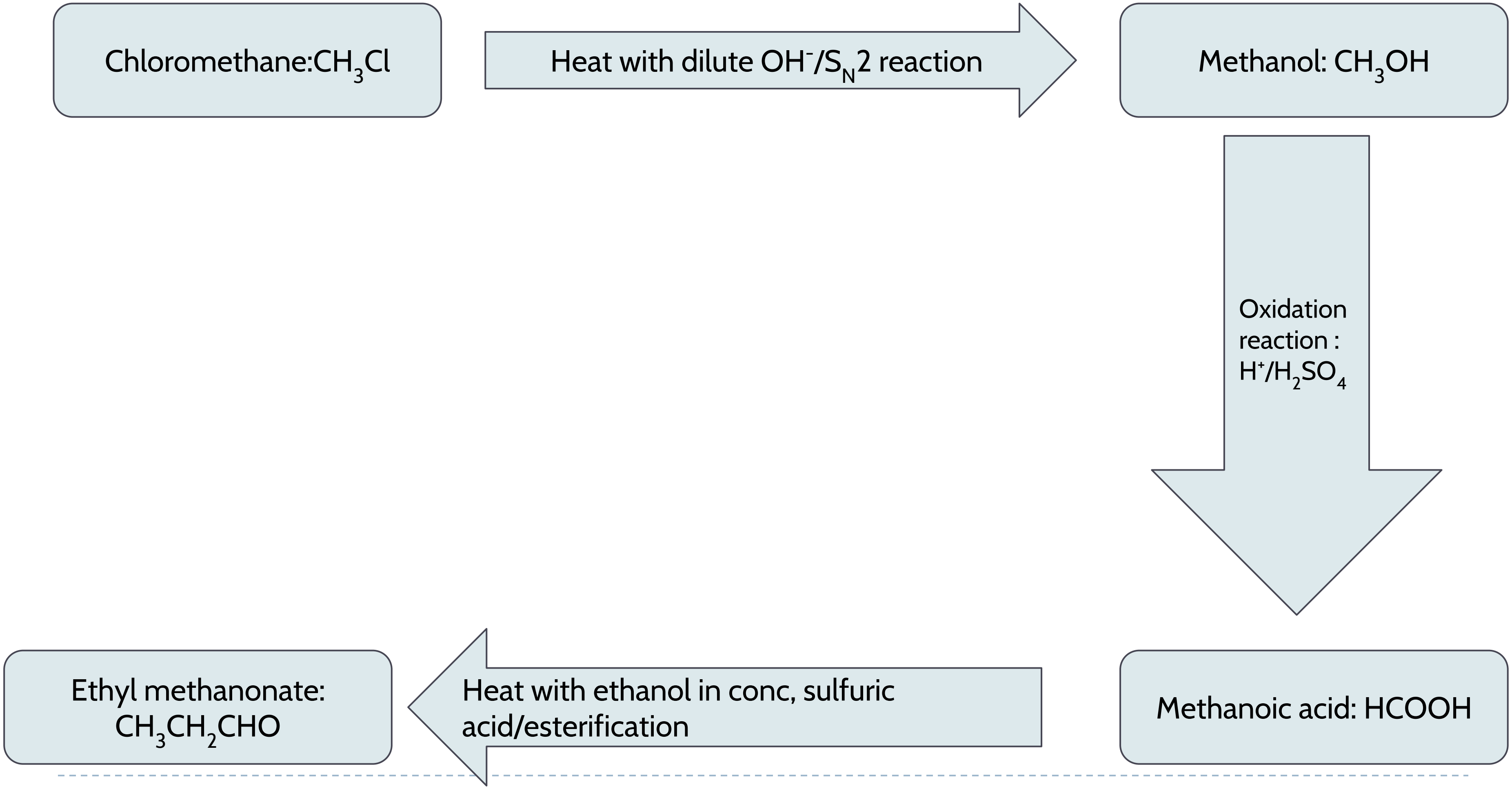
Design a synthetic route to produce ethyl methanoate from chloromethane

Step 3:

- The starting material, chloromethane, needs to be converted to methanoic acid. Methanoic acid is the product of the oxidation of a primary alcohol.
- Chloromethane, a halogenoalkane, is a reactive compound which is susceptible to attack by nucleophiles such as OH^-

Design a synthetic route to produce ethyl methanoate from chloromethane

Step 4:



Chloromethane:CH_3Cl

Heat with dilute OH^-/S_N2 reaction

Methanol: CH_3OH

Oxidation reaction : H^+/H_2SO_4

Methanoic acid: HCOOH

Heat with ethanol in conc, sulfuric acid/esterification

Ethyl methanonate: CH_3CH_2CHO

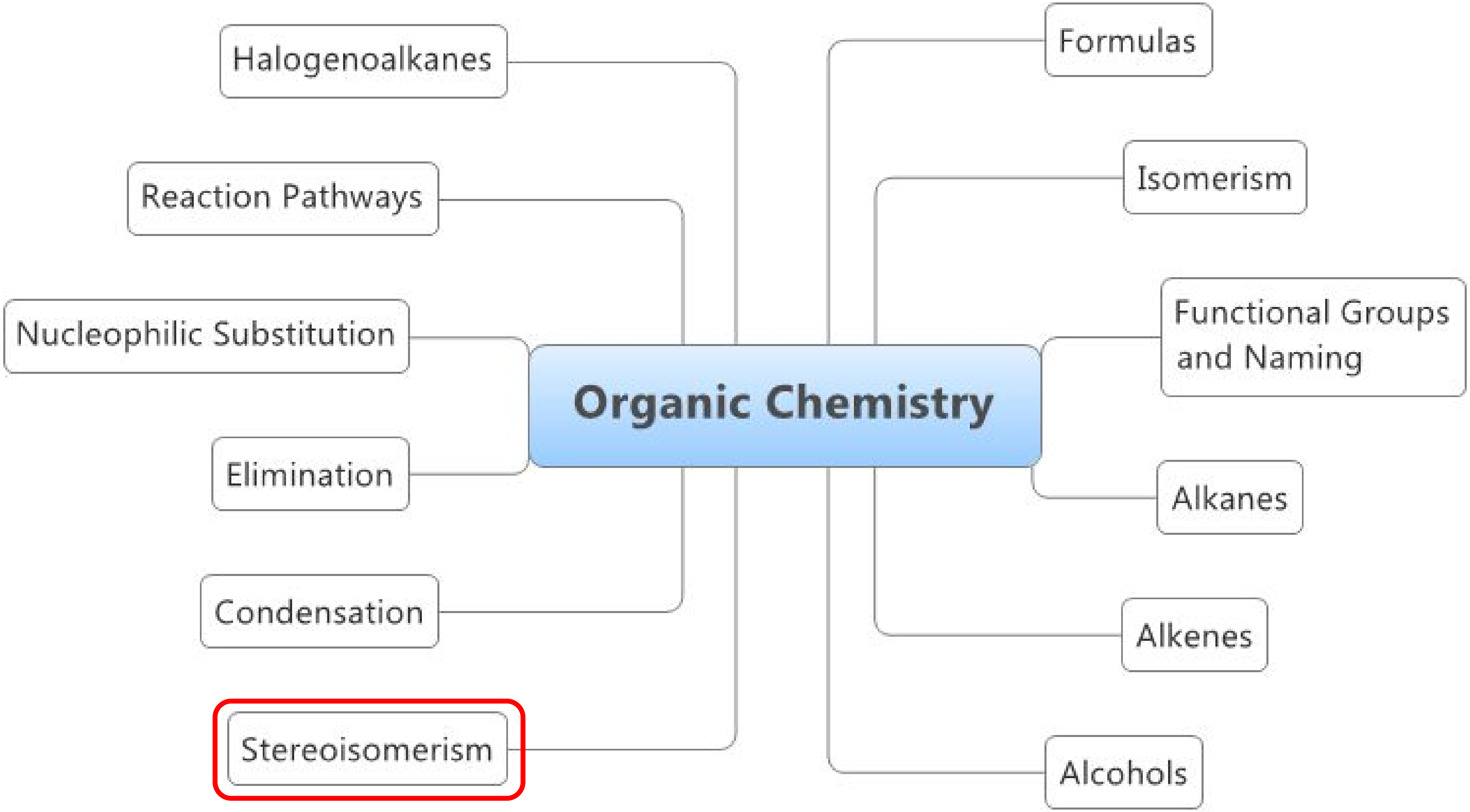
Main

Lesson 8

20.3 Stereoisomerism

Main
Menu

We Are Here



Organic Chemistry

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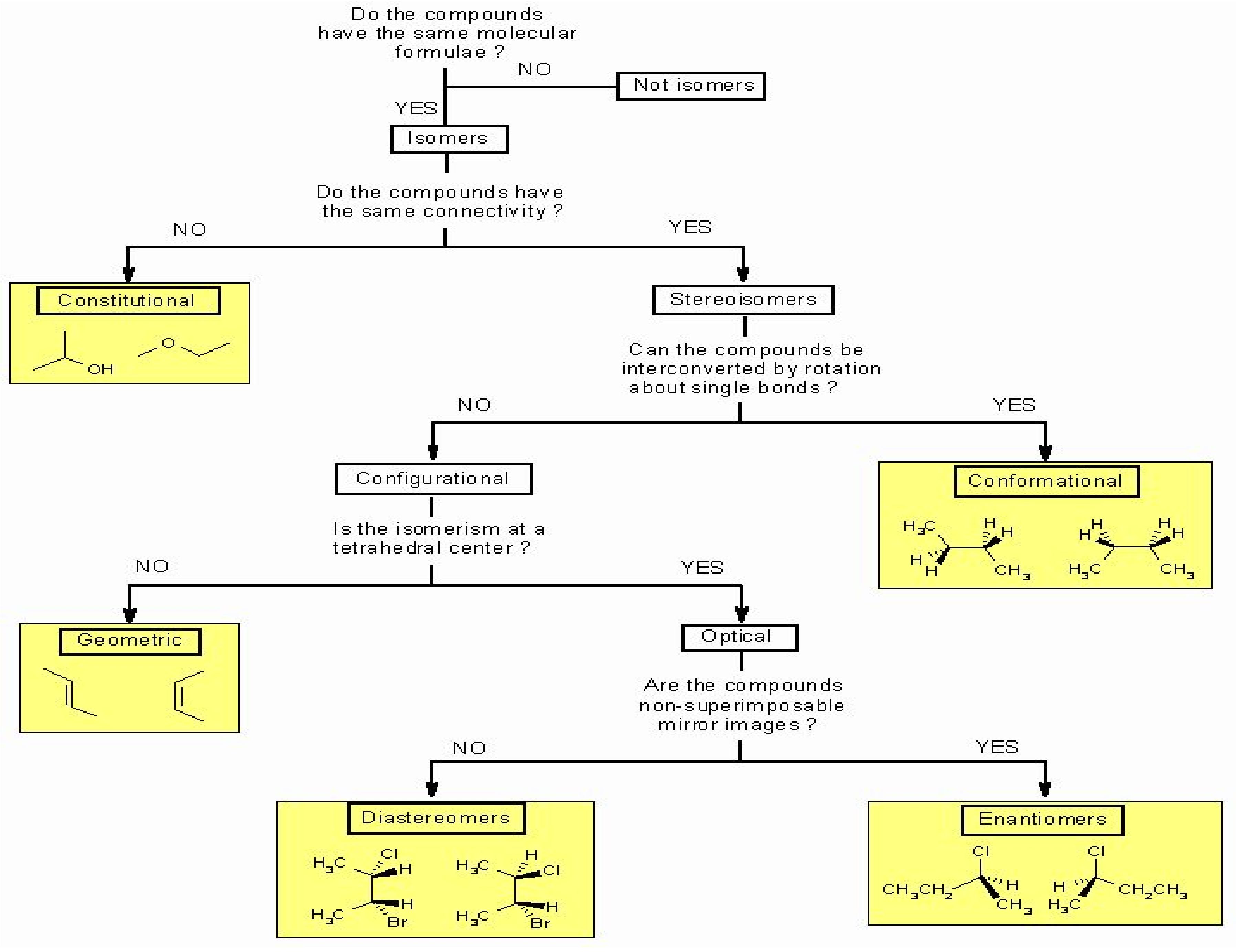

Do the compounds have the same molecular formulae ?
NO
Not isomers
YES
Isomers
Do the compounds have the same connectivity ?
NO
YES
Constitutional
OH
O
Stereoisomers
Can the compounds be interconverted by rotation about single bonds ?
NO
YES
Configurational
Conformational
H_3C
H
H
H
H
CH_3
H
H
H_3C
H
H
CH_3
Is the isomerism at a tetrahedral center ?
NO
YES
Geometric
Optical
Are the compounds non-superimposable mirror images ?
NO
YES
Diastereomers
H_3C
Cl
H
H_3C
H
Br
H_3C
H
Cl
H_3C
H
Br
Enantiomers
Cl
CH_3CH_2
H
CH_3
Cl
H
H_3C
CH_2CH_3

Isomers

- Stereoisomers are subdivided into two classes
  - Conformational isomers, which interconvert only by breaking and reforming a bond.
  - Configurational isomers are further subdivided into cis-trans and E/Z isomers and optical isomers.

- Cis-trans isomers can occur in alkenes or cycloalkanes (or heteroanalogues) and differ in the positions of atoms (or groups)

Stereoisomerism

- Stereoisomers are compounds with the same structural formula but different 3D arrangement of atoms

- There are two types of stereoisomerism:
  - Geometrical isomerism
  - Optical isomerism

Main

Geometrical (cis-trans isomerism)

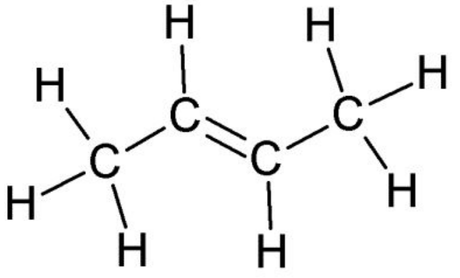
- Geometric isomerism involves the arrangement of groups around a double bond
  - Or a single bond that can't rotate freely such as in a cyclic compound

- It happens because double bonds are not free to rotate

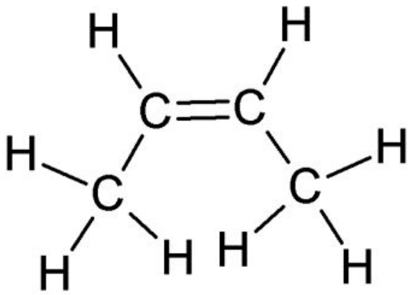
- Each C=C carbon must have two different groups attached to it.

- In the **trans** isomer, the substituents (the $-CH_3$ groups) are on opposite sides of the double bond

- In the **cis** isomer, the substituents are on the same side of the double bond



trans-but-2-ene

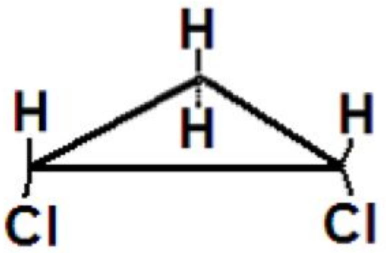


cis-but-2-ene

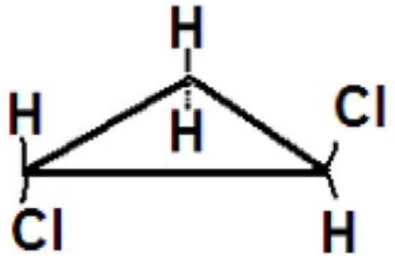
Main

Cis vs Trans

- Ring structures like C=C restrict rotation and therefore can result in cis and trans isomers



cis-1,2-dichlorocyclopropane

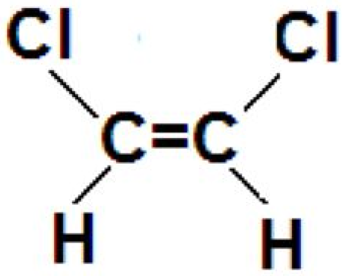


trans-1,2-dichlorocyclopropane

Main

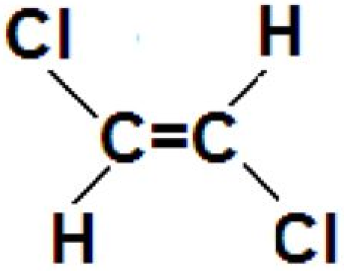
Physical Properties

- The chemical properties of geometrical isomers tend to be similar but their physical properties are different



Boiling point
= 60.3 °C

cis 1,2-dichloroethane



Boiling point
= 47.5 °C

trans 1,2-dichloroethane

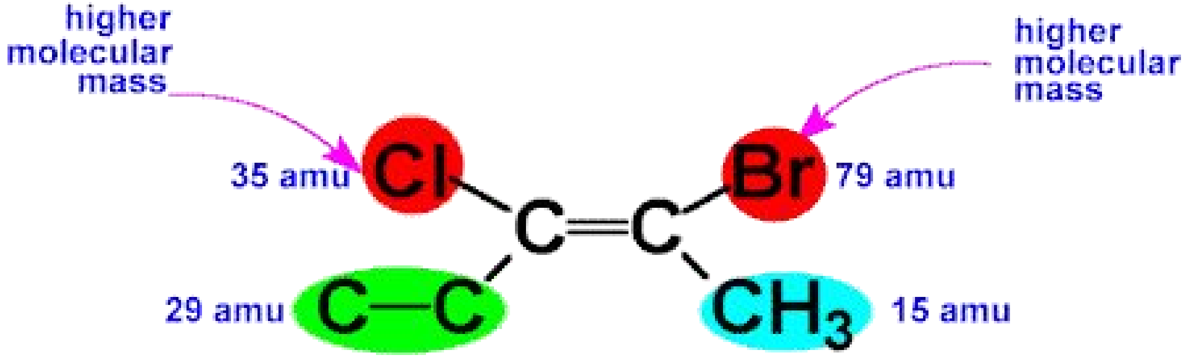
Cis: polar

Trans: non-polar

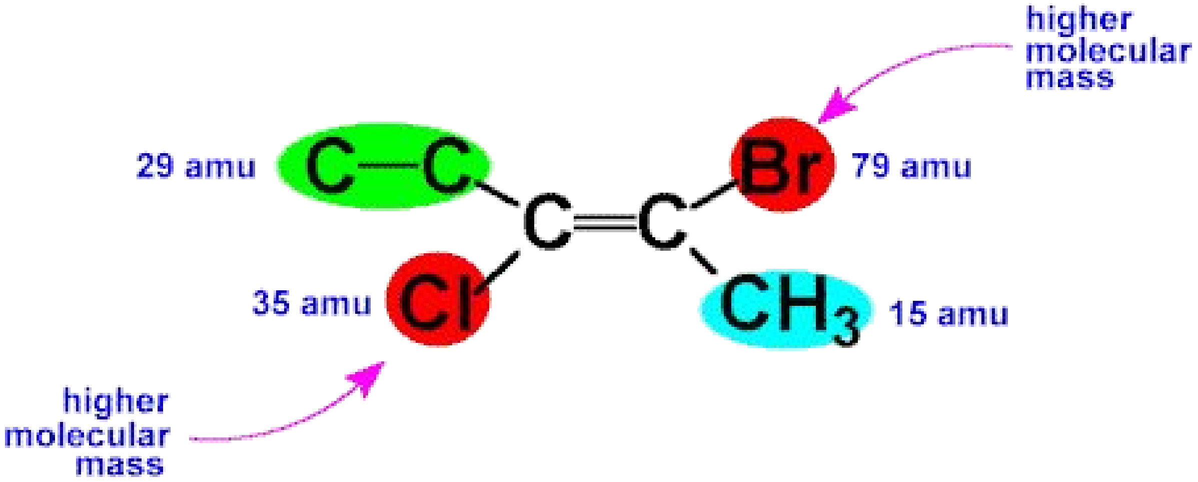
Main

E/Z Isomers

- More general way of naming isomers
- Cahn-Ingold-Prelog priority
  - Give priority to atoms attached to the C=C bond that have the highest atomic number



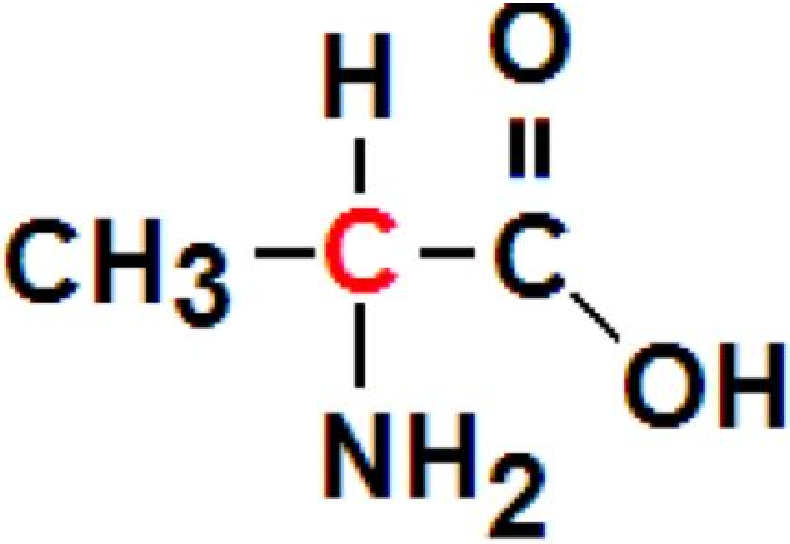
Z = same side for highest molecular masses



E = opposite sides for highest molecular masses

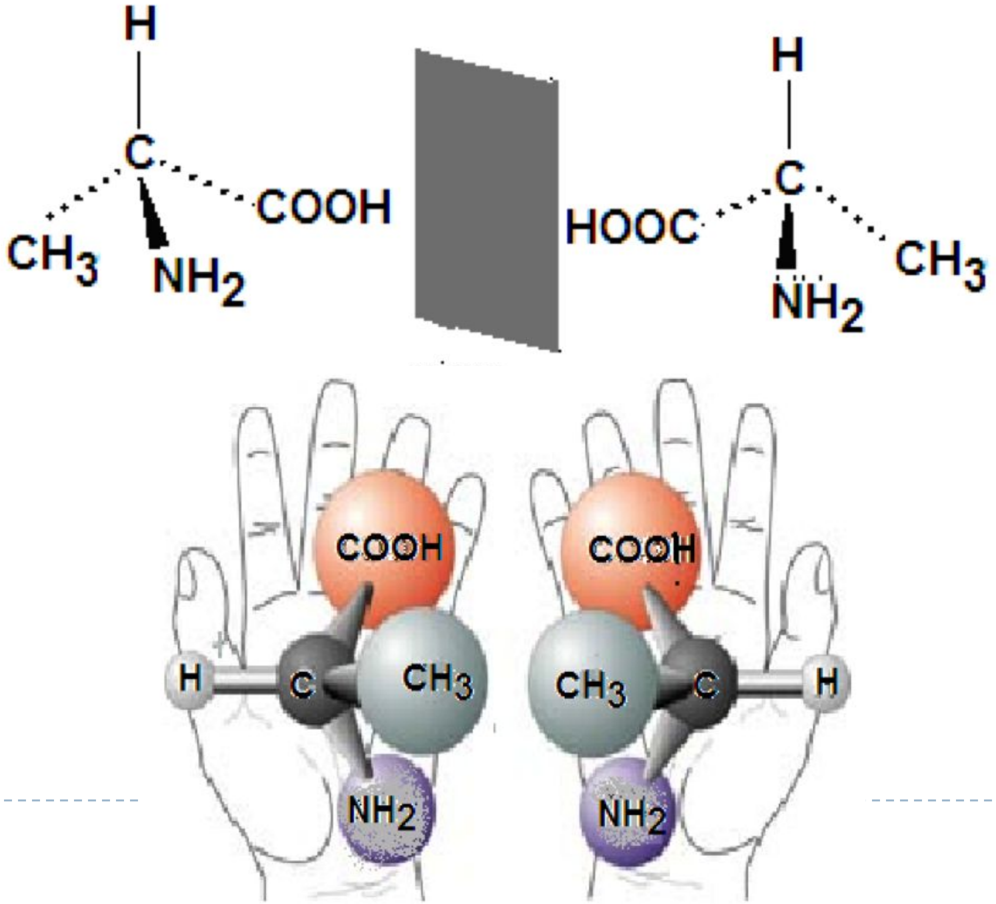
Optical Isomers

- Optical isomerism is present in all compounds that contain at least one asymmetric (chiral) carbon atom
- An asymmetric carbon atom has four different atoms or groups attached



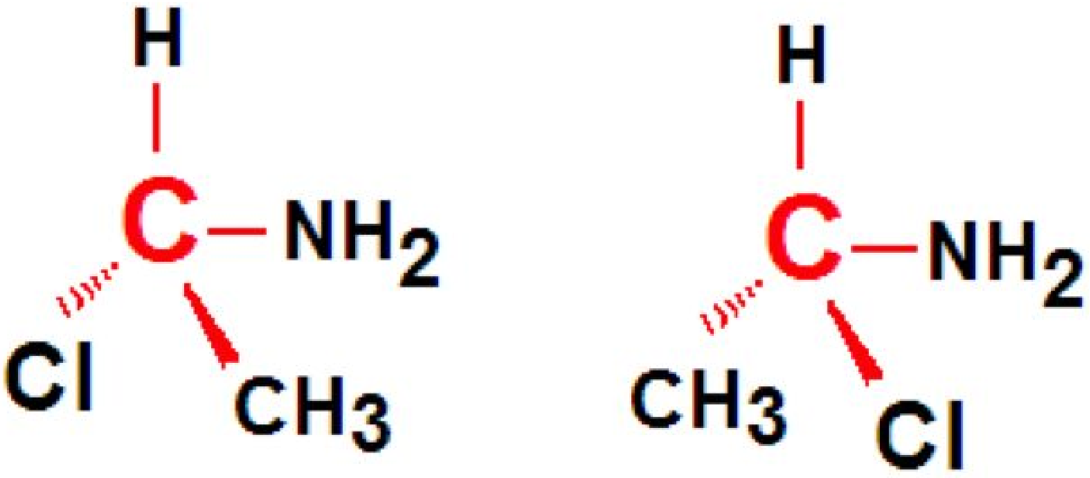
Optical Isomers

An optically active compound can rotate the plane of polarized light as it passes through a solution of the compound. Optical isomers are enantiomers. Enantiomers are non-superimposeable mirror images of each other. Diastereomers are not mirror images of each other



Enantiomers

While these structures may look identical, in three dimensions they are mirror images of each other. Such molecules are called **enantiomers**

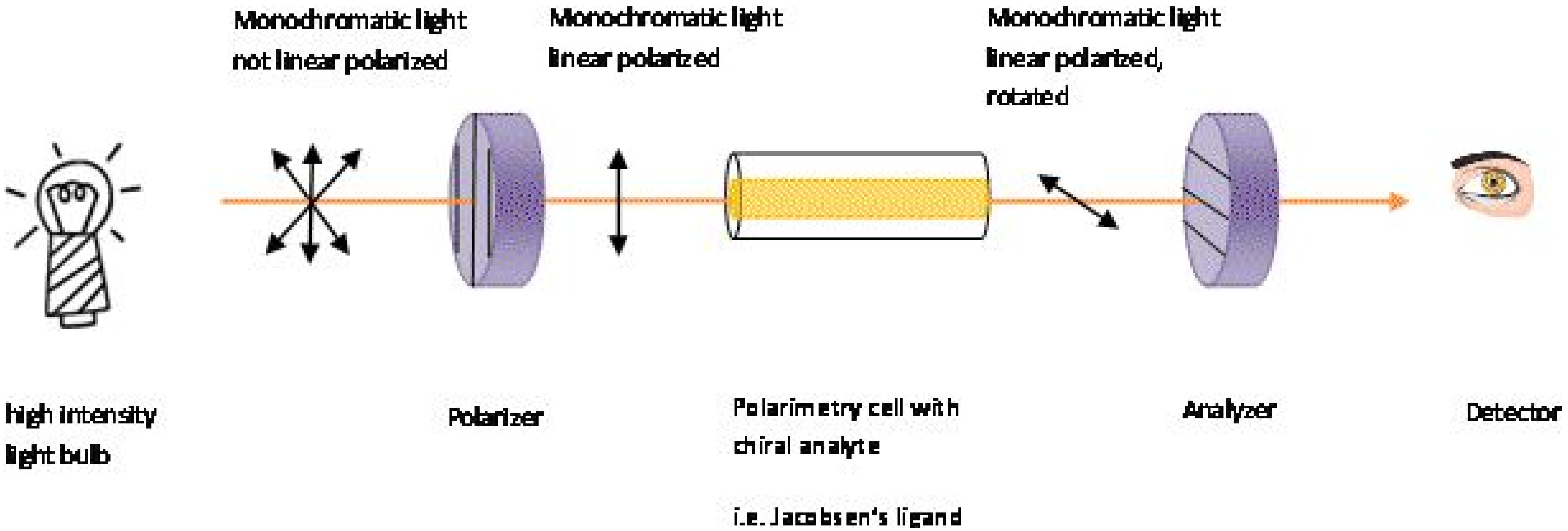


If a molecule has a plane of symmetry it will not exhibit optical isomerism

Main

Polarized Light

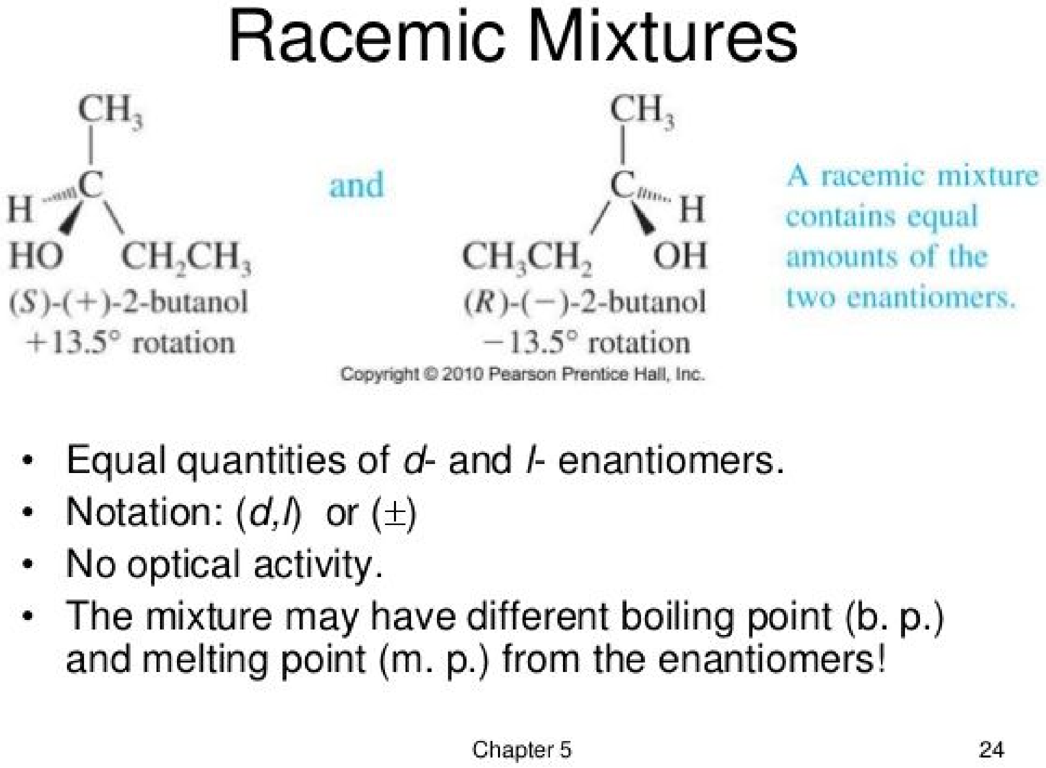
Optical isomers rotate the plane of plane-polarized light in opposite directions



Main

Racemic Mixture

A racemic mixture (or racemate) is a mixture of two enantiomers in equal amounts and is optically inactive



Racemic Mixtures

(S)-(+)-2-butanol
+13.5° rotation

and

(R)-(−)-2-butanol
−13.5° rotation

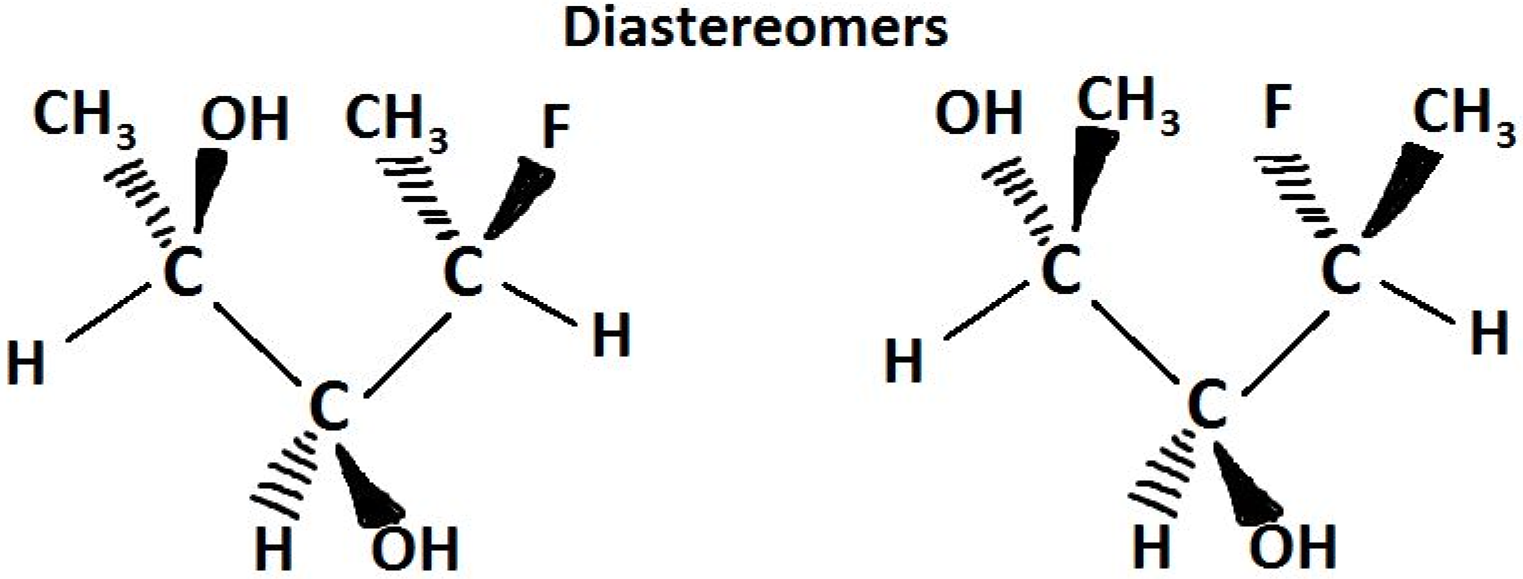
A racemic mixture contains equal amounts of the two enantiomers.

- Equal quantities of *d*- and *l*- enantiomers.
- Notation: (*d*,*l*) or (±)
- No optical activity.
- The mixture may have different boiling point (b. p.) and melting point (m. p.) from the enantiomers!

Main

Diastereomers

- Cis-trans isomers are diastereomers
- Arise from presence of more than one chiral center
- Physical and chemical properties are different for each



Wedge out of the page (toward you)

Dash in the page (away from you)

Main