07/09/26 (1) Prof Famuyiwa

CHM 202

Introduction to Organic Chemistry

Organic Chemistry is the study of organic compound. Organic compounds are the compounds of Carbon except CO_2, CO, bicarbonate e.g Sodium bicarbonate and ~~inorganic~~ hydrogen ~~compounds~~ Carbon is able to form compounds than other elements in the periodic table put together. It is unique

Classification of Organic Compound

They are classified into groups according to the functional group present in the compound. The functional group is part of the compound that influences the chemical & physical part.

1. Alkane - Paraffin is the common name. Single bond btw C and H - functional group. Each C has 4 bonds — C_nH_{2n+2}
2. Alkene - Common name - Olefin
3. Alkynes - Acetylene (common name) $C \equiv C$ - No geometrism
4. Arenes Common name - Benzene or Aromatics
5. Halo alkane - Alkyl halides

1-4 : Hydrocarbon

(2)

6. Alkane - Ether
7. Alkanol - Alcohol
8. Alkanal - Aldehyde
9. Alkanone - Ketone
10. Alkanoic acid - Carboxylic acid

Derivative
a.) Esters b.) Amides c.) Acid halides

Alkanamide - Amides of Alkyl Carboxylic group.

Nomenclature of

This involves naming of simple organic compounds and it is can be divided into to 2 namely:

a.) Systemic / IUPAC
b.) Non-systemic

First 20 Org. e.g Methane

Undecane | Duo | Tri | Tetra | Penta .... Icos ane

a) Systemic/IUPAC - follows a pattern. The IUPAC of aliphatic (straight chain) alkane forms the basis of IUPAC nomenclature for other classes of Organic compound. It should be noted that each alkane differs from the preceding member by CH_2. A series of compound where each member differs by a constant are called homologous series - Homologues e.g Alkane, Alcohol.

for other classes of organic compound

The last letter 'e' of alkane is replaced by a group of letters suffix e.g -ol, -al, -one, -oic acid

b) Non-systemic - these are names of some organic compounds were called before the advent of IUPAC nomenclature. Though, IUPAC nomenclature was established for standardizing nomenclature of all types of compounds.

i) Its not as strong as electrovalent bonding, so it breaks faster. except Diamond which has high m.p

But common names of some compounds were maintained e.g formamide IUPAC (Methanal) Propanone IUPAC (Acetone), Acetic acid IUPAC (Ethanoic acid).

Physical General prop of Organic Compound

Odor/sc

i) Organic compounds are generally low melting point solid or low boiling point liquid or gases because they are largely covalent compounds.

2) The molecules are held together by either weak van der waal forces, dipole dipole, or hydrogen bond

3) These bonds are INTERMOLECULAR FORCE OF ATTRACTION.

These intermolecular forces of attraction has effect on the following physical properties:

i) Melting point

ii) Boiling point

iii) Viscosity

iv) Solubility

decreasing mp, bp & viscosity

Ionic bond > Covalat > H-bond > Dipole-dipole > Van der waals

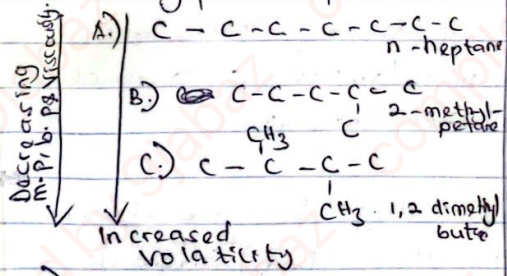
Boiling point, Melting Point & Viscosity of organic compound follows the same trend.

1.) These physical properties increase with relative molecular weight in a series of compounds which follows a regular patter in an homologous series.
(CH_3OH - ethanol)

2.) Straight chain isomer have higher melting, boiling point are more viscous than branched isomers.

Note: Branching reduces B.p, M.p & Viscousity.

3.) The more branching the less the melting point, m.p & viscous.



4.) Organic compounds with hydrogen bonds has high melting point, boiling point & viscosity than organic compounds having dipole bonds, which in turn has higher boiling point & melting point & is more viscous than organic compounds with vanderwaal forces.

Volatility

1.) It decreases with increase in relative molecular weight in a homologous series.

2.) Branched chain isomers are more volatile than the straight chain isomers.

3.) The more the branching, the greater the volatility

4.) Organic compounds with Vander waal forces is more volatile than organic compounds with dipole dipole which in turn is more volatile than the one in Hydrogen bonding.

(Missing « Solubility » b/f)

General chemical properties of Organic Compounds

In organic reaction, bonds are broken (FISSION) & simultaneously bonds are formed (FUSSION).

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Read more Textbook, Halogenation of Alkane

Fission

There are two ways fission can occur in organic reaction. e.g

i) Homolytic - This happens when a bond breaks & each atom requires 1 electron each.

$A \div B \rightarrow A^{\cdot} + B^{\cdot}$

(· - are called free radicals.)

Example of this rxn is found in the chlorination of methane, (halogenation of alkane)

e.g $Cl_2 \xrightarrow{\text{sunlight}} Cl^{\cdot} + Cl^{\cdot}$

The above rxn is called chain initiation.

Methane; $CH_4 + Cl^{\cdot} \rightarrow CH_3^{\cdot} + HCl$

- methane radical is produced.

$CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$

is known as chain propagation

$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow CH_3 - CH_3$

$CH_3^{\cdot} + Cl^{\cdot} \rightarrow CH_3Cl$

$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$

} Chain termination

2) Heterolytic happens when a bond breaks and two bonding electrons are found in one of the atoms.

2 - Partially ∂

$A \overset{\delta}{-} B \rightarrow A^{\delta+} + B^{\delta-}$

The reason why atoms moves to the B part is because it is more electronegative.

They produces ions not radical

atoms that produce +ve charge

C^+ - carbocation

-ve charge C^- → carbanion

Example of this found where carbon is bonded to electronegative atom e.g Alcohol, Ether, CN (amine/amide), C-O, C-Cl.

C - Mg (to more electropositive atom) Grignard reagent.

The stability of carbocation & carbanion

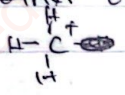
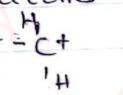
They are classified into:

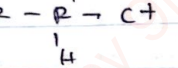
1) Primary carbocation

2) Secondary carbocation
3) Tertiary carbocation

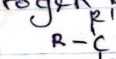
Primary

C^+ - B that is attached to other other atoms

e.g  or 

Secondary 

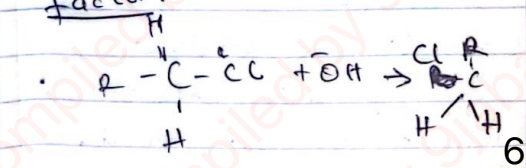
Tertiary - No hydrogen bond

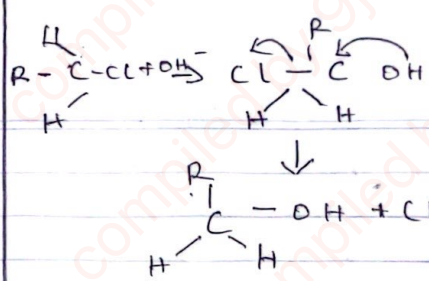
In carbocation, 

Tertiary is the most stable $ it is the opposite reverse for carbanion (It is the least stable)

Factors influencing organic reaction

An attack by species on a substrate may be enhanced or enhibited by the distribution of electrons in the region of where the attack is taking place is called (1) electronic factor.





The reactants specie is a nucleophile (OH^-) — seeks an electron deficient center.

electrophile - electron loving specie

And other by the nature and size of the atom or groups of atom surrounding the size is called (2) steric factor.

Electronic is divided into Inductive & Meso meric effect

b/f

Solubility

(i) Generally, organic compounds are insoluble in water except those that form hydrogen bonds with water e.g Alcohol, Carboxylic acid, amine, sugar.

(ii) Solubility decreases as the hydrocarbon part of the molecule increases in a particular homologous series.

Ionic compounds are soluble in water.

Some organic compounds (polar-covalent) or that have hydrogen bonding are also soluble in water.

(ii) Solubility Decreases cont'd:

CH_3OH
CH_3CH_2OH
$CH_3CH_2CH_2OH$

Decreases solubility as the hydrocarbon part increases

The OH^- group is responsible for solubility.

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Factors influencing Organic reaction cont'd

Electronic effect is divided into Inductive & Mesomeric effects.

$C^{\delta+} \rightarrow Cl^{\delta-}$ | Nucleophile will attack

Carbon to high electronegative element. When electron is being drawn away from the center midst it is inductive effect

$-I \rightarrow$ Inductive effect

$C \Leftarrow Mg$

Electron being pushed to Carbon. Electrophile will attack.

+I effect - +ve Inductive effect.

Mesomeric effect

Happens when electrons are withdrawn from Carbon in a sigma bond.

e.g $C=O \rightleftharpoons C^{\delta+} - O^{\delta-}$

They transform to conjugate effect due to their arrangements

$C=C-C=C-C=C-C=O$

In conjugation, effect will be fast through the

$sp^3 \rightarrow -\overset{|}{\underset{|}{C}}-$
Notes

chain.

For Inductive, effect is negligible in the first C.

C → C → Cl

Inductive effect - This happens when sp^3 (Carbon atom) is attachment to a more electronegative atom creating a Permanent dipole. The effect is transmitted along the chain but tends to be insignificant beyond the second carbon atom.

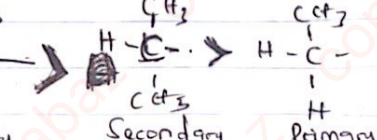
Electronegative atoms or group of atoms (e.g OH⁻) will draw electrons from Carbon atom to themselves, thereby, exerting negative effect. It is denoted by -I.

However, certain atoms or group of atoms notable alkyl groups (C - methyl CH_3; (C_2H_5 ethyl)

e.g C ← CH_3

donate electrons to Carbon atoms away from themselves thereby, exerting +ve Inductive effect, +I.

The bulkier the alkyl group the greater the +I effect i.e tertiary alkyl group exert greater positive +I effect than secondary alkyl group which in turn exert greater +I effect than primary alkyl group.



* -ve I & +ve I effect can be used to predict the acidity & basicity strength of organic acids & bases. e.g

Acid

-ve I effect increases acidity while +I effect decreases acidity.

+I increases basicity & -I decreases basicity.

Amine $R-\ddot{N}H_2$ (lone pairs) → They are bases

$R-\ddot{N}H$ (R¹) Secondary

$R-\ddot{N}-R''$ (R¹) Tertiary

The bulkier the Amine, the more basicity due to the alkyl group in the structure.

$CH_3COOH \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-O^- + H^+$

The more the reactants can release a H^+ product, the more acidic it is.

FCH_2COOH is more electronegative than $ClCH_2COOH$

$ClCH_2COOH \rightleftharpoons ClCH_2-\overset{O}{\overset{\|}{C}}-O^- + H^+$

Mesomeric effect

It is denoted by M, it happens when $sp^2(-\overset{|}{\underset{|}{C}}=)$ Carbon atom or $sp(-C\equiv)$ is attached to a more electronegative atom thereby creating a shift of pi electrons in the multiple bonds towards the more electronegative atom.

$-\overset{|}{C}=O$

STERIC FACTOR

$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$

Carboxylic acid + Alcohol $\xrightarrow{C_2H_5COOH+H^+}$

$CH_3-\overset{O}{\overset{\|}{C}}-OH \quad HOCH_3$

$CH_3-\overset{O}{\overset{|}{C}}(OH)(O_+CH_3)H \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{+}{O}(H)CH_3$

The bulkier the alkyl group, the slower the rate of reaction to produce ester.

Asc 1) Isomers

Read on: Types of Organic Reactions: Substitution

Soln

1.) Substitution
2.) Elimination
3.) Addition
4.) Rearrangement

Dictated

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Isomerism

- This is an occarence where two or more compounds have the same molecular formula but different structural formular.
- Isomerism is divided into: Structural and stereo.

SPFT

Structural Isomerism

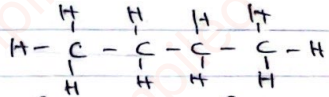
+ Skeleton / chain Isomerism
+ Position al Isomerism
+ Functional group Isomerism
+ Tautomerism Isomerism

Structural Isomerism

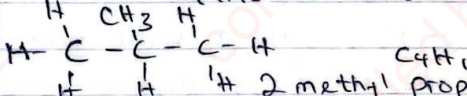
This type of isomerism involves an order of atoms' connectivity within the compounds are different i.e The way the atoms are connected to one another is different from one compound to the other.

+ Skeleton / Chain Isomerism

Examples include: Butane & 2 methyl propane are isomers under chain isomerism where Butane has 4 Carbon atoms:



C_4H_{10} Butane

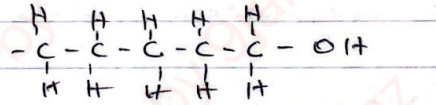


C_4H_{10} 2 methyl propane

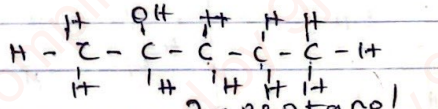
Same molecular formular but different connectivity.

+ Positional Isomerism

Examples include: Pentanol & 2-pentanol



Pentanol / 2-pentanol



2-pentanol

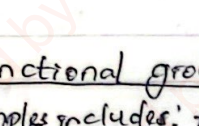
Note: The position of the "OH" is different.

* The first example structure can also be called 5-pentanol & the other 4-pentanol but that is WRONG. When you have 2 possible

name for a particular isomer, the one with the lowest number [e.g 1 pentanol & 2 pentanol] is correct

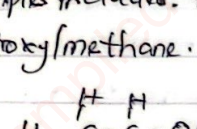
+ Functional group isomerism

Examples includes: Ethanol & methoxylmethane.



Ethanol

C_2H_6O Functional Group is Alcohol.

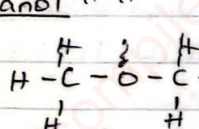


Methoxylmethane

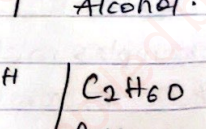
C_2H_6O Ether

+ Tautomerism Isomerism

Examples include: Ethenol & Ethanol



Ethenol (C_2H_4O)



Ethanol (C_2H_4O)

Note: When you have the same carbon carrying the double bond and also the -OH group. It will have a corresponding Carbonyl group.

STEREO ISOMERISM

This type of isomerism does not involve the order of atoms connectivity within the compound.

Actually, the order of connectivity remains the same but the special arrangement of the atom differs from one compound to another.

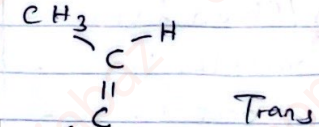
It is divided into: Geometrical and Optical Isomerism.

+ Geometrical Isomerism

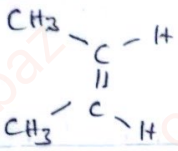
This occurs when rotation between carbon atoms is restricted. This can be seen in Alkene & Cycloalkanes.

Two good examples: But-2-ene & 1-2 dichlorocyclohexane.

$CH_3-CH_3=CH-CH_3$;



Trans

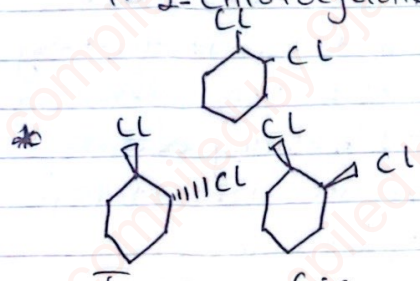


cis

The 2 are the two isomers for But-2-ene.

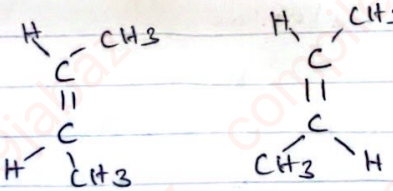
Note: Same thing opposite each other is Trans but if it is on same line different, it is Cis.

1-2-Chlorocyclohexane



Trans Cis

For But-2-ene



[I] [II]

Cis (Z-configuration) Trans (E-configuration)

[Hint (Trans): It looks like (S)Z but it is the opposite i.e E]

Case Between carbon 2 & 3 is not possible

∴ The methyl group on carbon 2 & 3 are viewed in structure I are on the same side while that of structure II are on the opposite side.

The 2 structures are not the same.

I is cis or Z configuration while structure II is trans or E-configuration.

+ Optical Isomerism

This occurs when two compounds of the same molecular formular & same order of atom connectivity but different special arrangement of the atom rotate plain polarized light in opposite direction. Compounds that exhibits this property must have stereo / chiral centre.

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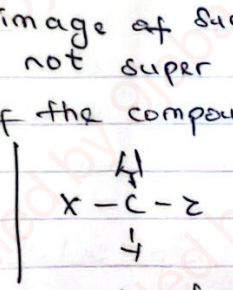
Chirality in Organic Chemistry

Chirality is a carbon centre that has 4 (sp^3 atoms) different groups attached to it. It result into right & left handedness

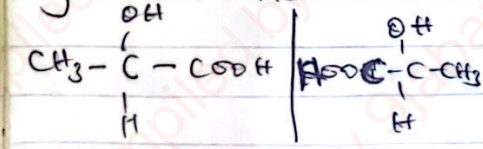
The mirror image of such compound is not super imposable of the compound.



Just like a left hand is not super imposable as the right hand.

Such isomers will exhibit isomer optical isomerism in which One isomer will rotate plane polarized light to the right & the other will rotate plane polarized of the same degree to the left.

Eg Lactic Acid

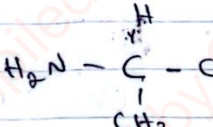


Lactic acid will exhibit optical isomerism Isomers that rotate plane polarize to the right are designated +ve and those that are designated to the left are -ve. & +ve are known to be dextrorotatory. & while -ve - levorotatory.

All naturing occurring sugar are dextrorotatory.

D-glucose means dextrorotatory glucose.

Nature synthesize L-alanine



Alanine

(L & D)

The isomers are known as Enantiomers and the mixtures and the equal amount of enantiomers are not expected to rotate plane polarized light either to the left or right.

Racemic

11)

This type of mixture is called Racemic (equal amount of elantiomers) The elantiomers are given R & S configuration. and it is the most used configuration.

Rules of R & S configuration

1) For illustration, consider lactic acid, the 4 group around sp^3 carbon atom are numbered 1-4. According to the atomic masses & the highest atomic mass no 1 & the lowest no 4.

2.) Groups that are attached to the sp^3 atom with the same element, next element will be considered until there is a difference in the element of the groups & elements with higher atomic mass will be given priority.

3) The carbon atom in the group with multiple bonds will be considered to have same number of atoms to which it is bonded to.

eg C = O is C(-O)(=O)

C ≡ N is C(-N)(≡N)

4.) The least group that is given No 4 will be pushed inwards & the remaining 3 groups are left

5.) When counting the numbers from 1 to 3, and it is clockwise R-configuration is applied but S-configuration is assigned when it is anticlockwise

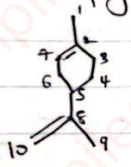
eg $H_3C-\overset{OH}{\underset{H}{C}}-COOH$ (3, 1, 2)

Brief Chemistry & Biological properties of an Elantiomers

Elantiomers have both physical & chemical properties the same except its chemical reaction with another Chiral Compound. Center of

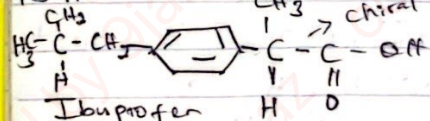
2) They possess different

biological activities differences e.g
One elantiomeric form of a compound called limonene is primarily responsible for the odour of orange while the other form is responsible for lemon. (because of their different configuration)



Limonene

5 is the chiral centre.
The S- configuration of Anti-inflammatory drug is Ibuprofen is effective while the R-configuration is not.



Ibuprofen

The Anti-hyper drug Methyl dopa also own it effect exclusively to the S-imoser.

Structure

The right handed thalidomide causes morning sickness in pregnant woman while the left handed thalidomide causes birth defect.

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VSEPR PROJECTION FORMULA

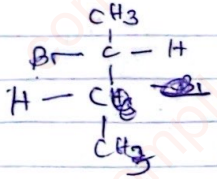
It is not easy to represent 3-dimensional structure. of especially molecules with 2 or more chiral centre. Chemists sometimes represent structure for Chiral molecule with 2 dimensional formula called FISCHER

By Convention,
Projection are written with main Carbon chain, extending from top to bottom & with all groups eclipsed vertical lines represents bonds that projects behind the plane

of the paper or that line in it.

Horizontal line represents bonds that projects out of the plane of the paper.

The intersection of vertical and horizontal lines represents the Carbon atom usually the one that is at stereo center.



2-dimensional

Compounds with more than 1 chiral centre

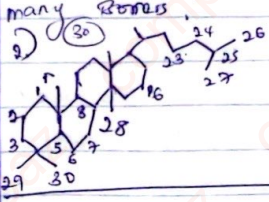
2) They can be synthesized in lab

1) They occur in nature examples Sugar, Lautaric acid, Cholesterol.

The number of isomer, such compound will have to depend on the no. of chiral centre, and it is given by 2^n (n is the number of chiral centre) e.g from the $2^n = 4$.

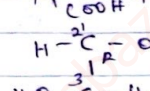
Ans

If they are 8 chiral centre, how many isomers?

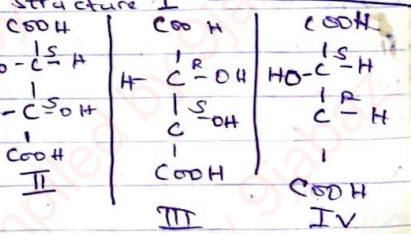
2) 

e.g A compound with 2 chiral centres will have 4 isomers and 2 pairs of enatiomers

e.g.



Structure I Tataric acid



II III IV

In all the structures, Carbon 2 & 3 are chiral centers. This is a achiral of 2 centre & 4 isomers.

Structure 1 & 2 are mirror images of each other, likewise 3 & 4.

1 & 2 are Enationmers same with 3 & 4 but 1 & 3 are not mirror images of one another they are isomers, likewise 2 & 4. These types of isomers are referred to diastereomers.

The configuration in Carbon 2 & 3 in all the structures are indicated as for structure 3 - R, S. 4 is S, R. 1 is R, R. 2 - S, S.

Enatiomers will exact opposite configuration in the chiral center of each other while diastereomers will have opposite configuration in one chiral center and 1 same.

Structure 1 is the same as structure 2

Mesocompounds

They have chiral center but they exhibit achirality i.e They don't rotate/deflect/ polare.

When there is plane of symmetry, they will not display.

Structures 3 and 4 are meso compounds though they have chiral centers they will exhibit characteristics of a mesocompound

There is no plane of symmetry in 1 & 2 Tataric acid have 3 isomers not 4. Because structure 3 & 4 are same compound. 2 enatiomers & 1 mesocompounds are possessed in Tataric acid.

I & II - Enatiomers

III & IV are one structure

Compounds with chiral centers, plane of symmetry will exhibit achirality.

Alkyl halides / Haloalkane

They have R—X as their general formula.

R can be Alkyl or Aryl group or halide group.

Benzene

CH_3Cl - methyl chloride

CH_3CH_2Br - ethyl bromide

Nomenclature

Non-systematic: The Halides are treated as the parent names while the alkyl group are added as prefix e.g methyl chloride

CH_3Cl, CH_3CH_2Br - ethyl bromide.

Systematic / IUPAC:

The halogens are treated as substituted on the parent alkane

CH_3Cl - chloromethane &

CH_3CH_2Br - bromoethane.

General physical properties

1) Because of dipole force of attraction in their molecules, they tend to have higher boiling point than alkane of comparable relative molecules

2) Boiling point of corresponding alkane increase

less than

Fluoro < Chloro < Bromo < Iodo

e.g $CH_3F < CH_3Cl < CH_3Br < CH_3I$

3) Halo alkanes are insoluble in water because of their inability to form hydrogen bond in water.

23/04/26

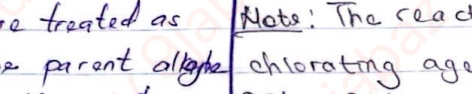
Preparation of Alkyl Halides

1) Reaction of alcohols with hydrogen chloride in the presence of zinc chloride as catalyst.

$CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$. (No need to balance)

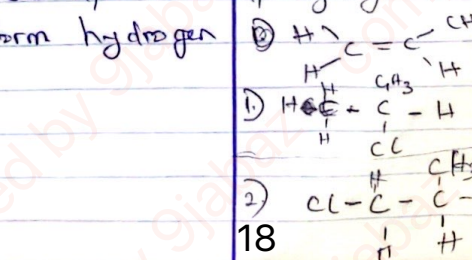
Note: The reaction of alcohols with chlorating agent e.g $SOCl_2$, PCl_3, PCl_5.

2) Addition of Hydrogen Halides to Alkenes.

e.g 

Markonikov's

Mac Konikov Rule states that The addition of Hydrogen halide molecule across the unsymmetrical double bond of an alkene. The hydrogen atom acts to the carbon atom of the double bond that has the higher number of hydrogen atom.



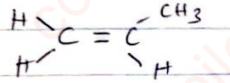
To give:

1) 2-chloropropane

2) Chloropropane

$Cl_2, H_2 \Rightarrow$ Symmetrical.

In case when hydrogen is absent in the unsymmetrical molecule (e.g HCl). The addition is the positive n of the unsymmetrical molecule will be attached to the carbon with the higher number of hydrogen. For example in ICl.



I^+ will prefer the first part.

2) Anti-Markonikov Addition is two radical addition of unsymmetrical molecule across the double bond of unsymmetrical alkane in the presence of peroxides. (H_2O_2)

3.) Free radical Halogenation of Alkane

e.g $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
or $CH_2Cl_2 + HCl$
or $CHCl_3 + HCl$
or $CCl_4 + HCl$

The first step is Initiation followed by propagation step and followed by termination step which is the 3rd step.

Initiation breaks Cl_2 in the presence of sunlight

$Cl_2 \xrightarrow{h\nu} Cl^{\cdot} + Cl^{\cdot}$

Reaction of Haloalkanes

There are reactive δ undergoes nucleophilic substitution of halogen atom by: OH^- (to form alcohol) $\ominus$ $-OR$ (alkoxy), $-$ [illegible] $-CH_3COO^-$, $-CN$, $-NH_2$

They are commonly employed in the preparation of Alcohol, Ethers, Esters, Amines.

Primary & Secondary Haloalkane undergo alkaline hydrolysis to the alcohol.

Water alone acts slowly at room temperature but Primary

hydrolysis Tertiary Haloalkane.

24/10/26

Preparation of Alcohol

Primary & Secondary Haloalkane undergo alcohol hydrolysis to give alcohol. water alone acts slowly at room temp but rapidly hydrolyse tertiary haloalkane.

$CH_3CH_2Br + -OH \rightarrow CH_3CH_2OH + Br^-$

Primary haloalkane.

In the presence of NaOH/KOH.

Secondary haloalkane $CH_3CH(CH_3)Br$

When an halogen (x) is attached to 1 known alkyl, the halo alkane is Primary e.g $CH_3-\underset{H}{\overset{H}{C}}-Br$ or $H-\underset{H}{\overset{H}{C}}-Br$

Secondary $\Rightarrow$ $CH_3-\underset{H}{\overset{CH_3}{C}}-Br$

It has two attached alkyl group

Tertiary - 3 - $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$

Secondary preparation

$CH_3CH(CH_3)Br + OH \rightarrow CH_3CH(CH_3)OH + Br^-$

Tertiary preparation

$CH_3C(CH_3)_2Br + OH$

Preparation of Ether

$R-O-R$ Alkoxyl alkane

Williams synthesis in which alkoxide Sodium or Potassium prepared by dissolving a alkaline metal in excess of the appropriate alcohol react with an alkane to form ether.

$CH_3-Br + CH_3O^- \rightarrow CH_3OCH_3 + Br$

Preparation of Nitrile

This is formed by heating the halo alkane with Sodium Cyanide

$CH_3Br + NaCN \rightarrow CH_3CN + NaBr$

Preparation of Ester

IE can be prepared by the Alcoholic solution of silver (I) salt of carboxylic acid react bond with halo alkane. $(CH_3COO)Ag$

$CH_3Br + CH_3COO^- \rightarrow CH_3OOCH_3 + Br^-$.

methyl methanoate.

Preparation of Amine

Alkanation of Ammonia takes place if an alcohol solution of ammonia is heated with haloalkane in a sealed tube mixture of different classes of amines is formed.

a) $CH_3Br + NH_3 \rightarrow CH_3-NH_2 + HBr$

Above, is a Primary amine.

b) $CH_3-Br + CH_3-NH_2 \rightarrow CH_3-\underset{CH_3}{NH} + HBr$

c) $CH_3-Br + CH_3NHCH_3 \rightarrow CH_3\overset{CH_3}{\underset{CH_3}{N}} + HBr$

d) $CH_3-Br + CH_3\overset{CH_3}{\underset{CH_3}{N}} \rightarrow CH_3\overset{CH_3}{\underset{CH_3}{N}}CH_3 + Br$

Alkyl halide undergo Substitution

NUCLEOPHILIC SUBSTITUTION REACTION

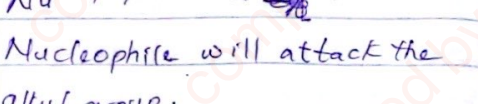
There are 2 main mechanisms:

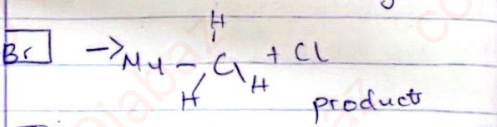
1. S_N2
2. S_N1.

S_N2 – the transition stage obtained in this mechanism shows bond breaking and bond formation simultaneously

Nucleophile will attack the alkyl group.

e.g





product

Two molecules are involved in the transition stage which is rate determining step. Hence, S_N2 (Substitution Nucleophilic bi-molecular)

This mechanism favours primary haloalkane but as the hydrocarbon part of the haloalkane increases, the substitution reaction slows down. The order of reactivity in S_N2 mechanism is methyl halide which in turns

greater than secondary and it is:

$CH_3X > CH_3CH_2X > (CH_3)_2CHX$

is not found in 3°.

It is noted that S_N2 reaction mechanism always leads to inversion of configuration.

S_N1 - This gives two intermediate. distinct transition state where one breaking and one formation occurs one after the one.

i) $H_3C-Cl \rightarrow \cdot CH_3^+ + Cl^-$

ii) $CH_3^+ + :Nu \rightarrow CH_3-Nu$

One molecule leaves completely before the nucleophile attack. Hence S_N1 which is Substitution Nucleophilic unimolecular. This mechanism favours the tertiary halo alkane.

Dr Fadare-Coord

27/04/26

Outline

HYDROCARBON

(Alkanes, Alkenes, Alkyne, Benzene & Derivative)

- Nomenclature
- Reactions
- Lab. Preparations.

(Textbooks & PQ) ⇒ Exam.

L. G. Wade Organic

DR FADARE

Hydrocarbons

They are the largest group of organic compound and consists majorly of hydrogen and Carbon.

⇒ Where can you get largest hydrocarbon? Crude oil.

Ass 1

1) Write out the fractions gotten from fractional distillation of Crude oil &
2) Examples of the kind of hydrocarbons contained in each fraction.
3) Petrochemicals definition.

Petrochemicals forms the basis of every industry chemically oriented.

Industries that rely on Petrochemicals are called petro-allied industry.

i) List every petro-allied industry & list the kind of ~~petro-allied~~ petrochemicals used in the petro-allied industry.

(Dangote Refinery is where petrochemicals are gotten from)

Petro-allied industry e.g Paints, Plastics.

Rubber - An hydrocarbon gotten from plants.

Another source of hydrocarbons is essential oils found in plants (they are not as plenty as crude oil or petroleum.

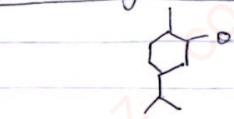
Ass 3

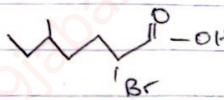
- What are essential oils
- What are the different types (minimum of 50 examples) and Terpenoids.

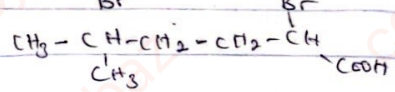
Essential oils are a subset of Terpenoids

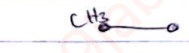
- Draw the structure of the 50 examples & write their common names.

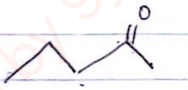
Line-Angle Drawing





from 





Ass: In not e & in a full scalp sheet (Submission Thursday)

Assignment Solution

1) Refinery Gases, Gasoline (Petrol), Naphtha, Paraffin (Kerosene), Gas oil (Diesel oil), Residue (Bitumen), Fuel oil,

2) (i) Refinery gases - C_1 to C_4
(ii) Gasoline (Petrol) - C_5 to C_{10}
(iii) Naphtha - C_7 to C_{10}

(iv) Paraffin (Kerosene) - C_{10} to C_{16}
(v) Gas oil (Diesel oil) - C_{14} to C_{20}
(vi) Fuel oil - C_{20} to C_{40}
(vii) Residue (Bitumen) - C_{70}
(viii) Lubricating oil - C_{30} to C_{50}

2.) Petrochemicals are the chemical compounds obtained from petroleum and natural gas.

b)(i) Plastic industry - Ethylene, Propylene, Benzene & Ethylene, Vinyl Chloride Monomer (VCM).

(ii) Pharmaceutical industry - Benzene & Phenol, Ethylene Glycol & Propylene Glycol.

(iii) Textile & Synthetic Fiber Industry - Paraxylene, Benzene, Propylene.

(iv) Paints, Coatings and Adhesives Industries - Toluene & Xylenes, Propylene & Methanol, Phenol (from Benzene) & Acetone.

(v) Agrochemical Industry - Methane, Ethylene Oxide & Alkylphenols, Benzene & Toluene derivatives.

(vi) Detergents, Soaps and Cosmetics Industries - Ethylene Oxide, Benzene & Propylene, Propylene Glycol

(vii) Synthetic Rubber (Elastomer) Industry - Butadiene, Isobutylene (from Butane).

3.) Essential oils are highly concentrated extracts from different plants that are used in aromatherapy or topically for various conditions.

b.) 1)

Myrcene $C_{10}H_{16}$

2)

Limonene $C_{10}H_{16}$

3)

etc . . . .

22/05/26

Reaction of Alkanes

Alkane undergoes SUBSTITUTION REACTION

$R-H \xrightarrow[UV\ Light]{Br_2} R-X$

where X is halogen

Mechanisms -

Initiation step
Propagation
Termination.

It is an uncontrollable reaction. Why is it uncontrollable and the implication?

ALKENES

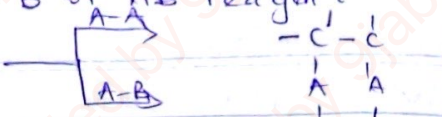
$-\overset{|}{C} = \overset{|}{C}-$

They are more reactive than Alkanes.

They undergo ADDITION reaction. In addition reaction, the reagent is added across the double bond. [Opening the double bond]

A - A or A_2 reagent

A - B or AB reagent



Types of reaction

1.) Hydrogenation
H_2 H - H

2.) Chlorination
Cl_2 Cl - Cl

3.) Bromination
Br_2 Br - Br

4.) Hydroxylation
HO - HO

5.) Hydration H - OH

6.) Polymerization

7.) Hydrochlorination
H - Cl

8.) Hydrobromination
H - Br.

9.) Ozonolysis.

It mainly addition across the double bond.

$CH_3-CH=CH-CH_3 \xrightarrow{H_2/Pd/C} CH_3-CH_2-CH_2-CH_3$ (Hydrogenation)

$CH_3-CH=CH-CH_3 \xrightarrow{Cl_2}$ Chlorination $CH_3-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_3$

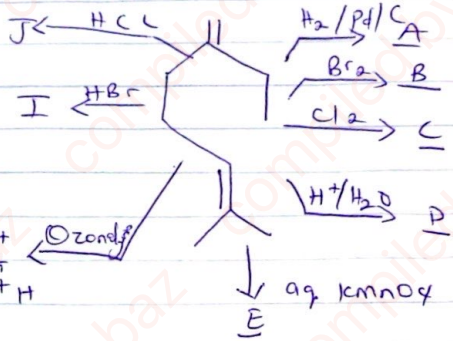
22/05/26

Reaction

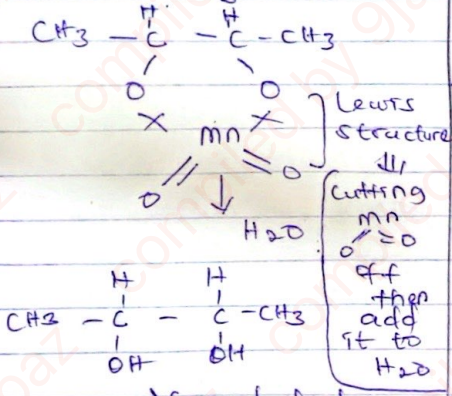
Hydration $CH_3-CH_2-\underset{OH}{CH}-CH_3$ (H_2O/H^+)

Hydroxylation $CH_3-CH=CH-CH_3$ (aq $KMnO_4$) $CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$

Ass



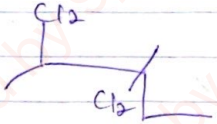
$CH_3-CH=CH-CH_3$ (aq $KMnO_4$)

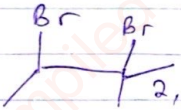


Exercise 5Dln

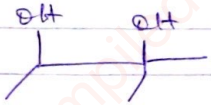
A.) 

2-methyl Butane

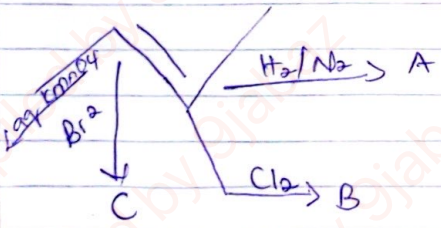
B.) 

C.) 

2,3 Bromo 2-methyl Butane

D 

Exercise



MARKOVNIKOV ADDITION

Note ⇒ Last section.

25/05/06

Anti-Markonikov Addition of water ⇒ final product is an Alcohol

The diff btw Markonikov

Ozonolysis

Polymerization

Synthesis of Alkane

Prep

The diff btw Markonikov & Anti-markonikov is the addition of Bromine. (In the addition of water

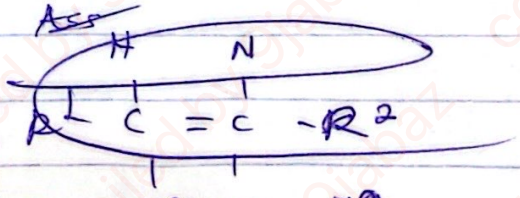
→ Preparation of Alkanes

Zaytsev rule

The most substituted alkane is the most stable alkane.

Tetra substituted is more stable than Trisubstituted.

Disubstituted is more stable than monosubstituted.



$R^2\ C - C^{\oplus} - H$

Which is most stable?

di $R^1 - \overset{H}{\underset{|}{C}} = \overset{H}{\underset{|}{C}} - R^2$

di $R - \overset{R^2}{\underset{|}{C}} = C - H$

mono $R^1 - \overset{H}{\underset{|}{C}} = \overset{H}{\underset{|}{C}} - H$

01/06/25

Undergoes Substitution rxn.

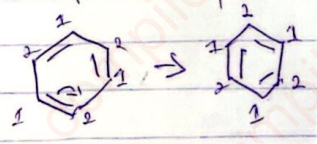
Benzene

C_6H_6

Double bonds. It hardly ever undergoes Addition reaction. It need to be forced under very harsh conditions to undergo addition reaction.

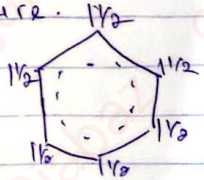
It is unsaturated.

Because of the delocalization of the pi-electrons.



The bond order is changing in delocalization.

The resonance hybrid structure.



The broken lines is to show the delocalization.

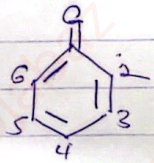
The bond order here is 1½

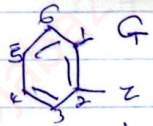
∴ It explains why there is unsaturation. It cannot undergo addition reaction because there is no double bond in the delocalization.

 → Don't draw this in kb class bcoz of mechanism of benz.

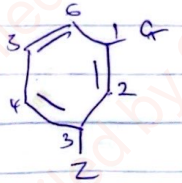
The Derivatives of Benzene (Nomenclature)

Every carbon atom on the benzene is equal, either clockwise or anticlockwise.

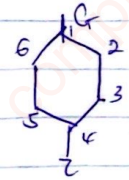




When you have 1,2-Substitution, you have ~~orto~~ ortho or O



1,3-Substitution is meta or m.



1,4-Substitution is Para

fg

Bromo benzene

chloro benzene

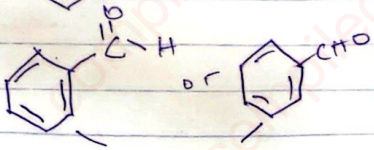
hydroxyl benzene
(phenol)

nitrobenzene

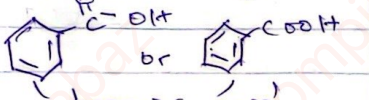
Aniline
Aminobenzene

Methylbenzene
(Toluene)

Methoxy
benzene
(anisole)

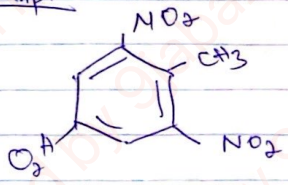


benzaldehyde



benzoic acid

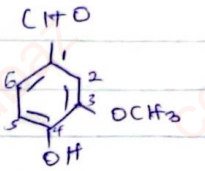
Example



CH_3 connected to Benzene is a priority (- Toluene)

methyl - 2, 4, 6 - trinitro benzene
or
2, 4, 6 - trinitro toluene (- very popular)
TNT

2.)



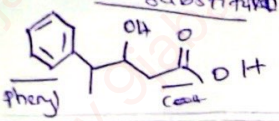
~~COOH > CHO > OH > OCH3~~ 1, 4
or

Order of Priority
$-COOH > -CHO > -NH_2 > -OH >$

~~OCH3~~

Answer
4-hydroxy - 3-methoxy benzaldehyde
It is a natural product found in certain type of legumes.
Used in cosmetics
It is ⇒ Vanilin
A major ingredient in Vanilla

Substituent

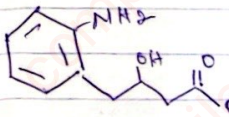


Once, a benzene is behaving a substituent, the benzene will be phenyl

3-hydroxyl - 4 - phenyl pentanoic acid

methyl, ethyl, propyl

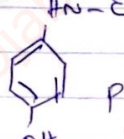
phenyl.



3-hydroxy -4- ~~phenyl~~ (2-aniline) phenyl pentanoic acid

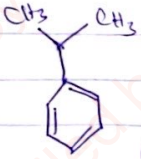
Ass

1) Structure of Cumene, xylene, ibuprofen

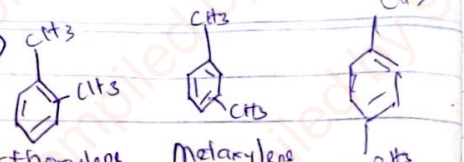


paracetamidophenol (paracetamol)

Solution

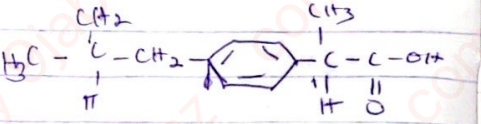
1) 

Cumene

2.) 

Orthoxylene Metaxylene Paraxylene

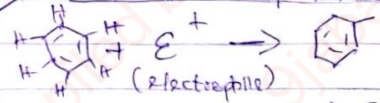
Xylene

3.) 

Ibuprofen

05 07/06/26

Reactions of Benzene



To give a substituted Benzene. This reaction is called an Electrophilic Aromatic Substitution (EAS)

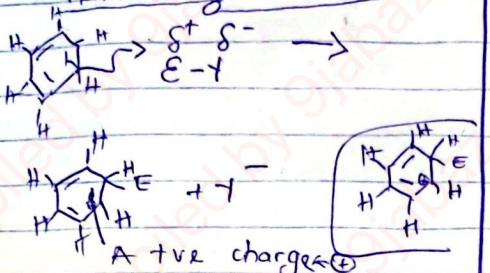
Types of EAS

1.) Halogenation
2.) Friedel - Crafts Alkylation
3.) Friedel - Crafts Acylation
4.) Sulfonation

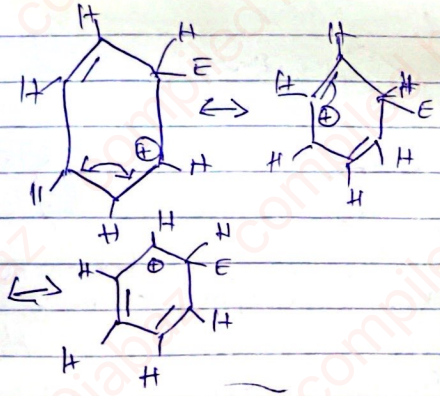
Describe Benzene as if it is a nucleophile

5) Nitration

General Mechanism



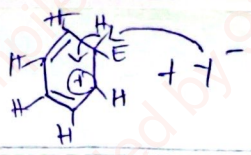
This is an Intermediate carbocation



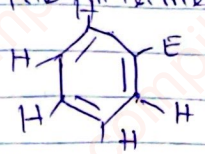
These are resonance stabilized intermediate carbocation.

Act 1

- What is the name of the intermediate carbocation

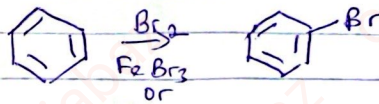


From the intermediate carbocation



We have a substitution product.

HALOGENATION



Br_2 is a slow reaction unless catalyst (Lewis acid e.g $FeBr_3$ or $AlCl_3$) is added.

Mechanism

Br_2 & $FeBr_3$ will form an addduct

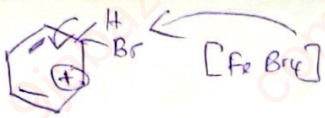
To give

$[Br^{\delta+}-Br^{\delta-}-FeBr_3]$

It polarize the Br faster.

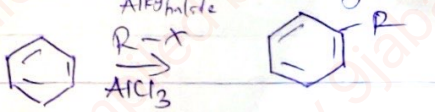
 will attack $[Br^{\delta+}-Br^{\delta-}-FeBr_3]$

To give



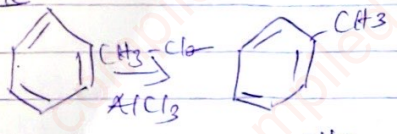
To give Bromo-benzen

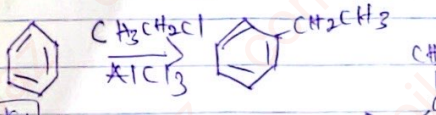
Friedel's Crafts Alkylation



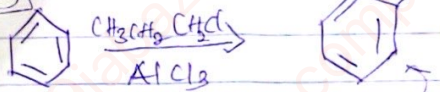
To get, Alkyl Benzem

Example (A.D.C)





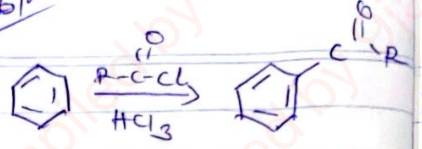
Tricky



To get Iso propylbenzene. instead of the expected propylbenzene.

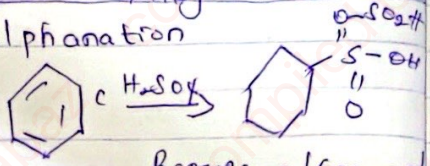
Qy: Why & How did it happen

05/06/26



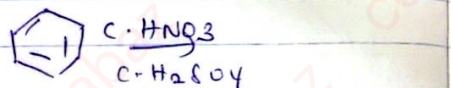
Friedel Craft's Alkylation

Sulphonation



Benzene sulfonic acid

Nitration



LABS

Used in detergent, Liquid soap, shampoo etc.

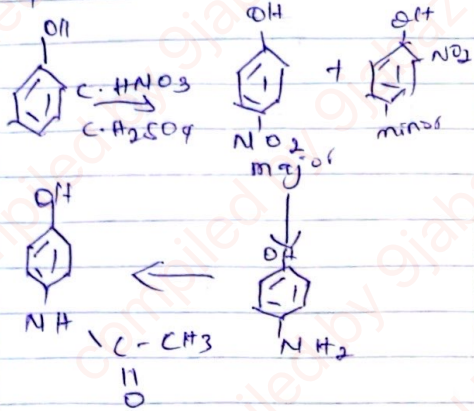
To derive this, friedel craft acylation followed reduction

* Names of the reduction and reagents.

Which happens in acidic medium.

Which happens in basic medium

Why is friedel craft acylation before reduction.



Reactions of substituted Benzene

EWG: Electron withdrawing Group

EDG: Electron donating group.

Electron withdrawing Group deactivate the benzene.

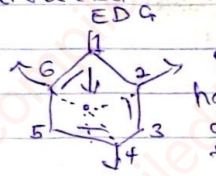
A deactivated benzene ring is meta directed.

Implication of deactivated Benzene ring.

The benzene ring will no longer be susceptible to electrophilic aromatic substitution.

EDG: Donate electron towards Benzene ring, the electrons are pumped towards the centre and then dissipated towards the surroundings.

Thus, benzene ring is activated.



Position 2, 4 & 6 have higher electron density than the rest.

A benzene ring that is activated will be Ortho-para directing.

Electron withdrawing Group.

It withdraws inductively and mesomerically.

Inductively & mesomerically

$-\overset{O}{\overset{\|}{C}}-OH$ inductively

$-\overset{O}{\overset{\|}{C}}-R$ inductively.

EDGs

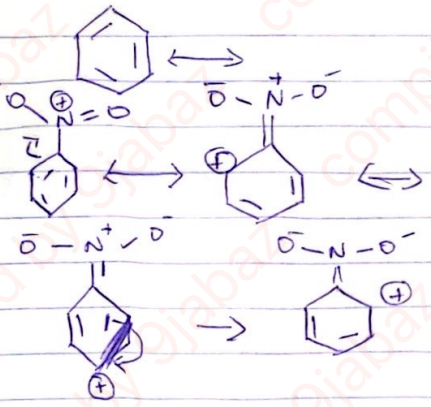
- $-\ddot{N}H_2$
- $-\ddot{O}H$
- $-\ddot{O}R$

} Highest donating Cap

- $-NH-COR$
- $-O-CO-R$

R (alkyl group) donate inductively.

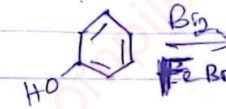
Alkyl group activates benzene ring but not as much as the ones above.

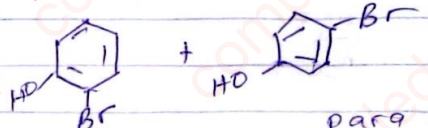


09/06/25

c- conc.

Examples

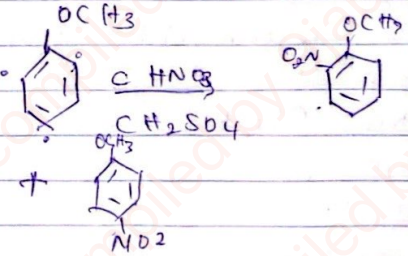


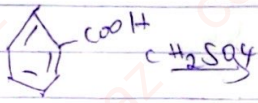


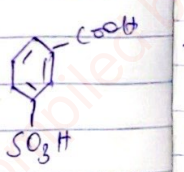
ortho product sterically hindered (minor)

para Product major prod

Ortho :- Two constituents are close together & there is a tendency for a steric hinderance (minor). Para product will be the major product





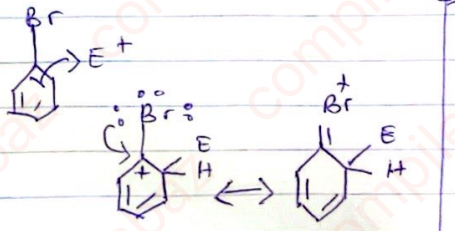


meta product

Halo benzene (special case)

Br withdraws electron (it does it inductively)

However, it can donate electrons (mesomerically) in a way that stabilizes the intermediate arenium ion when the electrophile (E^+) is added to either the ortho or para position

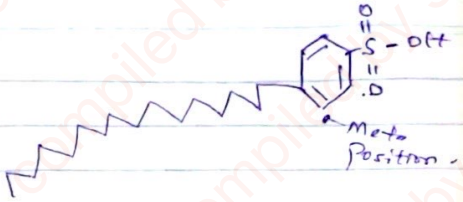


The reaction will be slow because Benzene ring will be deactivated.

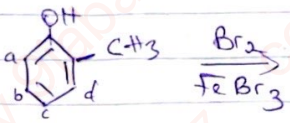
The products will either be ortho or para product.

The yield will be low.

The possibility of ending up with a mixture is very high.



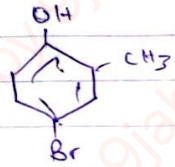
Start with Friedel Craft reaction first.

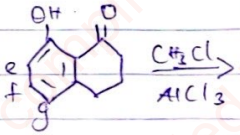


Br will be added to (c)

⇒ OH activates the rings than CH_3

To give,



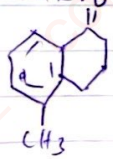


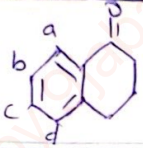
e is ortho to OH

g is Para to OH because there is less steric hindrance

CH_3 is added to (g)

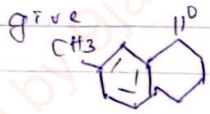
To give,

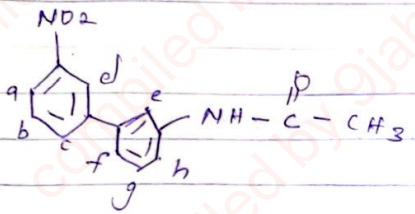




(b) Is preferred.

To give





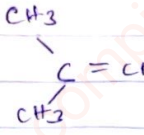
NO_2 will go to (e)

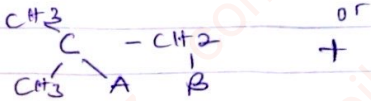
Test.

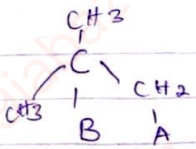
Missed Note

22/05/26

MARKOVNIKOV ADDITION







-) $CH_3 - \overset{CH_3}{\underset{}{C}} = CH_2$ HCl

$CH_3 - \overset{CH_3}{\underset{Cl}{C}} - CH_3$

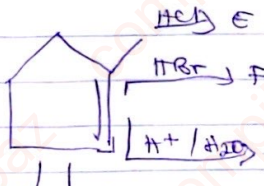
Holiphilic carbon.

Add hydrogen to the holiphilic carbon [CH_2] with the highest hydrogen atom.

-) $CH_3 - \overset{CH_3}{C} = CH_2$ H_2O

$CH_3 - \overset{CH_3}{\underset{OH}{C}} - CH_3$

Exercise

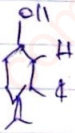


H.) 

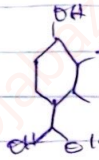
Addition of Br_2 across the double bond

I.) 

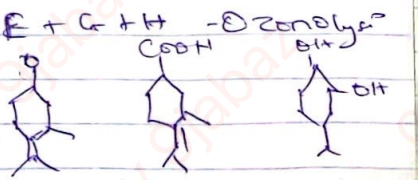
Addition of Cl_2 across the double bond

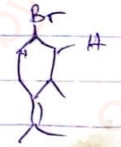
J.) H^+/H_2O 

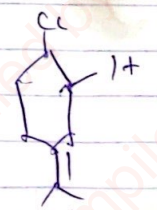
Acid catalyzed Hydration

K.) 

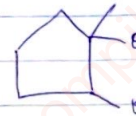
Dilute KMnO4, 'mild' oxidation with dilute KMnO4.

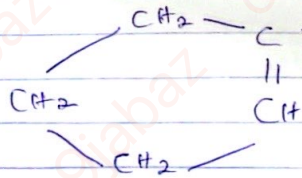
L.) 

M.) HBr 

N.) HCl 

Addition of HCl across the double bond.

I. 



Ass solution

A.) 

Hydrogenation of double bond.

THIRD PART

11/06/26

Prof Famuyiwa

CHM cont'd

E1 & E2

Elimination rxn. of haloalkane

Mechanism

The reaction of haloalkane in alcoholic solution of sodium or potassium hydroxide will dissolve into elimination reaction aka De-Hydrogenation

$R-CH_2-CH_2-X \xrightarrow[KOH]{Alcohol} R-CH=CH_2$

In an elimination reaction where two products are possible, Zaytsev rule is used to produce the major / minor.

For example, 2-chlorobutane

$CH_3-\underset{Cl}{\overset{H}{C}}-CH_2-CH_3$ elimination

To give

$CH_3-\overset{H}{C}=CH-CH_3 + HCl$

and

$CH_3-\overset{H}{C}=C-CH_3 + HCl$

ZAITSAV rule says the more substituted an alkane, the more stable the alkane

There are 2 main mechanism of elimination named: E2 & E1.

E2 mechanism

This is bi-molecular elimination (2 atoms at the same time leave simultaneously in the transition state).

Ex: In the reaction of 2-bromopropane in alcoholic solution of NaOH.

What will be the product?

Soln

$CH_3 - C - CH_3$
|
Br

To give

$CH_2 = C - CH_3 + HBr$

The reaction (E2) mechanism favor the transition state where less stable Carbocation is formed.

(Primary carbocation is less stable)

E1 Mechanism - Unimolecular elimination.

The two leaving atoms leave one after the other in transition state

In the reaction of tertiary butane

$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - Cl$ floride.

The reaction mechanism E1 favors transition state when more stable carbon cation is found.

Tet-butyl carries the functional group.

When secondary carbon cation, the shape matter when hydrocarbon is less E1 is favoured. When hydrocarbon is more, E2 is favoured.

e.g $CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - Cl$

Ans: 2-methyl Propane

$CH_2 = \overset{CH}{\underset{CH_3}{C}} -$

15/06/26

S_N2 Mechanism

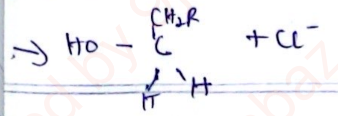
Substitution

H → R'
H → R''

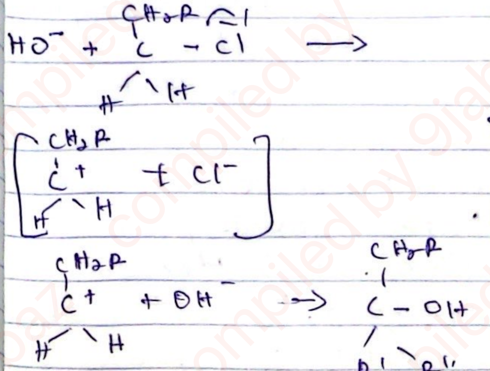
$HO^- + \overset{CH_2R}{\underset{H}{\overset{|}{C}}} - Cl \longrightarrow$

$\left[HO \cdots \overset{CH_2R}{\underset{R' \quad R''}{\overset{|}{C}}} \cdots Cl \right]$

Transition state



SN 1



Secondary can be SN2 & SN1 depending on the R

For SN2, the carbocation should be primary. $ Tertiary for SN1.

*Re

SN2

This mechanism favours the primary haloalkane but as the hydrocarbon part of the haloalkane increases, the substitution reaction slows down due to steric effect as it is shown in the table below:

SN2

Compound	Rate
CH_3-X	30
CH_3-CH_2-X	1
$(CH_3)_2-CH-X$	0.02
$(CH_3)_3-CH_2-X$	0.00001
$(CH_3)_3\ C-X$	0

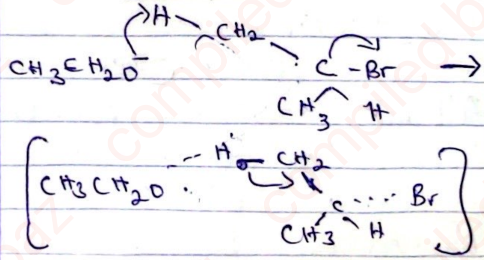
It will be noted that SN2 reaction mechanism always leads to inversion of configuration especially with a compound that contain stereo centre.

~~ELIMINATION REACTION OF HALOALKANE~~

$CH_3CH_2O^- + CH_3CHBrCH_3$

$\longrightarrow CH_3CH=CH_2 + CH_3CH_2OH + Br^-$

Mechanism.

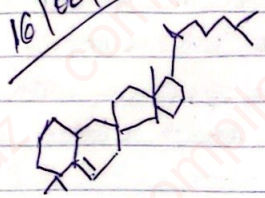


The rxn mechanism favours the transition state where less stable carbocation is found - SN_2

~~[illegible]~~

16/06/26

Revision



a) How many chiral centre are in this structure? 7

b) Isomers - 27 ⇒ 128

{- Line structures}

How many ~~tautiomer~~?

What are nucleophile and electrophile?

SUBSTITUTION VS ELIMINATION

All nucleophiles are potential bases and all bases are potential nucleophiles.

Therefore, nucleophilic substitution reaction and elimination reaction

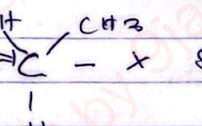
~~All nucleophiles are potential bases & all ba~~

Often compete with each other.

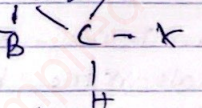
Let consider SN_2 and E_2

SN_2 occur when nucleophile or a base attacks a carbon atom that carries the halogen.

while E_2 occurs when base or nucleophile attacks a bitter hydrogen, hence the competition.



Nu - Nucleophile attacks ~~Hydrogen~~, X - substitution



Base attacks H - Elimination

When the substrate is a primary halide and the base is a etoxide

ion. Substitution is highly favoured.
When the subtrate is a secondary halide & the base is ethoxide ion; elimination is favoured.
With tertiary haloalkane, SN2 reaction do not occur. So, the elimination reaction will dominate. and highly favoured especially when the reaction is carried out at high temperature.
Elimination will be preferred to Substitution.

- Increase in temperature favours elimination reaction over ~~elimination~~ substition reaction
- Strong sterically ~~hindered~~ base such as But~~ty~~t-Butoxide ion

favours elimination over substitution.

SN1 vs E1

Since the E1 and SN1 reaction proceed through the formation of a common intermediate, E1 reaction are favoured by substrate that can form stable carbocation. [Tertiary halide]. They are also favoured by poor nucleophile (weak base) and they are generally favoured by the use of polar solvents.
Finally, increasing the temperature of the reaction favours reaction by E1 mechanism at the expense of the SN1 mechanism.
If the elimination product is desired. It is more convenient to add a strong base & force an E2 reaction to take place instead.

Q. Which is more & least stable?

$(CH_3)_3C^+$,
$(C_2H_5)_3C^+$, $(C_2H)_3C^+$
, $(C_4H_9)_3C^+$

The bulkier - the more stable

2.) What is the major product of the rxn between 2-methyl propene and ~~Iodine~~ Iodine Chloride.

Answer:

3.)