



*Organic chemistry for
non-chemistry students (233).*

Summary



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Chapter 1

Bonding and Isomerism

Ionic compounds: metal with non-metal.

Covalent molecules: all atoms are non-metal.

Bond energy: energy required to break 1 mol of bond (endothermic)

$c-c < c=c < c\equiv c$ (the strongest bond)

Bond length: distance between two nuclei of atoms.

as bond energy \uparrow the bond length \downarrow .

covalent bond: *Polar *non-polar: (c-H)

Hydrocarbons: compounds contain only carbon and hydrogen atoms .

***Alkanes:** no double bonds nor triple bonds .

*** Alkenes:** contain carbon-carbon double bond.

*** Alkynes:** contain carbon-carbon triple bond.

Electronegativity: ability of an atom to withdrawn electrons (in the bond) to itself .

H					
		C	N	O	F
				S	CL
					Br
					I

 (increase)

C	N	O	F
		S	CL
			Br
			I

σ Bond is stronger than π bond.

Hybridization:

If carbon atom forms 4 σ bonds : SP^3 hybridization, bond angle 109.5° and geometry is **tetrahedral** .

If carbon atom forms 3 σ bonds : SP^2 , bond angle 120° , **trigonal planar**.

If carbon atom forms 2 σ bonds : SP , bond angle 180° , **linear**.

***Resonance :** 1) σ bonds and atoms are localized

2) π bonds and lone pair of electrons are delocalized

3) Total formal charges are equal on both structures .

Formal charge: actual charge of a given atom. = (number of valence electrons) – (number of intervening electrons around atom after homolytic cleavage) .

*Hybrid structure(real structure)

Isomers: molecules have the same molecular formula .

Constitutional isomers (structural) : have the same molecular formula but different arrangement of atoms.

End of chapter

Chapter 2

Alkanes and cycloalkanes

Alkanes: Acyclic hydrocarbons which have a general formula C_nH_{2n+2} , each carbon is SP^3 hybridized .

Physical properties:

1) Alkanes are insoluble in H_2O ; due to the absence of hydrogen bonding with H_2O molecules (hydrocarbons are non-polar molecules).

Alkanes are soluble in non-polar solvents.

2) In general alkanes have low boiling point (b.p) since intermolecular force among alkanes molecules is **van der waals** (weak forces) **however as molar masses of alkanes increases the b.p increase.**

*For identical molar masses , asymmetrical increases the b.p increase.

Nomenclature of alkanes:

First :for continuous chain (unbranched alkanes)

CH_4 methane

C_2H_6 ethane

C_3H_8 propane

C_4H_{10} butane

C_5H_{12} pentane

C_6H_{14} hexane

C_7H_{16} heptane

C_8H_{18} octane

C_9H_{20} nonane

$C_{10}H_{22}$ decane

Second: for branched alkanes

- I. Locate the longest continuous carbon chain to determine the parent's name .
- II. Number the chain from the end nearer to the first substituent .
- III. Determine the position of each substituent on the longest carbon chain.

IV. If 2 or more identical substituent are present, use the prefixes (Di for 2/Tri for 3/Tetra for 4) .

V. Write substituents (based on alphabetical order) first then parent name.

VI. Naming of substituents: **halogens**: F: fluoro , Cl: chloro , Br: bromo, I iodo. **Alkyl group** (C_nH_{2n+1}): CH_3 methyl , C_2H_5 ethyl

$CH_3-CH_2-CH_2$ (is called **propyl**)

$CH_3CH_2CH_2CH_2$ (is called **butyl**)

$(CH_3)_2CHCH_2$ (is called **iso butyl**)

CH_3CHCH_3 (is called **isopropyl**)

$CH_3CHCH_2CH_3$ (is called **sec-butyl**)

$CH_3C(CH_3)_2CH_2$ (is called **tert-butyl**)

VII. If you have 2 equal long of carbon chain, select one with the most branches.

VIII. If branching occurs at equidistant ; number, the chain from the end according to the alphabetical order of substituent . (just compare the first digit then select a lower one) .

IX. Prefixes are not included in comparison of the alphabetical order of substituents but iso is included .

*Drawing of molecules: start drawing of parent name then number the chain from any end and finally draw substituents .

*(n): normal: on branching .

Classification of carbon atoms:

1° : primary

2° : secondary

3° : tertiary

4° : quaternary

Cycloalkanes: they are cyclic hydrocarbons with a general formula (C_nH_{2n}).

Naming of cycloalkanes

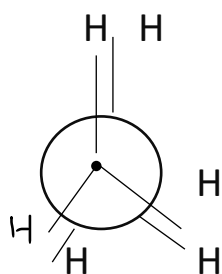
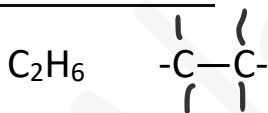
1- present of 1 sub (no need for numbering)

2- present of 2 sub: a) give no1 for carbon atom in the cyclic that a sub based on alphabetical order.

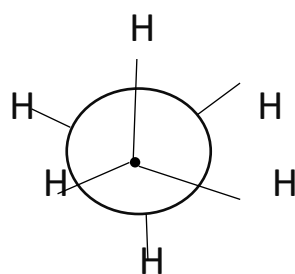
b) give the second sub a lower no .

Conformation of alkanes and cycloalkanes

First: alkanes



Eclipsed



staggered

Staggered conformer is more stable than eclipsed conformer.

Conformers (Conformational isomers) they are isomers (same molecular formulas) with same arrangements of atoms (not constitutional isomers) they are obtained by interconvertible rotation around σ bond (single bond) .

Second: cyclohexane : it has no angle strain (bond angle 109.5°) , two conformational structures are present.

In chair conformation each carbon has 1 axial bond in the plane and 1 equatorial bond in the plane, so each carbon has 1 ax and 1 eq bonds.

eq bond is more stable than an ax bonds and large groups atoms prefer eq bonds .

If ring flips: each ax bond becomes eq bond and each eq bond becomes an ax bond.

cis- trans isomerism in cycloalkanes:

If a cyclic has 2 sub and these sub are not located at same carbon, we should use the cis-trans.

*Cis: same side (up-up/down-down)

*Trans: opposite sides (up-down)

-Include cis-trans in the naming .

*No relation between up/down and eq/ax.

They have different physical properties (boiling point, melting point) and can be separated using physical methods(such as distillation)

Summary of isomerism

*Isomers: same molecular formula

1- Structural isomers(constitutional)

2- stereoisomers(same arrangement of atoms)

a) Conformers(rotation around σ bond

(Eclipsed - staggered / ax-eq)

b) Cis-trans

*Note: you can't find a relationship (cis-trans) and (conformers) at the same time.

The relationship:

(Cis-trans, conformers, identical, constitutional isomers, resonance, not isomers)

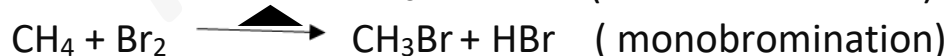
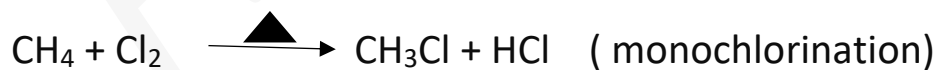
Reaction of alkanes :

1) Combustion of hydrocarbons



2) Radical substitution reaction

Radical: odd number of electrons it is very reactive.

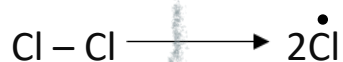


*different environment of H will produce different products (structural isomers).

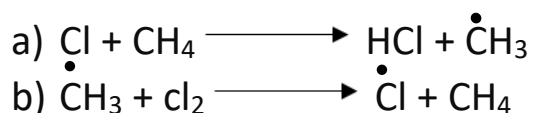
***Mechanism of reaction:**



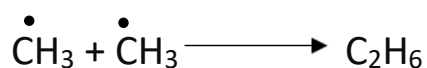
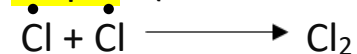
Step 1 : (initiating step) : production of radical



Step 2 : (chain-propagating step)



Step 3 : (chain-terminating)



(Radical is consumed and no radical is produced)

*Radical is consumed in reactant and another radical is produced in product, step 2 will be repeated to get more.

End of chapter

Chapter 3

Alkenes and alkynes

Alkenes have general formula: C_nH_{2n} (as cycloalkanes).

Alkynes have general formula: C_nH_{2n-2} .

*Cumulated: $C=C=C$

*Conjugated: $C=C-C=C-C=C$

*Isolated: $C=C-C=C-C-C=C-C=C$

* Nomenclature of Alkenes and alkynes:

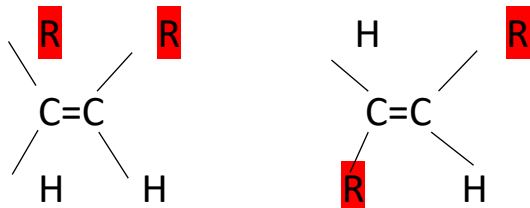
- I. Select the longest carbon chain that contain $C=C$ or $C\equiv C$.
- II. Number the chain from the end nearer to double or triple bond if numbering is equidistant number the chain from end nearer to 1st sub ... if equidistant numbering based on alphabetical order of sub.
- III. Indicate the position of $C=C$ or $C\equiv C$ using a lower number.
- IV. The parent's name is ended by: ene for alkene, yne for alkyne.

Notes: if molecule contain double and triple bond and equidistant, start numbering from alkene.

* $CH_2=CH$ (is called: vinyl)

* $CH_2=CH-CH_2$ (is called allyl)

Cis-trans isomerism in alkenes



CIS

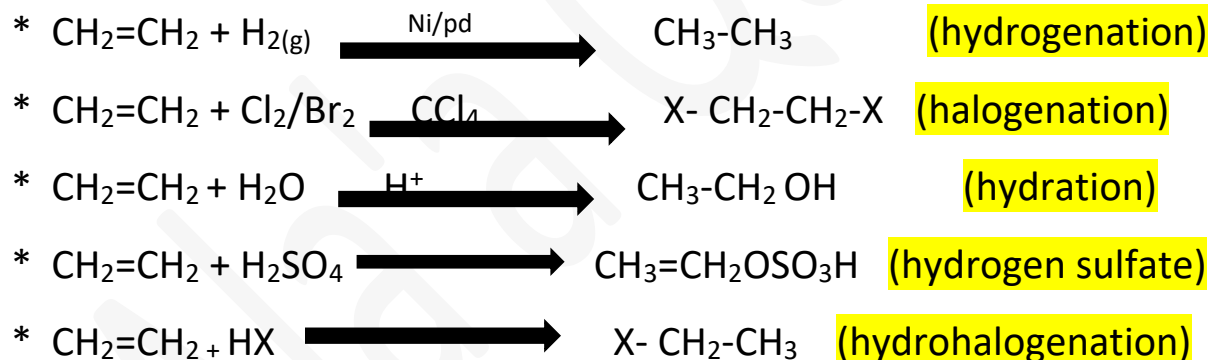
trans

Note: if alkene has identical group (atom) on the same carbon of C=C
There is no cis nor trans.

Reaction of alkenes:

π Bond is broken in reaction and new σ bonds are formed in the product.

1) Addition reaction (electrophilic addition reaction)



2) Oxidation reaction

1- using KMnO_4



2- Ozonolysis using O_3 then Zn/H^+

σ and π bonds are broken of C=C.

markovnikov's rules: electrophile(H^+) is added to carbon of C=C that has more hydrogens that are attached directly to the carbon.

Explain: 3° carbocation that more stable > 2° carbocation > 1° carbocation > methyl.

Notes: $\text{CH}_2=\text{CH}_2 \xrightarrow[\text{H}_2\text{O}_2:\text{O}^-\text{H}]{\text{BH}_3:\text{THF}}$ (anti markovnikov)

Reaction of alkynes:

1) With X_2

*excess $\text{X}_2 \rightarrow$ alkanes

*1 mol $\text{X}_2 \rightarrow$ alkenes

2) With $\text{H}_{2(\text{g})}$. Pt/Ni \rightarrow alkanes

But in the present of lindlar's catalyst: alkene is not affected and just 1 π bond is broken in alkynes and cis product is obtained.

3) With HX

*Excess HX

*1 mol HX

4) with strong base (NaNH_2) (terminal alkyne)

For SP carbon hydrogen is the most acidic, while for SP³ hybridized carbon the acidity is the weakest.

5) with H_2O ($\text{H}^+ / \text{Hg}^{2+}$)

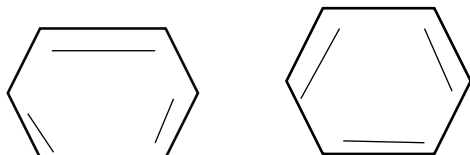
$\text{R}-\text{C}\equiv\text{C}-\text{H} \rightarrow \text{R}-\underset{\text{O}}{\text{C}}-\text{CH}_3$ (keto form).

End of chapter

Chapter 4

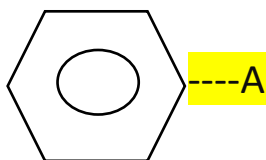
Aromatic compound

Benzene C₆H₆



There is no equilibrium rather there is a resonance relationship (extra stabilization), bond length of C-C is an intermediate between single bond and double bond, each carbon SP² hybridization.

Nomenclature: (Common name) (monosubstituted)



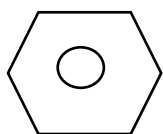
- A** : OH = phenol
- : CH₃ = toluene
- : NH₂ = aniline
- : C=C = styrene
- : CO₂H = benzoic acid
- : CHO = benzaldehyde
- : COCH₃ = acetophenone
- : SO₃H = benzenesulfonic acid
- : OCH₃ = anisole
- : isopropyl = cumene

Disubstituted:

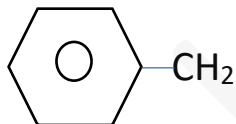
- 1) Select common name if present
- 2) Give a second sub a lower no
- 3) Don't give number for carbon outside and inside the ring
- 4) You can use (o) ortho (1,2 disub), (m) meta (1,3), (p) para (1,4)
(Two subs on the same benzene).
- 5) If common name is not present, use alphabetical order of sub then give a second sub a lower number.

3 or more sub:

- *Select common name if present then give sub lower number.
- *If common name is not present give sub the lower no.
- *Equidistant → based on alphabetical order .



As sub is called (phenyl)



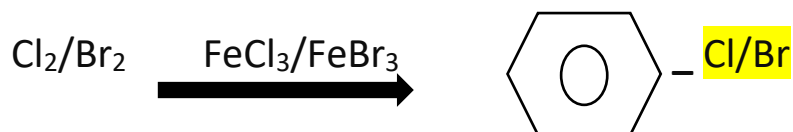
As sub is called (benzyl)

Reactions of benzene (electrophilic aromatic substitution)

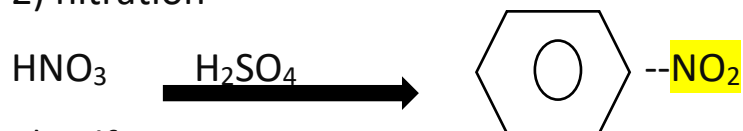


+

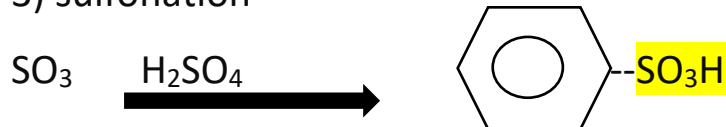
- 1) halogenation (chlorination or bromination)



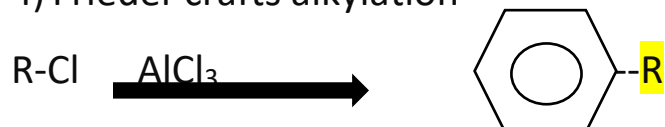
2) nitration



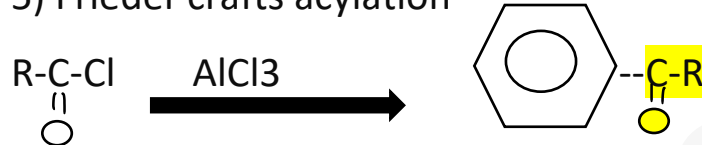
3) sulfonation



4) Friedel-Crafts alkylation

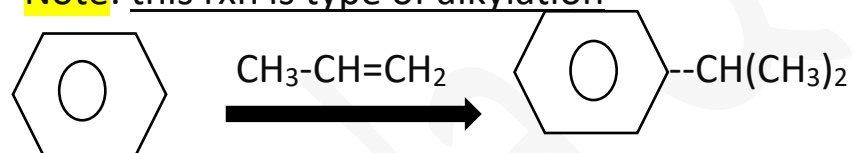


5) Friedel-Crafts acylation



One hydrogen atom in benzene is replaced by X, NO₂, SO₃H, R, R-C=O.

Note: this rxn is type of alkylation



Ring activating and deactivating substituents.

*Reactivity (fast rxn and slow rxn relative to benzene)

Activating groups: electron-releasing/donating.

(Decreases reactivity)

NH₂, NHR, NR₂

OH, OR

NH-CO-R

↓ R(alkyl)

Deactivating groups: electron-withdrawing.

(Decreases reactivity)

CO-R, COOH

COOR, CONH₂

SO₃H

CN

NO₂

*Orientation (which hydrogen in monosubstituted benzene should be replaced ortho, meta or para).

-electron-withdrawing groups direct a second substituent mainly meta position.

-electron-releasing group direct a second electrophile mainly ortho and para.

*Halogens direct ortho and para position but deactivate electrophilic aromatic substitution .

End of chapter

#First exam#

Chapter 5

Stereoisomerism

Stereoisomerism: deals with arrangement of atom in the space.

Chiral molecules: a molecule that contains at least one chiral center.

chiral center (stereogenic center): it is a SP^3 carbon that has 4 different atoms (or group), (no plane of symmetry).

*Don't look just on adjacent atoms, look on the whole chain.

Achiral molecule: molecule that has no chiral center (contains plane of symmetry).

*Configuration of a chiral center: (rules)

1. Give the priority for each atom (or group) around the chiral center according to the atomic number of the atom that is attached directly to a chiral center. (a,b,c,d)
2. If 2-atom that attached directly to a chiral center is identical, observe the 1st point of difference.
3. The group (d) should be located on back bond, but if it is located on front bond invert the configuration.
4. Look to path (a,b,c) if a direct is clockwise chiral center has R-configuration, if counterclockwise chiral center has S-configuration.
5. *Special case*: if group (d) is located on plane:
step1 :exchange between group (d) and (c) .
step2: find configuration for new drawing.
Step3: invert the configuration.

(R) and (S) is written before the name.

C	N	O	F
		S	Cl
			Br
			I

Enantiomers: pair of molecules which are mirror image to each other, but not superimposable.

If the configuration is opposite to each other, we have enantiomers relationship, but if configuration is the same the relationship is identical.

Notes:

*Enantiomers should have the same molecules formula (isomers) and same arrangement of atoms(not constitutional isomers).

*Any achiral molecules with its mirror image are identical.

Properties of enantiomers

They have identical physical properties such as melting point and boiling point, they cannot separate using physical methods.

They are differing in two concepts:

- a) Reaction with chiral reagent
- b) Direction of rotation for a plane polarized light.

Polarized light and optical activity

Instrument called: polarimeter

Polarizer : makes light beam in parallel planes.

Polarized light will enter from the first window and exit from the second window (both windows are glass and colorless)

In the tube we have a solution of organic compound.

*Principle of this instrument:

*When we add certain organic solution into a polarimeter tube these molecules may affect on the direction of the polarized light and when they exit from a second window, they polarized lights have been rotated.

Direction of the polarized light could be:

Clockwise: organic molecules are said to have dextrorotatory (D)(+) .

Counterclockwise: organic molecules are said to have leno rotatory (L) (-).

α : amount of rotation: observed rotation.

$[\sigma]$: specific rotation = $\alpha / \{\text{length of tube (dm)} * \text{concentration of organic substance (g/ml)}\}$

Some organic molecules have no effect on the direction of the polarized light ($\alpha=0$) No rotation(optically inactive) .

a) achiral molecules

b) racemic mixture: same rotation of enantiomers.

Chiral molecules :optically active.

We do not determine unless do an experiment.

Enantiomers they have same value of α but opposite sign.

E-Z convention for cis-trans isomers

- 1) It is applied only for alkene
- 2) E: opposite side , Z: same side (according to the atomic number)
- 3) Include in the naming.

*Fischer projection formulas

-Representation of chiral molecules in 2 dimensions instead 3 dimensions.

Step1: determine (a,b,c,d) .

Step2: direction from (a,b,c)

Clockwise: R-configuration

Counterclockwise: S-configuration

*If d-group locates at horizontal lines invert the configuration.

Diastereomers: compound with more than one chiral center.

One configuration is kept as is, while another configuration is inverted.

They are not mirror image to each other.

Diastereomers have different physical properties and can be separated using physical methods.

If molecules contain only 1 chiral center it cannot be a diastereomers.

Summary of relationship

1) Constitutional isomers

2) Stereoisomers:

a) Conformers

b) Configurational isomers:

1. Enantiomers(all configurations are inverted)

2. Diastereomers:

a. Cis-trans

b. E-Z

c. Some configurations are inverted, and other configuration are kept as.

Meso compound: contain at least 2 chiral center and plane of symmetry (achiral molecules).

Plane of symmetry: bisects a molecule into 2 identical parts.

No meso compound has only 1 chiral center.

Any molecule that has identical atoms (group) at 2 chiral center and one chiral center has S-configuration and other chiral center has R-configuration this molecule is a meso compound.

To calculate the maximum possible number of stereoisomers: $(2)^n$

N: no of chiral center+ no of double bonds.

Reactant has no chiral center: one chiral center is present (racemic mixture).

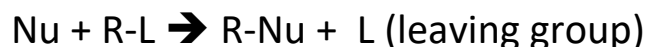
Reactant has already one chiral center: diastereomers.

End of chapter

Chapter 6

Substitution and elimination reactions

First: nucleophilic substitution (S_N) reaction.



Examples of Nu:

* Nitrogen Nu : NH_3 , R-NH_2 , $\text{R}_2\text{-N-H}$

* Oxygen Nu: O^- , H_2O , RO^- ,

* Carbon Nu: C^- , $\text{R-C}\equiv\text{C}^-$

* Sulfur Nu: S^- , SR^-

* Halogen Nu: I^- , Br^- , Cl^-

-no S_N reaction for SP^2 .

* S_N^2 :

1) Rate of rxn \propto [Nu] and [R-X].

2) rxn occurred in one step "no intermediate" .

3) reactive: (methyl) > 1° alkyl halide > 2° alkyl halide > 3° alkyl halide).

4) there is inversion of configuration .

5) strength of Nu increases the rate of reaction is also increased.

neutral nu is weaker than -ve charged nu.

6) prefer aprotic polar solvents.

[acetone /DMF/DMSO]

C	N	O	F
		S	CL
			Br
			I

*S_N¹:

- 1) rate of rxn \propto [RX].
- 2) rxn occurred in more than 1 step.
- 3) reactivity : 3° > 2° > 1° > methyl.
- 4) If reactant has a chiral center product will be formed in a racemic mixture.
- 5) prefer protic polar solvents [CH₃O-H / F-H / NH₃ / H₂O].

Second: elimination reaction.

π bond is formed

E2: Rxn occurred in one step.

E2: Rxn occurred in more than 1 step.

*1° Alkyl halides :

Bulk nu : S_n² Not bulk Nu : E2

*2° Alkyl halides :

S_N¹: H₂O / ROH , S_N²: C⁻N / S⁻H , E2 : O⁻R / O⁻H / C⁻H₃ / N⁻H₂

*3° Alkyl halides :

S_N¹: H₂O / ROH , E2 : O⁻R / O⁻H / C⁻H₃ / N⁻H₂ / C⁻N

End of chapter

Chapter 7

Alcohols and phenols

Alcohols have the general formula R-OH (OH called hydroxyl group)

Phenols have OH group attached directly to a benzene ring.

Nomenclature of alcohols: name is ended by -ol.

Classification of alcohols: 1°, 2°, 3°.

Physical properties of alcohols:

- 1) They can form hydrogen bonding among their molecules → have high boiling points
- 2) Low molar masses of alcohols are soluble in water (while as molar mass increase the solubility in water decrease)

Alcohols as acid: $\text{ROH} \rightarrow \text{RO}^-$

Alcohols as base : $\text{ROH} \rightarrow \text{RO}^+\text{H}_2$

CH_3O^- : methoxide

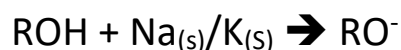
$\text{C}_2\text{H}_5\text{O}^-$: ethoxide

*Phenols is more acidic than alcohols.

*Electron-withdrawing group increase the acidity, while electron-donating group decrease the acidity.

***Reactions:**

1) acidity



We cannot use base (NaOH), since alcohols is very weak acid, but for phenols we use (NaOH).

2) oxidation of alcohols:

1° alcohol + jone's reagent (CrO_3, H^+ , acetone) \rightarrow Carboxylic acid

1° alcohol + PCC \rightarrow aldehyde

2° alcohols + jone's reagent / PCC \rightarrow ketone

3° alcohols + jone's reagent / PCC \rightarrow can't be oxidized

3) With H_2SO_4 (dehydration of alcohols to form alkane "removal of water").

Mechanism: E1

*More stable form since more alkyl group around $\text{C}=\text{C}$.

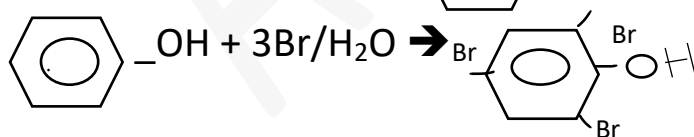
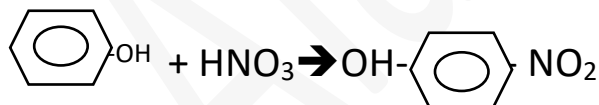
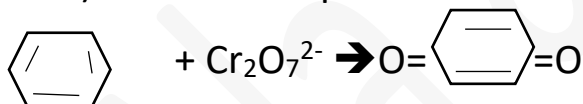
4) Preparation of alkyl halides from alcohols

$\text{ROH} + \text{HX} \rightarrow \text{R-X}$

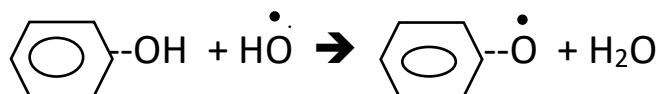
$\text{ROH} \xrightarrow{(\text{SOCl}_2/\text{PCl}_3)} \text{R-Cl}$

$\text{ROH} \xrightarrow{(\text{PBr}_3)} \text{R-Br}$

5) oxidation of phenol



6) phenols as antioxidants



Thiols (mercaptans): have the general formula RSH (-SH is called sulfhydroxyl group) .

Thiols are more acidic than alcohols .

Synthesis: $RX + S^-H \rightarrow RSH$ (S_N^2)

Reactions: Oxidation (use I_2/H_2O_2)

$RSH \rightarrow RS-SR$ (Disulfide) .

End of chapter

Chapter 8

Ethers

have the general formula: $R-O-R^*$

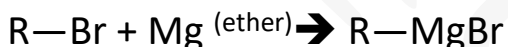
name is ended by ether.

If $R-O$ is a substituent: (CH_3O : methoxy, C_2H_5O : ethoxy)

Physical properties:

- 1) No hydrogen bonding is present among ether molecules \rightarrow they have low boiling point.
- 2) Ether can form hydrogen bonding with alcohols.

*Ether is inert \rightarrow can be used as organic solvents in preparation of Grignard reagent.



Note: $R-MgBr$ and $R-Li$ are strong bases and nucleophiles.

Synthesis: Williamson method

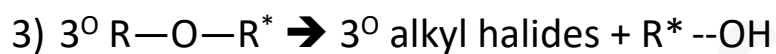
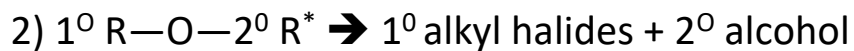
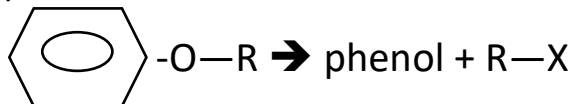
Alcohol ($R-OH$) + $Na_{(s)}/K_{(s)} \rightarrow$ alkoxy(RO^-) + alkyl halide [methyl or primary halide only] (R^*X) $\xrightarrow{S_N2} R-O-R^*$

Note: methanol + $(CH_3)_2C=CH_2 \xrightarrow{H^+} (CH_3)_3C-OCH_3$

Reactions: cleavage of ether



1)



End of chapter

#Sacond exam#

Chapter 9

Aldehydes and ketones

- Aldehydes have a general formula: RCHO
- Ketones have a general formula: RCOR*

Nomenclature: 1) aldehydes:

Name is ended by -al

OH, as sub is called hydroxy.

Use carbaldehyde if CH=O is attached directly to a cyclic.

2) ketone:

Name is ended by -one

Synthesis:

1) 1° alcohol $\xrightarrow{\text{PCC}}$ aldehyde

2) 2° alcohol $\xrightarrow{\text{PCC/ Ione's}}$ ketone

3) $\text{R-C}\equiv\text{C-H} + \text{H}_2\text{O} \xrightarrow{\text{H}^+/\text{Hg}^{2+}} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$

4) Friedel- crafts acylation

Physical properties:

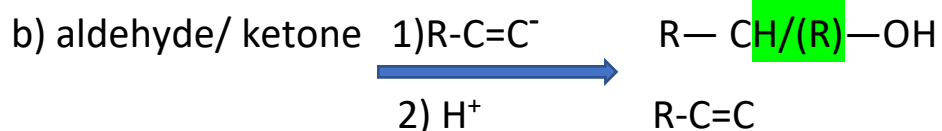
Aldehyde and ketone can't form hydrogen bonding among their molecules but can form dipole-dipole interaction therefore have a low boiling point.

Reactions: (nucleophilic addition)

1) For carbon Nu

a) aldehyde/ ketone $\xrightarrow{\text{HCN / KOH}}$ $\text{R}-\underset{\text{CN}}{\text{CH}}(\text{R})-\text{OH}$

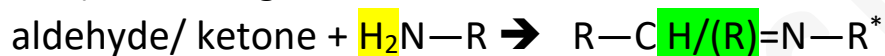
Cyanohydrin: CN and OH at the same carbon.



C) with $\text{R}-\text{MgX}$



2) For nitrogen Nu



$\text{C}=\text{N}$: imine bond

$\text{C}=\text{N}-\text{OH}$: oxime

3) For oxygen Nu

aldehyde/ ketone +

1 mol alcohol \rightarrow hemiacetal (OH and OR at the same carbon)

2 mol alcohol \rightarrow acetal (2 OR group at the same carbon).

Acetals and hemiacetals are stable in basic media, but they undergo hydrolysis in the present of large amount of water.

4) For hydride(reduction of aldehyde and ketone)

Reduction: no of H atoms increase / no of O atoms decrease

Aldehyde + reduction agent $\rightarrow 1^\circ$ alcohol

Ketone + reduction agent $\rightarrow 2^\circ$ alcohol

Reduction agent: NaBH_4 / LiAlH_4

Oxidation of aldehyde and ketone

Aldehyde + tollen's reagent or KMnO_4 or Ag_2O \rightarrow carboxylic acid

Cyclic ketone + $\text{HNO}_3 / \text{V}_2\text{O}_5$ \rightarrow $\text{OH}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$

Aldehyde is more reactive than ketone as Nu.

End of chapter

Chapter 10

Carboxylic acids and their derivatives

Carboxylic acids have the general formula: RCOOH

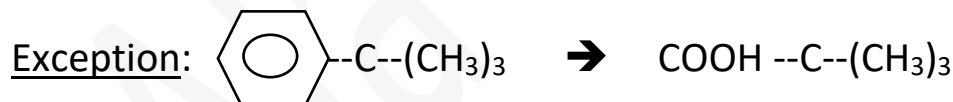
C=O as sub is called **oxo**

Physical properties:

- 1) Carboxylic acids are polar molecules and among their molecules there are hydrogen bonding and dipole-dipole interactions.
- 2) They have a higher boiling point.
- 3) Low molar masses of carboxylic acids are soluble in water.

***Synthesis:**

- A. Oxidation of 1° alcohol by jone's reagent or oxidation of aldehydes.
- B. Oxidation of side chain of benzene (regardless length of R).

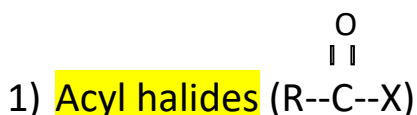


- C. Hydrolysis of nitriles.
- D. Reaction of Grignard reagent with carbon dioxide then addition of H^+ .

Carboxylic acid derivatives:

- 1- Acyl halide
- 2- Acid anhydride
- 3- Ester
- 4- Amide

Mechanism is Nu acyl substitution.

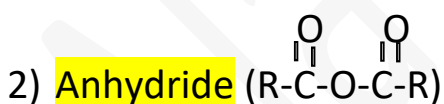


Synthesis:

Carboxylic acid + $SOCl_2$ / PCL_5 \rightarrow acyl halide

Reactions:

- 1) Hydrolysis \rightarrow carboxylic acid
- 2) Acyl halides + $R-\overset{\overset{O}{\parallel}}{C}-O$ \rightarrow Anhydride
- 3) Acyl halides + $R-OH$ \rightarrow ester
- 4) Acyl halides + R_2-NH \rightarrow amide



Synthesis:

- a) From acyl halide
- b) For cyclic anhydride: heating of dicarboxylic acids

Reaction:

- 1) Hydrolysis \rightarrow carboxylic acid
- 2) Anhydride + $R-OH$ \rightarrow ester
- 3) Anhydride + R_2-NH \rightarrow amide

3) Ester ($\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}^*$)

Synthesis:

- a) From acyl halide
 - b) From anhydride
 - c) From carboxylic acid + alcohol (esterification)
- *Alcohol and carboxylic acid in the same molecule \rightarrow cyclic ester(lactone).

Reaction:

- a- Ester + $\text{H}_2\text{O}/\text{OH}^- \rightarrow \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$
- b- Ester + $\text{R}_2\text{-NH} \rightarrow$ amide
- c- Ester + 2 mol $\text{RMgX} \rightarrow 3^\circ$ alcohol
- d- Ester + strong reduction agent $\rightarrow 1^\circ$ alcohol

4) Amide ($\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\text{R}_2$)

* 1° and 2° amides can form hydrogen bonding among their molecules, while 3° amines can't.

Synthesis:

- 1) From acyl halide
- 2) From anhydride
- 3) From ester
- 4) Carboxylic acid + $\text{R}_2\text{-NH} \rightarrow$ amide

Reaction:

1- Amides + H₂O /H⁺ → carboxylic acid

2- Amides + H₂O /OH → R-C(=O)-O⁻

3- Amides + LiAlH₄ → amines

The order of reactivity of Nu acyl sub:

acyl halide > anhydride > ester > amide

*For acidity:

Carboxylic acid > phenol > thiol > alcohol

End of chapter

Chapter 11

Amines

Organic bases derived from: NH_3

Classification: 1° , 2° , 3° .

NH_2 as sub is called amino.

Physical properties:

- 1) Only 1° and 2° amines can form hydrogen bonding among molecules, while with water molecules all amines can form hydrogen bonding.

2) For b.p

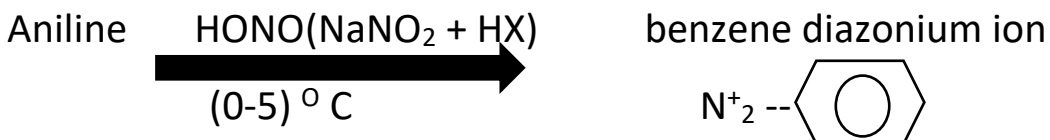
Carboxylic acid > alcohol > amines > aldehydes and ketones > alkanes.

Synthesis of amines:

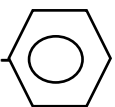
- a) Reduction of amides by LiAlH_4
- b) Reduction of nitriles to produce 1° amines
- c) Reduction of nitro group to prepare 1° aromatic amines (use $(3\text{H}_2/\text{Ni})$ or (1. SnCl_2/HCl 2. NaOH))
- d) Reduction (use NaBH_3NC) amination of aldehydes/ketones .

Reactions:

- 1) As base
- 2) As Nu
- 3) Diazotization reaction for 1° aromatic amine



benzene diazonium ion +

- 1) $\text{HBF}_4 \rightarrow$ Fluoro benzene
- 2) $\text{HCl}/\text{Cu}_2\text{Cl}_2 \rightarrow$ chloro benzene
- 3) $\text{HBr}/\text{Cu}_2\text{Br}_2 \rightarrow$ bromo benzene
- 4) $\text{KI} \rightarrow$ iodo benzene
- 5) $\text{H}_2\text{O}/\text{H}^+ \rightarrow$ phenol
- 6) $\text{H}_3\text{PO}_2 \rightarrow$ benzene
- 7) $\text{KCN}/\text{Cu}_2(\text{CN})_2 \rightarrow \text{CN}-$ 

Amines can act as bases

Aliphatic amines are stronger than aromatic amines

Amides are weaker than aromatic amines.

Electron-donating groups increase the basicity .

End of chapter

#Final exam#

The End 