A2 ORGANIC CHEMISTRY NOTES

by

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"Nothing is Particularly Difficult if you Break it Down into Small Jobs"
"A little more Persistence, a little more Effort, and you might not be the Hopeless Failure you think you are, Genius and Failure don't happen overnight"

Introduction to Organic Chemistry

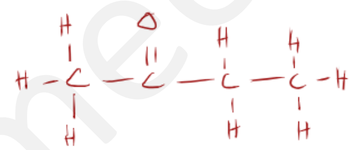
Organic - Chemistry of carbon compounds
- biological molecules
- fossil fuels

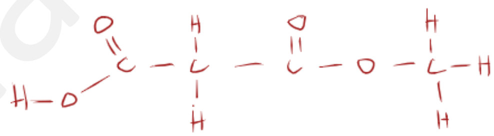
formulas:

molecular formula: $C_2H_4O_2$ total no. of atoms of elements in a molecule (no information about structure)

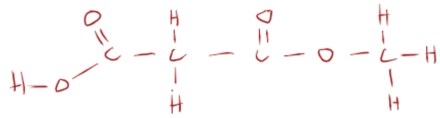
structural formula

1. **fully displayed formula**
   all atoms and bonds shown
   - C - 4 bonds
   - N - 3 bonds } lone pairs can form dative bonds
   - O - 2 bonds }
   - H - 1 bond
   - Halogen - 1 bond

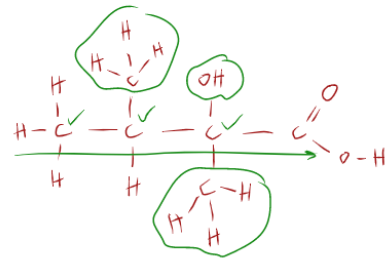




2. condensed structural formula



$HOOC\ CH_2\ COOCH_3$



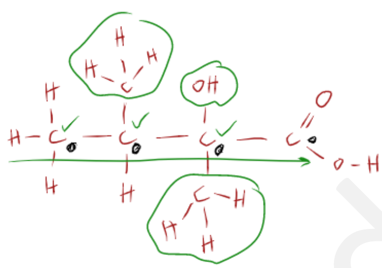
$CH_3\ CH(CH_3)\ C(OH)(CH_3)\ COOH$

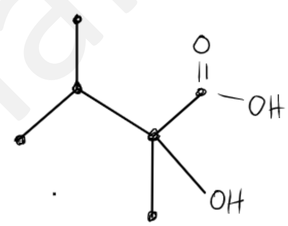
aldehydes

$R-CHO$

3. Skeletal formula

C − C bonds shown only any functional group.





Naming (Simple naming)

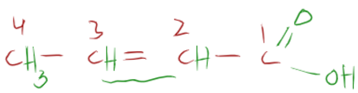
prefix

prefix	
meth	1C
eth	2C
prop	3C
but	4C
pent	5C
hex	6C
hept	7C
oct	8C
non	9C
dec	10C

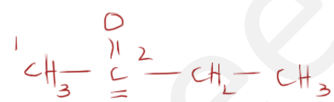
an or en

suffix

- alkane – ane
- alkene – ene (position of C=C)
- alcohol – ol (position of OH).
- carboxylic acid – oic acid
- nitriles – nitrile
- aldehyde – al.
- ketones – one (position of C=O).



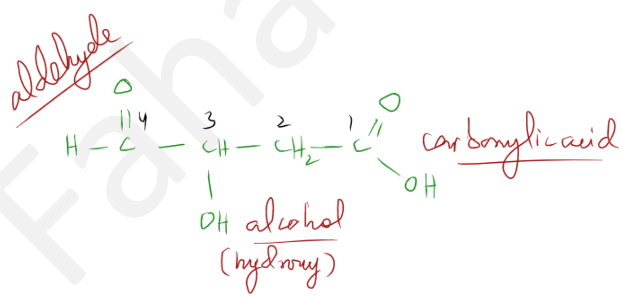
but-2-en oic acid



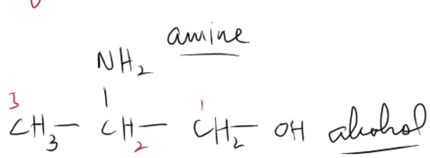
butan-2-one

> Counting is done from side which gives smaller # to higher precedence group. → suffix

RCOOH > nitriles > aldehyde > ketones > alcohols > amines > C=C
(hydroxy branch) (amino branches)



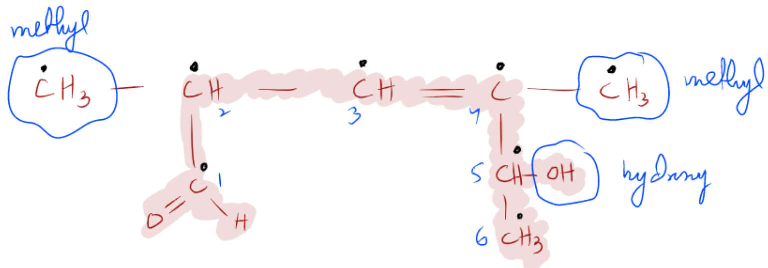
3-hydroxy butan-4-al oic acid



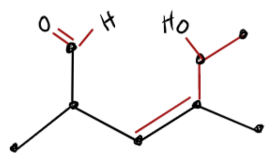
2-amino propan-1-ol

Branches

position – branch – longest carbon atom chain
alphabetical
- more substituent groups
- max C=C
- highest precedence group



5-hydroxy 2,4-dimethyl hex-3-en al



Isomers

Structural Isomers

same molecular formula different structural formula
(different arrangement of atoms)

(a) chain / branch isomers

C_5H_{12} $CH_3-CH_2-CH_2-CH_2-CH_3$ $CH_3-CH_2-CH(CH_3)-CH_3$ $CH_3-C(CH_3)_2-CH_3$

(b) Positional Isomer

change position of a functional group

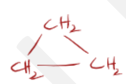
$CH_3-CH_2-CH=CH_2$ but-1-ene $CH_3-CH=CH-CH_3$ but-2-ene

(c) Functional group isomer

$CH_3-CH_2-C(=O)-H$ propanal $CH_3-C(=O)-CH_3$ propanone

$CH_3-CH_2-C(=O)-OH$ carboxylic acid $CH_3-C(=O)-O-CH_3$ ester

$CH_3-CH=CH_2$ alkene



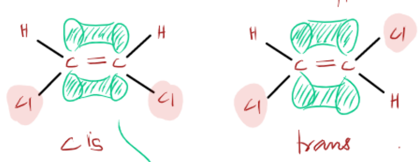
cycloalkane

Stereo Isomers

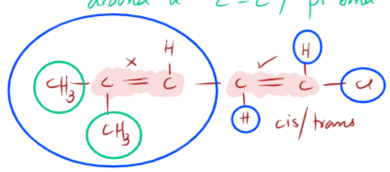
same molecular formula, same structural formula but different 3-dimensional geometry

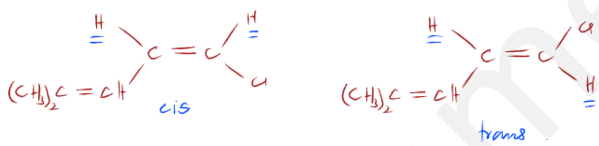
(a) geometric isomers

- C = C present
- each C must be bonded to two different groups



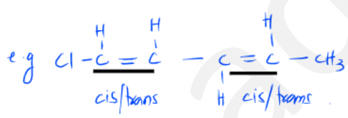
rotation is restricted around a C = C / pi bond





unsymmetric molecule

n × (C = C) cis/trans ⟶ 2^n different geometric isomers.



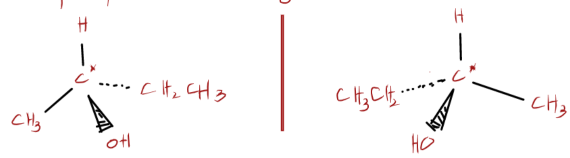
$2^2 = 4$

cis	cis
trans	trans
cis	trans
trans	cis

Optical Isomers (enantiomers, a mixture of enantiomers → racemate/racemic mixture)

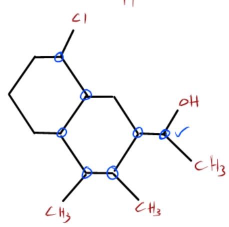
Chiral Carbon – sp_3 hybridized / tetrahedral, 109.5°
C makes 4 single bonds with 4 different groups.

↘ two non superimposable mirror images.



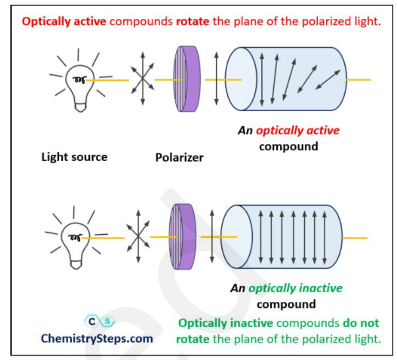
(+) (−)

both enantiomers, rotate plane polarized monochromatic light in opposite direction (clockwise / anticlockwise)



small enantiomers usually have exactly the same chemical and physical properties

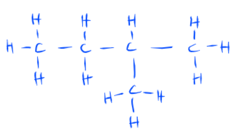
- large biologically / shape specific will have drastically different functions if stereochemistry is changed.



Alkanes

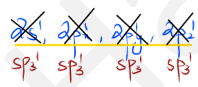
saturated hydrocarbons

C_nH_{2n+2}

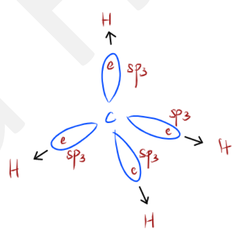


2 methyl butane

sp_3 hybridization – all single bonds, no π bond / double bond.



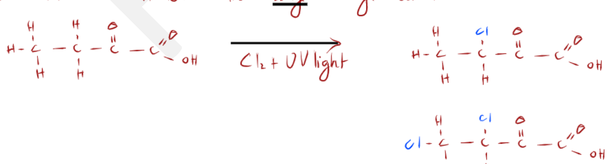
hybridization – mixing of orbitals to form new hybrid orbitals during bond formation



Free radical substitution

Cl_2 or Br_2 + UV light

× substitute Cl or Br into any alkyl chain.

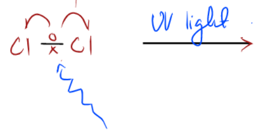


+ HCl by product

number/position of H atoms being substituted is random / multiple products produced.

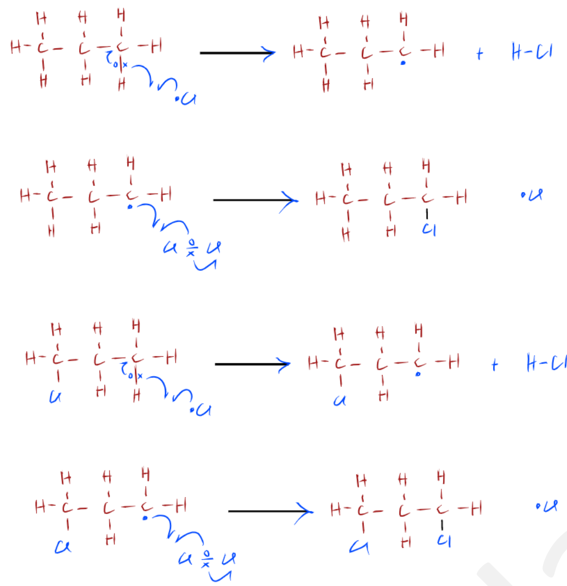
MECHANISM

1- Initiation: free radicals are produced

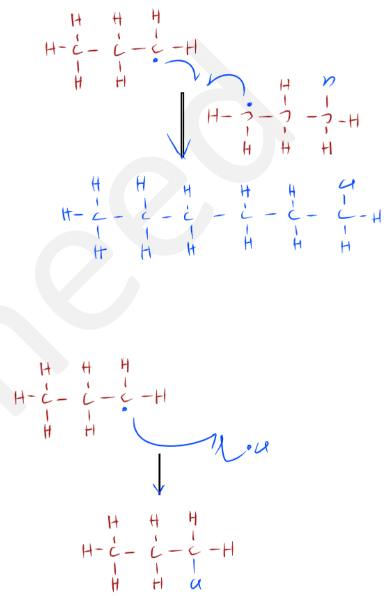


free radical: specie with unpaired e-
very reactive

2- Propagation: radicals attack H atoms



3- Termination: free radicals combine randomly.

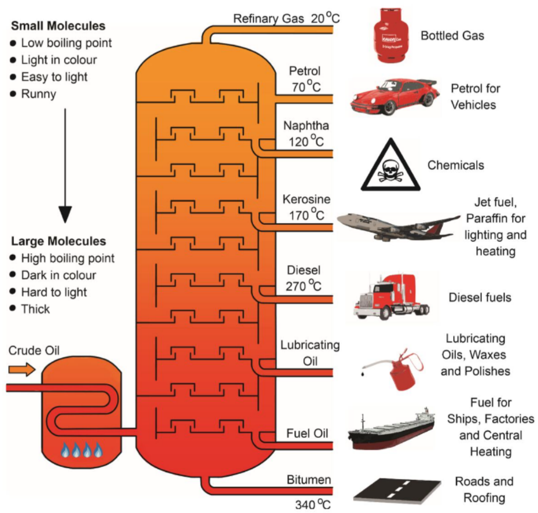


Crude Oil

source of most hydrocarbon

Fractional Distillation of Crude Oil

When crude oil reaches the refinery it is heated until it evaporates. As the vapour (*hydrocarbon gases*) condense back into liquids, the column sorts the different fractions from each other and removes them from the sides of the column. The larger hydrocarbons, with the high boiling points, turn back into liquids at the base of the column and the smaller hydrocarbons stay as gases. They rise up the column and condense at different levels. At the top of the column there are a number of hydrocarbons with low boiling points (between 20ºC and 70ºC) - these remain as gases.



Cracking

Zeolites / Pumice

Al_2O_3 + T°C > 450°C

long Chain hydrocarbon → smaller chain

- not very useful
- big molecules / more van der waals
- high MP/BP/ viscosity
- low flammability

smaller chain:

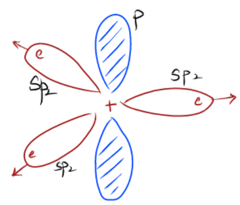
- alkanes
- alkene
- hydrogen
- more flammable
- less viscous
- low MP / BP
- lesser Van der Waals

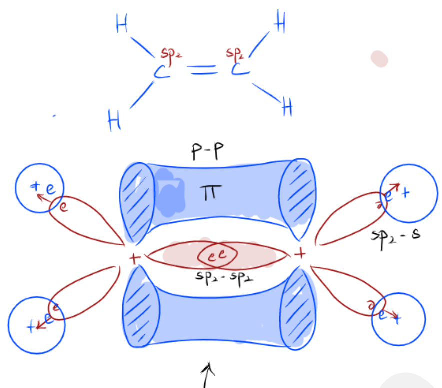
Structure of Benzene and Alkene

Alkenes "C = C"

↳ Carbon is sp_2 hydrized

~~2s¹, 2px¹, 2py¹~~ (2pz¹) (sp_2 sp_2 sp_2)



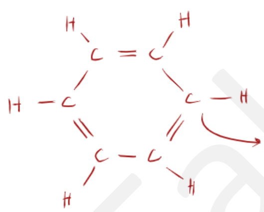


high e^- charge density
Attracts electrophiles VERY STRONGLY

Benzene

simplified version / Kekule structure
(don't use this) (1:1 ratio is only possible in benzene)

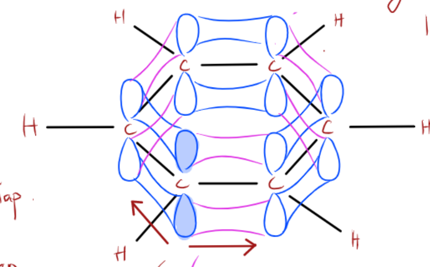
C_6H_6

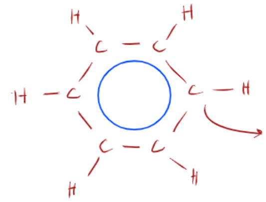


→ sp_2 hybridized
(all carbon atoms in benzene)

hexagonal planar
120°

C−C σ bonds
sp_2-sp_2 overlap.
C−H σ bonds
sp_2 - s overlap
π bonds − p-p overlap.





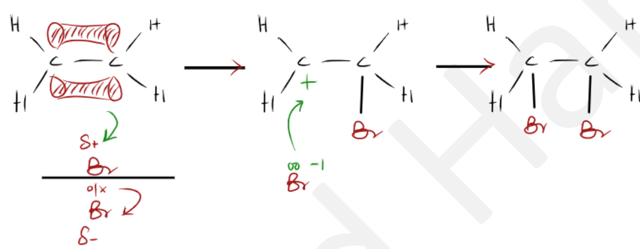
ring of delocalized π electrons.

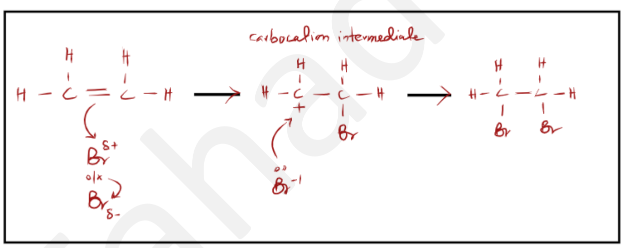
e^- density in π e^- cloud is significantly lower compared to an alkene π e^- cloud.

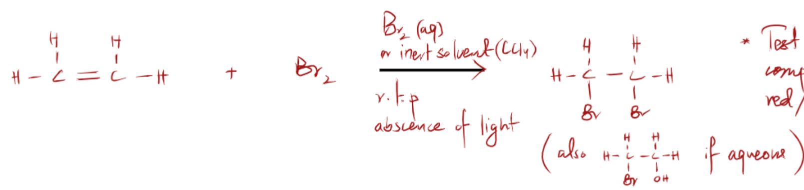
C − C	alkane	350 KJ/mol
C ⋯ C	benzene	520 KJ/mol
C = C	alkene	610 KJ/mol

Electrophilic Addition

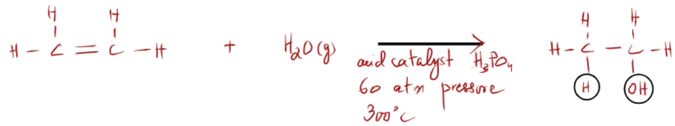
high e^- density π bond strongly polarizes Br_2

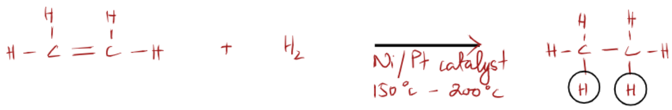




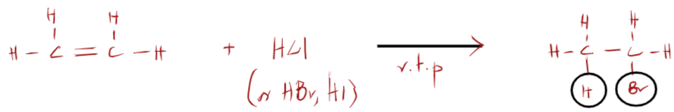


* Test for unsaturated compounds
red/orange Br_2 decolorizes



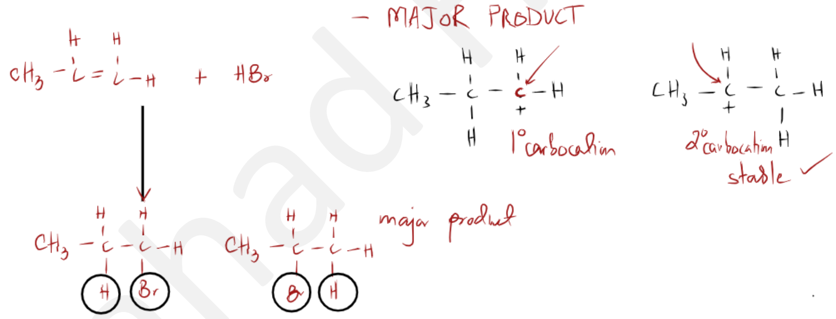


unsaturated → saturated
(smaller) (bigger)
low MP higher MP
(unsaturated vegetable oil) → (margarine)

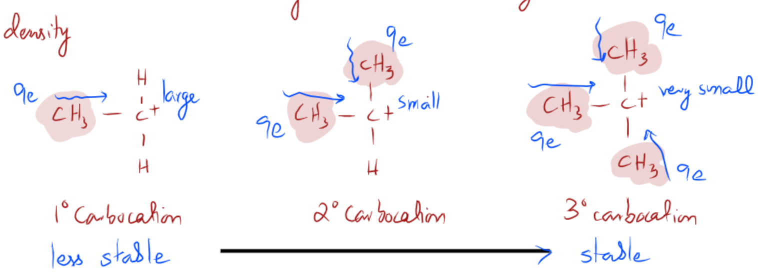


Markovnikov's Rule

unsymmetric alkene → H gets bonded to C in C=C which is already bonded to more H atoms
– MAJOR PRODUCT

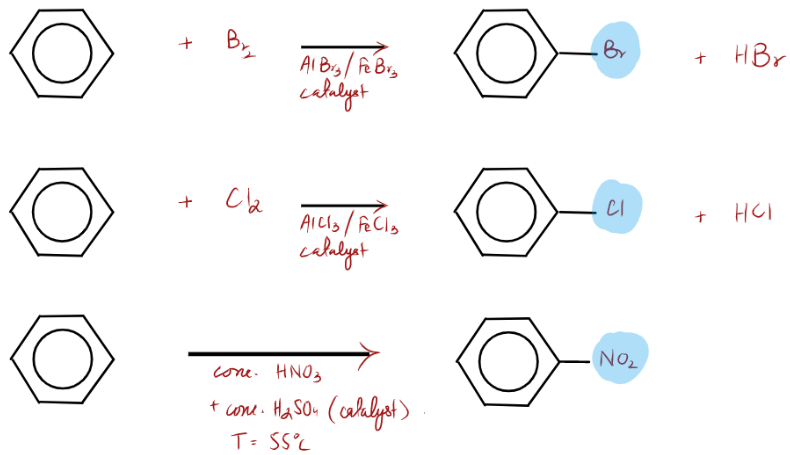


Carbocations with more e⁻ donating alkyl chains are more stable as they have a lower charge density



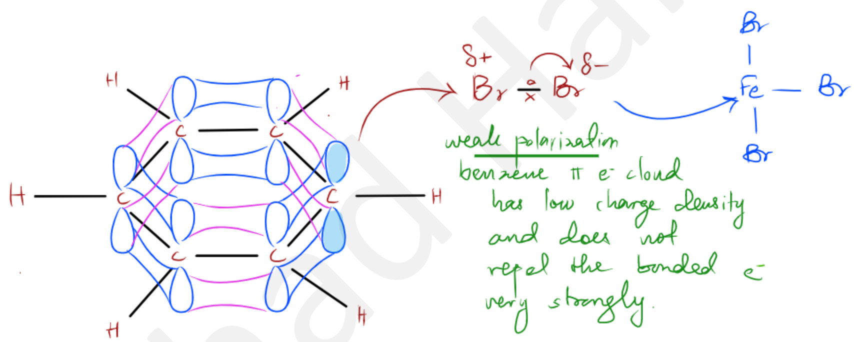
Electrophilic Substitution

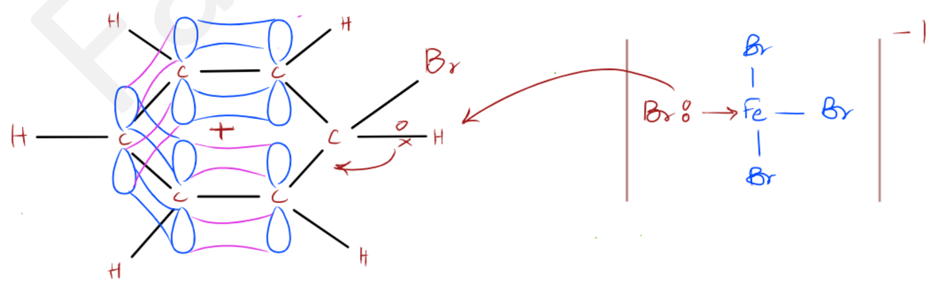
Electrophilic Substitution in Benzene

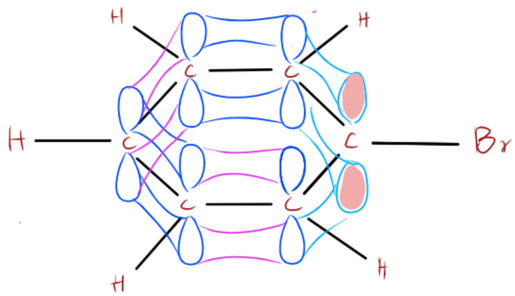


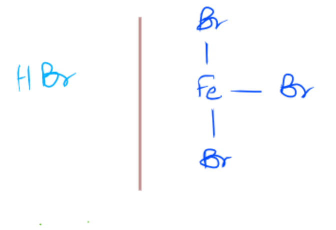
Electrophilic Substitution Mechanism

1. Bromination (or chlorination)

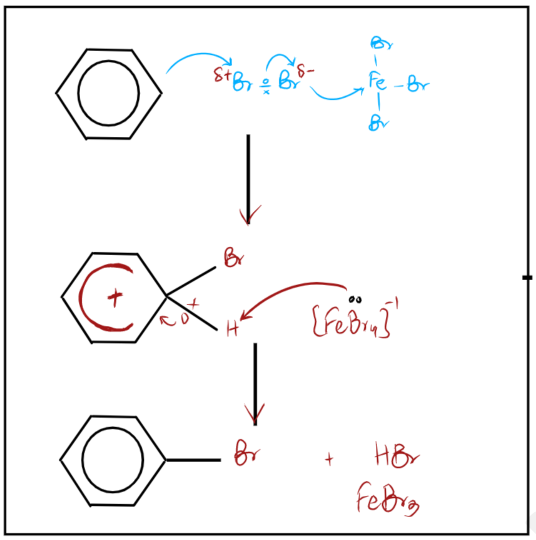




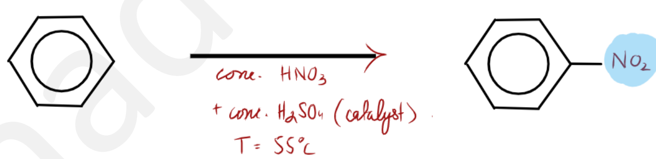




Exam - Mechanism



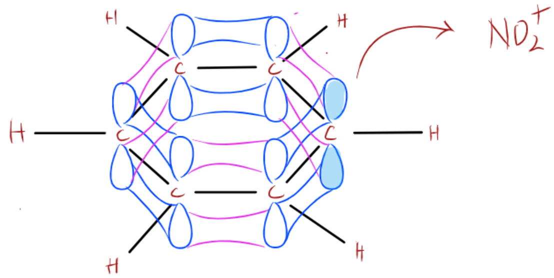
Nitration mechanism

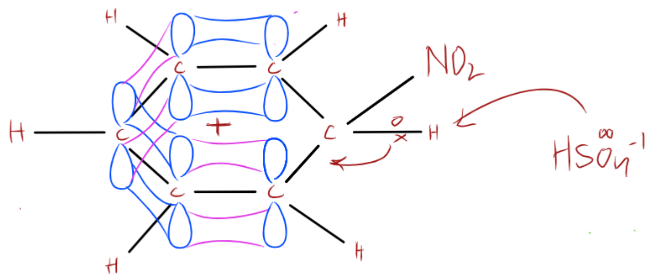


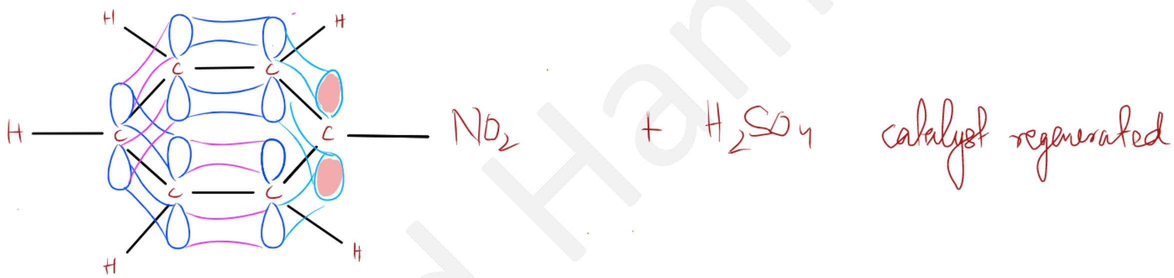
conc. HNO_3 + conc. H_2SO_4 react

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

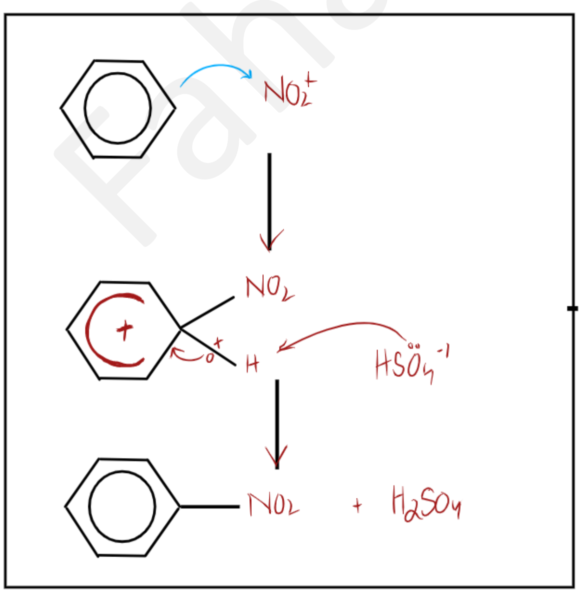
nitronium electrophile







Exam - Mechanism



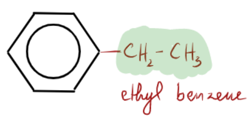
Electrophilic Substitution (2,4,6 and 3,5 Directing Groups)

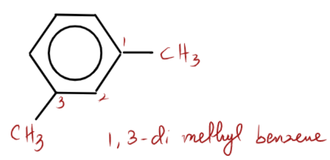
Electrophilic Substitution of Benzene Derivatives

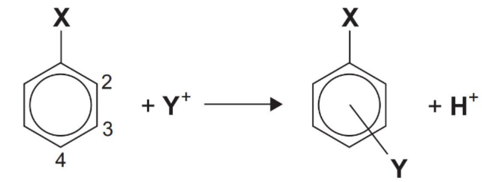
2-4 (6) directing groups

1- Electrophilic Substitution of Arenes

Arene → benzene + alkyl chain



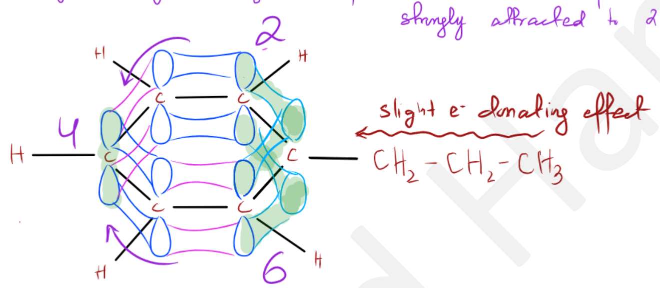


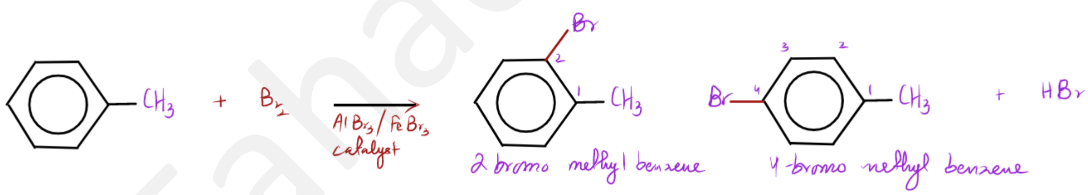


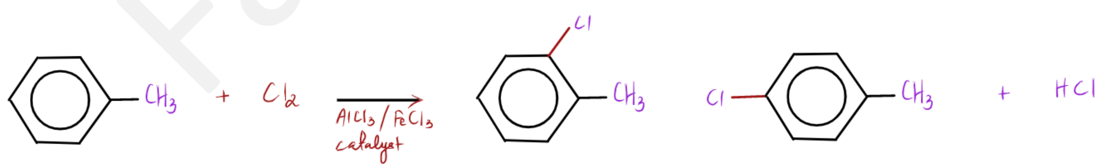
X- groups that direct the incoming **Y** group to the 2- or 4- positions	**X**- groups that direct the incoming **Y** group to the 3- position
$-NH_2$, $-NHR$ or $-NR_2$	$-NO_2$
$-OH$ or $-OR$	$-NH_3$
$-NHCOR$	$-CN$
$-CH_3$, $-$alkyl	$-CHO$, $-COR$
$-Cl$	$-CO_2H$, $-CO_2R$

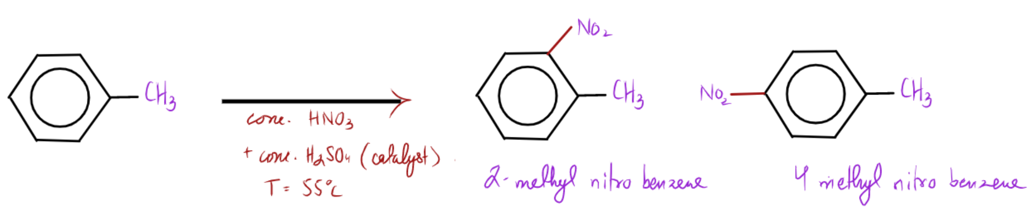
2-4(6) directing groups are e^- donating groups

higher charge density at position 2, 4(6), electrophiles will be strongly attracted to 2,4,6 position







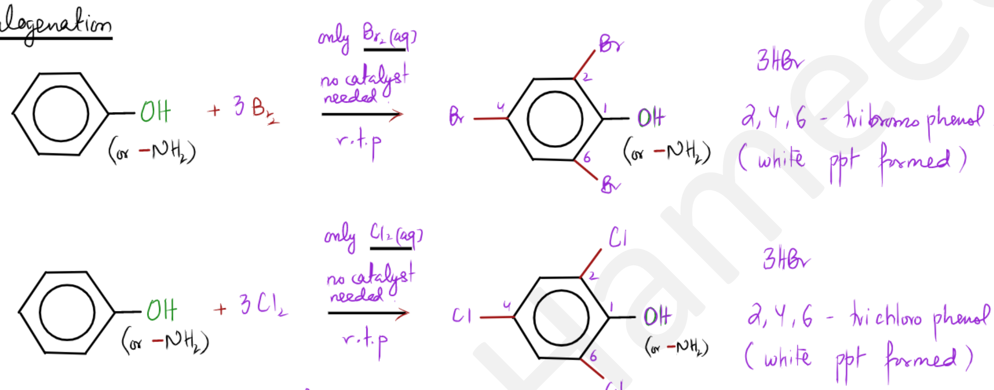


Electrophilic Substitution of Phenols and Phenylamine

$-OH$, $-NH_2$ 2, 4, (6) directing groups

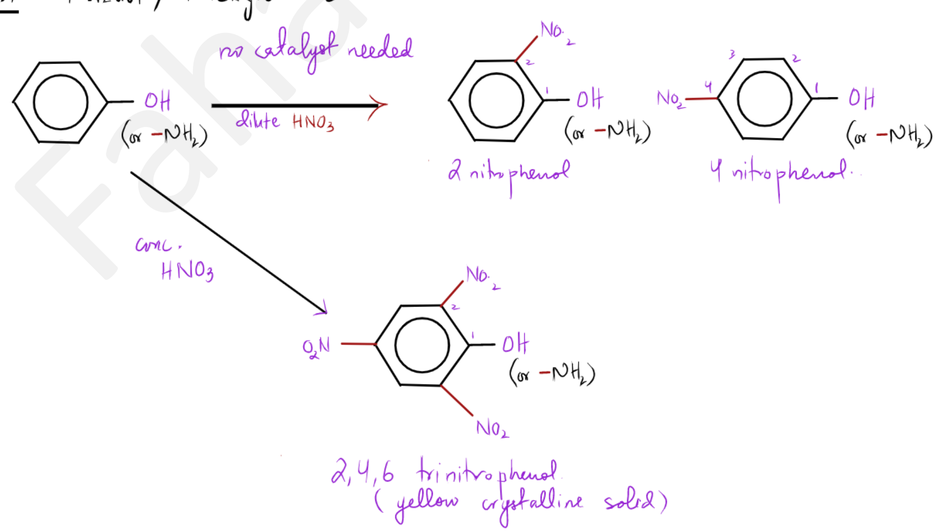
* lone pair on O in hydroxy group (or N in NH_2) overlap with benzene's π e⁻ cloud and significantly increase the π e⁻ cloud density
  - electrophiles (NO_2^+ / Br^+) will be strongly attracted to benzene
  - faster reaction, milder conditions

halogenation



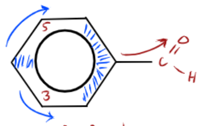
Test for identification of phenols
red/orange Br_2 (aq) decolorizes and produces a white ppt

Nitration Phenol / Phenylamine

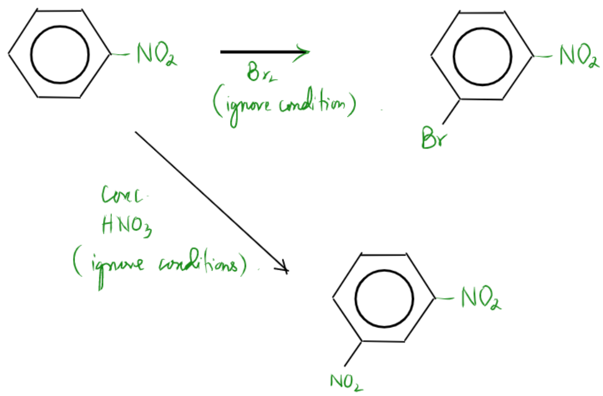


3(-5) directing groups

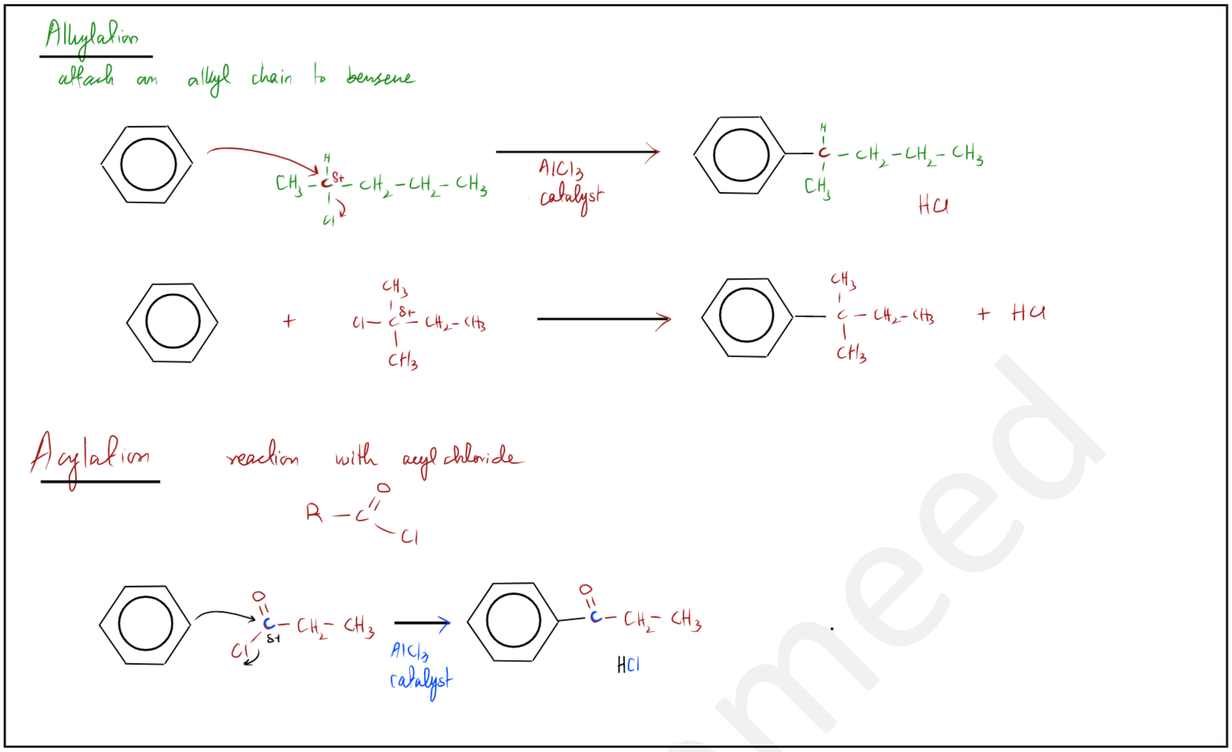
electron withdrawing groups NO_2, CHO, COOH, $-NH_3^+$, CN



relatively higher e⁻ density at position 3 (and 5)
Overall benzene becomes deactivated, e⁻ density in benzene π e⁻ cloud is very less, less attraction for electrophiles, slower reactions / higher T / higher conc.

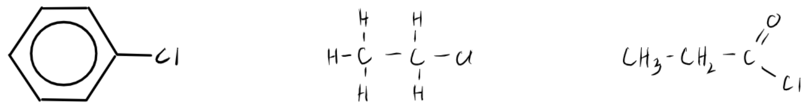


Electrophilic Substitution : Alkylation and Acylation



Hydrolysis of Chlorinated Compounds

Hydrolysis of Cl related compounds



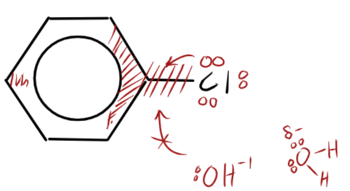
chlorobenzene | halogenoalkanes | acylchloride

halogenoalkanes: NaOH (aq), heat with reflux

acylchloride: vigorous reaction even with cold water; white fumes of HCl(g)

No Hydrolysis ⟶ Strong Hydrolysis

No Hydrolysis of Chlorobenzene



-ve ion is repelled by the high charge density π e⁻ cloud

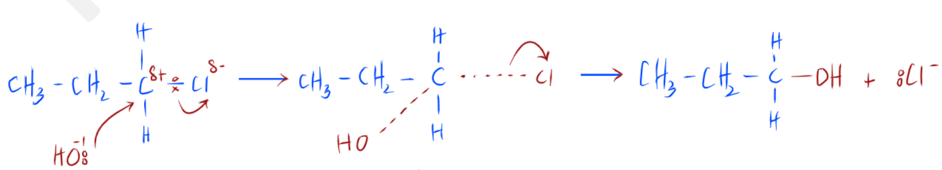
lone pair on Cl overlap with benzene's π e⁻ cloud which increases the strength of the C–Cl bond so high charge density e⁻ cloud repel OH^- ions / nucleophiles

Hydrolysis of Halogenoalkanes

1 - Primary Halogenoalkane S_{N2} ⟶ rate would depend on both reactants

$$CH_3-CH_2-CH_2-Cl + OH^- \longrightarrow CH_3-CH_2-CH_2-OH + Cl^-$$

NaOH(aq) heat with reflux

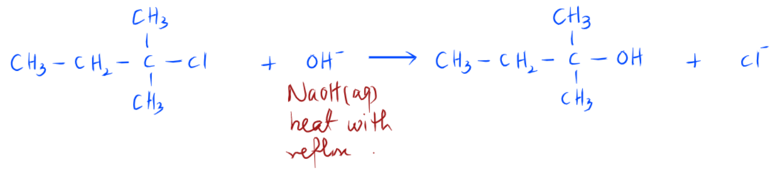


nucleophile: $:CN^{-1}$, $:NH_3$

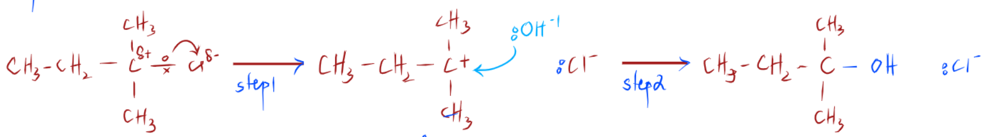
transition state

one step mechanism

2 - Tertiary halogenoalkane S_N1

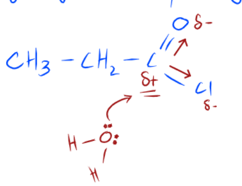


2 step mechanism

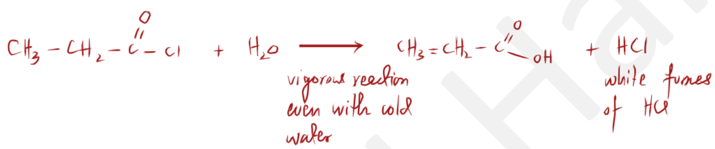


easier to form a tertiary carbocation
more e⁻ donating alkyl chains
lower the charge density

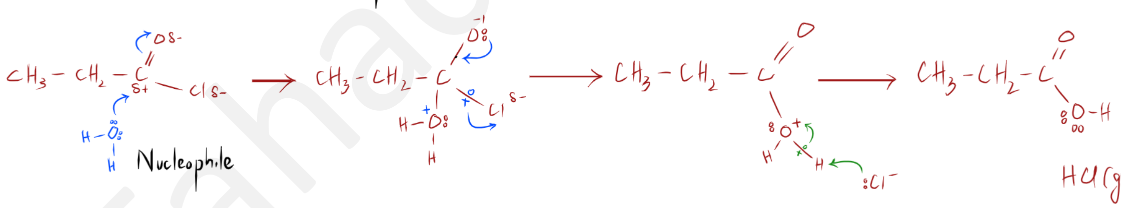
Strong Hydrolysis of Acylchlorides



C in acylchloride is attached to two very electronegative element, oxygen and Chlorine. So δ+ charge density is very high. Nucleophiles H_2O: are very strongly attracted.



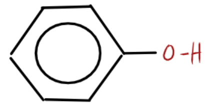
Addition - Elimination Mechanism (Nucleophilic)



Comparison of Weak Acids

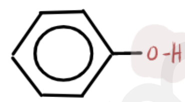
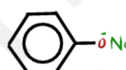
Weak Acids

all organic acids are weak acids
(partially ionise, produce fewer H^+ ions)

CH_3-CH_2-OH alcohol | H_2O |  phenol | $CH_3-CH_2-C(=O)-OH$ carboxylic acid

weakest acid → stronger acid

weak acid → strongest acid

		CH_3-CH_2-OH alcohol	 phenol	$CH_3-CH_2-C(=O)-OH$
redox	reactive metal Na	very slow reaction $CH_3CH_2\text{-}O^-Na^+ + H_2$	 $O^-Na^+ + H_2$ Sodium phenoxide	$CH_3-CH_2-C(=O)-O^-Na^+ + H_2$
acid, base reactions	strong base NaOH	no reaction	 $O^-Na^+ + H_2O$ Sodium phenoxide	$CH_3-CH_2-C(=O)-O^-Na^+ + H_2O$
	weak base Na_2CO_3	no reaction	no reaction	$CH_3-CH_2-C(=O)-O^-Na^+ + H_2O + CO_2$
	weak base NH_3	no reaction	no reaction	$CH_3-CH_2-C(=O)-O^-NH_4^+$

Explaining acid strength

alcohols are the weakest of the weak acids

ionizes even less than water (produces 1×10^{-7} mol/dm³ H^+ ions).

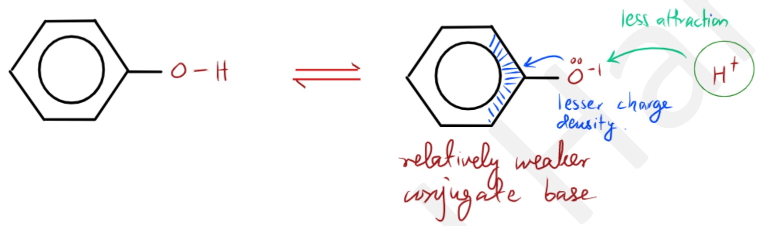
$$CH_3-CH_2-O-H \rightleftharpoons CH_3-CH_2-O^{-1} + H^+$$

e⁻ donating alkyl chain. large -ve charge density.

alkyl chain has e⁻ donating effect which increases charge density of $CH_3-CH_2-O^{-1}$ ion, making it unstable, stronger attraction for H^+ ions, less dissociation, O-H bond strength increases.

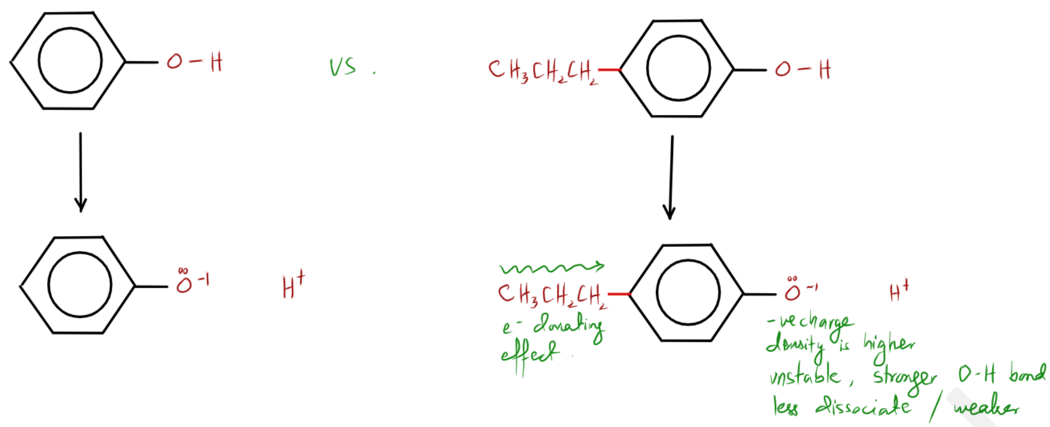
Phenols are slightly stronger acids compared to alcohols

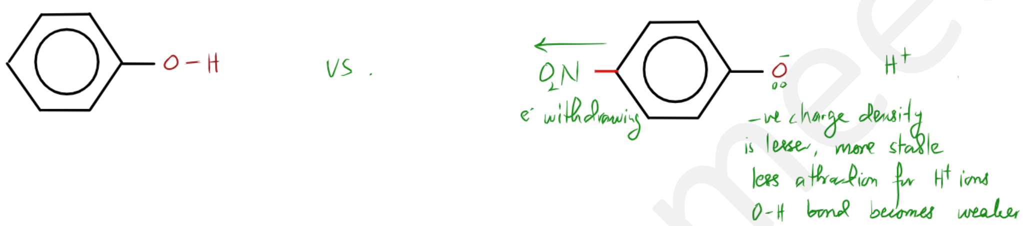
they can react with Na (reactive metal) and NaOH (strong bases)



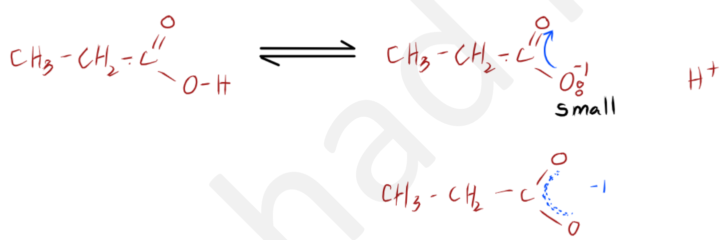
lone pairs on the phenoxide ion $C_6H_5O^{-1}$ overlap with benzene's pi electron cloud, charge density on phenoxide ion decreases, making it more stable (less attraction for H^+, -O-H bond weakens) hence more dissociation

Comparison of acid strength within phenols



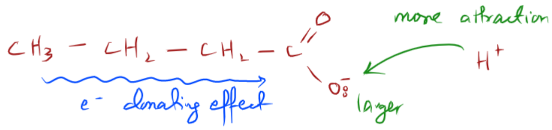


Why are carboxylic acids (relatively) the strongest acid



In Carboxylic acids, a highly electronegative oxygen in C=O has strong electron withdrawing effect, which decreases -ve charge density in $RCOO^-$ ion / making it stable less attraction for H^+ ions, O-H bond strength decreases more dissociation / relatively strong acid

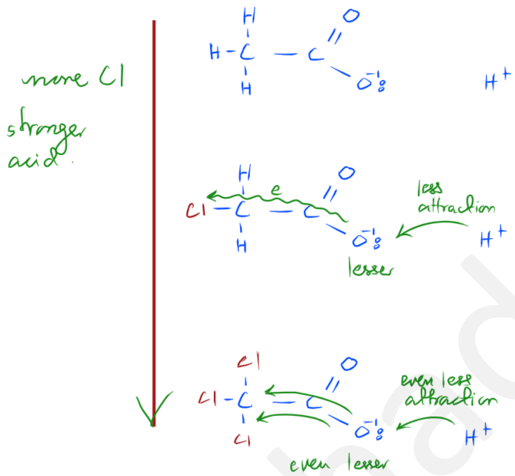
alkyl chain length → carboxylic acid strength



large e^- donating effect in bigger alkyl chains

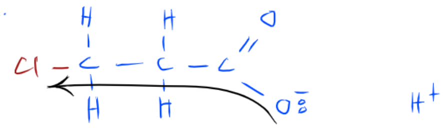
higher -ve charge density in $RCOO^-$ making it unstable, more attraction for H^+ ions stronger O-H bond, less ionization → **weaker acid**

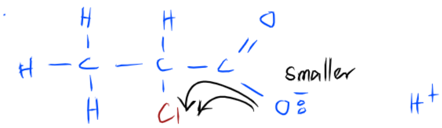
Cl substituted carboxylic acid



Cl has e^- withdrawing effect
$RCOO^-$ charge density decreases, becomes more stable, O-H is weaker
less attraction for H^+ → stronger acid
more ionization.

Position of Cl





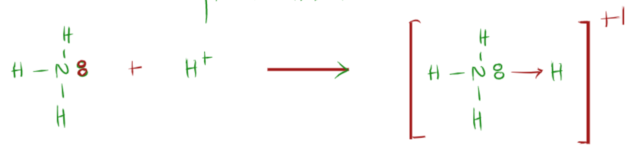
stronger acid.

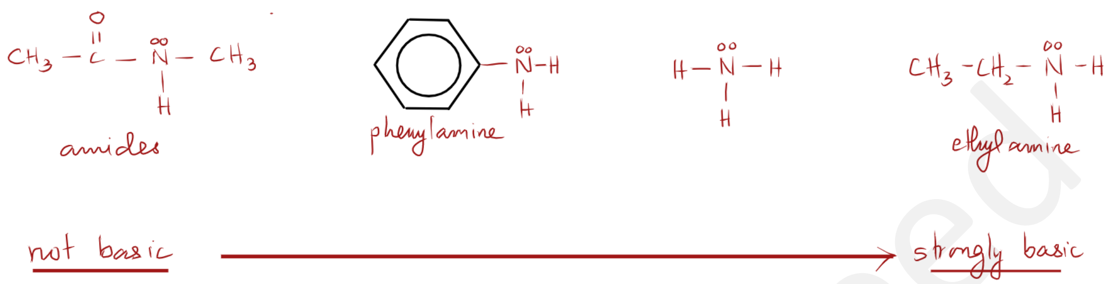
Cl is closer, more e⁻ withdrawing effect
RCOO⁻ becomes more stable
lower charge density, less attraction for H^+
O-H bond becomes weaker → more dissociation.

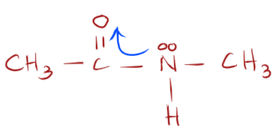
Comparison of Weak Bases

Stregnth of bases. (all are weak)

Nitrogen bases
accepts H^+ ions.



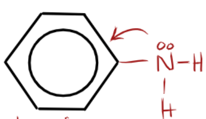




amides

not basic

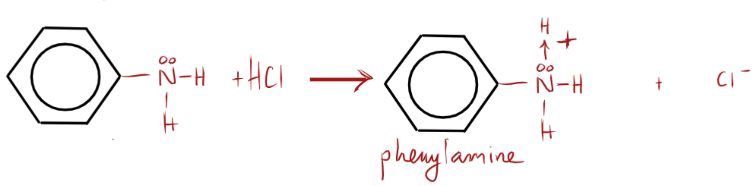
lone pair on N in amide. overlaps with π e⁻ cloud in C=O as oxygen has strong e⁻ withdrawing effect, lone pair on N is not available to accept H^+ ions.

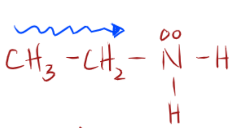


phenylamine

weakly basic

lone pair on N overlaps with benzene's π e⁻ cloud and its charge density decreases. hence weaker attraction for H^+ ions, weakly basic





ethylamine

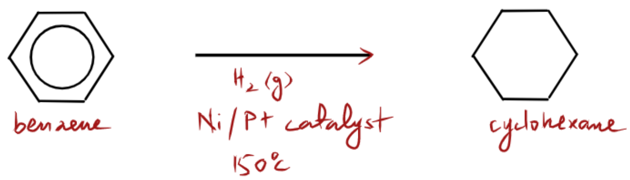
strongly basic

alkyl chain has e⁻ donating effect charge density on lone pair on N increases more attraction for H^+ ions, stronger base.

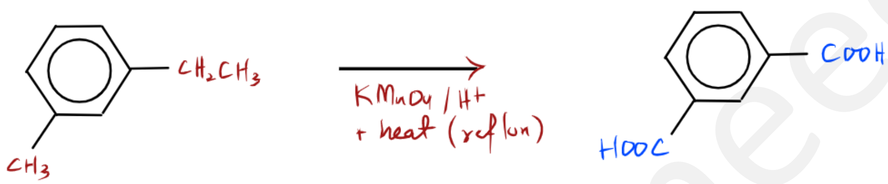
All Redox Reactions (Including AS)

Redox Reactions

Hydrogenation of benzene



Oxidation of Arenes

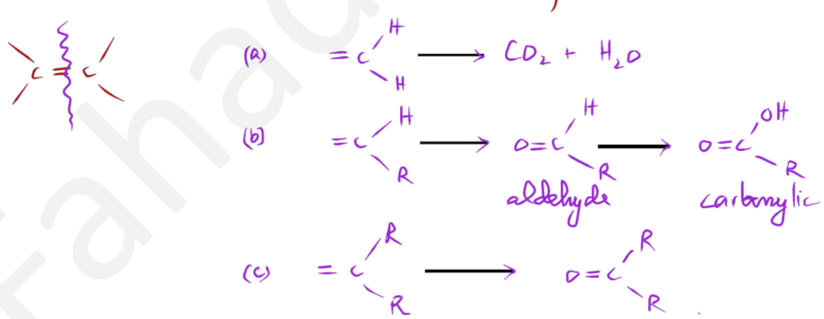


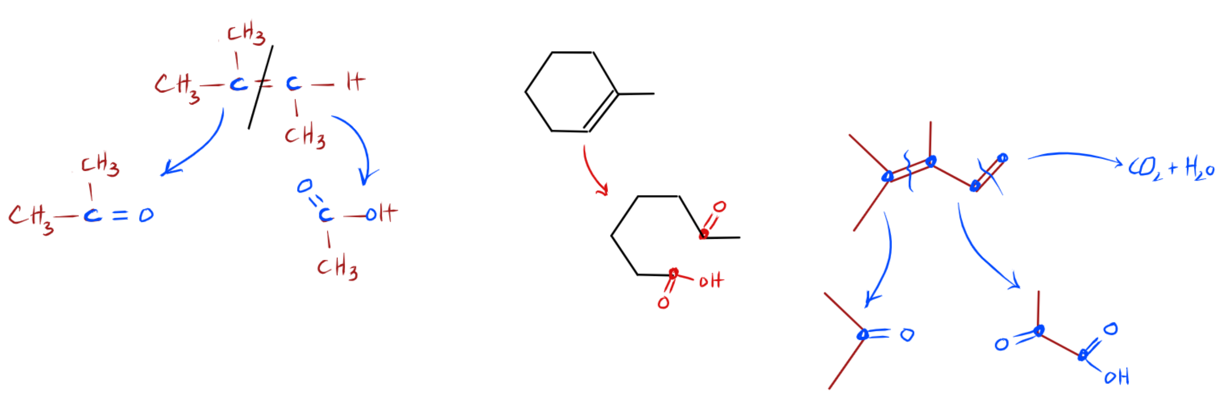
Oxidation of Alkenes

1- mild oxidation

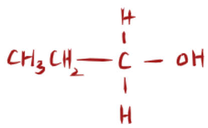
$CH_3-CH=CH-H \xrightarrow{\text{cold/dilute } KMnO_4} CH_3-CH(OH)-CH(OH)-H$

2- strong oxidation — hot, concentrated, acidified $KMnO_4$





Primary Alcohol —oxidation→ **aldehyde** —oxidation→ **carboxylic acid**



Primary alcohol → aldehyde:

1. $K_2Cr_2O_7/H^+$ reflux, heat — orange to green
2. $KMnO_4/H^+$ reflux, heat — purple to colorless

Aldehyde → carboxylic acid:

1. $K_2Cr_2O_7/H^+$ reflux, heat — orange to green
2. $KMnO_4/H^+$ reflux, heat — purple to colorless
3. Tollen Reagent $[Ag(NH_3)_2]^{+1}$ — silver mirror / black ppt
4. Fehling's Reagent + heat: $Cu^{2+} \rightarrow Cu_2O$ — brick red ppt of Copper (I) oxide

to stop at aldehyde and prevent further reaction

~~reflux~~ → distillation

aldehyde have much lower melting and boiling as they dont form hydrogen and they evaporate easily

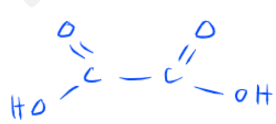
only two carboxylic acids are oxidized.

most carboxylic are resistant to oxidation

1. methanoic acid → $CO_2 + H_2O$

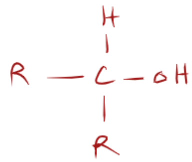
1. $K_2Cr_2O_7/H^+$/ reflux
2. $KMnO_4/H^+$/ reflux
3. Tollens $[Ag(NH_3)]^+$
4. Fehling solution + heat

2. Ethanedioic acid (Oxalic acid)

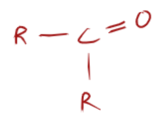


→ $CO_2 + H_2O$ ($KMnO_4/H^+$, reflux)

Secondary Alcohols —oxidation→ **Ketones**

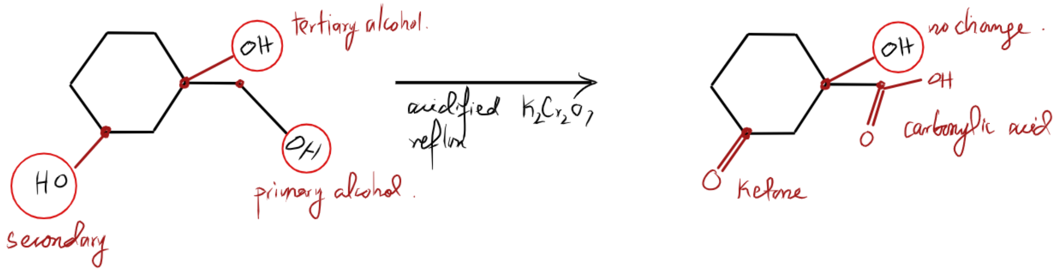


1. $K_2Cr_2O_7/H^+$
   reflux, heat
   orange to green
2. $KMnO_4/H^+$
   reflux, heat
   purple to colorless



tertiary alcohols no oxidation

Example

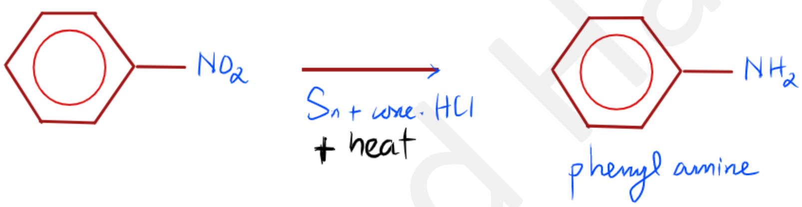


Reduction

Carboxylic acid $\xrightarrow[\text{LiAlH}_4]{\text{Lithium hydrido Aluminate}}$ aldehyde $\xrightarrow[\text{LiAlH}_4\,/\,\text{NaBH}_4]{}$ primary alcohol.

Ketones $\xrightarrow[\text{LiAlH}_4\,/\,\text{NaBH}_4]{}$ secondary alcohol

Reduction of Nitrobenzene



Reduction of Amides

$$R-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R \xrightarrow[\text{LiAlH}_4]{-O,\ +2H} R-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{N}}-R$$

Reduction of nitriles

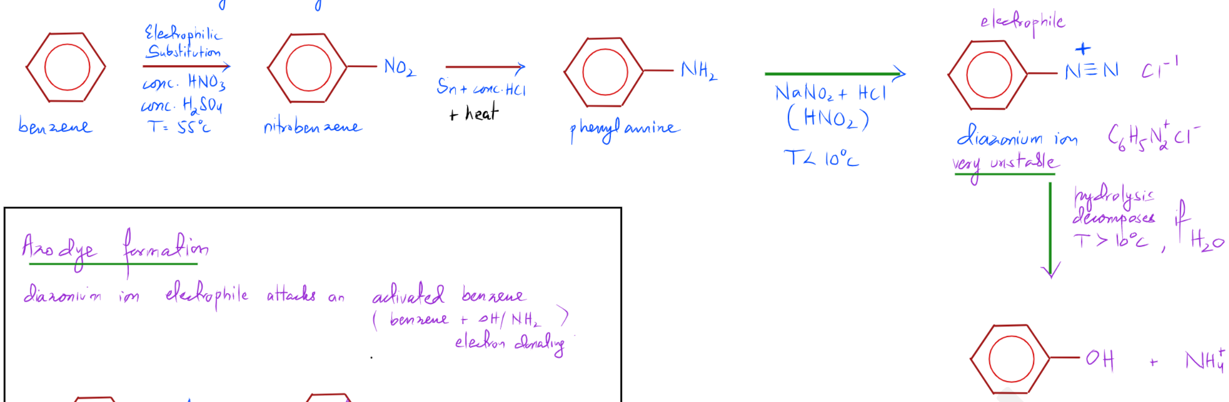
$$R-C\equiv N \xrightarrow[\substack{150^\circ C \\ \text{or} \\ \text{LiAlH}_4}]{H_2\ +\ \text{Ni catalyst}} R-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{N}}-H$$

allyl amine

Dye Stuff : Azo Dyes

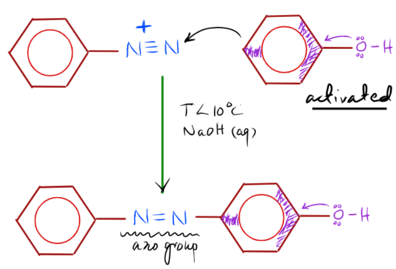
Dye Stuff / Azo Dyes

"Paints" → azo dyes are very stable

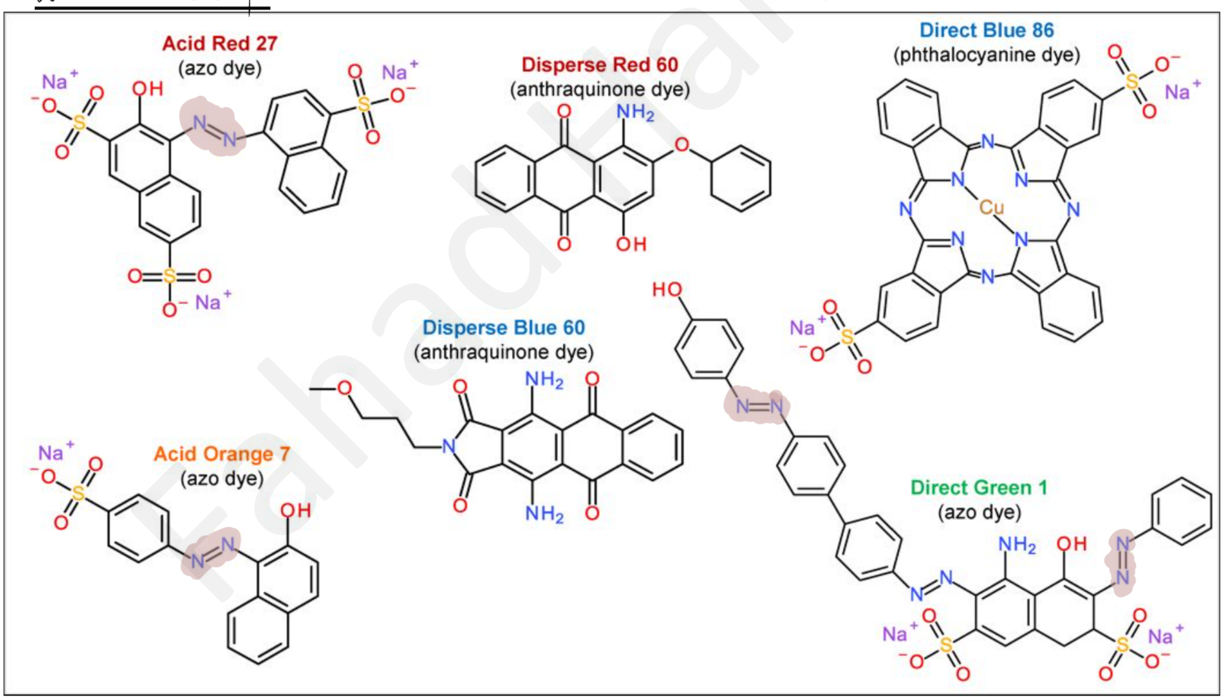


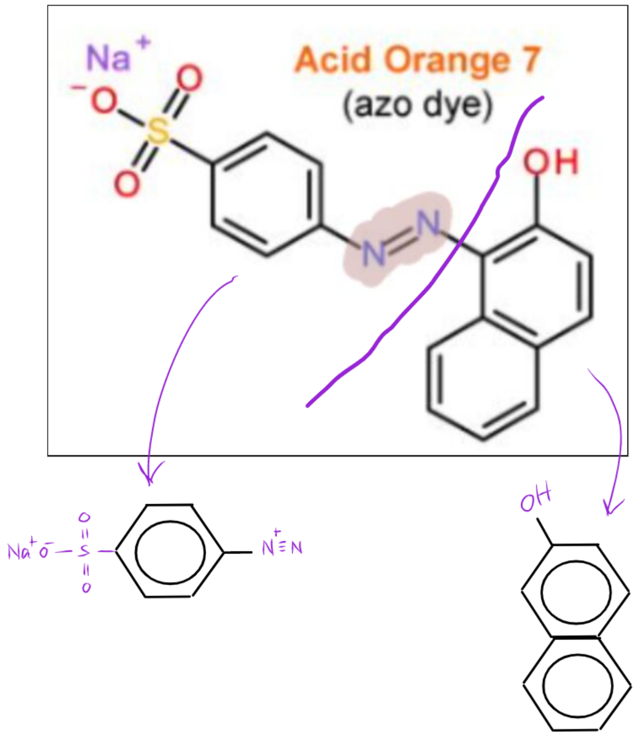
Azo dye formation

diazonium ion electrophile attacks an activated benzene
(benzene + OH / NH_2) electron donating



Just as an Example





Find original reactants

- $\overset{+}{N}≡N$ that comes from the inactive benzene

Formation of Acyl Chlorides

Acyl chlorides $R-C(=O)-Cl$

Formation

$$R-C(=O)-OH \longrightarrow R-C(=O)-Cl$$

PCl_3 + heat
$SOCl_2$ + heat
PCl_5 (+ heat)

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + HCl + POCl_3$$

$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$$

Esters & Amides

Formation of Esters

Addition - Elimination
"condensation"

1. Alcohol + carboxylic acid $\rightleftharpoons$ ester + H_2O

Forward: conc. H_2SO_4 + reflux

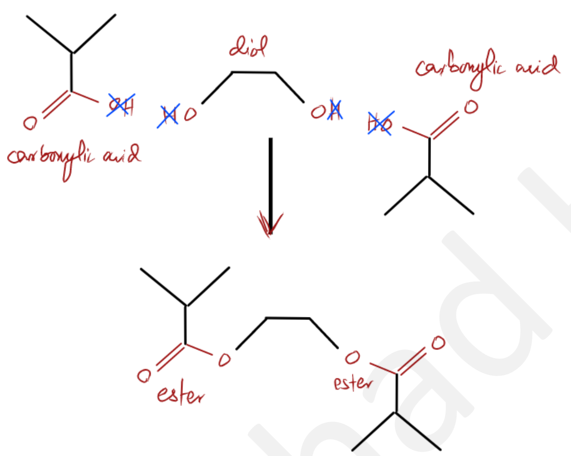
Reverse: dilute H_2SO_4 / NaOH reflux (acid or alkaline hydrolysis)

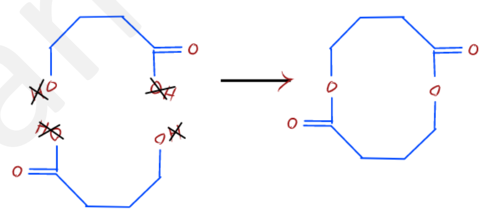
CH_3-CH_2-OH + $CH_3-CH_2-C(=O)-OH$ ⟷ $CH_3-CH_2-C(=O)-OH$ ... $H-O-CH_2-CH_3$ (δ+ on C)

$CH_3-CH_2-C(=O)-O-CH_2-CH_3$ + H_2O

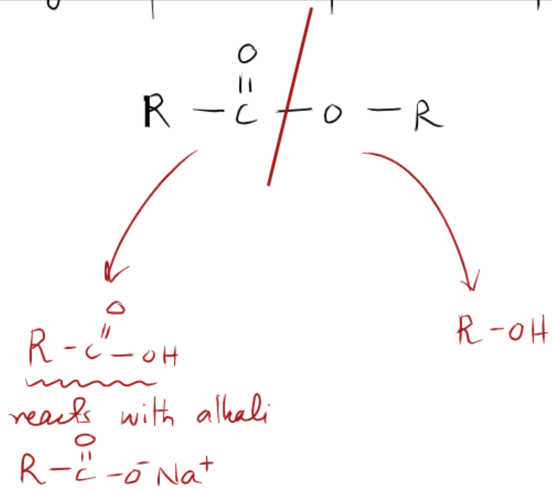
propanoate | ester link | ethyl

ethyl propanoate





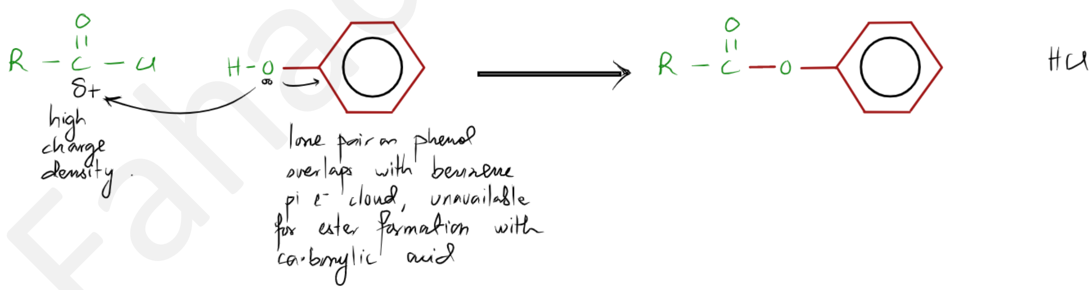
* Alkaline hydrolysis of Esters produces soaps



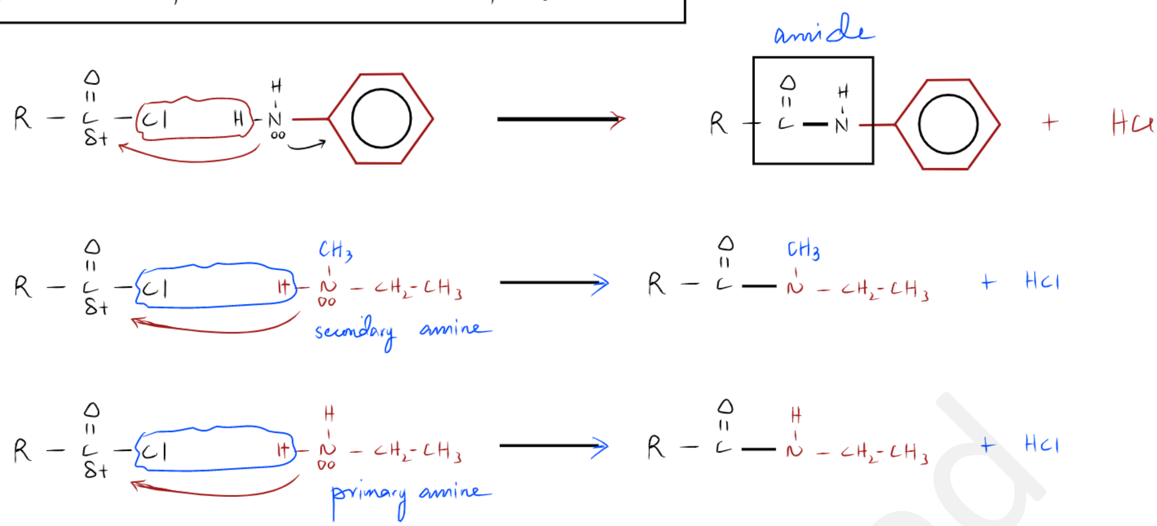
Acylchlorides + alcohols ⟶ Ester + HCl

fast vigorous reaction. no conditions needed

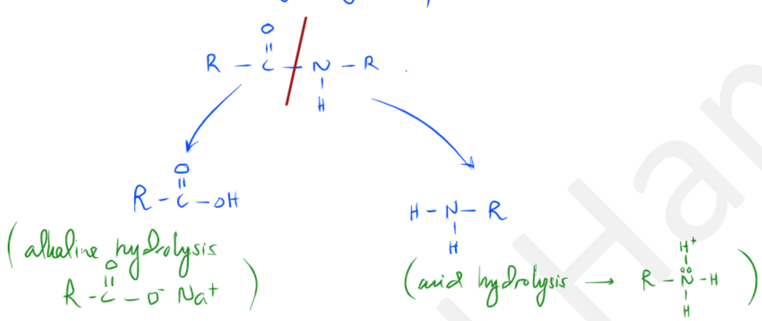
Phenols only form Esters with acylchlorides



Acyl chlorides form amides with phenyl amine

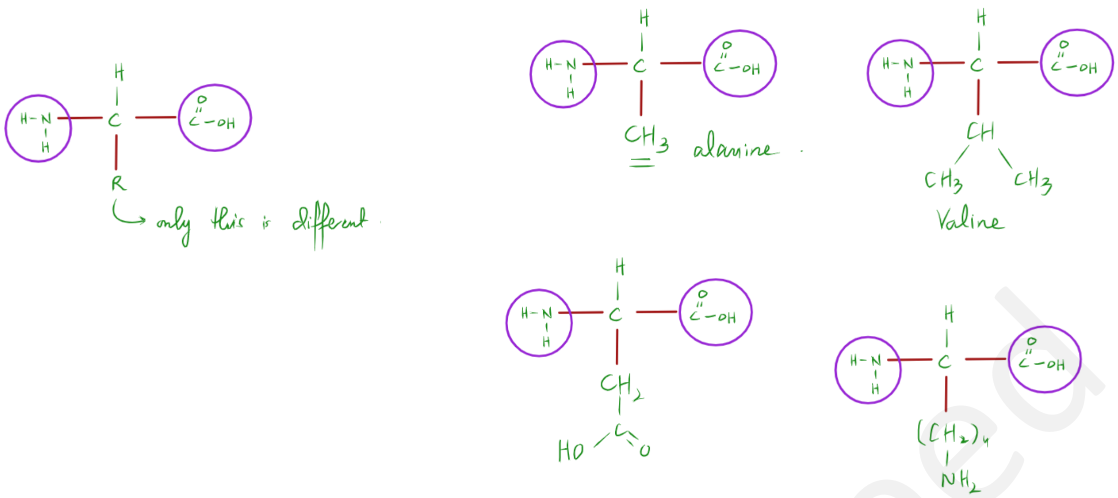


Acid / alkaline hydrolysis of amides

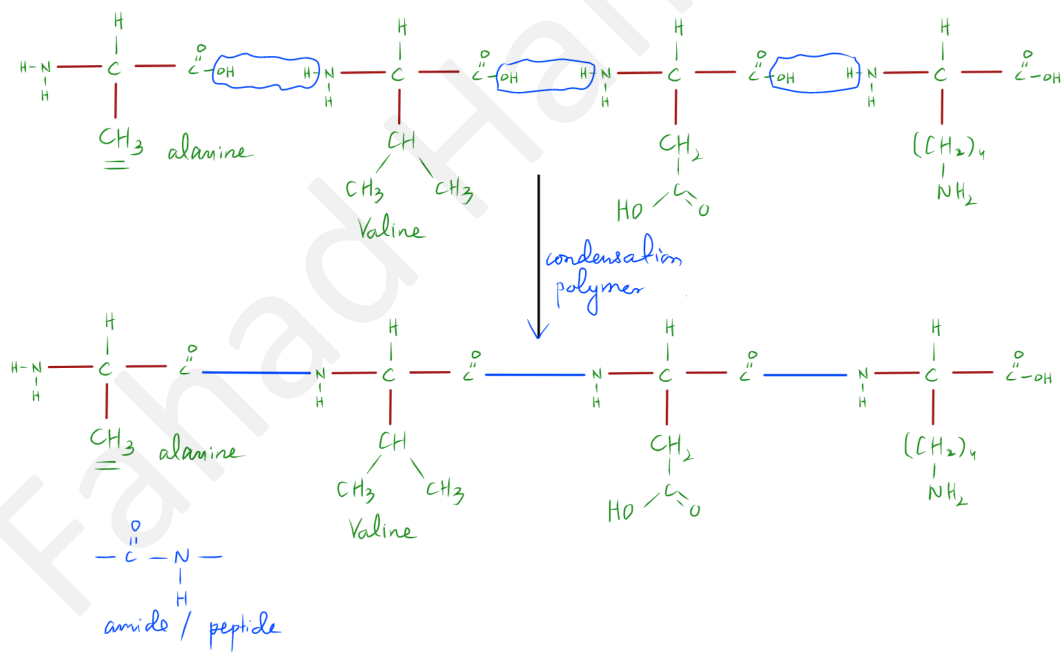


Amino Acids, Polymerization

Amino Acids (monomer) → Protein (polymer)

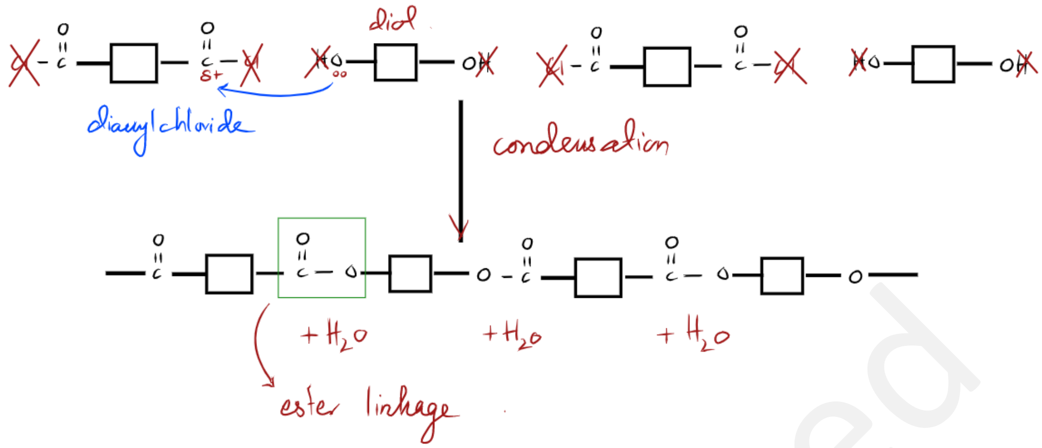


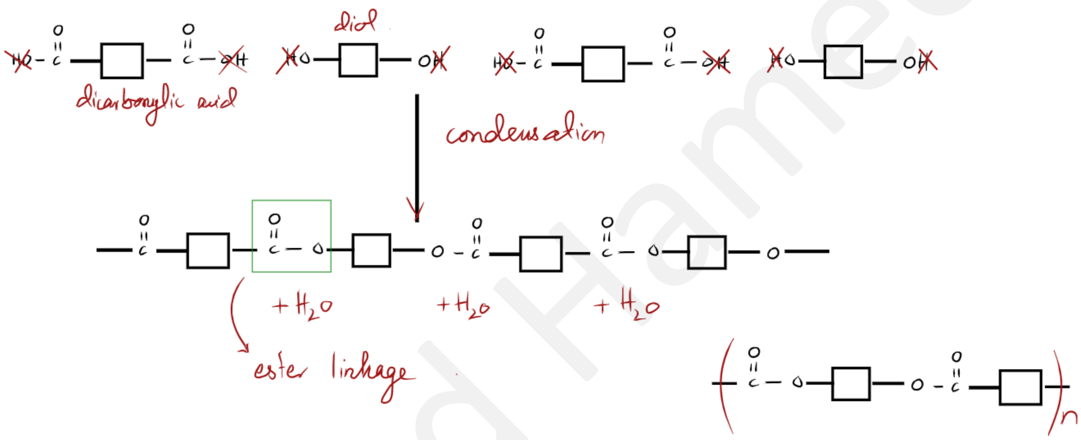
Primary Structure / simple polypeptide (Condensation Polymers)



Condensation Polymerization

1. Polyester

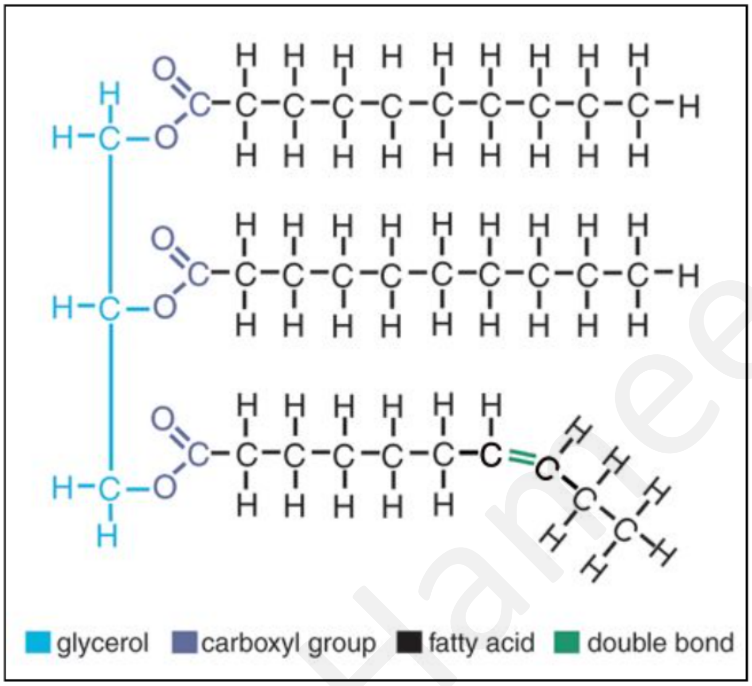




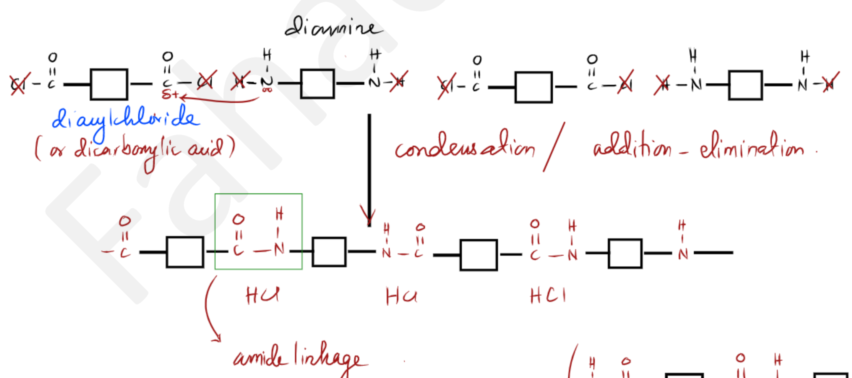
Examples

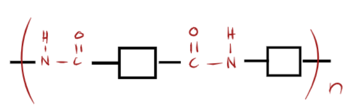
Terylene - fabric, clothing

natural polyesters - fats



2. Polyamide



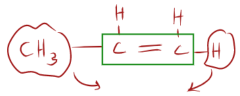


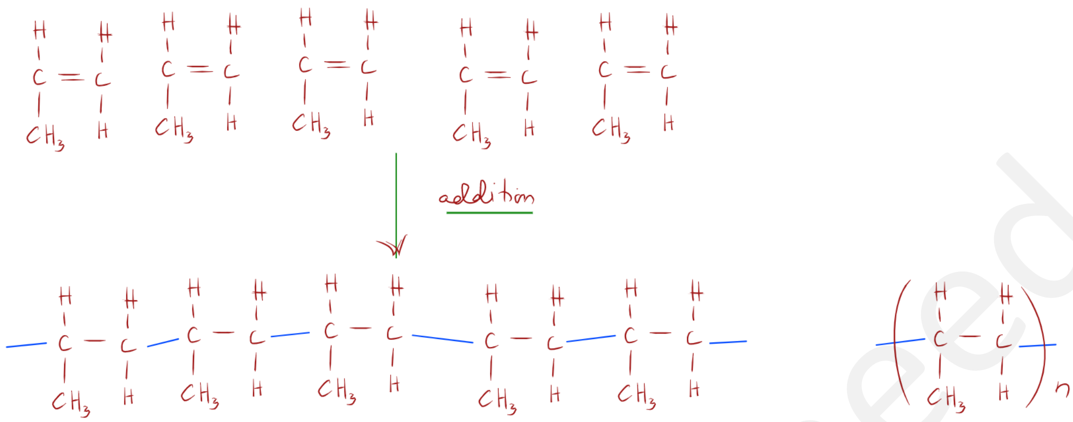
Examples

Kevlar, Nylon ; natural proteins

Addition Polymers

monomer = alkene





polypropene

repeat unit

Addition Polymers vs Condensation Polymers

Addition Polymers

- inert, non biodegradable
- PVC, Polyethene, Poly propene
- linkage ⟶ nonpolar carbon chain, very stable and unreactive

Condensation Polymers

- very polar linkages

- very reactive, hydrolyse easily
- × heat / boil with dilute acid or dilute alkali