

Hydroxy Compounds



Preparation of Alcohols

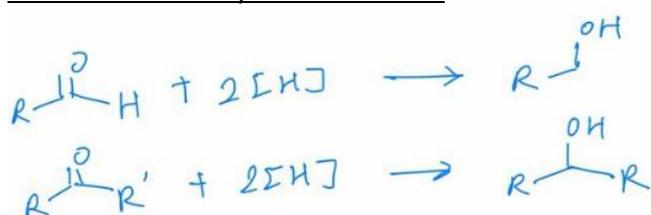
Electrophilic Addition of Alkenes

- Refer to Alkene Lecture

Nucleophilic Substitution of Halogenoalkanes

- Refer to Halogen Derivatives Lecture

Reduction of Aldehydes and Ketones

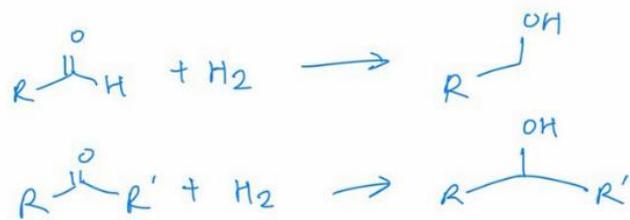


Reagent & Condition

LiAlH₄ in dry ether, r.t.p.

OR

NaBH₄ in ethanol, r.t.p.



Reagent & Condition

H₂, Ni/Pd/Pt catalyst, r.t.p.

Reduction of Carboxylic Acids



Reagent & Condition

LiAlH₄ in dry ether, r.t.p.

Reactions of Alcohols

Combustion

- Refer to Mole Concept Lecture

Dehydration of Alcohol

- Refer to Alkene Lecture

Nucleophilic Substitution to form halogenoalkane

- Refer to Halogen Derivatives Lecture

Oxidation of Primary Alcohol

(a)



Reagent & Condition

K₂Cr₂O₇ aq, H₂SO₄ aq, immediate distillation

↳ obs: Orange K₂Cr₂O₇ aq turns green



Reagent & Condition

K₂Cr₂O₇ aq / KMnO₄ aq, H₂SO₄ aq, heat

↳ obs: Orange to green ↳ obs: Purple to Colourless

Oxidation of Secondary Alcohol



Reagent & Condition

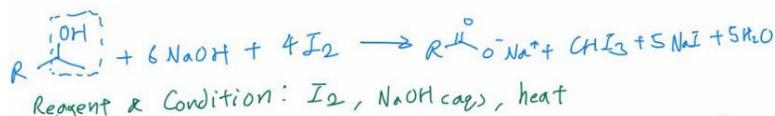
K₂Cr₂O₇ aq / KMnO₄ aq, H₂SO₄ aq, heat

↳ obs: Orange to green ↳ obs: Purple to Colourless

Exception for Oxidation: Tertiary Alcohol



Tri-iodomethane/Iodoform reaction



Reagent & Condition: I₂, NaOH aq, heat

↳ obs: Brown I₂ decolourises, pale yellow ppt CHI₃ form

Ester Formation (Nucleophilic Acyl Substitution)



Reagent & Condition

conc. H_2SO_4 catalyst, heat under reflux



Reagent & Condition

r.t.p.

Phenol



Chemical Reactions of Phenol

Combustion

- Refer to Mole Concept Lecture

Ester Formation (Nucleophilic Acyl Substitution)



Reagent & Condition

1. $NaOH$ cat., r.t.p
2. $R'-C(=O)-Cl$, r.t.p

No reaction of Phenols with Carboxylic Acid as:

- 2p orbital of O atom in -OH overlap with pi electron cloud in benzene -> lone pair delocalize into benzene -> lone pair less available for donation to electrophile
 - o Phenol is less nucleophilic

Phenol can react with acyl chloride as:

- Acyl Chloride is more electrophilic

Reactions involving benzene ring

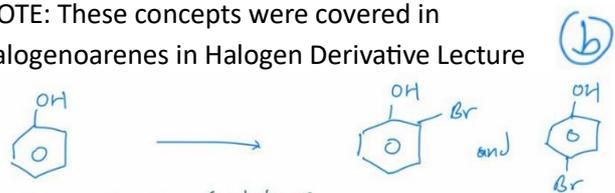
Nucleophilic Substitution using -OH

- 2p orbital of O atom in -OH overlap with pi electron cloud in benzene -> lone pair delocalize into benzene
 - o Partial double bond character in C-O bond, stronger C-O bond and requires more energy to break
- Benzene will repel the nucleophile due to pi electron cloud

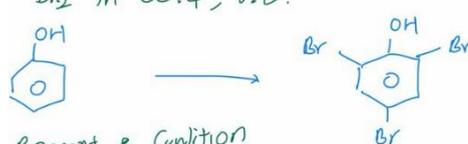
Electrophilic Substitution

- 2p orbital of O atom in -OH overlap with pi electron cloud in benzene -> lone pair delocalize into benzene
- Thus, -OH group is activating group, make benzene ring more susceptible for electrophilic substitution
 - o Phenols only need milder conditions
- -OH group is 2,4-directing
- NOTE: Refer to Data Booklet

NOTE: These concepts were covered in halogenoarenes in Halogen Derivative Lecture

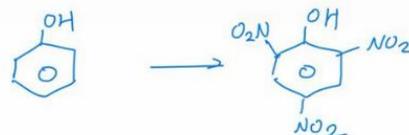


Reagent & Condition
 Br_2 in CCl_4 , r.t.



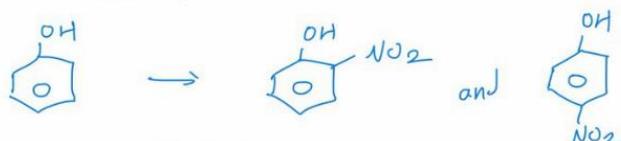
Reagent & Condition
 Br_2 aq., r.t.

↳ Obs: Orange Br_2 decolorise, white ppt of product form



Reagent & Condition

conc. HNO_3 , r.t.



Reagent & Condition

dilute HNO_3 , r.t.

Acidic properties of Alcohols and Phenols

pKa: ethanol > water > phenol > carboxylic acid

- Ethanol is weaker acid:
 - o Electron-donating R group that intensifies negative charge on $\text{CH}_3\text{CH}_2\text{O}^-$ ion, so ion not preferably formed
- Phenol stronger acid than water and ethanol
 - o 2p orbital of O atom in -OH overlap with pi electron cloud in benzene -> lone pair delocalize into benzene
 - o Negative Charge of $\text{C}_6\text{H}_5\text{O}^-$ dispersed, stabilizing the ion via resonance -> more preferentially formed

NOTE: when looking at acidity in organic chemistry, pay attention to the negative charge on the ion and hence stability of the ion

Reaction with Na and Bases

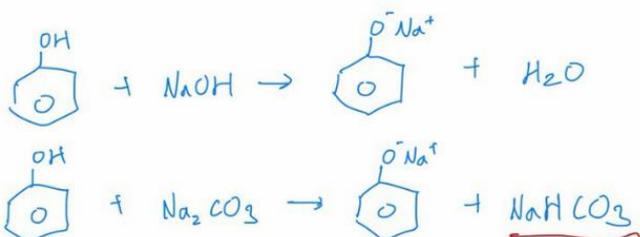
Both Aliphatic Alcohol and Phenol can react with Na



Aliphatic Alcohol cannot react with Bases as not acidic enough

Phenol can react with Bases as acidic enough

- NOTE: not acidic enough to form CO_2 when reacting with Na_2CO_3



Identification tests for Aliphatic Alcohol

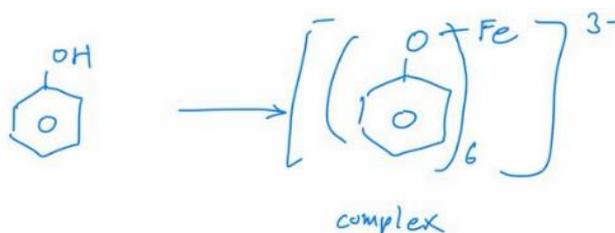
- Nucleophilic Substitution
 - o Refer to Halogen Derivatives Lecture
- Acid – Metal Reaction with Na
 - o Obs: Effervescence of H_2 that gives 'pop' sound with lighted splint
- Oxidation
 - o Refer to above section (a)

Identification Test for Phenol

Electrophilic Substitution by Br_2

- Refer to above section (b)

IMPT: Complex Formation using Neutral FeCl_3



Reagent & Condition

Neutral FeCl_3 (aq), r.t

↳ Obs: Solution turns violet