Faculty of Engineering

Cairo University

Chemical Engineering Department,

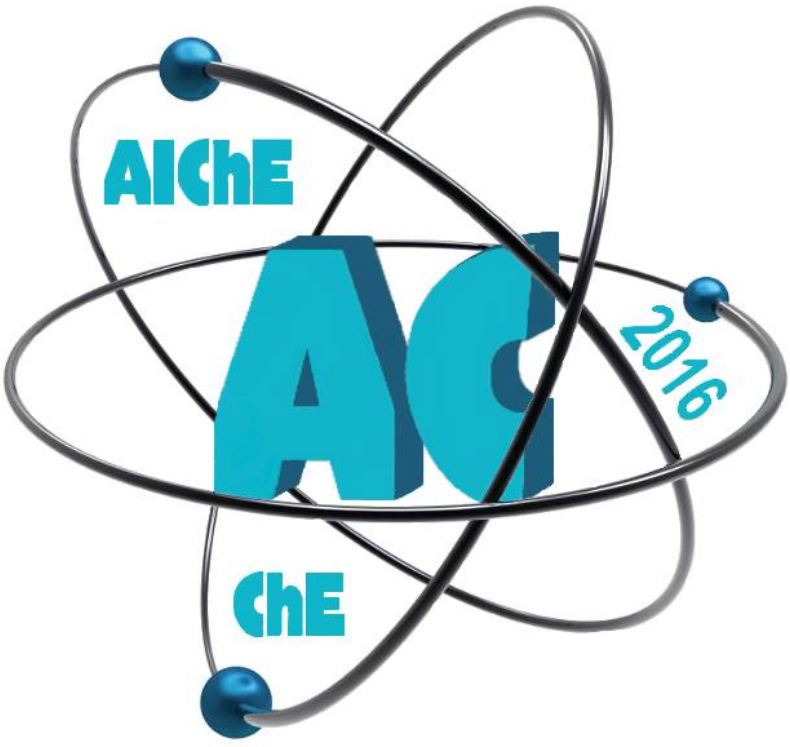
AIChE-AC-ChE 2016

#1

Organic Chemistry

Contents:

- *Summary until midterm*



#1

Organic

Organic Compounds

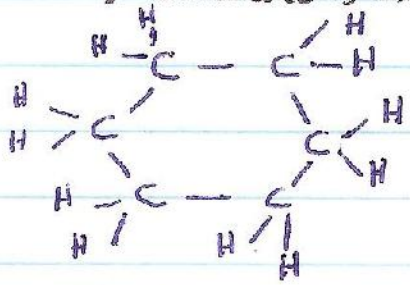
- Open Chain (aliphatic) $CH_3-CH_2-CH_2-\cdots$
- Closed Chain (cyclic)

- Hetero Cyclic (Ring Contain foreign atom)

Pyridine

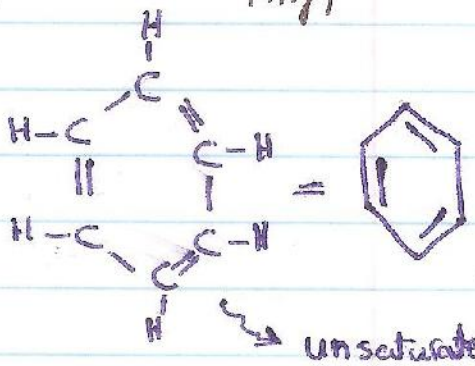
Furan

- Homo Cyclic (Ring Composed of the same element)
  - Alicyclic (aliphatic cyclic) → "Saturated as aliphatics"



Cyclohexane

  - Aromatic (Compound Contain Benzene ring)



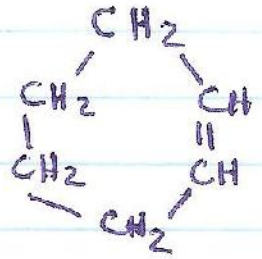
unsaturated

Benzene

(Cyclohexa-1,3,5-triene)

#2

Cyclohexene (Partially saturated)



⇒ Destructive distillation of Coal

Heating Coal in absence of air for 17 hours at 1000°C to 3000°C, Producing:

Coal gas

* 97% flammable gases
  - 50% H_2, 35% CH_4, 8% CO, 4% (C_2H_2 + C_2H_4 + C_2H_6)
  - 3% (H_2S + NH_3 + CO_2)
    - → make SO_2 then H_2SO_4
    - → Fertilizers
    - → used in beverages

Coke

→ used in steel industry

Coal Tar

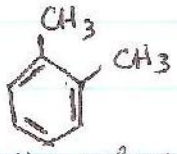
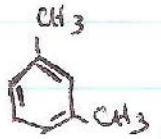
** Due to fractional distillation @ T < 350°, We get
a) light oil (< 200°C)
b) Middle oil (200 - 250°C)
c) Heavy oil (250 - 300°C)
d) Anthracene oil (300 - 350°C)
e) Pitch

* flammable gased are recycled & used in heating.

** Fractional distillation at T < 350°C to avoid thermal cracking.

#3

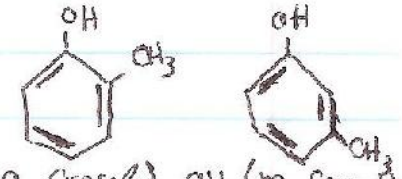
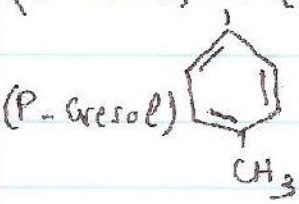
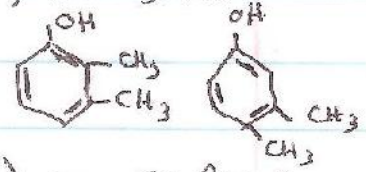
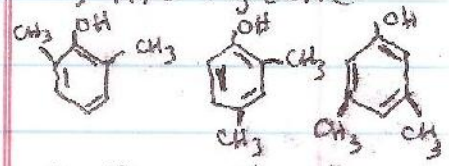
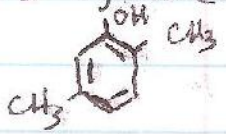
a) light oil compounds (ene)

Name	B.P	Mol. Form	Structural Form
Benzene	80°C	C_6H_6	
Toluene "Methyl Benzene"	110°C	$C_6H_5CH_3$ C_7H_8	
Xylenes "Di Methyl Benzene"	14°C	C_8H_{10}	 ortho-xylene  Meta-xylene  Para-xylene
Pyridine	115°C	C_5H_5N	

*(ine) is used instead of (ene) because the compound is not a hydrocarbon.

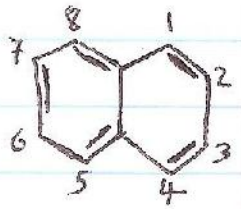
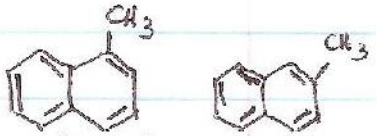
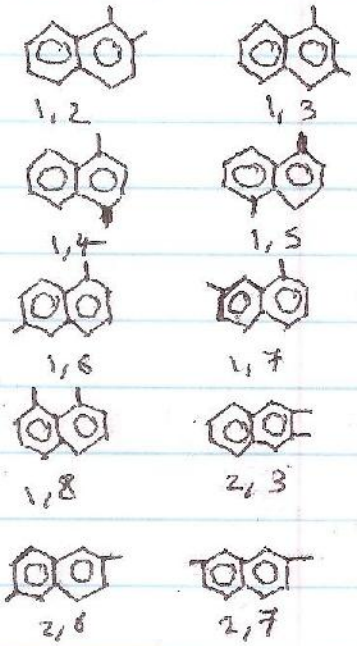
#4

b) Middle oil Compounds (oil)

Name	Molecular formula	Structural formula
Phenol	C_6H_6O	
Cresols (Methyl phenol)	C_7H_8O	 (O-Cresol) (m-Cresol)  (P-Cresol)
xylenols (Dimethyl phenol)	$C_8H_{10}O$	* xylenols have 6 Isomers generat from a) o-xylene  b) m-xylene  c) P-xylene 

#5

c) Heavy oil Compounds

Name	Molecular Formula	Structural Formula
Naphtalene	$C_{10}H_8$	 α-Position @ (1, 4, 5, 8) β-Position @ (2, 3, 6, 7)
Methyl Naphtalene	$C_{11}H_{10}$	 α-methyl naphtalene β-methyl naphtalene
Di Methy Naphtalene	$C_{12}H_{12}$	- have 10 isomers 
Acenaphtalene	$C_{12}H_{10}$	 Tricyclic Compound

*6

d) Antheracenes oil Compounds

Name	Molecular Formula	structural formula
Anthracene	$C_{14}H_{10}$	 - the centers of the rings are collinear
phenanthrene	$C_{14}H_{10}$	 - the centers are not linear
flaurene	$C_{13}H_{10}$	
Carbazole	$C_{12}H_9N$	

*7

- Benzene general formula (C_nH_{2n-6}), so it is highly unsaturated.

- Q: Prove that Benzene is unsaturated cyclic Compound with explaining its structure.

- A: ① In addition reactions the double bond attaches to two monovalent (ثنائي تكافؤ) atoms.

So, 2 atoms were added ⟶ one double bond

4 atoms were added ⟶ two double bond

By applying this to benzene

$C_6H_6 \xrightarrow[\text{sunlight}]{3Cl_2} C_6H_6Cl_6$ benzene hexachloride

$C_6H_6 \xrightarrow{3H_2} C_6H_{12}$ hexa hydro benzene

6 atoms added ⇒ ∴ Benzene Contains 3 double bonds.

② Bayer who invented cyclisation reaction:

1,5-dichloro Pentane $Cl-CH_2-CH_2-CH_2-CH_2-CH_2-Cl \xrightarrow{Zn\ dust}$  C_5H_{10}

Cyclo pentane

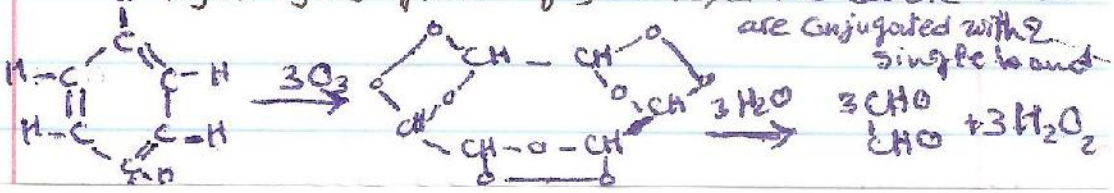
1,6-dichloro hexane $Cl-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-Cl \xrightarrow{Zn\ dust}$  C_6H_{12}

Cyclo hexane

⇒ he found that on hydrogenation of benzene, it produces (hexa hydro Benzene) which is identical to (cyclo hexane) ⇒ ∴ Benzene is a cyclic Compound

$C_6H_6 \xrightarrow{3H_2} C_6H_{12}$

③ Ozonolysis of benzene gives (trizonide) which on hydrolysis gives glyoxal ⇒ The double bonds are conjugated with 2 single bonds

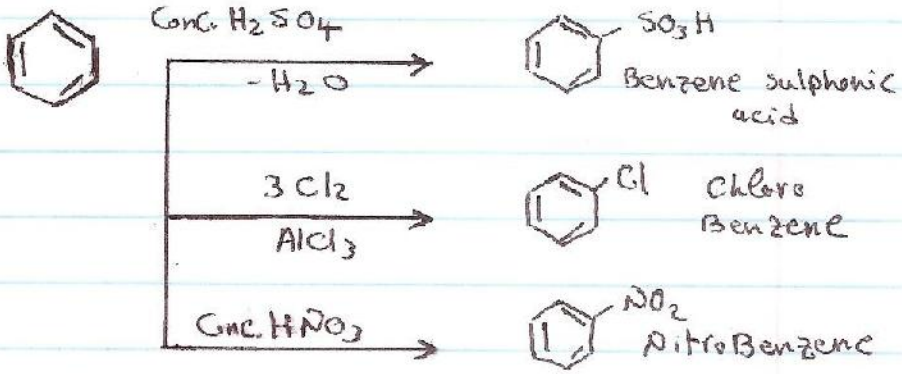


8

Q: Write Notes about "Aromaticity".

- It is the Aromatic properties which rised due to the difference between the 3 double bonds in Benzene & the usual double bonds of aliphatic Compounds.

Q: Prove that Carbon atoms in benzene are equivalent & mono substituted benzene has no isomers.



- Each of these reactions give one and the same Compounds, even if the molecule is added to different Carbon atoms.

* "لما عادت دي بتبقي ناتج واحد و هو نفس الناتج حتى لو دخلت الجزيء التفاعل على ذرة كربون أخرى"

This prove that

1- Carbon atoms in benzene are equivalent.

"لو دخلت جزيء على أي ذرة كربون مش هتفرق معاك"

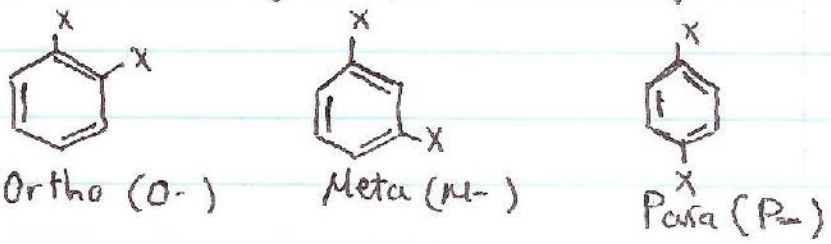
2- Mono substituded benzene has no isomers.

"الناتج يكون واحد عندما يحدث تفاعل تبادل بين البنزين وأي جزيء (واحد)"

*9

Kekule's formula

On substituting 2 hydrogen atoms in one benzene ring, 3 products are given.

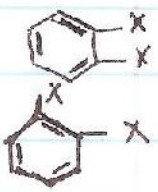


Ortho (O-) Meta (M-) Para (P-)

Critics to Kekule's formula

Landenberg attacked Kekule's formula on the basis that 4 isomers should be formed on di-substitution.

1 meta, 1 para, 2 ortho

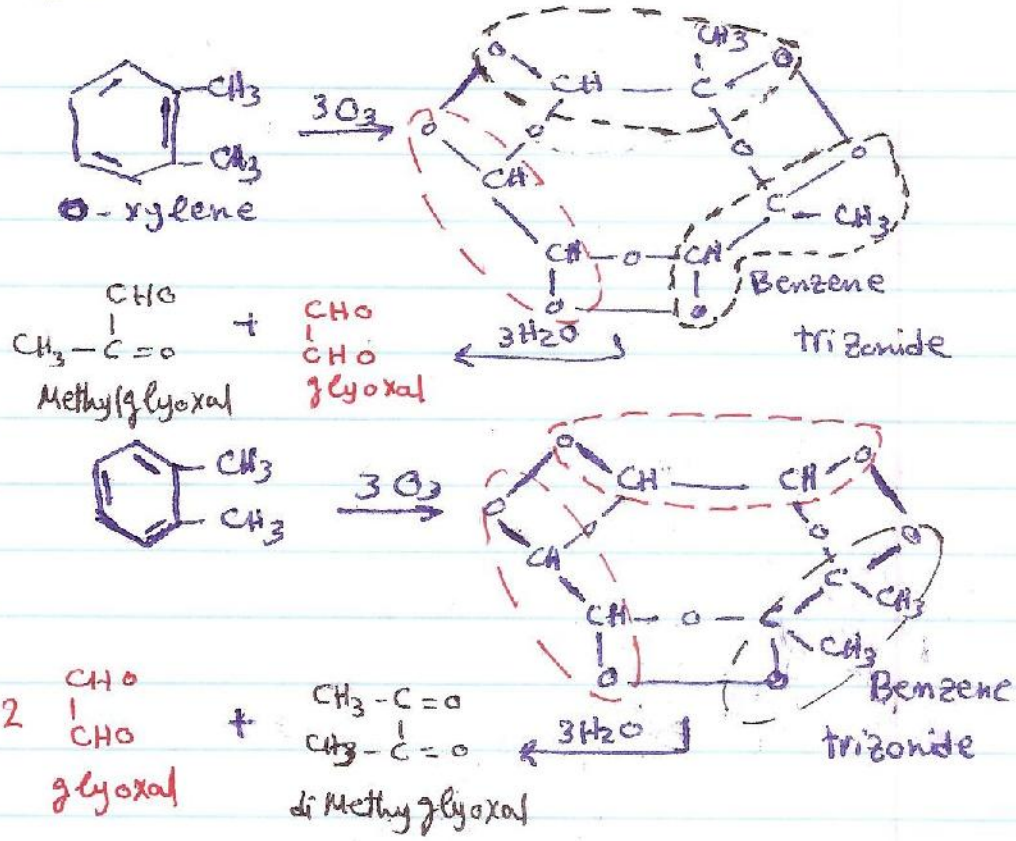


Kekule overcome critics

The single and double bonds in benzene ring are not fixed position but oscillate between two positions. This known as "Resonance"

- when O-xylene subjected to ozonolysis gives trizonide which decompose to give glyoxal, methyl glyoxal & di methyl glyoxal, these compounds can't be obtained unless 2 forms of O-xylene are present.

10



- In aliphatic compounds C–C (1.54 Å) C=C (1.34 Å)
- In Benzen ring, (–) & (=) have equal length (1.4 Å)

Q: The two formula of benzene are identical. Explain that.

A: Because the π-electrons forming the double bonds are free to travel between carbon atoms in circular path.

Orientation in benzene ring

The assigning of the position of substituents in disubstituted or polysubstituted derivatives of benzene.

*II

- Different studies on Orientation

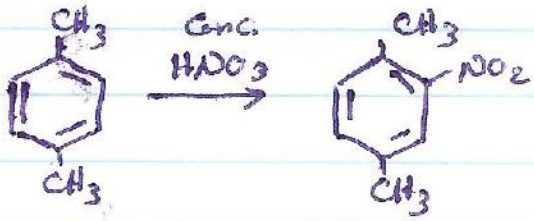
① Korner absolute method

A- 3rd Sub. + Para isomer → 1 tri Sub. derivative of benzene

B- 3rd Sub. + Ortho isomer → 2 tri Sub. derivative of benzene

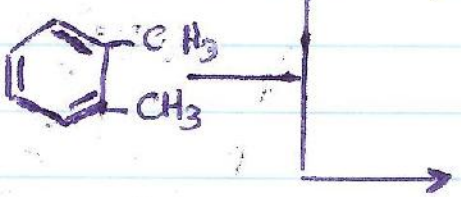
C- 3rd Sub. + Meta isomer → 3 tri Sub. derivative of benzene

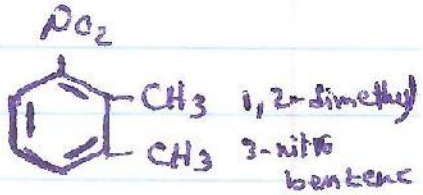
A-



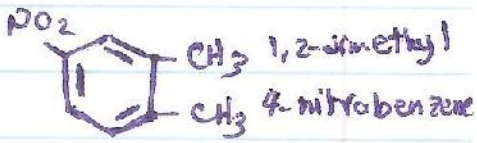
1,4- dimethyl 2- nitrobenzene

B-



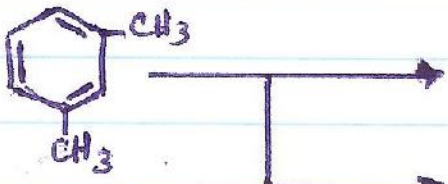


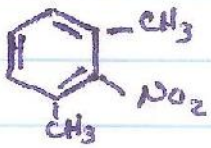
1,2-dimethyl 3-nitro benzene



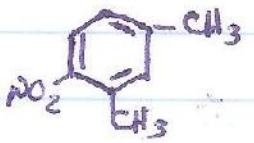
1,2-dimethyl 4-nitrobenzene

C-

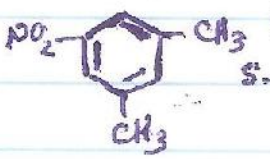




1,3-dimethyl 2-Nitrobenzene



1,3-dimethyl 4-Nitro benzene



1,3-dimethyl 5-Nitro benzene

* 12

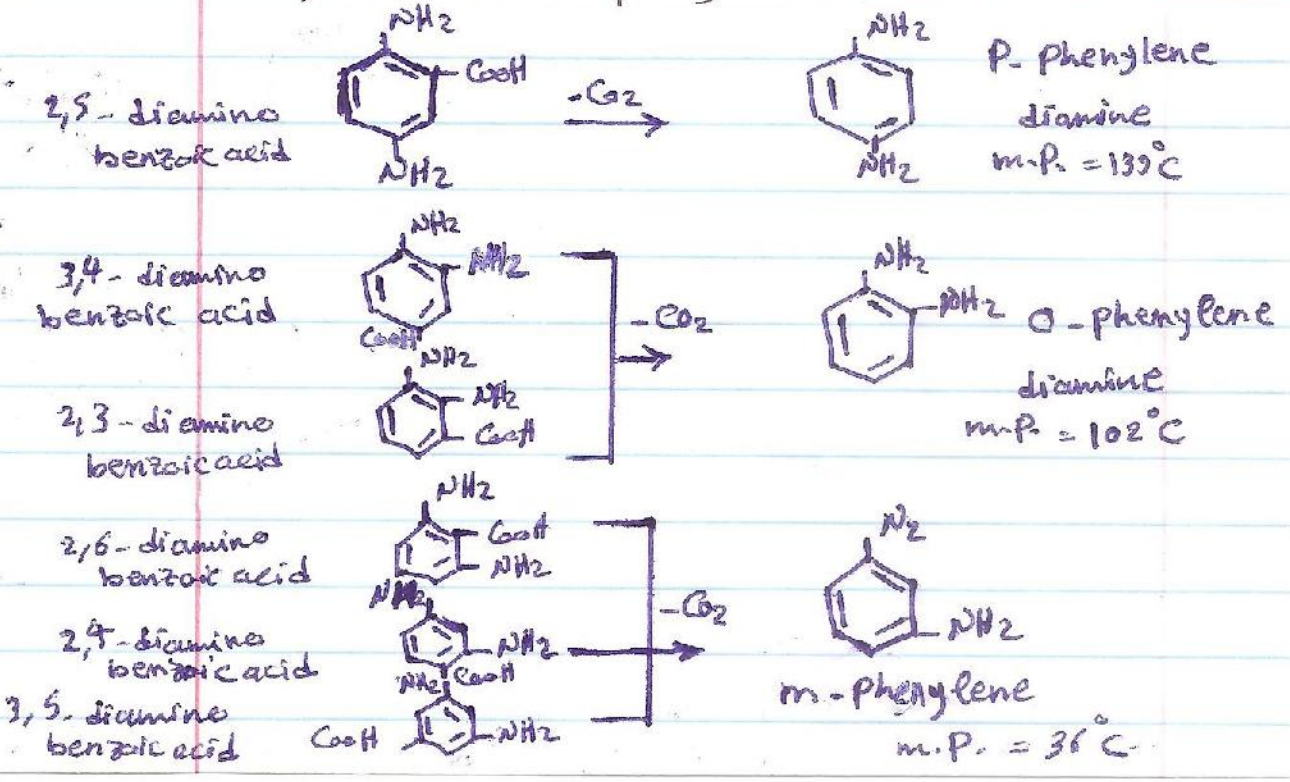
Q: Explain how to determine the position (structure) of xylene isomer.

A: By nitrating xylene.

- if one product is produced the isomer is Para
  " Write Reaction A in Page 11 "
- if two products are produced the isomer is Ortho
  " Write Reaction B in Page 11 "
- if 3 product are produced the isomer is Meta
  " Write Reaction C in Page 11 "

2) Greiss method

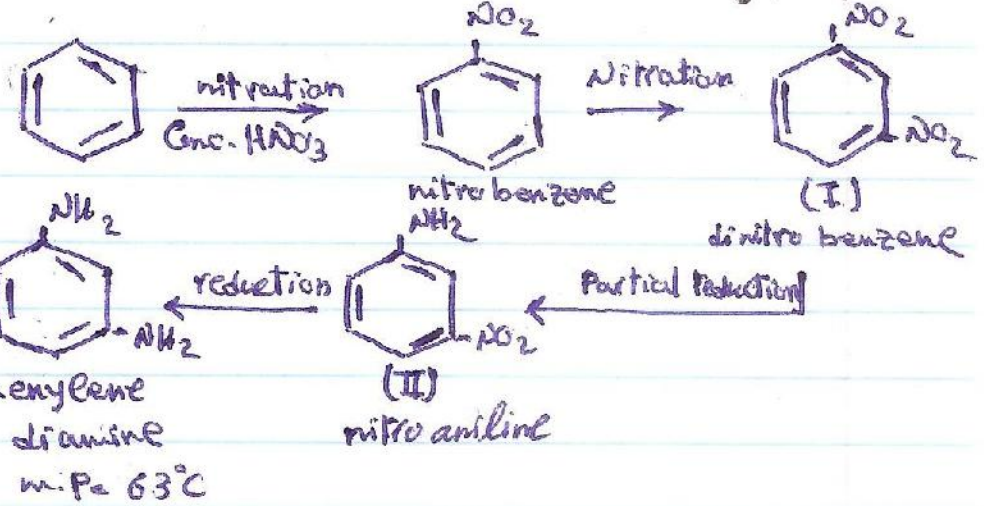
The reverse of Korner method by decarboxylation of 6 isomeric diamino benzoic acids To give 3 different phenylene diamine.



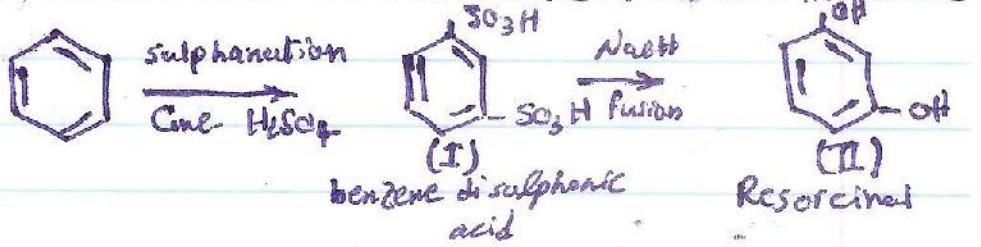
#13

3) The Relative method

This method based on the assumption that atoms or groups remain in the same position or exchange position with the incoming group.

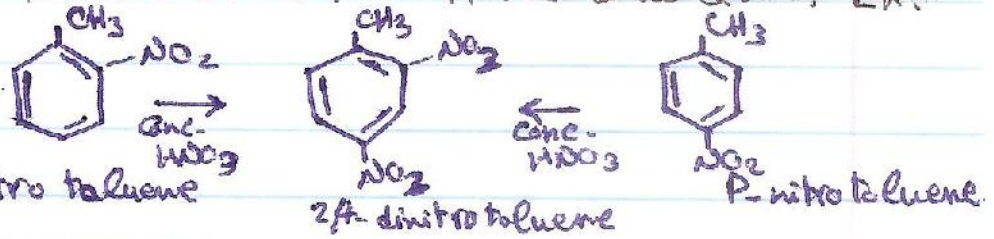


* Phenylene diamine produced is meta Compound, so (I) is m-dinitro benzene, (II) is m-nitro aniline



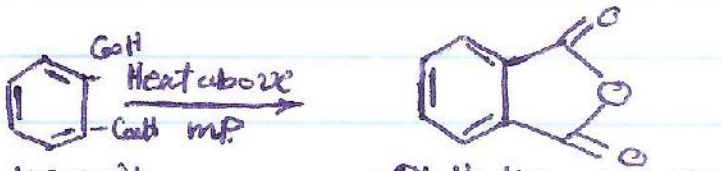
* Resorcinol (m-dihydroxybenzene) produced is meta Compound so (I) is m-benzene disulphonic acid.

* This method Can't be applied to all Cases, Ex:-

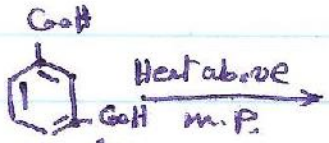


#14

4) Formation of cyclic Compound

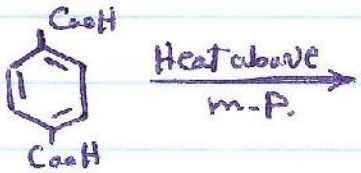


Phthalic acid — Phthalic anhydride



No changes

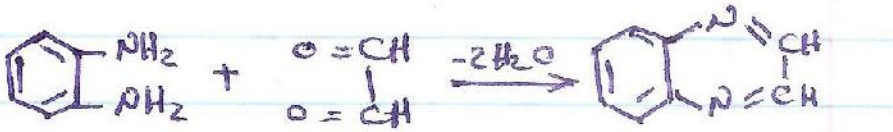
isophthalic acid



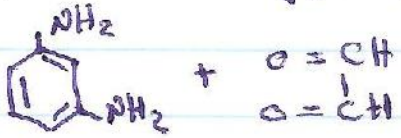
No changes

terephthalic acid

* When the three isomeric acids are heated above their m.p the isomer that lost water and give anhydride must be ortho.

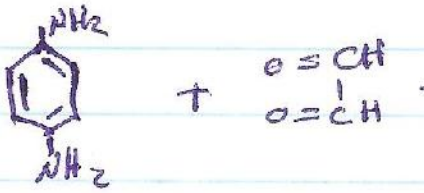


o-phenylene diamine — glyoxal — quinoxaline



No reaction

m-phenylene diamine



No reaction

P-phenylene diamine

* When the three isomers of phenylene diamine were reacted with glyoxal, the isomer that gave a cyclic compound is ortho.