

AROMATIC HYDROCARBONS.

(NEW COURSE)

P-1

CHAPTER NO. 9

WHAT ARE AROMATIC COMPOUNDS? WRITE THEIR CLASSIFICATION & NOMENCLATURE.

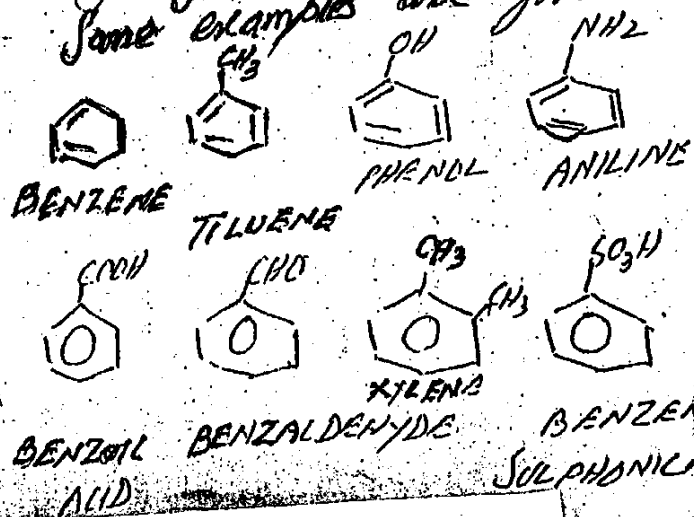
DEFINITION: The term aromatic was derived from Greek word "AROMA" meaning "FRAGRANT". These are special class of organic compounds which have low Hydrogen to Carbon ratio. These compounds have characteristic odour.

However some compounds are aromatic but do not have any odour and some compounds are not aromatic but they are fragrant. Now a days aromatic compounds are defined as "AROMATIC HYDROCARBONS INCLUDE BENZENE AND ALL THOSE COMPOUNDS WHICH ARE STRUCTURALLY RELATED TO BENZENE".

Benzene has a characteristic structural feature. It has regular planar hexagonal structure. On the basis of number of benzene rings aromatic compounds can be divided into following classes

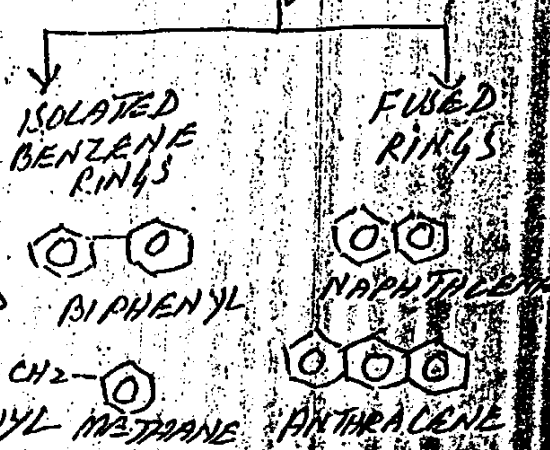
MONOCYCLIC AROMATIC COMPOUNDS.

They have one benzene ring. Some examples are given below



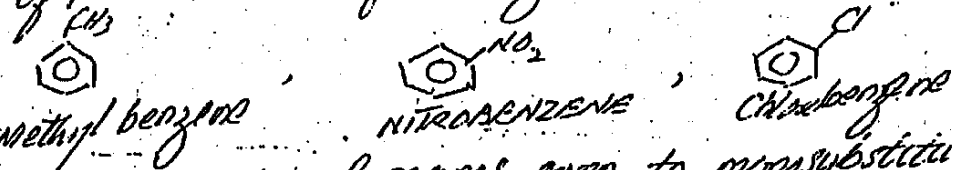
POLYCYCLIC AROMATIC HYDROCARBONS

They have two or more benzene rings. These are divided into two types

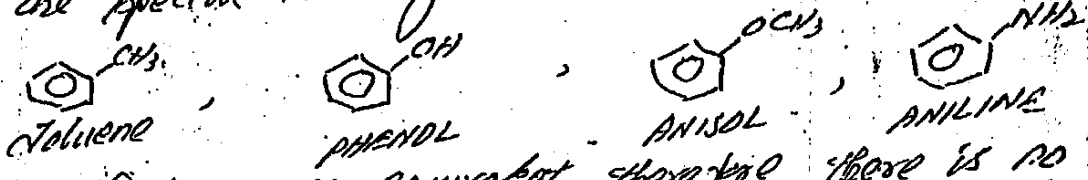


RULES OF NOMENCLATURE:

1. Monosubstituted derivatives are named by writing name of substituent before benzene. For example

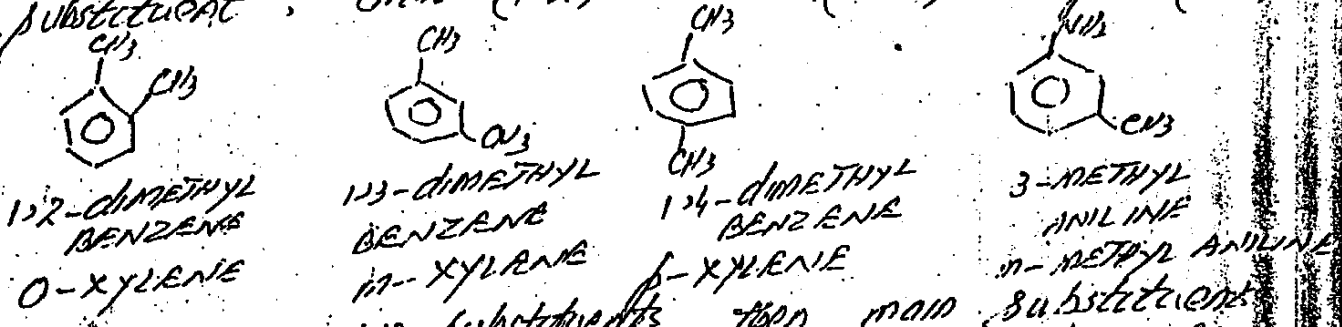


2. There are special names given to monosubstituted products like

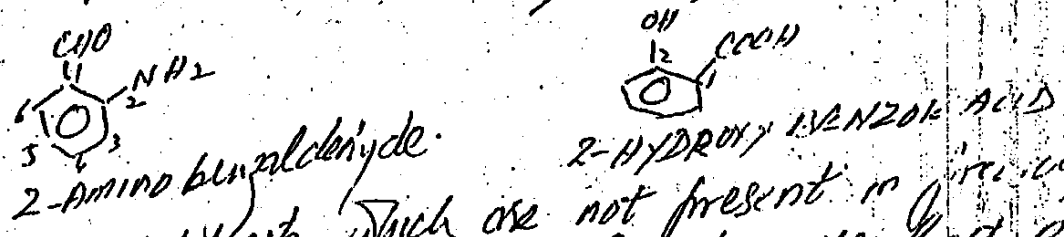


3. Since all positions are equivalent therefore there is no need to mention position of one substituent. There is only one monosubstituted product of benzene

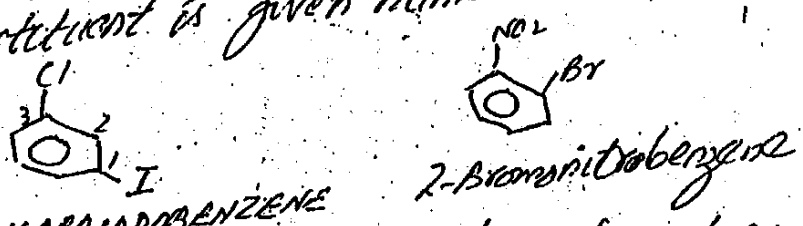
4. There are two methods to mention position of second substituent, ortho (1,2), meta (1,3) and para (1,4)



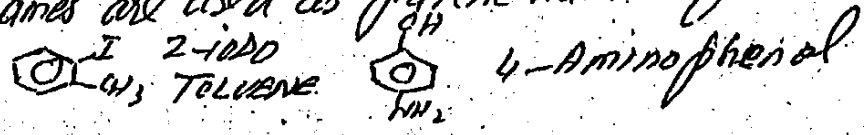
5. When there are two substituents then main substituent is given position 1 and numbers the ring in such a way that second substituent gets minimum possible number. The priority order is -COOH > -CHO > -COCH₃ > -OH > -NH₂ > -OR > -R



6. The substituents which are not present in priority order are named in alphabetical order if no last named substituent is given number 1

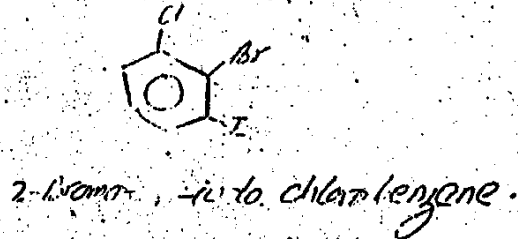
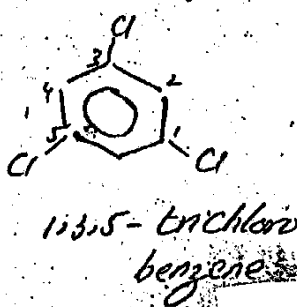
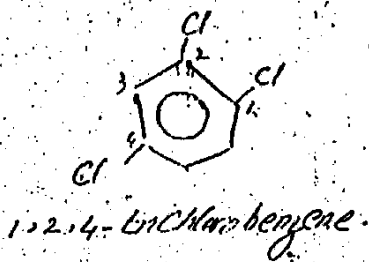
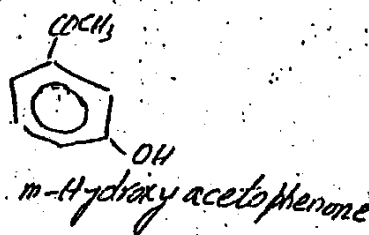
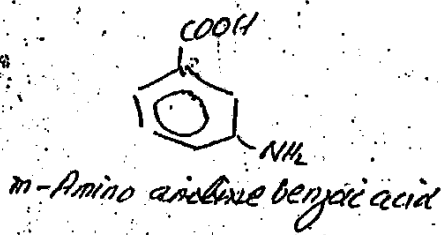
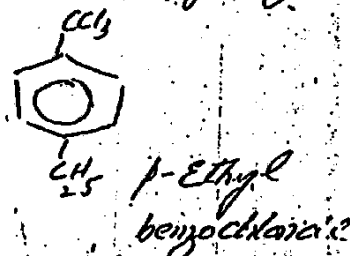
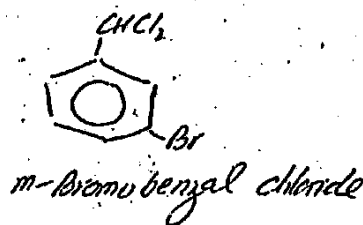
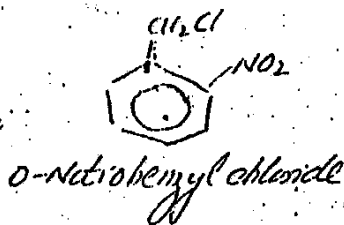
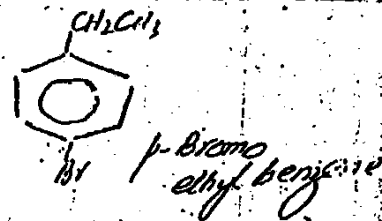
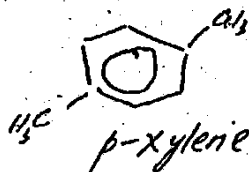
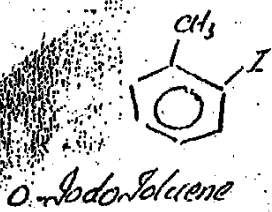
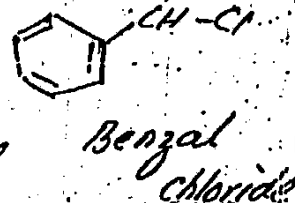
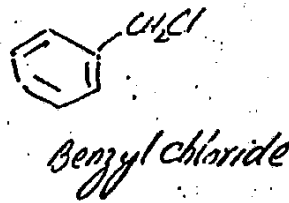
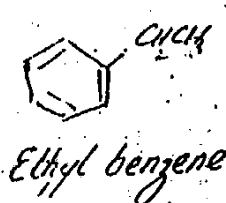
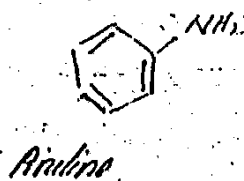
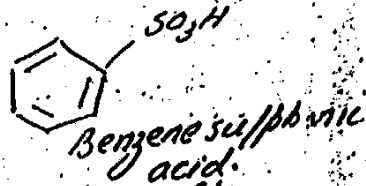
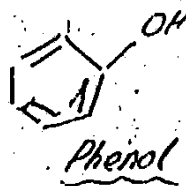
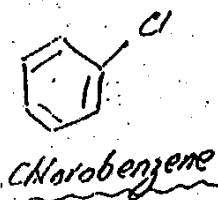
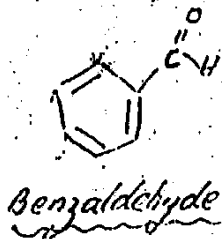
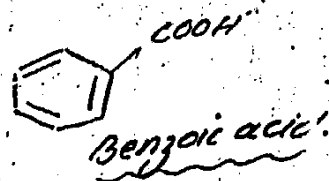
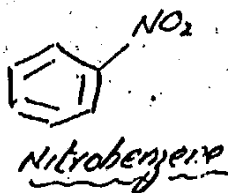
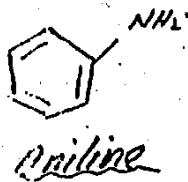
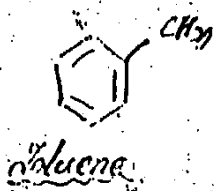


7. The special names are used as parent names of molecules



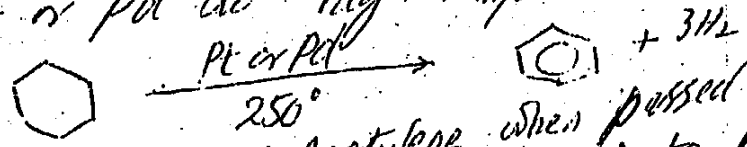
NOMENCLATURE OF DERIVATIVES OF BENZENE. p-3

Most of derivatives of benzene are given common names which are accepted by I.U.P.A.C. system. Some examples are given below.

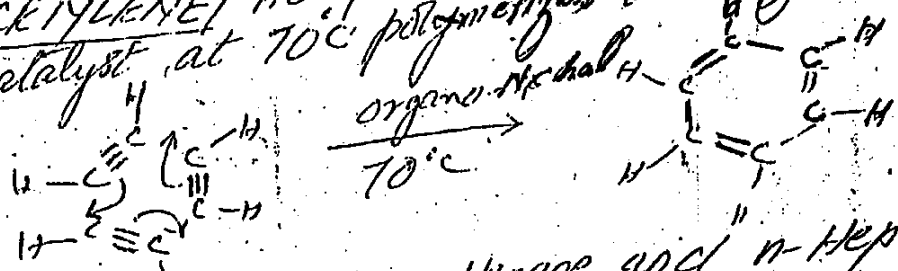


WRITE METHODS OF PREPARATION OF BENZENE P-4

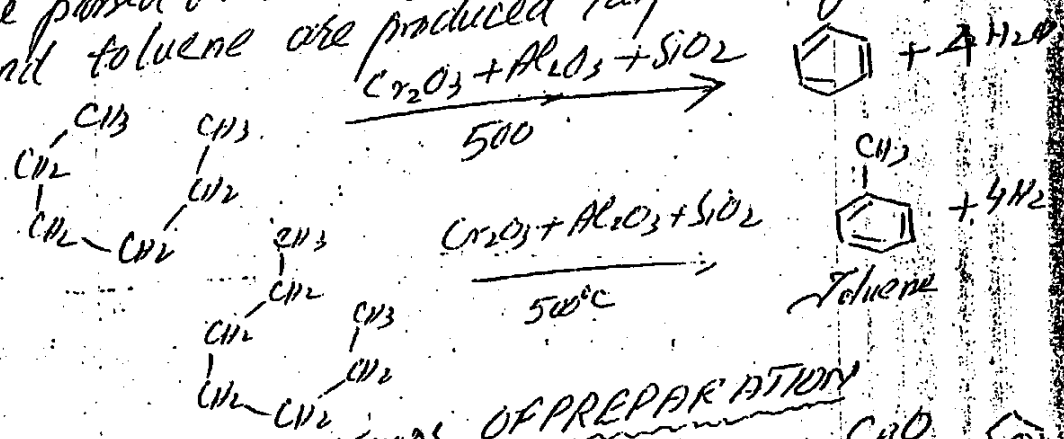
DEHYDROGENATION OF CYCLOHEXANES | The dehydrogenation of cyclohexane and other derivatives produces benzene and its derivatives. The reaction is carried out in presence of Pt or Pd at high temperature.



2 FROM ACETYLENE | Acetylene when passed over organo-nickel catalyst at 70°C polymerizes to Benzene.

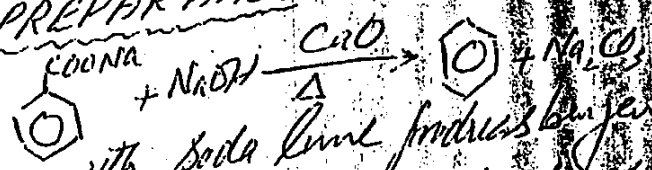


3- FROM ALKANES | When n-Hexane and n-Heptane are passed over Cr₂O₃, Al₂O₃ and SiO₂ at 500°C benzene and toluene are produced respectively.



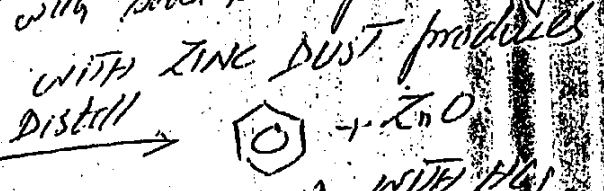
4) LABORATORY METHODS OF PREPARATION

(a) FROM SODIUM BENZOATE

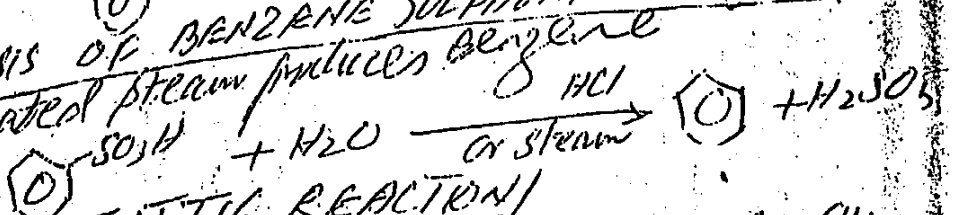


Sodium benzoate on heating with soda lime produces benzene.

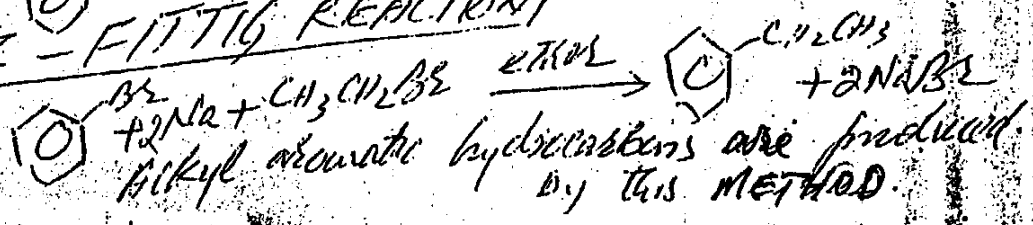
(b) REDUCTION OF PHENOL



(c) HYDROLYSIS OF BENZENE SULPHONIC ACID WITH HCl
or super-heated steam produces benzene.



5) WURTZ-FITTING REACTION



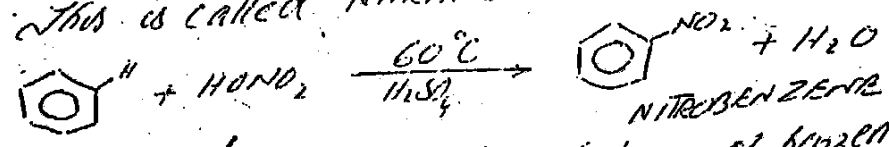
Bikyl aromatic hydrocarbons are produced by this method.

WRITE REACTIONS IN WHICH BENZENE BEHAVES LIKE A SATURATED HYDROCARBON. ALSO WRITE REACTION TO SHOW THAT IT BEHAVES LIKE AN UNSATURATED HYDROCARBON.

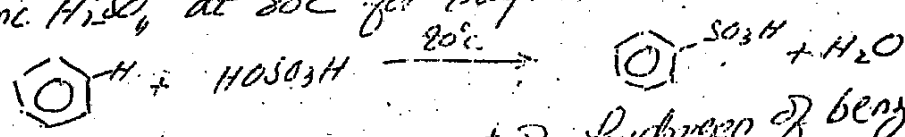
Benzene shows reactions of both saturated and unsaturated hydrocarbons. Some of these reactions are given below.
REACTIONS OF SATURATED HYDROCARBONS. (SUBSTITUTION REACTION)

The most important characteristic of saturated hydrocarbons is that they undergo substitution reactions. Benzene also undergoes following substitution reactions.

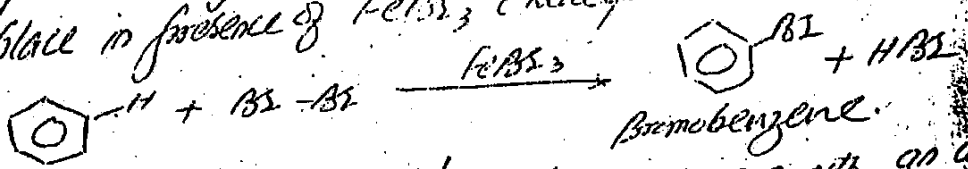
1. NITRATION / When benzene is treated with conc. Nitric acid and conc. H₂SO₄ (nitrating mixture) hydrogen is replaced by -NO₂ group. This is called NITRATION OF BENZENE.



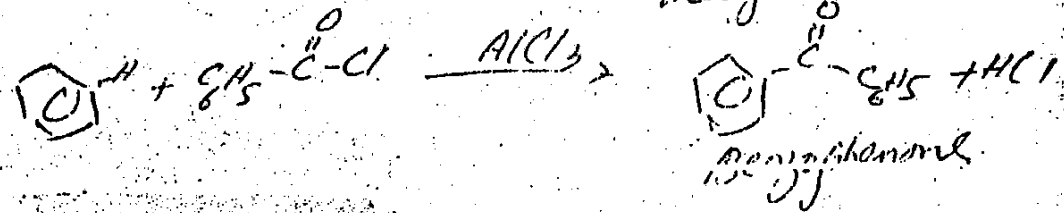
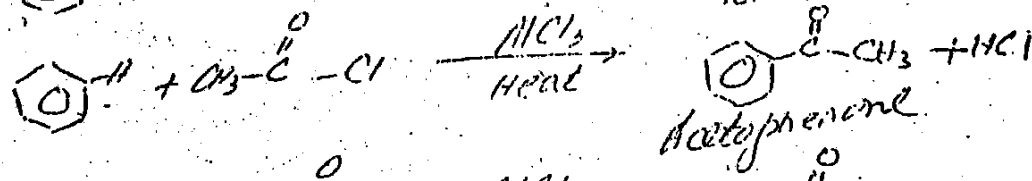
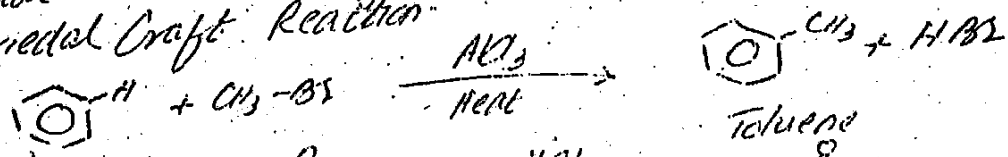
2. SULPHONATION / The replacement of hydrogen of benzene by a sulphonic acid group is called sulphonation. Benzene is treated with conc. H₂SO₄ at 80°C for sulphonation.



3. HALOGENATION / The replacement of hydrogen of benzene by a halogen group is called halogenation. Halogenation takes place in presence of FeBr₃ catalyst.



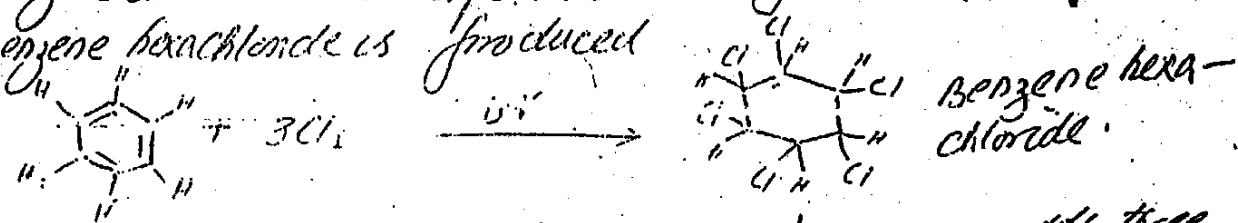
4. FRIEDEL CRAFT REACTION / Reaction of benzene with an alkyl halide or acid halide in presence of Lewis acid catalyst is called Friedel Craft Reaction.



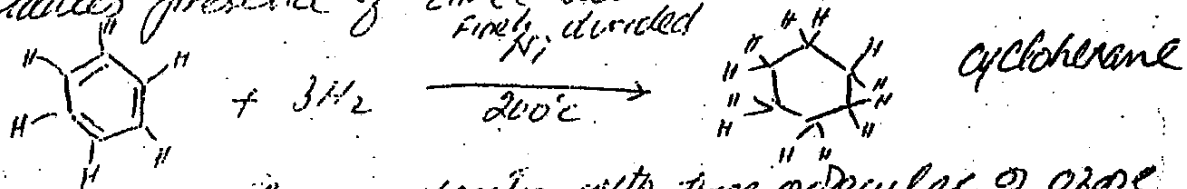
REACTIONS OF UNSATURATED HYDROCARBON: - (ADDITION REACTIONS)

The most important characteristic of unsaturated hydrocarbons is the addition reactions. Benzene undergoes following addition reactions

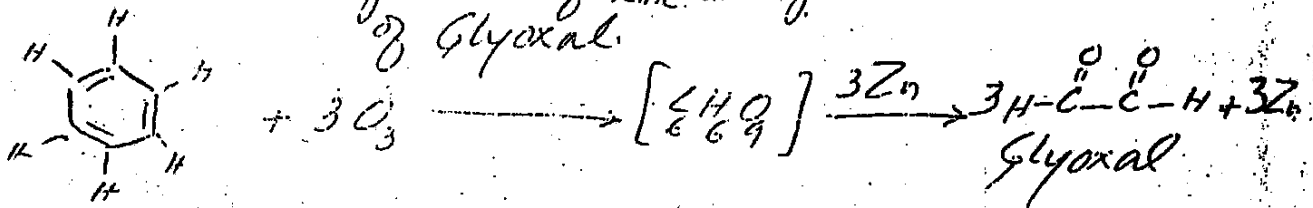
1. ADDITION OF CHLORINE: When chlorine is bubbled through boiling benzene or mixture is exposed to U.V. light an addition compound benzene hexachloride is produced



2. ADDITION OF HYDROGEN (REDUCTION) Benzene adds three molecules of H_2 in presence of Ni at 200°C to produce cyclohexane. It indicates presence of three double bonds.



OZONOLYSIS: Benzene reacts with three molecules of ozone in presence of Zinc and produces three molecules of Glyoxal.

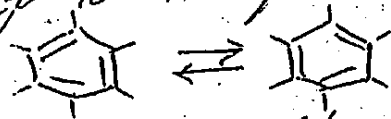


The molecular formula of benzene is C_6H_6 which indicates that it must be highly unsaturated.

STRUCTURE OF BENZENE: - The structure of benzene remained a problem for chemists for so many years. It shows reactions of both saturated and unsaturated hydrocarbons. Its formula " C_6H_6 " shows it to be highly unsaturated but it does not decolorize Bromine water and dil KMnO_4 . Further it shows substitution reactions which is characteristic of saturated hydrocarbon. This structure remained a problem for chemists for many years. Let us consider classical and modern methods to determine structure of benzene.

CLASSICAL STRUCTURE OF BENZENE

A German scientist Kekule proposed cyclic structure of Benzene. According to Kekule Benzene is cyclic hexagonal structure with three alternating double and single bonds. Later on he proposed that benzene has a benzene is an equilibrium mixture of following two

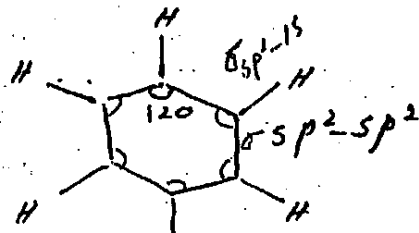
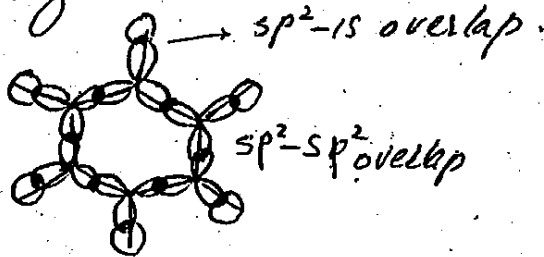
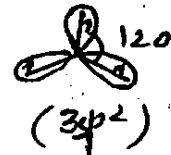


These structures explain addition reactions of benzene but cannot explain substitution reactions of benzene.

MOLECULAR ORBITAL TREATMENT OF BENZENE:-

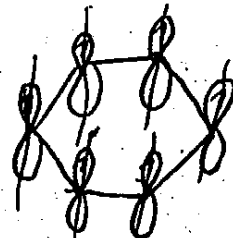
Spectroscopic analysis have shown that Benzene has hexagonal, regular, planar structure with each bond angle 120° . It suggests that each carbon in benzene is sp^2 -hybridized. In sp^2 hybridization each carbon has three hybrid orbitals situated at an angle of 120° . One unhybridized p orbital is present perpendicular to these hybrid orbitals. $1s^2 2s^2 2p^1 2p_x^1 2p_y^1 2p_z^1$

In benzene there are six carbon atoms so there are 18 sp^2 hybrid orbitals in benzene as shown below



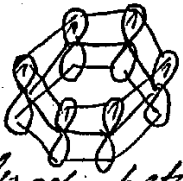
12 sp^2 hybrid orbitals are utilized in 6(C-C) sigma bond formation. Each C-C sigma bond is formed due to sp^2-sp^2 overlap. 6 sp^2 are utilized in 6(C-H) σ bond formation. Each σ is formed due to sp^2-1s overlap.

One unhybridized p -orbital is still present on each carbon. Thus there are six p orbitals each with one electron. These p orbitals have their axes parallel to each other. If it is considered similar



to alkene, then there should be three alternate π -bonds between carbon atoms. But in Benzene six p-orbitals have their axis parallel to each other and these overlap simultaneously and form an electron cloud of π -electrons above and below benzene ring.

The π -electrons are completely delocalized.



π -delocalized π -electrons.

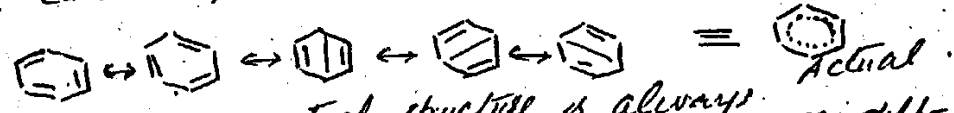
In ethene on the other

hand π -bond is localized between two carbons.

Due to delocalized π -electrons, these electrons are not easily donated to an electrophile. Thus benzene does not undergo ~~addition~~ electrophilic addition reactions under normal conditions. But under drastic conditions when a powerful electrophile is available, it can attack these π -electrons. Thus delocalization of π -electrons is responsible for stability and special behaviour of benzene. Compounds having alternate double and single bonds are called conjugated systems. All conjugated systems have delocalized bonding.

Q: WHAT IS RESONANCE? EXPLAIN STABILITY OF BENZENE IN TERMS OF RESONANCE ENERGY.

When a compound can be represented by more than one Lewis structures and actual structure is hybrid of all these structures the compound is said to possess resonance. For example benzene C_6H_6 can be represented by following canonical structures:



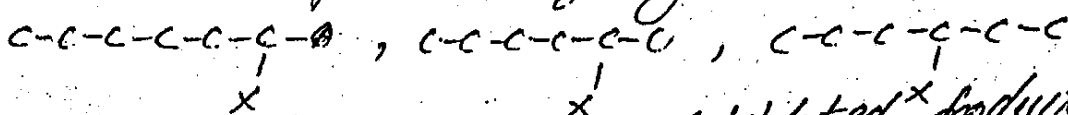
Resonance Energy: The actual structure is always more stable than any one of canonical structures, the difference of energy between actual structure and most stable canonical structure is called Resonance Energy.

It is calculated from heat of hydrogenation data.

Heat of hydrogenation of Kekulé structure	=	3×119.6	=	358.8 kJ
Heat of hydrogenation of Actual benzene	=		=	208.8 kJ
Thus benzene has Resonance Energy	=		=	150 kJ

Thus benzene is more stable than non-resonating system by 150.5 kJ energy.

monosubstituted products of benzene 10

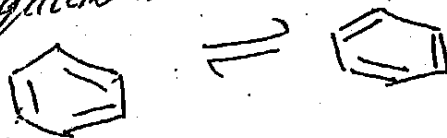


but benzene has only one monosubstituted product of benzene.

3 The molecular formula of benzene C_6H_6 , neither corresponds to alkane, alkene or alkyne. Thus it is concluded that benzene cannot have open chain structure.

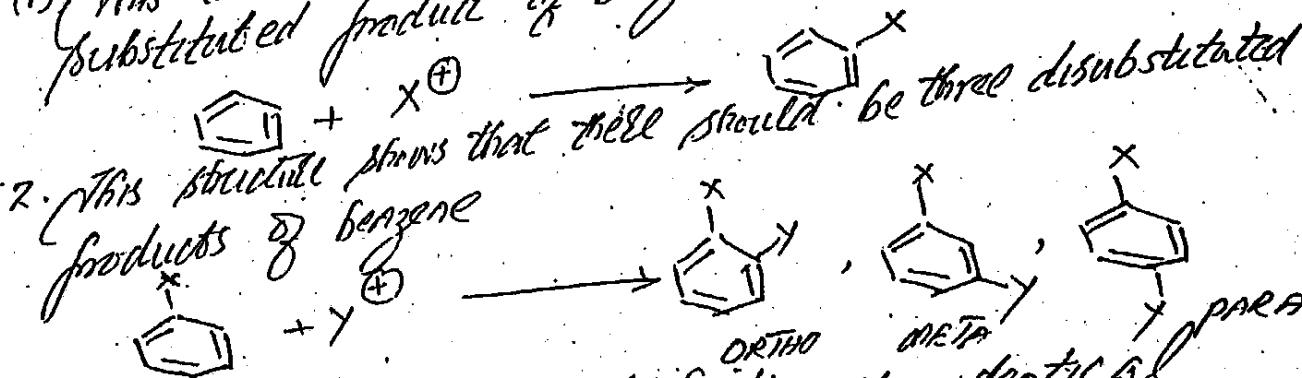
WHAT IS KEKULE STRUCTURE OF BENZENE? WRITE ITS ADVANTAGES & DISADVANTAGES.

Kekule suggested a cyclic, regular, hexagonal structure of benzene with three alternate double bonds. He suggested that benzene has following two structures which are in equilibrium with each other.



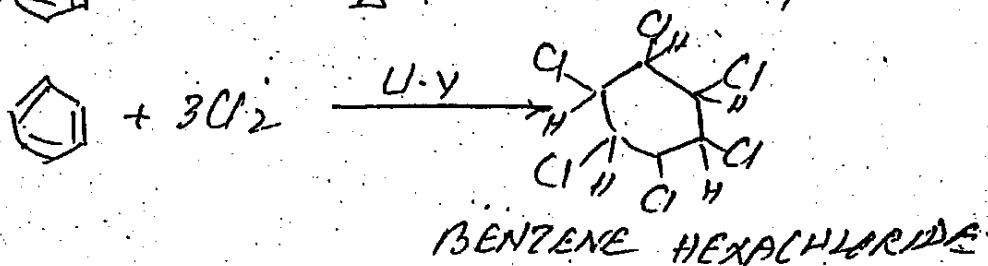
ADVANTAGES

(1) This structure shows that there should be one monosubstituted product of benzene.



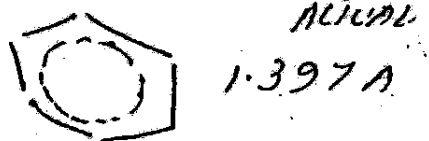
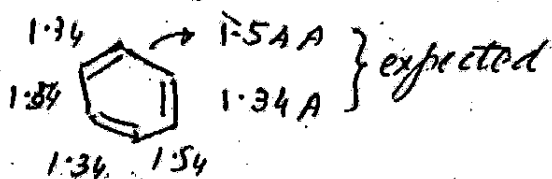
These points suggest that all positions are identical.

3. This structure justifies addition of 3-moles of H_2 and three moles of Cl_2 to each mole of benzene.



OBJECTIONS TO KEKULE'S STRUCTURE: (P-11)

1. This Kekule structure does not explain substitution reactions of benzene
2. The Kekule structure does not explain extra stability of benzene
3. The Kekule structure suggests benzene to be highly unsaturated but it behaves like saturated compounds
4. Kekule structure suggests that bond lengths in benzene should be alternately C-C and C=C lengths (1.34 Å and 1.54 Å respectively) but actually bond lengths are 1.397 Å which are neither equal to single bond length nor equal to double bond lengths.



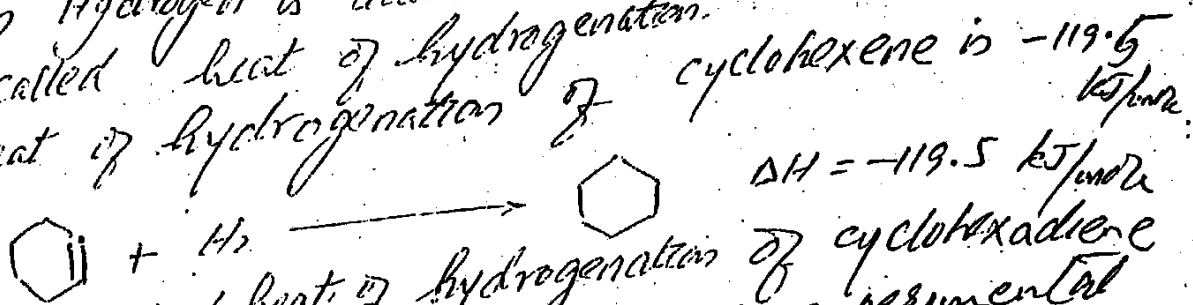
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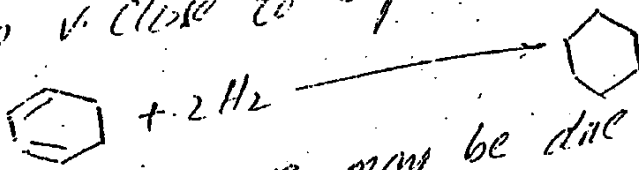
WRITE A NOTE ON STABILITY OF BENZENE.

Benzene is an extraordinarily stable molecule. The increased stability of benzene is due to delocalized π -electron cloud. The increased stability of benzene can be explained on the basis of heat of hydrogenation data.

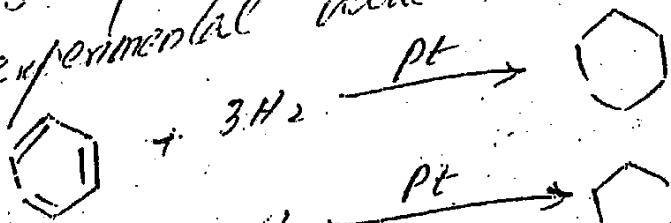
When Hydrogen is added to an unsaturated compound is called heat of hydrogenation. The amount of heat evolved



The expected heat of hydrogenation of cyclohexadiene is $-119.5 \times 2 = -239 \text{ kJ/mole}$. The experimental value is v. close to expected value $\Delta H_{\text{exp}} = -239 \text{ kJ}$
 $\Delta H_{\text{actual}} = -231.5 \text{ kJ}$



The minor difference may be due to conjugated d.b. The expected heat of hydrogenation of 1,3,5-cyclohexatriene is $-119.5 \times 3 = -358.5 \text{ kJ}$
 The experimental value is -208 kJ/mole



This actual structure of benzene is more stable than 1,3,5-cyclohexatriene. This difference between actual structure and most stable canonical structure is called Resonance energy

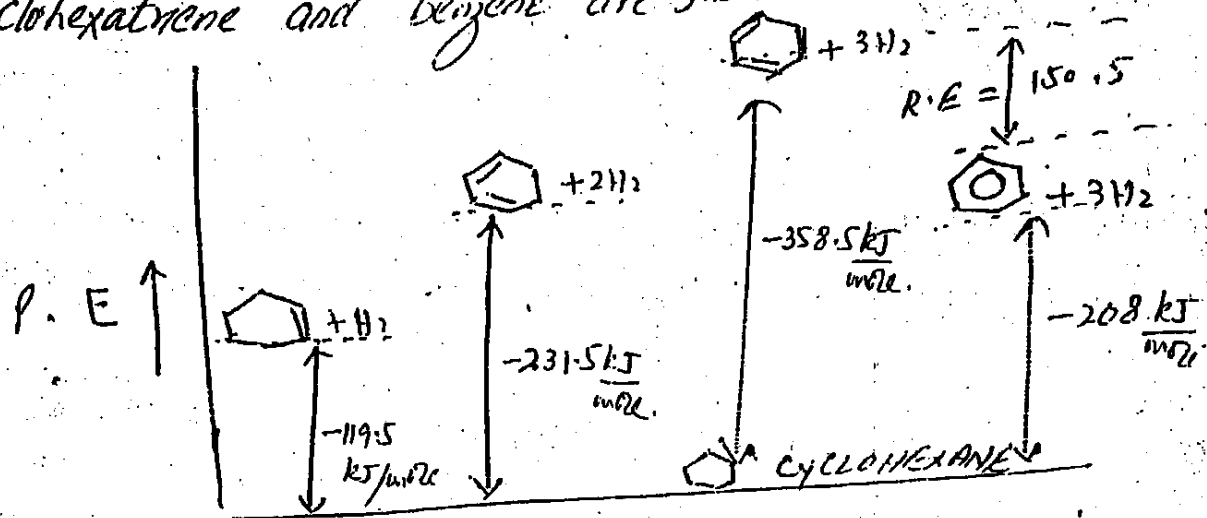
$$\text{Resonance energy} = -358.5 - (-208)$$

$$= 150.5 \text{ kJ/mole}$$

13

P-13

The relative energies of cyclohexene, cyclohexadiene and cyclohexatriene and benzene are shown below.



The relative energy diagram shows that benzene is much more stable than 1,3,5-Hexatriene.

Q: COMPARE RELATIVE REACTIVITIES OF ALKANE, ALKENE AND BENZENE.

Ans: The order of reactivities of alkane, alkene and benzene is $\text{Alkene} > \text{Benzene} > \text{Alkane}$.

ALKANES are least reactive compounds. The low reactivity is due to non-polar nature and very strong sigma bonds. They can undergo only substitution reactions which involve FREE RADICALS.

ALKENES are very much reactive compounds. This is due to weak π bond which is localized. The electrophile can attack π -electrons very easily. Thus alkenes undergo addition reactions quite easily. Alkenes can also undergo addition polymerization and oxidized easily.

BENZENE is quite stable and less reactive compound. It has delocalized π -electrons which are not easily available to an electrophile. Thus only a powerful electrophile can attack these π -electrons in presence of catalyst and under drastic conditions. Benzene undergoes substitution reactions. But these reactions

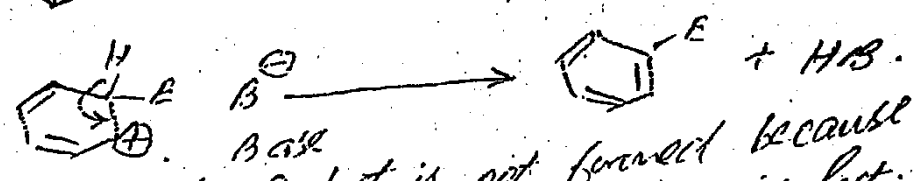
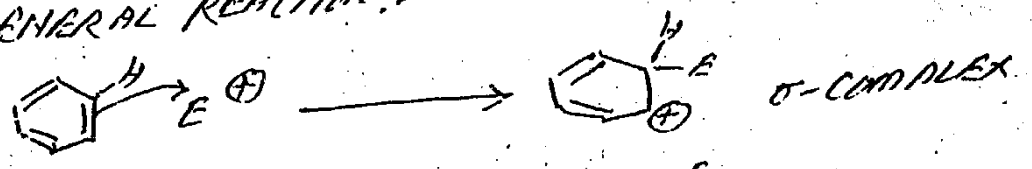
do not involve free radicals. These are electrophilic substitution reaction. Benzene can also undergo addition reactions. These addition reactions require much more drastic conditions. Benzene does not undergo polymerization and it is resistant to oxidation.

Thus benzene is more reactive than Alkanes but less reactive than Alkenes.

GENERAL PATTERN OF REACTIVITY OF BENZENE:-

Due to delocalised π -electrons the weak electrophile cannot attack benzene ring. Only a powerful electrophile can attack these π electrons. The initially formed σ -complex loses H^+ and a substituted product is formed.

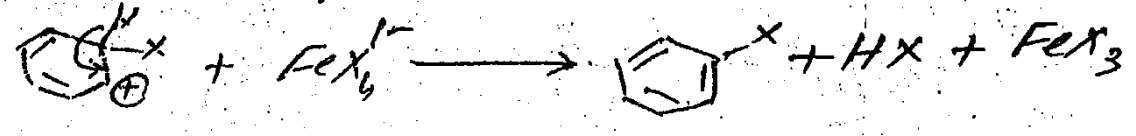
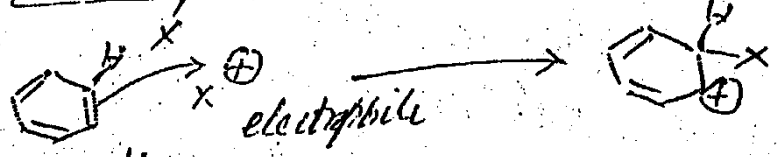
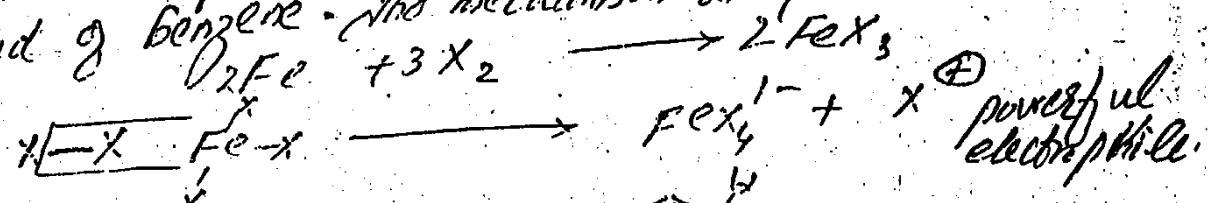
GENERAL REACTION:-



The addition product is not formed because in this case the characteristic stability of benzene is lost.

EXAMPLE - Halogenation of benzene. Takes place in presence of Iron or Iron halide catalyst. FeX_3 produced by reaction of halogen with iron is an electron deficient molecule.

It reacts with another molecule of halogen to form powerful electrophile called HALOGENONIUM ION X^+ . This electrophile can break continuous sheath of π electron cloud of benzene. The mechanism is shown below.



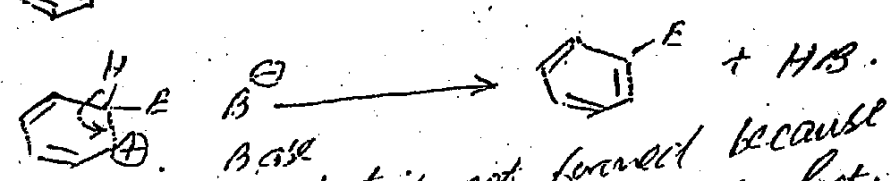
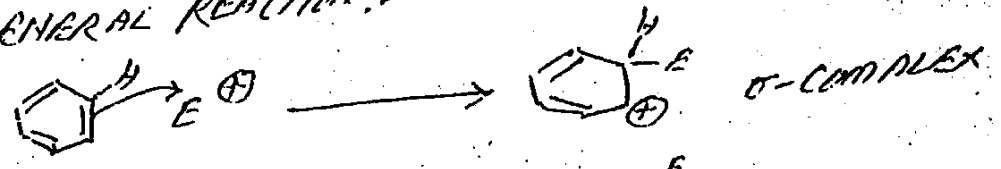
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Thus benzene is more reactive than Alkanes but less reactive than Alkenes.

GENERAL PATTERN OF REACTIVITY OF BENZENE:-

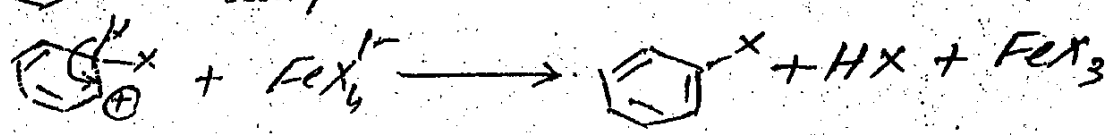
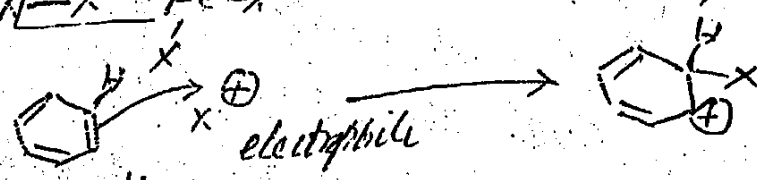
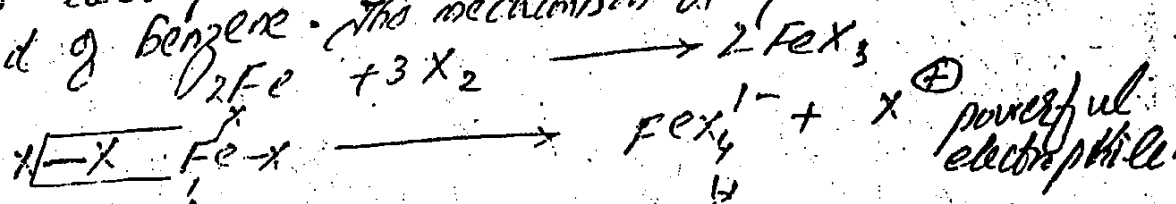
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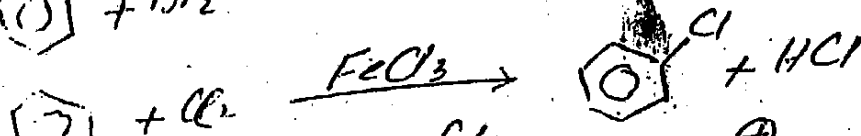
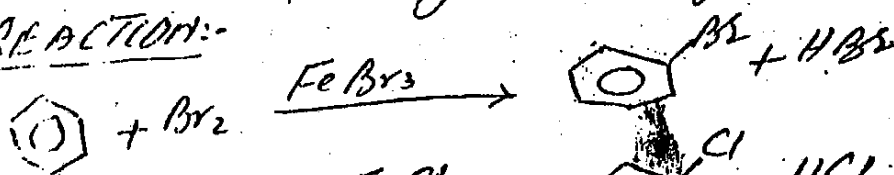
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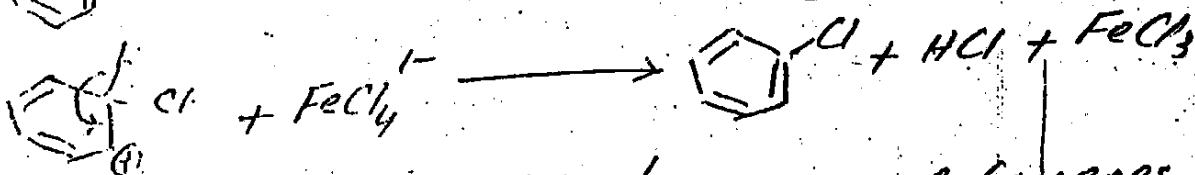
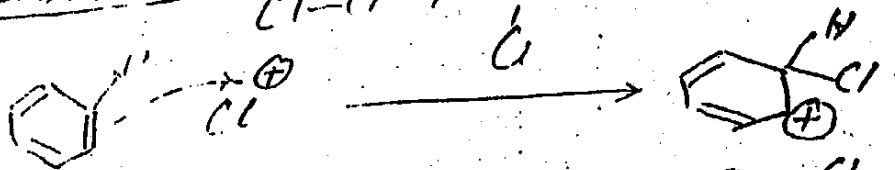
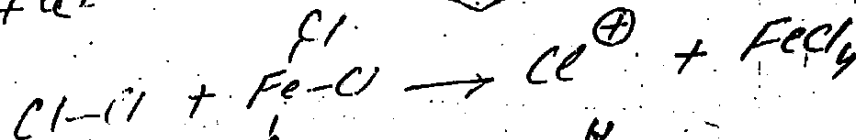
WRITE NOTE ON HALOGENATION OF BENZENE P-15

The replacement of hydrogen of benzene by halogen group is called HALOGENATION. When benzene is treated with halogen in presence of catalyst, hydrogen is replaced by halogen atom. The order of reactivity is $F_2 > Cl_2 > Br_2 > I_2$. Fluorination is too vigorous to control and iodination gives poor yield.

NET REACTION:-

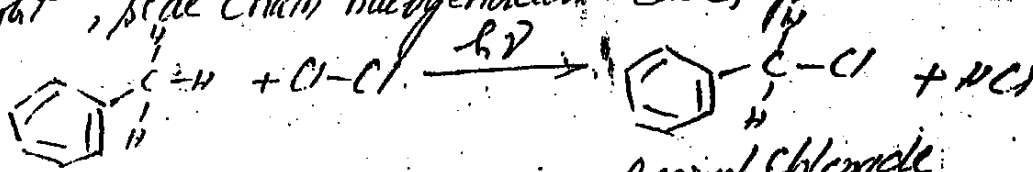


MECHANISM:

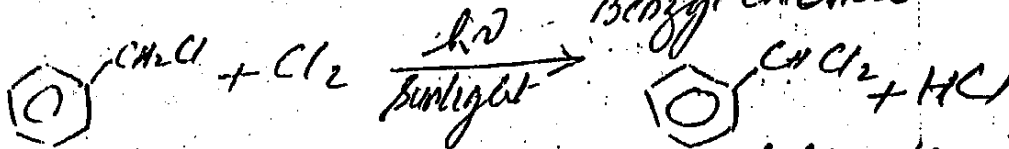


SIDE CHAIN HALOGENATION:

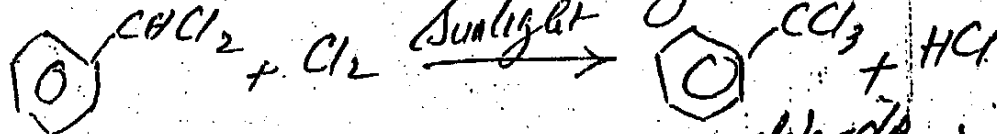
When alkyl benzenes are treated with chlorine or bromine in presence of sunlight, side chain halogenation takes place.



Benzyl chloride

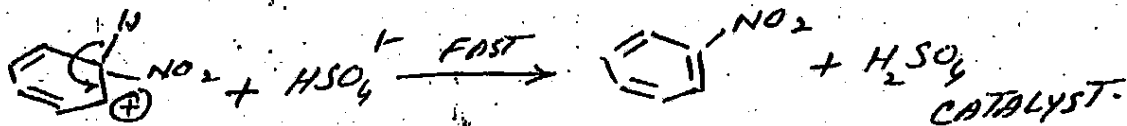
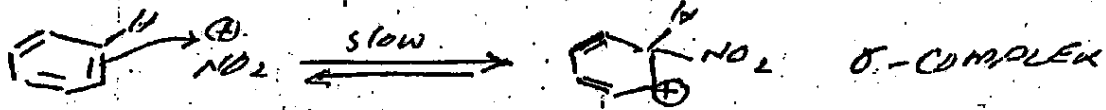
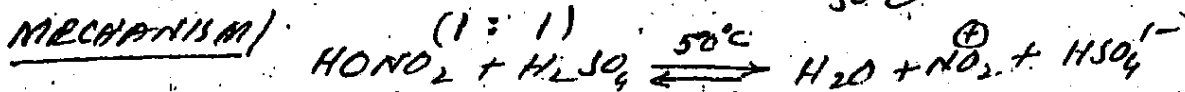
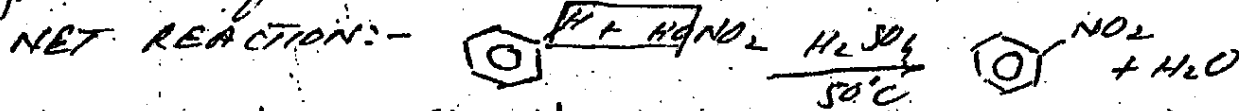


Benzal chloride



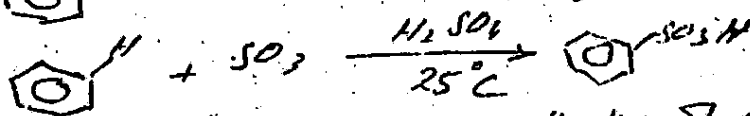
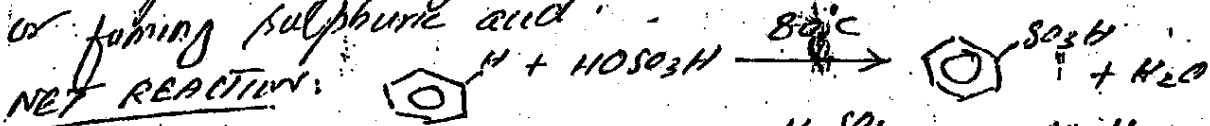
Benzotrichloride

NITRATION OF BENZENE:- The replacement of hydrogen of benzene by a nitro group is called NITRATION. When benzene is treated with nitric acid and H_2SO_4 (conc), nitration takes place. The reaction proceeds through formation of nitronium ion " NO_2^+ "



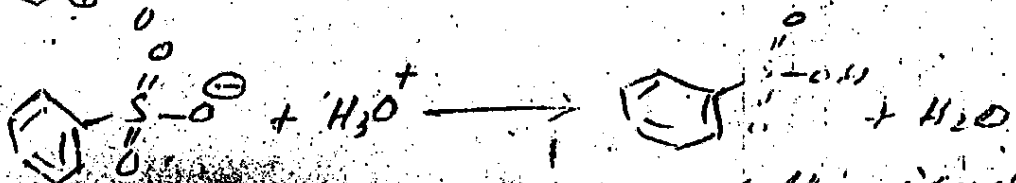
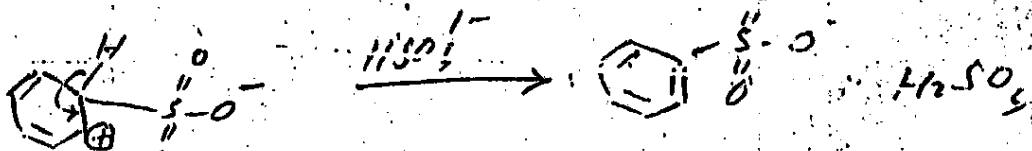
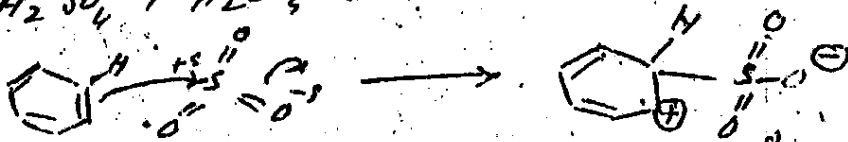
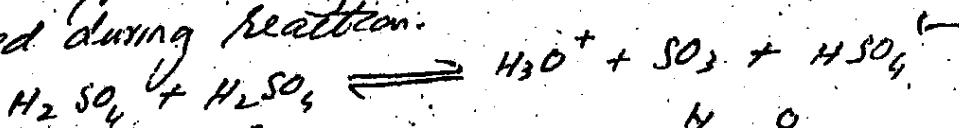
SULPHONATION OF BENZENE

The introduction of sulphonic acid group in benzene ring is called "Sulphonation". For sulphonation, benzene is treated with conc. H_2SO_4 or fuming sulphuric acid.



MECHANISM)

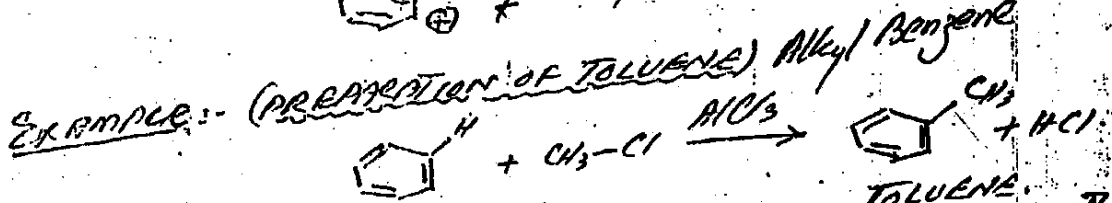
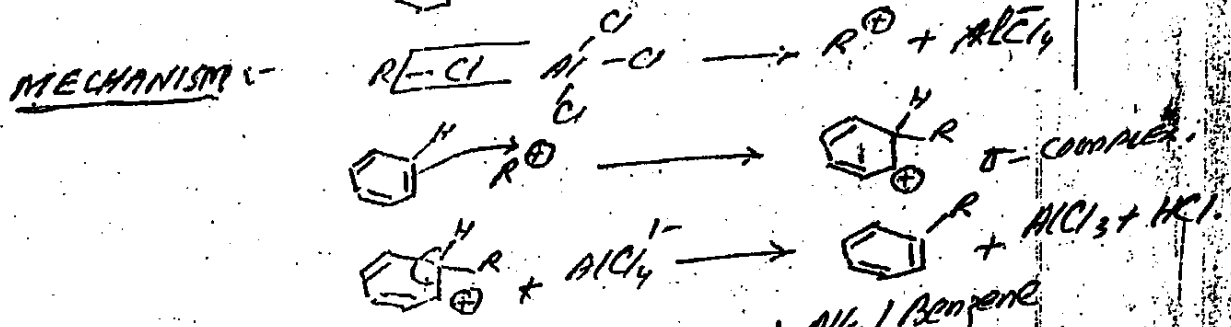
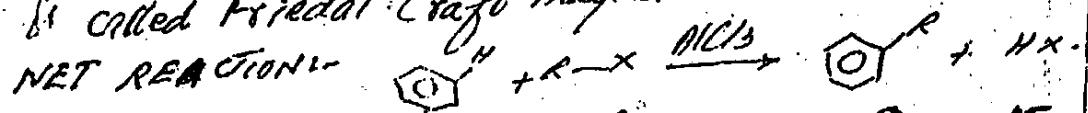
The attacking electrophile is " SO_3 " which is produced during reaction.



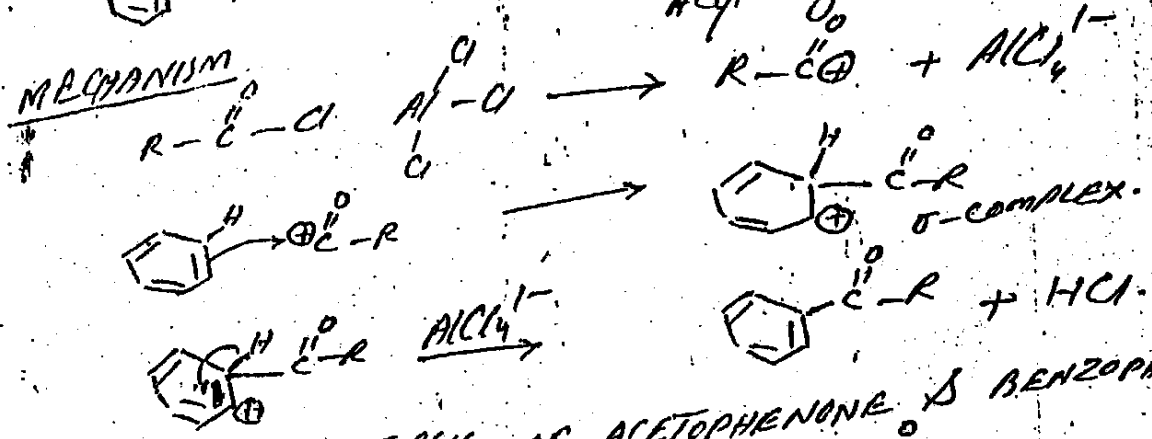
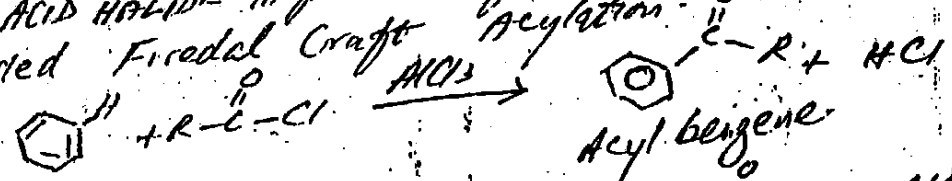
Benzene sulphonic acid.

FRIEDAL CRAFT REACTION:- The alkylation or acylation of benzene is called Friedal Craft Reaction. It may be divided into two types

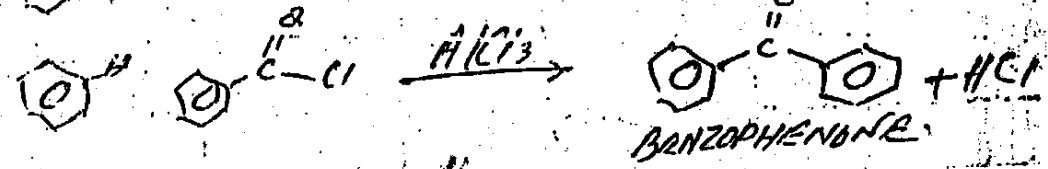
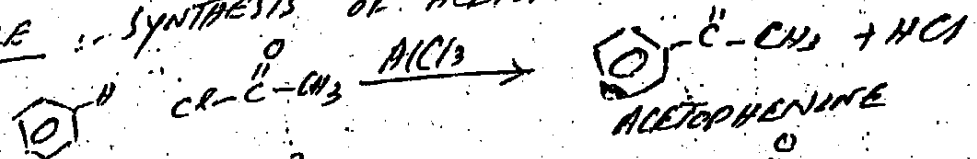
a) FRIEDAL CRAFT ALKYLATION:- The reaction of benzene with an alkyl halide in presence of a Lewis acid catalyst is called Friedal Craft Alkylation.



(b) FRIEDAL CRAFT ACYLATION:- The reaction of benzene with an ACID HALIDE in presence of Lewis acid catalyst is called Friedal Craft Acylation.

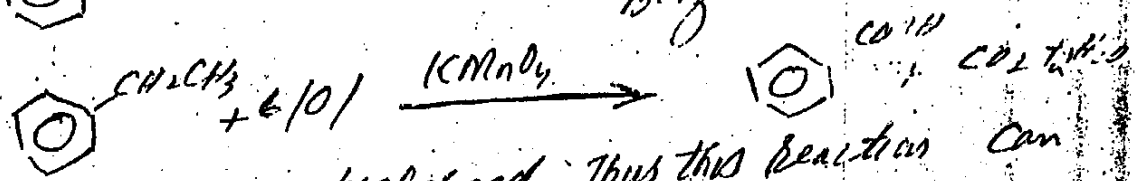
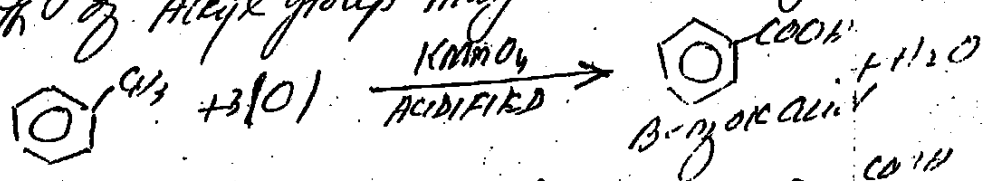


EXAMPLE:- SYNTHESIS OF ACETOPHENONE & BENZOPHENONE



WRITE NOTE ON FOLLOWING :-

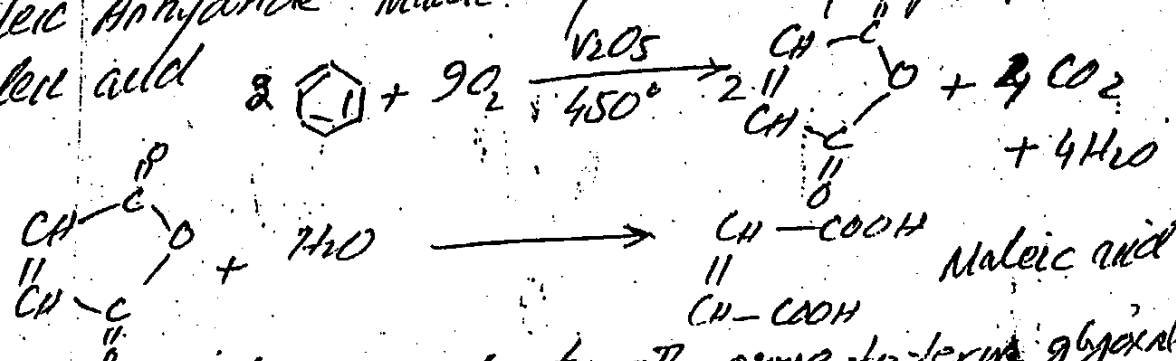
SIDE CHAIN OXIDATION OF BENZENE Alkyl benzenes are oxidized with dil acidified $KMnO_4$ or $K_2Cr_2O_7$. In these reactions the alkyl groups are oxidized to $-COOH$. The benzene ring is not affected. Whatever the length of Alkyl group may be it is oxidized to $-COOH$.



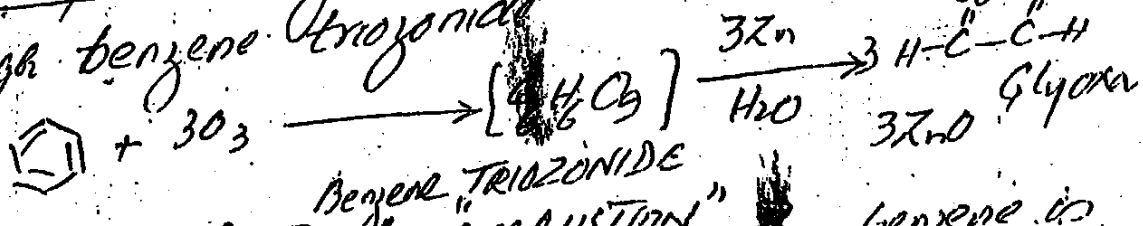
Colour of $KMnO_4$ is discharged. Thus this reaction can be used to identify Alkyl benzenes.

OXIDATION OF BENZENE

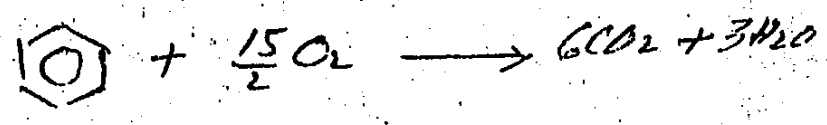
(a) by $KMnO_4$ or $K_2Cr_2O_7$. However when benzene is strongly heated in Air, in presence of V_2O_5 , it is oxidized to Maleic Anhydride. Maleic anhydride on hydrolysis produces Maleic acid.



(b) OZONOLYSIS Benzene reacts with ozone to form glyoxal through benzene triozonide.



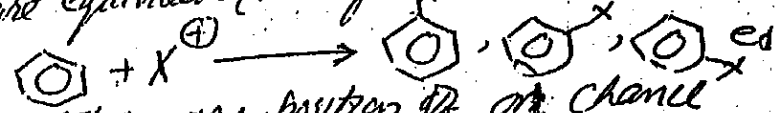
(c) COMPLETE OXIDATION OR COMBUSTION when benzene is burnt in free supply of oxygen it is completely oxidized to CO₂ and H₂O



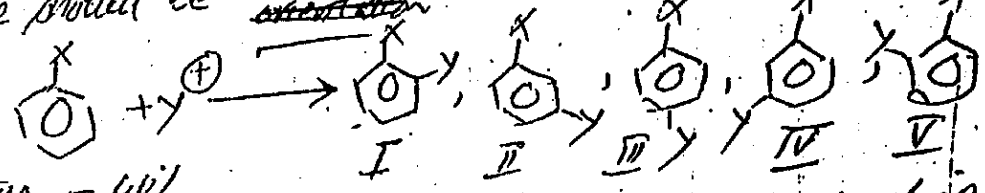
v. Imp: WRITE NOTE ON ORIENTATION IN BENZENE P-19

The substituent already present on benzene ring determines position of incoming electrophile. It is called orientation in benzene. Further some substituents increase reactivity of benzene ring and some other decrease reactivity of substituent. Thus it is also called directive influence of substituent.

There is only one monosubstituted product of benzene. As all positions are equivalent, the first substituent can take any position.

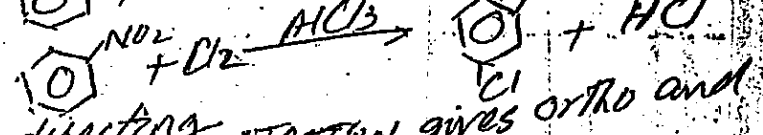
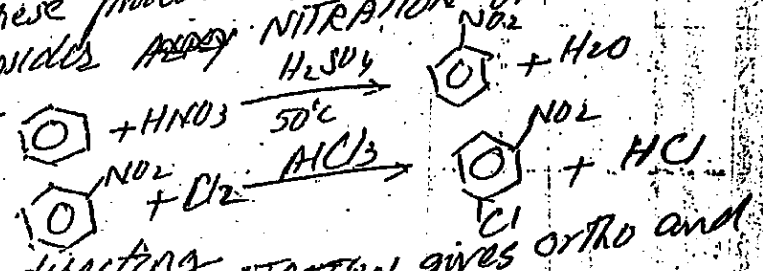


If 2nd substituent take any position of its chance bases, there should be 40% ortho, 40% meta and 20% para product.



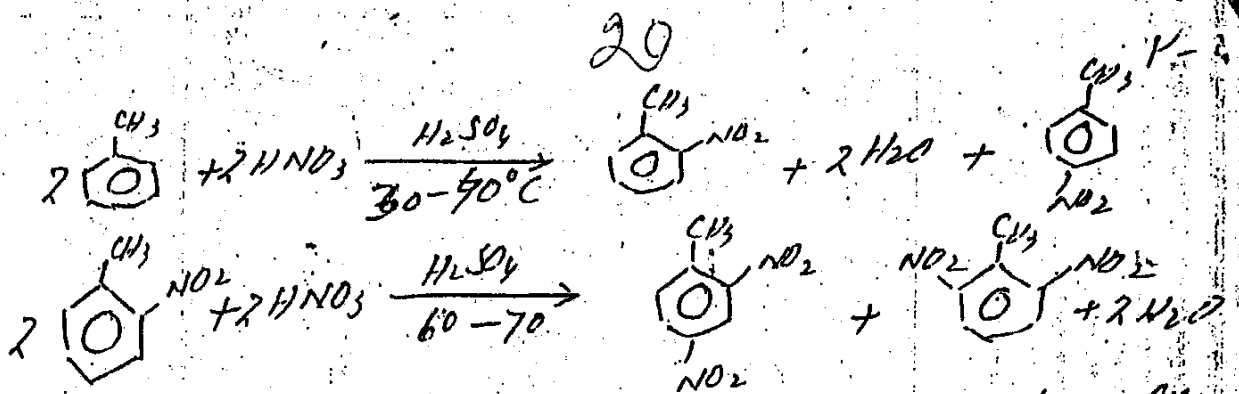
- I, V = ORTHO = 40%
- II, IV = META = 40%
- III = PARA = 20%

But in actual practice these products are not obtained in this ratio. Let us consider NITRATION OF BENZENE followed by halogenation.

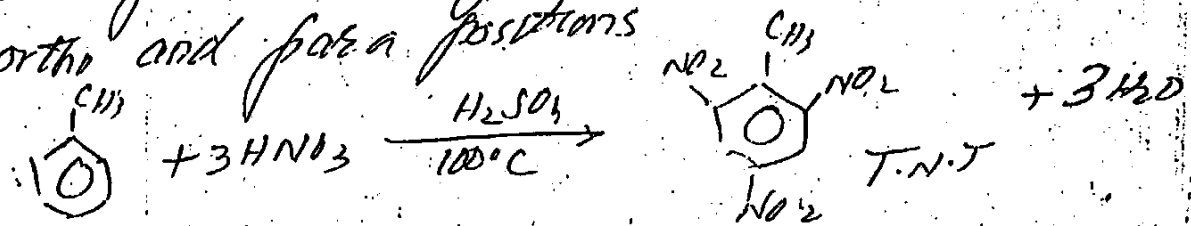


Only meta chloro nitro benzene is obtained. This nitro group is meta directing. HALOGENATION FOLLOWED BY NITRATION gives ortho and para products. Thus chlorine is ortho/para directing. GROUPS: The groups like NO_2 are ORTHO-PARA DIRECTING. The electrophile

$-\text{CH}_3, -\text{OH}, -\text{Br}, -\text{NH}_2$ direct incoming to ortho and para position. These are activating groups. They are electron releasing groups, they increase electron density at benzene ring hence increase reactivity of benzene. The increase in electron density is especially high at 'o' and para positions. Thus they are 'o' para directing and activating groups e.g. $-\text{R}, -\text{OH}, -\text{NH}_2, -\text{NHR}, -\text{OCH}_3$

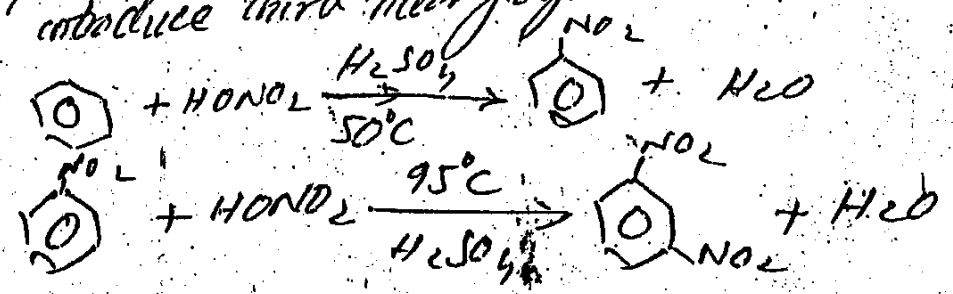


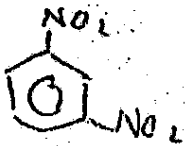
Due to increase in reactivity of benzene by $-\text{CH}_3$ it is possible to carry out nitration at all ortho and para positions



meta DIRECTING GROUPS

The groups which withdraw electron from benzene ring decrease electron density at benzene ring and decrease reactivity of benzene. The decreased in electron density is especially high at ortho and para positions. Thus electrophile cannot attack at ortho para position. The only position left for attack of electrophile is meta position. For example nitration of benzene takes place at $45-50^\circ\text{C}$ while nitration of nitrobenzene takes place at 95°C . It is not possible to introduce third nitro group because two nitro groups decrease reactivity to such an extent that it is not possible to introduce third nitro group.





21

12-21

+ α HNO₃ $\xrightarrow{H_2SO_4}$ NO REDUCTION

Some more m-directing groups are

-NO₂, -CHO, -COOH, -COCl, -CN etc

All groups having multiple bonds are meta directing.

COMPARISON OF REACTIVITIES OF ALKANE, ALKENE AND BENZENE.

"OR"

30

"GIVE REASONS:-

BENZENE IS LESS REACTIVE THAN ETHENE BUT MORE REACTIVE THAN ETHANE? WHY?

Ans. It is due to the fact that in ethene there is localized π -bond present between carbon and carbon. These π -electrons are easily donated to an electrophile. Therefore ethene undergoes addition reactions at room temp mostly. But in case of benzene the π -electrons are delocalized. Only a powerful electrophile under vigorous conditions can attack these π -electrons. Thus benzene is less reactive than ethene. Further in benzene there is resonance which makes it more stable (less reactive).

But benzene is more reactive than ethane because in ethane there is only σ -bond present between two carbons. There are no π -electrons. Sigma bond is very strong as compared to π -bond. Thus ethane is less reactive than benzene.