CONTINUATION OF BENZENE NOTES

(To be copied into the student's note book. In the process of copying the notes, one is at liberty to use the alternative structure of benzene- the one involving double bonds.)

A substituent affects the electrophilic substitution reactions of the benzene ring in two ways:

(i) The reactivity (i.e how readily the ring reacts)

(ii) The position on the ring to which the incoming electrophile is directed

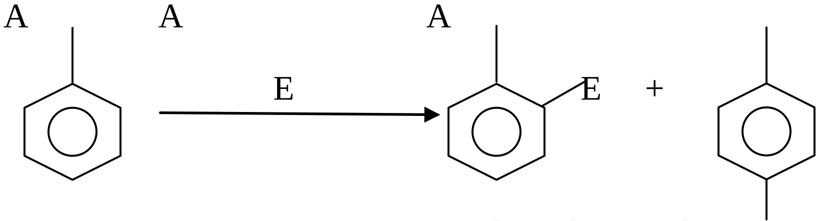
(a) Category1 of Substituents:

This includes substituents that affect the ring in the following ways:

(i) make the ring more reactive(i.e activate the ring)

(ii) direct the incoming electrophile into the ortho and para positions (i.e ortho-para directing)

i.e



ortho-substituted product

para-substituted product

These substituents activate the ring because they have a tendency to push electrons towards the ring, hence enriching it with electrons and as a result making the delocalized electrons to be more readily available for electrophilic attack.

The substituents activate all the ring positions but they do so morefor the ortho and para positions, hence the reason why they are ortho-para directing.

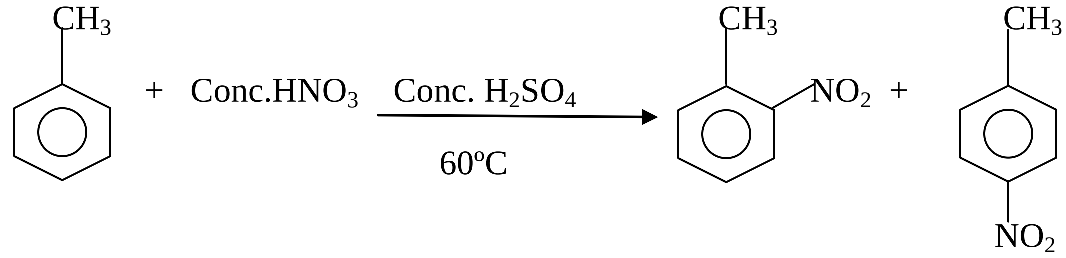
The substituents in this category are said to be <u>ortho-para directing with activation</u>. They include the following:

- -NH_2 group and derivatives (i.e –NHR , -N-R)

R^1

- -OH group and derivatives (i.e –OR)
- alkyl groups
- phenyl groups

e.g



<u>Quiz</u>:

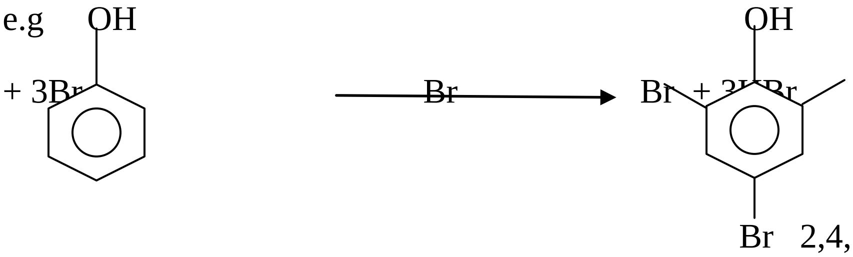
Explain why it is easier to nitrate methylbenzene than benzene

<u>Note</u>:

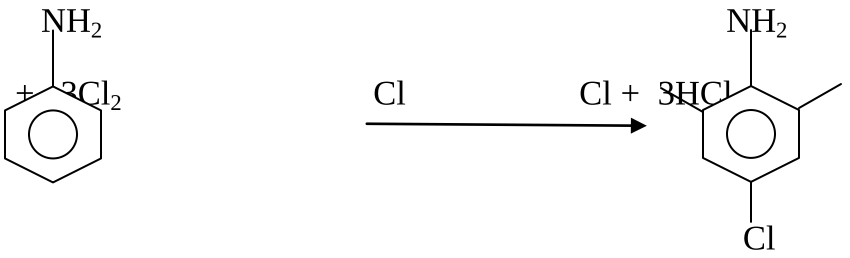
(i) Phenol and aminobenzene are much more reactive; in them the ring is <u>so much activated</u> (by the hydroxyl and amino groups respectively) that when reacting with a <u>halogen</u>,

- a halogen carrier (catalyst) is <u>not required.</u>
- all the <u>extra-activated</u> sites (ie ortho- and para- positions) on the <u>same ring</u>are substituted.

e.g



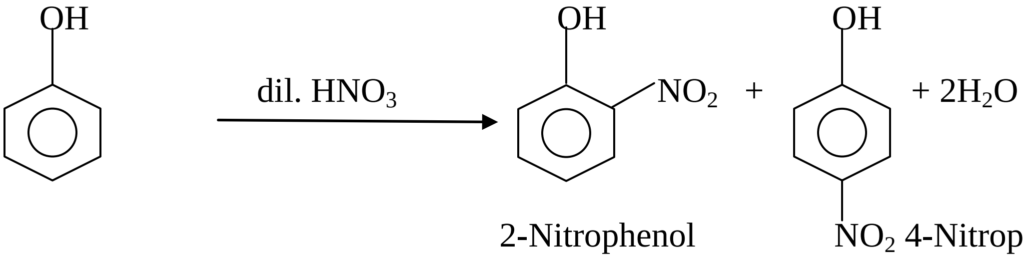
2,4,6-tribromophenol



2,4,6-trichloroaminobenzene

Further more, in the case of phenol, nitration can occur using just dilute nitric acid, in this case forming ortho- and para-substituted products.

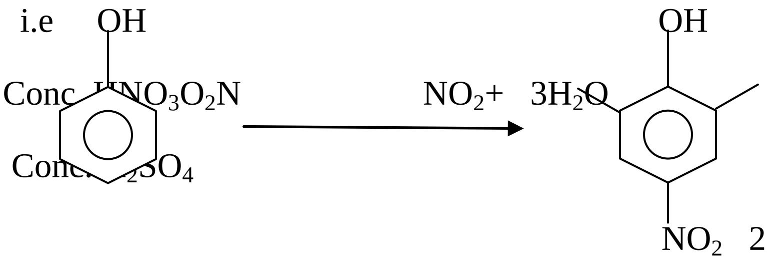
i.e



2-Nitrophenol 4-Nitrophenol

If the usual nitrating mixture (concentrated nitric acid and concentrated sulphuric acid) is used, a single product, in which all the extra-activated sites on the same ring is formed.

i.e

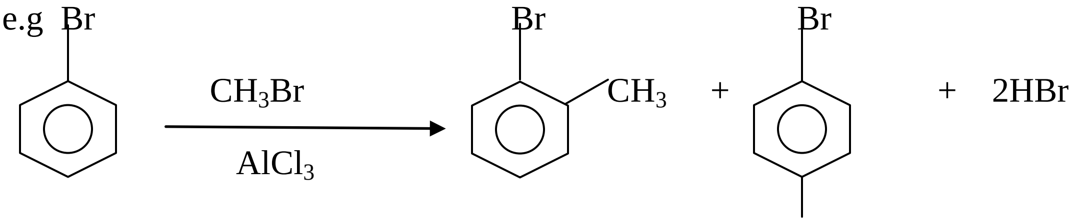


2,4,6-Trinitrophenol

(Also known as Picric acid)

(ii) The halogens are also ortho-para directing , but with deactivation.

e.g



2-bromomethylbenzene CH$_3$ 4-Bromomethylbenzene

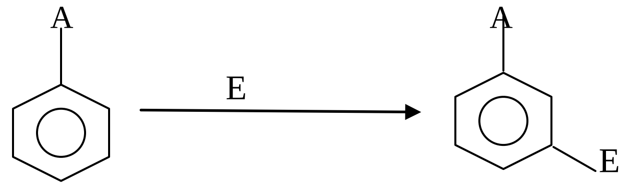
(b) Category 2 of Substituents:

This includes substituents that affect the ring in the following ways:

(i) make the ring less reactive(i.e deactivate the ring)

(ii) direct the incoming electrophile into the meta position (i.e meta- directing)

i.e



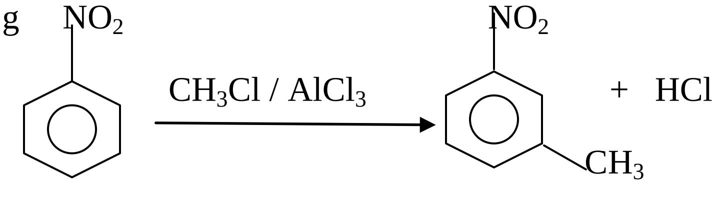
These substituents deactivate the ring because they have a tendency to withdraw (pull)electrons from the ring, and as a result making the delocalized electrons to be less readily available for electrophilic attack.

The substituents deactivate all the ring positions but they do so less for the meta position, hence the reason why they are meta-directing.

The substituents in this category are said to be meta- directing with deactivation. They include the following:

- -NO_2 group
- -COOH group
- -CHO group
- -SO_3H group
- -CN group

e.g



3-Nitromethylbenzene

Quiz:

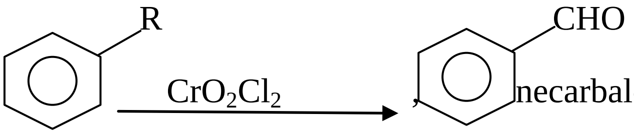
Explain why it is more difficult to nitrate nitrobenzene than benzene.

8. Effect of Benzene Ring on Akyl Group Attached to It:

The benzene ring has a <u>modifying effect</u> on the chemical property of the alkyl group attached to it. This effect is such that the alkyl group is rendered capable of undergoing <u>oxidation</u>to either an aldehyde group (-CHO) or a carboxyl group (-COOH) depending on the nature of the oxidizing agent used.

Oxidation to the aldehyde group (leading to formation of <u>benzenecarbaldehyde</u>) is effected by a <u>mild oxidizing agent</u>such as <u>chromium dichloride dioxide</u>, CrO_2Cl_2 (also commonly known as chromyl chloride) or <u>manganese(IV) oxide</u>, MnO_2 (in acidic medium).

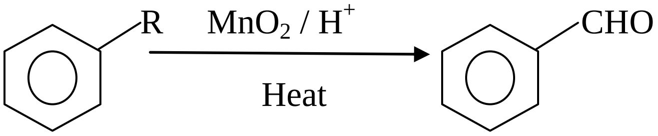
i.e



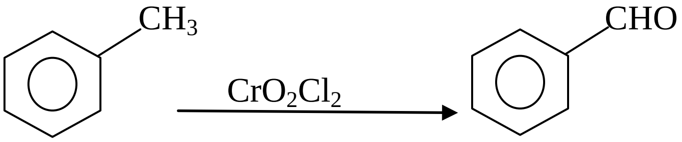
, necarbaldehyde

(also commonly called Benzaldehyde)

<u>OR</u>

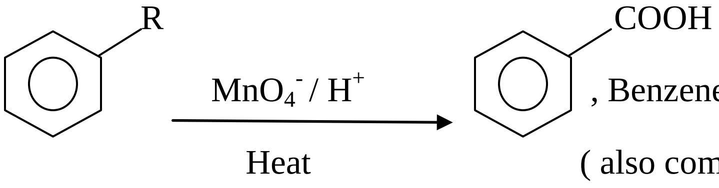


e.g



Oxidation to the carboxyl group (leading to formation of <u>benzenecarboxylic acid</u>) is effected by a <u>strong oxidizing agent</u>such as acidified potassium manganate(VII) solution or acidified potassium dichromate(VI) solution.

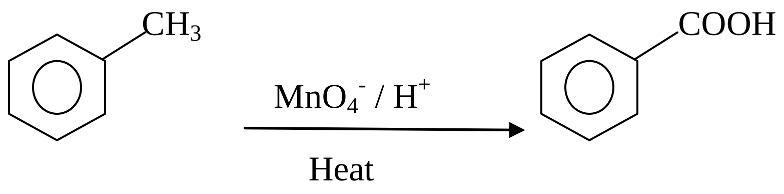
i.e



, Benzenecarboxylic acid

(also commonly called Benzoic acid)

e.g

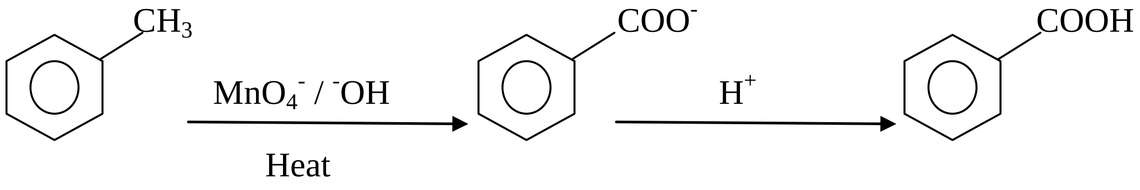


<u>Note</u>:

(i) In each of the above cases, the end product of oxidation of the alkyl group is always aldehyde group (-CHO) or carboxyl group (-COOH), regardless of the number of carbon atoms in the alkyl group.

(ii) Alkaline potassium manganite(VII) solution can also be used in the oxidation. In this case however, we first obtain a salt of the carboxylic acid (i.e benzenecarboxylate). The benzenecarboxylic acid is then obtained in a further step-by adding a dilute acid to the carboxylate.

e.g



<u>Quiz</u>:

Using equations only, show how each of the following conversions can be effected:

(a) Ethyne → Benzaldehyde

[<u>Hint</u>: Ethyne → Benzene → Methylbenzene

↓

Benzaldehyde]

(b) Phenol → Benzoic acid

(c) Cyclohexane → Benzoyl chloride