UNIT I
Benzene and its derivatives

Sub Topic: effect of substituents on reactivity and orientation of mono substituted benzene compounds towards electrophilic substitution reaction
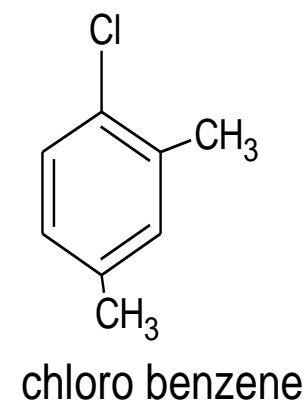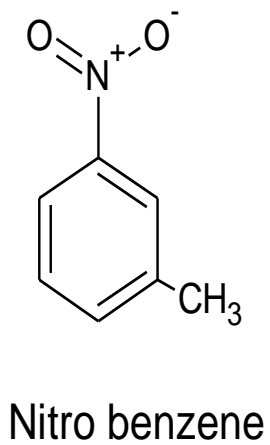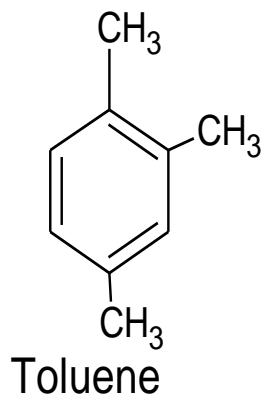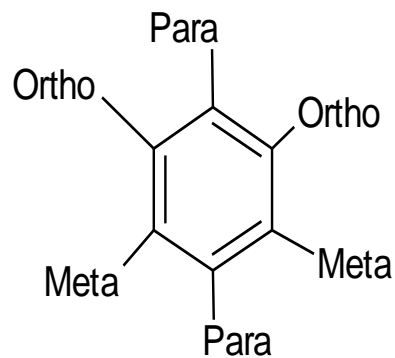
Presented by

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Para

Ortho

Ortho

Meta

Meta

Para

Toluene

Nitro benzene

chloro benzene

Reactivity : rate of reaction
orientation :arrangement of group or atoms in benzene

Maths	Physics	Chemistry
74	59	45
55	58	58
74	58	58

Classification of substituent groups

to determine the effects of a great number of groups on electrophilic substitution. As shown in Table nearly all groups fall into one of two classes: activating and ortho, para directing, or deactivating and meta-directing. The halogens are in a class by themselves, being deactivating but ortho, para-directing
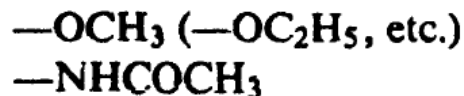
EFFECT OF GROUPS ON ELECTROPHILIC AROMATIC SUBSTITUTION
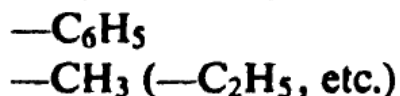
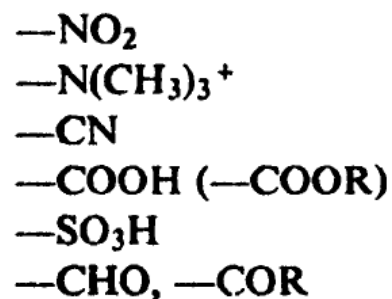**Activating: *Ortho,para* Directors**
Strongly activating
—NH_2 (—NHR, —NR_2)
—OH

Moderately activating
—OCH_3 (—OC_2H_5, etc.)
—$NHCOCH_3$

Weakly activating
—C_6H_5
—CH_3 (—C_2H_5, etc.)

Deactivating: *Meta* Directors
—NO_2
—$N(CH_3)_3{}^+$
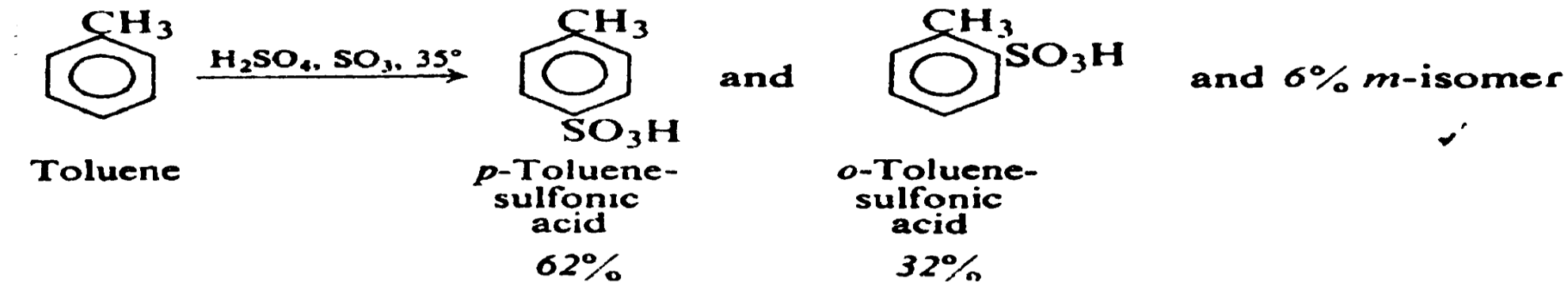—CN
—COOH (—COOR)
—SO_3H
—CHO, —COR

Deactivating: *Ortho,para* Directors
—F, —Cl, —Br, —I
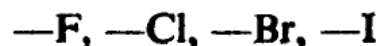
Effect of substituent groups

Like benzene, toluene undergoes electrophilic aromatic substitution : sulfonation,

for example. Although there are three possible monosulfonation products,

this reaction actually yields appreciable amounts of only two of them : the ortho and Para

Benzene and toluene are insoluble in sulfuric acid, whereas the sulfonic acids are readily

soluble; completion of reaction is indicated simply by disappearance of the hydrocarbon layer.

When shaken with fuming sulfuric acid at room temperature, benzene reacts completely within

20 to 30 minutes, whereas toluene is found to react within only a minute or two.

Studies of nitration, halogenation, and Friedel-Crafls alkylation of toluene give analogous results. In some way the methyl group makes the ring more reactive than unsubstituted benzene, and directs the attacking reagent to the ortho and para positions of the ring.

On the other hand, nitrobenzene, to take a different example, has been found to undergo substitution more slowly than benzene, and to yield chiefly the meta isomer.

Like methyl or nitro, any group attached to a benzene ring affects the reactivity of the ring and determines the orientation of substitution. When an electrophilic reagent attacks an aromatic ring, it is the group already attached to the ring that determines how readily the attack occurs and where it occurs.

A group that makes the **ring more reactive than benzene is called an activating group**. A group that makes the ring **less reactive than benzene is called a deactivating group.**

A group that causes attack to occur chiefly at positions ortho and para to it is called an ortho,para director. A group that causes attack to occur chiefly at positions meta to it is called a meta director.

Determination of orientation

To determine the effect of a group on orientation is, in principle, quite simple: the compound containing this group attached to benzene is allowed to undergo substitution and the product is analyzed for the proportions of the three isomers.

Identification of each isomer as ortho, meta, or para generally involves comparison with an authentic sample of that isomer prepared by some other method from a compound whose structure is known. In the last analysis, of course, all these identifications go back to absolute determinations of the Korner type

summarizes the orientation of nitration in a number of substituted benzenes.

Table 11.1 ORIENTATION OF NITRATION OF C_6H_5Y

Y	Ortho	Para	Ortho plus para	Meta
—OH	50–55	45–50	100	trace
—NHCOCH$_3$	19	79	98	2
—CH$_3$	58	38	96	4
—F	12	88	100	trace
—Cl	30	70	·100	trace
—Br	37	62	99	1
—I	38	60	98	2
—NO$_2$	6.4	0.3	6.7	93.3
—N(CH$_3$)$_3$$^+$	0	11	11	89
—CN	—	—	19	81
—COOH	19	1	20	80
—SO$_3$H	21	7	28	72
—CHO	—	—	28	72

A given group causes the same general kind of orientation predominantly ortho. para or predominantly meta whatever the electrophilic reagent involved. The actual distribution of isomers may vary, however, from reaction to reaction.

for example, compare the distribution of isomers obtained from toluene by sulfonation or bromination with that obtained by nitration

ORIENTATION OF SUBSTTTUTION IN TOLUENE

	Ortho	Meta	Para
Nitration	58	4	38
Sulfonation	32	6	62
Bromination	33	---	67

Determination of relative reactivity

A group is classified as activating if the ring it is attached to is more reactive than benzene, and is classified as deactivating if the ring it is attached to is less reactive than benzene. The reactivities of benzene and a substituted benzene are compared in one of the following ways.
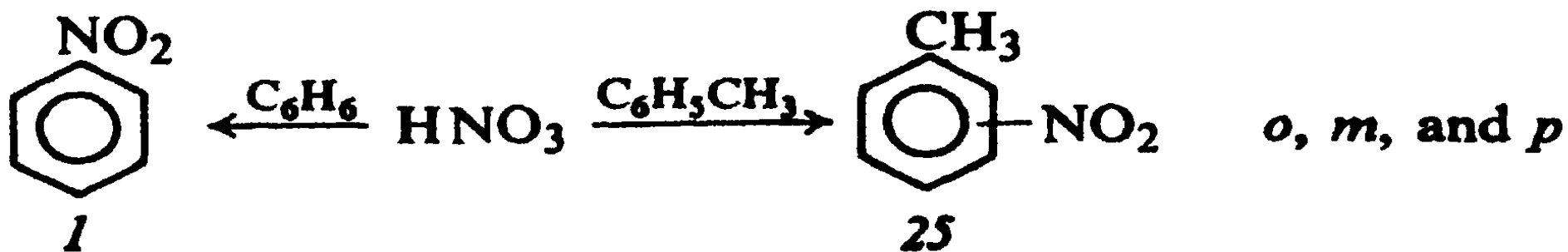
The time required for reactions to occur under identical conditions can be measured. Thus, as we just saw, toluene is found to react with fuming sulfuric acid in about one-tenth to one-twentieth the time required by benzene. Toluene is more reactive than benzene, and Methyl therefore an activating group.

The severity of conditions required for comparable reaction to occur within the same period of time can be observed. For example, benzene is nitrated in less than an hour at 60 by a mixture of concentrated sulfuric acid and concentrated nitric acid; comparable nitration of nitrobenzene requires treatment at 90 with fuming nitric acid and concentrated sulfuric acid. Nitrobenzene is evidently less reactive than benzene, and the nitro group, NO2 , is a deactivating group.
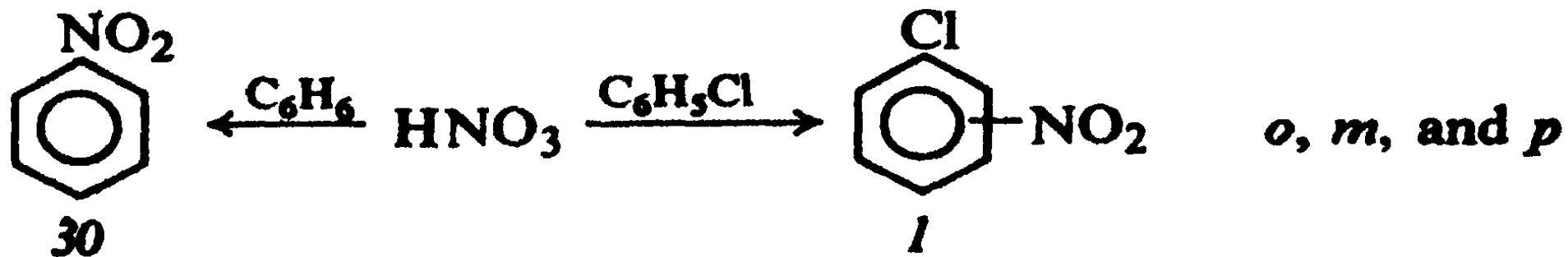
quantitative comparison under identical reaction conditions, competitive reactions can be carried out, in which the compounds to be compared are allowed to compete for a limited amount of a reagent . For example, if equimolar amounts of benzene and toluene are treated with a small amount of nitric acid

about 25 times as much nitrotoluene as nitrobenzene is obtained, showing that toluene is 25 times as reactive as benzene. On the other hand, a mixture of benzene and chlorobenzene yields a product in which nitrobenzene exceeds the nitrochlorobenzenes by 30: 1, showing that chlorobenzene is only one-thirtieth as reactive as benzene. The chloro group is therefore classified as deactivating, the methyl group as activating. The activation or deactivation caused by some groups is extremely powerful: aniline, $C_6H_5NH_2$, is roughly one million times as reactive as benzene, and nitrobenzene, $C_6H_5NO_2$, is roughly one-millionth as reactive as benzene.

Theory of orientation

Before we try to account for orientation in electrophilic substitution, let us look more closely at the facts.

An activating group activates all positions of the benzene ring; even the positions

Meta to it are more reactive than any single position in benzene itself. It directs ortho and para simply because it activates the ortho and para positions much more than it does the meta

A deactivating group deactivates all positions in the ring, even the positions meta to it. It directs meta simply because it deactivates the ortho and para positions even more than it does the meta.

Thus both ortho,para orientation and meta orientation arise in the same way:

the effect of any group whether activating or deactivating is strongest at the ortho and para positions.

In toluene in case of Para attack here structures I and III were formed and in that compound II was stable due to the carbon contain the positive charge contain the Electron releasing group –CH3 makes the ring more stable
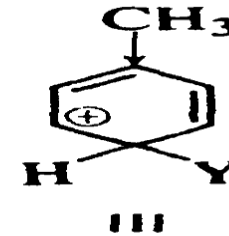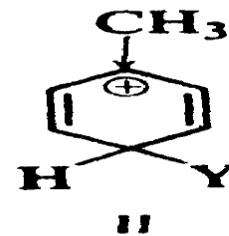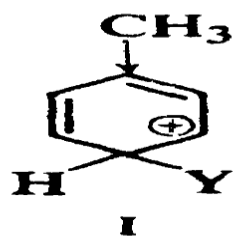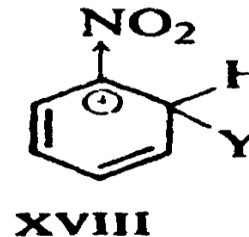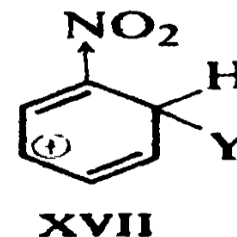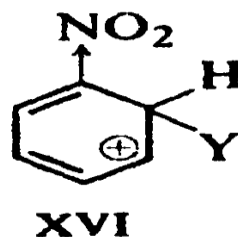

Especially stable: charge on carbon carrying substituent

In toluene in case of meta attack here structures IV and VI were formed and in that compounds was unstable due to the carbon contain the positive charge does not contain the Electron releasing group –CH3 makes the ring less stable
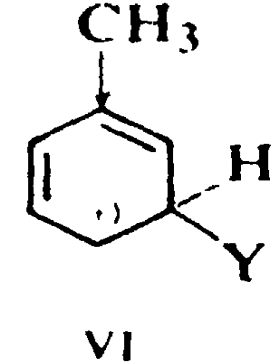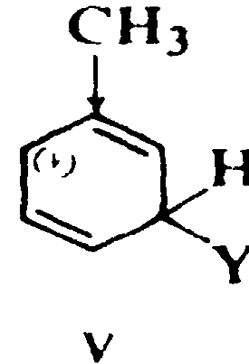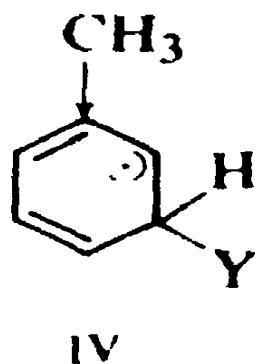
In toluene in case of ortho attack here structures VII and IX were formed and in that compound IX was stable due to the carbon contain the positive charge contain the Electron releasing group –CH3 makes the ring more stable
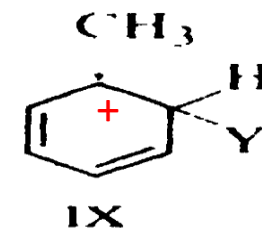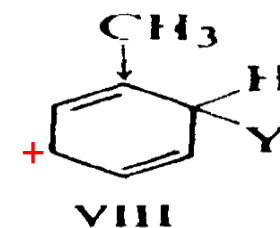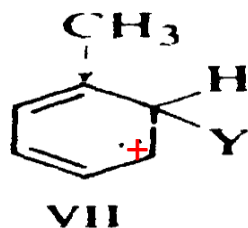
Especially stable: charge on carbon carrying substituent

Therefore conclude that the methyl group is para and ortho director group

In Nitrobenzene in case of Para attack here structures X-XII were formed and in that compound XI was un stable due to the carbon contain the positive charge contain the Electron with drawing group –NO2 makes the ring unstable
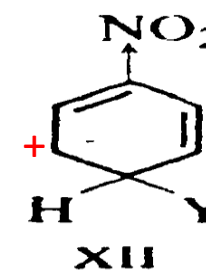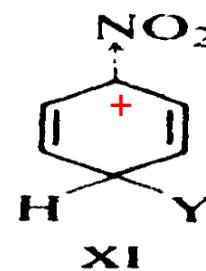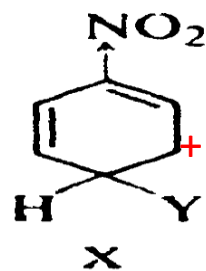

Especially unstable: charge on carbon carrying substituent

In Nitrobenzene in case of ortho attack here structures XVI-XVIII were formed and in that compound XVIII was un stable due to the carbon contain the positive charge contain the Electron with drawing group –NO2 makes the ring unstable

Especially unstable: charge on carbon carrying substituent

In Nitrobenzene in case of meta attack here structures XIII-XV were formed and in that compounds were stable due to the carbon contain the positive charge does not contain the Electron with drawing group –NO2 makes the ring stable
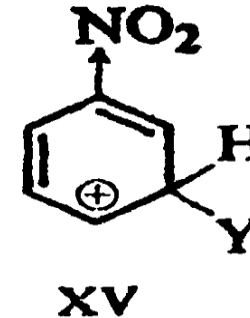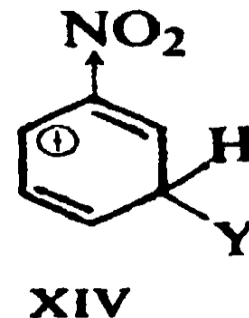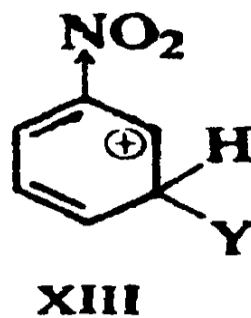
NH2
Amino Group
Substituent: E R G

NO2
Nitro group
Sub: EWR

N7
1s2 2S2 2P3

Electron release via resonance

We have seen that a substituent group affects both reactivity and orientation in electrophilic aromatic substitution by its tendency to release or withdraw electrons. So far, we have considered electron release and electron withdrawal only as inductive effects, that is, as effects due to the electronegativity of the group concerned. But certain groups (~NH2 and OH, and their derivatives) act as powerful activators toward electrophilic aromatic substitution, even though they contain electronegative atoms and can be shown in other ways to have electron-withdrawing inductive effects.

Although electronegative, the nitrogen of the NH2 group is basic and tends to share its last pair of electrons and acquire a positive charge. Just as ammonia accepts a hydrogen ion to form the ammonium ($NH_4 +$) ion, so organic compounds related to ammonia accept hydrogen ions to form substituted ammonium ions.

The OH group shows similar but weaker basicity; we are already familiar with oxonium ions, ROH2 +.


I   II   III   IV
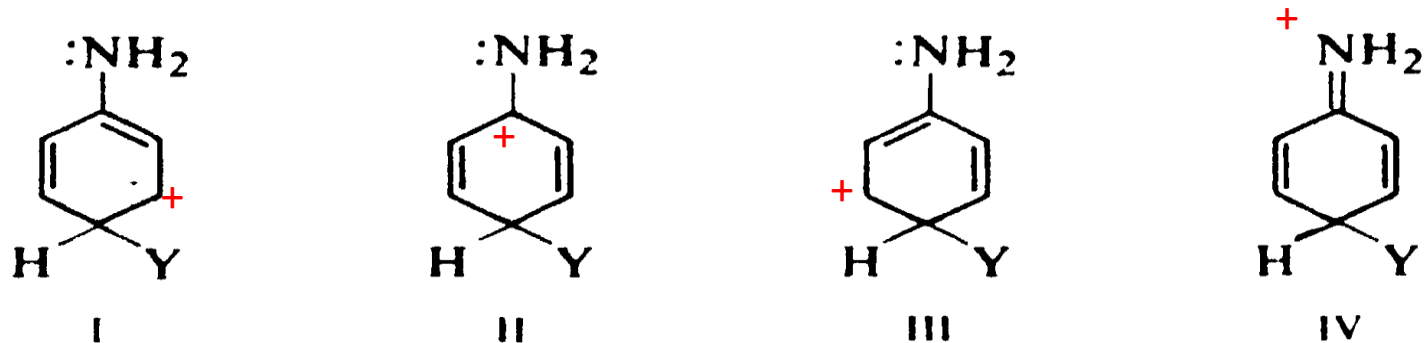
Especially stable: every atom has octet

Thus substitution in aniline occurs faster than substitution in benzene, and occurs predominantly at the positions ortho and para to NH2

V   VI   VII

VIII   IX   X   XI
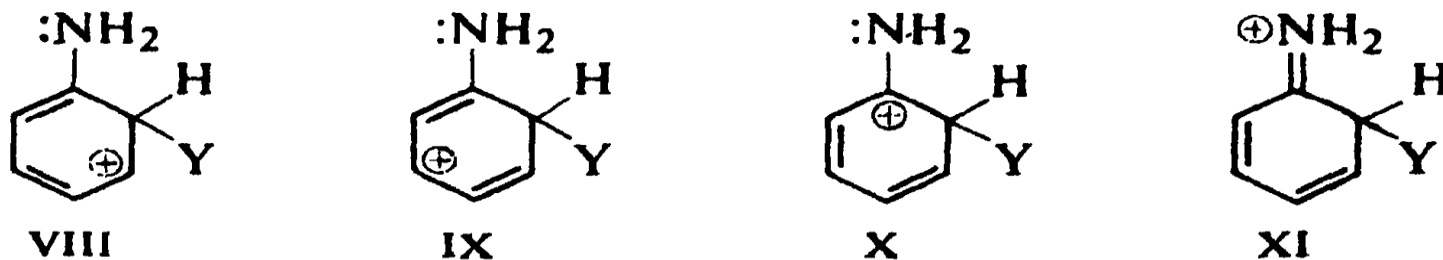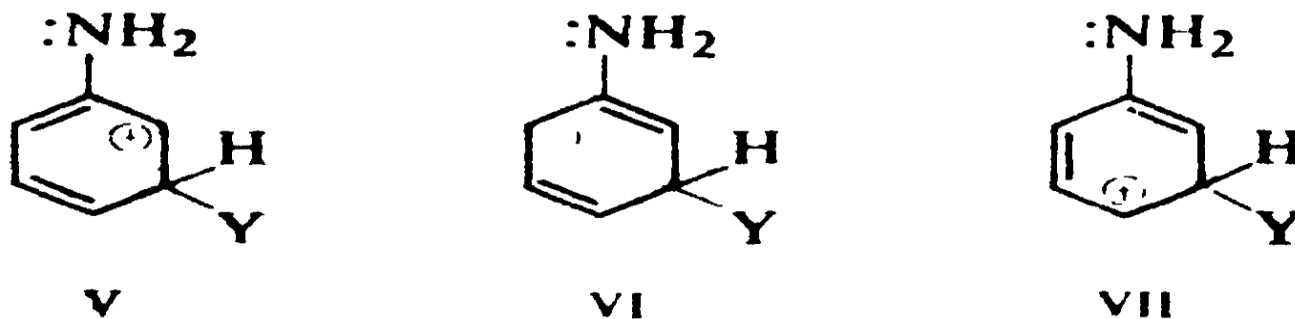
Especially stable: every atom has octet

same way activation and ortho and para orientation by the OH group is accounted for by contribution of structures like XII and XIII, in which every atom has a complete octet of electrons:

XII
Para attack

XIII
Ortho attack
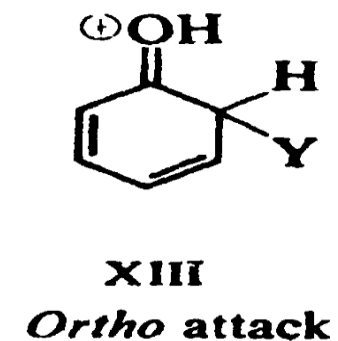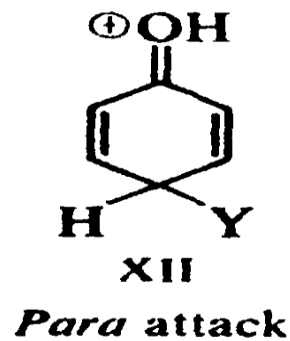
The similar effects of the derivatives of NH2 and OH are accounted for by similar structures (shown only para attack):


−NHCH₃

−N(CH₃)₂

−NHCOCH₃

−OCH₃
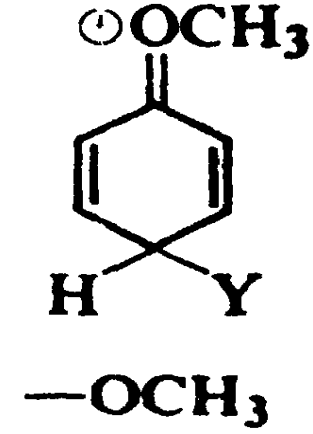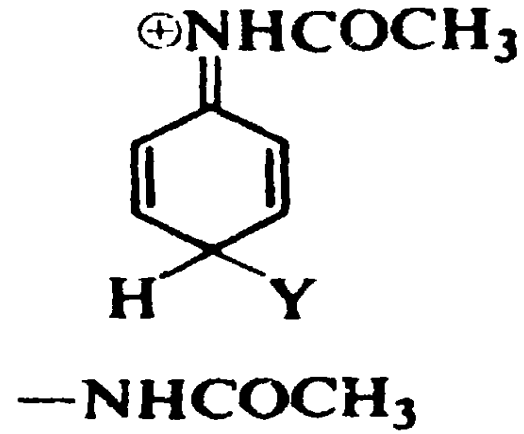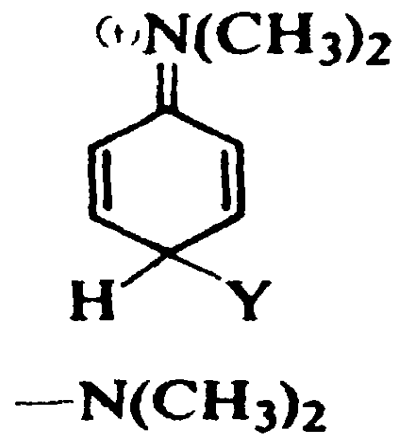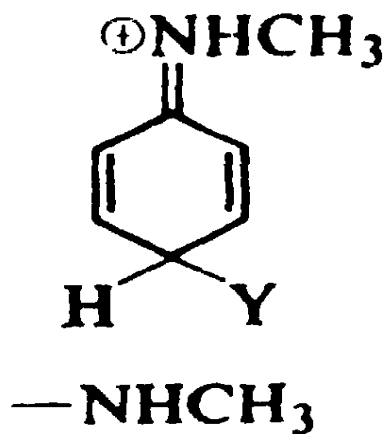
Effect of halogen on electrophilic aromatic substitution

Halogens are unusual in their effect on electrophilic aromatic substitution: they are deactivating yet ortho and para-directing. Deactivation is characteristic of electron withdrawal, whereas ortho and para orientation is characteristic of electron release. Can halogen both withdraw and release electrons? The answer is yes. Halogen withdraws electrons through its inductive effect, and releases electrons through its resonance effect. So, presumably, can the NH2 and OH groups,
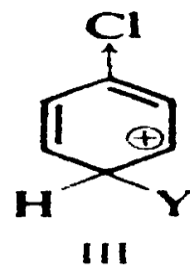
For halogen, the two effects are more evenly balanced, and we observe the operation of both. Let us first consider reactivity. Electrophilic attack on benzene yields carbonium ion I, attack on chlorobenzene yields carbonium ion II. The electron withdrawing inductive effect of chlorine intensifies the positive charge in carbonium ion II, makes the ion less stable, and causes a slower reaction.
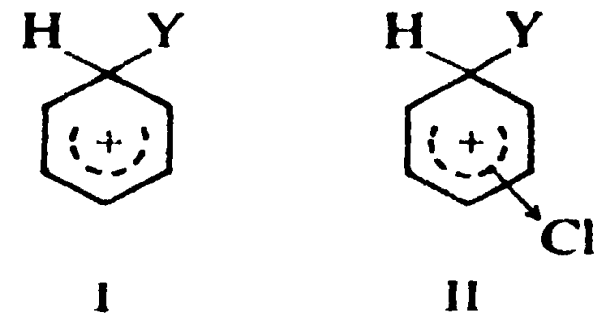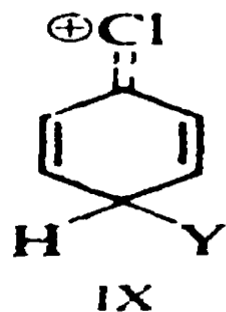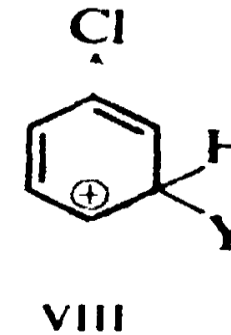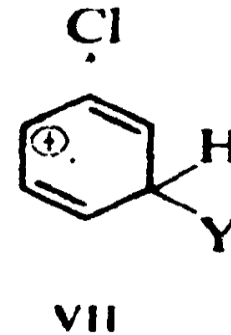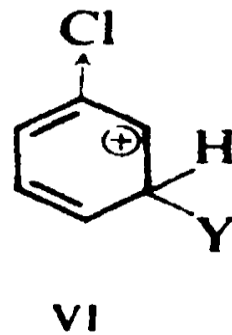

— Cl withdraws electrons: destabilizes carbonium ion, deactivates ring
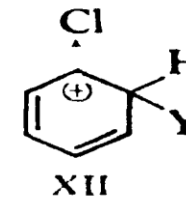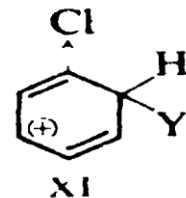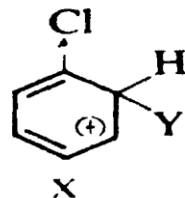
Cl -17= [Ne] 3s² 3p⁵ [3px 2 3Py 2 3Pz 1]
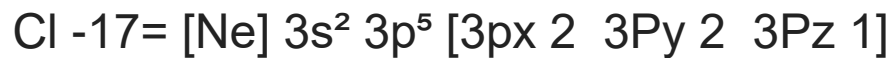
existence of halonium ions has shown us that halogen can share more than a pair of electrons and can accommodate a positive charge. Therefore **the halogen causes a stable carbocations at the para and ortho attack**
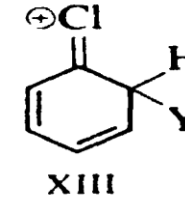
III

IV
Especially unstable: charge on carbon bearing substituent

V

VI

VII

VIII

IX
Comparatively stable: every atom has octet

X

XI

XII
Especially unstable: charge on carbon bearing substituent

XIII
Comparatively stable: every atom has octet