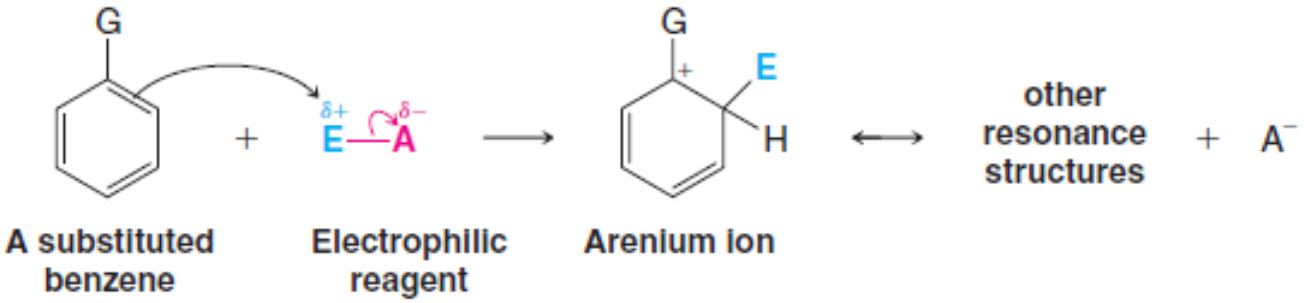
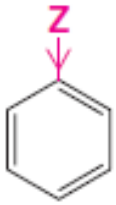
Organic Chemistry II
1st Semester,

Aromatic Compounds and Their Reactions

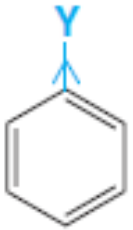
Based on Organic Chemistry, *T.W. GRAHAM SOLOMONS and CRAIG B. FRYHLE* ***10e.***

How Do Substituents Affect Reactivity?





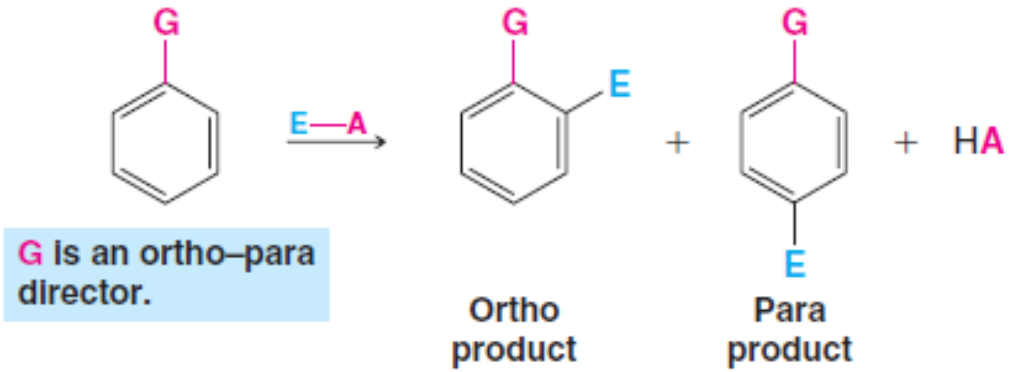
If Z donates electrons the ring is more electron rich and it reacts faster with an electrophile.



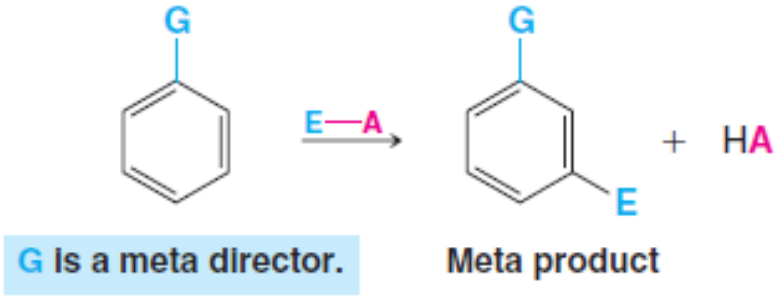
If Y withdraws electrons the ring is electron poor and it reacts more slowly with an electrophile.

Ortho–Para-Directing Groups and Meta-Directing Groups

Ortho–para directors predominantly direct the incoming group to a position ortho or para to itself.

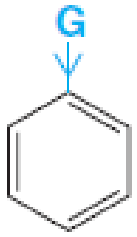


Meta directors predominantly direct the incoming group to a position meta to itself.

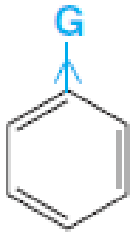


Electron-Donating and Electron-Withdrawing Substituents

- All electron-donating groups are activating groups and all are ortho–para directors.
- With the exception of halogen substituents, all electron-withdrawing groups are deactivating groups and all are meta directors.
- Halogen substituents are weakly deactivating groups and are ortho–para directors.



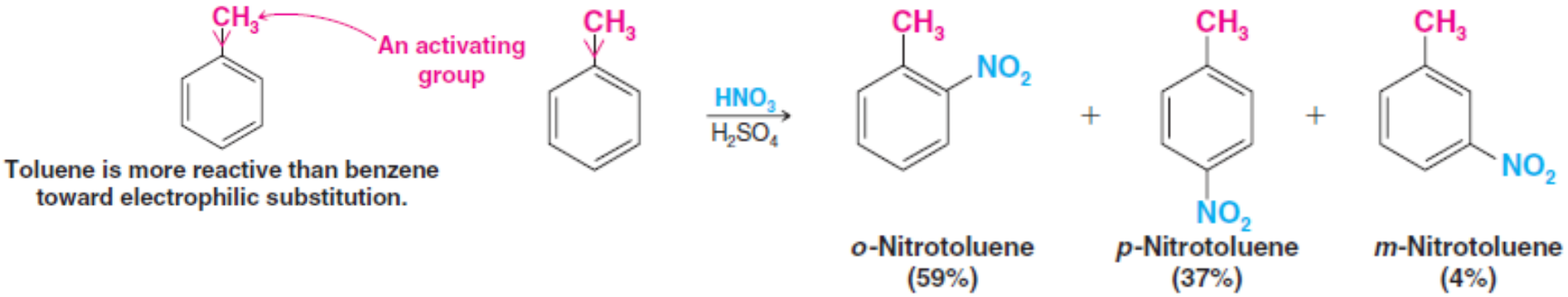
If G donates electrons the ring is activated; it reacts faster, and at an ortho or para position.



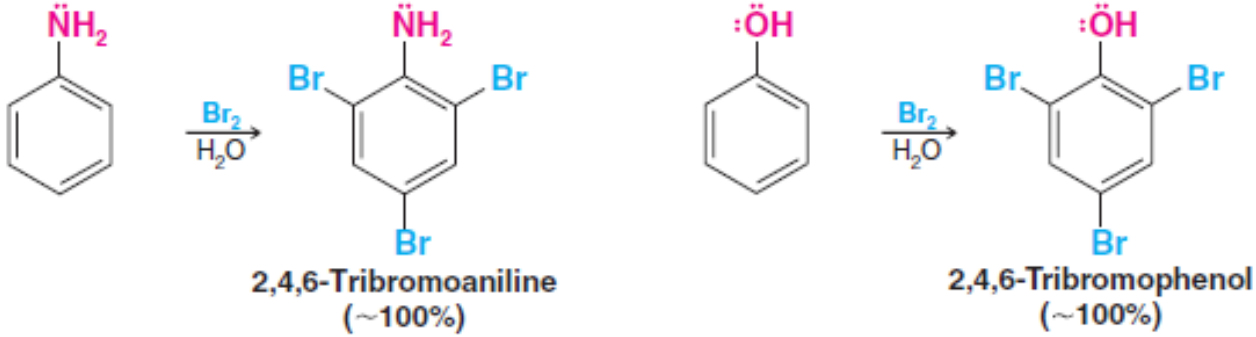
If G withdraws electrons the ring is deactivated; it reacts more slowly, and at a meta position (except when G is a halogen).

Groups: Ortho–Para Directors

Alkyl substituents are electron-donating groups and they are **activating** groups.
They are also **ortho–para directors**.



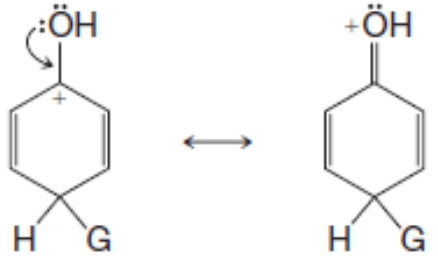
Groups that have an unshared electron pair on the atom attached to the aromatic ring, such as amino, hydroxyl, alkoxyl, and amides or esters with the oxygen or nitrogen directly bonded to the ring, are powerful activating groups and are strong ortho–para directors.



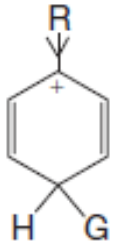
In general, substituent groups with unshared electron pairs on the atom adjacent to the benzene ring (e.g., hydroxyl, amino) are stronger activating groups than groups without unshared electron pairs (i.e., alkyl groups).

Contribution of electron density to the benzene ring through resonance is generally stronger than through an inductive effect.

Examples of arenium ion stabilization by resonance and inductive effects



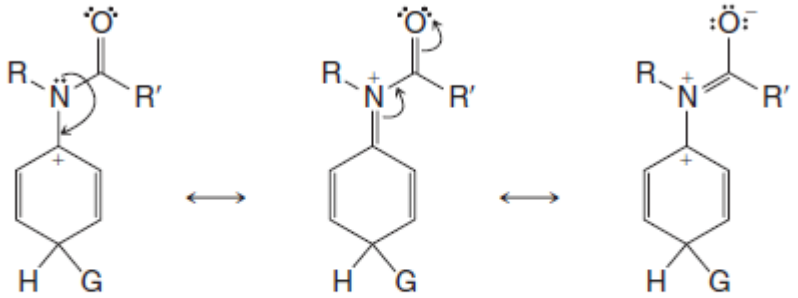
Electron donation through resonance



Electron donation through the inductive effect

As a corollary, even though amides and esters have an unshared electron pair on the atom adjacent to the ring, their activating effect is diminished because the carbonyl group provides a resonance structure where electron density is directed away from the benzene ring.

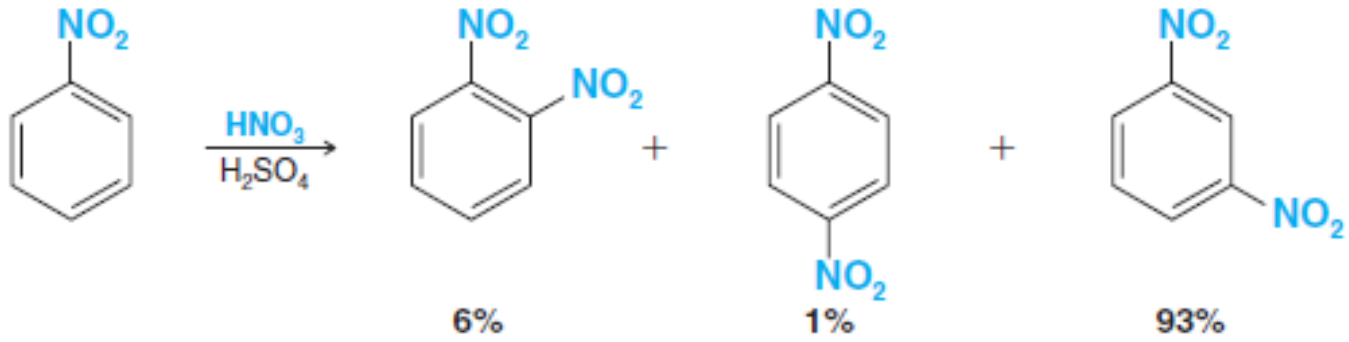
This makes amides and esters less activating than groups where the only resonance possibilities involve donation of electron density toward the benzene ring.



Electron donation to the ring by resonance is reduced when there is an alternative resonance pathway away from the ring.

Deactivating Groups: Meta Directors

The nitro group is a very strong **deactivating group** and, because of the combined electronegativities of the nitrogen and oxygen atoms, it is a powerful electronwithdrawing group.



The carboxyl group (CO_2H), the sulfonic acid group (SO_3H), and the trifluoromethyl group (CF_3) are also deactivating groups; they are also meta directors.

Halo Substituents: Deactivating Ortho–Para Directors

The chloro and bromo groups are ortho–para directors. However, even though they contain unshared electron pairs, they are deactivating toward electrophilic aromatic substitution because of the electronegative effect of the halogens.

Electrophilic Substitutions of Chlorobenzene

Reaction	Ortho Product (%)	Para Product (%)	Total Ortho and Para (%)	Meta Product (%)
Chlorination	39	55	94	6
Bromination	11	87	98	2
Nitration	30	70	100	
Sulfonation		100	100	

Similar results are obtained from electrophilic substitutions of bromobenzene.

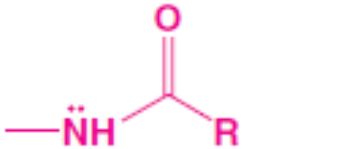
Classification of Substituents

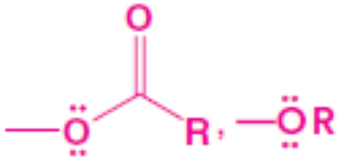
Effect of Substituents on Electrophilic Aromatic Substitution

Ortho–Para Directors

Strongly Activating

Moderately Activating



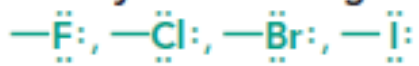


Weakly Activating

—R (alkyl)

—C_6H_5 (phenyl)

Weakly Deactivating

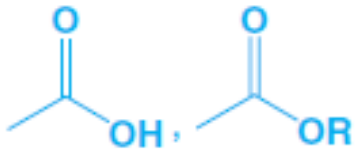


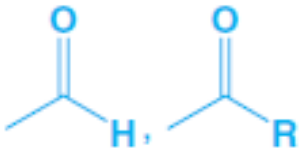
Meta Directors

Moderately Deactivating

—C≡N

—SO_3H





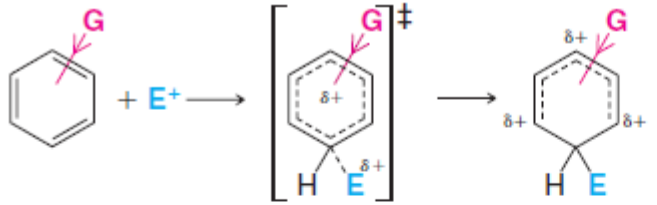
Strongly Deactivating

—NO_2

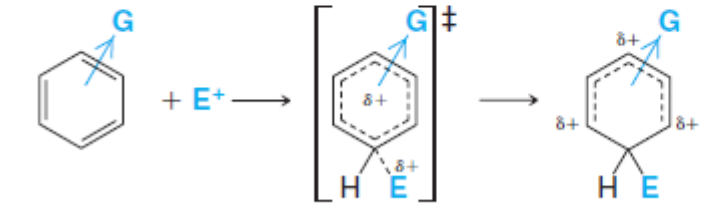
—NR_3^+

—CF_3, —CCl_3

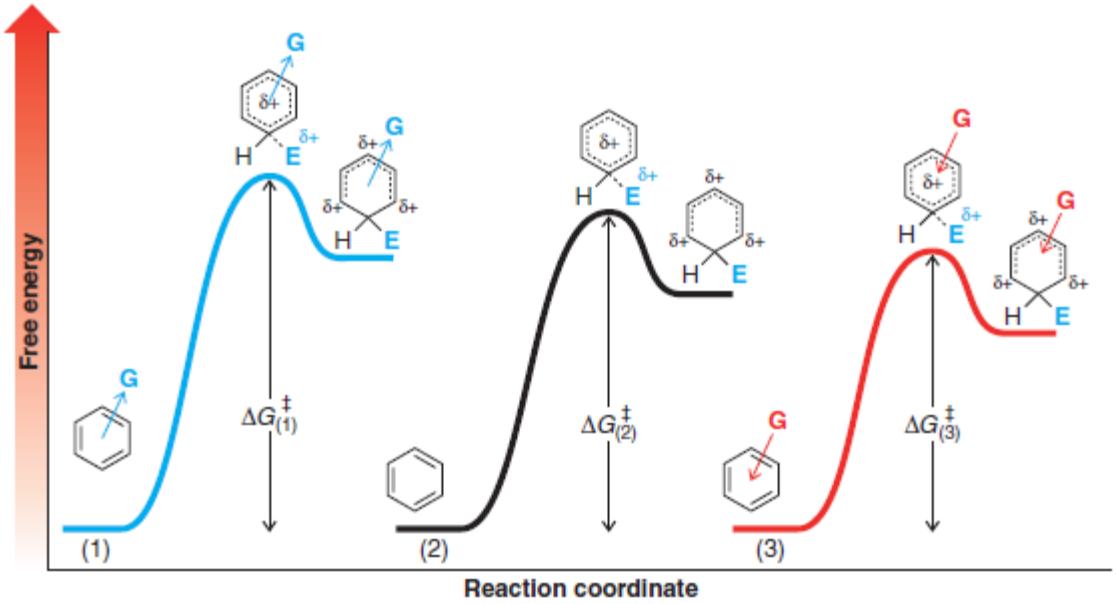
Reactivity: The Effect of Electron-Releasing and Electron-Withdrawing Groups:



When G is electron donating, the reaction is faster.



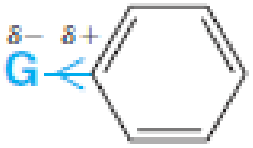
When G is electron withdrawing, the reaction is slower.



Inductive and Resonance Effects:

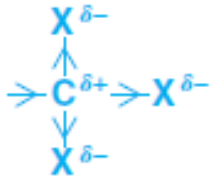
Theory of Orientation

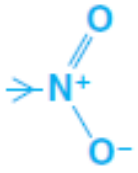
Inductive Effects The **inductive effect** of a substituent G arises from the electrostatic interaction of the polarized bond to G with the developing positive charge in the ring as it is attacked by an electrophile. If, for example, G is a more electronegative atom (or group) than carbon, then the ring will be at the positive end of the dipole:

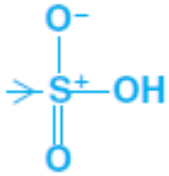


(e.g., G = F, Cl, or Br)

(R = alkyl or H)





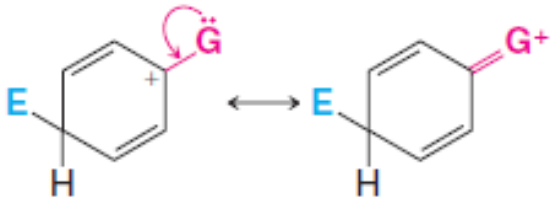


(G = H, R, OH, or OR)

Electron-withdrawing groups with a full or partial charge on the atom attached to the ring

Resonance Effects

The **resonance effect** of a substituent G refers to the possibility that the presence of G may increase or decrease the resonance stabilization of the intermediate arenium ion. The G substituent may, for example, cause one of the three contributors to the resonance hybrid for the arenium ion to be better or worse than the case when G is hydrogen. Moreover, when G is an atom bearing one or more nonbonding electron pairs, it may lend extra stability to the arenium ion by providing a *fourth* resonance contributor in which the positive charge resides on G:

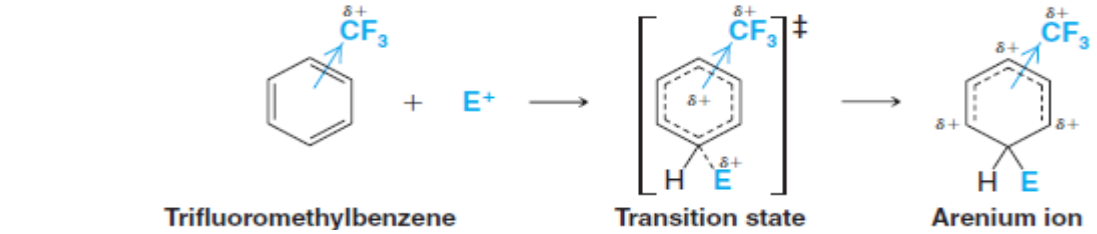


This electron-donating resonance effect applies with decreasing strength in the following order:

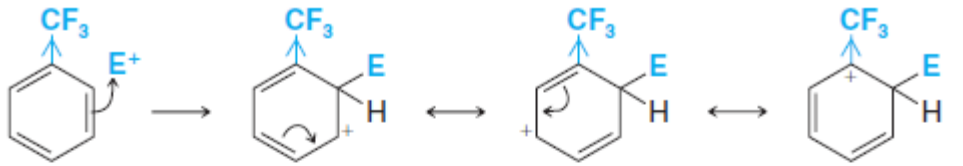
This is also the order of the activating ability of these groups.

Meta-Directing Groups

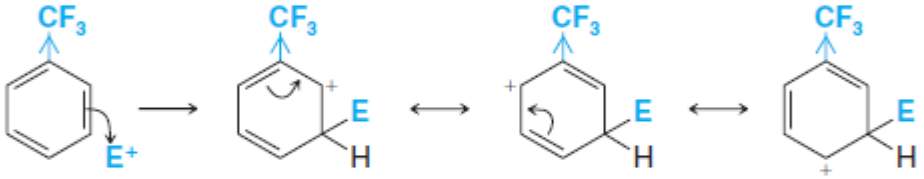
All meta-directing groups have either a partial positive charge or a full positive charge on the atom directly attached to the ring.



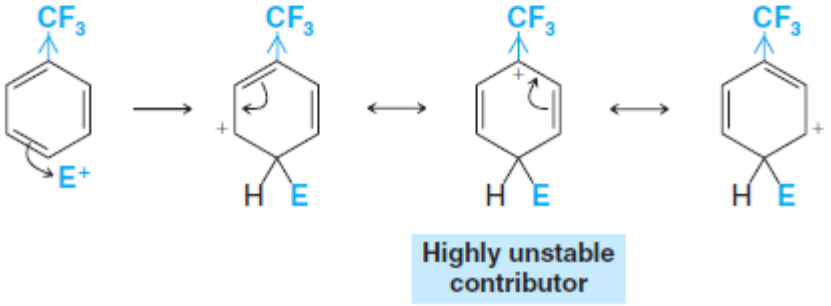
Ortho Attack



Meta Attack



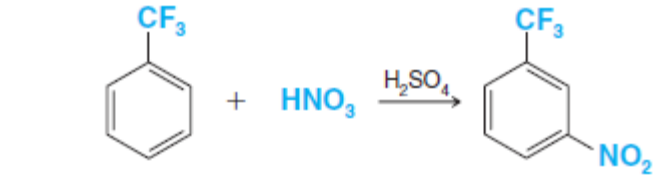
Para Attack



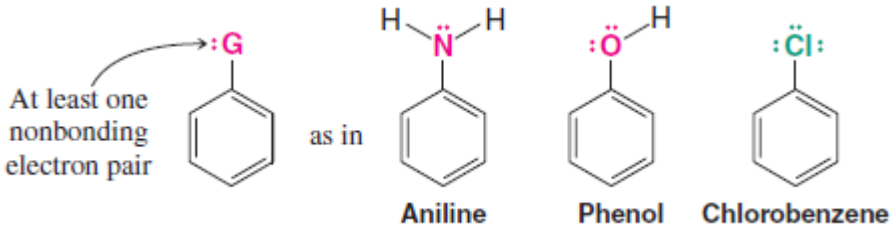
The arenium ion arising from ortho and para attack each has *one contributing structure that is highly unstable relative to all the others because the positive charge is located on the ring carbon that bears the electron-withdrawing group*.

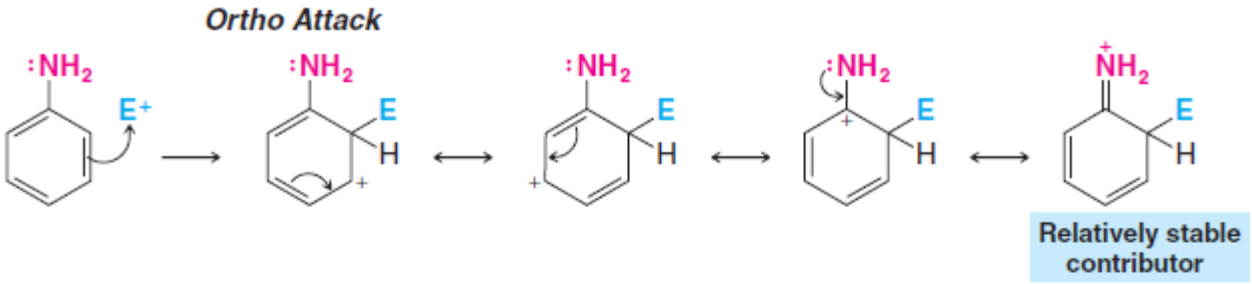
The arenium ion arising from meta attack has *no* such highly unstable resonance stucture.

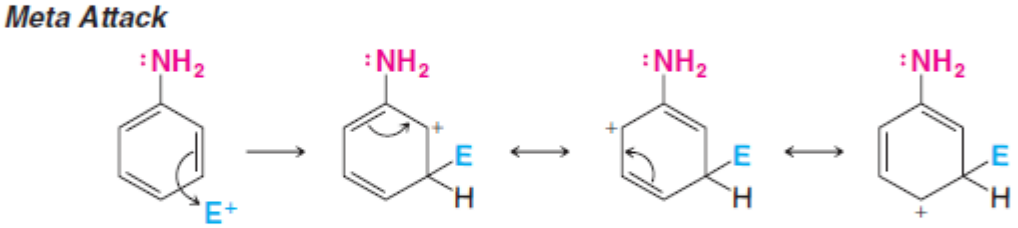
By the usual reasoning we would also expect the transition state leading to the meta substituted arenium ion to be the least unstable and, therefore, that meta attack would be favored.

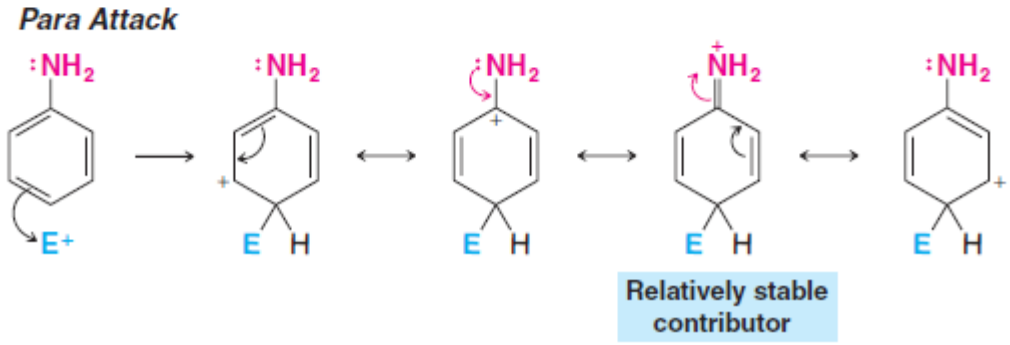


Ortho–Para-Directing Groups



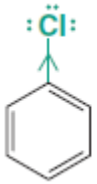






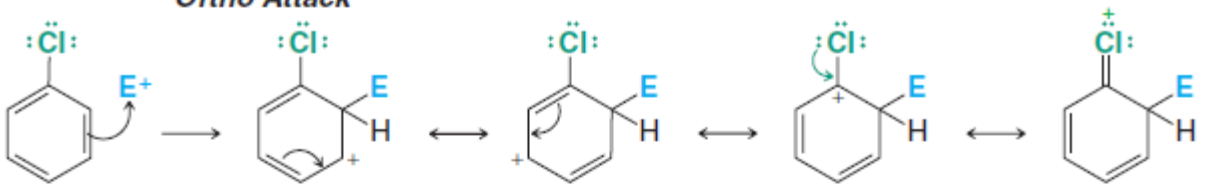
The directive and reactivity effects of halo substituents may, at first, seem to be contradictory.

The halo groups are the only ortho–para directors that are deactivating groups.



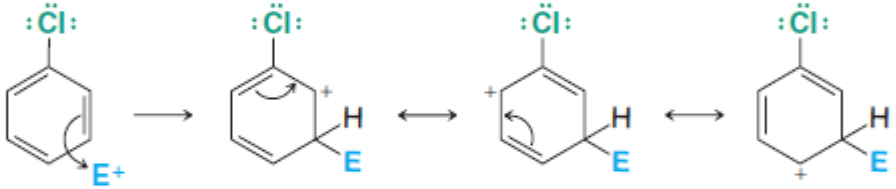
The inductive effect of the chlorine atom deactivates the ring.

Ortho Attack

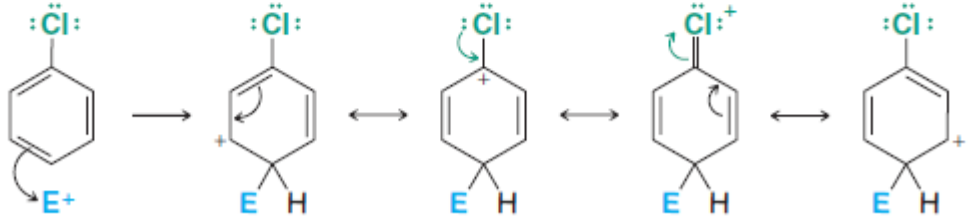


Relatively stable contributor

Meta Attack



Para Attack



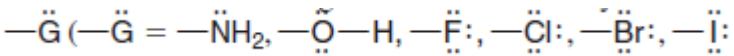
Relatively stable contributor

Through their electron-withdrawing inductive effect, halo groups make the ring more electron deficient than that of benzene. This causes the free energy of activation for any electrophilic aromatic substitution reaction to be greater than that for benzene, and, therefore, halo groups are deactivating.

Through their electron-donating resonance effect, however, halo substituents cause the free energies of activation leading to ortho and para substitution to be lower than the free energy of activation leading to meta substitution. This makes halo substituents ortho–para directors.

You may have noticed an apparent contradiction between the rationale offered for the unusual effects of the halogens and that offered earlier for amino or hydroxyl groups. That is, oxygen is ***more*** **electronegative than chlorine or bromine (and especially iodine). Yet the hydroxyl group is an activating group, whereas halogens are deactivating groups.**

An explanation for this can be obtained if we consider the relative stabilizing contributions made to the transition state leading to the arenium ion by resonance structures involving a group



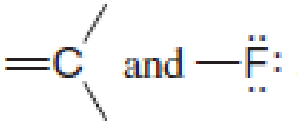
that is directly attached to the benzene ring in which G donates an electron pair. If -G is -OH or -NH_2, these resonance structures arise because of the overlap of a 2*p* orbital of carbon with that of oxygen or nitrogen. Such overlap is favourable because the atoms are almost the same size.

With chlorine, however, donation of an electron pair to the benzene ring requires overlap of a carbon 2*p* orbital with a chlorine 3*p* orbital. Such overlap is less effective; the chlorine atom is much larger and its 3*p* orbital is much further from its nucleus.

With bromine and iodine, overlap is even less effective.

Justification for this explanation can be found in the observation that fluorobenzene is the most reactive halobenzene in spite of the high electronegativity of fluorine and the fact that –F is the most powerful ortho–para director of the halogens.

With fluorine, donation of an electron pair arises from overlap of a 2*p* orbita of fluorine with a 2*p* orbital of carbon (as with - NH_2 and -OH).

This overlap is effective because the orbitals of  are of the same relative size.

Ortho–Para Direction and Reactivity of Alkylbenzenes