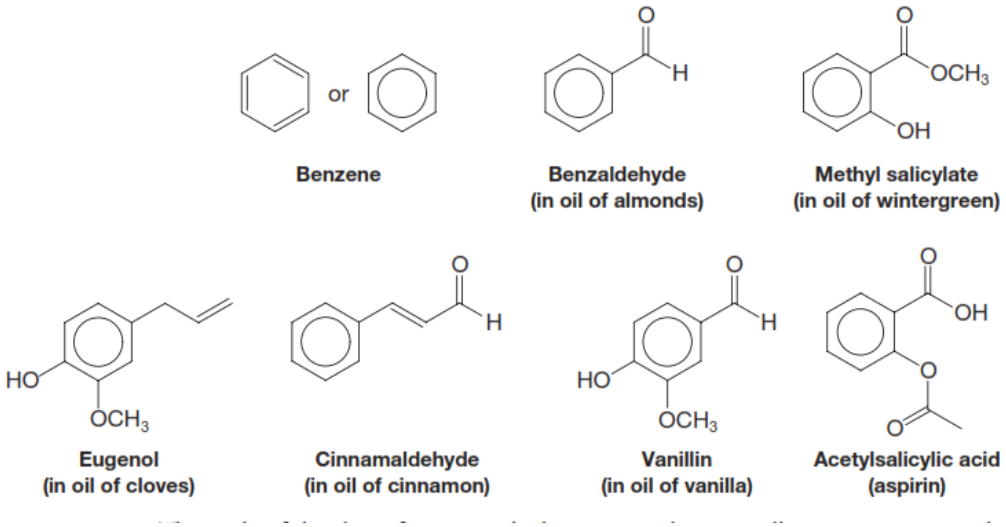
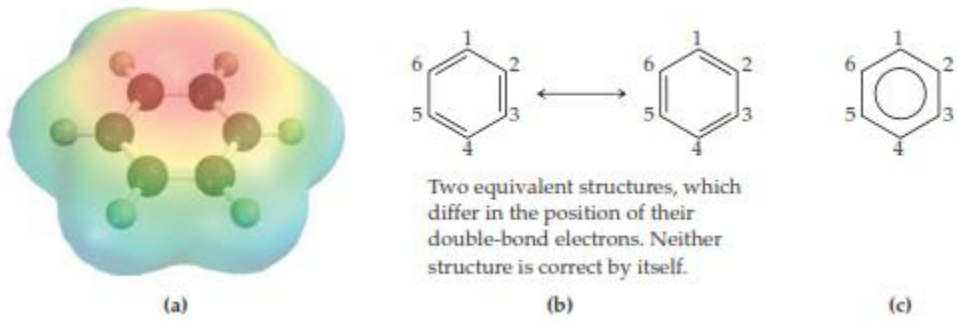
المركبات الاروماتية

وهي مركبات حلقية اشتق اسمها من كلمة Aromatic وتعني المركبات العطرية لان اغلب مركباتها ذات رائحة مميزه من امثلتها



البنزين

يعد البنزين ومشتقاته احد اهم صنف المركبات الاروماتية والبنزين عباره عن مركب حلقي سداسي يحوي على ثلاثه اواصر مزدوجه وثلاثه اواصر مفرده وتهجين جزيئة البنزين هو sp2 و طول الاصره في البنزين وجد انها تساوي 1.39 انكلستوم وهذه القيمه هي بين قيمة الاصره المفرده وبين الاصره المزدوجه حيث في الاثلين يكون طول الاصره 1.34 وفي الايثان هو 1.53 انكلستوم.وذلك بسبب الرنين resonance الشكل العام لحلقة البنزين هو



قاعدة هوكل للاروماتية Huckel's Rule for aromatic structure

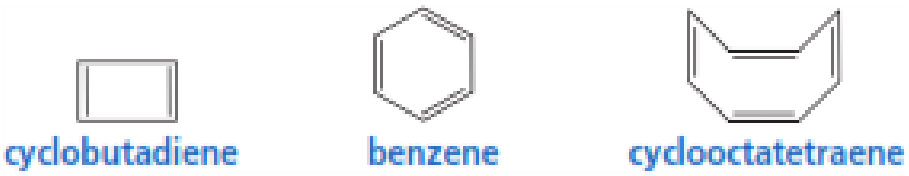
باستخدام هذه القاعده يمكن التميز بين المركب الاروماتي وغير الاروماتي.

Huckel's Rule $4n+2=\pi$ **electrons**

لكي يكون المركب اروماتي يجب ان تكون قيمة n تساوي عدد صحيح اي بدون كسور

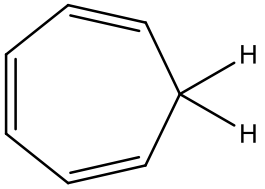
فعند تطبيق هذه القاعدع على البنزين نجد ان للبنزين 6 π

وبذلك فان 6 =4n+2 و بذلك تكون قيمة n =1

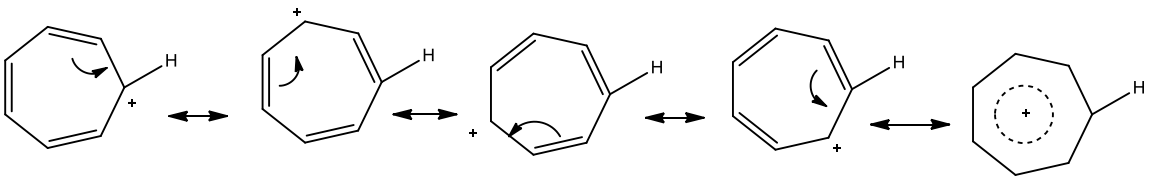


على عكس البنزين cyclobutadine يعتبر مركب غير اروماتي وذلك لان n=0.5اي عدد غير صحيح و المركب cyclooctatetraeneفهو مركب غير اروماتيا ايضا كذلك كون المركب لايقع بمستوى واحد (Not planer)وهو حاله ضروره للمركبات الاروماتيه ولرنين تلك المركبات.

كذلك بالنسبه للمركب Cycloheptatriene بالرغم ان له 6π الا انه يعتبر مركب غير اروماتي وذلك بسبب عدم تعاقب الاواصر المفرده والمزدوجه وهذا شرط اخر للمركبات الاروماتيه



بينما الكاربوكاتيون لهذا المركب يعد مركب اروماتي بسبب امكانية التعاقب من خلال الرنين



تسمية مشتقات البنزين

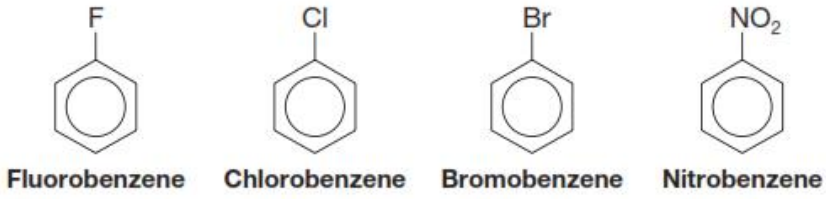
يوجد نظامين لتسمية مشتقات البنزين

الاول بذكر اسم المشتق ثم يتبعه كلمة benzene

Two systems are used in naming monosubstituted benzenes.

- In many simple compounds, *benzene* is the parent name and the substituent is simply indicated by a prefix.

For example, we have

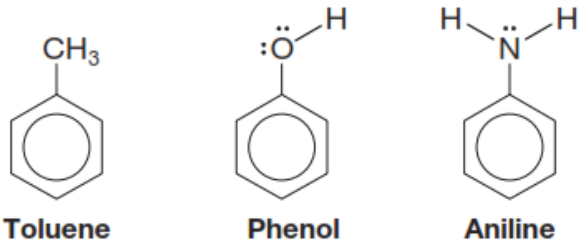


Fluorobenzene **Chlorobenzene** **Bromobenzene** **Nitrobenzene**

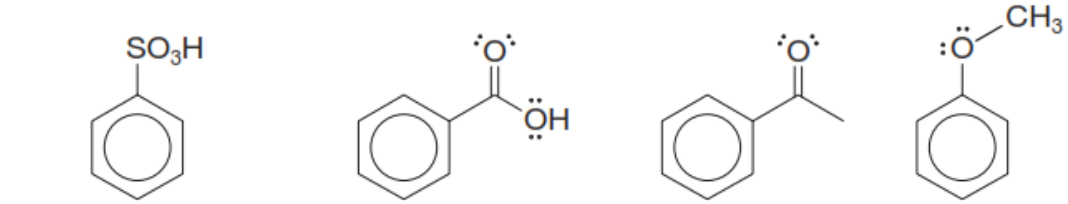
- For other simple and common compounds, the substituent and the benzene ring taken together may form a commonly accepted parent name.

لبعض مشتقات البنزين تسمية شائعه

Methylbenzene is usually called *toluene*, hydroxybenzene is almost always called *phenol*, and aminobenzene is almost always called *aniline*. These and other examples are indicated here:



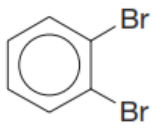
Toluene **Phenol** **Aniline**



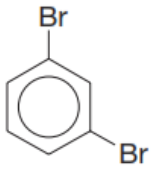
Benzenesulfonic acid **Benzoic acid** **Acetophenone** **Anisole**

- When two substituents are present, their relative positions are indicated by the prefixes ***ortho-***, ***meta-***, and ***para-*** (abbreviated ***o-***, ***m-***, and ***p-***) or by the use of numbers.

For the dibromobenzenes we have



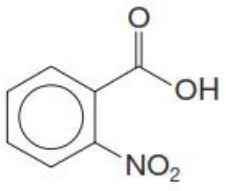
1,2-Dibromobenzene (*o*-dibromobenzene) ortho



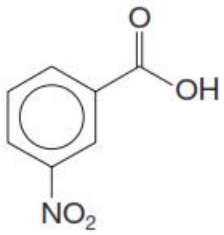
1,3-Dibromobenzene (*m*-dibromobenzene) meta

1,4-Dibromobenzene (*p*-dibromobenzene) para

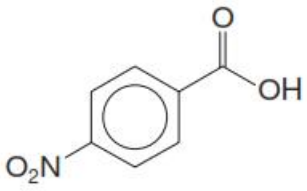
and for the nitrobenzoic acids



2-Nitrobenzoic acid (*o*-nitrobenzoic acid)

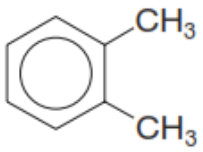


3-Nitrobenzoic acid (*m*-nitrobenzoic acid)

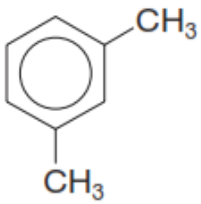


4-Nitrobenzoic acid (*p*-nitrobenzoic acid)

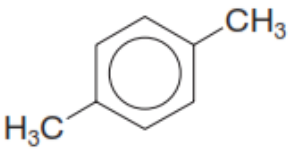
The dimethylbenzenes are often called *xylenes*:



1,2-Dimethylbenzene (*o*-xylene)



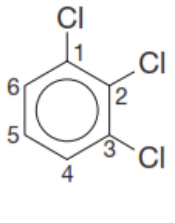
1,3-Dimethylbenzene (*m*-xylene)



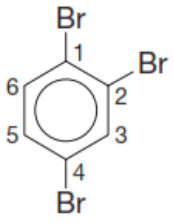
1,4-Dimethylbenzene (*p*-xylene)

- If more than two groups are present on the benzene ring, their positions must be indicated by the use of *numbers*.

As examples, consider the following two compounds:

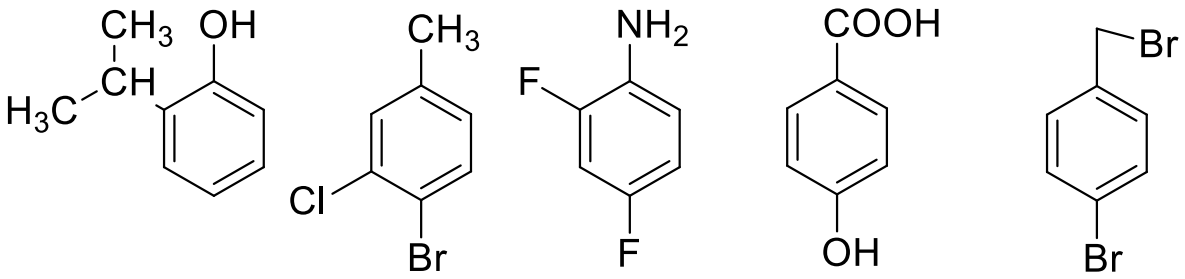


1,2,3-Trichlorobenzene



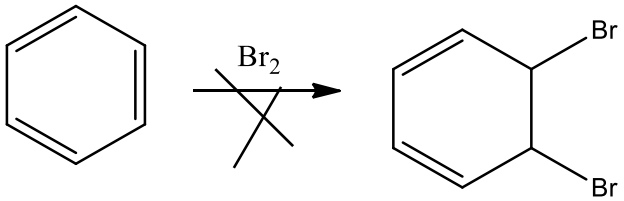
1,2,4-Tribromobenzene
(*not* 1,3,4-tribromobenzene)

سمي المركبات التالية **(homework)**



تفاعلات البنزين

بصوره عامه لا يتفاعل البنزين بنفس طريقة الالكينات حيث تفاعل البنزين مع البروم لا يزول لون البروم اي لا يعطي ثنائي البرومبن



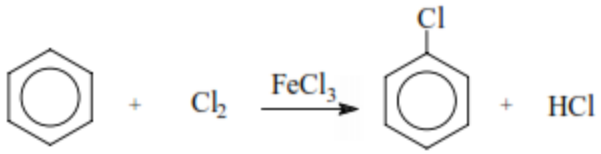
وانما يدخل البنزين تفاعل استبدال **substitution reaction** حيث يتم تعويض ذره او مجموعه باحد ذرات الهيدروجين وان ناتج هذا التفاعل يمكن ان يدخل التفاعل مره اخرى.

1- تفاعل الهلجنه

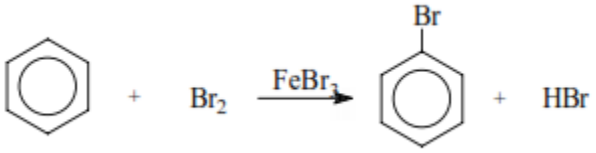
عند ادخال الكلور يسمى كلوره وعند البروم يسمى برمنه وهكذا

يتم هذا التفاعل بوجود حامض لويس اماFeX3 or ALX3

كما في المعادله التالية



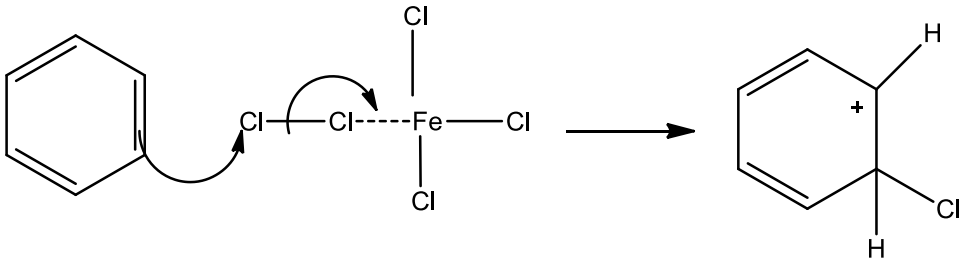
وايضا



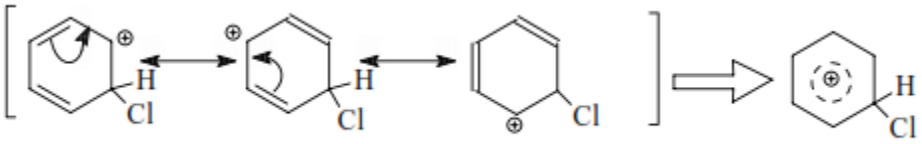
يسمى مثل هذا التفاعل بتفاعل الاستبدال او التعويض الالكتروفيلي

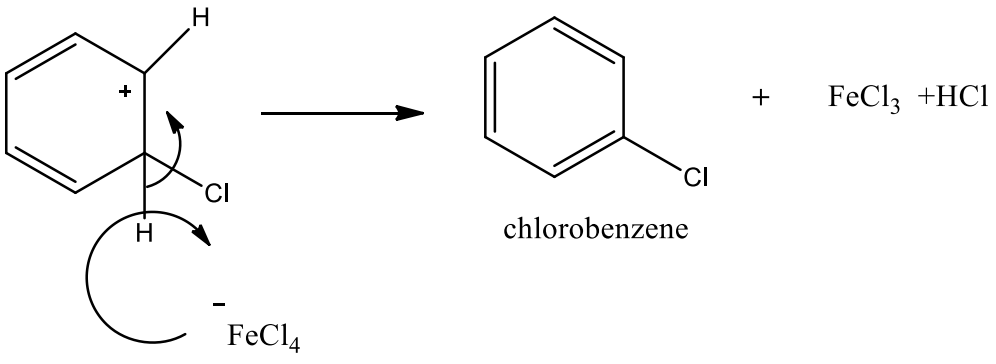
Electrophilic_aromatic **substitution**

يعمل العامل المساعد مثل $FeCl_3$(حامض لويسط) حيث يساعد على تجهيز التفاعل بالالكتروفيل اللازم للتفاعل



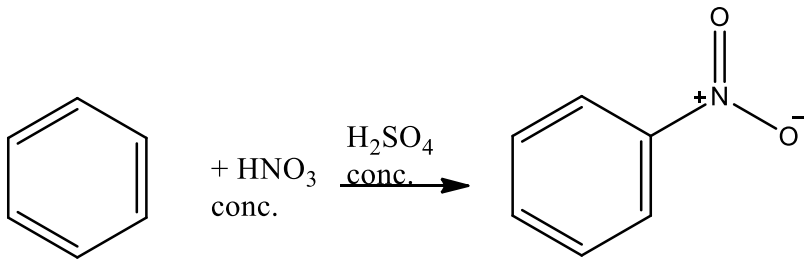
البنزونيوم المتكون (كاربوكاتيون) مستقر من خلال الرنين





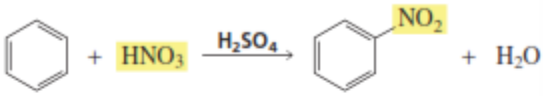
2-تفاعل النتره

يتفاعل حامض النتريك المركز مغ البنزين بوجود حامض الكبريت ليعطي nitrobenzene



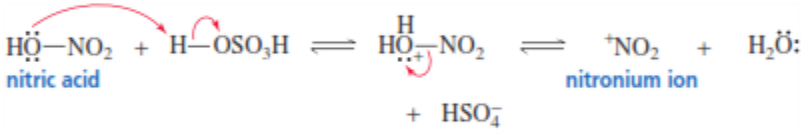
The nitration of benzene with nitric acid requires sulfuric acid as a catalyst.

nitration



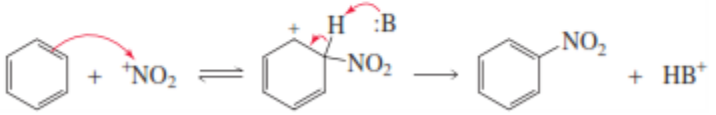
nitrobenzene

To generate the necessary electrophile, sulfuric acid protonates nitric acid. Protonated nitric acid loses water to form a nitronium ion, the electrophile required for nitration.



The mechanism for nitration is the same as the mechanisms described in Section 7.

mechanism for nitration

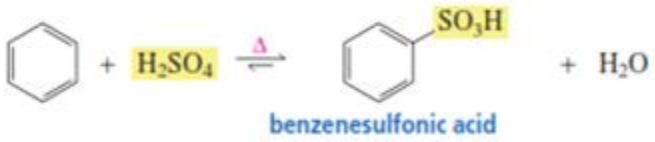


- The electrophile attaches to the benzene ring.
- A base (:B) from the reaction mixture (for example, H_2O, HSO_4^-, or solvent) removes a proton from the carbocation intermediate, thereby reforming the aromatic ring.

SULFONATION OF BENZENE

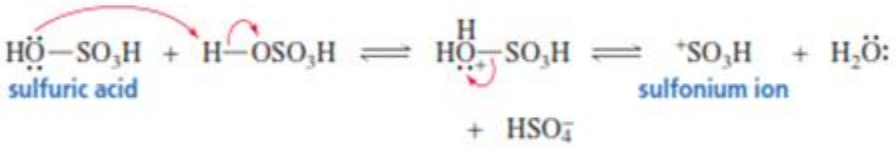
Fuming sulfuric acid (a solution of SO_3 in sulfuric acid) or concentrated sulfuric acid is used to sulfonate aromatic rings.

sulfonation



benzenesulfonic acid

Take a minute to note the similarities in the mechanisms for forming the $^{+}SO_3H$ electrophile for sulfonation and the $^{+}NO_2$ electrophile for nitration.

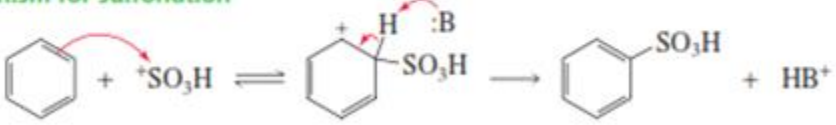


sulfuric acid

sulfonium ion

The mechanism for sulfonation is the same as the other mechanisms we have seen for electrophilic aromatic substitution.

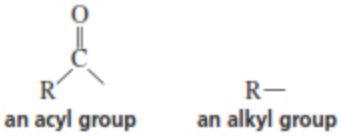
mechanism for sulfonation



- The electrophile attaches to the benzene ring.
- A base (:B) from the reaction mixture removes a proton from the carbocation intermediate, thereby reforming the aromatic ring.

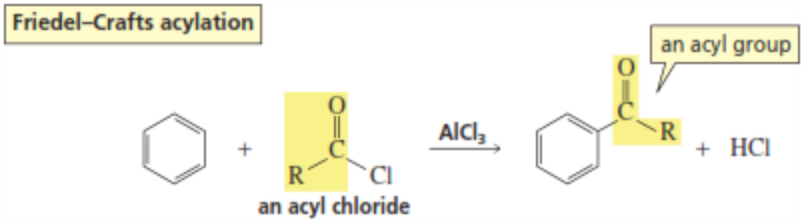
FRIEDEL–CRAFTS ACYLATION OF BENZENE

Two electrophilic substitution reactions bear the names of chemists Charles Friedel and James Crafts. *Friedel–Crafts acylation* places an acyl group on a benzene ring, and *Friedel–Crafts alkylation* places an alkyl group on a benzene ring.

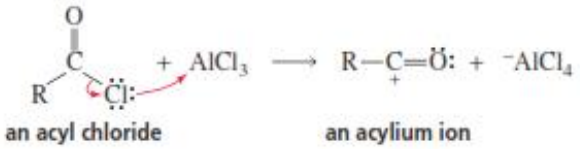


An acyl chloride is used to generate the electrophile for a **Friedel–Crafts acylation**. **An acyl chloride** has a Cl in place of the OH group of a carboxylic acid.

Friedel–Crafts acylation

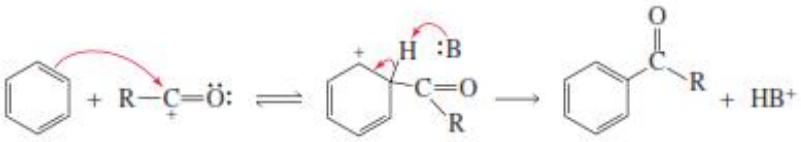


The electrophile (an acylium ion) is formed by the reaction of the acyl chloride with $AlCl_3$, a Lewis acid.



The mechanism for Friedel–Crafts acylation is shown below.

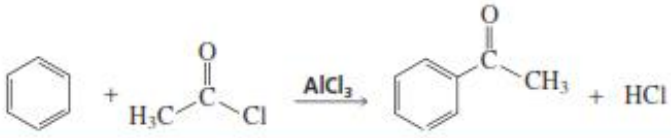
mechanism for Friedel–Crafts acylation



- The electrophile attaches to the benzene ring.
- A base (:B) from the reaction mixture removes a proton from the carbocation intermediate, thereby reforming the aromatic ring.

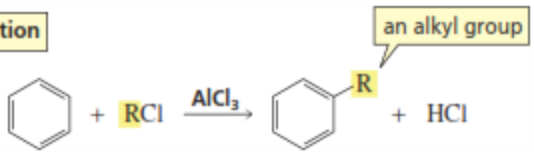
PROBLEM 9

Write the mechanism for the following reaction:

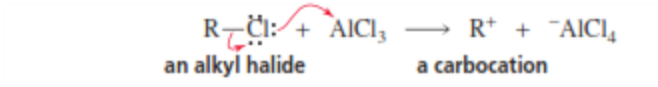


Friedel–Crafts alkylation places an alkyl group on a benzene ring.

Friedel–Crafts alkylation

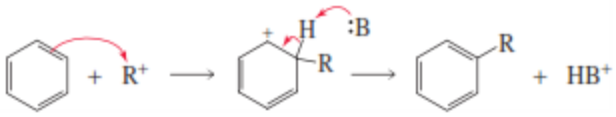


The electrophile in this reaction is a carbocation that is formed from the reaction of an alkyl halide with $AlCl_3$. Alkyl fluorides, alkyl chlorides, alkyl bromides, and alkyl iodides can all be used.



The mechanism for Friedel-Crafts alkylation is shown below.

mechanism for Friedel–Crafts alkylation



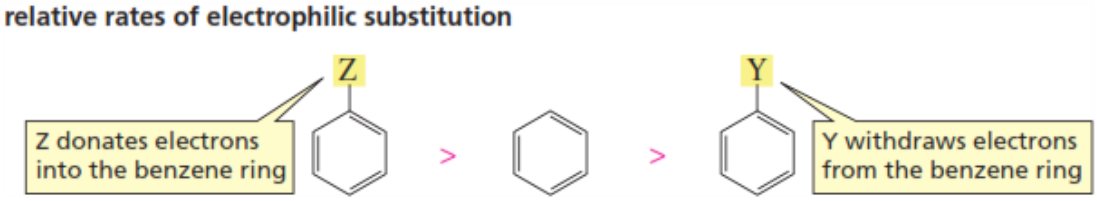
- The electrophile (R^+) attaches to the benzene ring.
- A base (:B) from the reaction mixture removes a proton from the carbocation intermediate, thereby reforming the aromatic ring.

The Effect of Substituents Group on Reactivity

اصبح من الواضح ان البنزين يتفاعل تفاعل تعويض (استبدال) الكتروفيلي electrophilic substitution reaction

والتي تم ذكرها في المحاضره السابقه(الهلجنه والنترته والسلفنه والاسيله والالكنه) ولكي نعرف فعالية المركبات الناتجه مقارنة بالبنزين اي هي فعاله اكثر او اقل من البنزين علينا فهم طبيعة هذه المعوضات وبصوره عامه تعتمد المعوضات على تاثير الحث (inductive effect) وتاثير الرنين(resonance effect) حيث المعوضات تزيد فعالية البنزين نحو التعويض الالكتروفيلي او تقلل فعاليتها كذلك تعمل على تحديد موقع الاضافه(اورثو او ميتا او بارا)

وبشكل عام



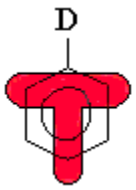
There are two ways substituents can donate electrons—*inductively* or by *resonance*. Substituents can also withdraw electrons *inductively* or by *resonance*.

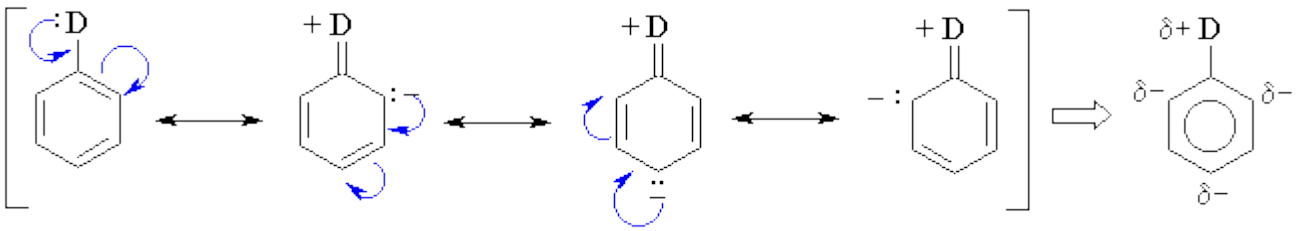
تاثير الحث

Inductive effect :the effects are those that occur through the σ system due to electronegativity type effects. These too can be either electron donating (*e.g.* -Me) where σ electrons are pushed toward the arene or electron withdrawing (*e.g.* $-CF_3$, $+NR_3$) where σ electrons are drawn away from the arene.

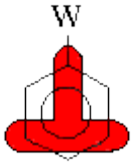
RESONANCE: effects are those that occur through the π system and can be represented by resonance structures. These can be either electron donating (*e.g.* -OMe) where π electrons are pushed toward the arene or electron withdrawing (*e.g.* -C=O) where π electrons are drawn away from the arene.

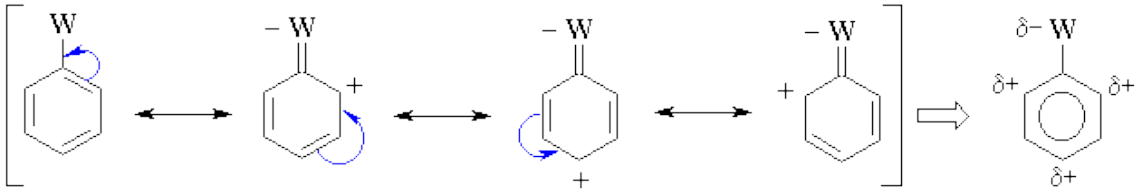
Electron donating groups (EDG) with **lone pairs** (*e.g.* -OMe, $-NH_2$) on the atoms adjacent to the π system **activate** the aromatic ring by increasing the electron density on the ring through a **resonance donating effect**. The resonance only allows electron density to be positioned at the **ortho-** and **para-** positions. Hence these sites are **more**nucleophilic, and the system tends to react with electrophiles at these **ortho-** and **para-** sites.





Electron withdrawing groups (EWG) with π bonds to **electronegative atoms** (*e.g.* -C=O, -NO_2) adjacent to the π system **deactivate** the aromatic ring by decreasing the electron density on the ring through a **resonance withdrawing effect**. The resonance only decreases the electron density at the ortho- and para- positions. Hence these sites are **less** nucleophilic, and so the system tends to react with electrophiles at the **meta** sites.





بصوره عامة المجاميع الدافعة للالكترونات تجعل موقعي اورثو وبارا اكثر سالبيه مما يزيد فعالية هذين الموقعين باتجاه التعويض الالكتروفيلي بهذين الموقعين

اما المجاميع الساحبه للالكترونات قانها تزيد الشحنه الموجبه على الموقعين اورثو وبار وبالتالي يسبب تنافر مع الالكتروفيل فلذلك توجه هذه المجاميع نحو ميتا

Donating and Withdrawing Electrons Inductively

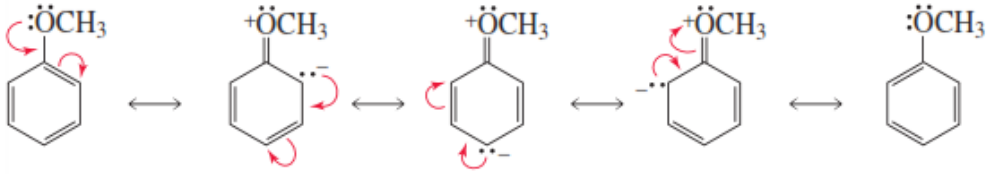
If a substituent that is bonded to a benzene ring is *less electron withdrawing than a hydrogen*, the electrons in the σ bond that attaches the substituent to the benzene ring will move toward the ring more readily than will those in the σ bond that attaches a hydrogen to the ring. Such a substituent donates electrons inductively compared with a hydrogen. Donation of electrons through a σ bond is called **inductive electron donation**. We have seen that alkyl substituents (such as CH_3) donate electrons inductively compared with a hydrogen.

If a substituent that is bonded to a benzene ring is *more electron withdrawing than a hydrogen*, it will draw the σ electrons away from the benzene ring more strongly than a hydrogen will. Withdrawal of electrons through a σ bond is called **inductive electron withdrawal**. The $^{+}NH_3$ group is an example of a substituent that withdraws electrons inductively because it is more electronegative than a hydrogen.

Donating and Withdrawing Electrons by Resonance

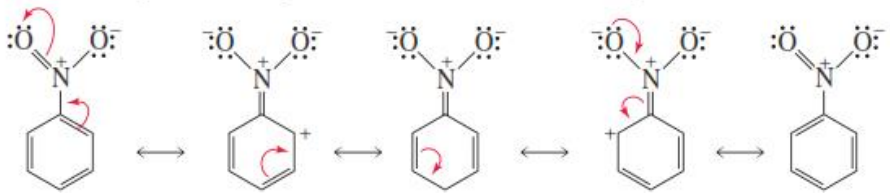
If a substituent has a lone pair on the atom directly attached to the benzene ring, the lone pair can be delocalized into the ring; these substituents are said to **donate electrons by resonance**. Substituents such as NH_2, OH, OR, and Cl donate electrons by resonance. These substituents also withdraw electrons inductively because the atom attached to the benzene ring is more electronegative than a hydrogen.

donating electrons by resonance into a benzene ring



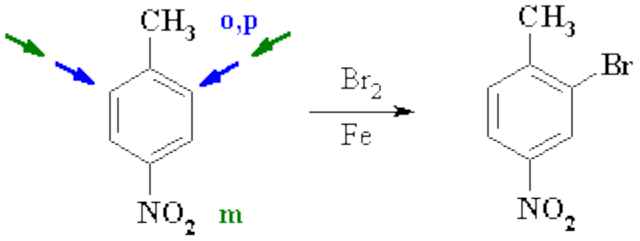
If a substituent is attached to the benzene ring by an atom that is doubly or triply bonded to a more electronegative atom, the π electrons of the ring can be delocalized onto the substituent; these substituents are said to **withdraw electrons by resonance**. Substituents such as C═O, C≡N, SO_3H, and NO_2 withdraw electrons by resonance. These substituents also withdraw electrons inductively because the atom attached to the benzene ring has a full or partial positive charge and, therefore, is more electronegative than a hydrogen.

withdrawing electrons by resonance from a benzene ring

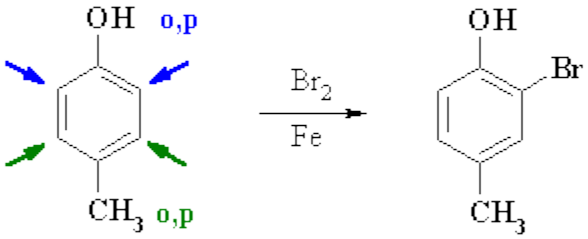


امثله على ذلك

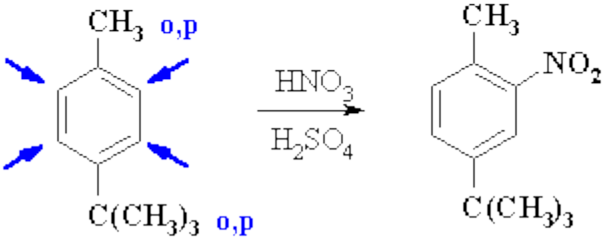
substituents reinforce each other



strongest activator controls



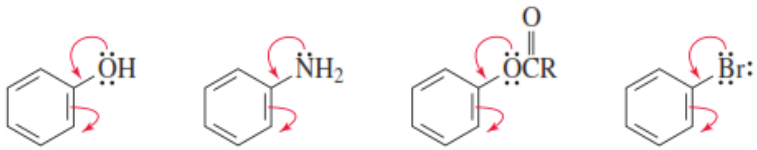
ctivating effects similar, but eric effects favour ortho to .e smaller methyl group



Relative Reactivity of Substituted Benzenes

The substituents shown in Table 1 are listed according to how they affect the reactivity of the benzene ring toward electrophilic aromatic substitution compared with benzene—in which the substituent is a hydrogen. *The* **activating substituents** *make the benzene ring more reactive toward electrophilic substitution; the* **deactivating substituents** *make the benzene ring less reactive.* Remember that activating substituents donate electrons into the ring and deactivating substituents withdraw electrons from the ring.

All the *activating substituents* (except for alkyl substituents) donate electrons into the ring by resonance and withdraw electrons from the ring inductively. The fact that these substituents have been found experimentally to make the benzene ring more reactive indicates that their electron donation into the ring by resonance is more significant than their inductive electron withdrawal from the ring.



We have seen that an alkyl substituent, compared with a hydrogen, donates electrons inductively.

The halogens are *weakly deactivating substituents*; they also donate electrons into the ring by resonance and withdraw electrons from the ring inductively. Because the halogens have been found experimentally to make the benzene ring less reactive, we can conclude that they withdraw electrons inductively more strongly than they donate electrons by resonance.

All the *substituents that are more strongly deactivating than the halogens* withdraw electrons both inductively and by resonance except for the ammonium ions

($^{+}NH_3$, $^{+}NH_2R$, $^{+}NHR_2$, and $^{+}NR_3$). The ammonium ions have no resonance effect, but the positive charge on the nitrogen atom causes them to strongly withdraw electrons inductively.

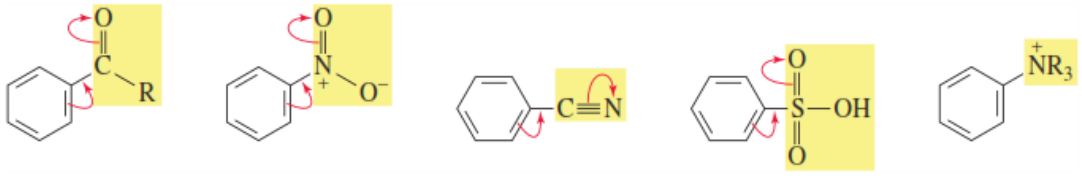
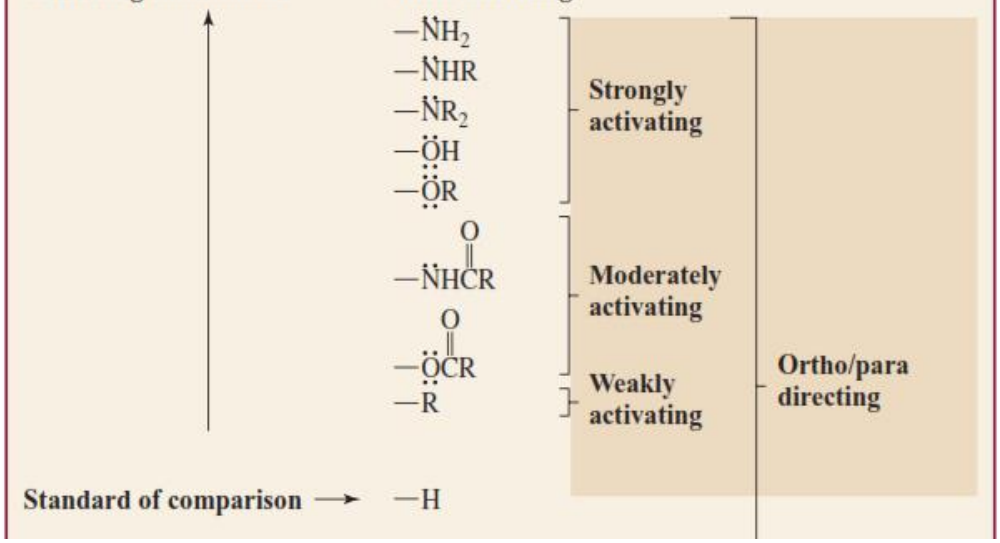
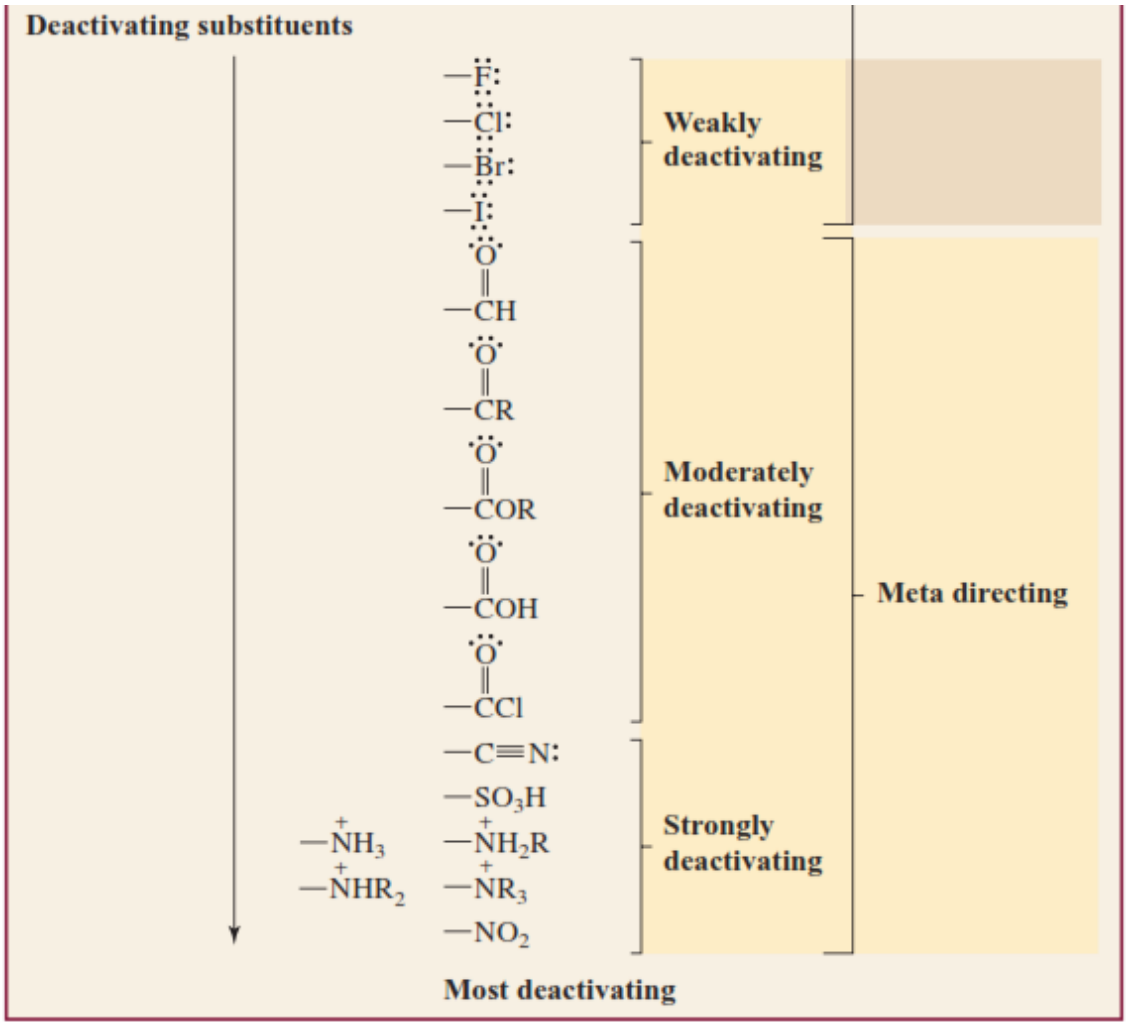


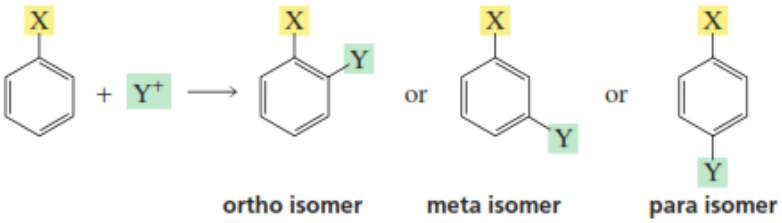
Table 1 The Effects of Substituents on the Reactivity of a Benzene Ring toward Electrophilic Substitution





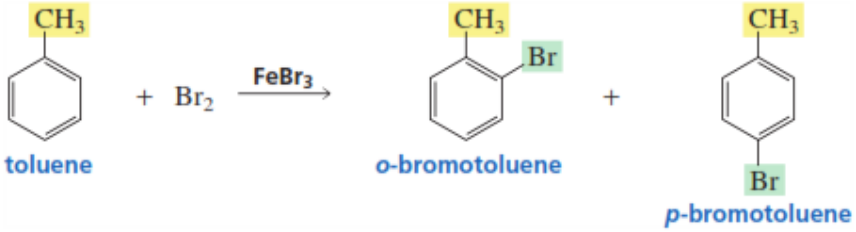
THE EFFECT OF SUBSTITUENTS ON ORIENTATION

When a substituted benzene undergoes an electrophilic substitution reaction, where does the new substituent attach itself? Is the product of the reaction the ortho isomer, the meta isomer, or the para isomer?

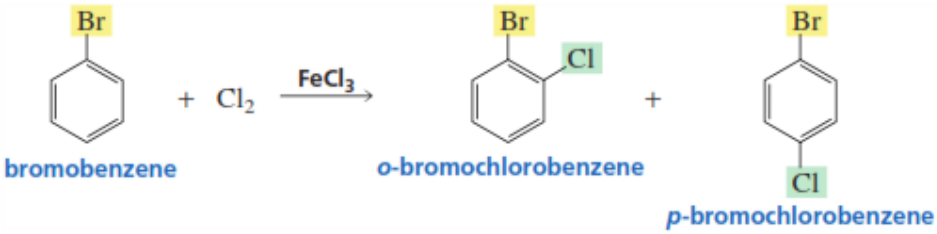


The substituent already attached to the benzene ring determines the location of the new substituent. The attached substituent will have one of two effects: it will direct an incoming substituent either to the ortho *and* para positions, or it will direct an incoming substituent to the meta position. All activating substituents and the weakly deactivating halogens are **ortho–para directors**, and all substituents that are more deactivating than the halogens are **meta directors**. Thus, the substituents can be divided into three groups:

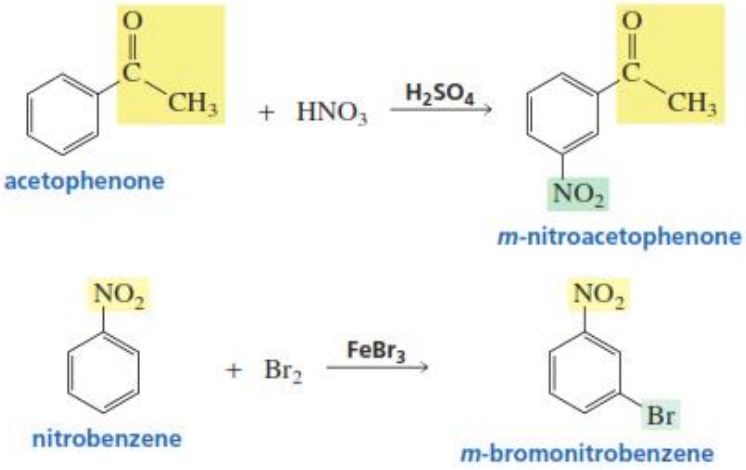
1. All *activating substituents* direct an incoming electrophile to the ortho and para positions.



2. The *weakly deactivating* halogens also direct an incoming electrophile to the ortho and para positions.



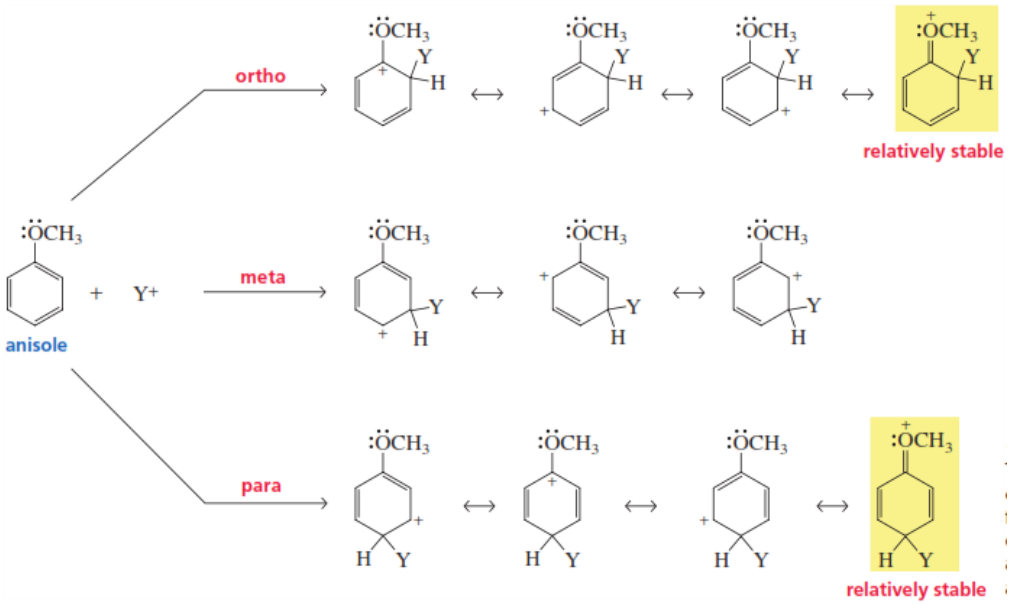
3. All *moderately deactivating and strongly deactivating* substituents direct an incoming electrophile to the meta position.



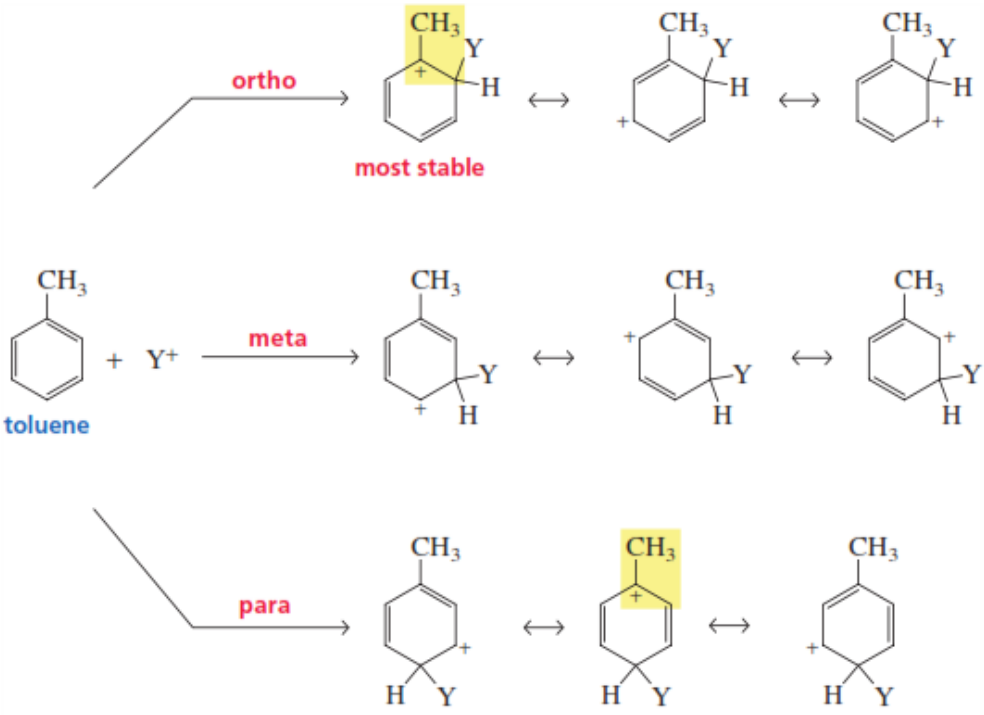
To understand why a substituent directs an incoming electrophile to a particular position, we must look at the stability of the carbocation intermediate, because as Figure 2 shows, formation of the carbocation is the rate-determining step.

When a substituted benzene undergoes an electrophilic substitution reaction, three different carbocation intermediates can be formed: an *ortho*-substituted carbocation, a *meta*-substituted carbocation, and a *para*-substituted carbocation (Figure 3). The relative stabilities of the three carbocations enable us to determine the preferred pathway of the reaction because the more stable the carbocation, the more stable the transition state for its formation, and the more rapidly it will be formed.

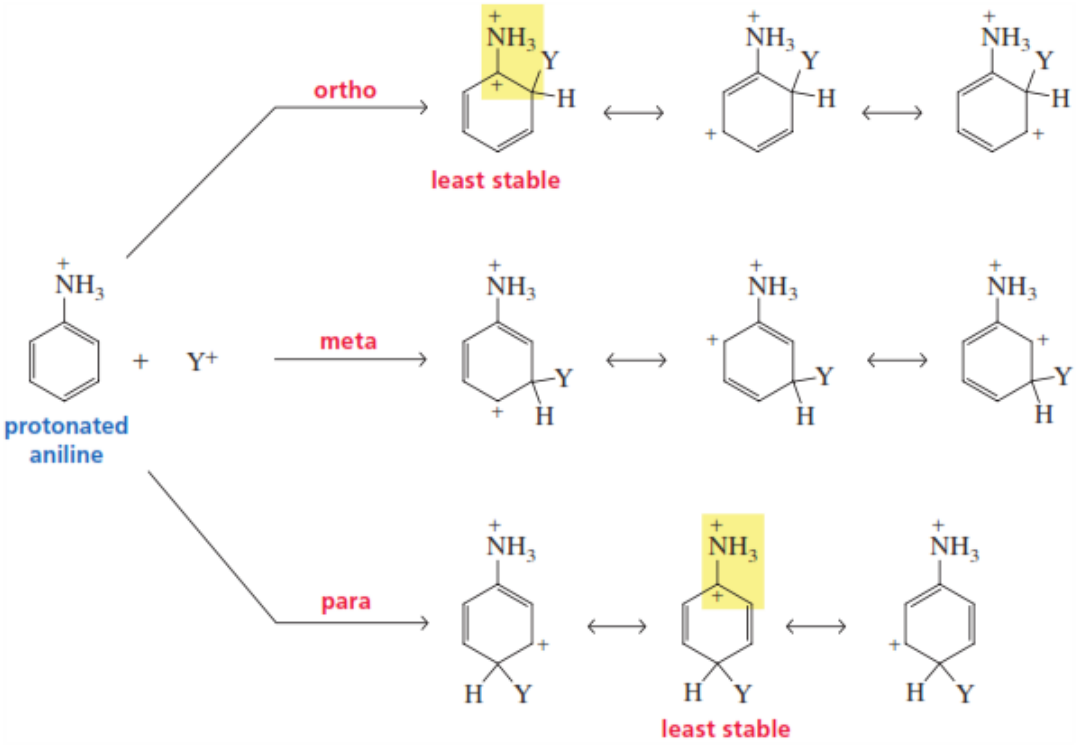
When the substituent is one that can donate electrons by *resonance*, the carbocations formed by putting the incoming electrophile on the ortho and para positions have a fourth resonance contributor (highlighted in Figure 3). This is an especially stable resonance contributor because it is the only one whose atoms (except for hydrogen) all have complete octets (that is, all have outer shells that contain eight electrons); it is obtained only by directing an incoming substituent to the ortho and para positions. Therefore, *all substituents that donate electrons by resonance are ortho–para directors.*



When the substituent is an alkyl group, the resonance contributors that are highlighted in Figure 4 are the most stable. In those contributors, the alkyl group is attached directly to the positively charged carbon and can stabilize it by inductive electron donation. A relatively stable resonance contributor is obtained only when the incoming group is directed to an ortho or para position. Therefore, *alkyl substituents are ortho–para directors.*



Substituents with a positive charge or a partial positive charge on the atom attached to the benzene ring will withdraw electrons inductively from the benzene ring, and most will withdraw electrons by resonance as well. For all such substituents, the resonance contributors highlighted in Figure 5 are the least stable because they have a positive charge on each of two adjacent atoms, so the most stable carbocation is formed



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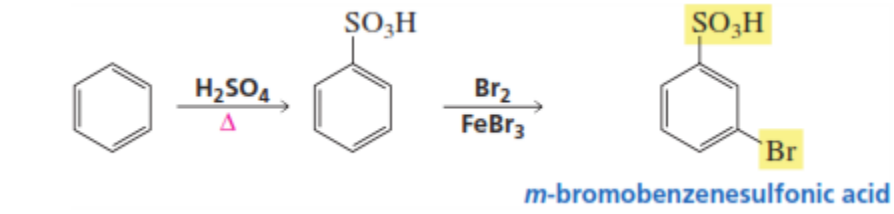

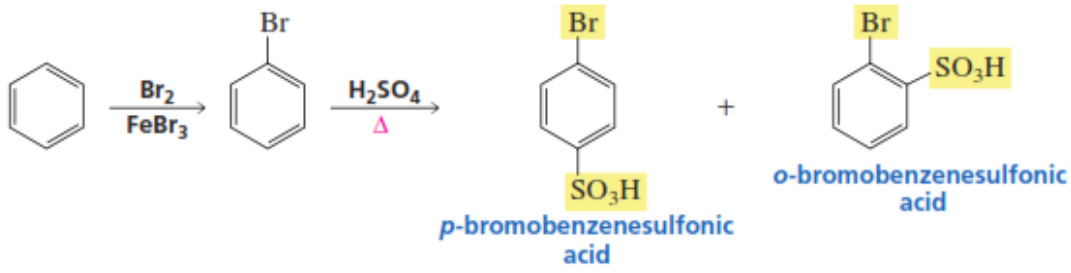

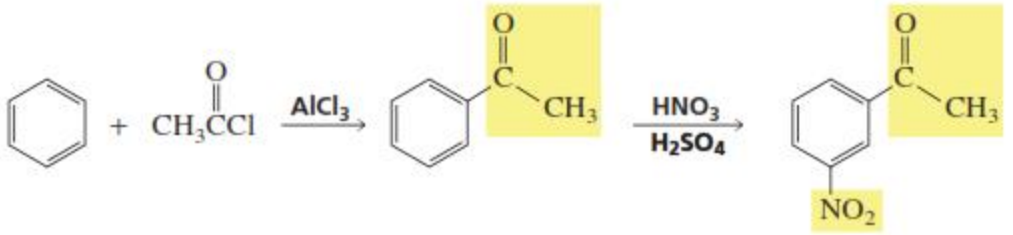

m-nitroacetophenone