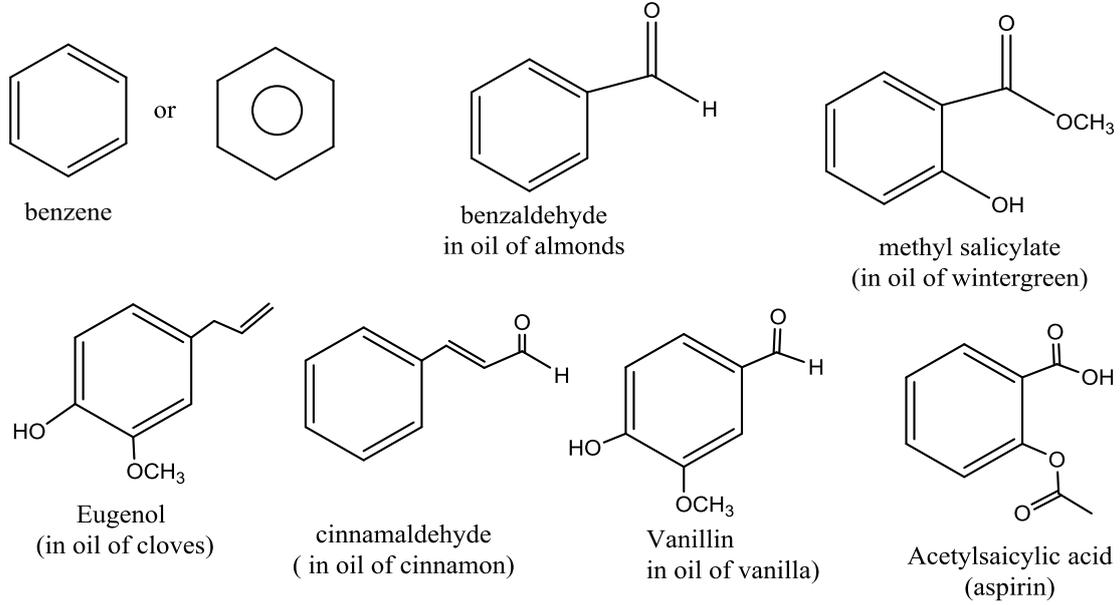


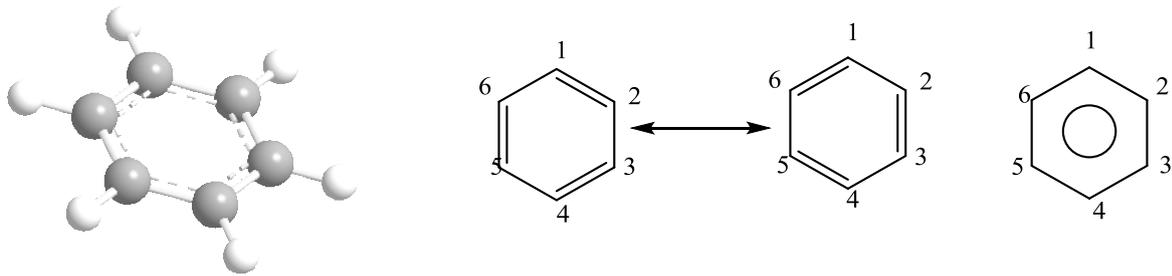
## الحلقات الأروماتية :-

هي مركبات حلقيه أشتق أسمها من كلمة Aromatic وتعني المركبات العطرية لان أغلب مركباتها ذات رائحة مميزة ومن أمثلتها



## البنزين

يعد البنزين ومشتقاته احد اهم صنف من المركبات الأروماتية والبنزين عباره عن مركب حلقي سداسي يحوي على ثلاثة اواصر مزدوجه وثلاثة اواصر مفردة وتهجينه هو  $sp^2$  وطول أصرته تساوي 1.39 انكستروم وهذه القيمه هي بين قيمة الاصرة المفردة وبين الاصرة المزدوجة حيث في الأثيلين يكون طول الأصرة 1.34 وفي الأيثان 1.53 انكستروم وذلك بسبب الرنين resonance والشكل العام لحلقة البنزين هو



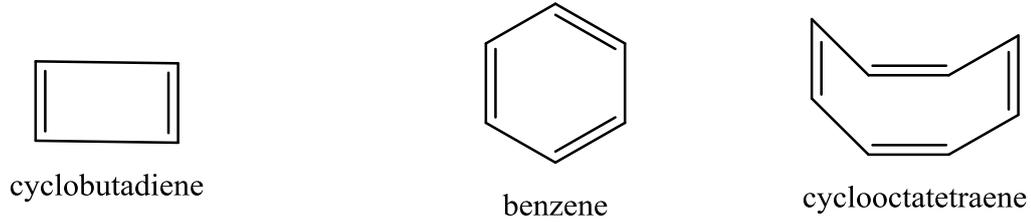
## قاعدة هيوكل للأروماتية Huckels Rule for aromatic structure

بأستخدام هذه القاعدة يمكن التمييز بين المركب الأروماتي وغير الأروماتي

$$4n + 2 = \pi \text{ electrons}$$

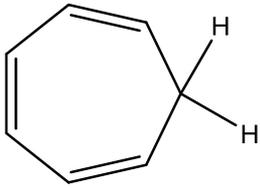
لكي يكون المركب أروماتي يجب ان تكون قيمة n عدد صحيح اي بدون كسور

فبعد تطبيق هذه القاعدة على البنزين نجد ان للبنزين  $6\pi$  وبذلك فان  $4n + 2 = 6$  وبذلك تكون قيمة  $n=1$

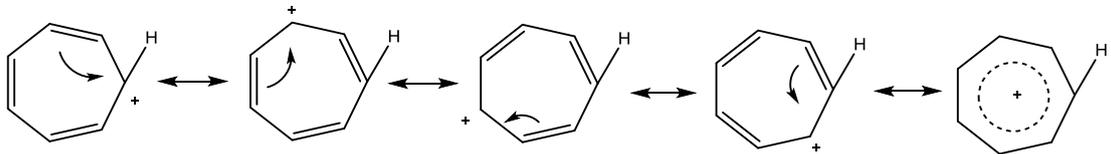


على عكس البنزين cyclobutadiene يعتبر مركب غير أروماتي وذلك لأن  $n=0.5$  عدد غير صحيح والمركب cyclooctatriene أيضا غير أروماتي كون المركب لا يقع بمستوى واحد (not planer) وهو حالة ضرورية للمركبات الأروماتية ولرنين تلك المركبات .

اما المركب cyloheptatriene بالرغم من ان له  $6\pi$  الا انه يعتبر مركب غير أروماتي وذلك بسبب عدم تعاقب الأواصر المفردة والمزدوجة وهذا شرط آخر للمركبات الأروماتية



بينما الكاروكاتيون لهذا المركب يعد مركب أروماتي بسبب امكانية التعاقب من خلال الرنين

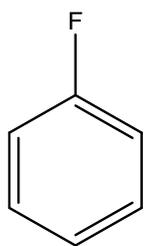


تسمية مشتقات البنزين

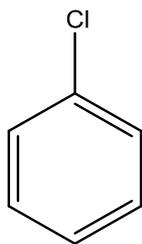
يوجد نظامين لتسمية مشتقات البنزين الأول يذكر اسم المشتق ثم يتبعه كلمة Benzene

Two systems are used in naming monosubstituted benzene .

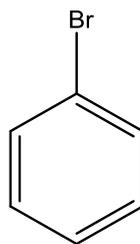
In many simple compounds , benzene is the parent name and the substituent is simply indicated by a prefix , for example we have



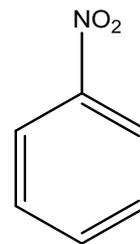
fluorobenzene



chlorobenzene



bromobenzene



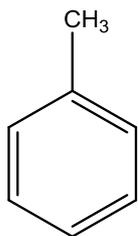
nitrobenzene

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

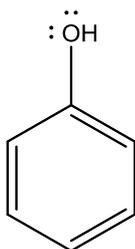
أبعض مشتقات البنزين تسميه شائعة

Methylbenzene is usually called toluene , hydroxybenzene is almost always called phenol , aminobenzene is almost always called aniline .

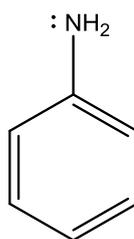
These and other examples are indicated here



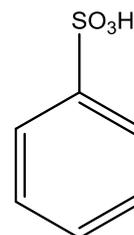
toluene



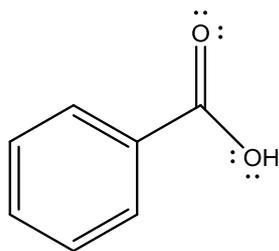
phenol



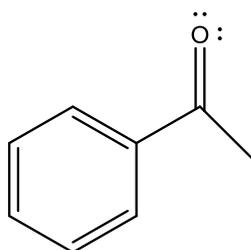
aniline



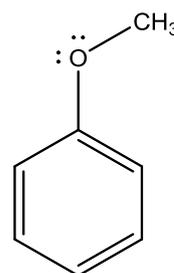
benzenesulfonic acid



benzoic acid



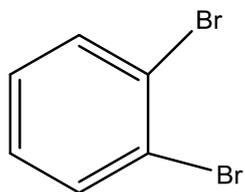
acetophenone



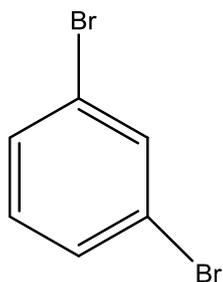
anisole

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

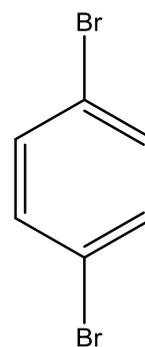
For the dibromobenzenes we have



1,2-dibromobenzene  
o-dibromobenzene

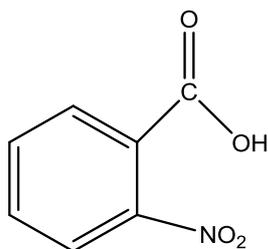


1,3-dibromobenzene  
m-dibromobenzene

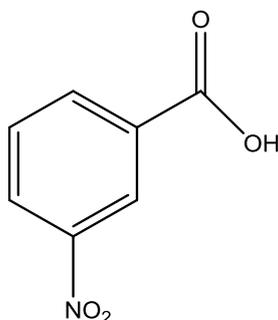


1,4-dibromobenzene  
p-dibromobenzene

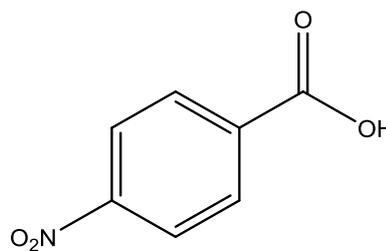
And for the nitrobenzoic acids



2-nitrobenzoic acid  
o-nitrobenzoic acid

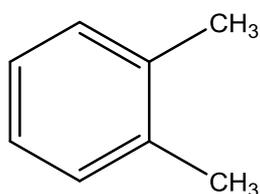


3-nitrobenzoic acid  
m-nitrobenzoic acid

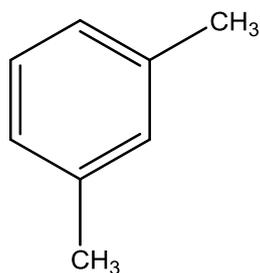


4-nitrobenzoic acid  
p-nitrobenzoic acid

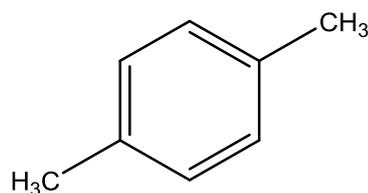
The dimethylbenzenes are often called xylenes:



*o*-xylene  
1,2-Dimethylbenzenes



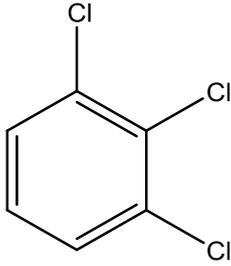
*m*-xylene  
1,3-Dimethylbenzenes



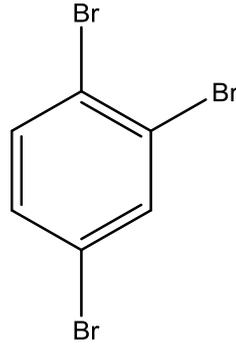
*p*-xylene  
1,4-Dimethylbenzenes

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

As examples, consider the following two compounds.

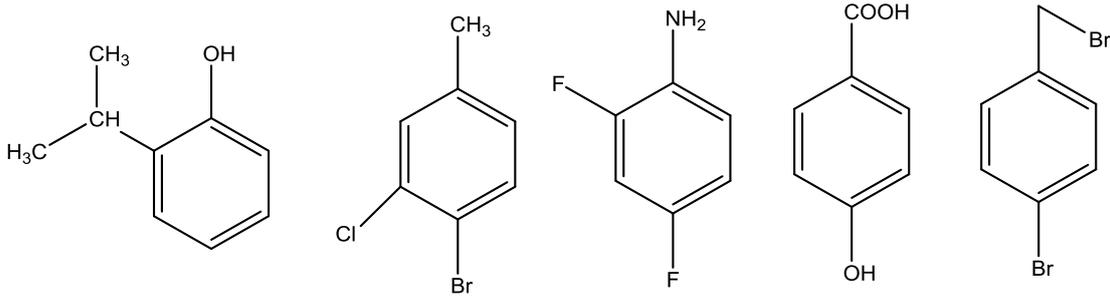


1,2,3-trichlorobenzene



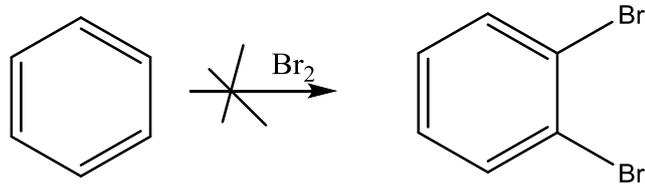
1,2,4-tribromobenzene

سمي المركبات التالية



تفاعلات البنزين

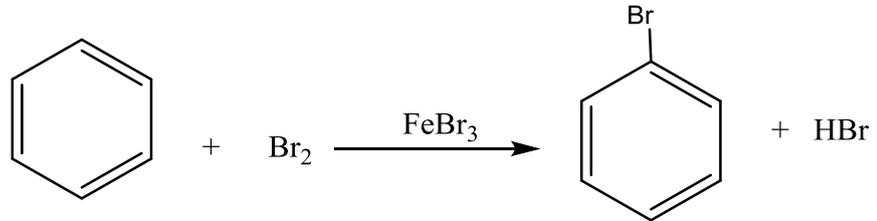
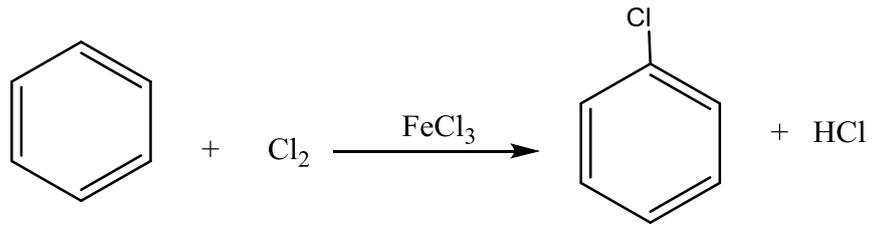
بصورة عامة لا يتفاعل البنزين بنفس طريقة الألكينات حيث تفاعل البنزين مع البروم لا يزول لون البروم اي لا يعطي ثنائي البرومين



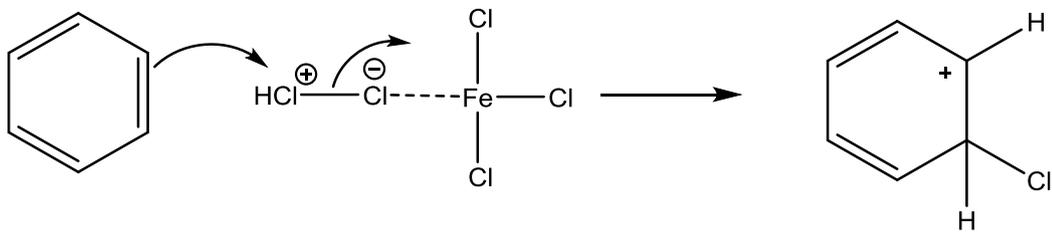
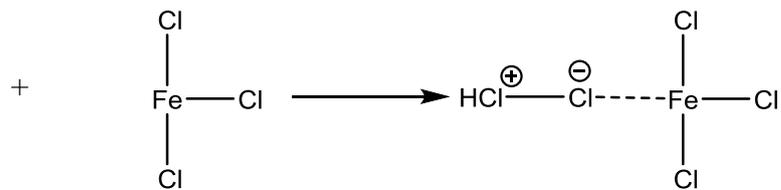
وانما يدخل ابنزين تفاعل استبدال Substitution reaction حيث يتم تعويض ذرة او مجموعة باحد ذرات الهيدروجين وان ناتج هذا التفاعل يمكن ان يدخل التفاعل مرة اخرى

1- تفاعل الهلجنة

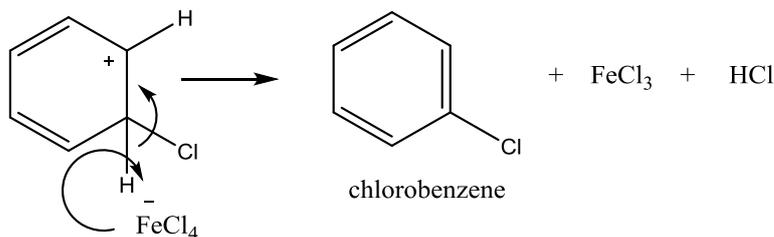
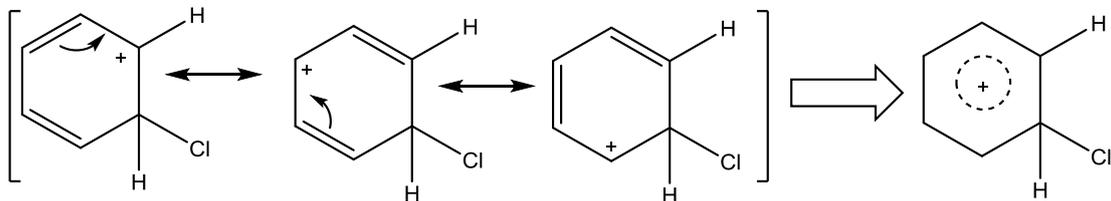
عند ادخال الكلور يسمى كلوره وعند البروم يسمى برمنه وهكذا يتم هذا التفاعل بوجود حامض لويس اما  $FeX_3$  or  $AlX_3$  كما في المعادلة التالية



يسمى هذا التفاعل بتفاعل الاستبدال او التعويض الألكتروفي ( Electrophilic aromatic substitution ) يعمل العامل المساعد مثل  $\text{FeCl}_3$  (حامض لويس) حيث يساعد على تجهيز التفاعل بالألكتروفيل اللازم للتفاعل .

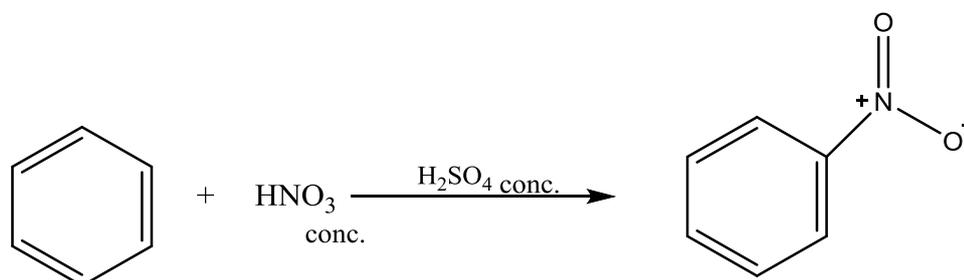


البنزونيوم المتكون (كاروكتيون) مستقر من خلال الرنين



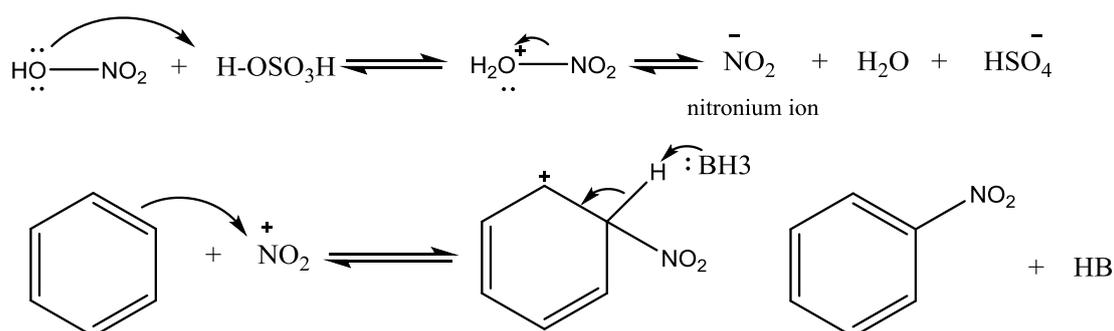
## 2- تفاعل النترنة

يتفاعل حامض النتريك المركز مع البنزين بوجود حامض الكبريتيك ليعطي nitrobenzene



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

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

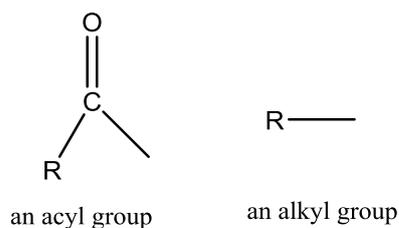


The electrophile attaches to the benzene ring

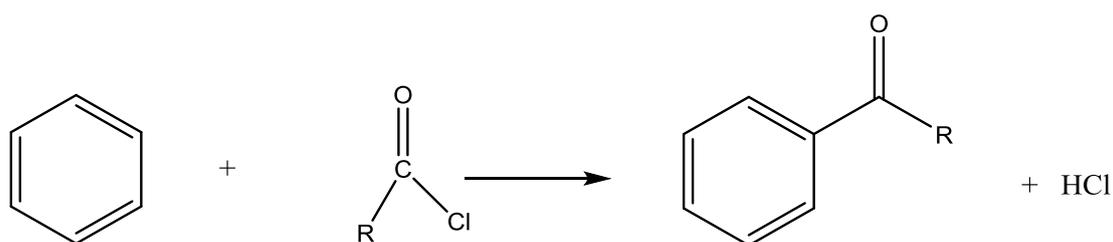
A base (B) from the reaction mixture (for example .H<sub>2</sub>O , HSO<sub>4</sub>, or solvent ) removes a proton from the carbocation intermediate thereby reforming the aromatic ring

## Friedel-crafts acylation of benzene

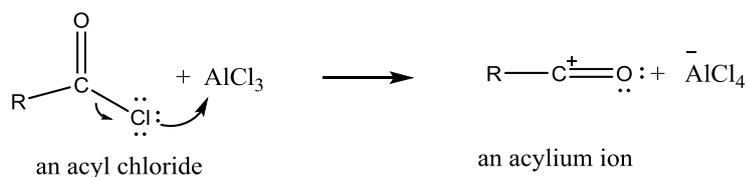
Two electrophile substitution reactions bear the names of chemists Charles Friedel and James Crafts . Friedel-Crafts acylation places an acyl group on a benzene ring and Friedel-Crafts alkylation places an alkyl group on a benzene ring .



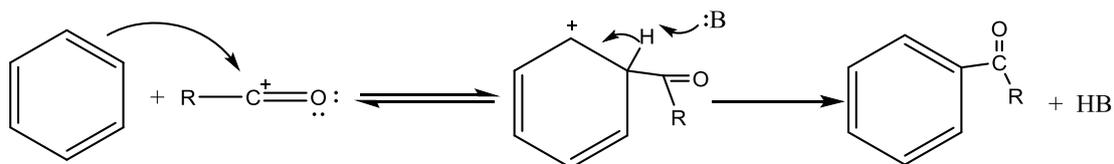
An acyl chloride is used to generate the electrophile for a Friedel-Crafts acylation an acyl chloride has a Cl in place of the OH group of a carboxylic acid .



The electrophile (an acylium ion is formed by the reaction of the acyl chloride with  $\text{AlCl}_3$  a lewis acid .

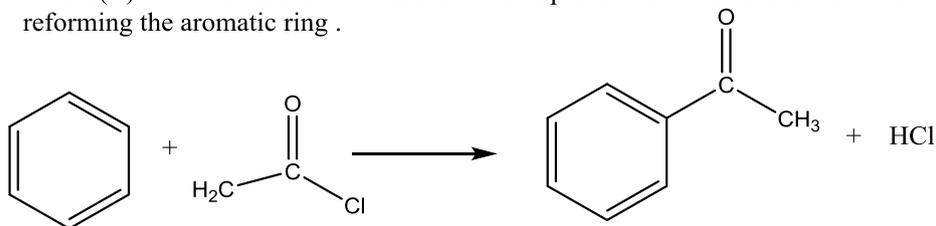


The mechanism for Friedel-Crafts acylation is shown below



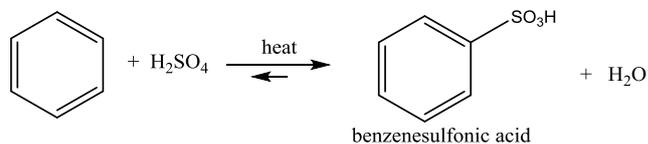
The electrophile attaches to the benzene ring

A base(B) from the reaction mixture removes a proton from the carbocation intermediate . thereby reforming the aromatic ring .

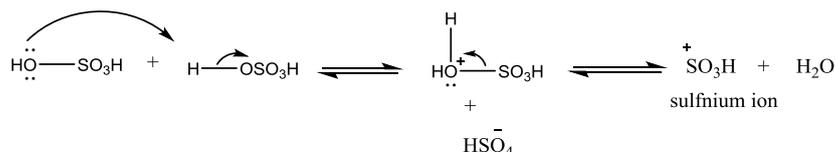


### SULFONATION OF BENZENE

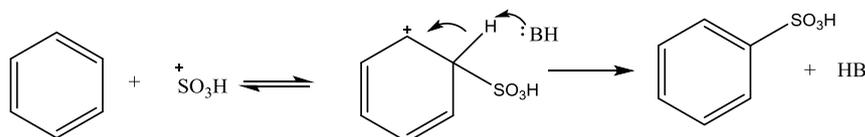
Fuming sulfuric acid (a solution of  $\text{SO}_3$  in sulfuric acid) or concentrated sulfuric acid is used to sulfonate aromatic rings.



Take a minute to note the similarities for forming the  $\overset{+}{\text{S}}\text{O}_3\text{H}$  electrophile for sulfonation and the  $\text{NO}_2^+$  electrophile for nitration.



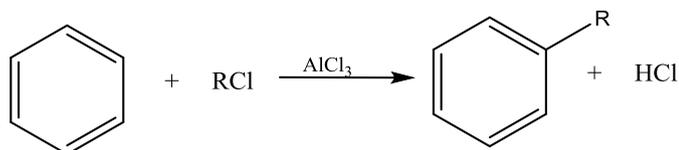
The mechanism for sulfonation is the same as the other mechanisms we have seen for electrophilic aromatic substitution.



The electrophile attaches to the benzene ring.

A base ( $\text{B}$ ) from the reaction mixture removes a proton from the carbocation intermediate, thereby reforming the aromatic ring.

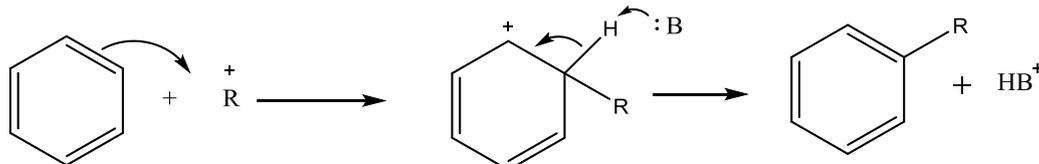
Friedel-Crafts alkylation places an alkyl group on a benzene ring



The electrophile in this reaction is a carbocation that is formed from the reaction of an alkyl halide with  $\text{AlCl}_3$ . Alkyl fluorides, alkyl chlorides, alkyl bromides, and alkyl iodides can all be used.



The mechanism for Friedel-Crafts alkylation is shown below



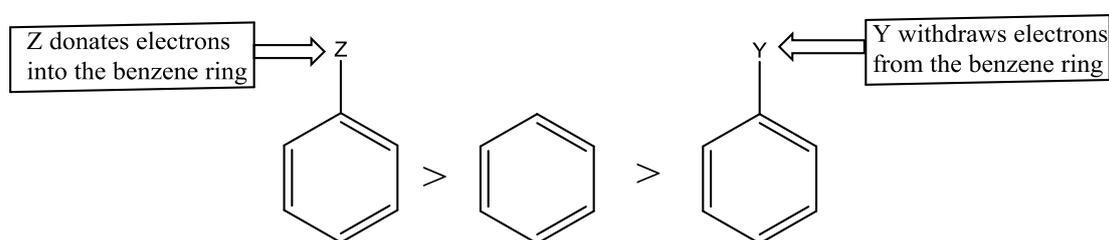
The electrophile ( $\text{R}$ ) attaches to the benzene ring.

A base ( $\text{B}$ ) from the reaction mixture removes a proton from the carbocation intermediate, thereby reforming the aromatic ring.

## The effect of Substitution Group on Reactivity

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

والتي تم ذكرها في المحاضرة السابقة (الهلجنة والنترتة والسلفنة والأسيلة والألكنة) ولكي نعرف فعالية المركبات الناتجة مقارنة بالبنزين أي هي أكثر فعالية أو أقل من البنزين علينا فهم طبيعة هذه المعوضات وبصورة عامة تعتمد هذه المعوضات على تأثير الحث وتأثير الرنين (inductive effect and resonance effect) حيث المعوضات تزيد فعالية البنزين نحو التعويض الألكتروفيلي أو تقلل فعاليتها كذلك تعمل على تحديد موقع الأضافة (أورثو أو ميتا أو بارا)



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

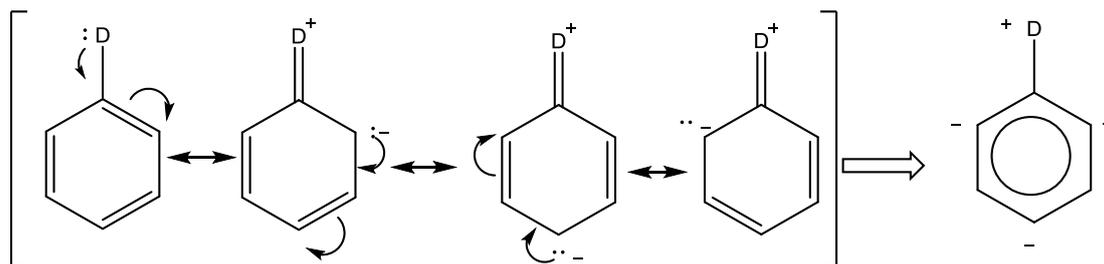
### تأثير الحث :-

**Inductive effect:** the effects are those that occur through the  $\sigma$  system due to electronegativity type effects. These too can be either electron donating (e.g  $-\text{Me}$ ) where  $\sigma$  electrons are pushed toward the arene or electron withdrawing (e.g  $-\text{CF}_3$  ,  $\text{NR}_3$  ) where  $\sigma$  electrons are drawn away from the arene .

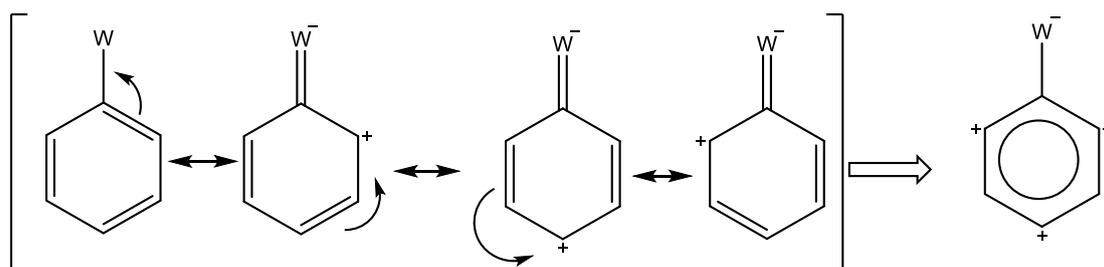
**Resonance effect:** the effects are those that occur through the  $\pi$  system and can be represented by resonance structures . These can be either electron donating (e.g  $-\text{OMe}$ ) where  $\pi$  electrons are pushed toward the arene or electron withdrawing (e.g  $-\text{C}=\text{O}$ ) where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

**Electron donating groups (EDG) with lone pairs** (e.g  $-\text{OMe}$  ,  $\text{NH}_2$ ) on the atoms adjacent to the  $\pi$  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  $\pi$  bonds to **electronegative** atoms (e.g  $-\text{C}=\text{O}$  ,  $-\text{NO}_2$ ) adjacent to the  $\pi$  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 site are **less nucleophilic** , and so the system tends to react with electrophiles at the **-meta** sites

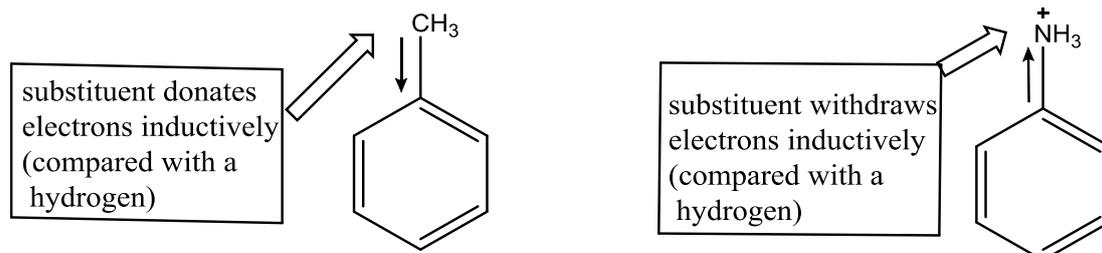


بصورة عامة المجماميع الدافعة للألكترونات تجعل موقعي أورثو وبارا أكثر سالبية مما يزيد فعالية هذين الموقعين باتجاه التعويض الألكتروفيلى بهذين الموقعين

اما المجماميع الساحبة فأنها تزيد الشحنة الموجبة على الموقعين أورثو وبارا وبالتالي يسبب تنافر مع الألكتروفيل فلذلك توجه نحو الموقع ميتا

## Donating and Withdrawing electrons Inductively

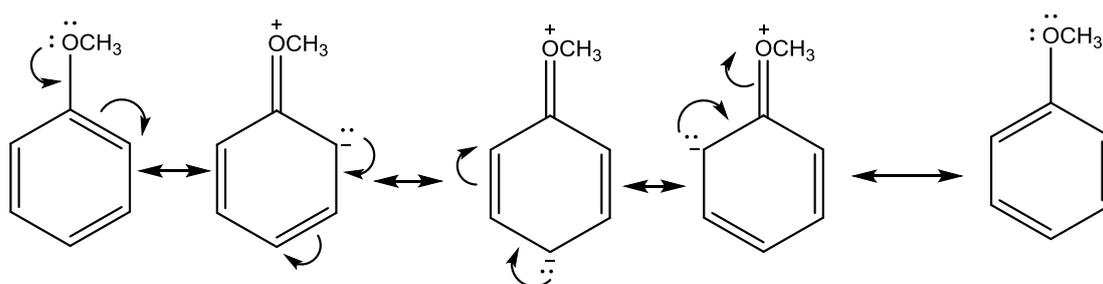
If a substituent that is bonded to a benzene ring is less electron withdrawing than a hydrogen , the electrons in the  $\sigma$  bond that attaches the substituent to the benzene ring will move toward the ring more readily than will those in the  $\sigma$  bond that attaches a hydrogen to the ring . Such a substituent donates of electrons inductively compared with a hydrogen . Donation of electrons through a  $\sigma$  bond is called **inductive electron donation** . We have seen that alkyl substituents (such as  $\text{CH}_3$ ) donate electrons inductively compared with a hydrogen



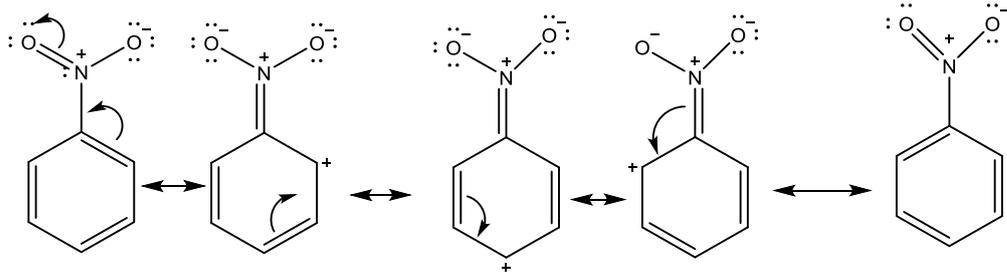
If a substituent that is bonded to a benzene ring is more electron withdrawing than a hydrogen, it will draw  $\sigma$  electrons away from the benzene ring more strongly than a hydrogen will. Withdrawal of electrons through a  $\sigma$  is called **inductive electron withdrawal**. The  $+NH_3$  group 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.

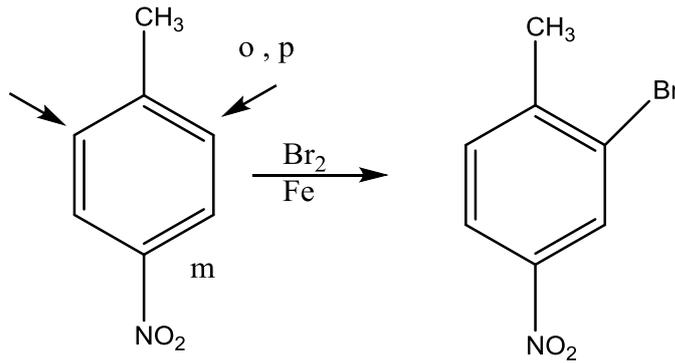


If a substituent is attached to the benzene ring by an atom that is doubly or triply bonded to a more electronegative atom, the  $\pi$  electrons of the ring can be delocalized onto the substituent. Such substituents are said to **withdraw electrons by resonance**. Substituents such as  $C=O$ ,  $C=N$ ,  $SO_3H$ , 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.

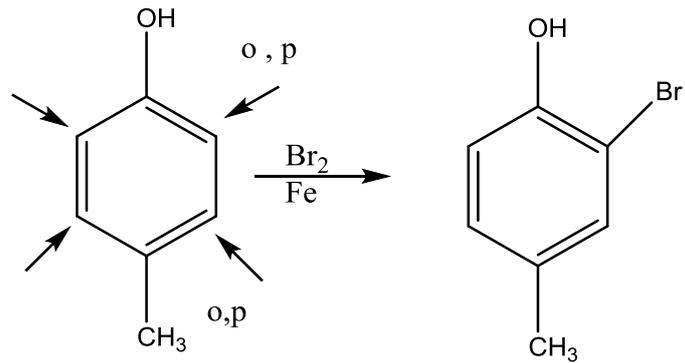


أمثلة على ذلك

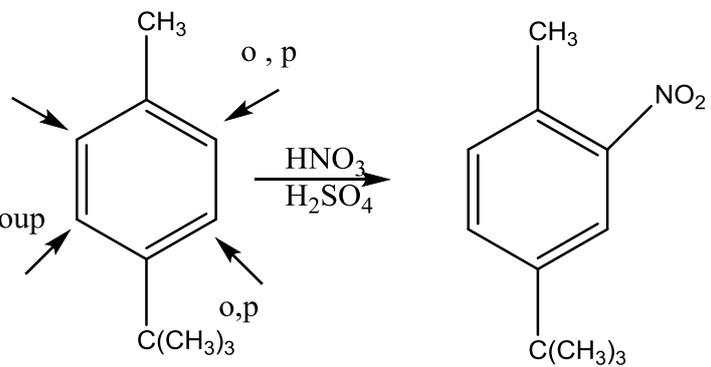
Substituents reinforce each other



Strongest activator controls



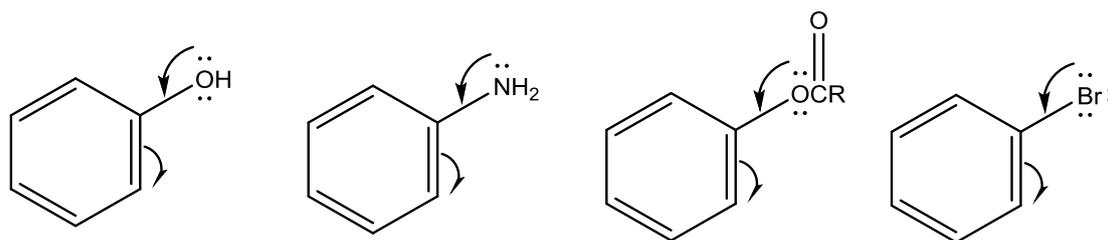
Activating effects similar, but steric effects favour ortho to are smaller methyl group



## Relative r Reactivity of Substituted Benzene

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 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.

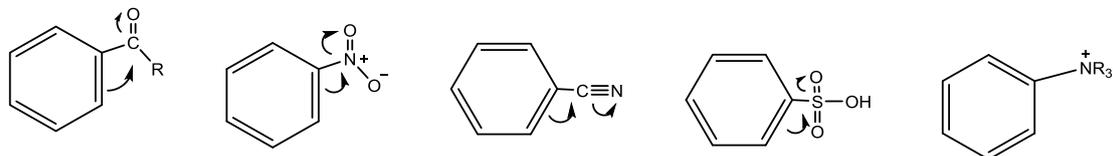


We have seen that an alkyl substituent , compared with a hydrogen , donates electrons inductively .

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 the 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

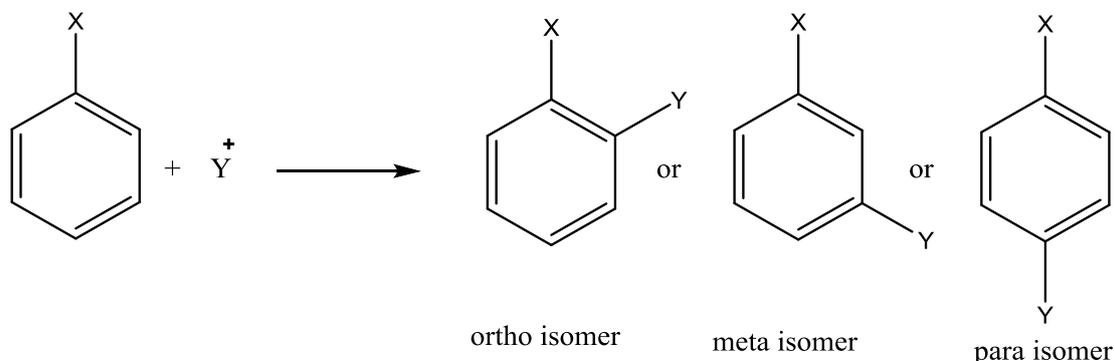
( $+NH_3$ ,  $+NH_2R$ ,  $+NHR_2$  and  $+NR_3$ ). The ammonium ions have no resonance effect, but the positive charge on the nitrogen atom causes them to strongly withdraw electrons inductively





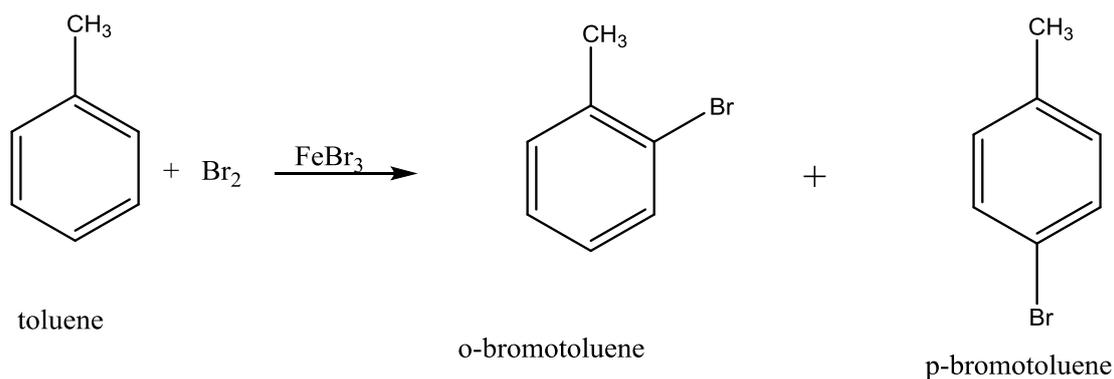
## THE EFFECT OF SUBSTITUTION ON ORIENTATION

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?

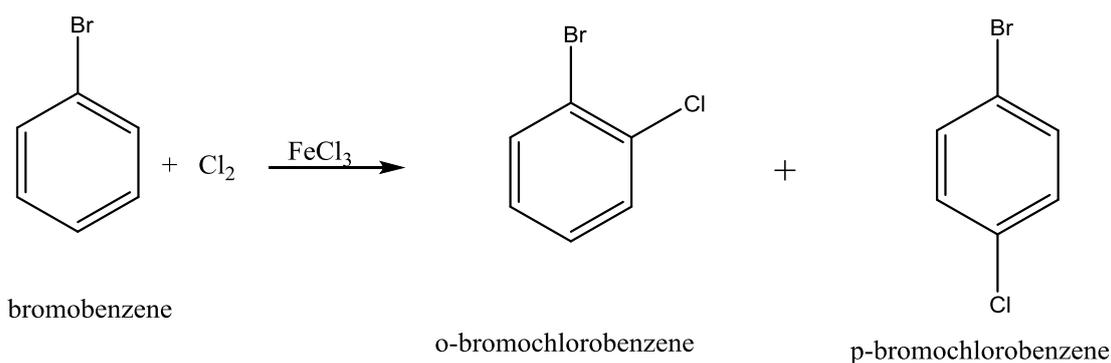


The substituent already attached to the benzene ring determines the location of the new substituent will have one of two effects an incoming substituent either to the **ortho** and **para** positions, or it will direct an incoming substituent to the **meta** positions. All activating substituents and 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:

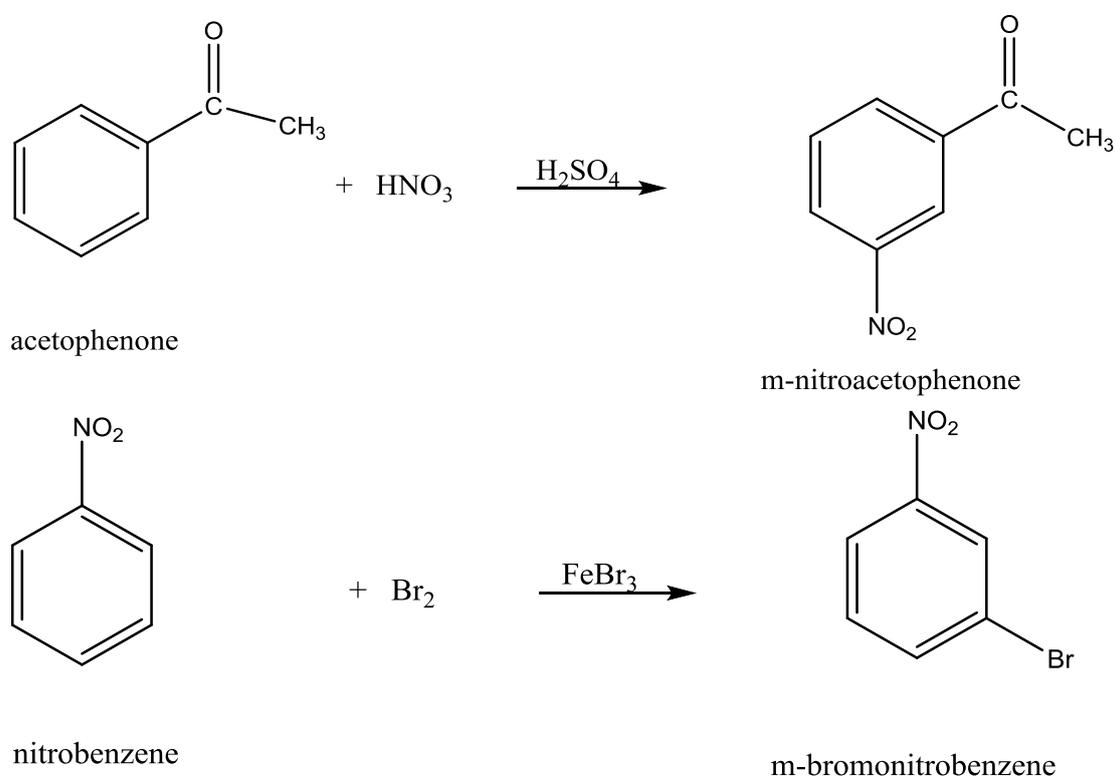
1- All activating substituents direct an incoming electrophile to the ortho and para positions



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

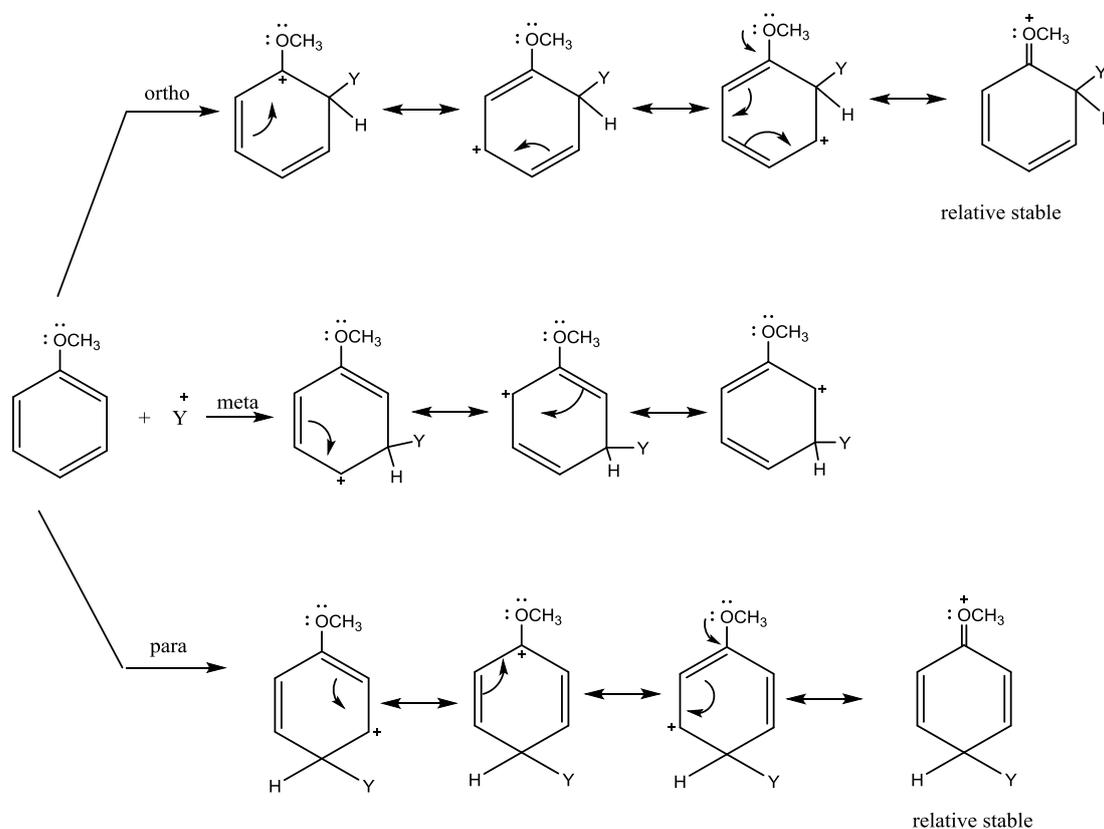


To understand why a substituent directs an incoming electrophile to a particular position, we must look at the stability of the carbocation intermediate, because as Figure 2 shows formation of the carbocation is the rate-determining step.

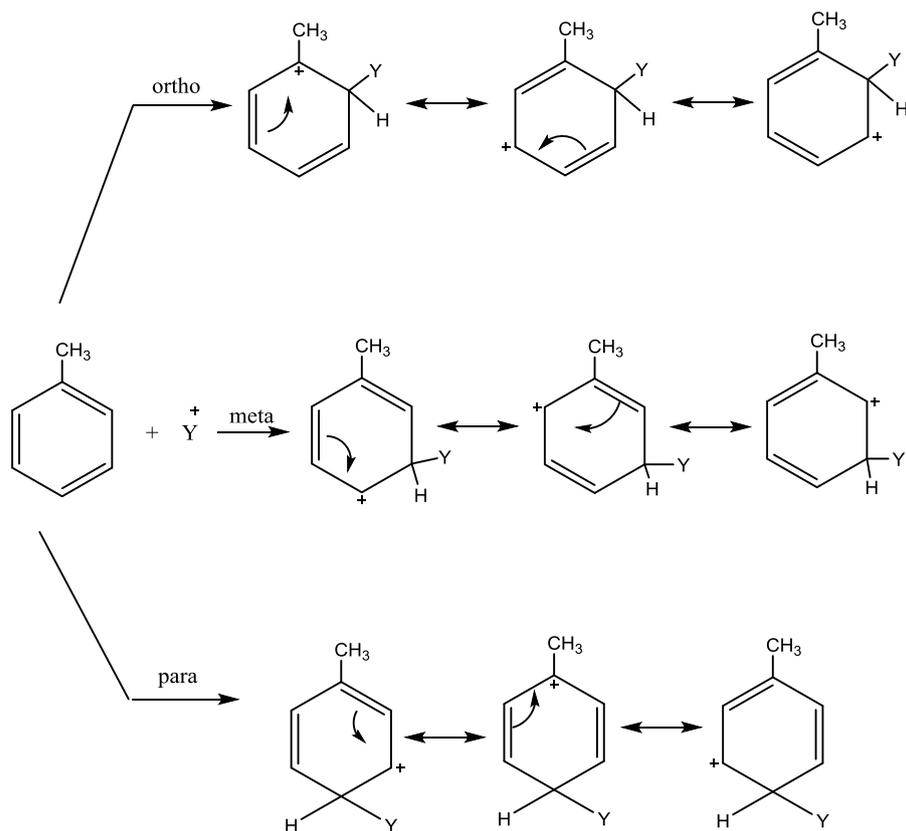
When a substituted benzene undergoes an electrophile substitution reaction, three different carbocation intermediates can be formed: an ortho-substituted carbocation, a meta-substituted carbocation, and a para-substituted carbocation (Figure 3). The relative stabilities of the three carbocations enable us to determine the preferred pathway of the reaction.

because the more stable the carbocation, the more stable transition state for its formation, and 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 stable carbocation is formed

