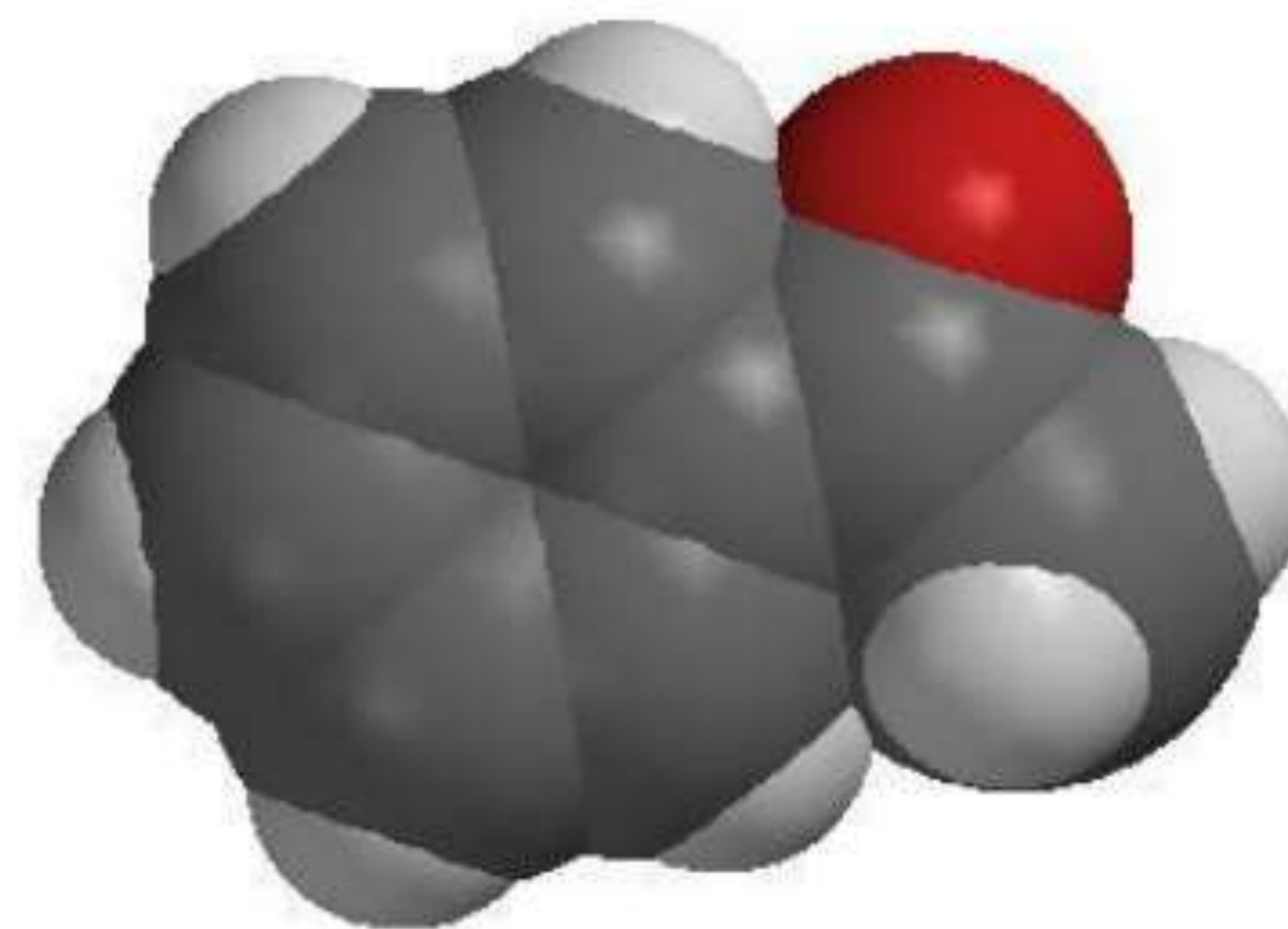


Chapter 4: Aromatic Compounds



① خصائص البنزين:

Cyclic Compound (1)

6 C (2)

6 H (3)

3 double bond (4)

2 x Db $6 \pi e^-$ (5)

general form $\rightarrow C_6H_6$ (6)

trigonal planar sp^2 120° bond angle (7)

(8) مستقر بنوكليوني

2 resonance structure that is equivalent in energy (9)

(11) كل H \leftarrow

Chemically Equivalent \leftarrow يعني متساوي التباديل مع Br مع H طالبت أي وحدة
رج اختياراً نفهم كلهم نفس معنى

(12) لتكافؤ فاصية Resonance \leftarrow قيام الرابطة التساوية (π) بتعويض متعاضداً داخل الحلقة
بسرعة مائلة اسم العام الي اكتشفه [Kekule]



* عشان صيغ البنزين عنده 2 Resonance stru \rightarrow Equivalent in energy

البنزين فعلياً بالنص

bond order Db \rightarrow 1 \leftarrow \leftarrow bond order = 1.5 (10)
bond order single bond \rightarrow 2 \leftarrow

* مع تطور العلم اكتشفنا انه



انه هاض التكل متى هو التكل الحقيقى للبنزين لأنه لعل البنزين أملاً مانيه لا رباط double و single الى فالواتح منلياً هو خلافة انه فضينا 3d_z, 3s, و 3d_{xy} رخلع عندي البنزين

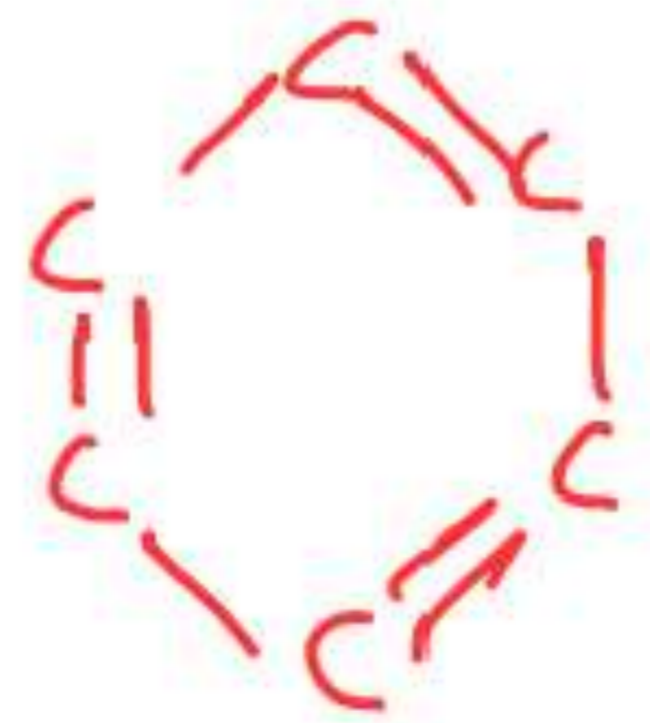
مغندي الرباط ابى هعن يكون طولها جاي بالنفس بين الأحادية والناتية ← 1.5 [أقصر من 1.5 و أطول من 1.5]
[الطول لكل الرباط متساوي]

تم تسميته بعدين بال Resonance hybrid structure
فليط



التكل الحقيقى
للبنزين

* همه بالامتنان مغلياً رح يجيبوا البنزين بعابى ال 3 صوره ←

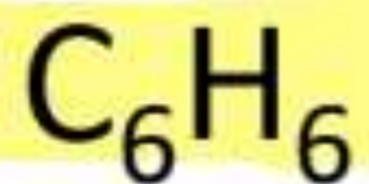


General Properties

Benzene:

System
ال
مخالف مجموع

— formula:



Conjugated

— IHD:

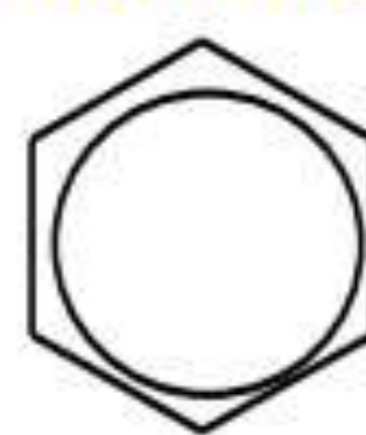
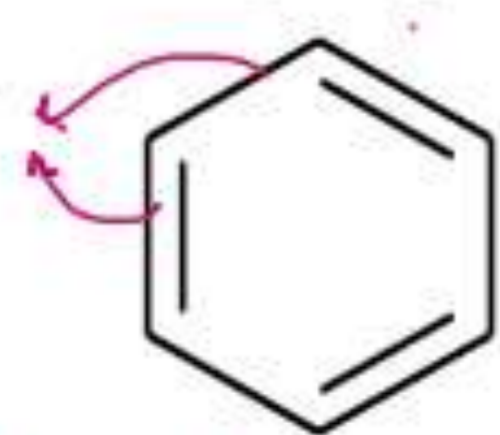
4 (highly unsaturated)

- chemical reactivity: substitution, but only 1 product \therefore all H atoms must be equivalent
- structure: cyclic, planar, sp^2 hybridized

طابقت بائي
مرهه رخ العمل
التفاعل.

- Benzene is **cyclic**, is **planar**,
- has an **interrupted cloud of π electrons**,
- and has **three pairs of electrons in the π cloud**.

Resonance
لا تميز بين
bond C
مخالف مجموع
مخالف مجموع
مخالف مجموع



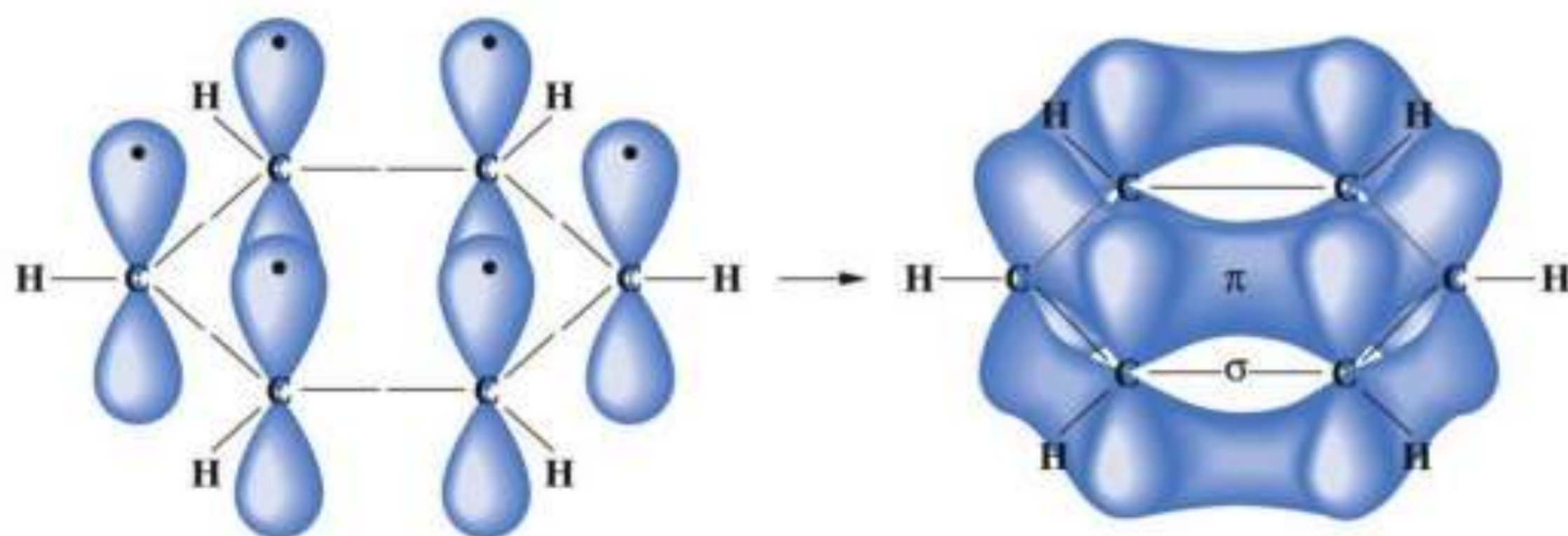
Kekule structure

Robinson structure

General Properties

Benzene:

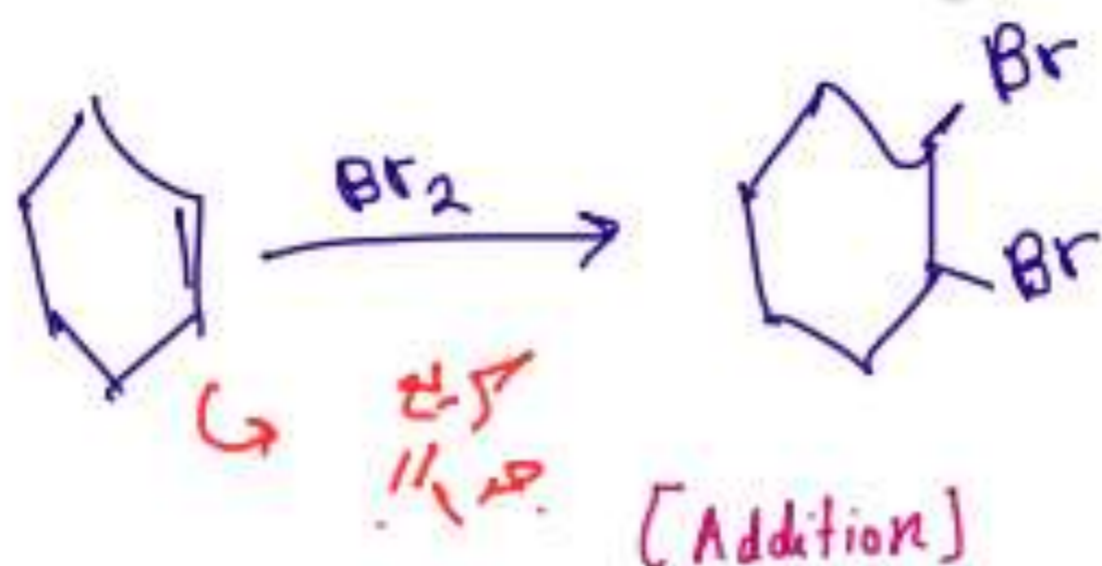
- C-C bond length: 1.39 Å
 - Intermediate to C-C (1.54 Å) and C=C (1.34 Å)
 - All C-C bond lengths are the same → resonance!



2

General Properties

Benzene:



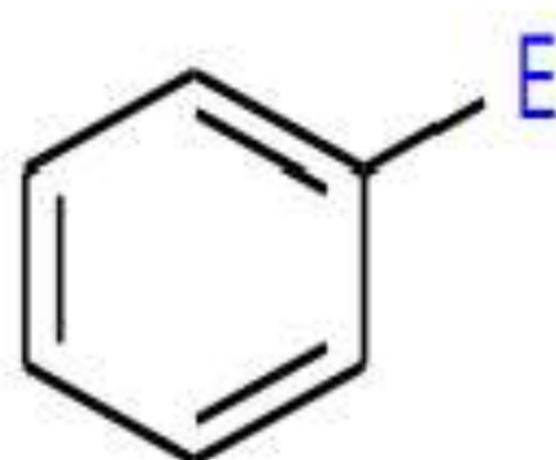
يعني مكانه
تحاول يحافظ
Resonance
structure

Chemical reactivity: electrophilic substitution

[Substitution]
لحفظ يحافظ

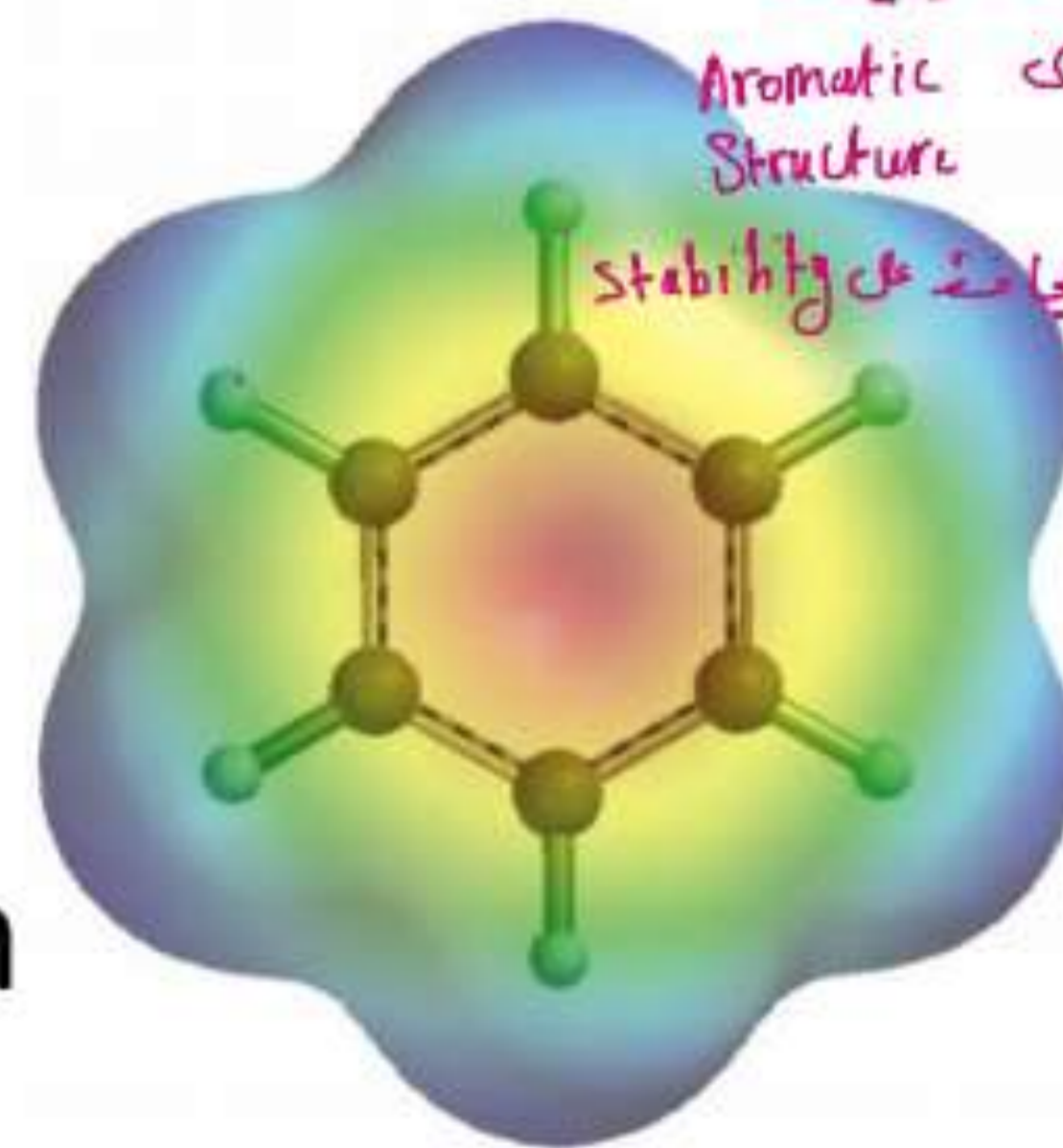


E^+

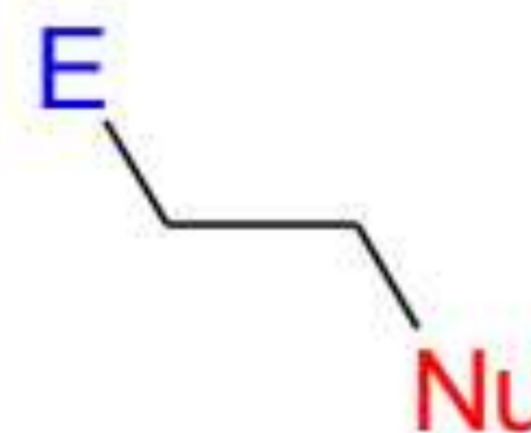
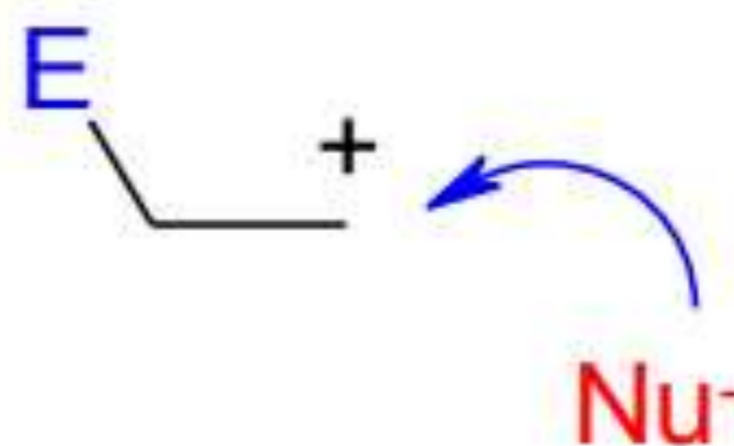
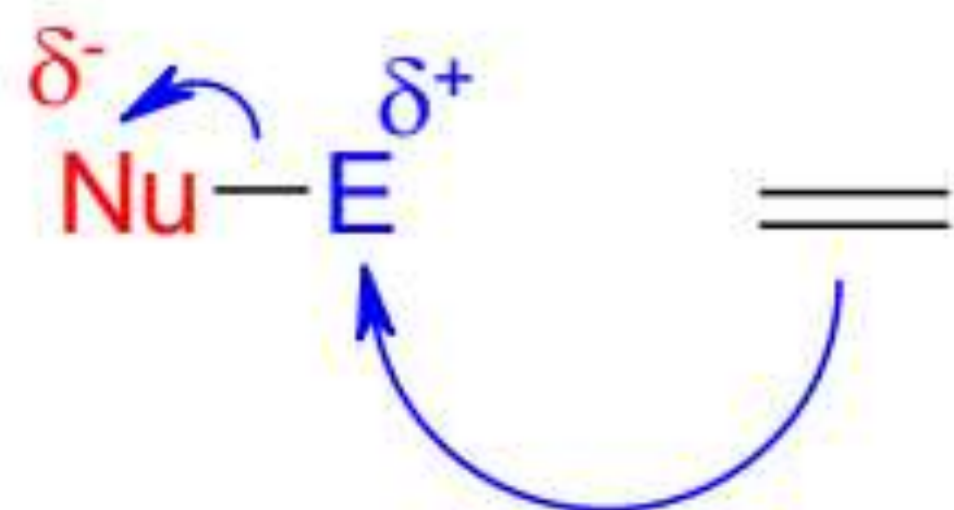


H^+

Aromatic
Structure
ويحافظ على stability



as opposed to electrophilic addition



General Properties

Why the difference between benzene and an alkene?

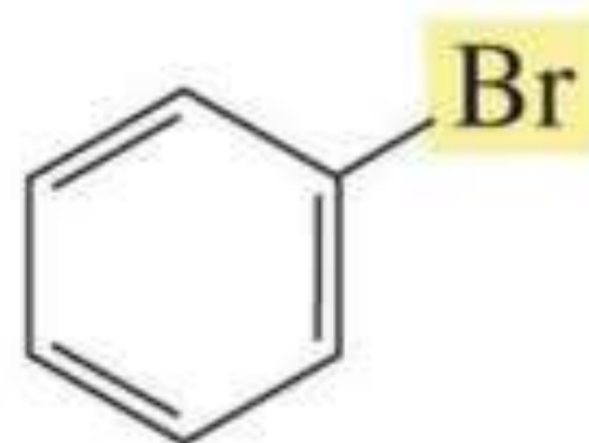
Aromaticity: the extra stability associated with aromatic compounds.

Aromatic compounds are:

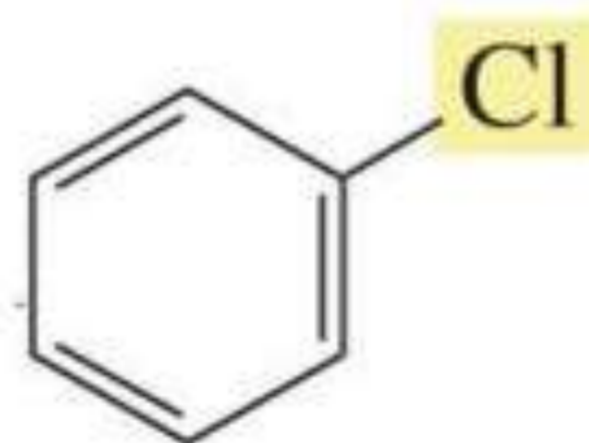
- Cyclic
 - planar
 - fully conjugated
 - contain $4n + 2 \pi$ electrons ($n=1,2,3\dots$) (Huckel's rule: equivalent to an odd number of π electrons pairs in the ring system).
- Handwritten notes:*
نظير في استوى واحد (في جانب بعض) →
* إذا التزمت طبق هامي القاعدة تكون Aromatic عدد صحيح →
 $4(1) + 2\pi = 6\pi$
 $4(2) + 2\pi = 10\pi$
 $4(0) + 2\pi = 2\pi \dots$
Aromatic

Naming Monosubstituted Benzenes

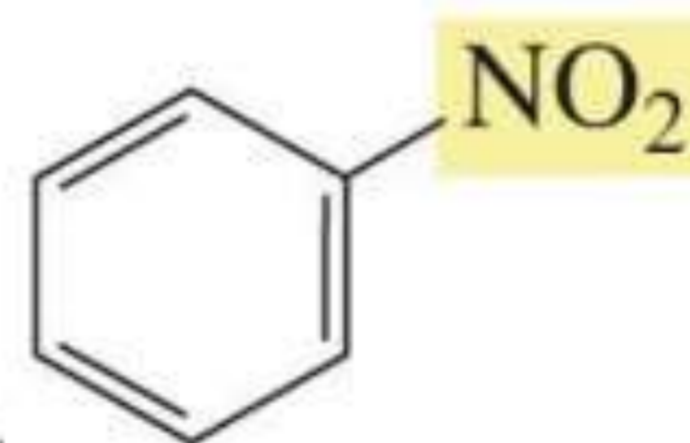
Some monosubstituted benzenes are named by **adding the name** of the substituent to “**benzene.**”



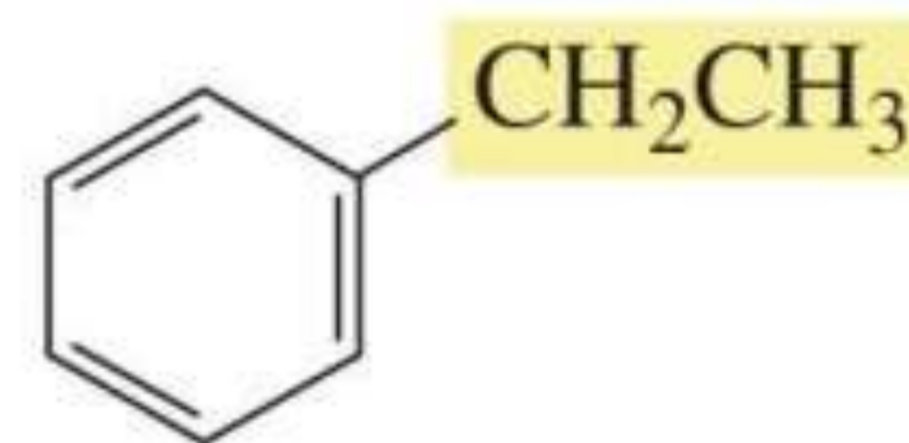
bromobenzene



chlorobenzene



nitrobenzene



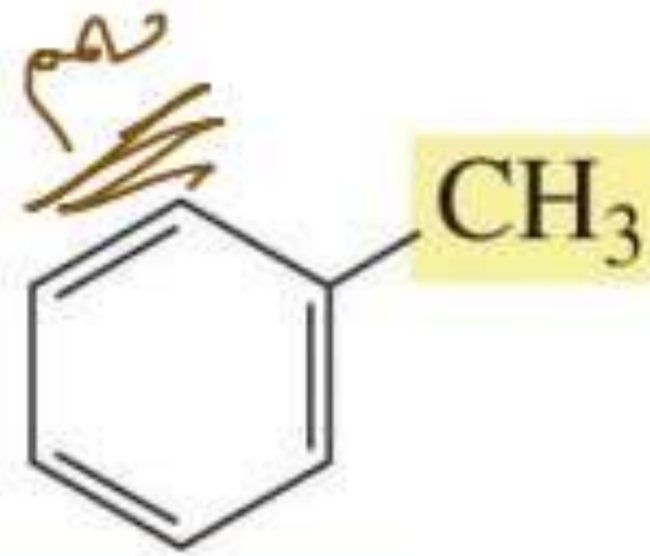
ethylbenzene

للمركبات العطرية
Cycloalkane

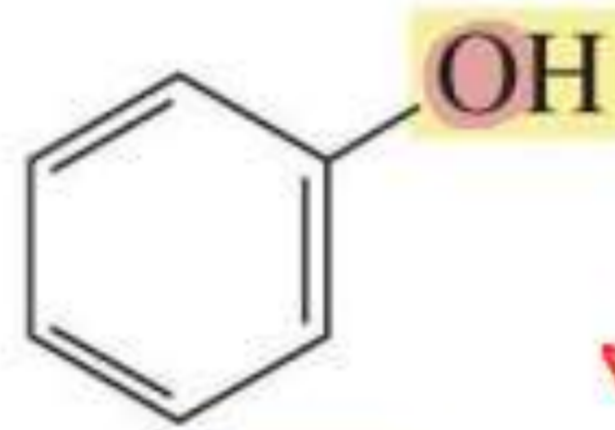
Naming Monosubstituted Benzenes

حفظ

Some monosubstituted benzenes have names that incorporate the substituent.

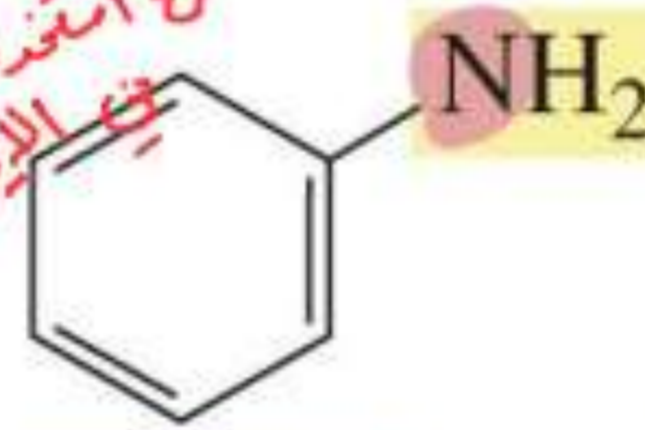


toluene



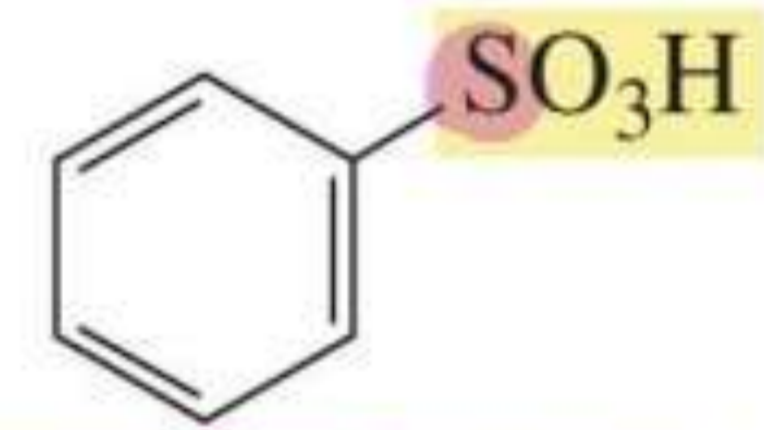
phenol

Alkyl Group ← المجموع هو
As root name استخدموا
في الأيوباء



aniline

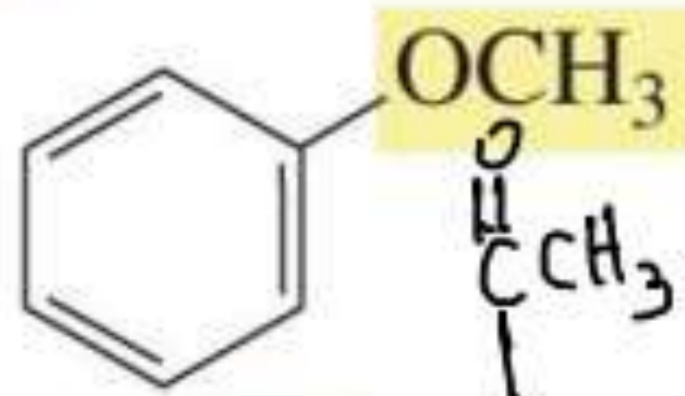
لأنه أمين



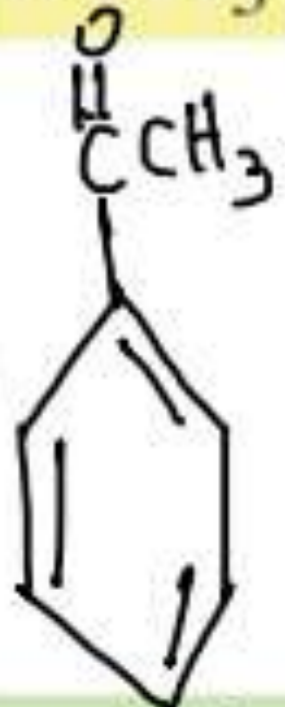
benzenesulfonic acid

[Common name]
لبعض الفروع

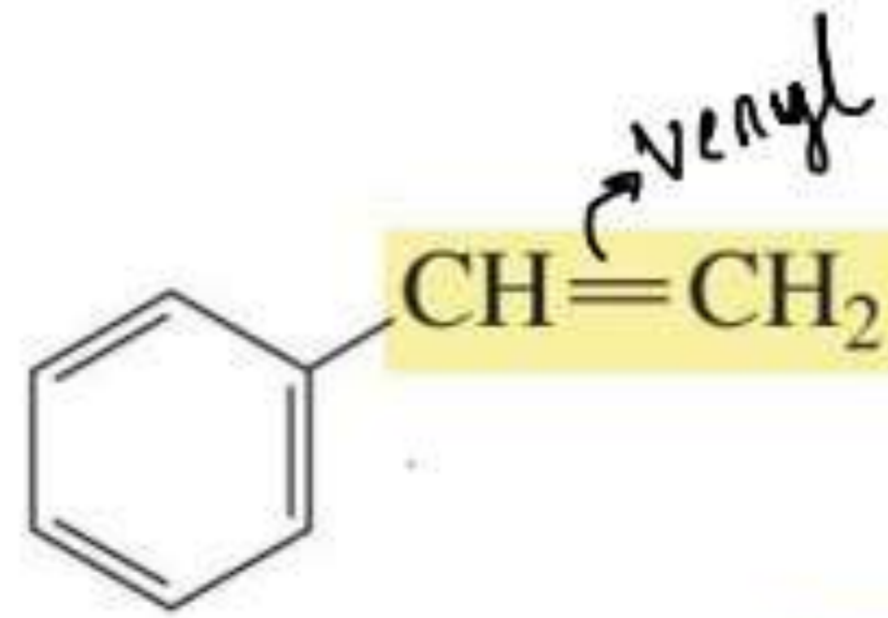
لأنه قادر على
التلون
أولئك أسماء تولين



anisole

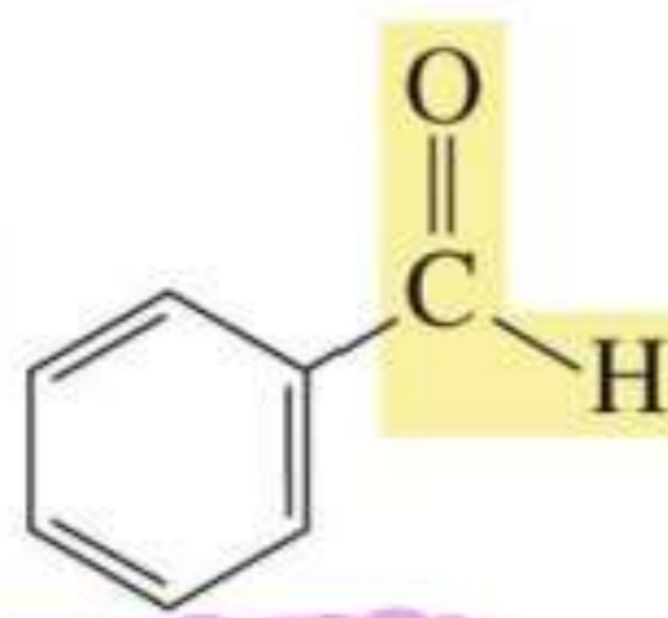


Acetophenone

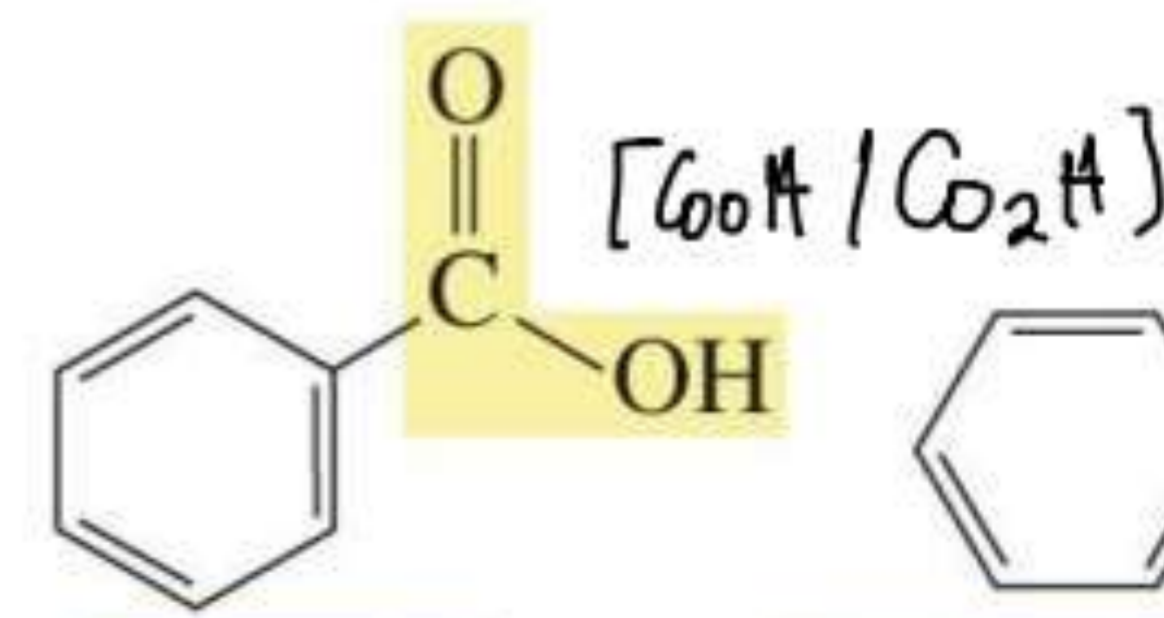


styrene

vinyl

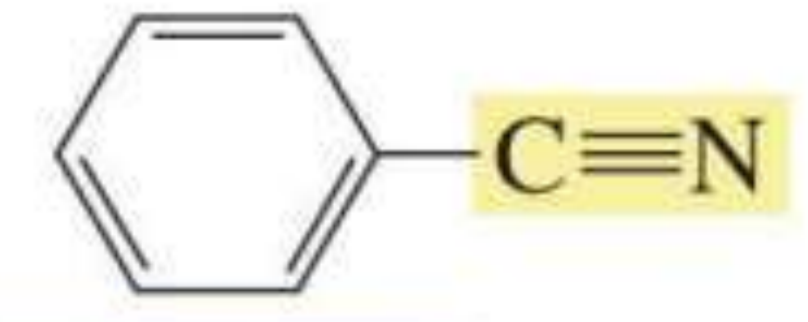


benzaldehyde



benzoic acid

[COOH / CO2H]



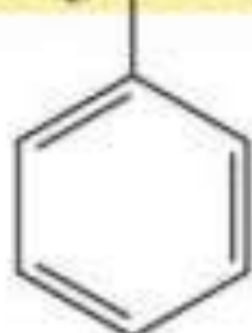
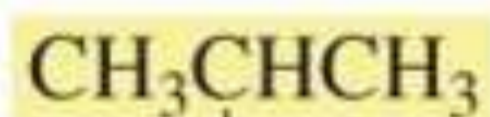
benzonitrile

Alkyl-Substituted Benzenes

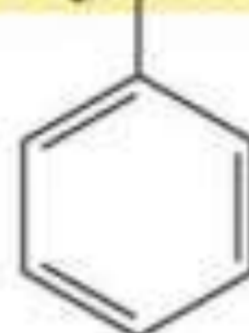
[تفرع واحد] → Named as alkyl benzene.

نفسه انه ما يحط
اقم قبل الـ ٣

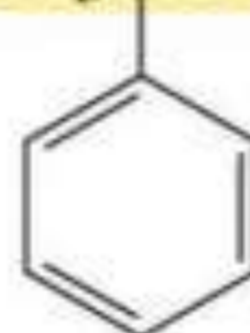
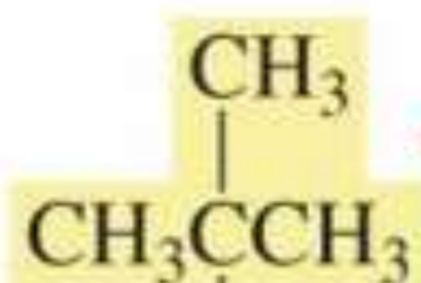
يقوم بتذكر
جموعه الألكيل
المتصلة بالبنزين
بعض لحظ ٢٥٥



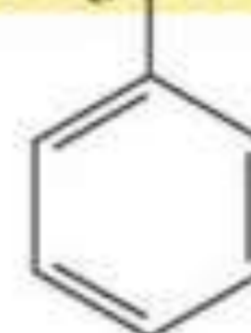
isopropylbenzene
cumene



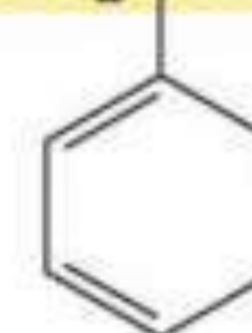
sec-butylbenzene



tert-butylbenzene



2-phenylpentane



3-phenylpentane

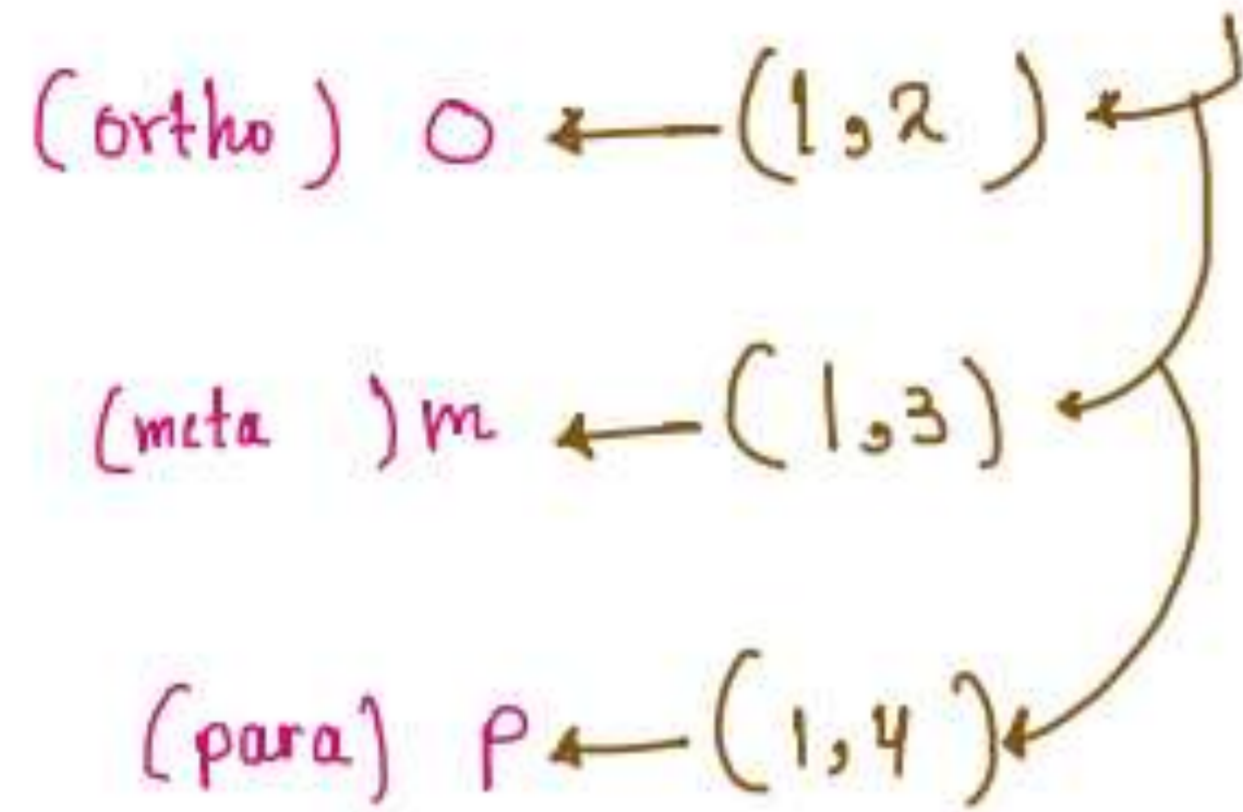
Name as an **alkyl-substituted benzene**
when the alkyl group has a name.

Otherwise, name as a **phenyl-substituted alkane**.

Toluene (methyl substituent on benzene) is an exception.

* اسمه بالا متجان غالباً يجب البنزين الي عليه تفرعين وضوت

* اسمه في البنزين ذر التفرعين فقط
 يوجد حالة خاصة للتعيين عن مواقع التفرحات بالأحرف
 بدل التفرحات :-

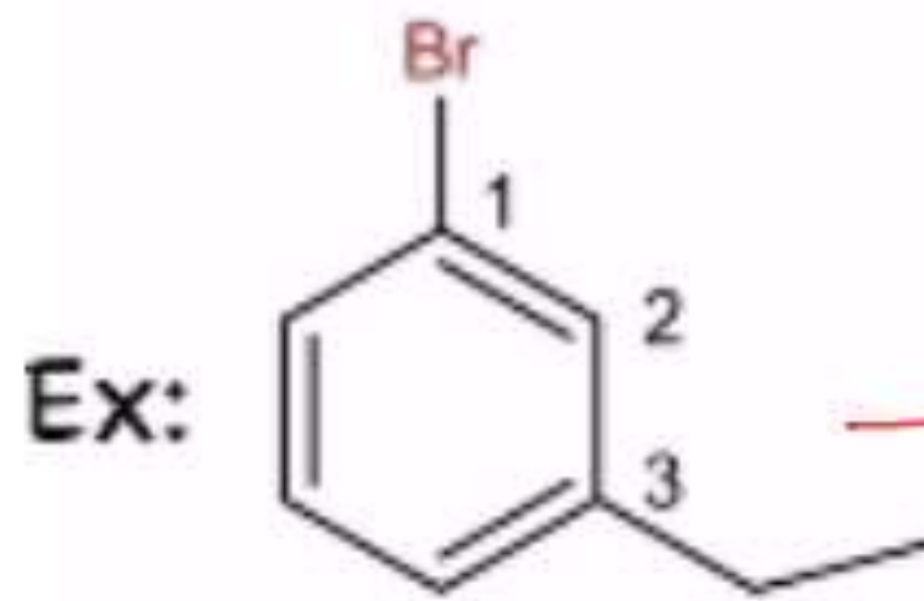


(2) البنزين الي عليه تفرعين :-

- (1) كلا من التفرعين not common
- (2) واحد common والثاني not common
- (3) كلا منهم common

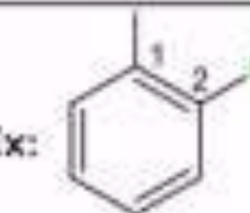
① الحالة الأولى :-

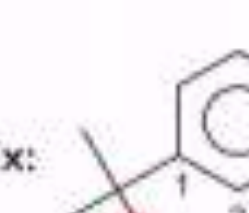
نسمه التفرع الي يوجد ثم اهو للتفرع الي الاله الارادية بجانباً بعدين لترجم بحيث الثاني يوجد أقل ترتيب



→ m-bromoethyl benzene / 1-bromo-3-Ethylbenzene

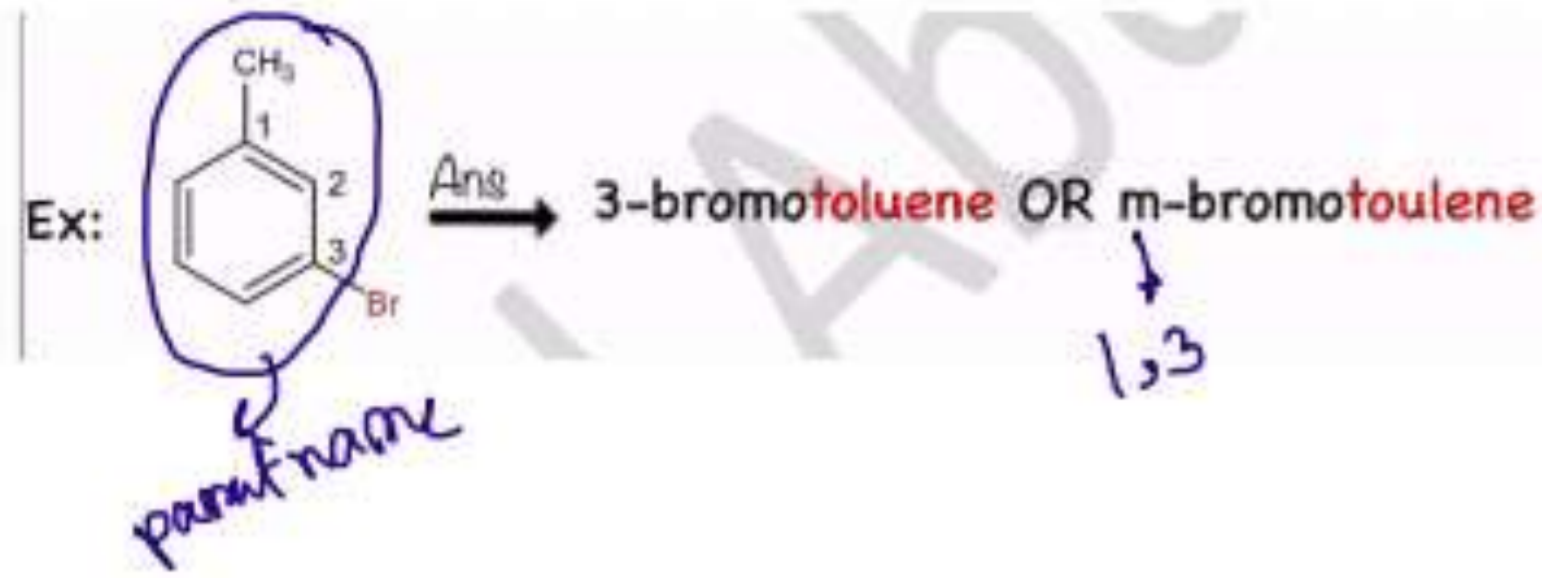
التنين مع يعني
 بحيث بالخيارات
 واحد منهم ليس

Ex:  Ans: 1,2-dichloro benzene OR o-dichloro benzene

Ex:  Ans: 1-tert-butyl-4-fluoro benzene OR p-tert-butylfluoro benzene

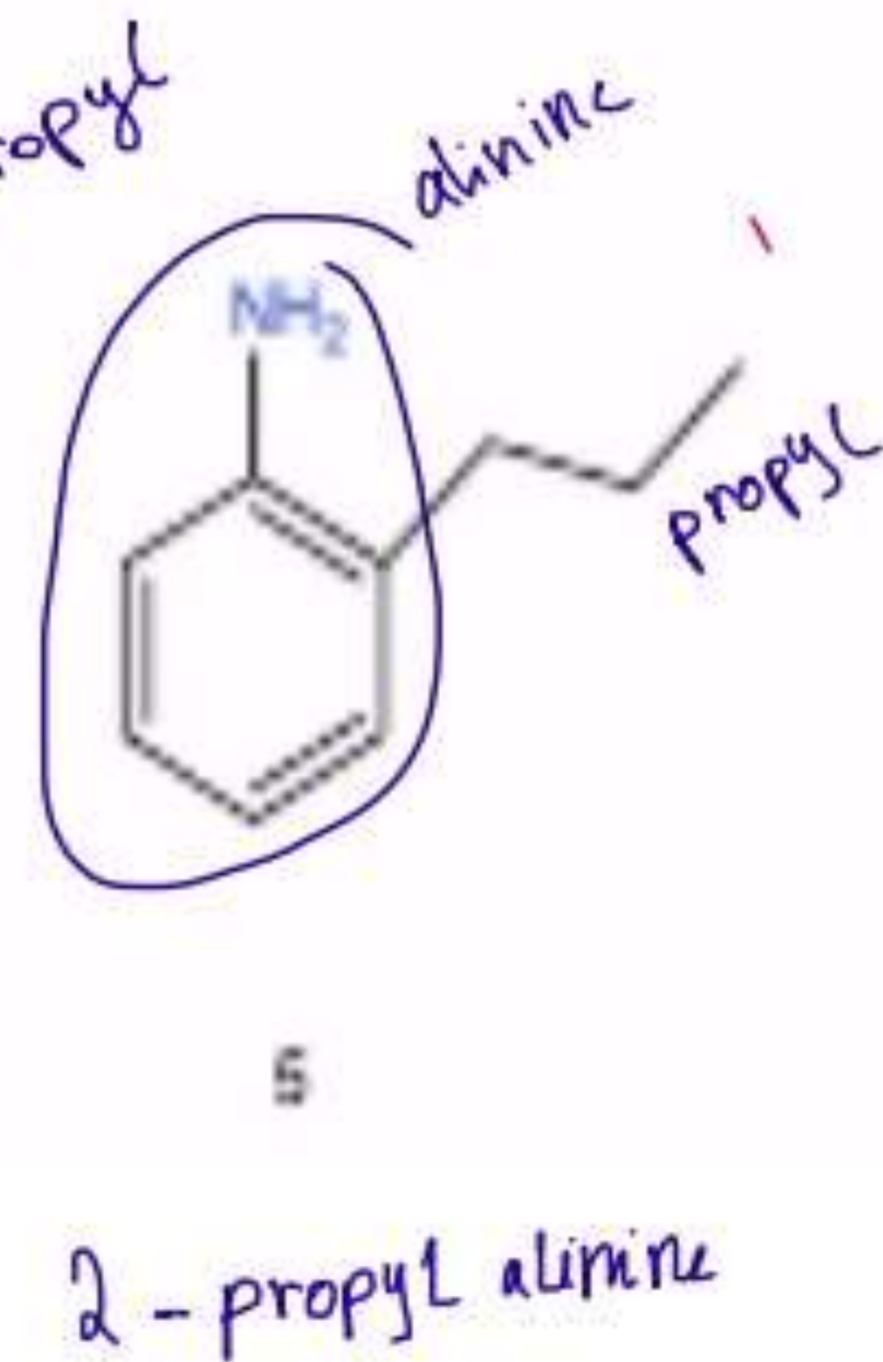
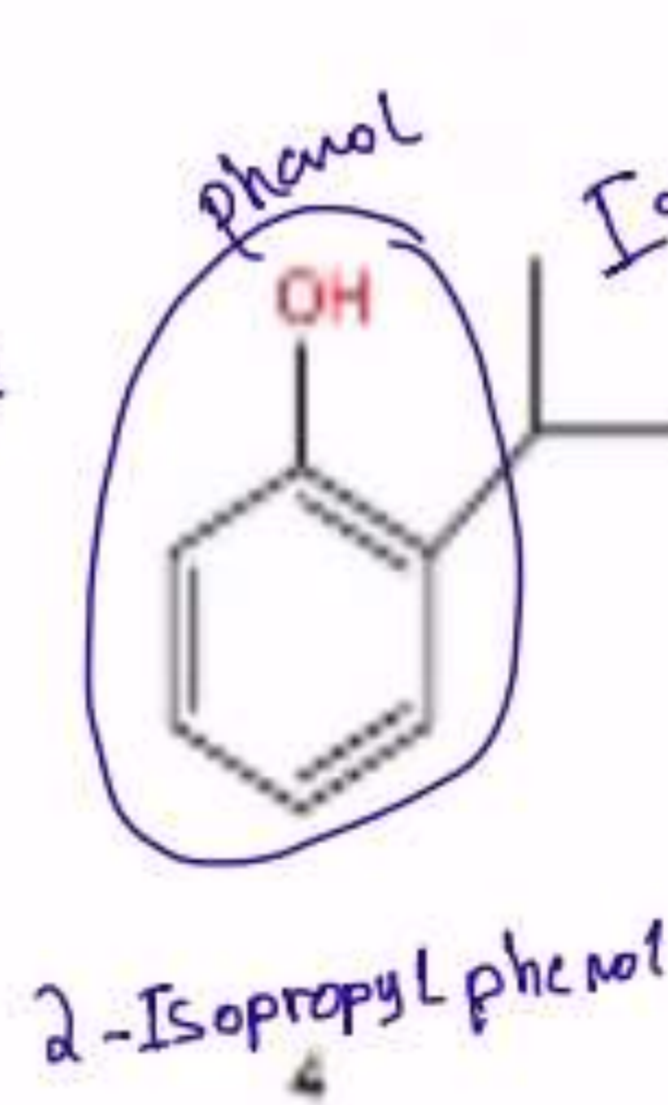
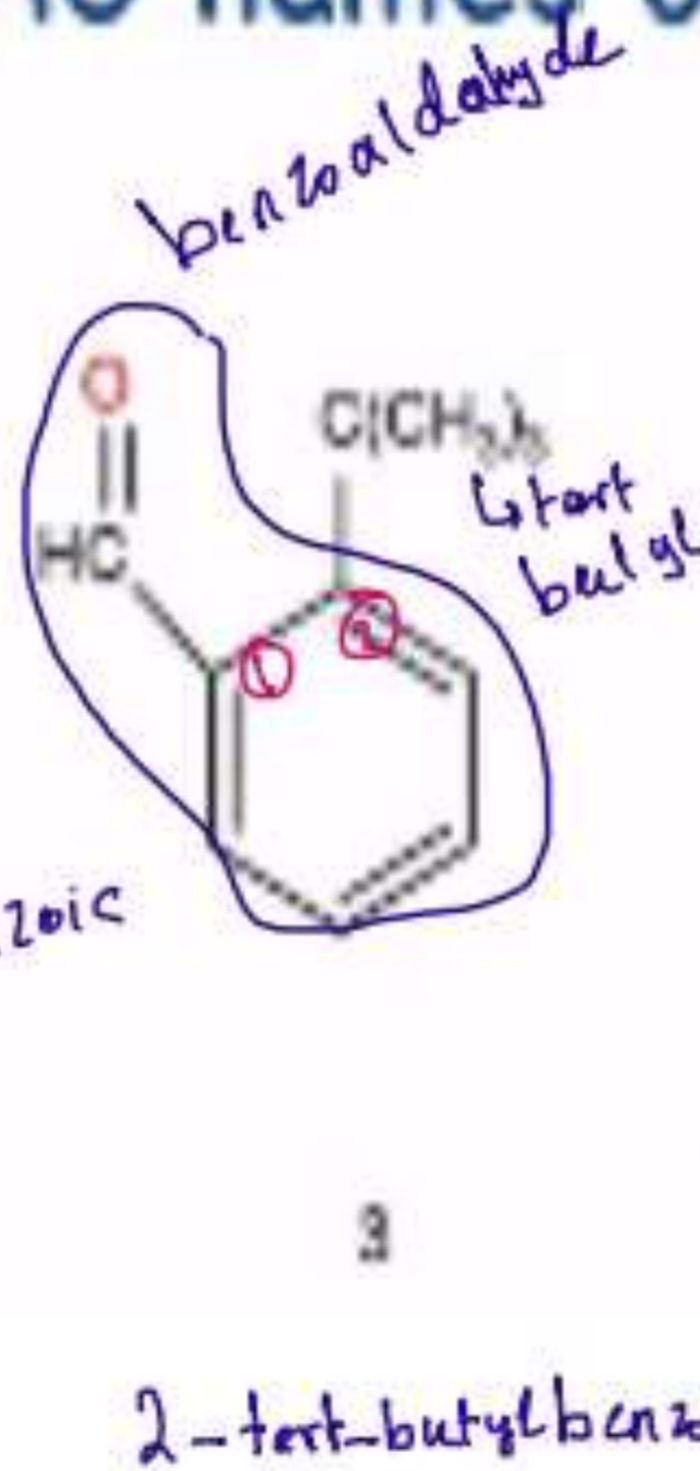
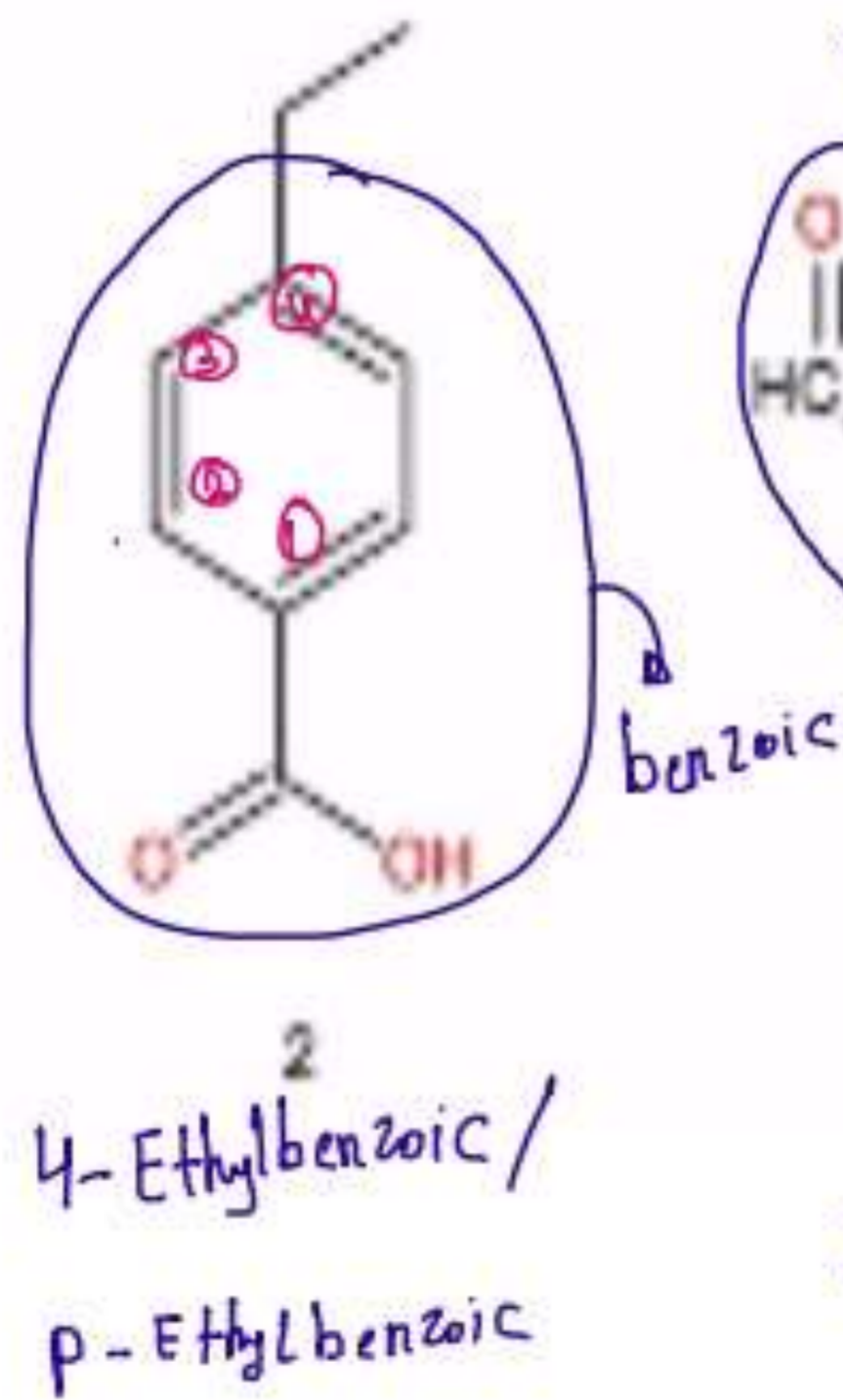
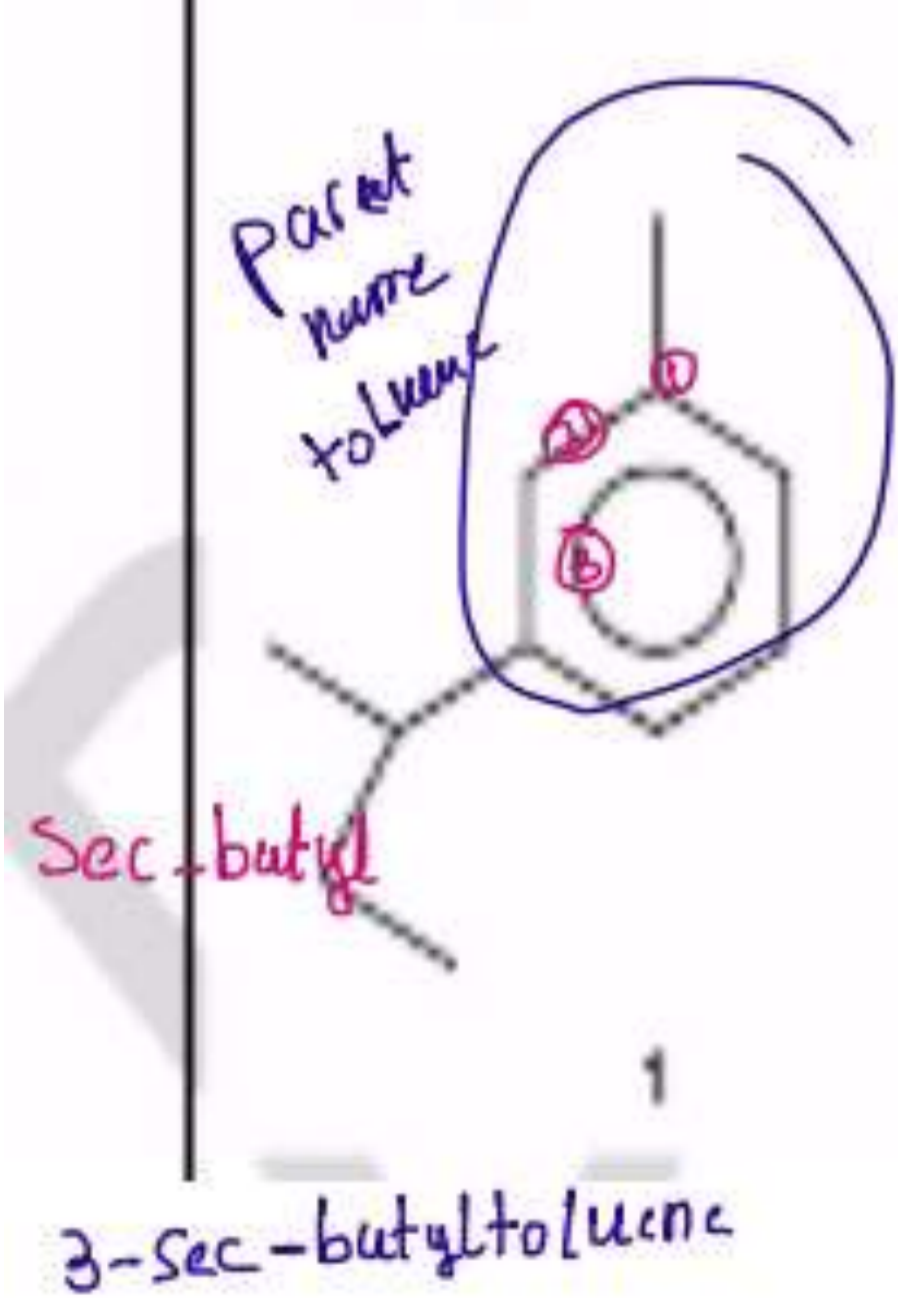
ملاحظة :- انه مايسر ابدل بالاماكن
 بعد اضافة يعني اخط methyl قبل chloro مثلا

Common parent name يكون باسم التفرع أو Common بعدد لا Not Common وال



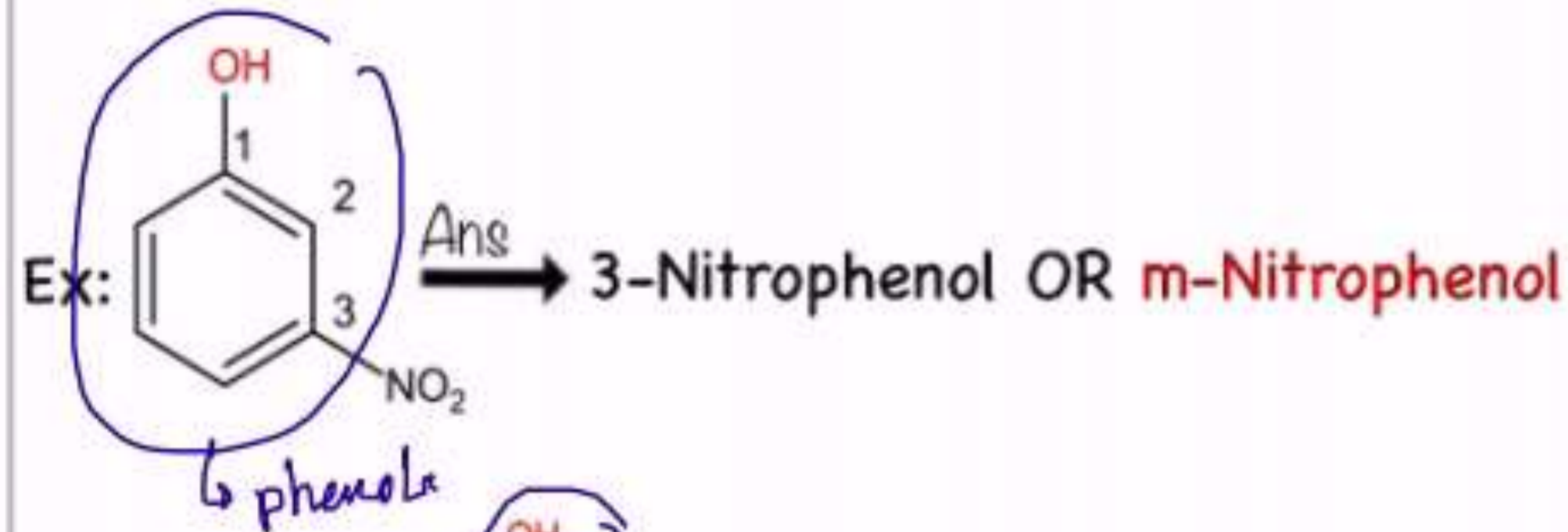
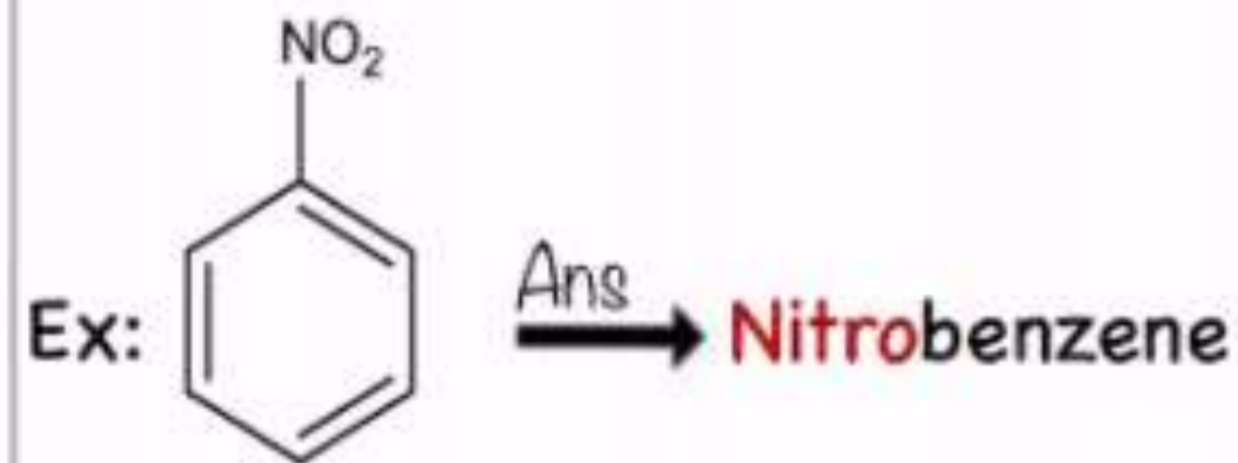
Let's Practice

Give the IUPAC names of the following compounds?



* ملاحظة - في عندي تفرع هـ هو NO₂ اسمه (Nitro) ويعتبر تفرع (Not common).

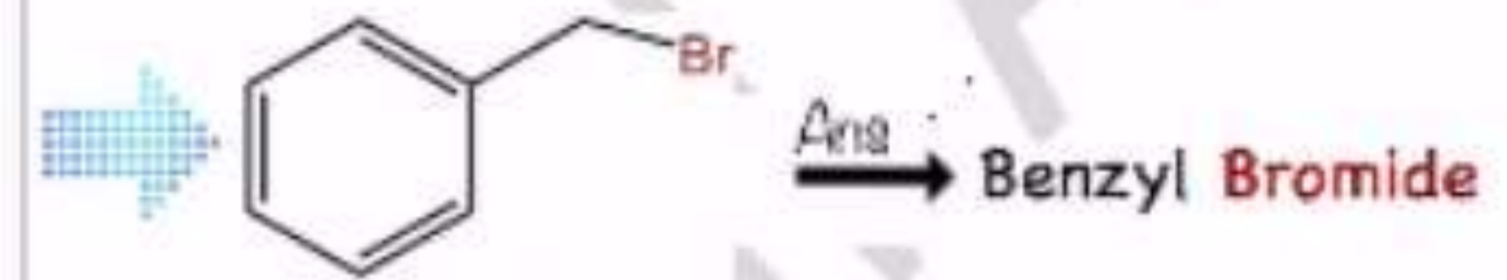
.. هذا التفرع هو (NO₂) واسمه (Nitro) ويعتبر تفرع (Not common):



التفرع (benzyl)
benzene + CH₂

phenole
[parent name]

Q: Give the common name of this compound?

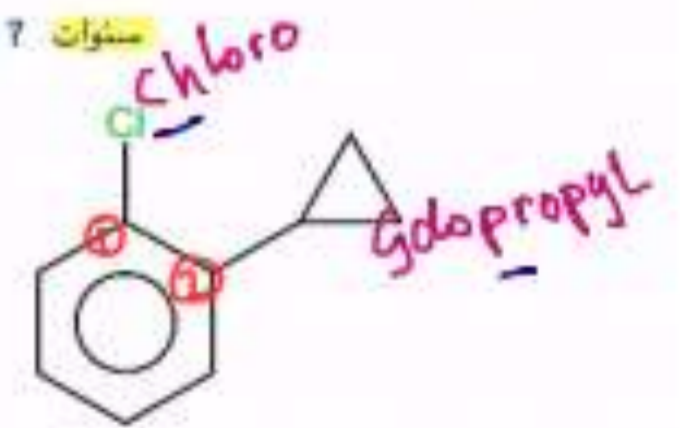


ال common name لاي
مركب فيه هالوجين يشطب
على الهالوجين ويسمي الي
متصل فيه كتفرع ويحط
للهاالوجين على شكل ide

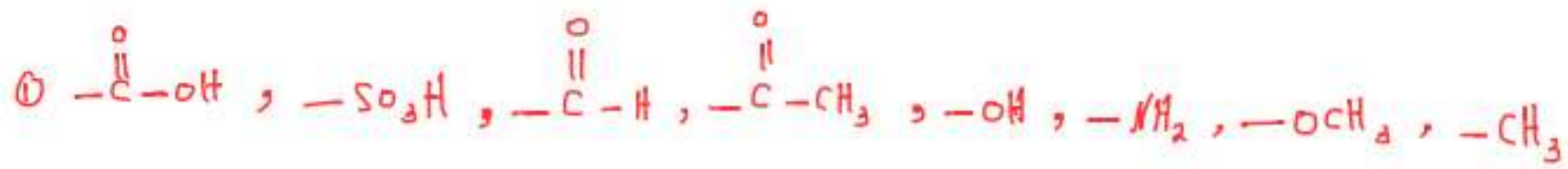
هـ في عندي

Q: What is the IUPAC name of this compound?

- (A) o-chlorocyclopropylbenzene
- (B) o-cyclopropylchlorobenzene
- (C) chlorophenyl cyclopropane
- (D) cyclopropylchloro benzene



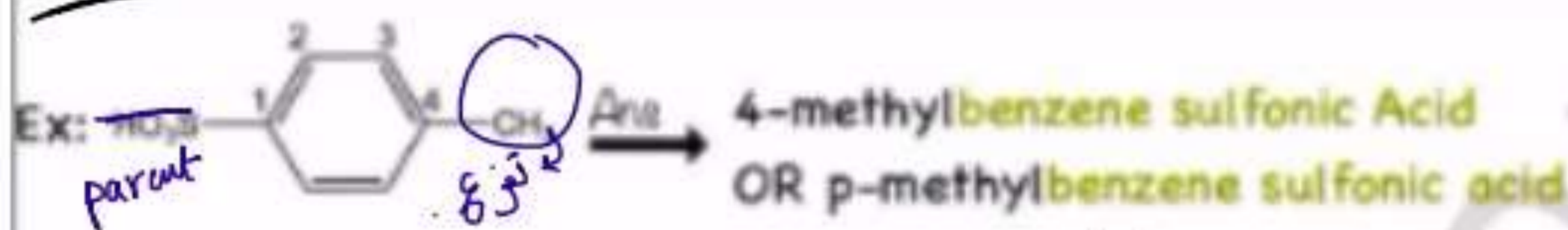
(3) الحالة (ج)



الأقل أولوية → الأمثل أولوية

COOH

لبنوات



هنا ال (SO3H) هي التي تأخذ رقم 1 ونسمي المركب باسمها (benzene sulfonic acid) لان لها اولوية على ال (CH3) حسب الترتيب فوق



Commones ← كتفزع

OCH_3 ← methoxy

NH_2 ← Amino

$-\text{C}(=\text{O})\text{CH}_3$ ← oxo

$-\text{C}(=\text{O})\text{H}$ ← Formyl

الترتيب الى عليه ٣ ترتيبات: [صم]

* لا نستخدم $(0, p, m)$ هون بس بستعملهم بأبوالترتيب

هل الترتيبات Not Common
واحد Common أو أكثر

① الحالة الأولى :-

* نفس تسمية GlobalKane الى د ch 2

* باختصار جتار C رقم البعدية بكم الترتيب بناء على الترتيب الى يعطى أقل ترتيب و ال C رقم البرض جتارها بناء على الى روح تعطينا أقل ترتيب
وإذا تشارك الترتيب بلجا المعاني

② الحالة (2) :-

* ال Common هو الي بوجه رقم البعدية برقم حسب الترتيب الأخرى

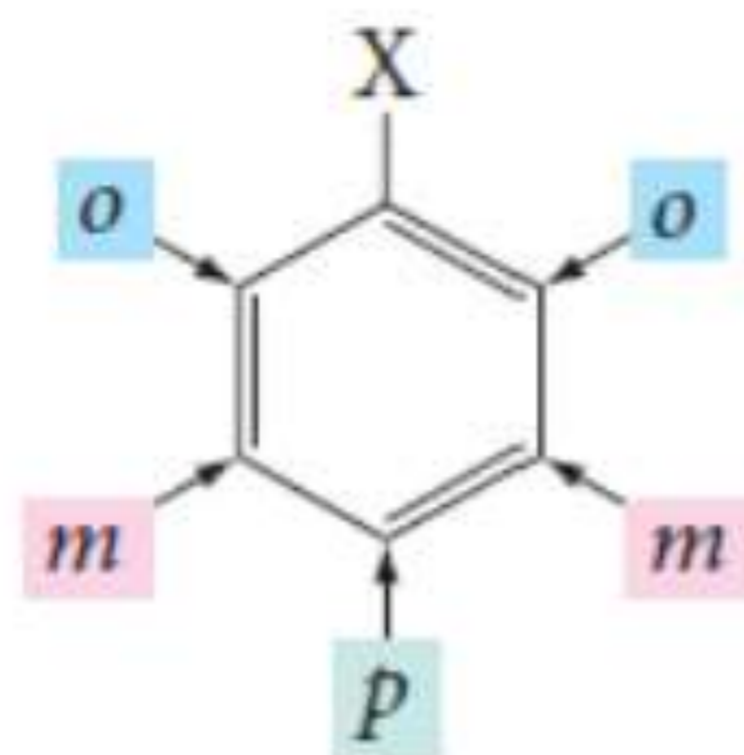
* إذا كان في عند Common 2 الي بوجه رقم (1) حسب الأدلية يكون بعد الي بوجه رقم 2 هي الي تعطى الترتيب الأخرى

* في طريقة تناو هدها أيام
المررة على نطلع الأخرى ترتيب
هي انه نجمع الأرقام و الترتيب الى
لحظي المجموع الأخرى هو الي بوجه

مثال 1) $1+6+4 = 13$

2) $1+3+5 = 9$

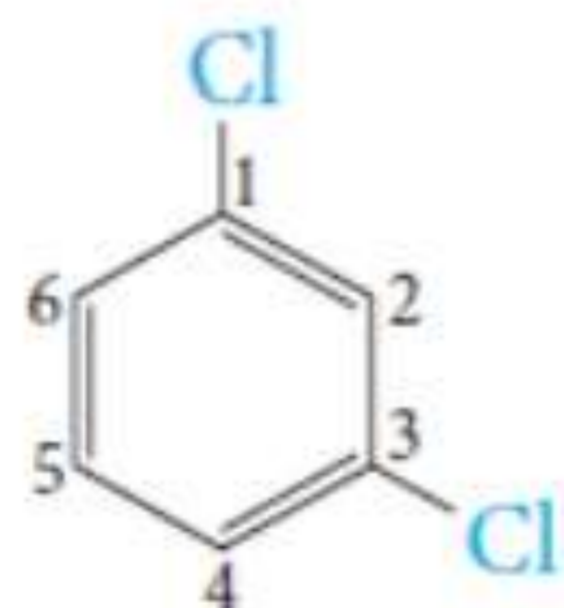
When two substituents are present, three isomeric structures are possible.



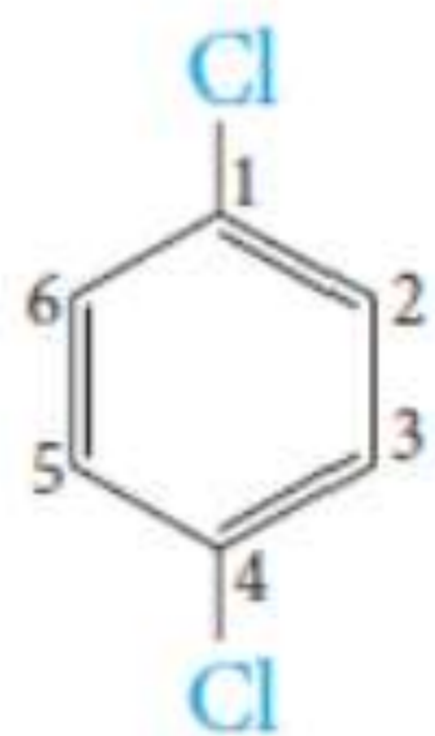
Specific examples are



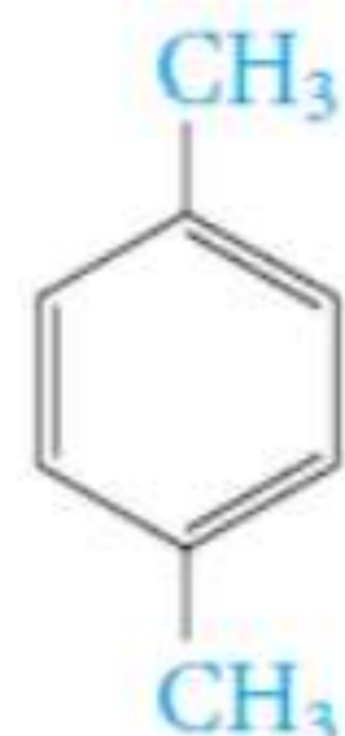
ortho-dichloro-
benzene



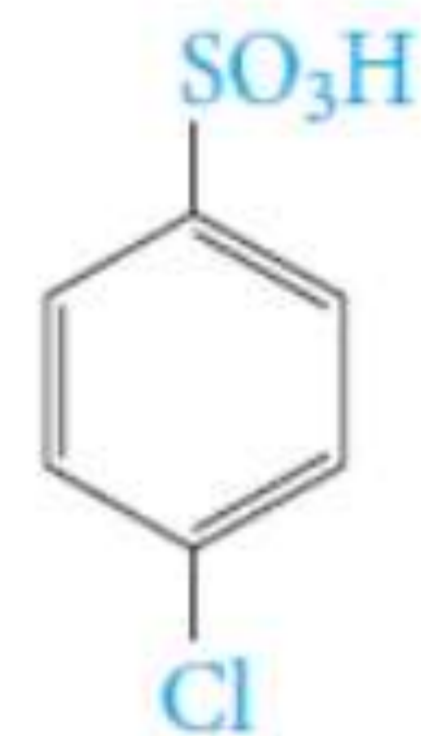
meta-dichloro-
benzene



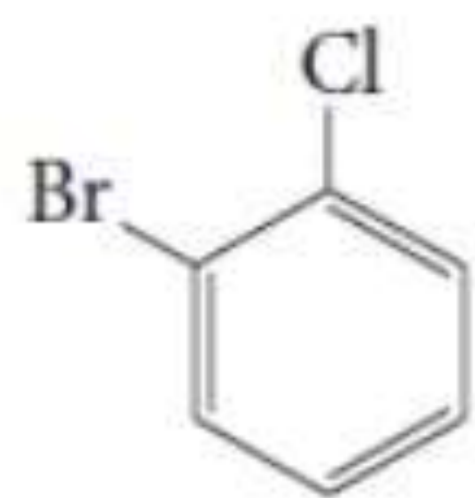
para-dichloro-
benzene



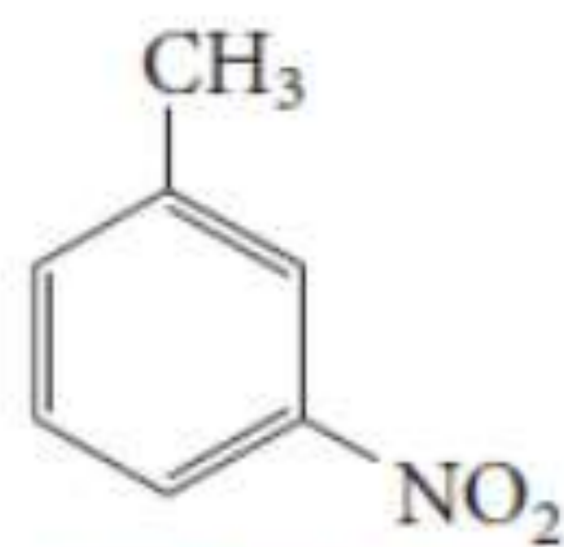
para-xylene**



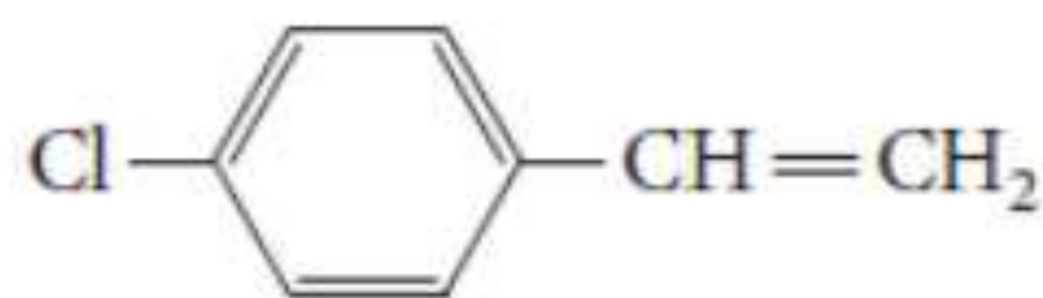
para-chlorobenzenesulfonic
acid



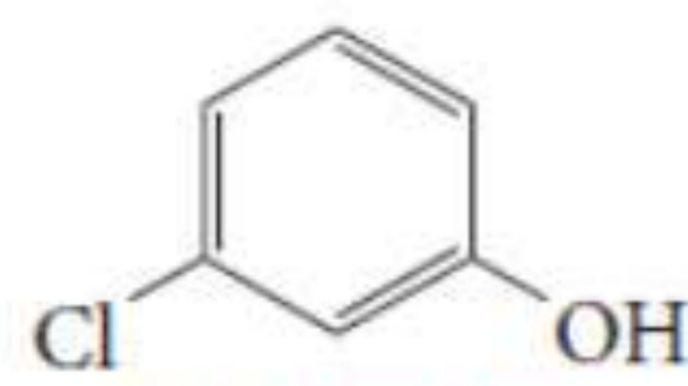
o-bromochlorobenzene
(note alphabetical order)



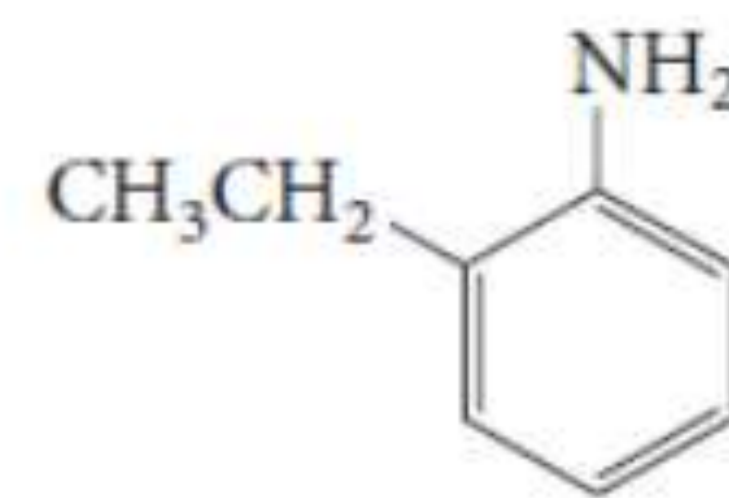
m-nitrotoluene



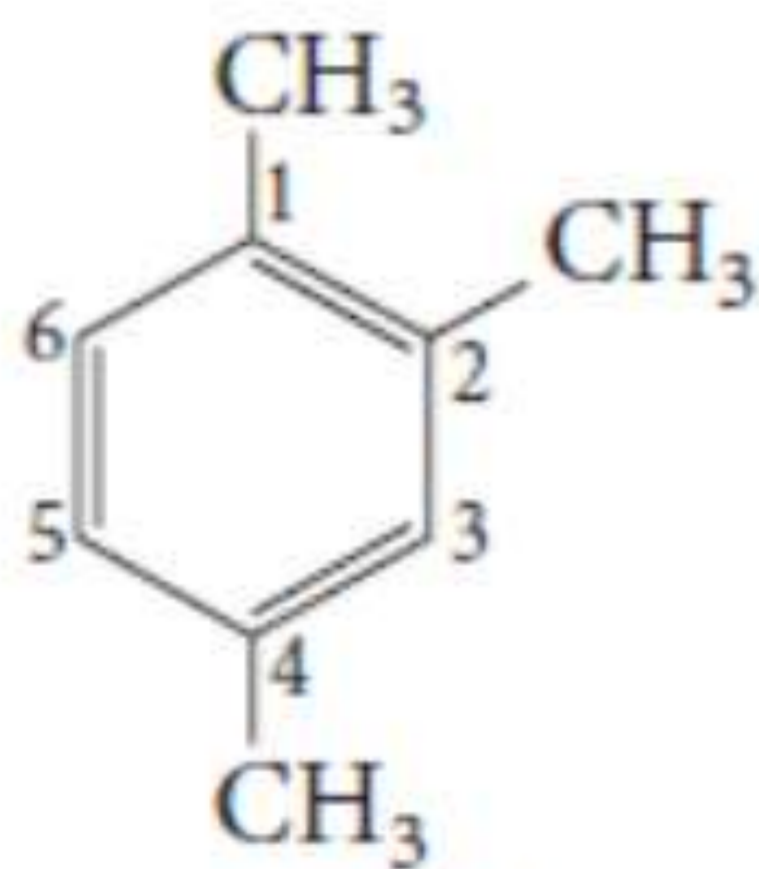
p-chlorostyrene



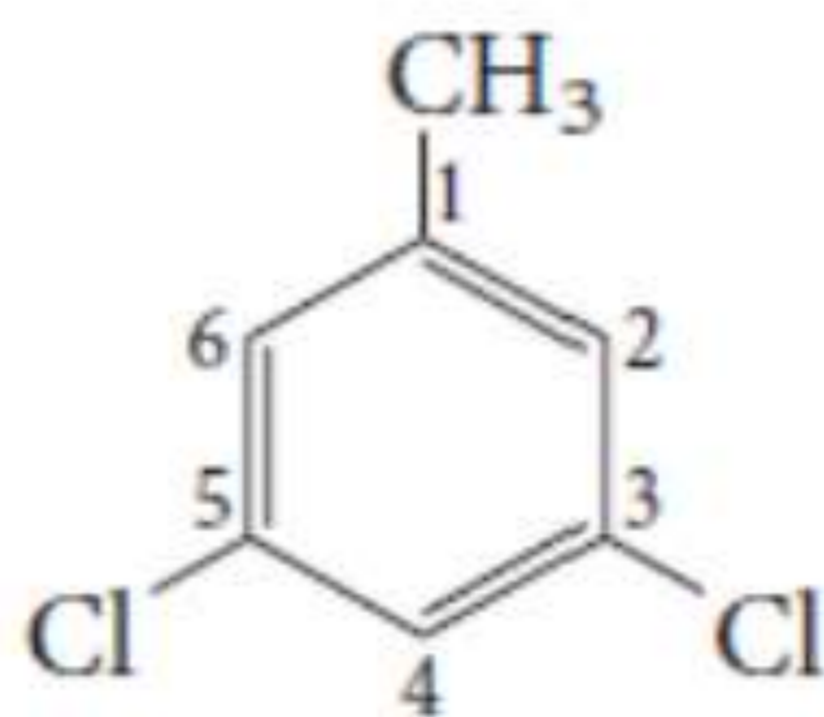
m-chlorophenol



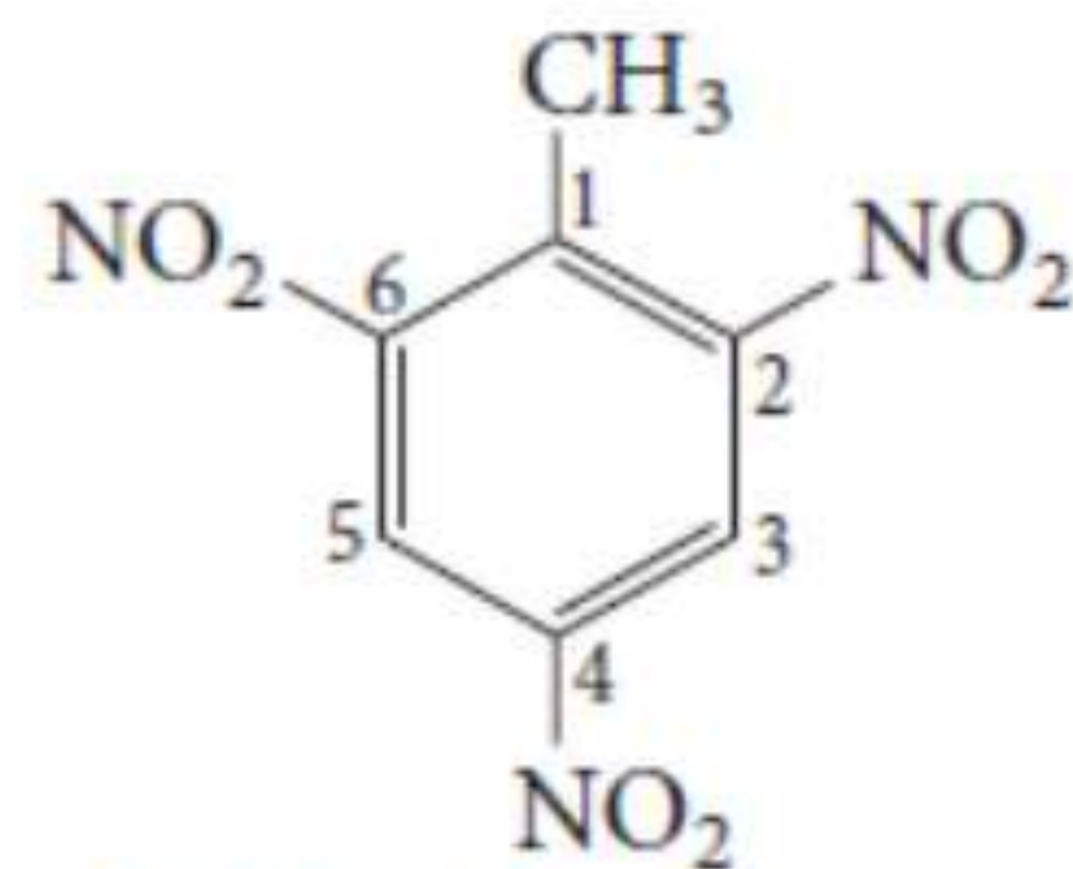
o-ethylaniline



1,2,4-trimethylbenzene



3,5-dichlorotoluene



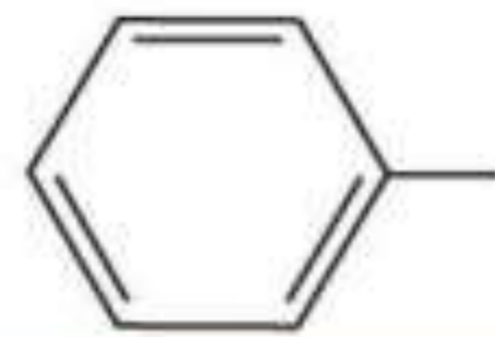
2,4,6-trinitrotoluene
(TNT)

As methyl (parent) ↷

Phenyl and Benzyl Substituents

له كما يكون البنزين هو

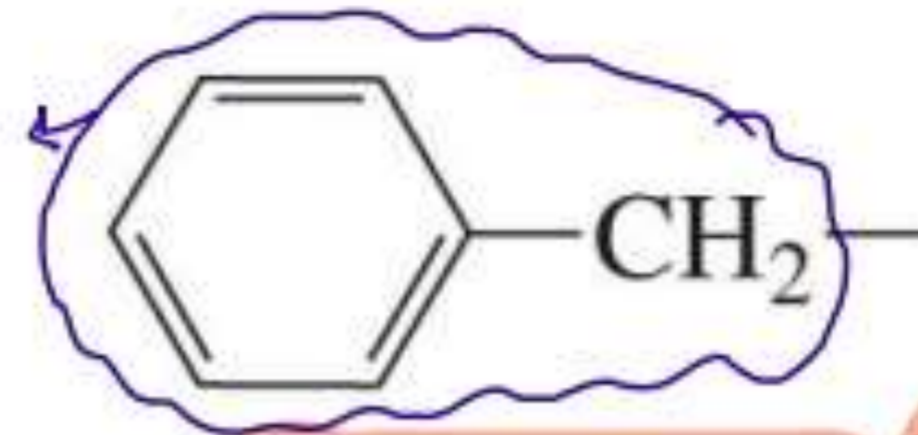
Alkyl Group



phenyl group (Ph)

له الاقصر

benzyl Group



benzyl group

$[C_6H_5CH_2]$

Alkane $\xrightarrow{-H}$ Alkyl Group

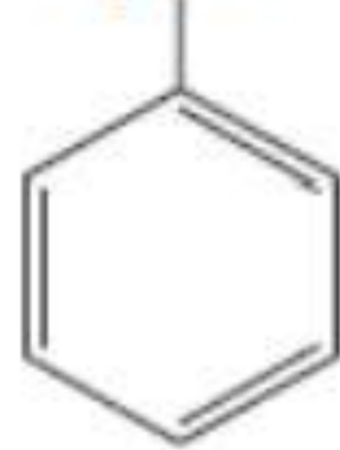
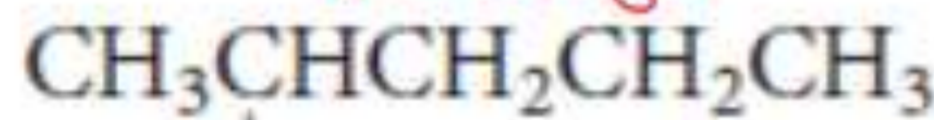
* البنزين كما يكون تفرع

لازم يكون موجود على

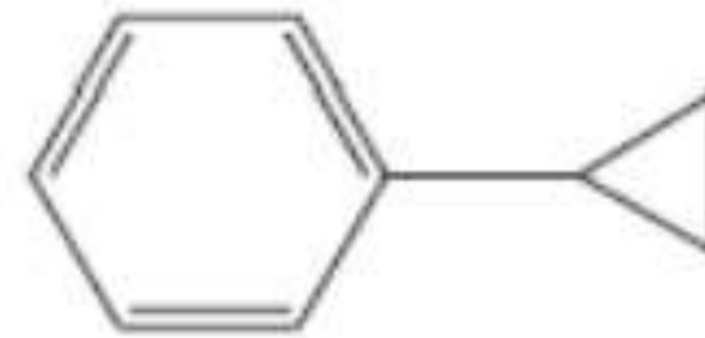
تحت واحد هيدروجين

له سطينا منه 11 فيتر تبطاً طول سلسلة هيدروجينية من الممكن اني
نر عنانه 11

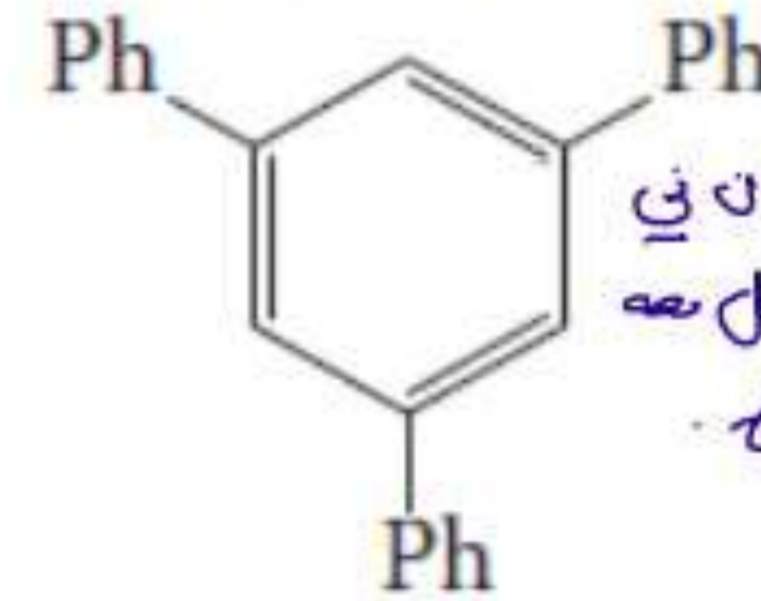
$[C_6H_5]$



2-phenylpentane
(or 2-pentylbenzene)



phenylcyclopropane
(or cyclopropylbenzene)



1,3,5-triphenylbenzene

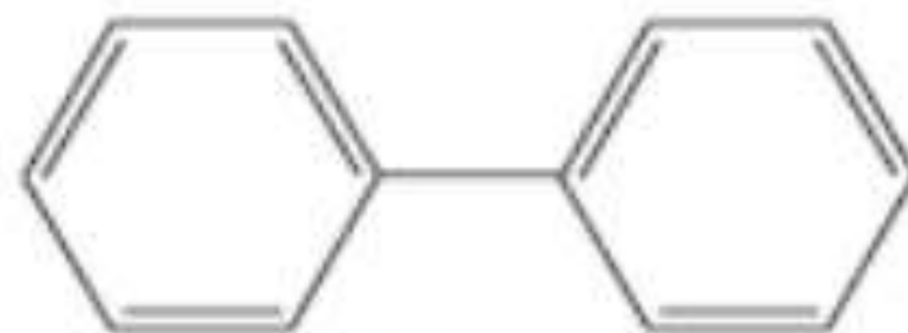
phenyl ← إذا كان له سلسله تفرع

benzyl ← إذا كان في هذا المثل مع التفرع

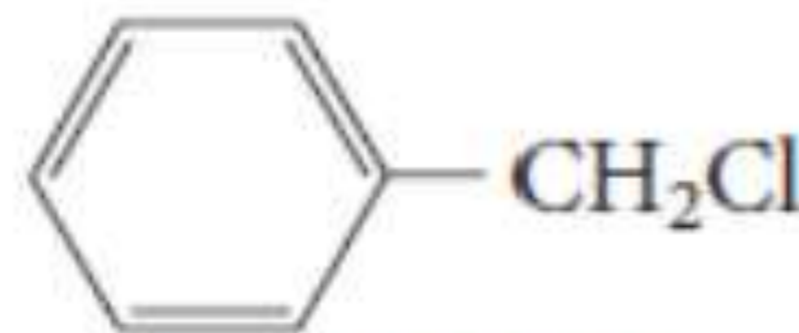
* يكون البنزين تفرع كما يكون

مفصل با تي انا أصلاً

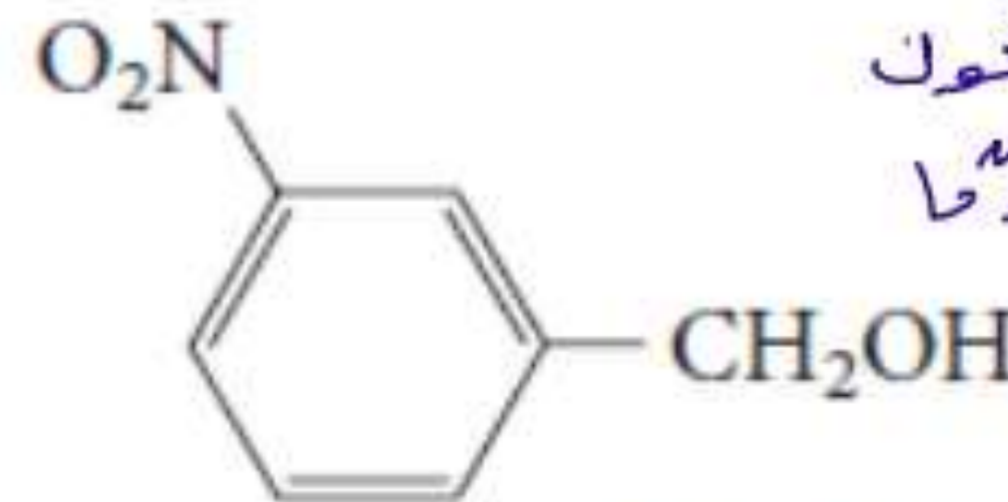
بفتر اسمه



biphenyl



benzyl chloride



m-nitrobenzyl alcohol

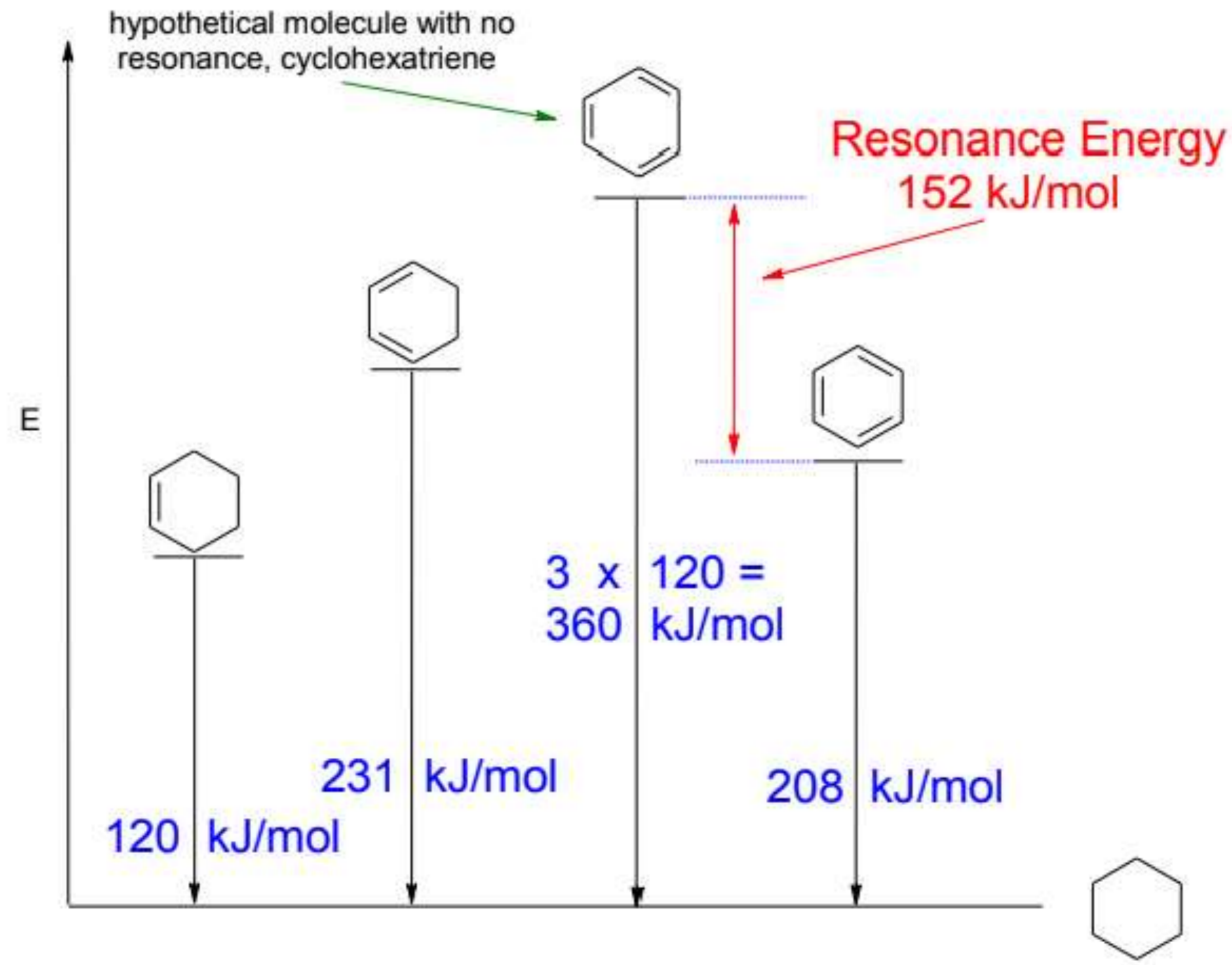


* هسه إذا كان يفرع تاني مع phenyl يعني حسب الحروف الأبجدية يعني مثلاً 1,2 أو 1,3 أو 1,4 قبل phenyl لأن الـ 1 قبل

بعض البنزين مركب كثير مستقر
بسبب املاكه الى Resonance
وبالتالي الطاقة التي يحفظها
ايها ليس يتفاعل مع تكون قليلة
مبدأ

Resonance Energy

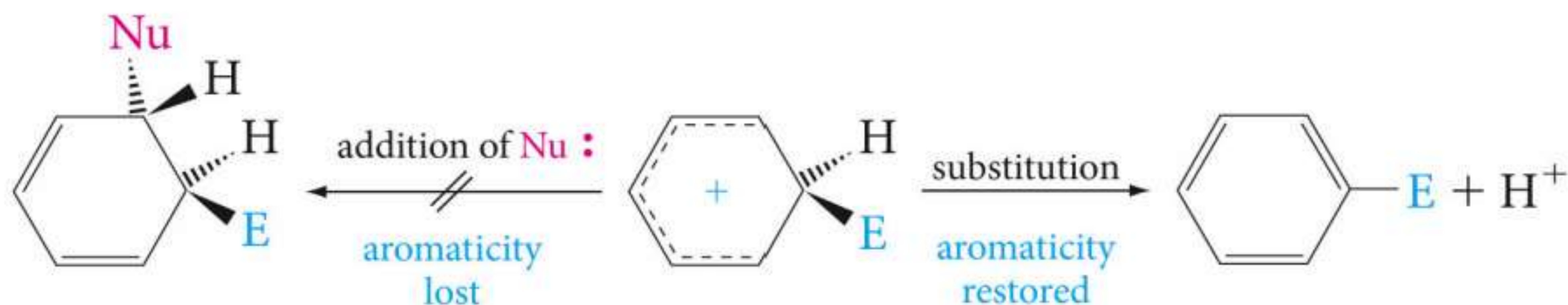
The resonance energy is a measure of the extra stability of the cyclic conjugated system compared to the corresponding number of isolated double bonds, i.e.



Resonance Energy

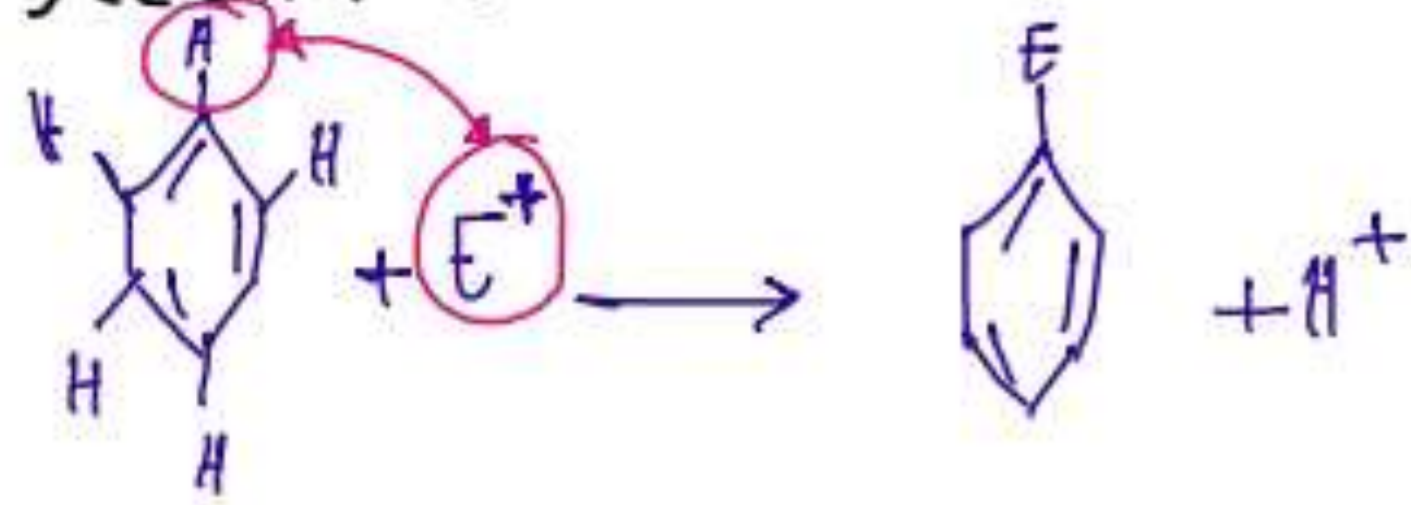
The large resonance stabilization energy seen in aromatic compounds results in two effects on their chemical reactivity:

- 1) Since the resonance stabilization energy is lost when an electrophile adds to the ring you need to use much stronger electrophiles than for alkenes/alkynes, generally this means using a catalyst.
- 2) The resonance energy can be regained if the intermediate carbocation loses a H^+ , this results in a substitution rather than the addition seen in alkenes/alkynes. The H^+ is lost to a base, even weak ones suffice here.



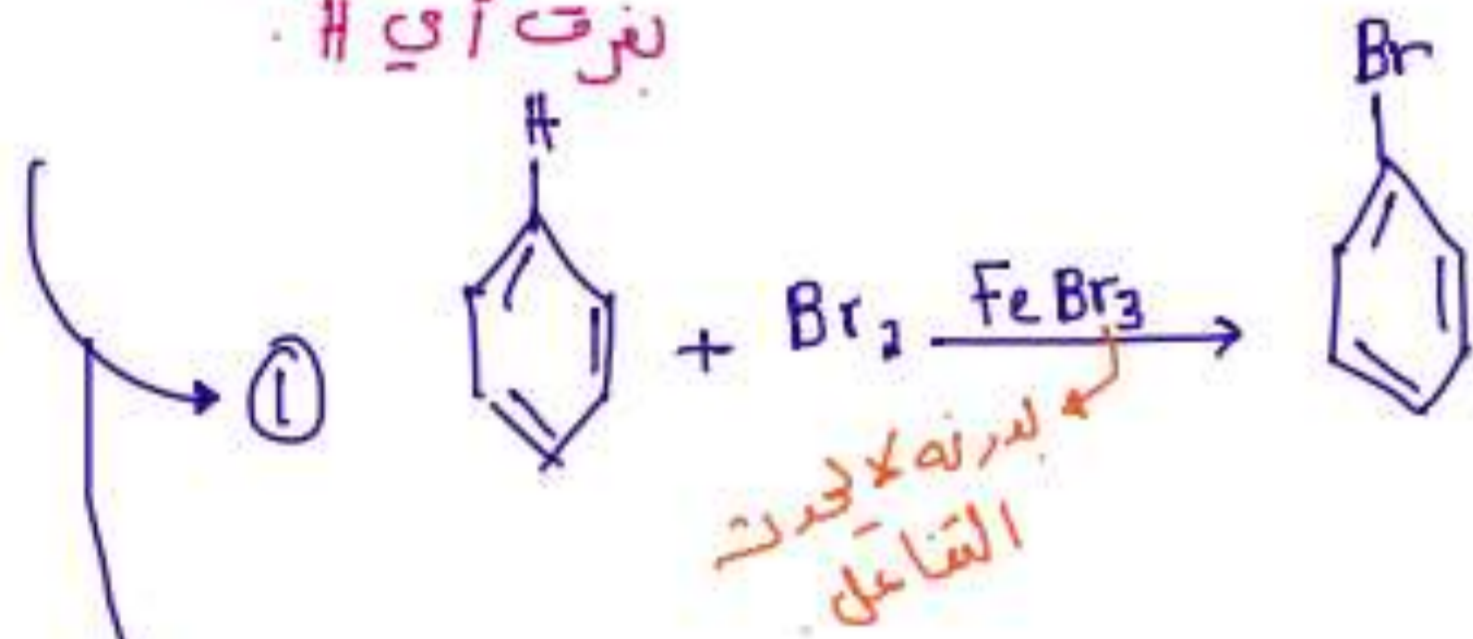
تفاعلات البترية :- * البترية لا يتفاعل بالاي حيافة بل يتفاعل بالاستبدال الا لكتروني
 [Electrophilic Aromatic substitution] [EAS]

Mechanism of substitution Reaction:-



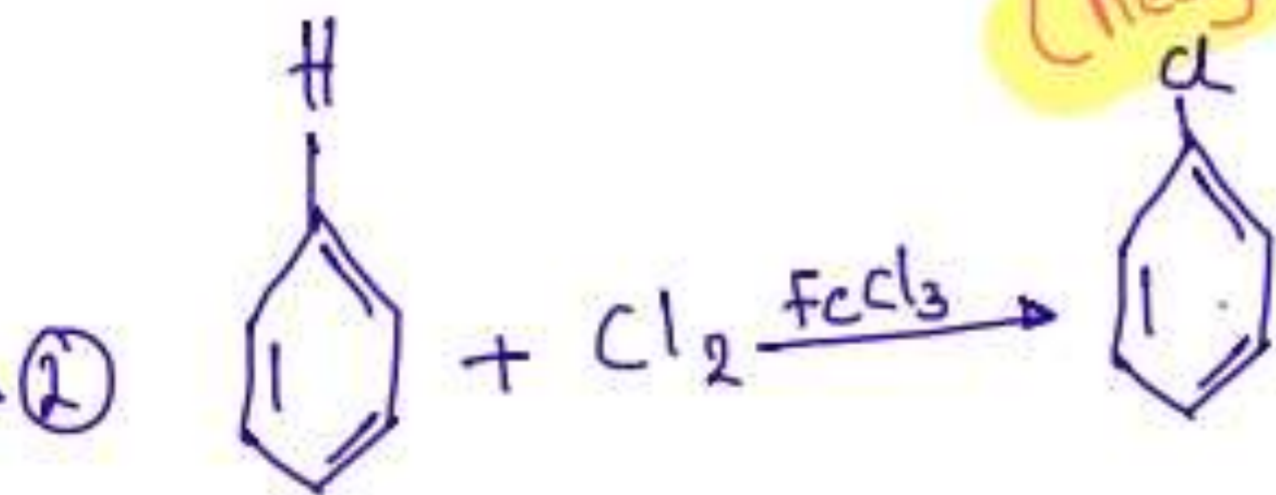
* لازم لكل امتحان تعرف البترية
 [Reagent + Catalyst] و ال [E+] (product) وال

* استبدال ذرة H
 بالالكتر وفضل واما
 بترت اي H



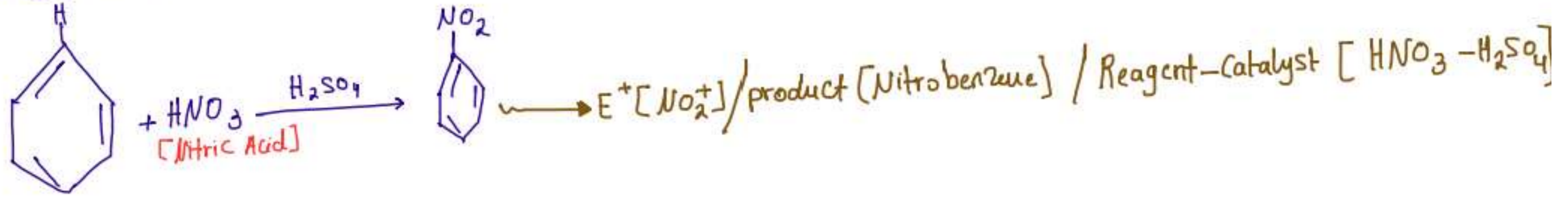
→ E+ [Br+] / product [bromobenzene] / Reagent - Catalyst [Br2 / FeBr3]

لذرة لا تحدث التفاعل
 FeBr3 مع Br2
 [Reagent + catalyst]

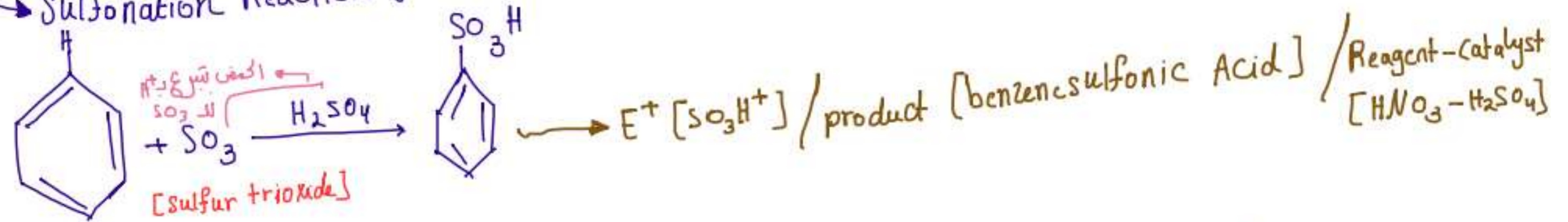


→ E+ [Cl+] / product [chlorobenzene] / Reagent - Catalyst [Cl2 - FeCl3]

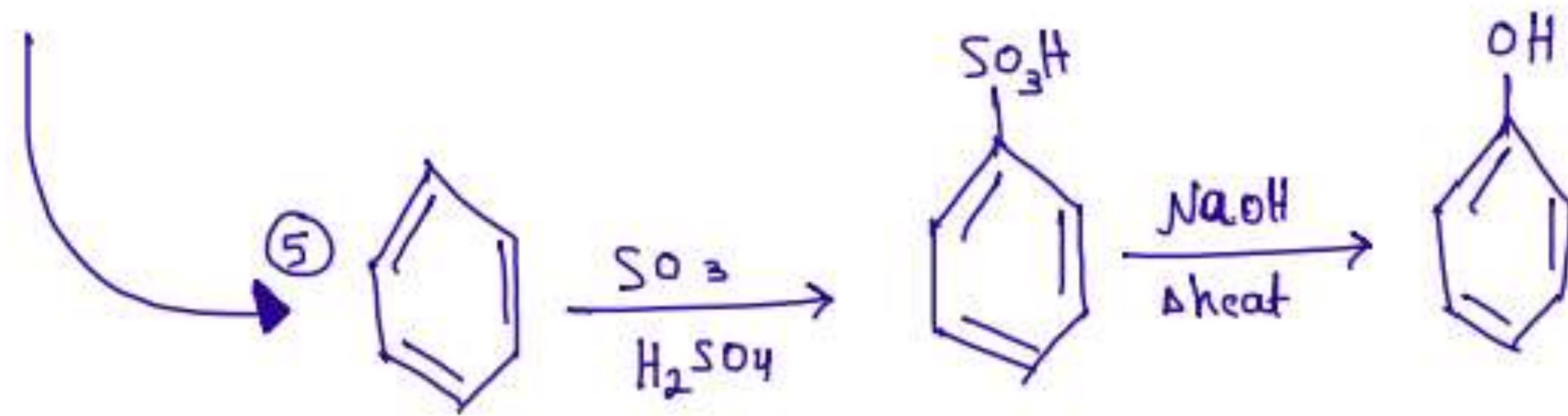
③ Nitration Reaction



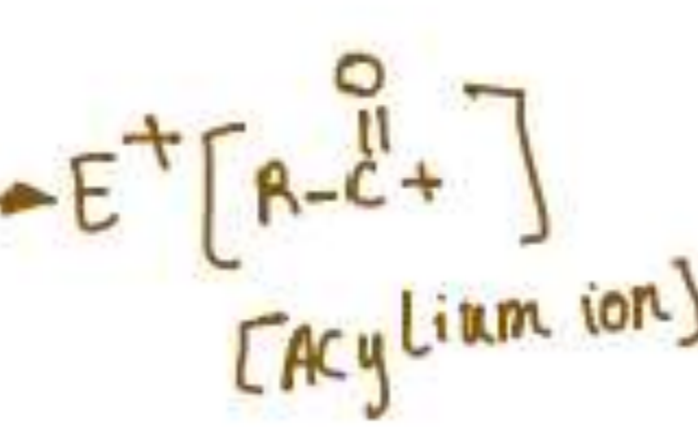
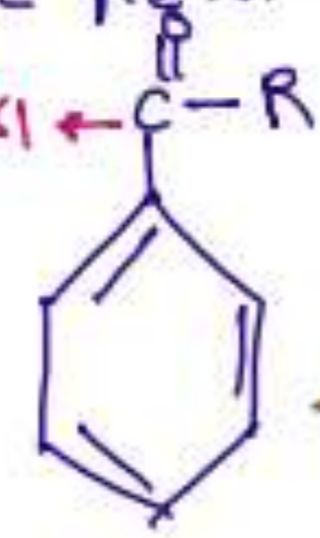
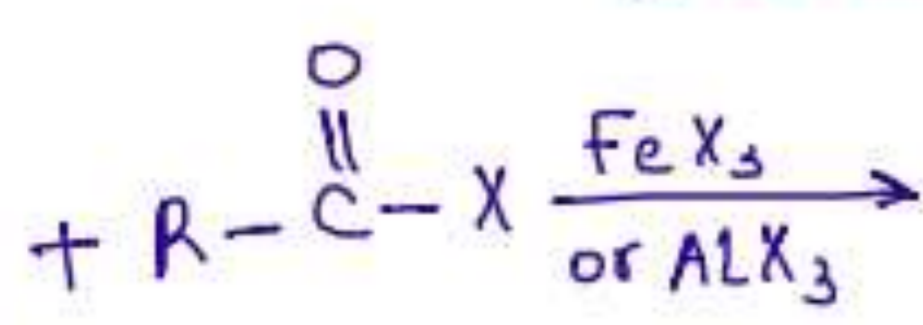
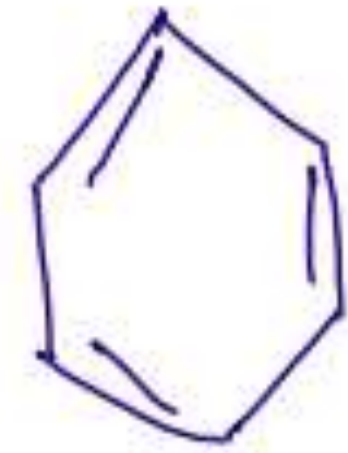
④ Sulfonation Reaction :-



* إذا جابلا نتجان حمض [Fuming sulfuric Acid] ← في نفس SO₃ بوجود H₂SO₄
 * لا يمكن تقيس ال phenol عن طريق مفاعلة البنزين مع NaOH لأن كلاهما NH₂



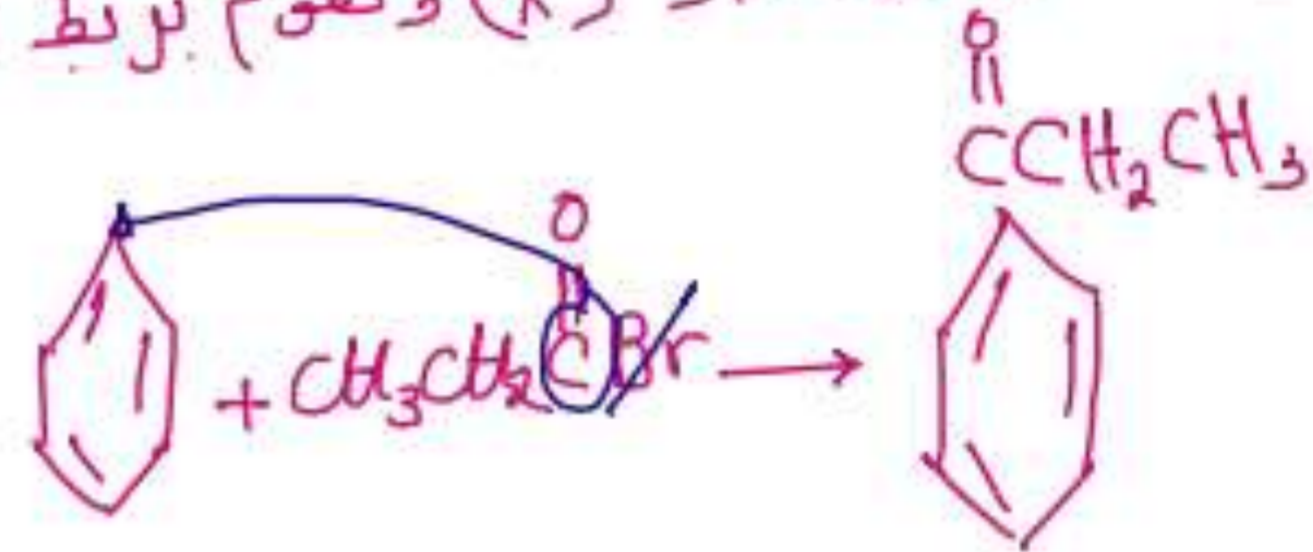
⑥ Friedel-Crafts Acylation Reaction * Acyl group: $\left[R-\overset{\text{O}}{\parallel}{C}-\{ \right]$



product [Acyl benzene] / Reagent - Catalyst
[Acyl halide / FeX_3 / AlX_3]

* لو كانت ال R عبارة عن CH_3 يكون الناتج (Acetophenone) ولو كانت جورد # بجمع الناتج [benzaldehyde]

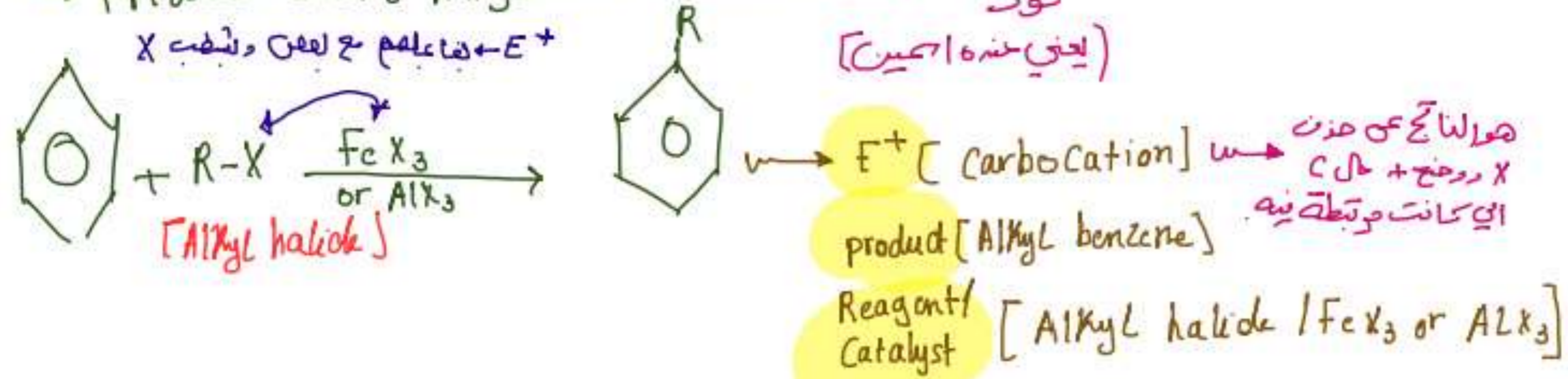
* لكتابة الناتج \leftarrow نكتب ال (X) ونقوم برابط مجموعة ال [Acyl] بالتزيين من عند $\left[\overset{\text{O}}{\parallel}{C} \right]$



مثال :-

⑦ Alkylation Reaction :

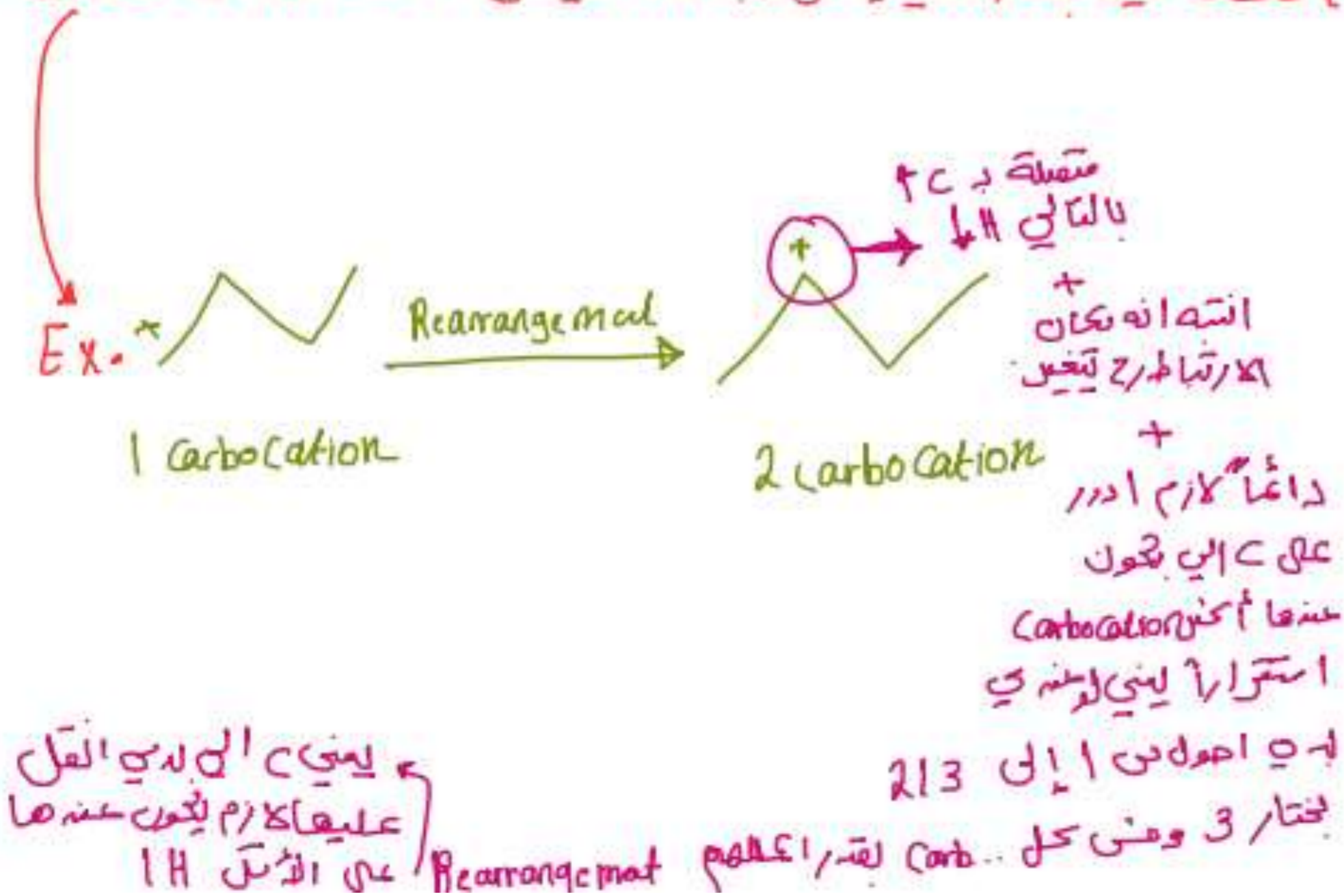
Friedel-Crafts Alkylation Reaction \rightarrow نفس الـ نوت (يعني منه احسين)



* لكتابة الناتج :

- نقول بتحويل R-X إلى Carbocation من طريق انه ينشط الـ X وينقل الحنة الحرة على C الي كانت متصلة X
- بعد ذلك Carbocation مع البنزين من C الي كانت متصلة الحنة الحرة

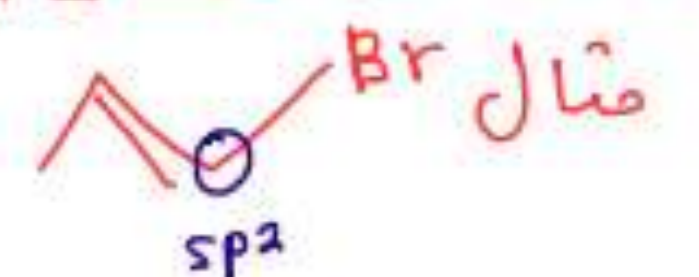
Carbocation مركباته بتحب تكون مستقرة وترتيبها حسب الـ stability يكون $3^\circ > 2^\circ > 1^\circ$ فشان هيك بقدرانه يعيد ترتيب هاله وينقل الحنة \oplus الى C ثانية ليعا أقل عدد H ليحول إلى أكثر استقرار



[Carbocation Rearrangement]

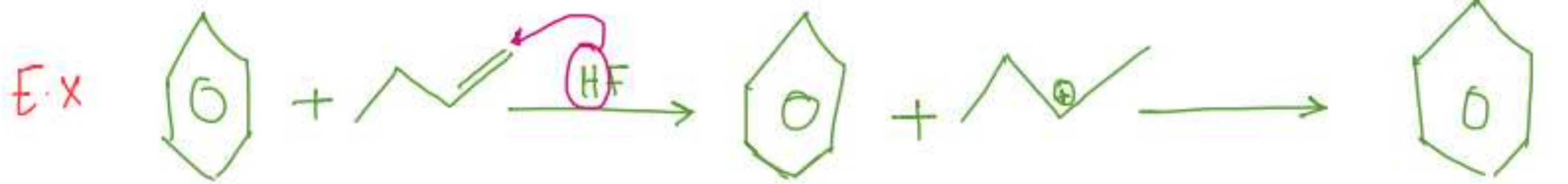
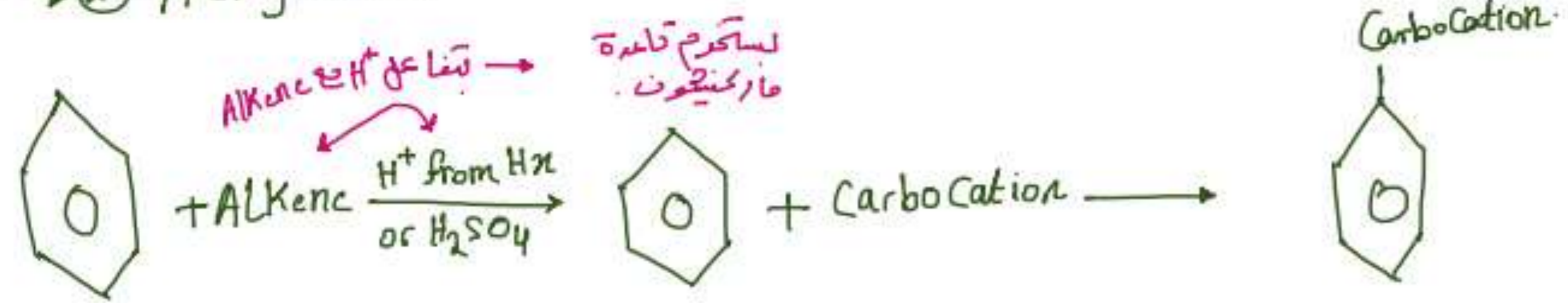
* لازم قبل ما نقل Carbocation اعلمها Rearrangement

* Alkyl halide الذي يكون فيه الـ X متصلة بـ C تعطينا sp² يعني بيها Db لا يستطيع التفاعل مع البنزين في [Friedel ...]



② Alkylation From Alkenes. Reaction :-

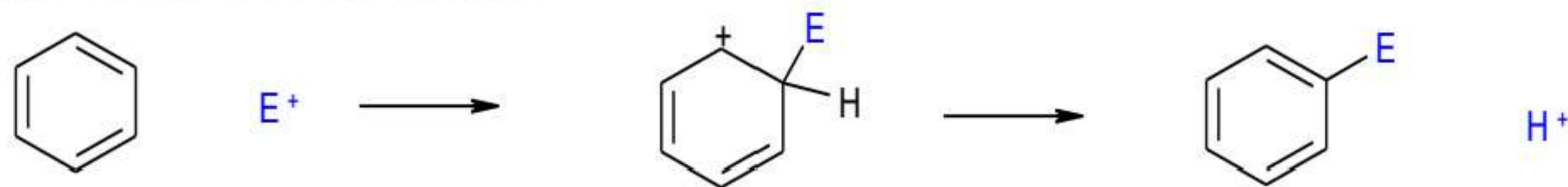
* لا يحدث Rearrangement في هذه الطريقة



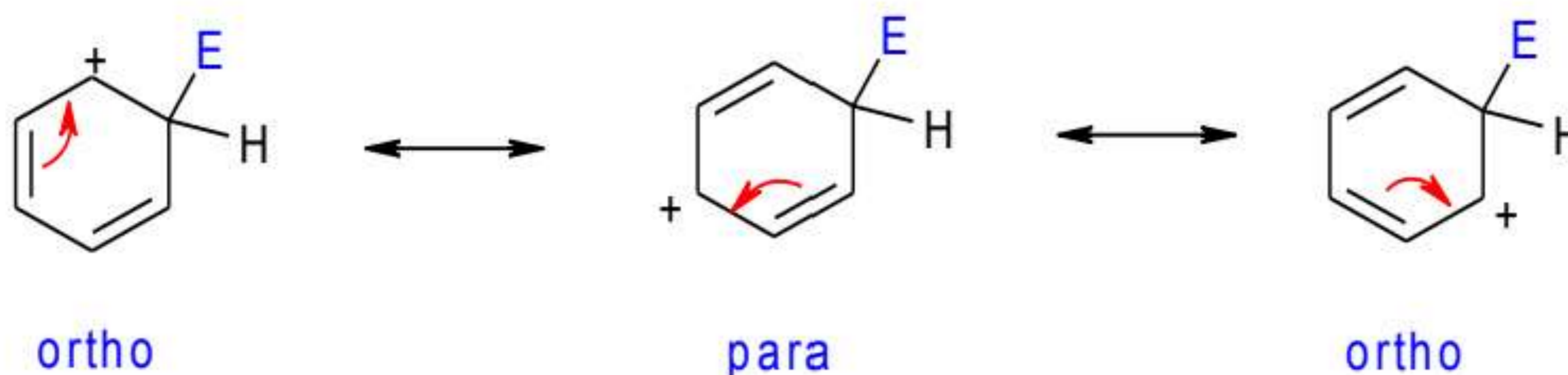
* جميع Catalysts في تفاعلات البنزين هم [Lewis Acid catalysts]

Mechanism of Electrophilic Aromatic Substitution (EArS)

In general all EArS reactions proceed by the same mechanism:



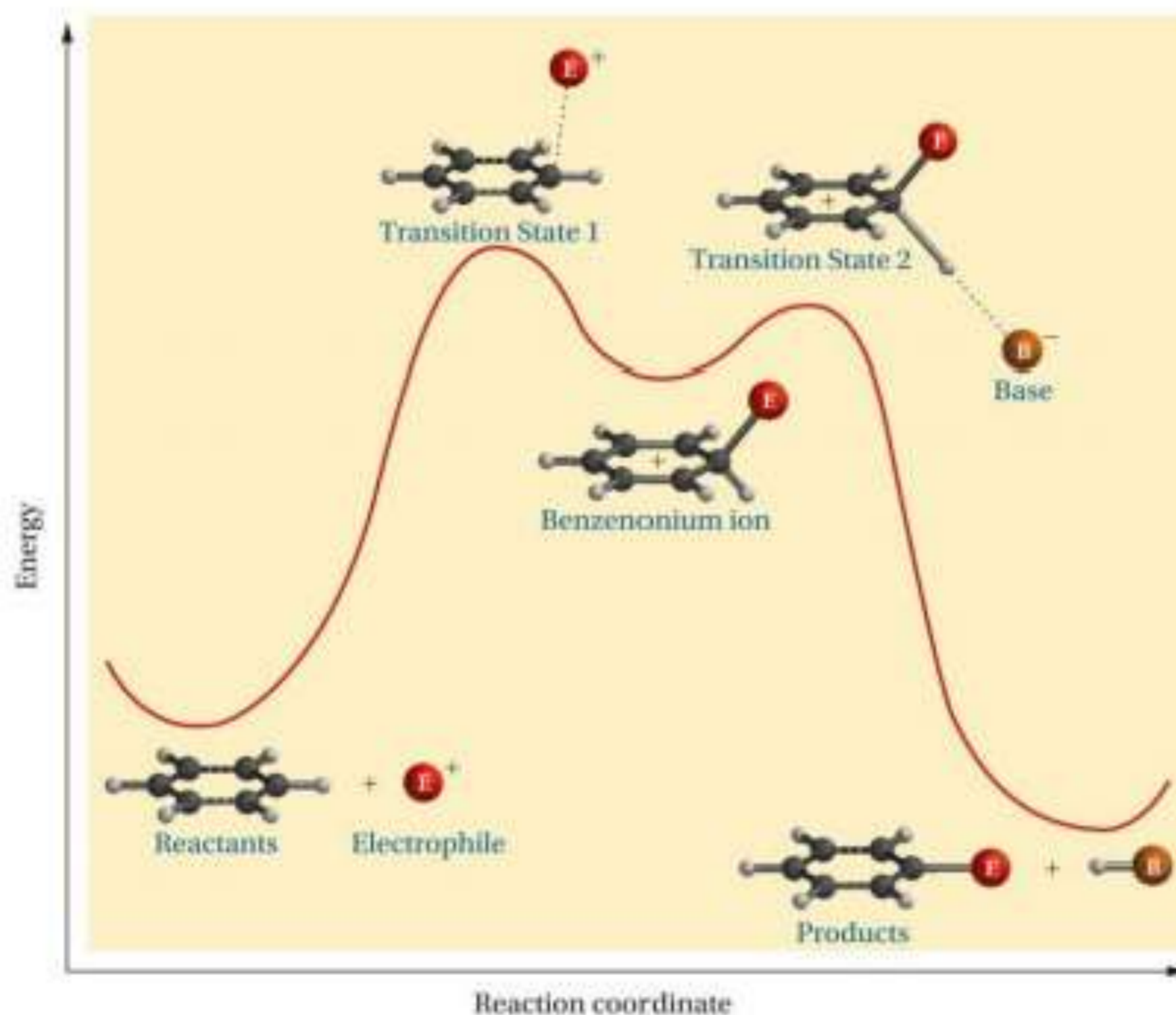
benzenonium ion
(a carbocation)



Benzenonium resonance structures

Mechanism of Electrophilic Aromatic Substitution (EArS)

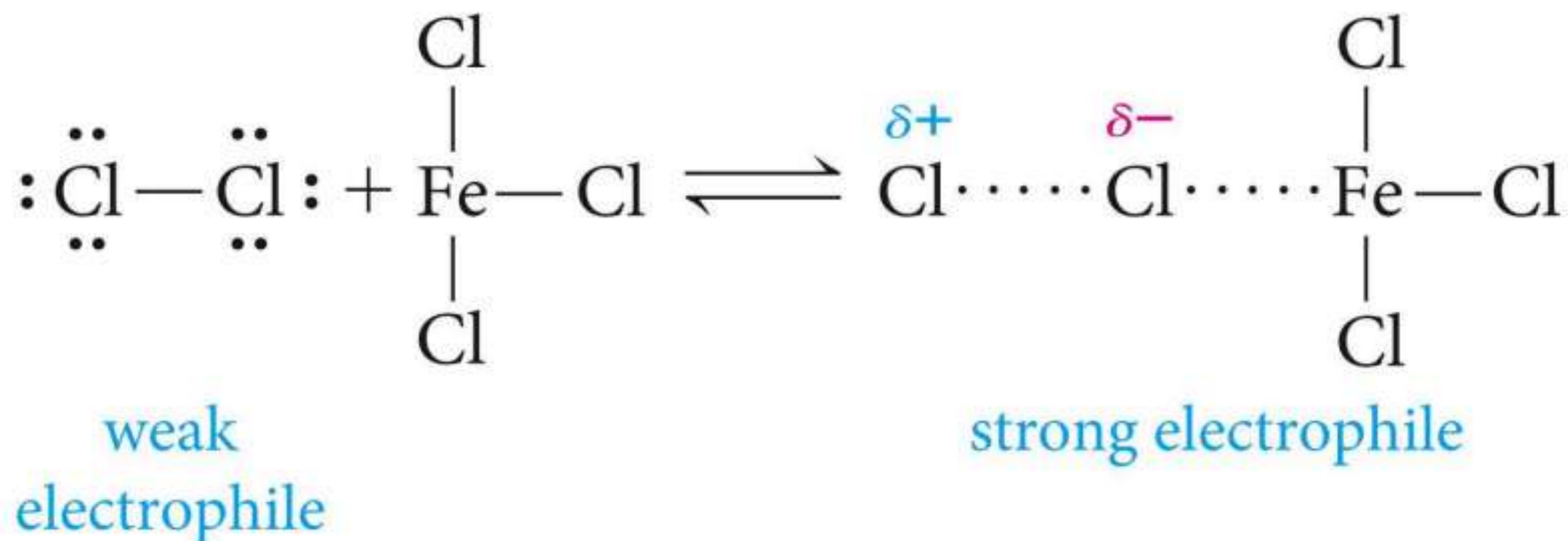
As with alkenes and alkynes, the carbocation generated by the addition of the electrophile is a stable intermediate, i.e.



The formation of the carbocation is the rate determining step as it takes energy to break the aromaticity.

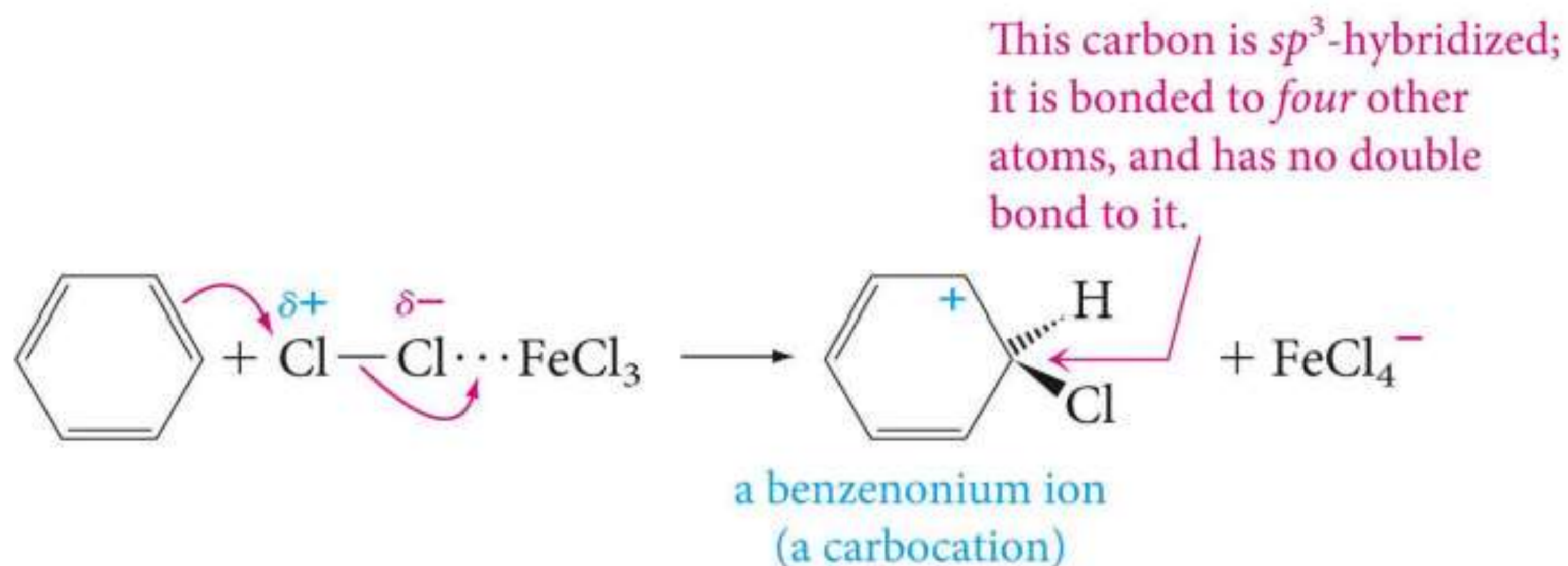
EArS - Halogenation

- Cl_2 and Br_2 are weak electrophiles on their own so need to be “activated” by using a Lewis acid catalyst.
- Commonly the corresponding iron trihalide is used, FeCl_3 or FeBr_3



EArS - Halogenation

The rate determining step is:

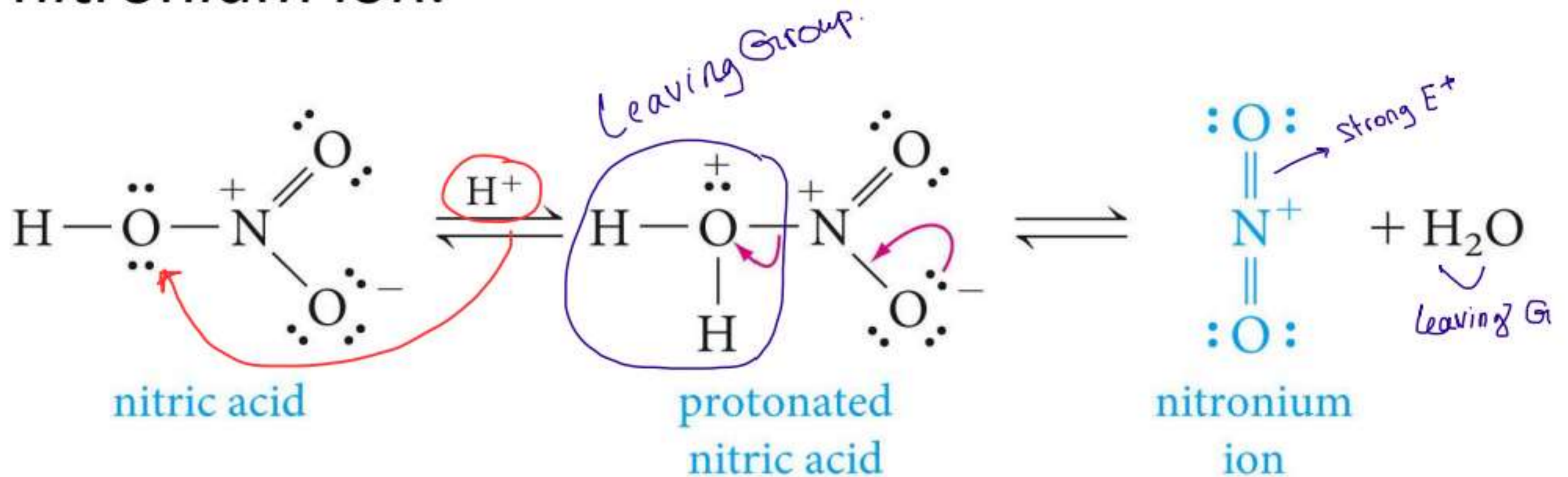


The base in this case is the chloride ion:



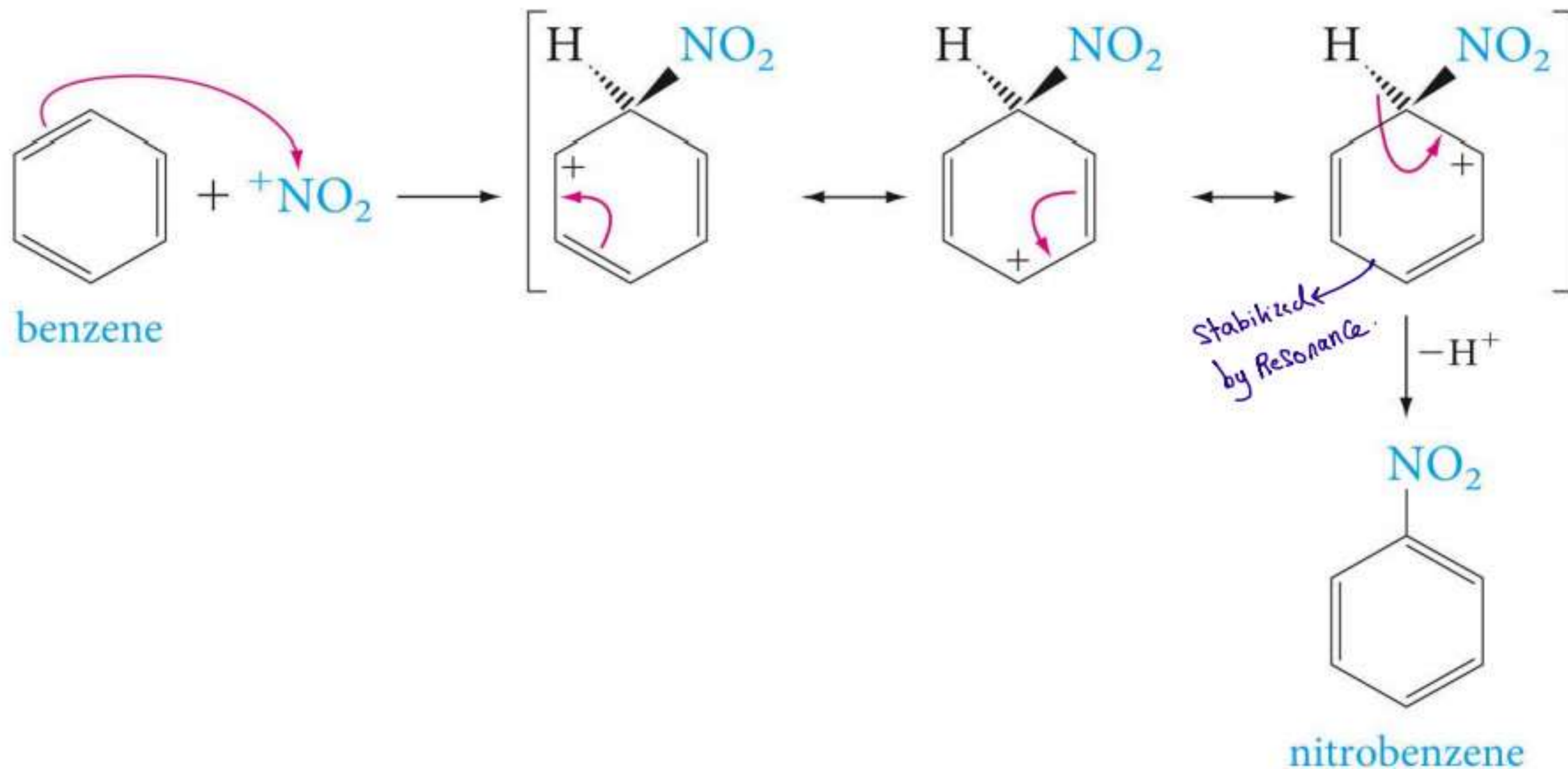
EArS - Nitration

In the case of nitration, sulfuric acid is used to generate a more reactivity electrophile, a nitronium ion.



EArS - Nitration

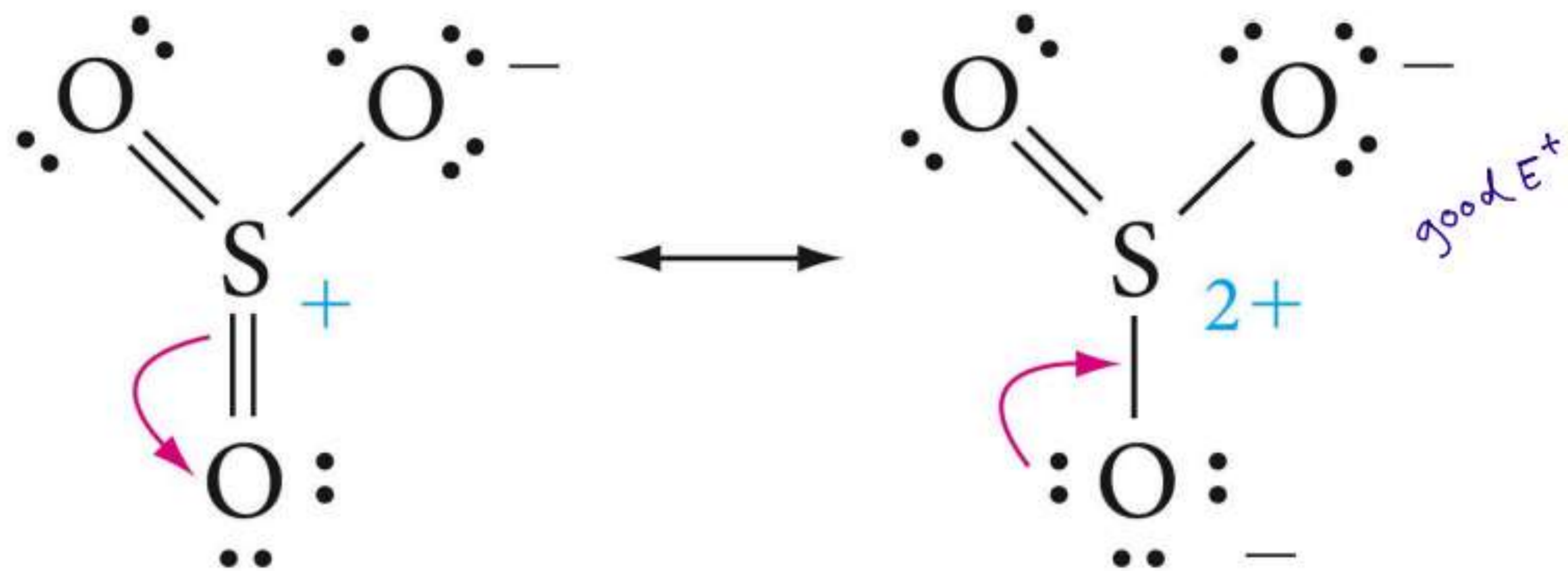
The product of the reaction is nitrobenzene, i.e.



EArS - Sulfonation

Sulfonation will generate a benzenesulfonic acid.

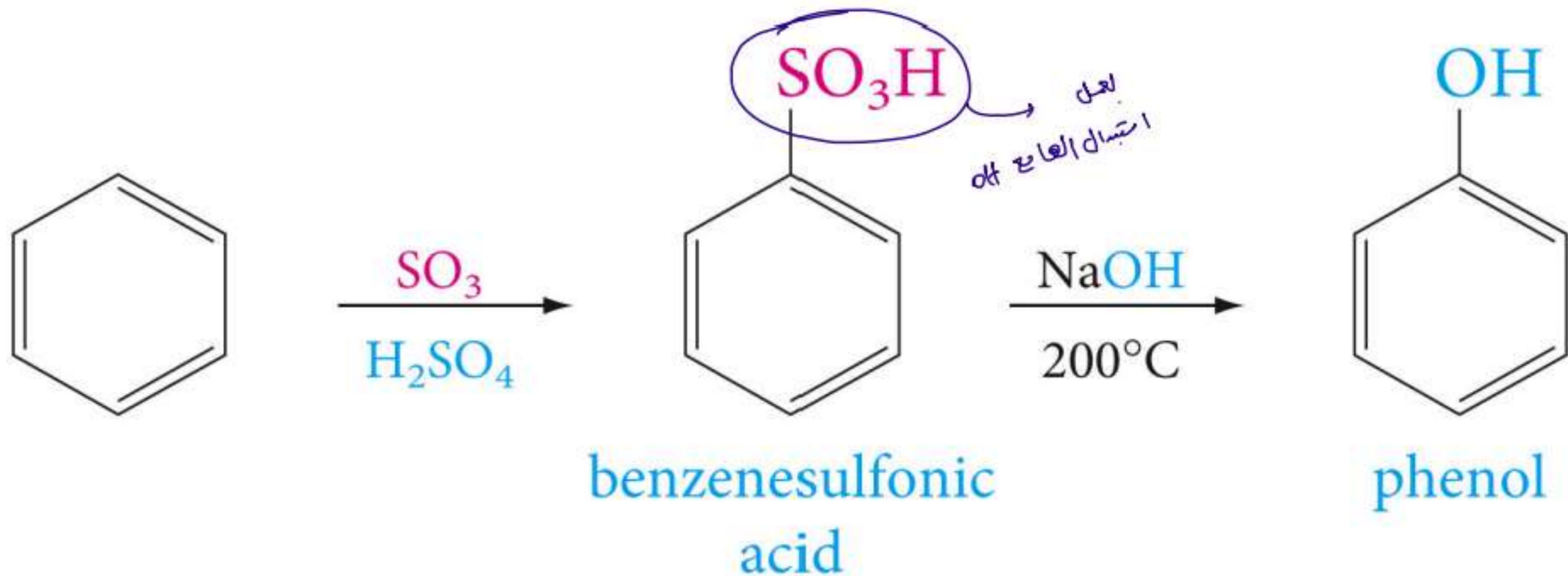
The electrophile used is sulfur trioxide, which is a strong electrophile, i.e.



بما انه صاف في عدي 20
عليه H وحدة صاف 2 توفد H⁺
2 بيبي SO₃ H وهو الـ E⁺


EArS - Sulfonation

While benzenesulfonic acids are useful in their own right, they are also convenient as they can be modified to a phenol easily, i.e.

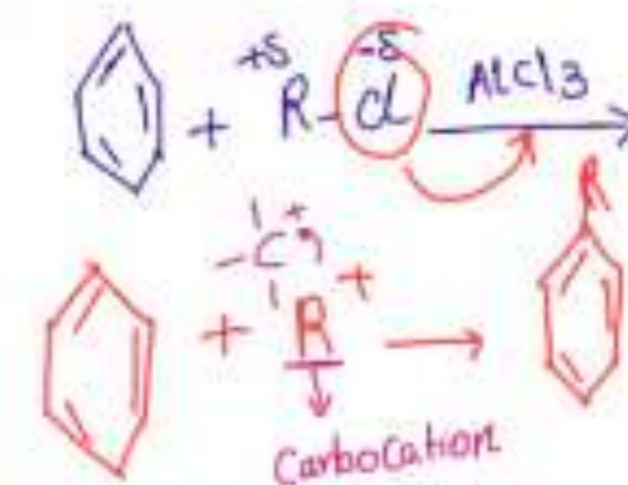


EArS - Alkylation

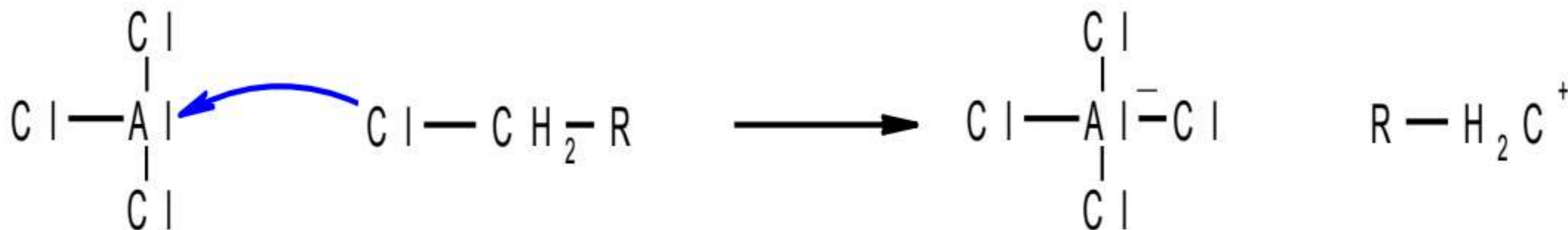
Alkylation will add an alkane group to benzene. In this case we need a carbocation as the electrophile. There are two ways to do this:

- 1) Friedel-Crafts alkylation
 - 2) Alkylation using an alkene and acid
- 

Friedel-Crafts Alkylation

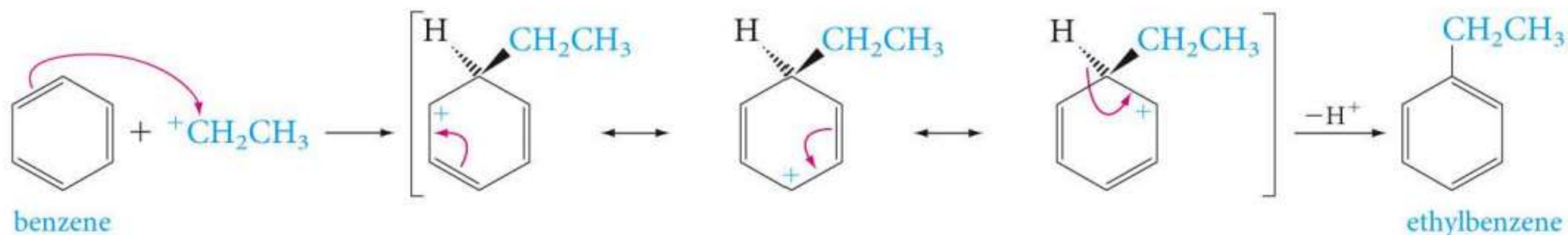


This process uses an alkyl halide (Cl or Br usually) and a Lewis acid catalyst similar to a halogenation reaction. In this case we use the corresponding aluminum trihalide as the Lewis acid catalyst.



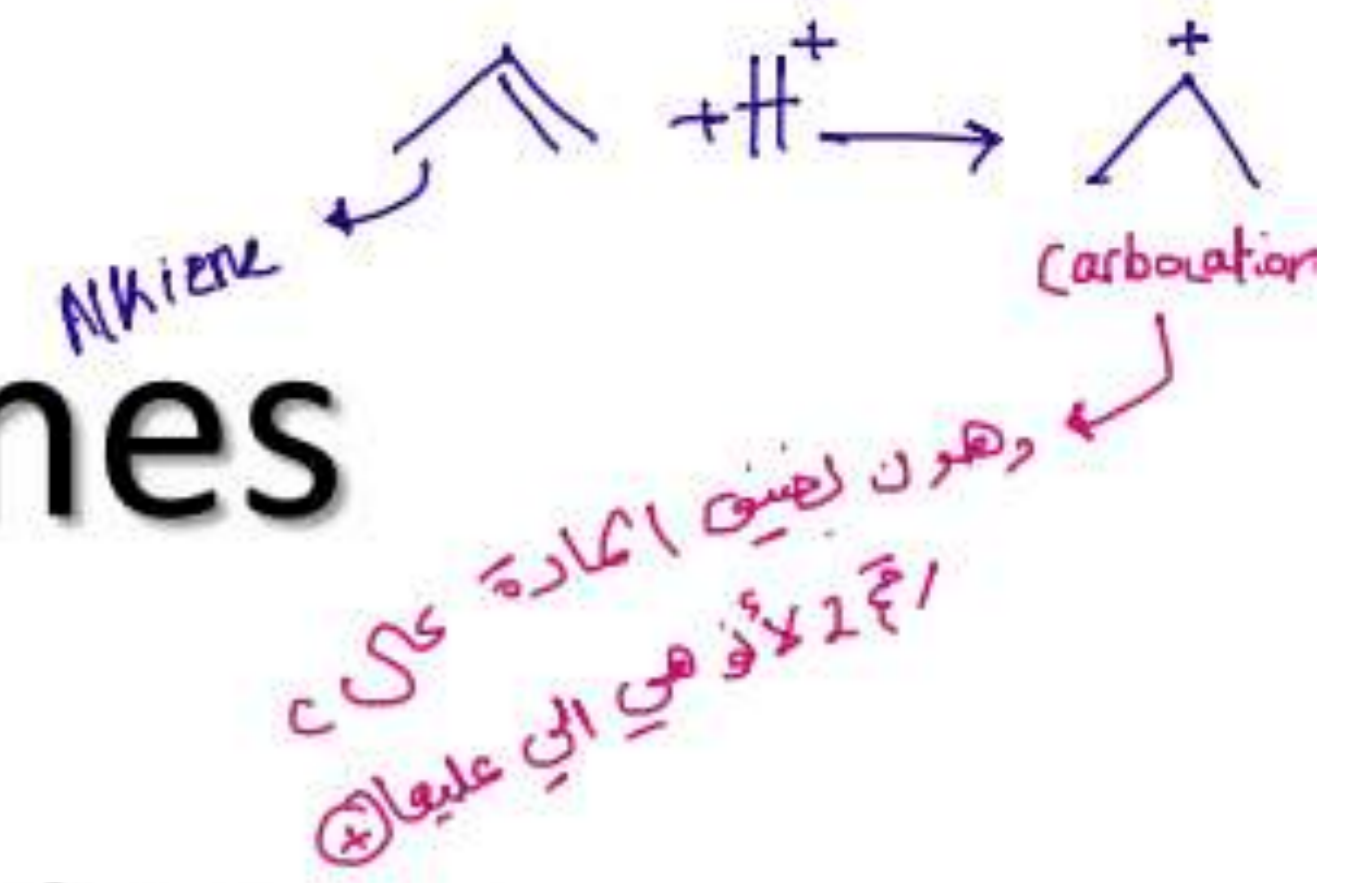
Friedel-Crafts Alkylation

The product is an alkylbenzene, i.e.



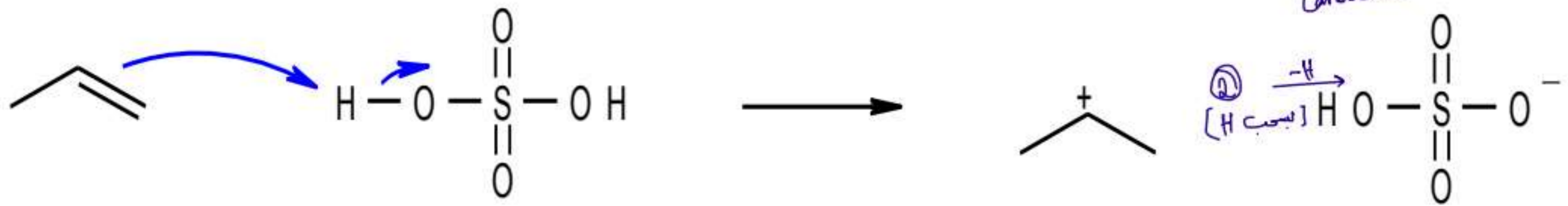
Note: there are limitations to Friedel-Crafts reactions, they can not be done on a nitrobenzene or benzenesulfonic acid as these group complex with the aluminum chloride catalyst deactivation it.

Alkylation from Alkenes



Alkylation can also be achieved by using an alkene and an acid (sulfuric as the conjugate base is a poor nucleophile), i.e.

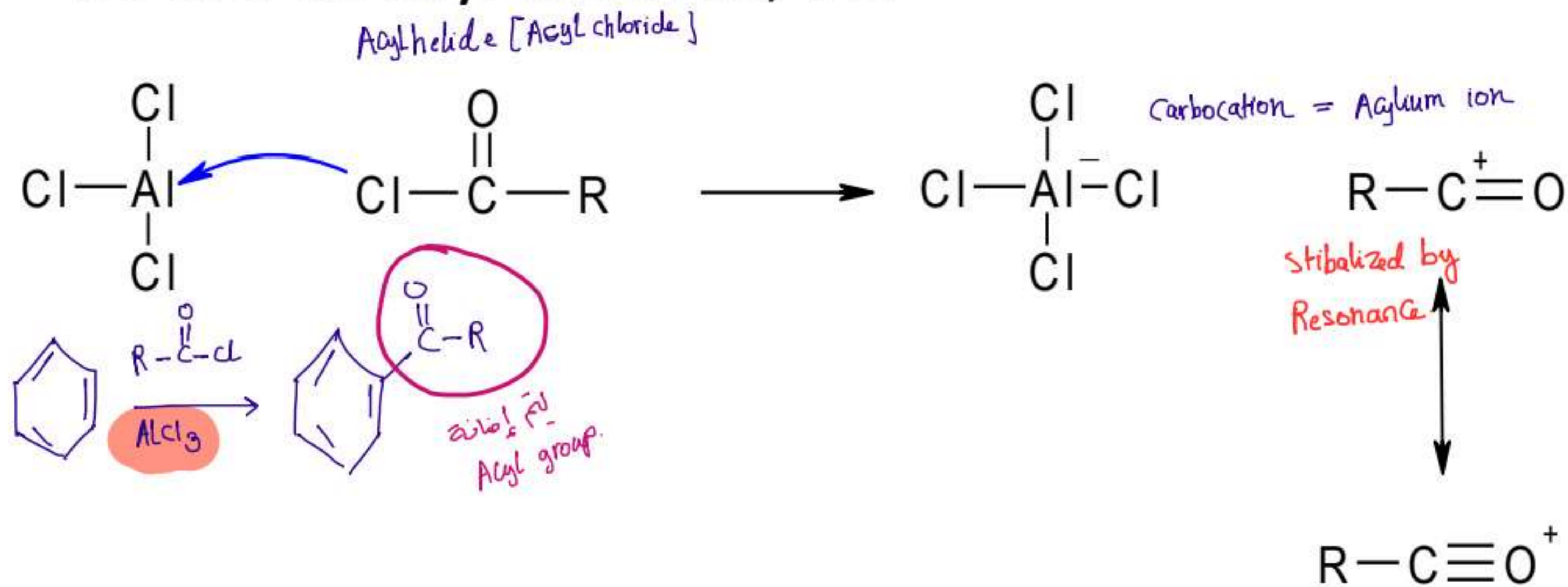
مهمه لارجا
البنزين يتفاعل
مع Carbocation



Note: this will generate the Markovnikov carbocation!

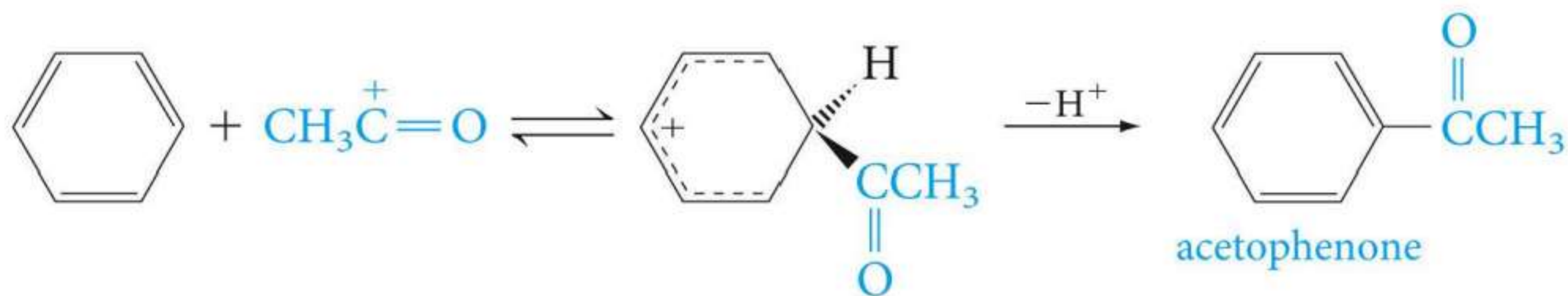
Friedel-Crafts Acylation

This process is identical to an alkylation except we use an acyl chloride, i.e.



Friedel-Crafts Acylation

The product is a phenyl ketone, i.e.

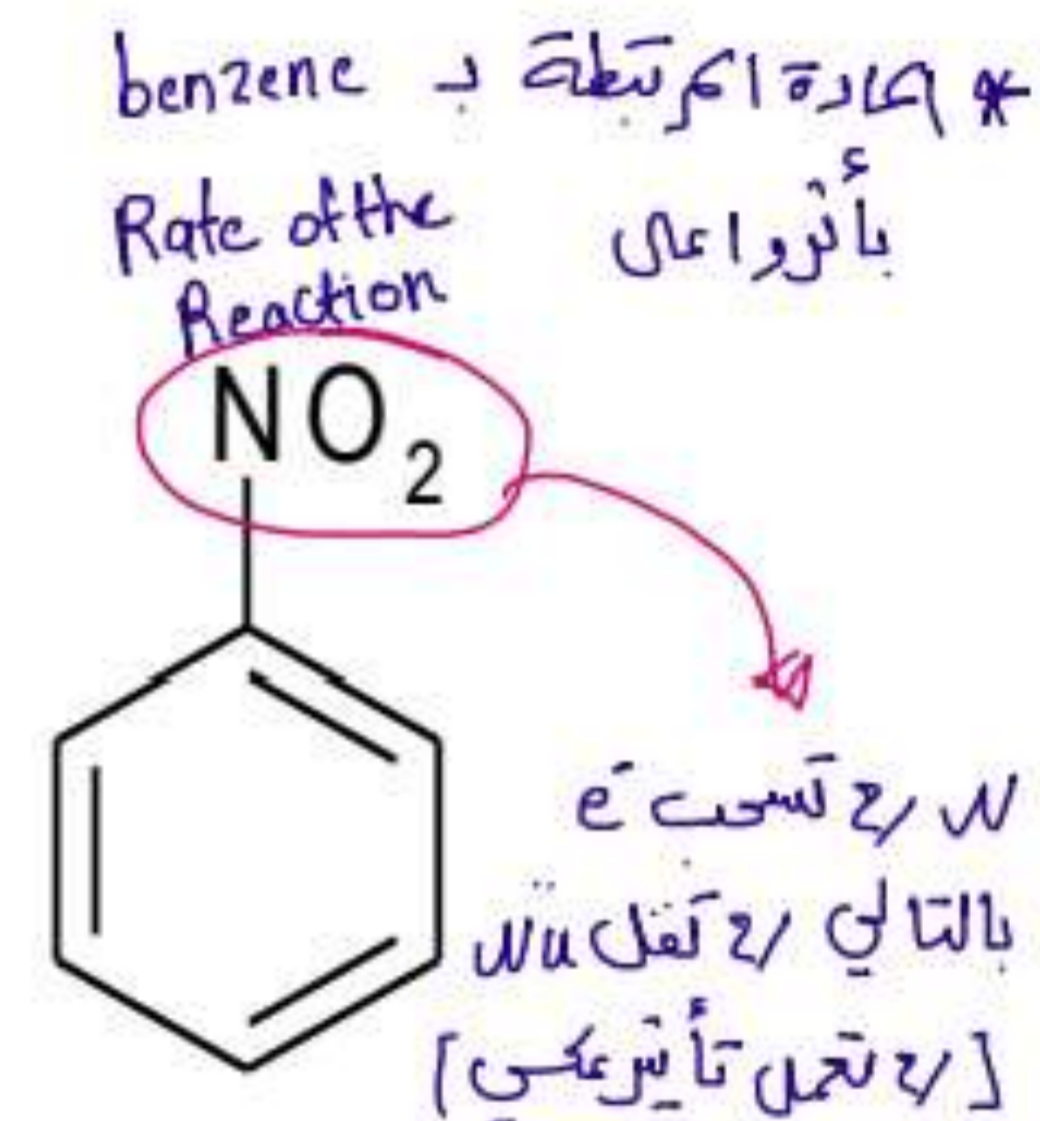
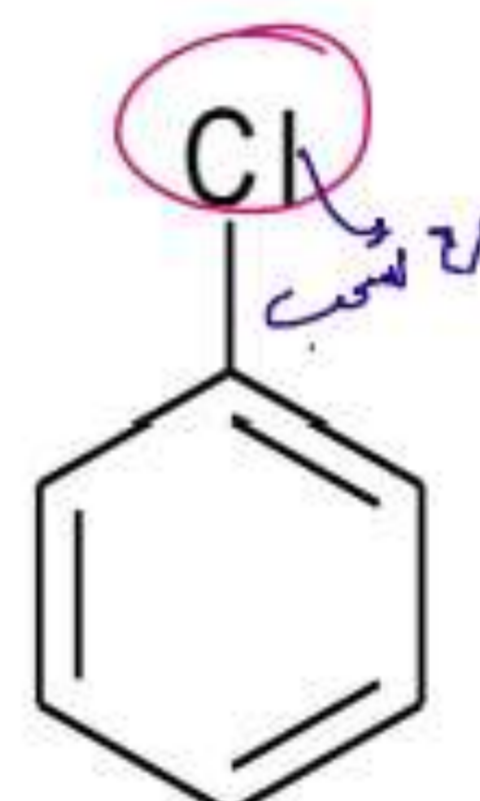
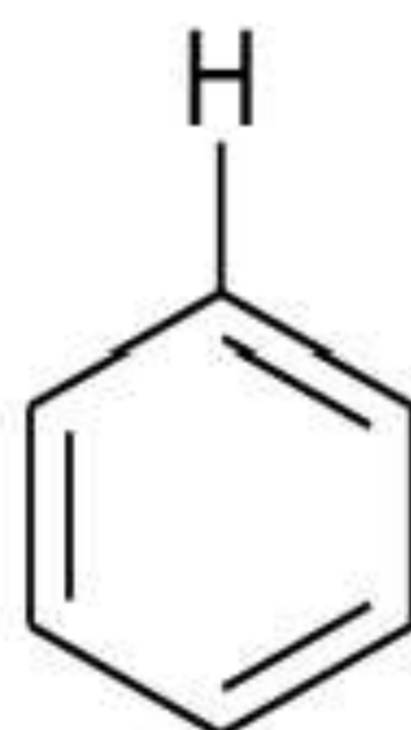
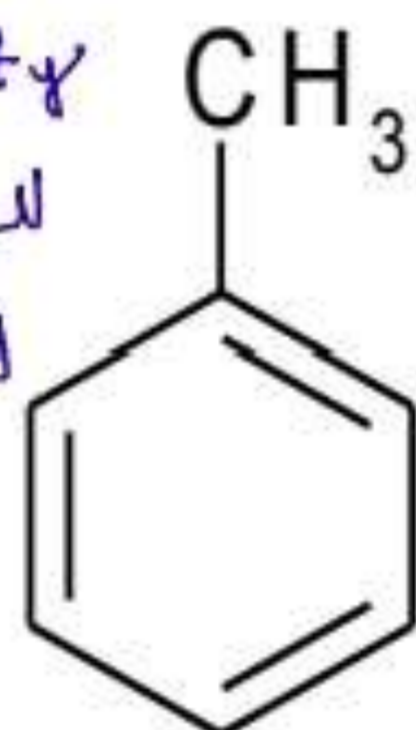
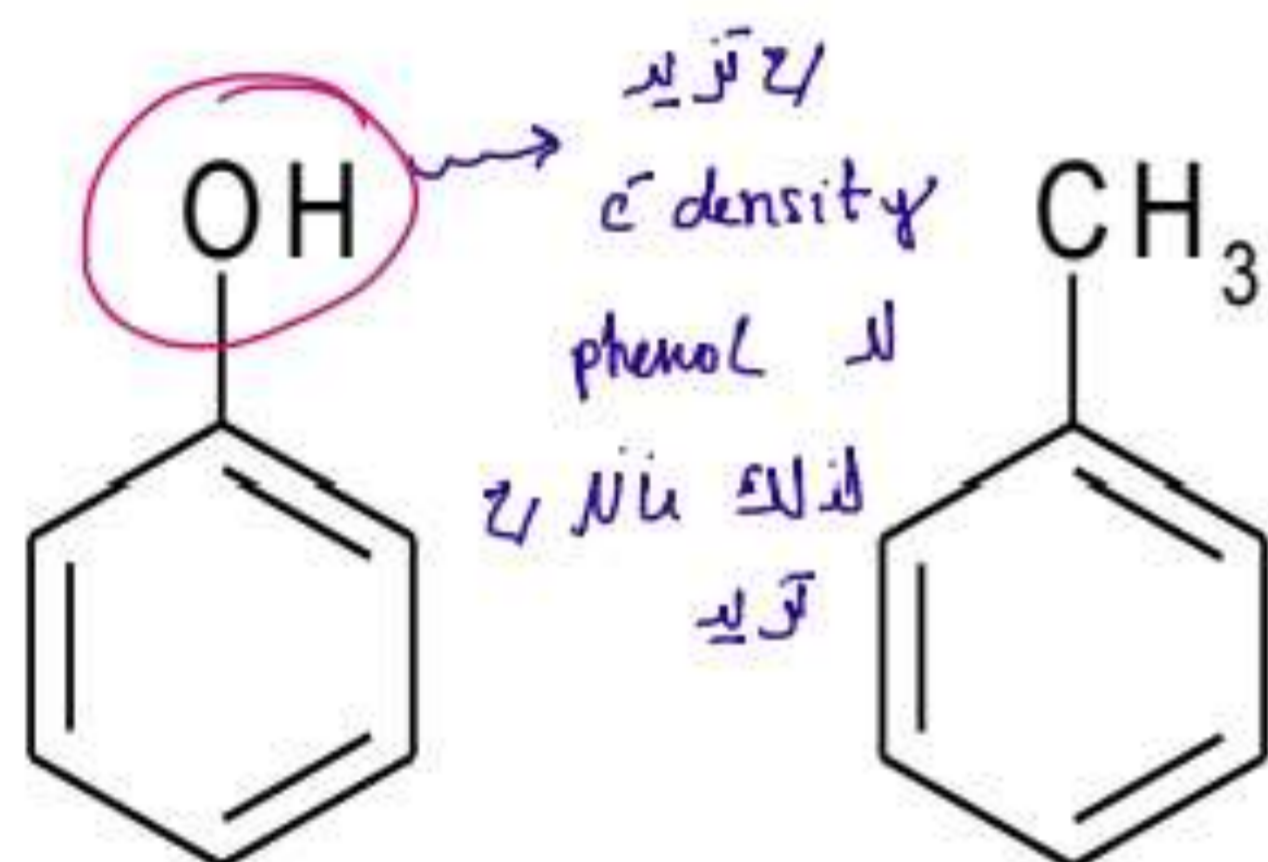


Note: the same limitations for nitro and sulfonic acid groups apply.

Reaction Rates

* هسه أنا عندني لواجبته استبدل
مع بنزين عادي غير أي H بس لو كان
البنزين أصلاً متصل باشي ثاني من قبل
هون رح يطلع عندني كذا ناتج [يعني
من محل H نفس بعين]

Experimentally you can observe the following relative rates of reaction:



phenol

1000

أسرع

toluene

24.5

أسرع

benzene

1

chlorobenzene

0.033

أبطأ

nitrobenzene

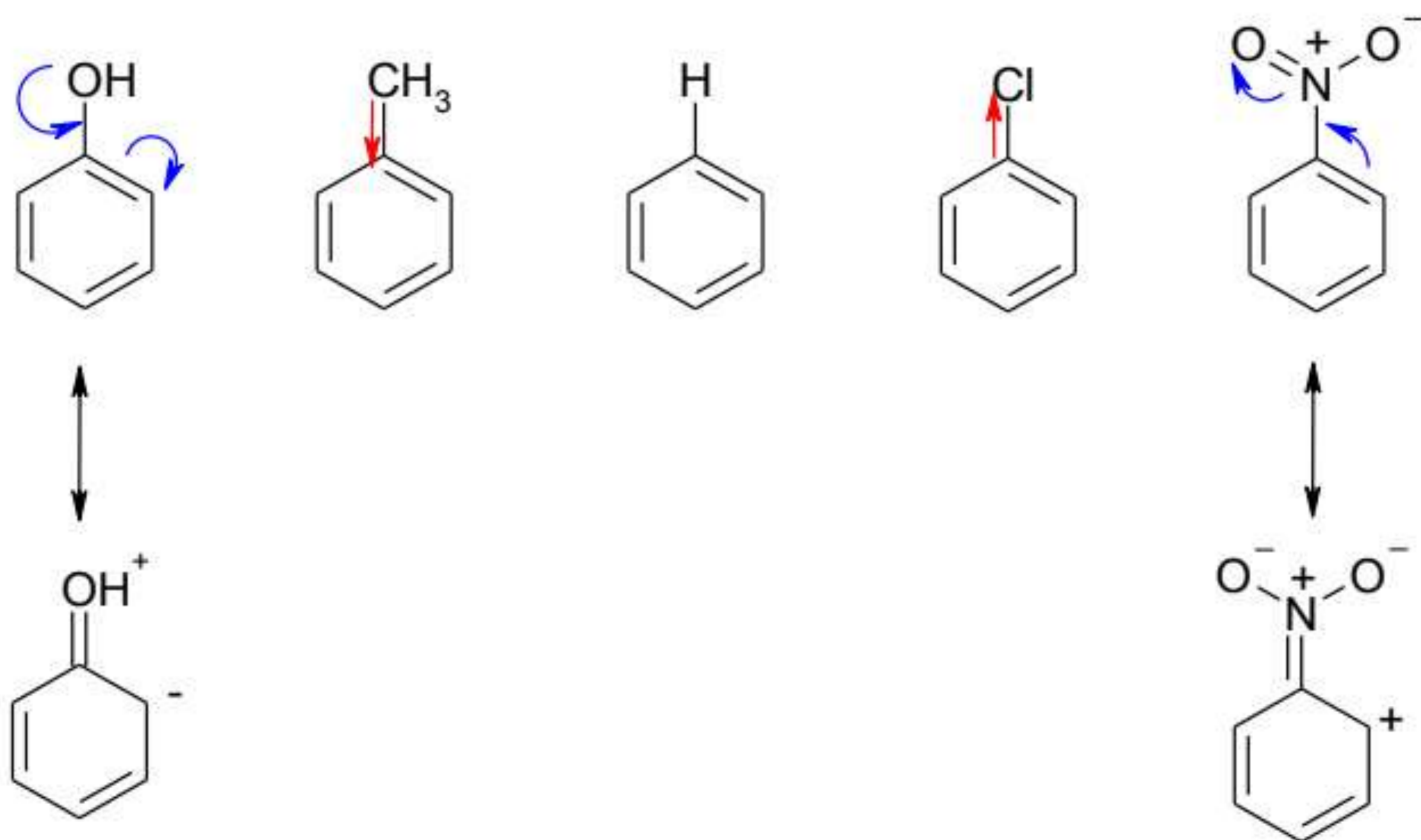
0.0000001

أبطأ

What is causing these differences?

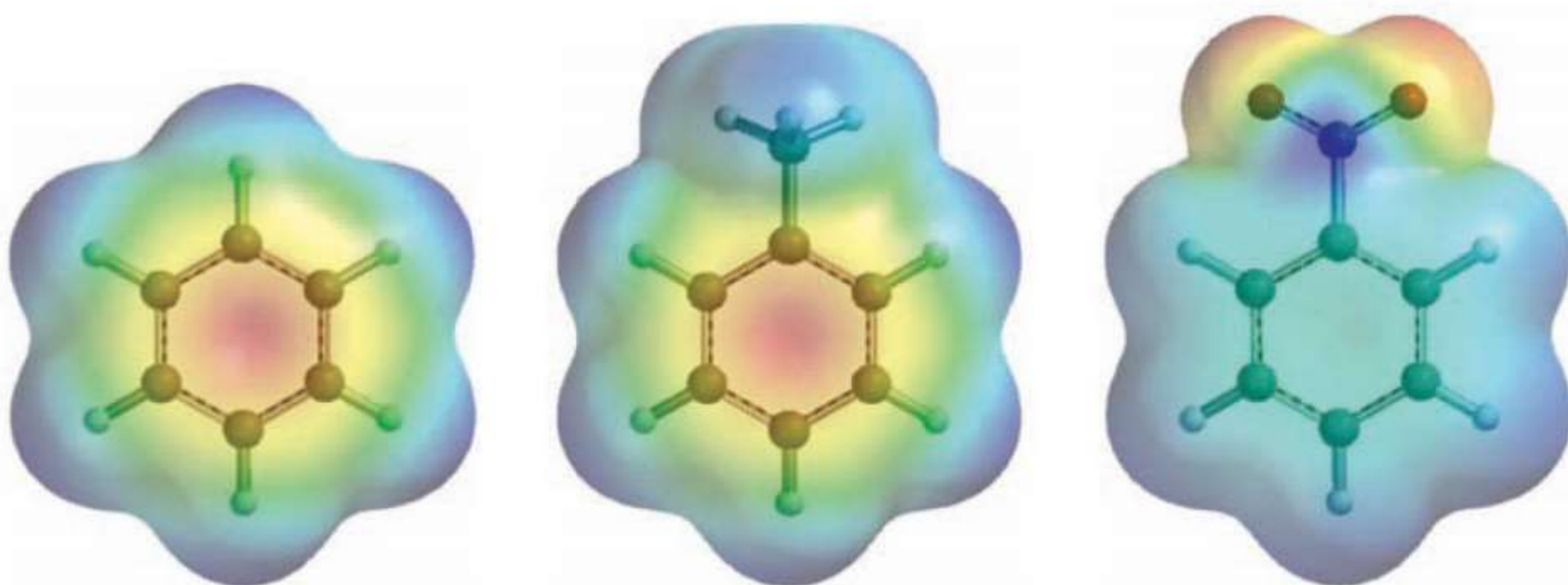
Reaction Rates

The reaction depends on the attack of an electrophile on the benzene ring, this means the charge density in the ring will be very important. Groups that increase the charge density will speed up the reaction while those that decrease charge density slow it down.



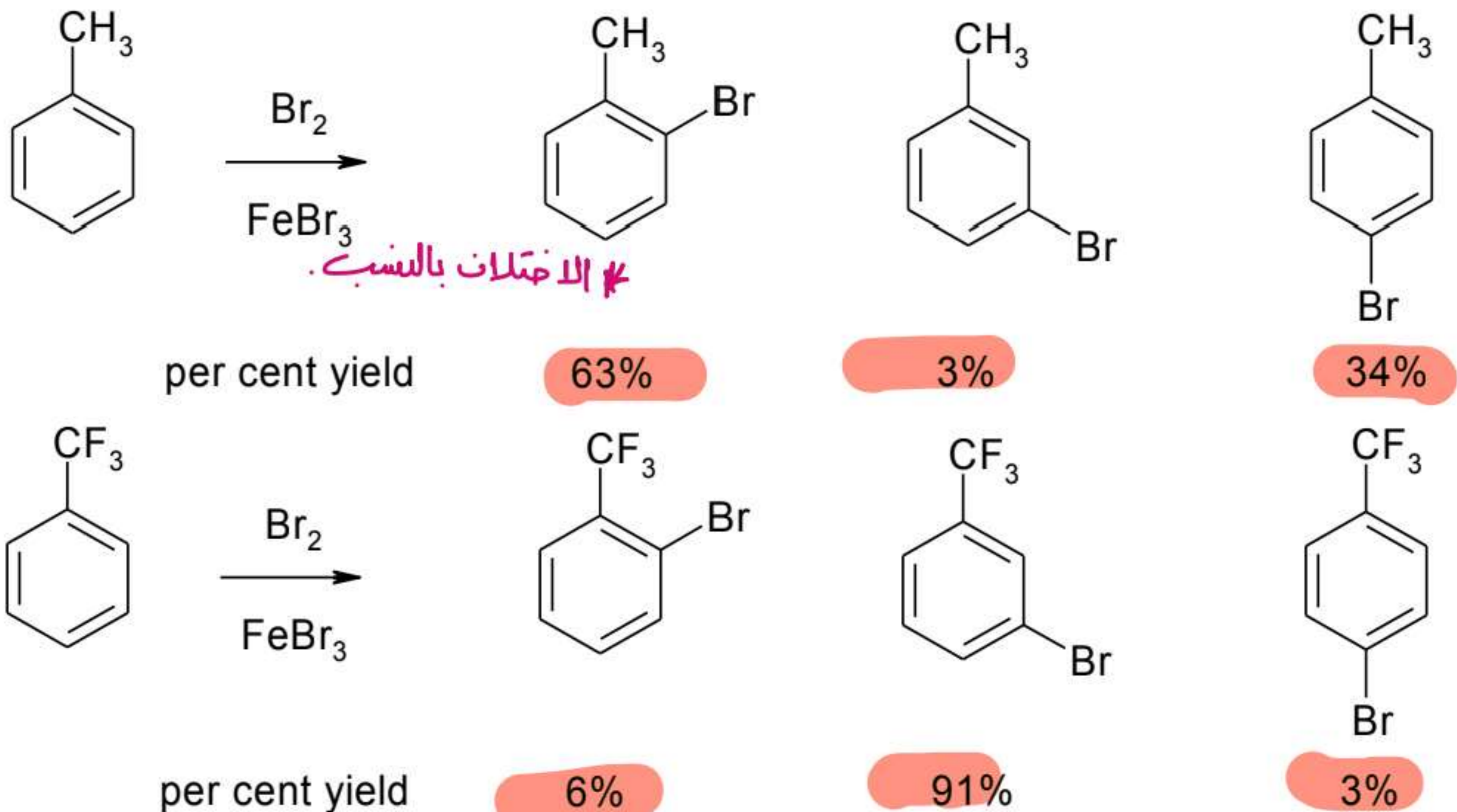
Reaction Rates

This can also be seen in the electron density of these molecules, i.e.



Directing Effects

A second experimental observation is:



Directing Effects

مفید ← موجودین تحت شرح د باسل بطریقتہ اسعمل

The directing effects are caused by the same processes that control the rate of the reaction. The table right groups substituents as o,p-directing or m-directing.

These are relative to an H atom.

Electron donating groups (EDG) activate the ring and are o,p-directing.

Electron withdrawing groups (EWG) deactivate the ring and are m-directing.

Why?

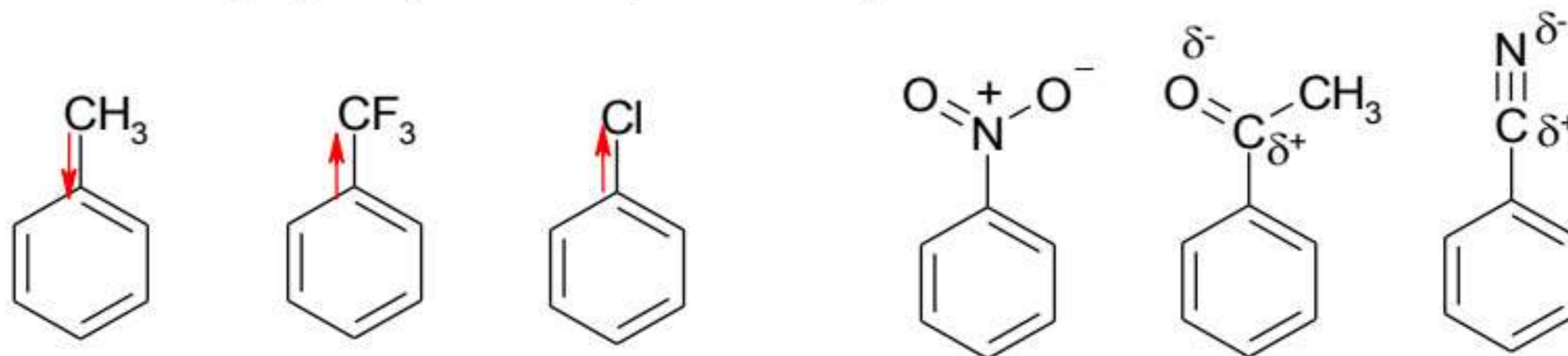
	Substituent group	Name of group	
Ortho, Para-Directing	$-\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{HR}, -\ddot{\text{N}}\text{R}_2$	amino	Activating
	$-\ddot{\text{O}}\text{H}, -\ddot{\text{O}}\text{CH}_3, -\ddot{\text{O}}\text{R}$	hydroxy, alkoxy	
	$-\ddot{\text{N}}\text{H}-\overset{\text{O}}{\parallel}-\text{R}$	acylamino	
	$-\text{CH}_3, -\text{CH}_2\text{CH}_3, -\text{R}$	alkyl	
	$-\ddot{\text{F}}:, -\ddot{\text{Cl}}:, -\ddot{\text{Br}}:, -\ddot{\text{I}}:$	halo	
Meta-Directing	$-\overset{\text{O}}{\parallel}-\text{C}-\text{R}$	acyl, carboxy	Deactivating
	$-\overset{\text{O}}{\parallel}-\text{C}-\ddot{\text{O}}\text{H}$		
	$-\overset{\text{O}}{\parallel}-\text{C}-\ddot{\text{N}}\text{H}_2$	carboxamido, carboalkoxy	
	$-\overset{\text{O}}{\parallel}-\text{C}-\ddot{\text{O}}\text{R}$		
	$-\overset{\text{O}}{\parallel}-\text{S}-\ddot{\text{O}}\text{H}$	sulfonic acid	
	$-\text{C}\equiv\text{N}:$	cyano	
$-\text{N}^+=\overset{\text{O}}{\parallel}-\ddot{\text{O}}:$	nitro		

Directing Effects

Two effects can account for these observations:

1) **Inductive effects**: this is the donation or withdrawal of electron density through the bond due to the EN of the atom.

- Alkyl groups are weakly EDG so activating
- Halides are more EN so weakly EWG and deactivating, but o,p-directing because of the lone pair electrons
- Any group where the atom attached to the ring has a formal or partial positive charge and no lone pair electrons, this includes nitro, cyano, carbonyl and alkyl halides.

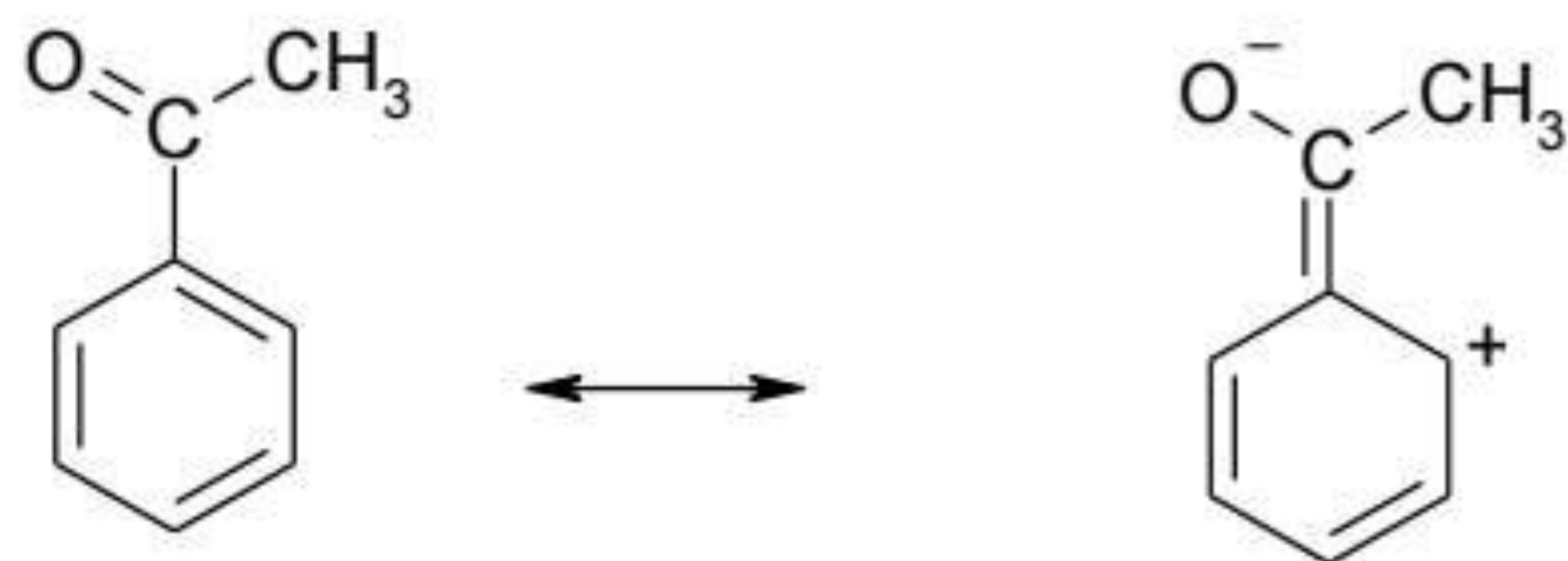
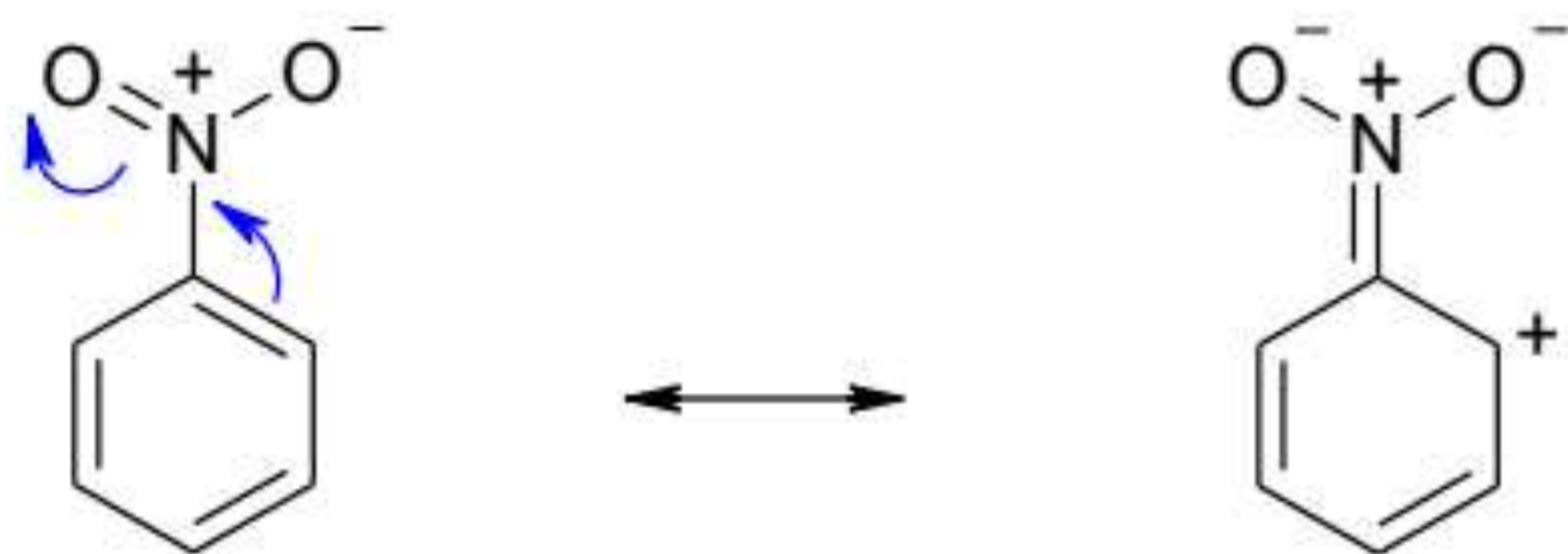


Directing Effects

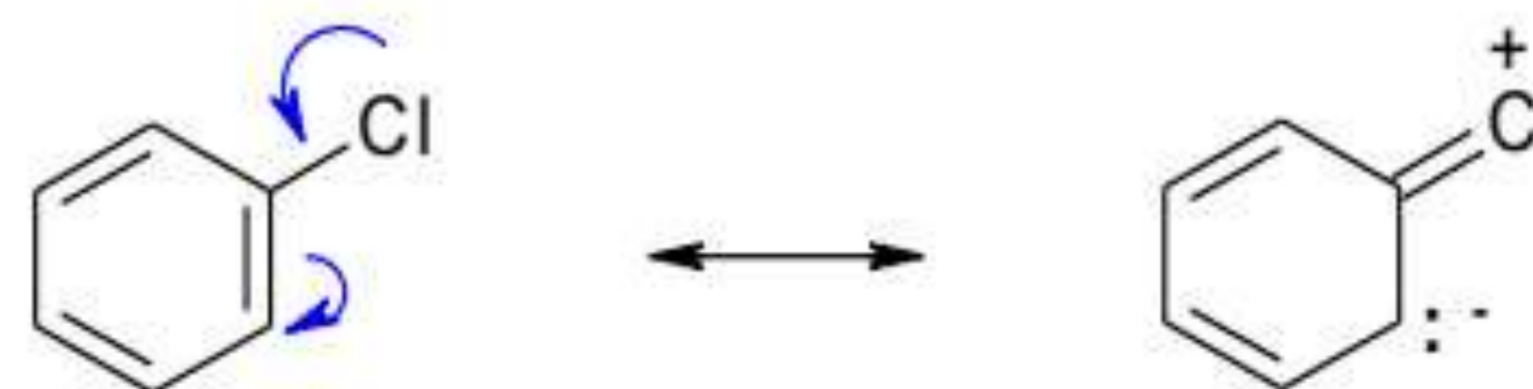
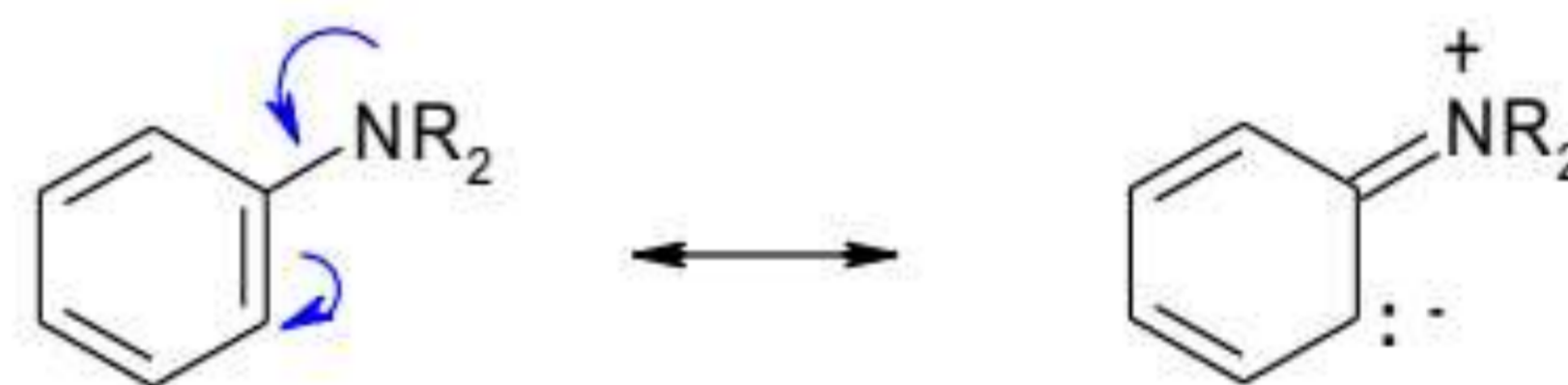
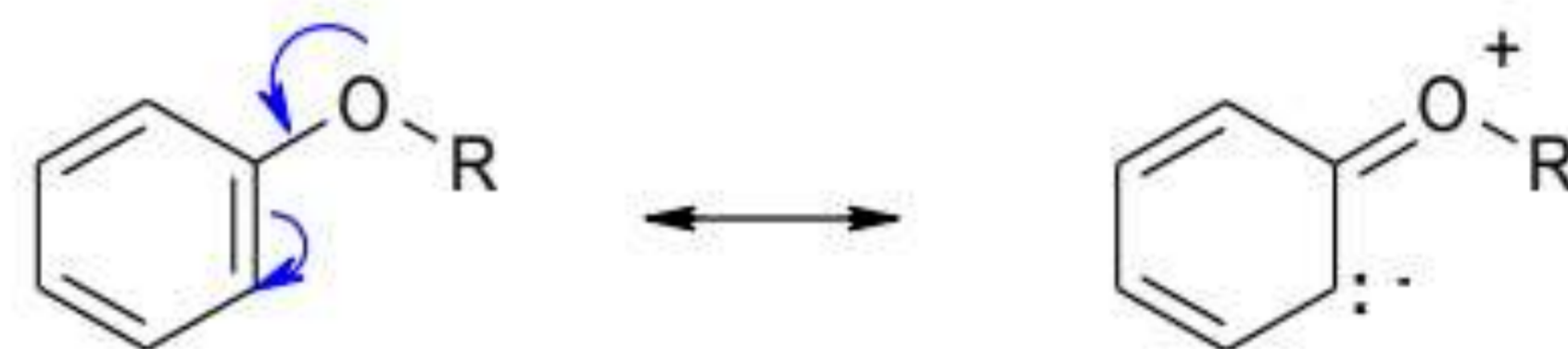
- 2) *Resonance effects*: this is the donation or withdrawal of electrons in the π system by resonance.
- Any group where the atom attached to the ring has a lone pair of electrons such as N and O. These are activating.
 - Halides are more EN so weakly EWG and deactivating, but o,p-directing because of the lone pair electrons
 - Any group where the atom attached to the ring has a formal or partial positive charge and no lone pair electrons but attached to a more EN atom by multiple bonds, this includes nitro, cyano, sulfonyl and carbonyl groups.

Directing Effects

Examples of resonance effects:



Electron withdrawal:

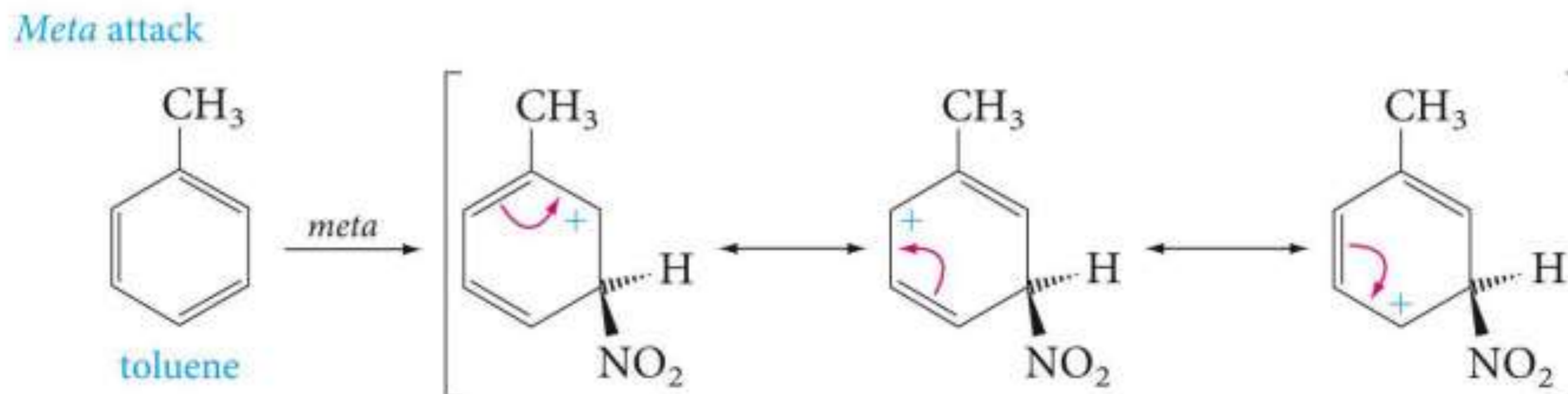
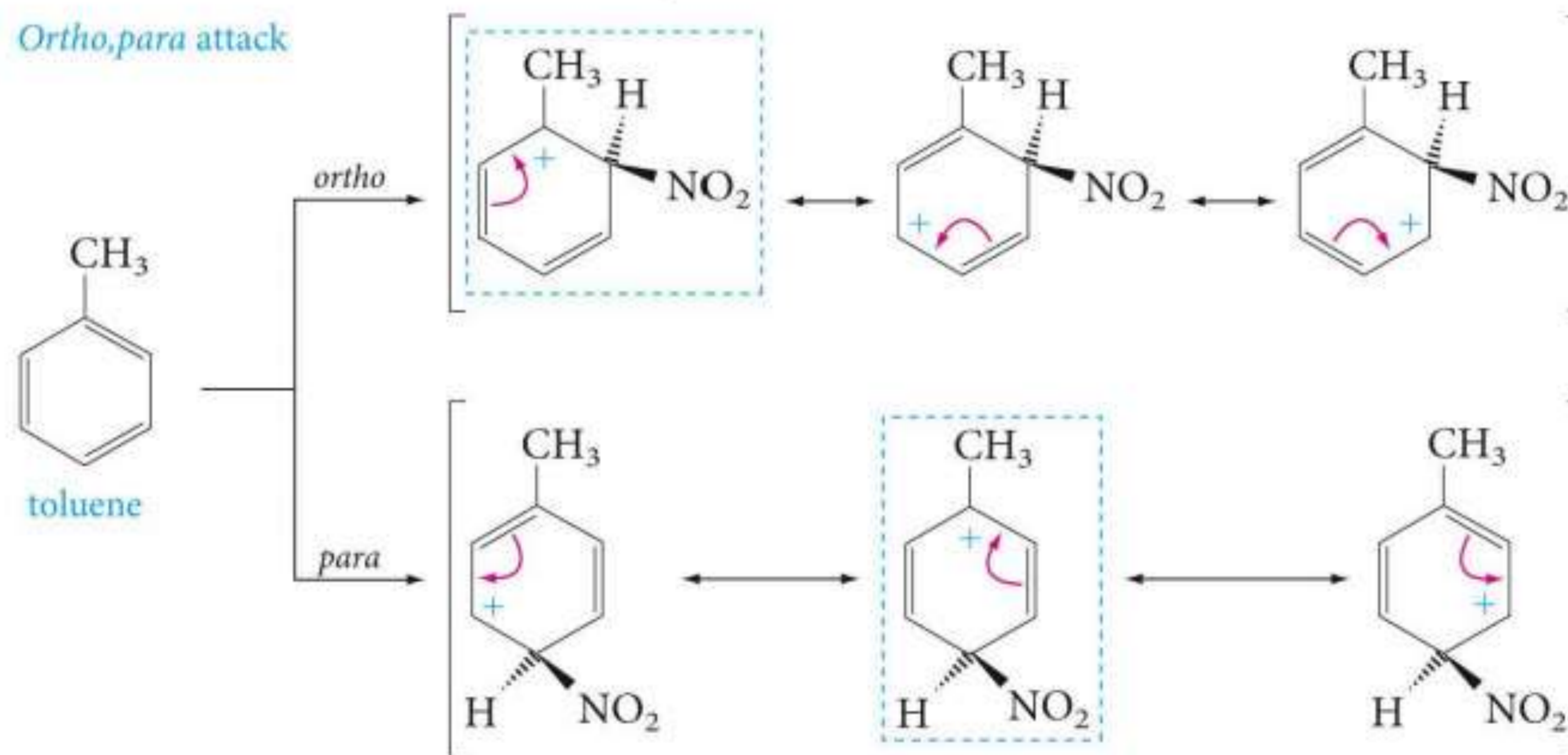


Electron donation:

Directing Effects

So how does this effect a reaction?

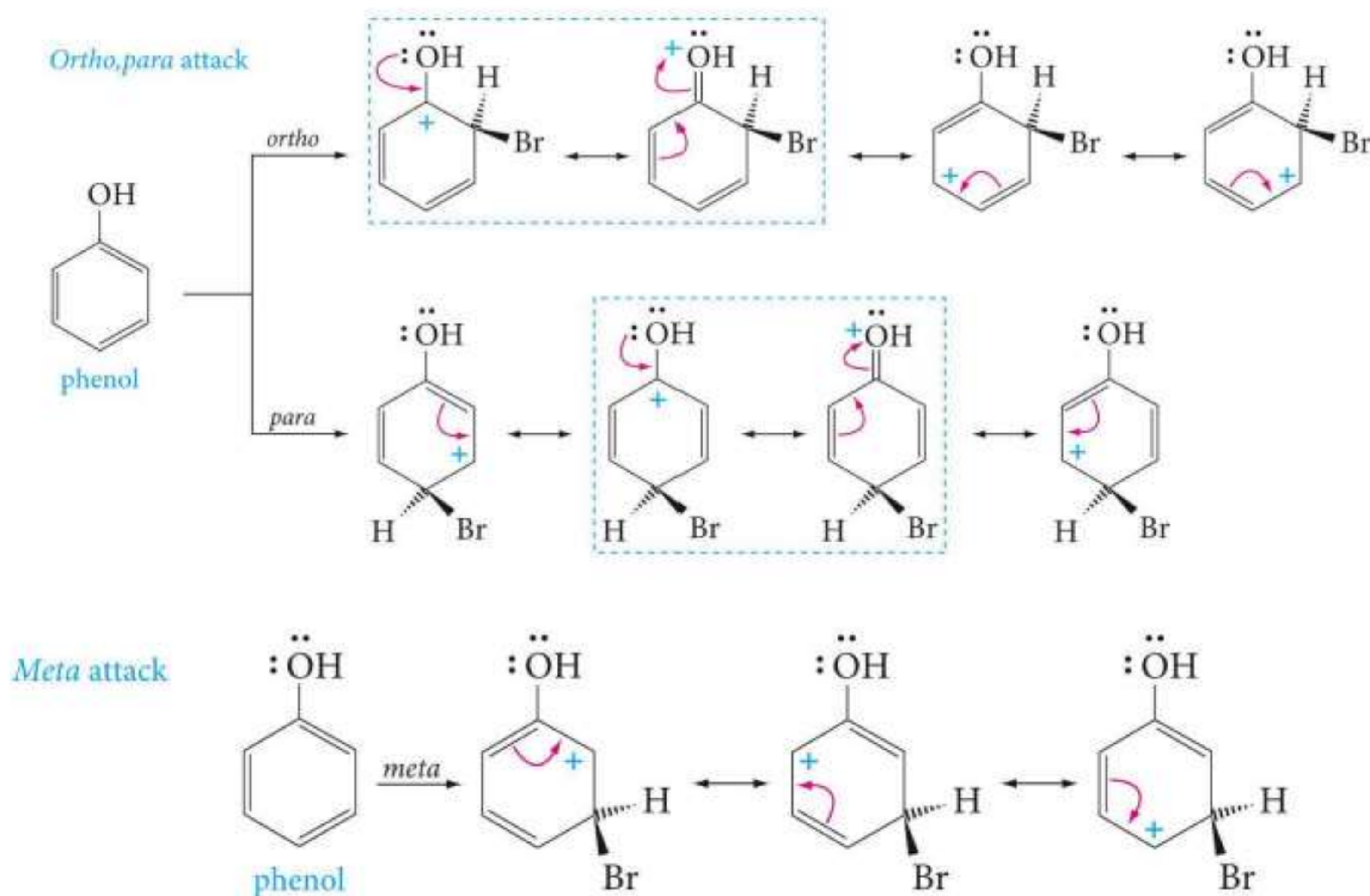
Activating o,p-directing group, i.e. CH₃



Directing Effects

So how does this effect a reaction?

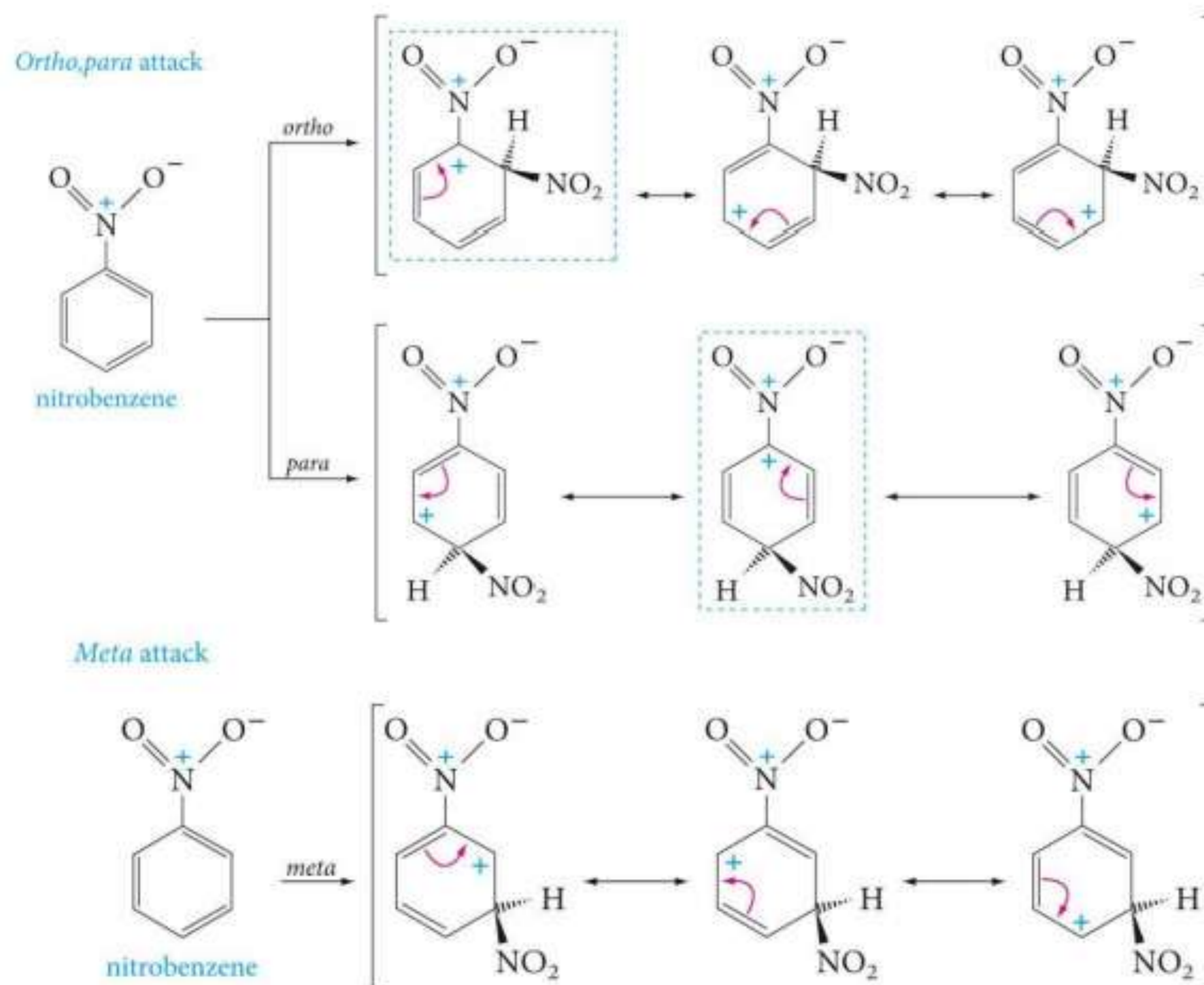
Activating o,p-directing group, i.e. OH



Directing Effects

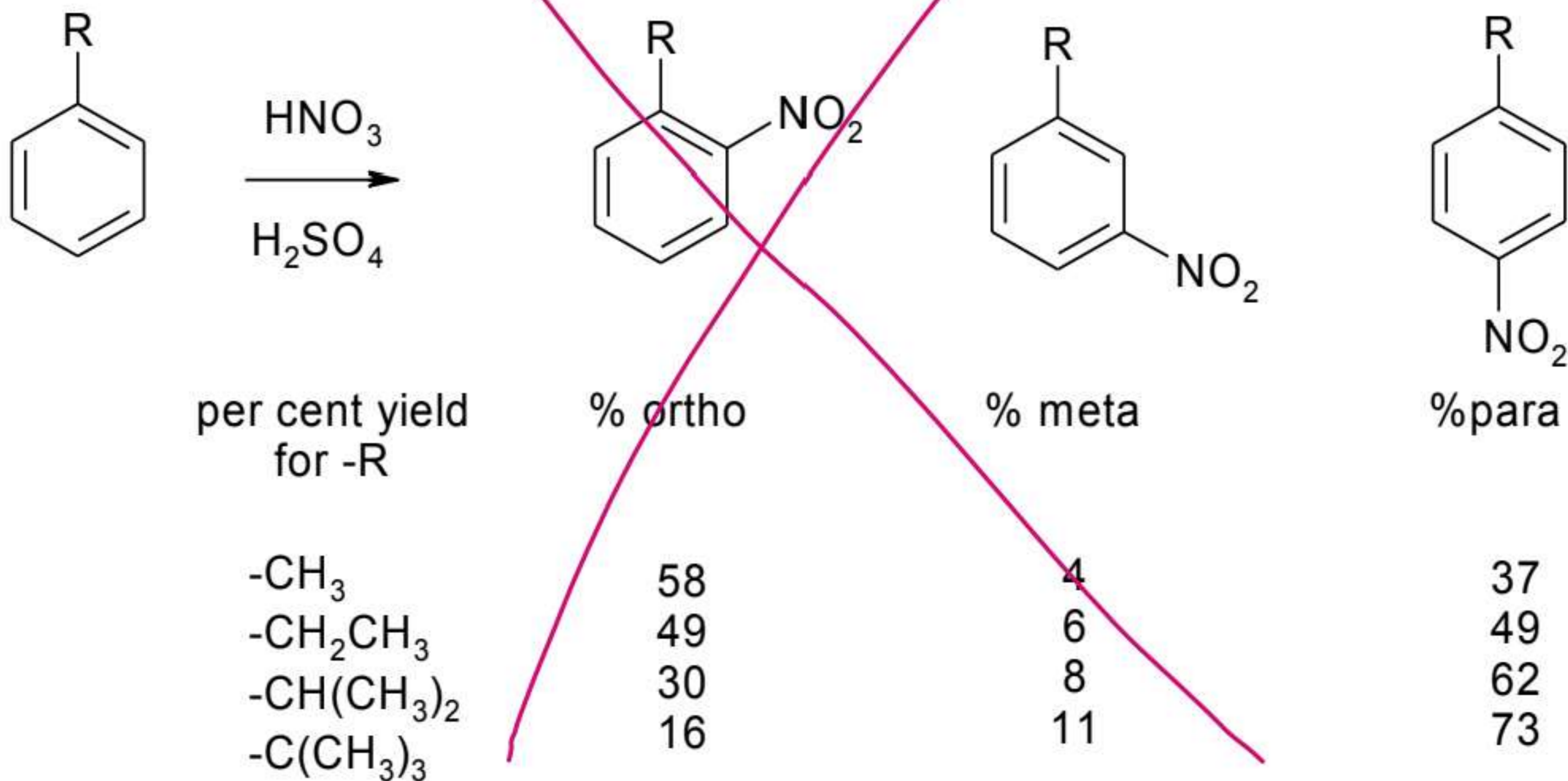
So how does this effect a reaction?

Deactivating m-directing group, i.e. NO_2



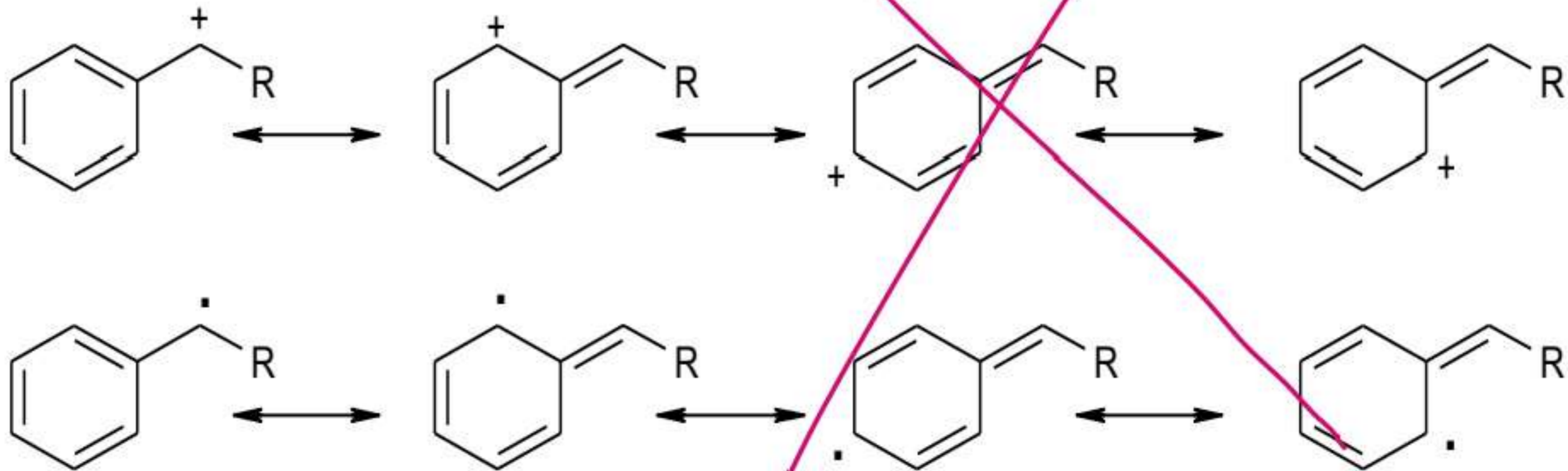
Directing Effects

Besides electronic effects the size of the substituent can effect the location of a subsequent reaction. These are *steric effects*, i.e.



Benzylic Reactions

The benzylic position has an enhanced reactivity similar to an allylic position, i.e.



As a result both benzylic cations and radicals form easily.

Second Electrophilic Aromatic Substitution reaction :- المركب يكون أحياناً عامل استبدال حامي أعلاه استبدال مرة ثانية

* التفرع إلى يكون موجود بالأساس على البنزين [عائق بالكلفة شيء إلى هسه بهي أضيفه] تحتكم بتخليق في التفاعل الثاني

نشاط البنزين وجرعته [Reactivity] سه ↑ النشاط ، ↑ جرعة التفاعل والعكس

تحتكم بموقع التفرع الجديد [يعني شيء كل || زي بعض لا يفرق]

← يا بوريه على [ortho, para]
← أو Meta

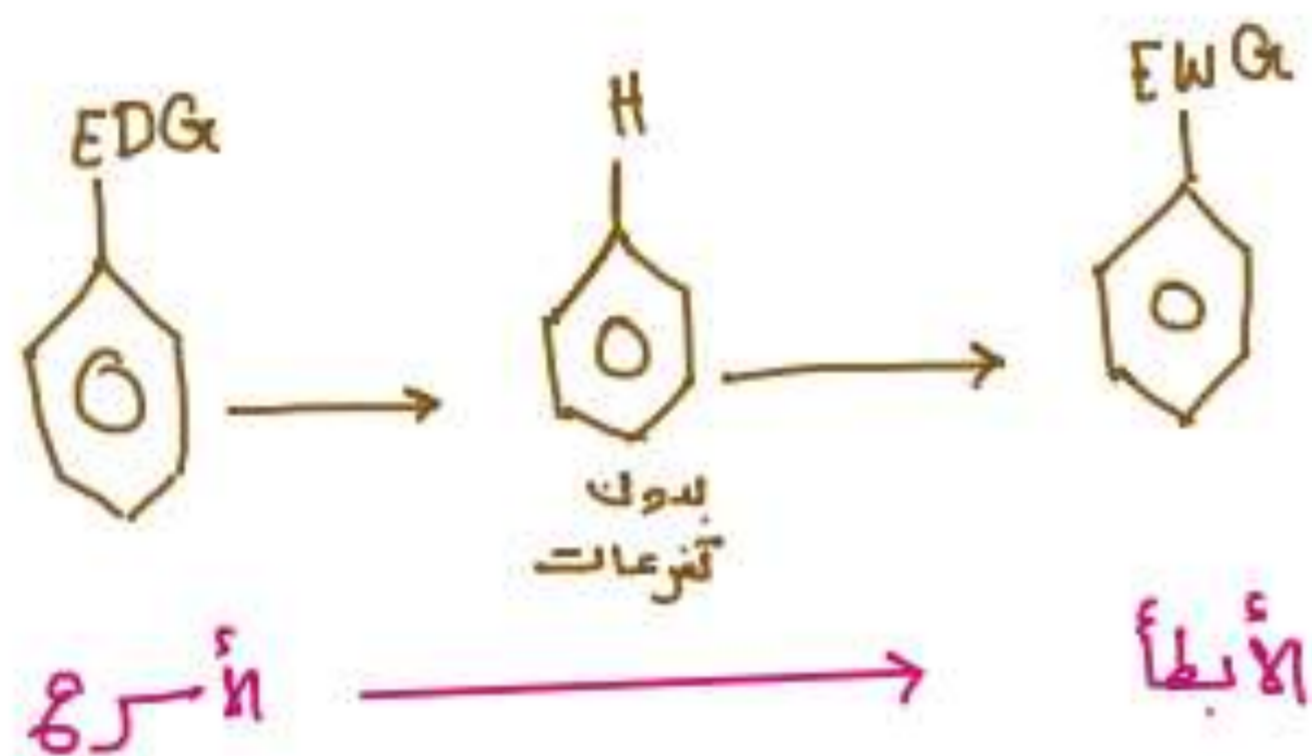
⇒ Reactivity of the benzene ring

→ EDG [e donating group] [Activators]

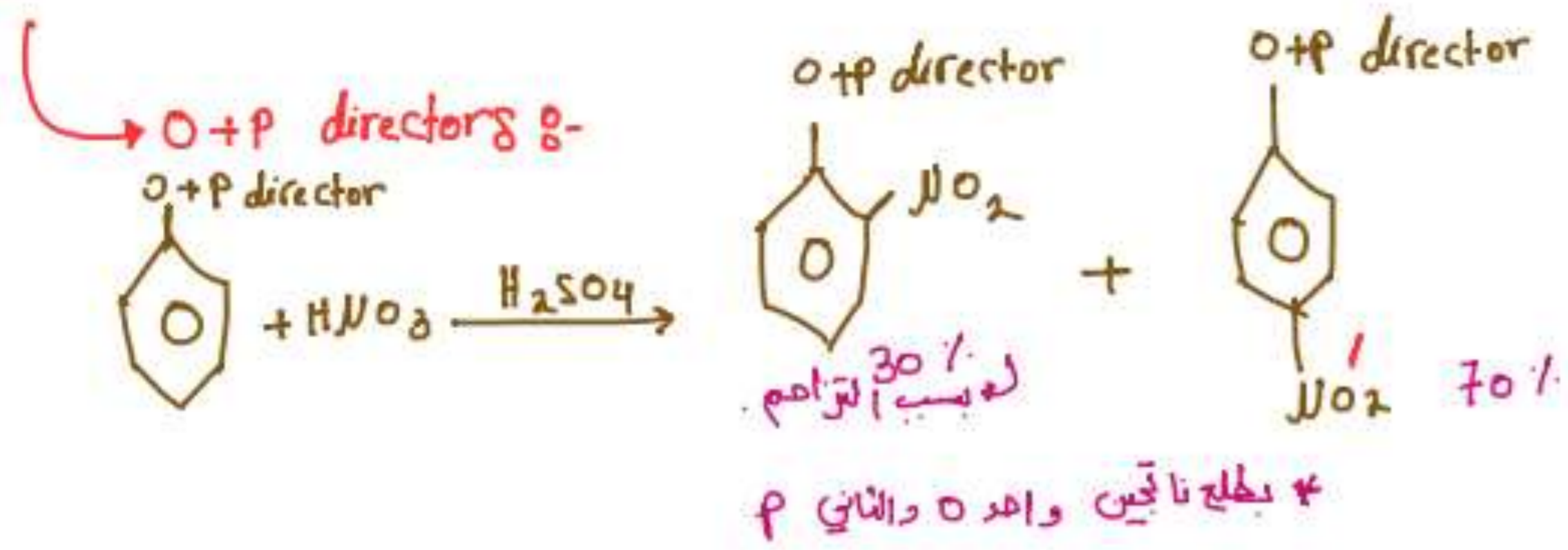
مجموعات منشطة [تزيد سرعة التفاعل]

→ EWG [e withdrawing Group] [deactivators]

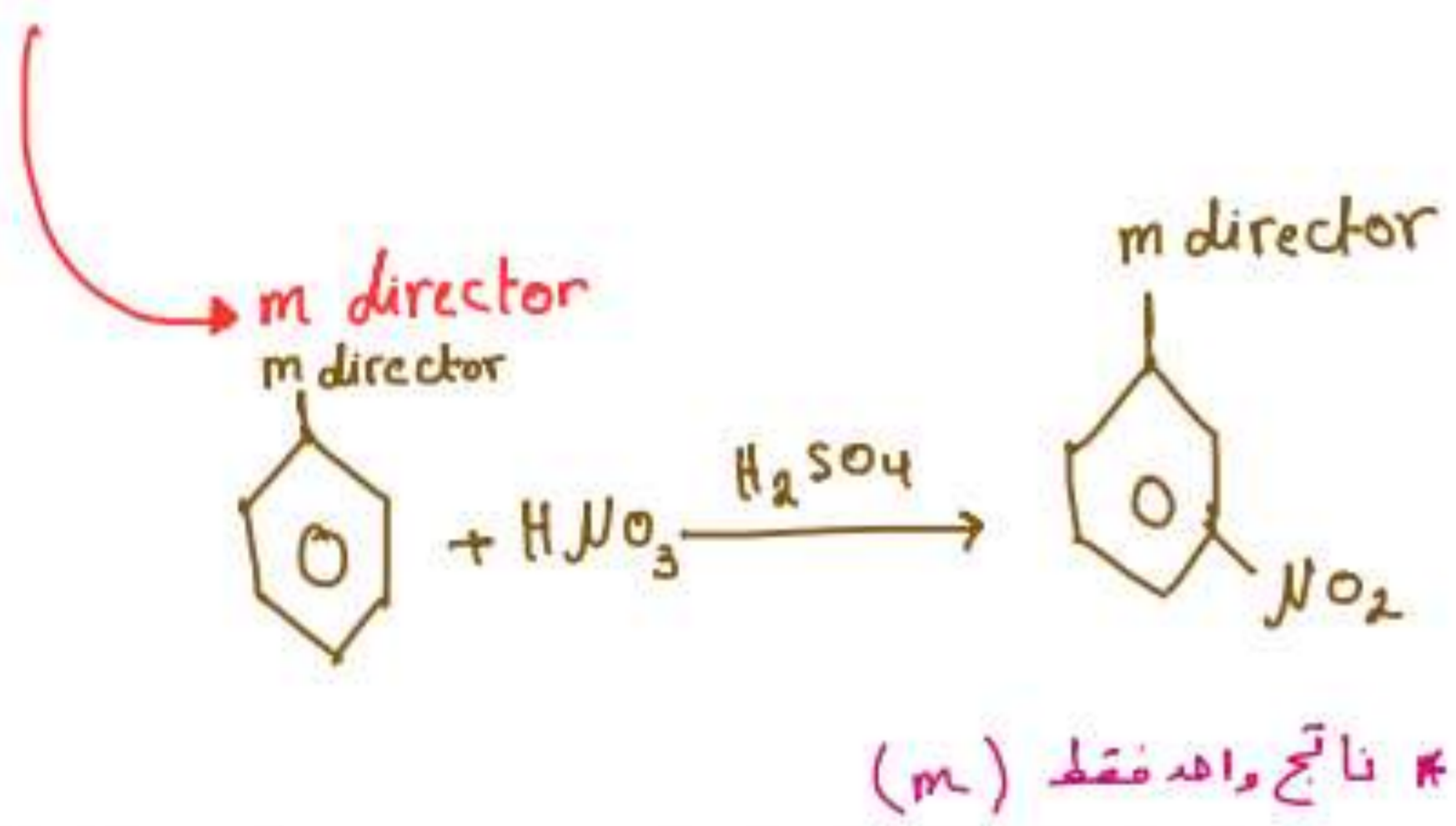
مجموعات منبطة (تقلل سرعة التفاعل)



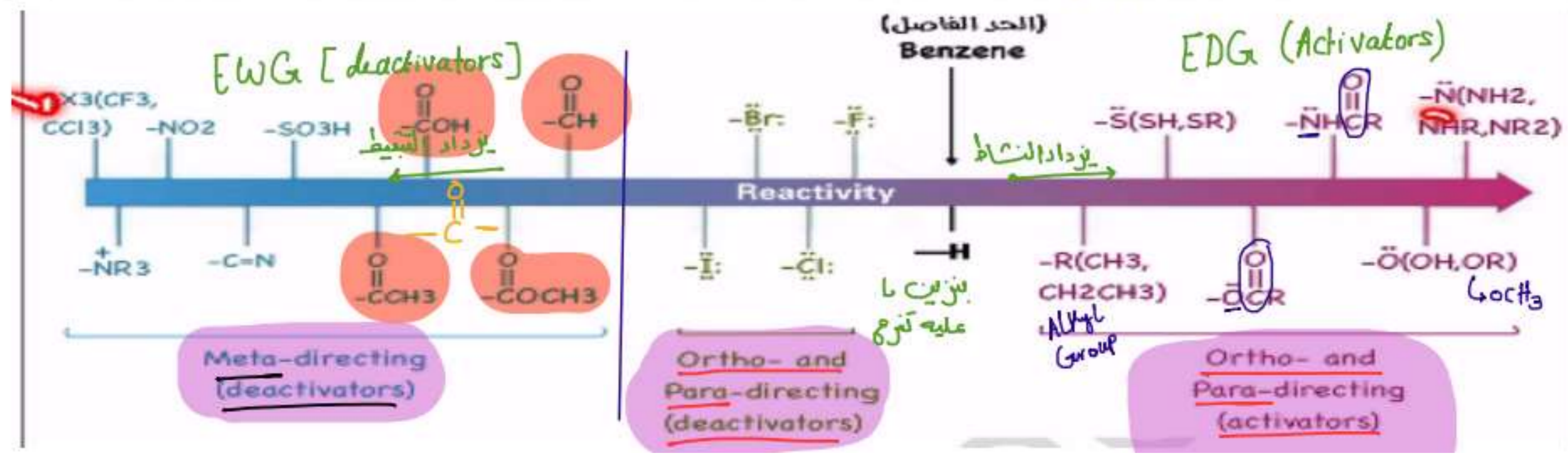
2) التكم بالموثق



* الي لحدد نشأه البنزين هو التفرع
 الأول فقط لا يوجد من الأساسي
 يعني الي يكون على الحلقة مني
 الي رح أضيفه



No No sir



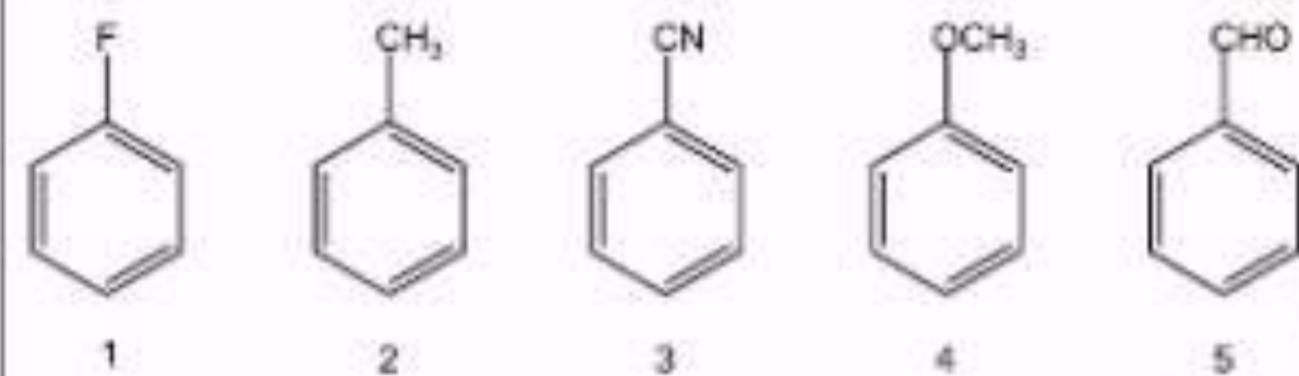
ما
 حفظ

ملاحظة: تم شرح كونهم EDG وهيك في part 8 بحكا عنهم مش مهمين فاذا حابين تفهمو ارجعو احضرو الفيديو لانني عملت سكب / لحد دقيقة 5

Examples on Reactivity :

IKP

Q: Rank the following compounds in order of increasing reactivity toward sulfonation reaction ?



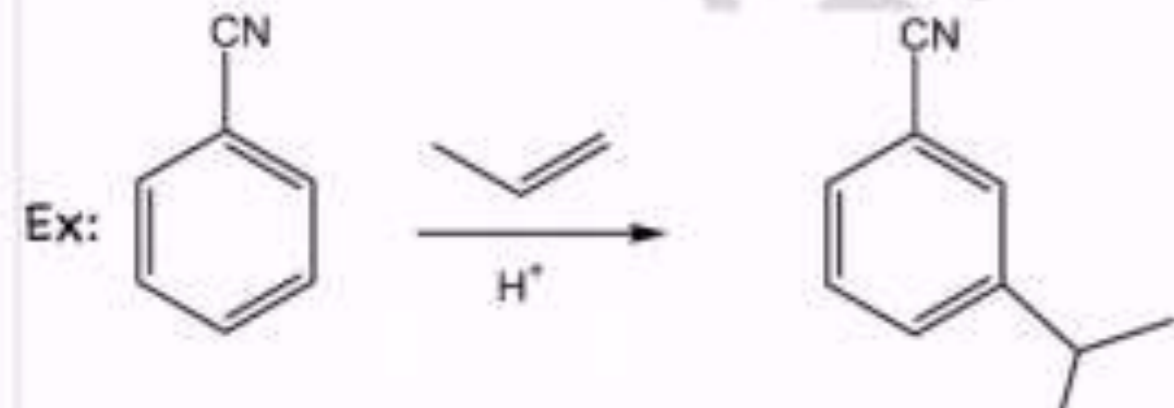
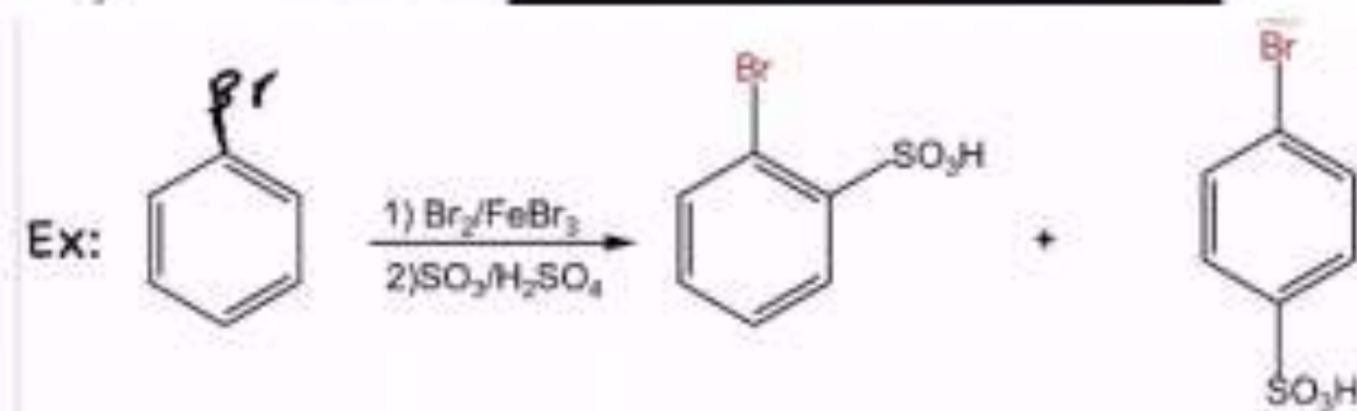
Ans : 4>2>1>5>3
امشي بالخط حيث كلما رحنا لليمن فيه زاد النشاط

Q: The order of decreasing reactivity towards electrophilic aromatic substitution is ?

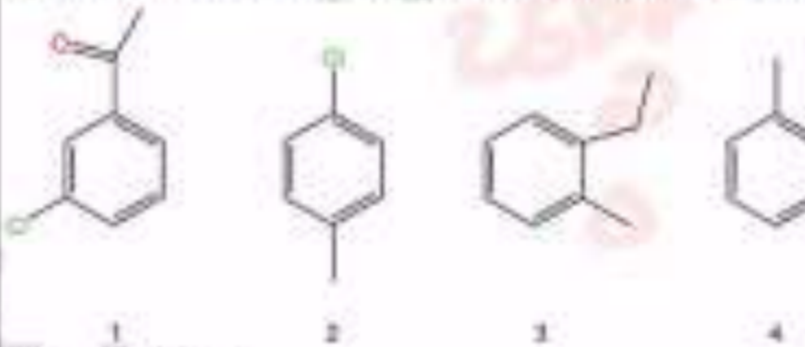
- 1) Benzene 2) Nitrobenzene 3) Benzaldehyde 4) Phenol 5) Ethylbenzene

Ans : 4>5>1>3>2
قم برسم التركيبات وقلرن حسب المنطق طبيعي

Q: Arrange the following compounds in order of increasing reactivity toward EAS ?



Q: Arrange the following compounds in order of increasing reactivity toward EAS ?



Ans : 3>4>2>1

منطقياً كل ما زاد عدد مجموعات الـ (EDG) زاد النشاط ليهك مركب (2) نشاطه اعلى من (1) لانه فيه مجموعتين (EDG) وليس واحدة ، وايضاً كلما زاد عدد مجموعات الـ (EWG) قل النشاط ليهك مركب (2) نشاطه اعلى من (1) لانه فيه مجموعة (EDG) ومجموعة (EWG) على طرف (1) التي فيه مجموعتين (EWG)

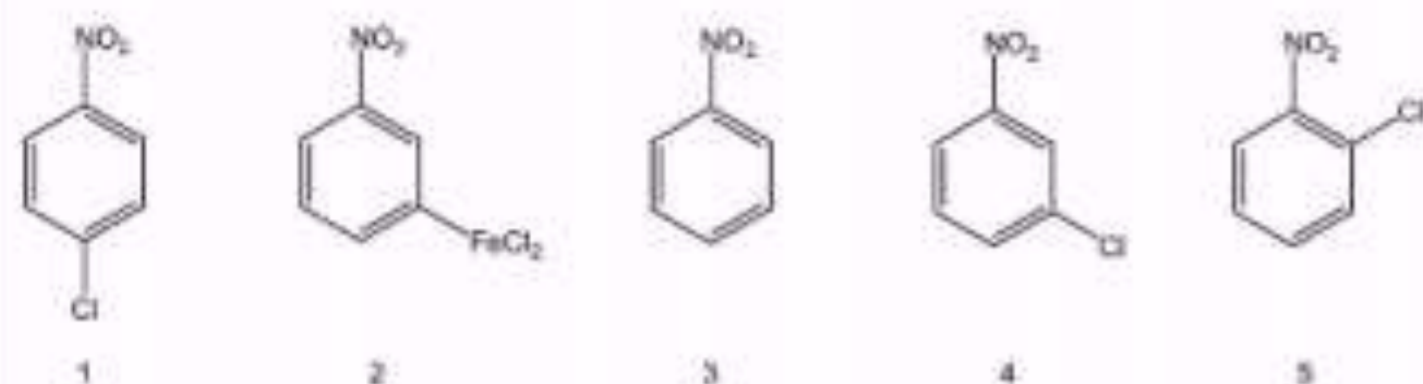
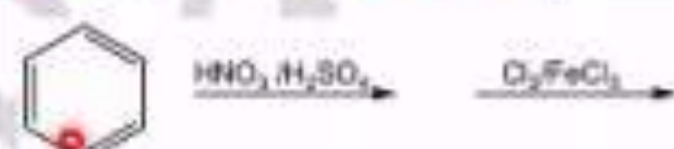
Bassil CHEMISTRY Abu

Examples on (O+P) or (m) directors :

Ex: c1ccc(C(=O)O)cc1 $\xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3}$ c1ccc(C(=O)O)cc1[N+](=O)[O-] (m) لذلك نضع

Ex: c1ccc(C)cc1 + CC(=O)Cl $\xrightarrow{\text{AlCl}_3}$ c1ccc(C)cc1C(=O)C + c1ccc(C)cc1C(=O)C (m) يتكون

Q: What is the major product(s) of the following reaction? سنوات



- A) 4
- B) 1+5
- C) 3+5
- D) 1+2

Ans : A

تجرع نل الجهل طول حياته

Bassil



ومن لم يثق مر التعلم ساعة

Aba-Ayoub

Q: What is the true answer(s) regarding the substituent effects of electrophilic aromatic substitution reactions? سنوات

- A. All activators are O, P-directors
- B. All deactivators are m-directors
- C. Halogens are activators O, P-directors
- D. All deactivators are m-directors except halogens
- E. A+D

Q: When considering electrophilic aromatic substitution reactions electron donating substituents (e.g methoxy) are described as? سنوات

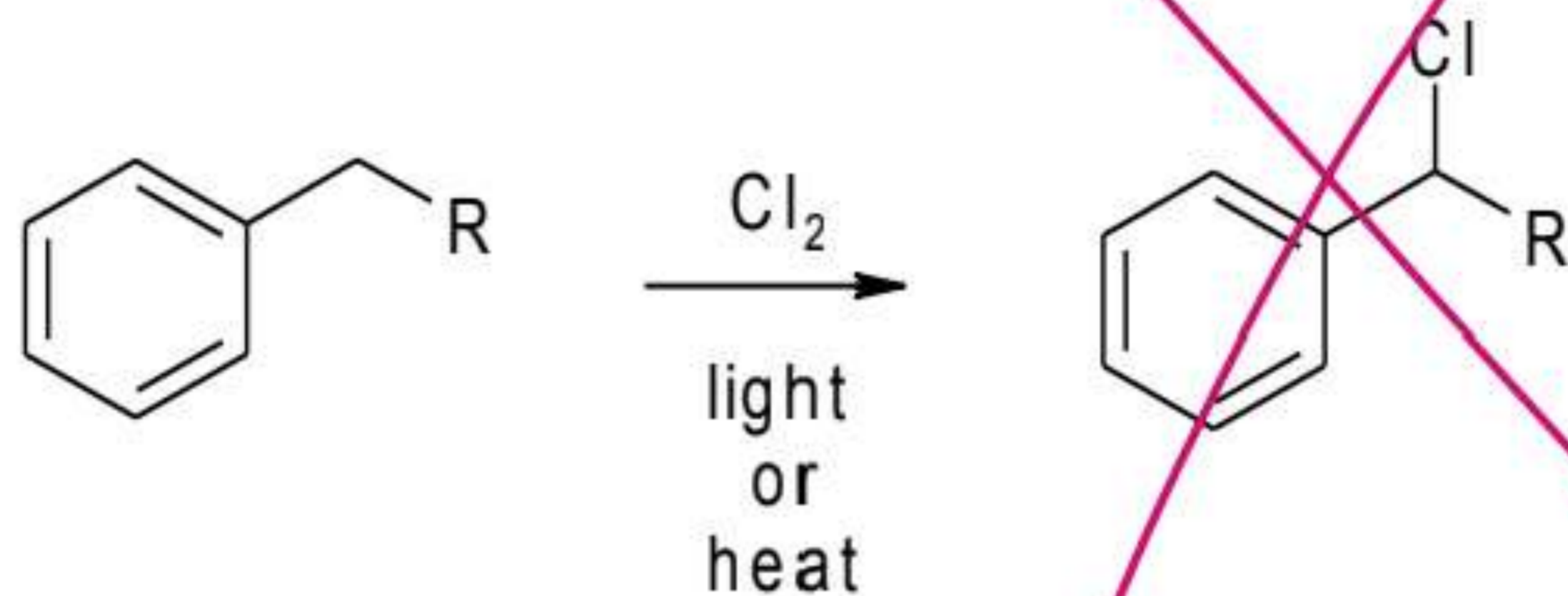
- A. Ortho/para directing and activating
- B. Ortho/para directing and deactivating
- C. Meta directing and activating
- D. Meta directing and deactivating

Ans : A (OCH3) هي (methoxy) اذا انت تاسي قال

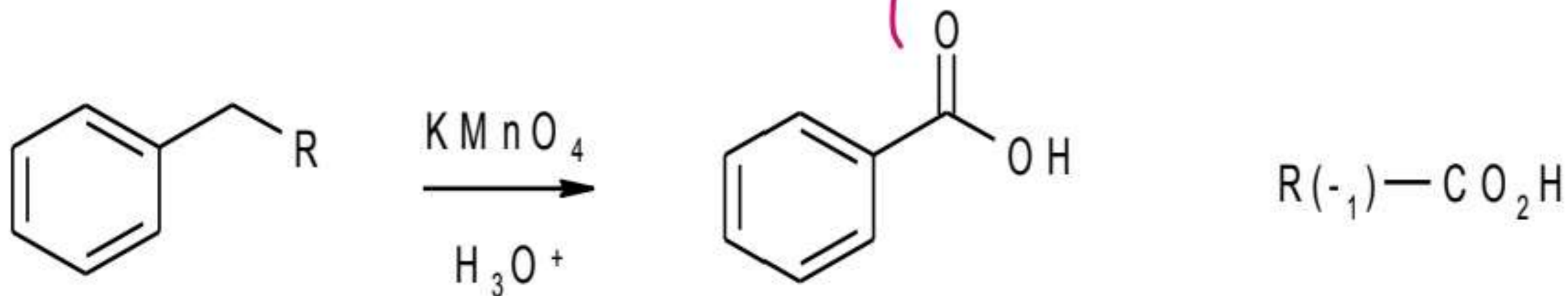
Benzylic Reactions

Common reactions for benzylic sites:

Radical halogenation:

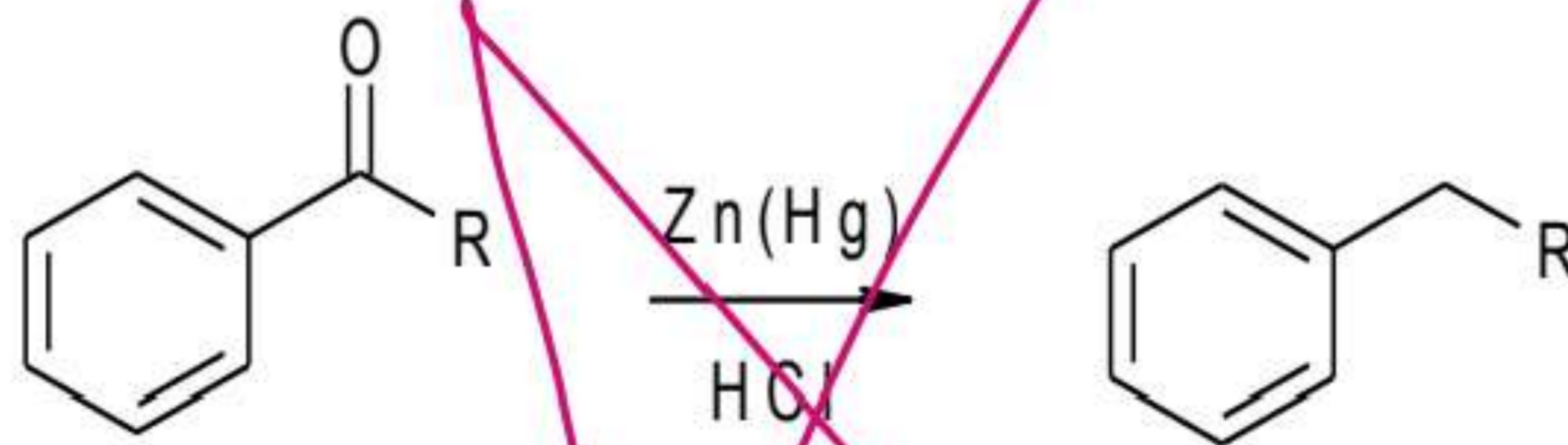


Oxidation:

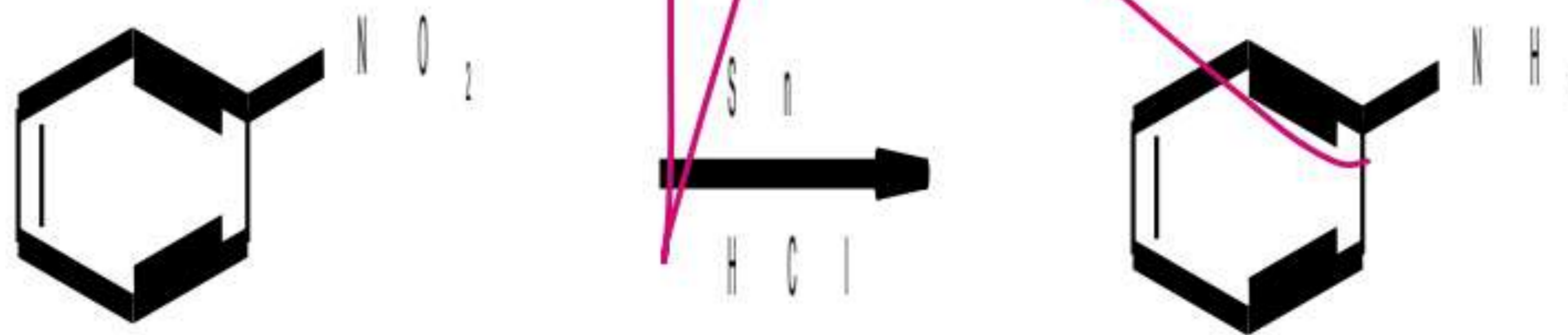


Other Functional Group Modifications

Reduction of carbonyls

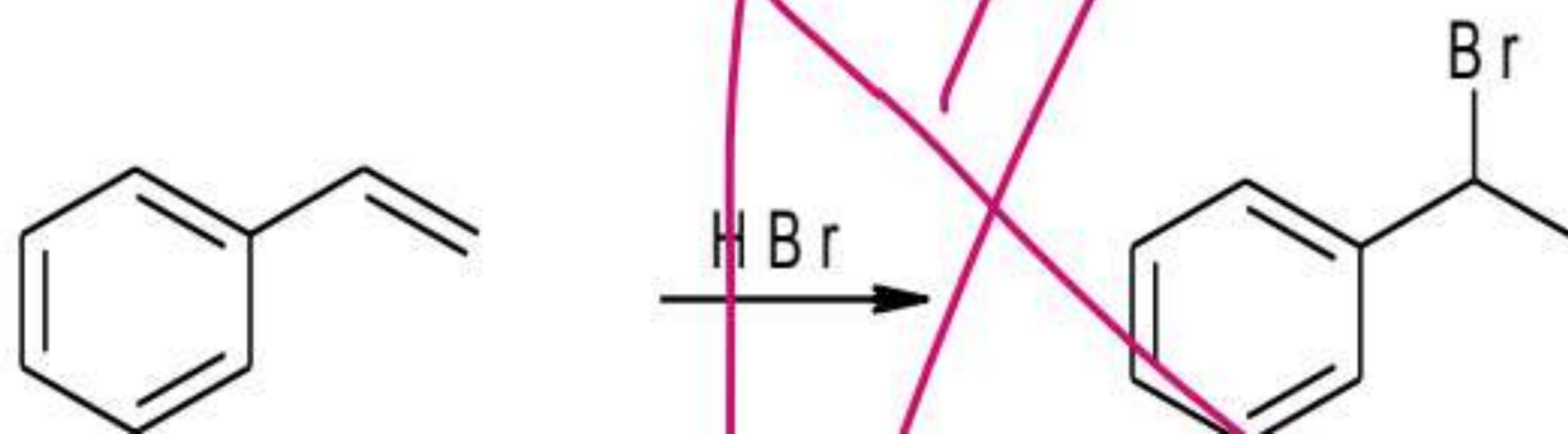


Reduction of nitro to amines

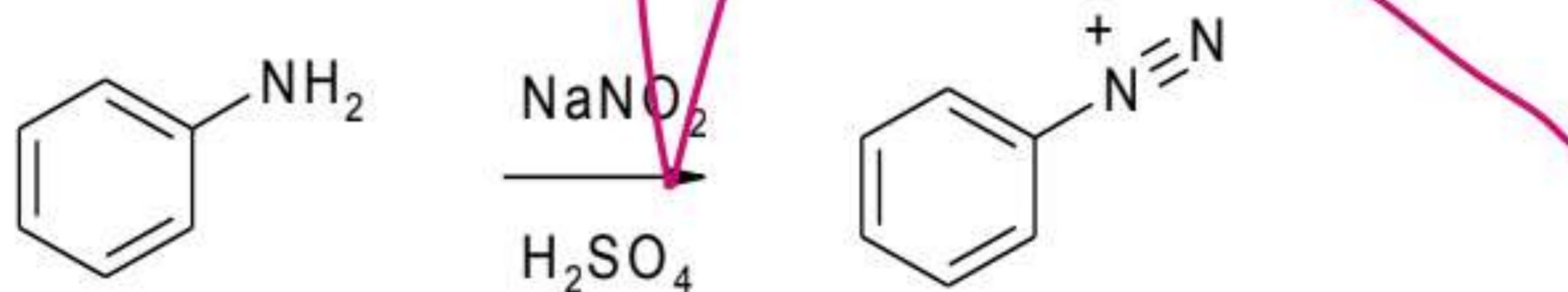


Other Functional Group Modifications

Addition to alkenes (Markovnikov addition product)

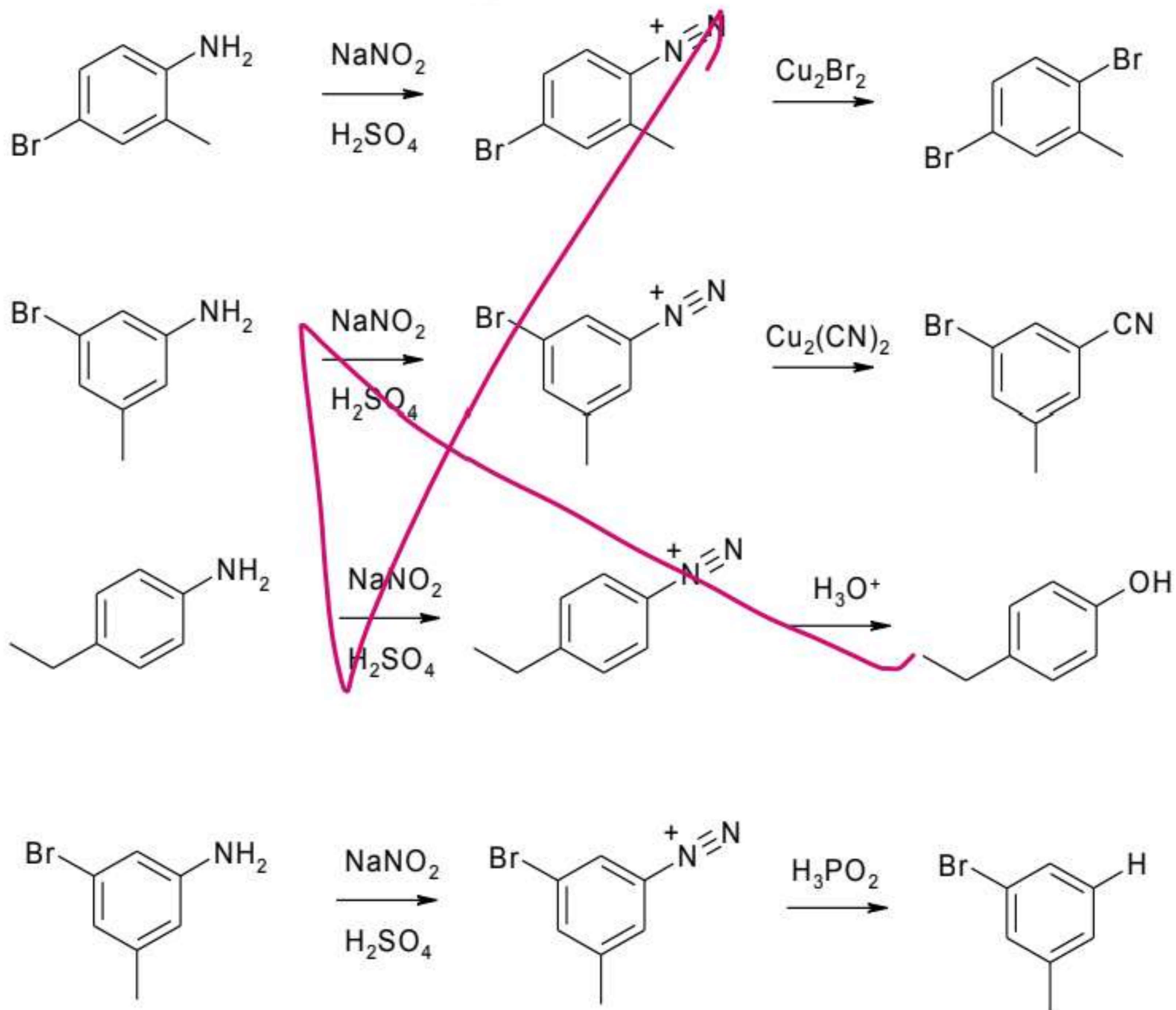


Diazonium salts allows for a Nucleophilic attack!



Examples of Using Diazonium Salts

Controlled synthesis!



Synthesis of Aromatic Compounds

You know what you want to make so the idea is to work backwards from the product, using well know reactions, to the starting material.

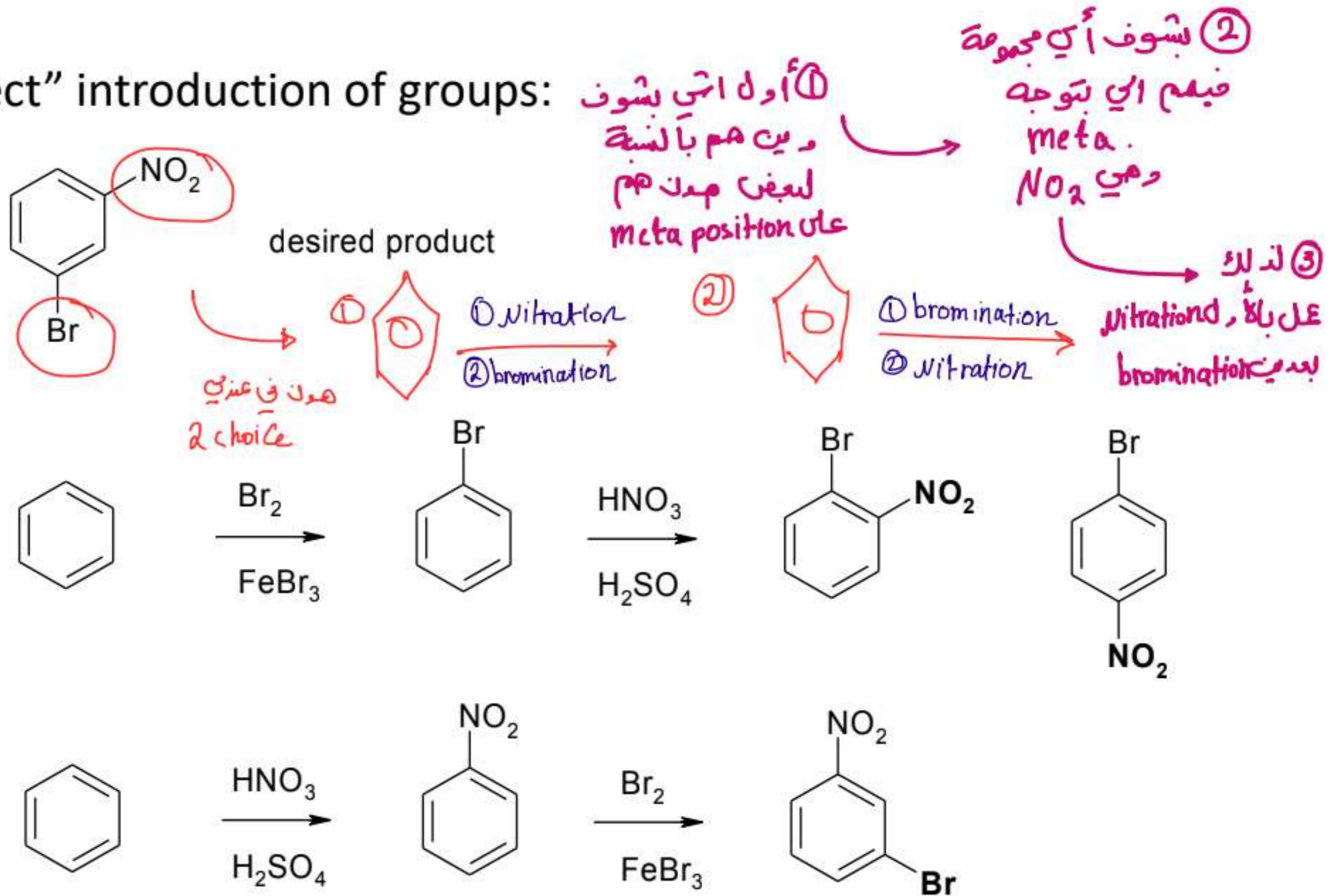
This process is known as *Retrosynthesis*.

لأرجع اجوع في المركب ←

This means you need to know how the reactions and their directing effects, i.e.

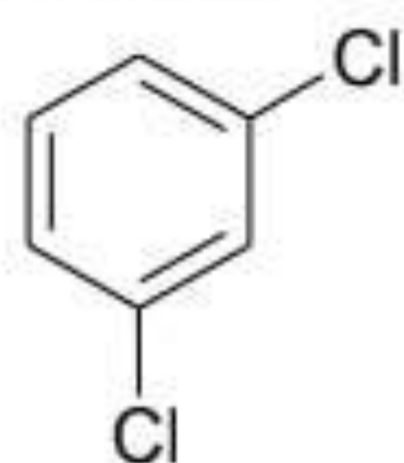
Synthesis of Aromatic Compounds

"Direct" introduction of groups:

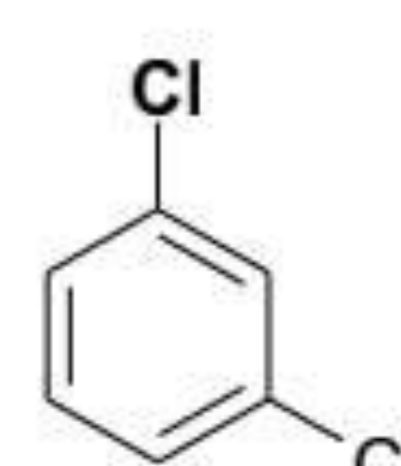
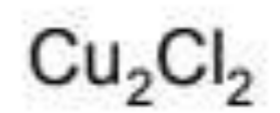
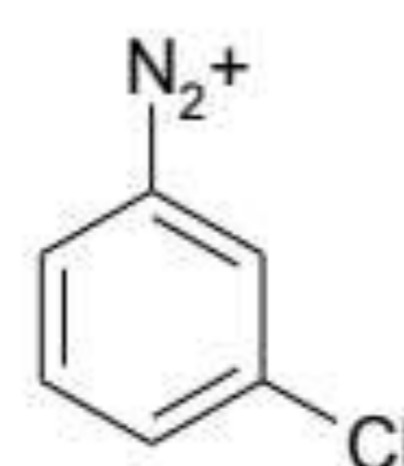
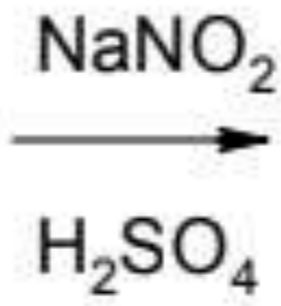
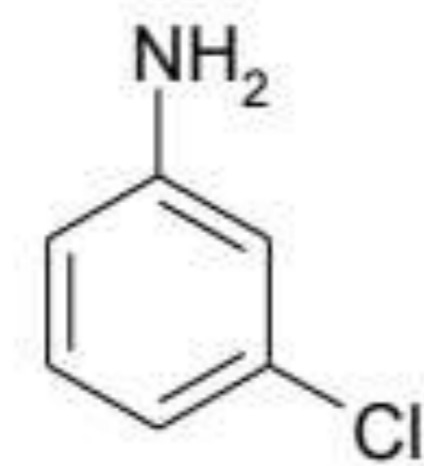
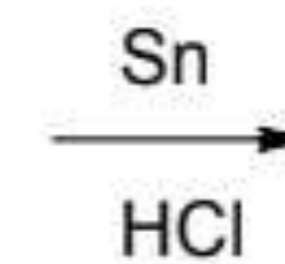
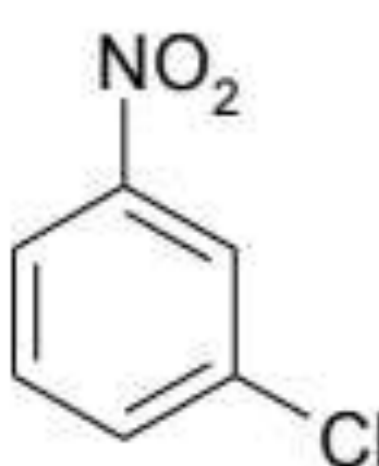
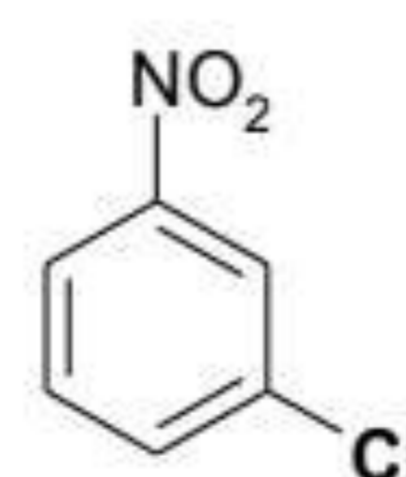
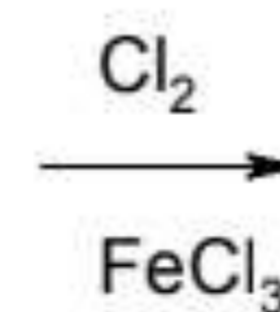
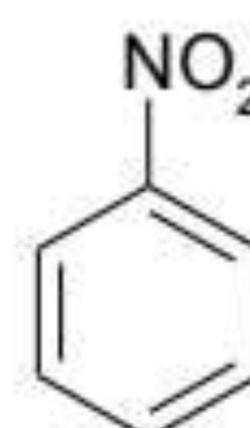
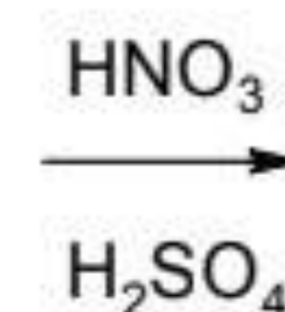
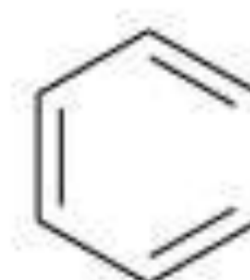
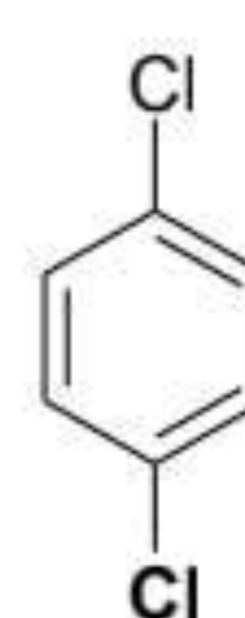
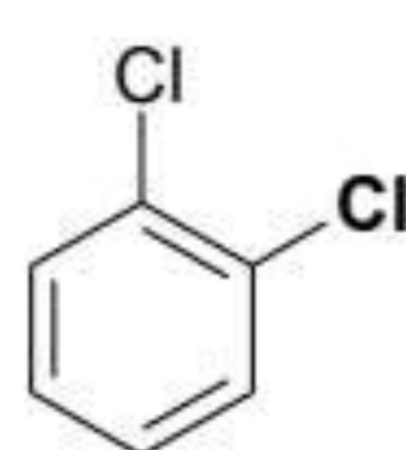
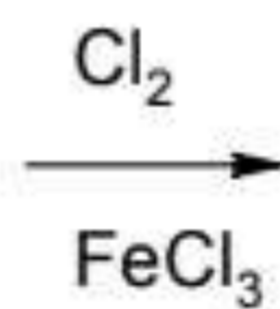
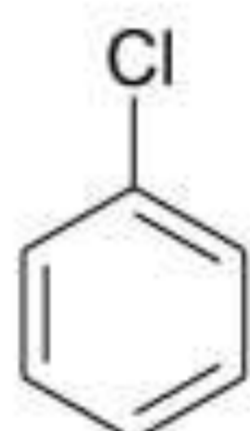
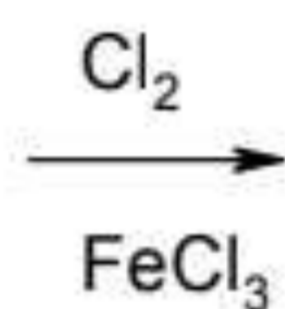
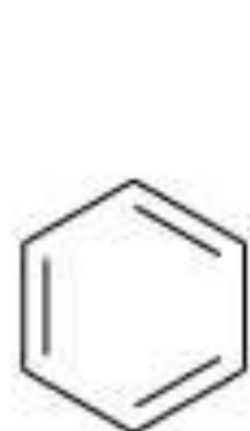


Synthesis of Aromatic Compounds

“Indirect” introduction of groups:

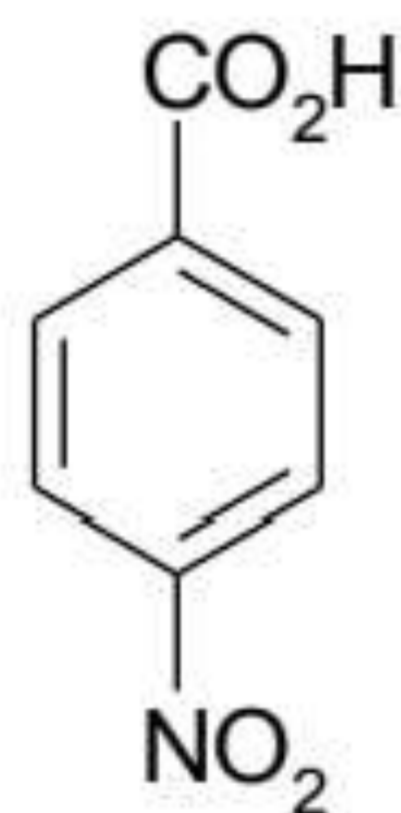


desired product

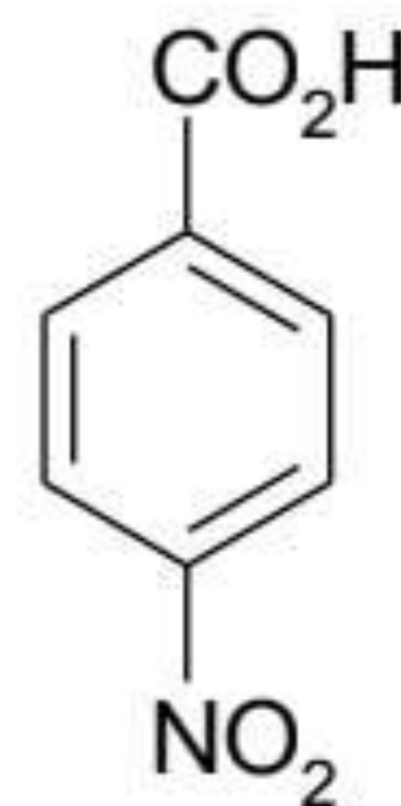
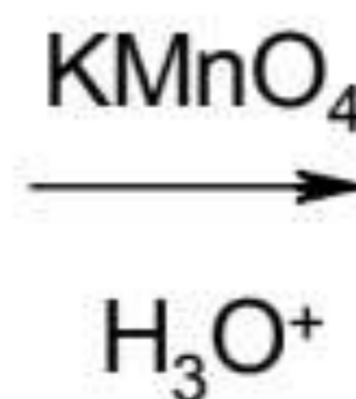
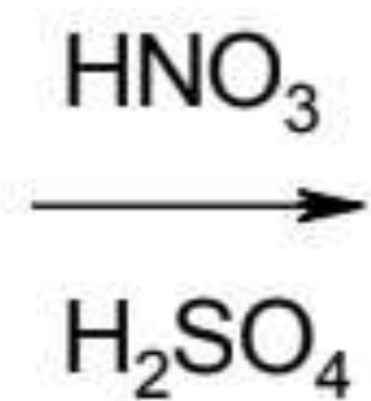
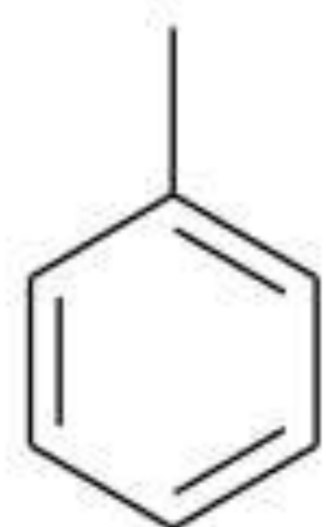
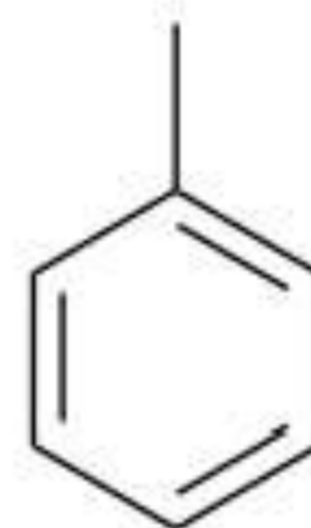


Synthesis of Aromatic Compounds

Unusual substitution patterns:

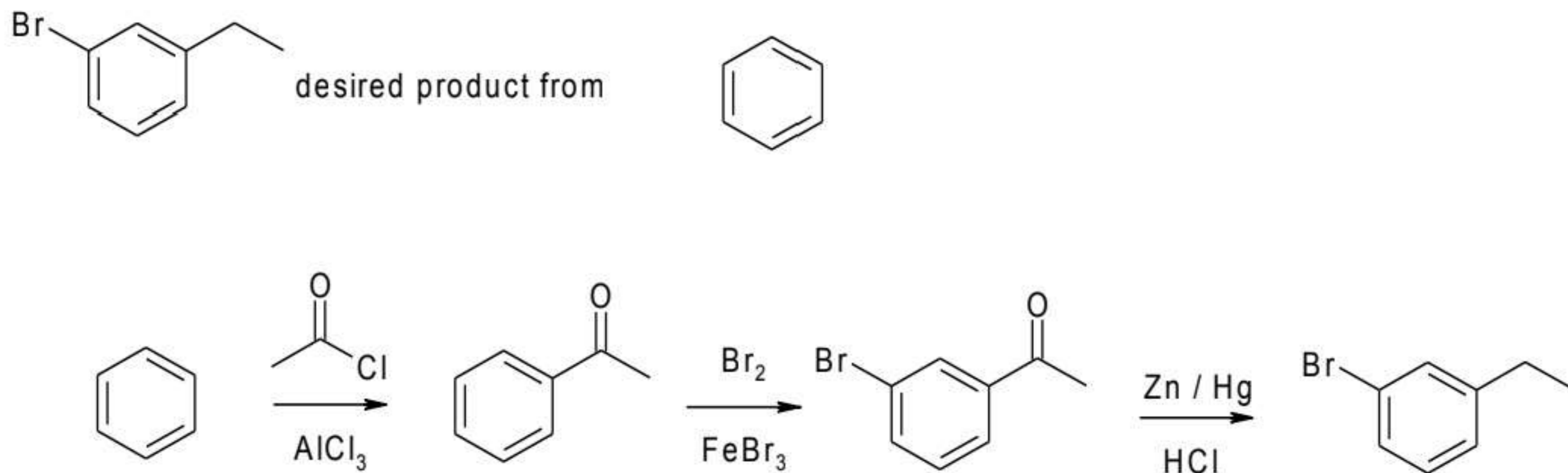


desired product from



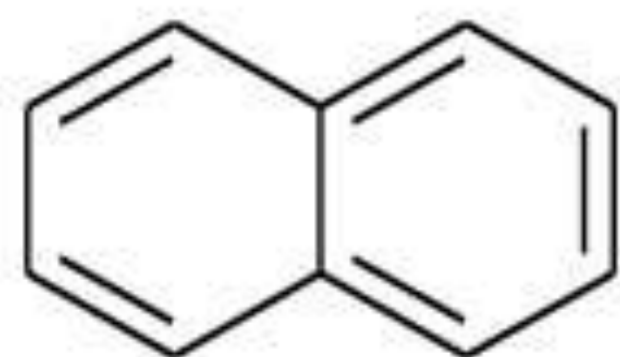
Synthesis of Aromatic Compounds

Unusual substitution patterns:

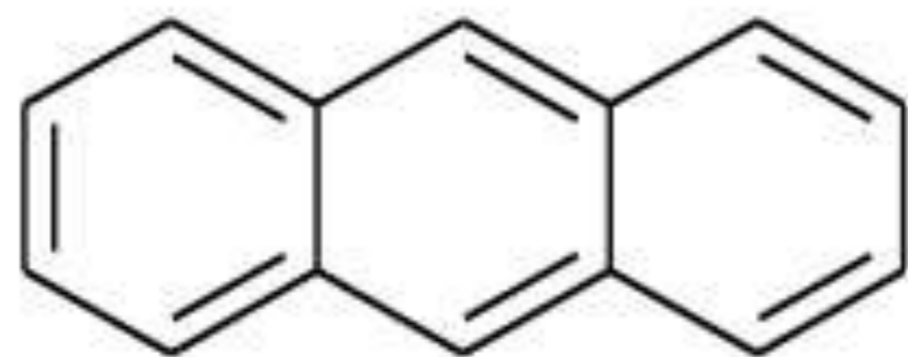


Polycyclic Aromatic Hydrocarbons

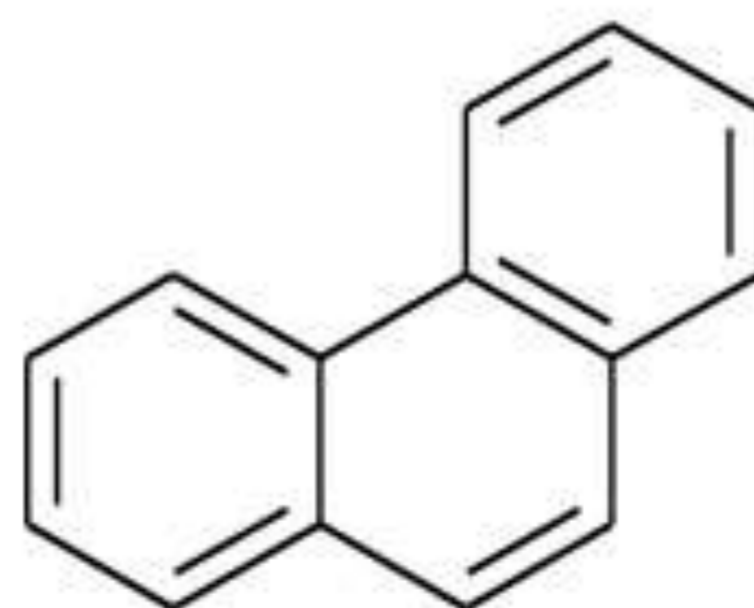
A number of polycyclic (multiple fused rings) hydrocarbons exist. They still obey Huckel's rule, alternating single & double bonds etc. They also exhibit a reduced reactivity to addition / substitutions and react by EArS.



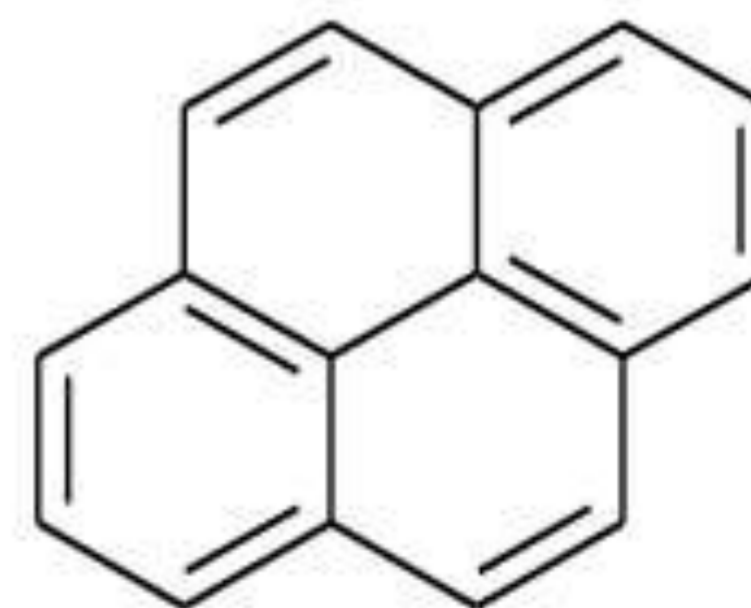
naphthalene



anthracene



phenanthrene



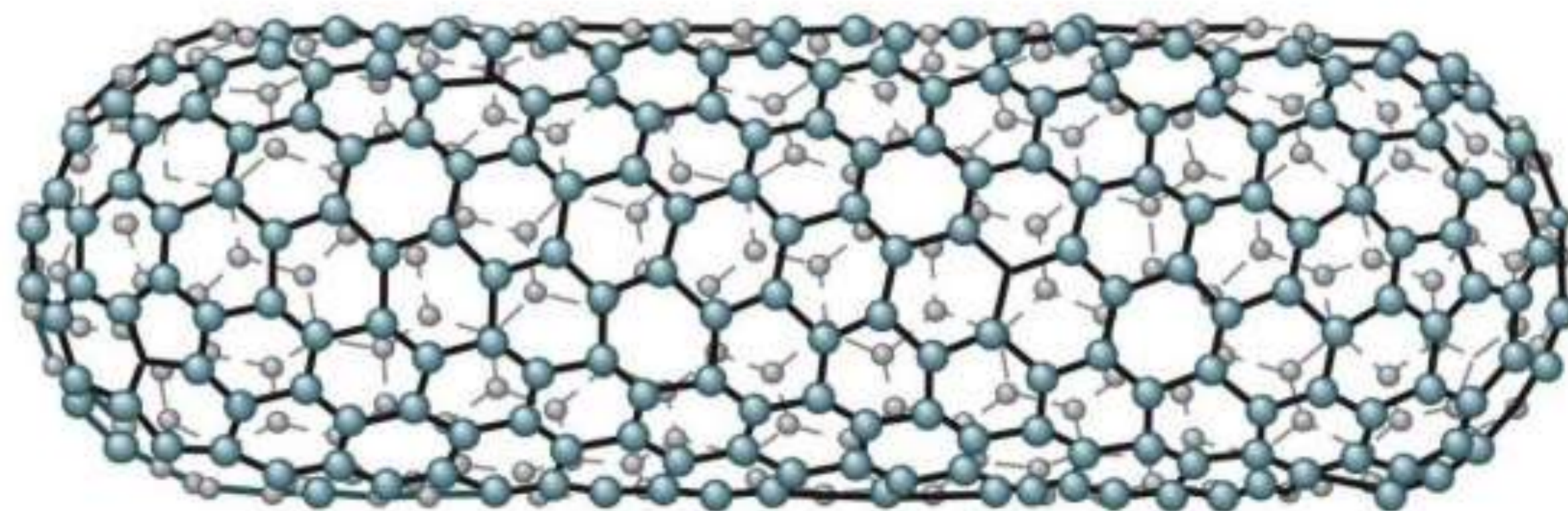
pyrene

Polycyclic Aromatic Hydrocarbons

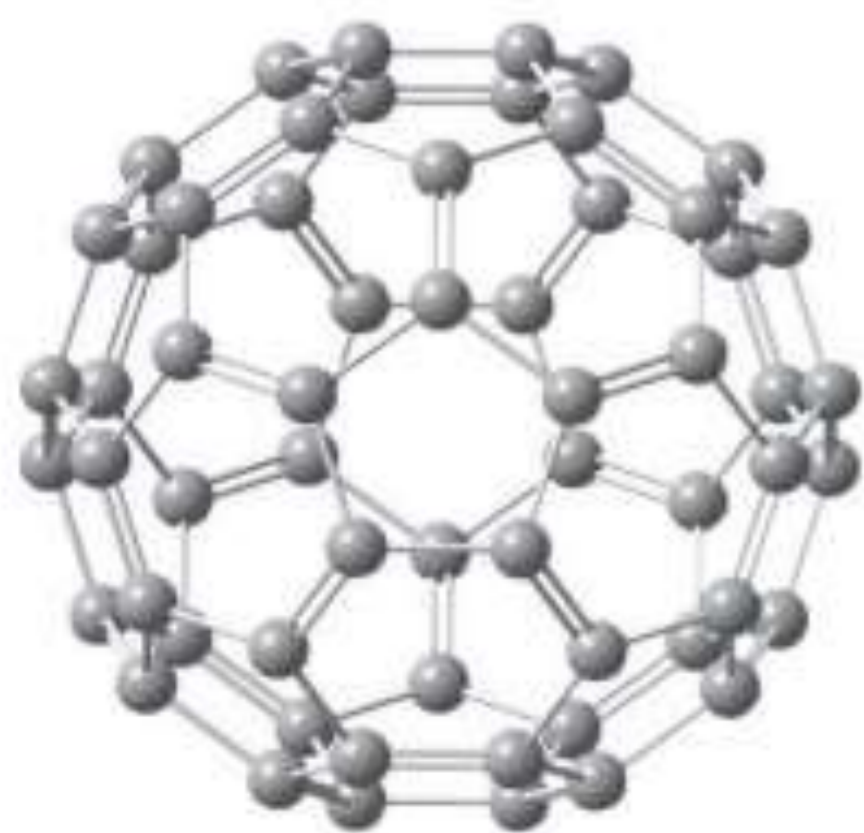
Two other cases of polycyclic hydrocarbons exist, fullerenes and carbon nanotubes. These compounds have interesting properties of electrical conductance and very high strength.



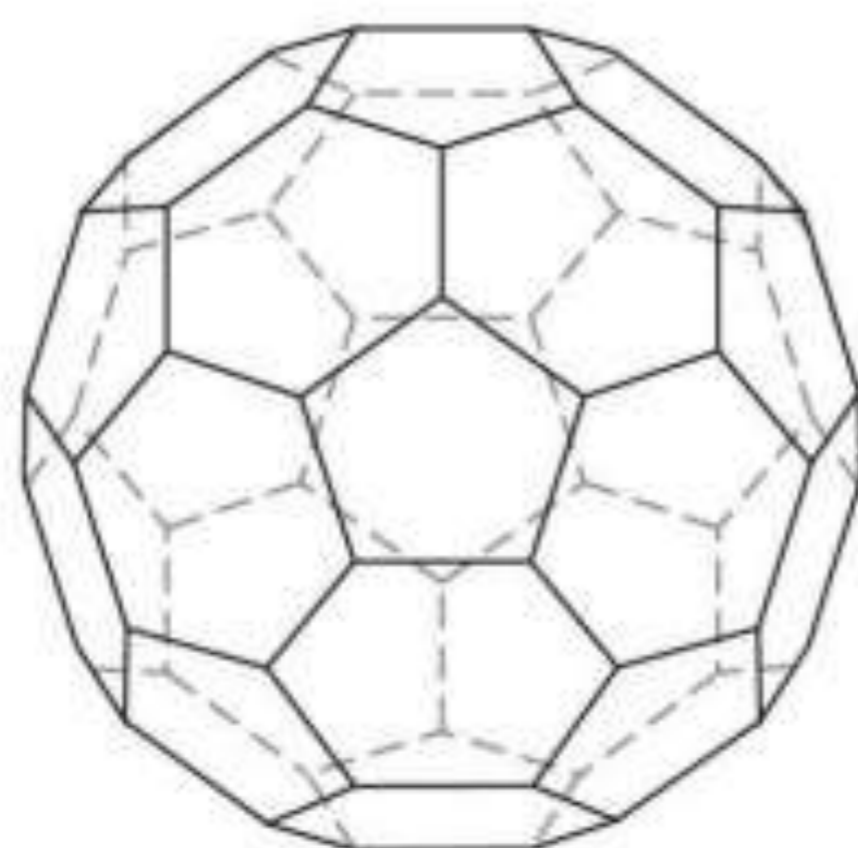
corannulene



Carbon nanotube¹



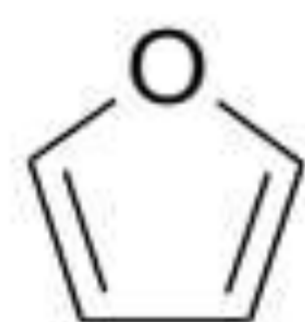
C₆₀ (the pi bonds are not shown)



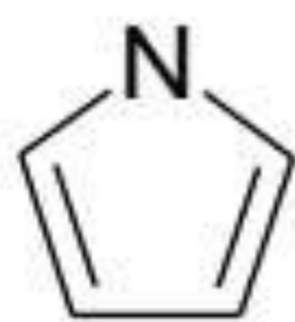
Heterocyclic Aromatic Compounds

Aromatic compounds with a non-carbon (hetero) atom in the ring are possible. In many cases that atom provides a lone pair of electrons as part of the $4n + 2 \pi$ electrons in the system.

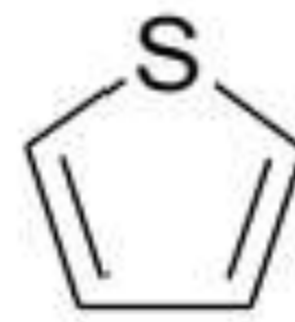
Examples include:



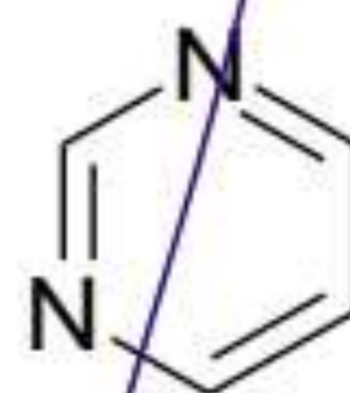
furan



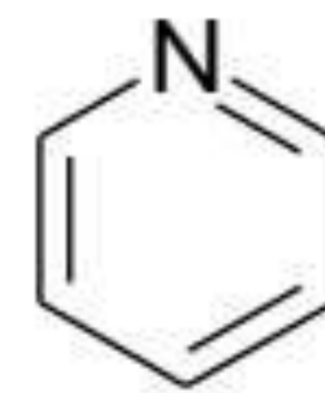
pyrrole



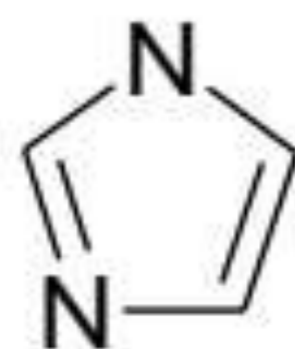
thiophene



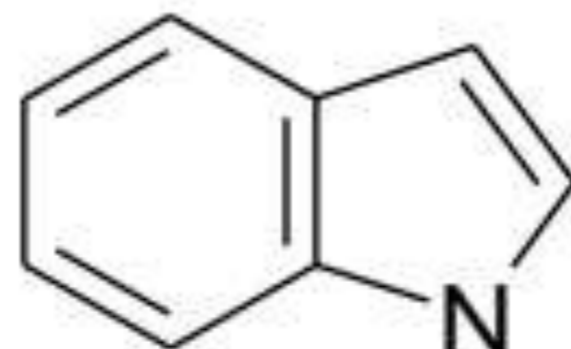
pyrimidine



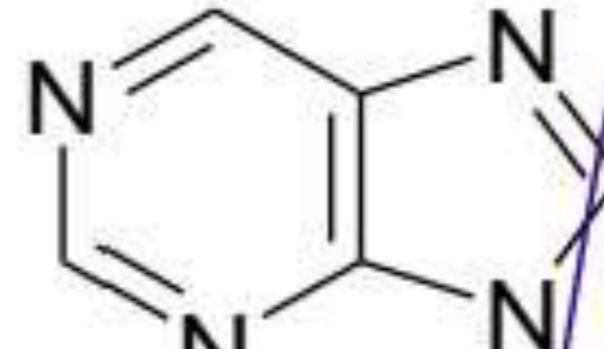
pyridine



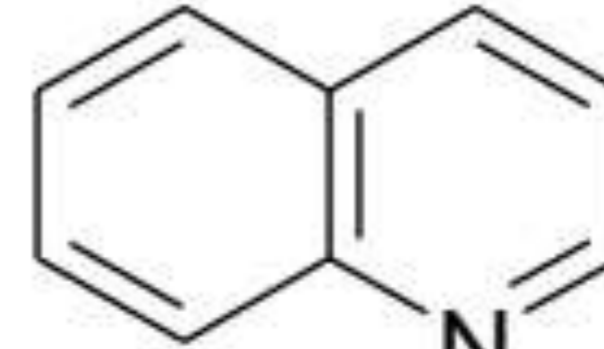
imidazole



indole



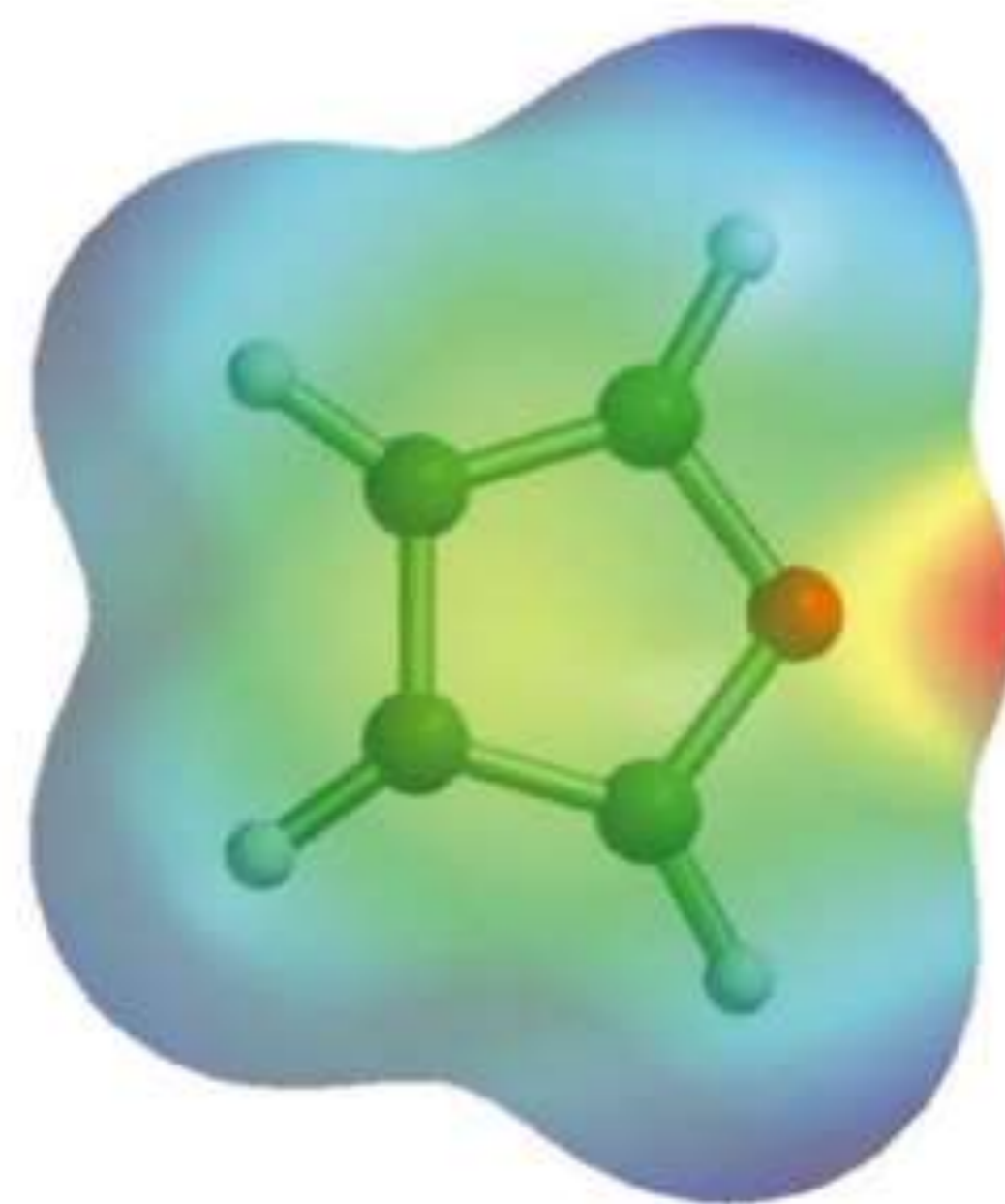
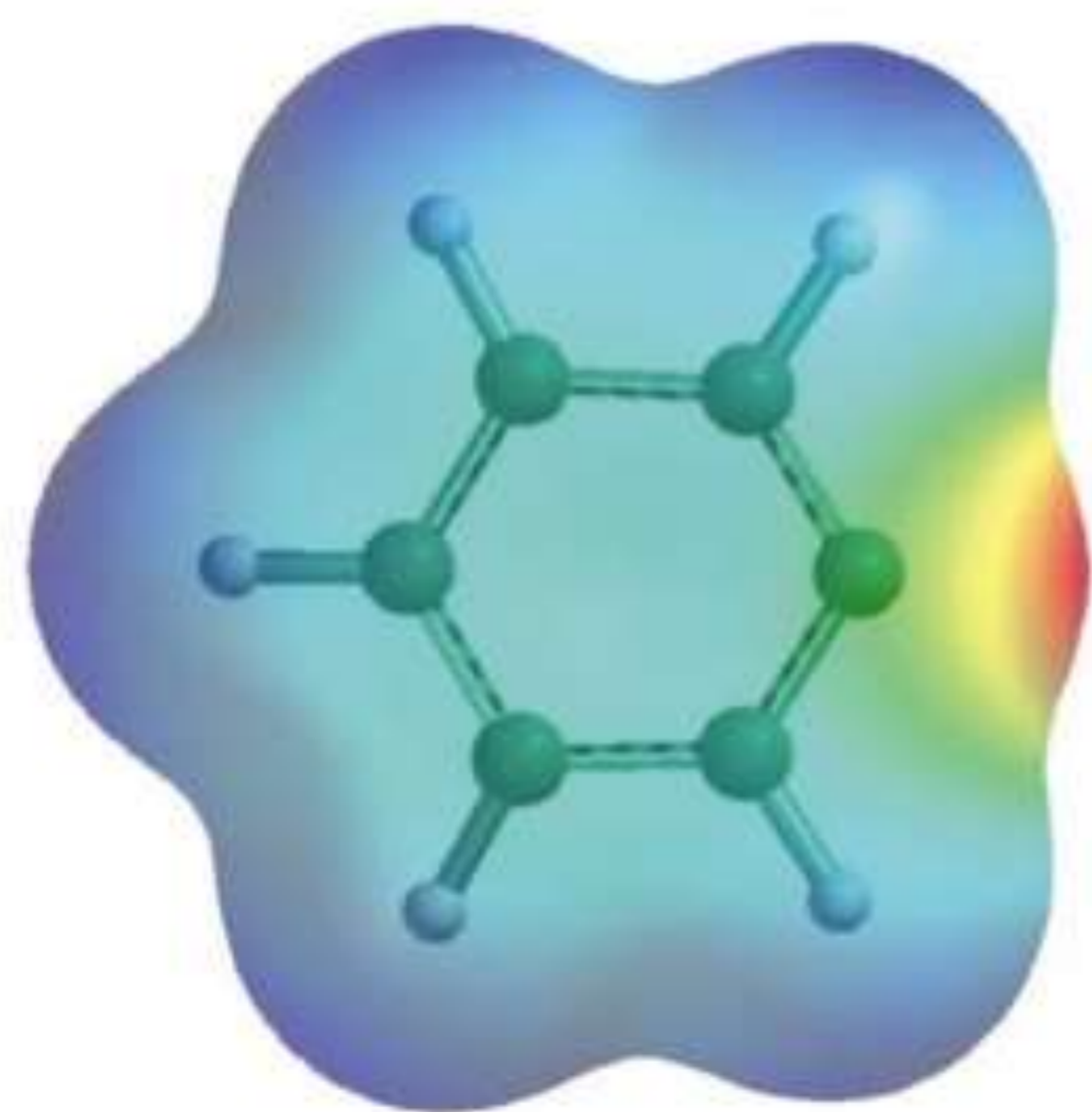
purine



quinoline

Heterocyclic Aromatic Compounds

- The heteroatom has significant effects on the chemical reactivity.
- They are commonly used as polar aprotic (no acidic H atom) solvents.
- They are very common in biology.
- For more information see Chapter 13.



1,3-dichlorobenzene *meta* di chloro

1,2-dichlorobenzene