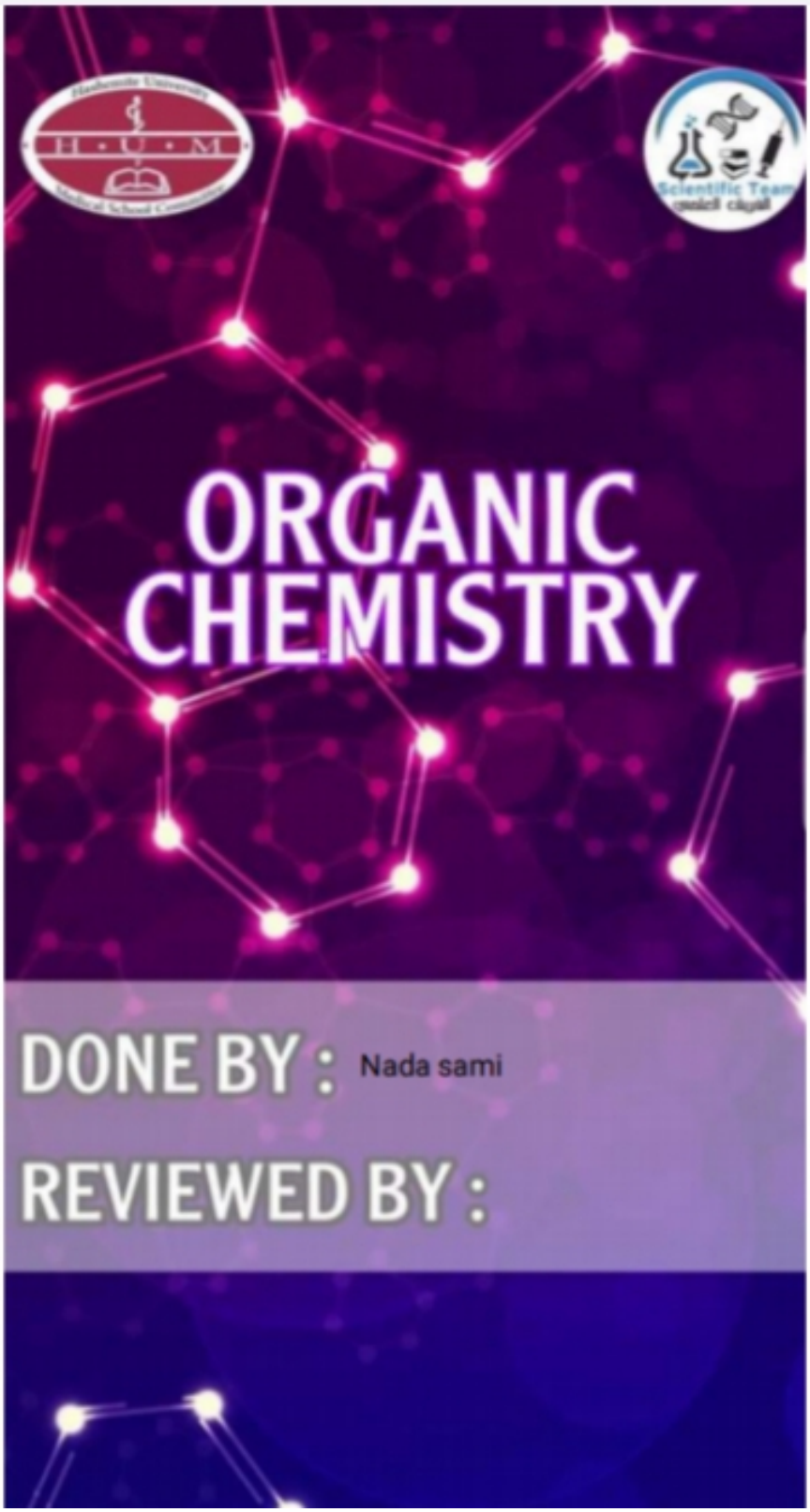
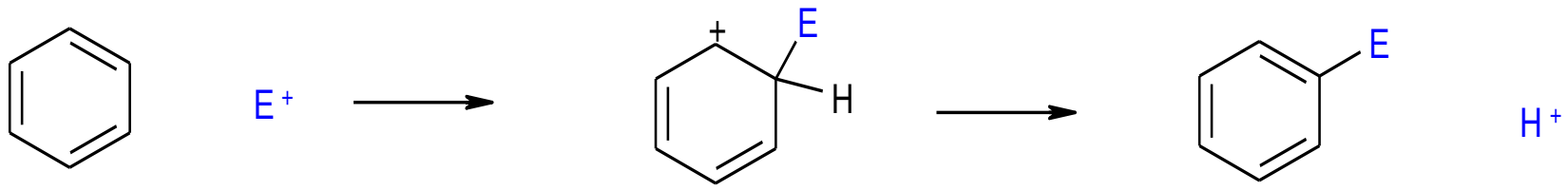
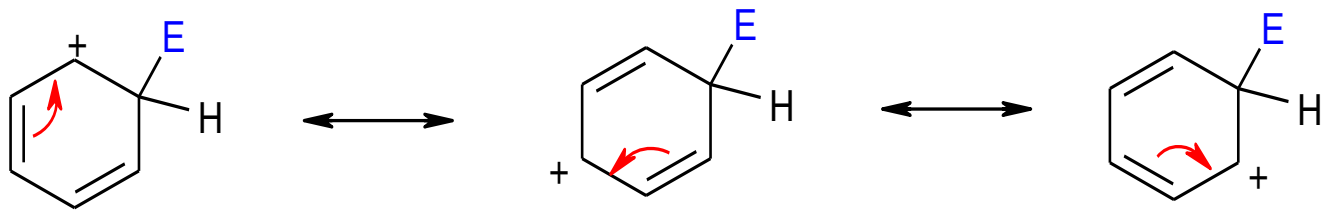

H.U.M
Scientific Team
ORGANIC
CHEMISTRY
DONE BY : Nada sami
REVIEWED BY :

Mechanism of Electrophilic Aromatic Substitution (EArS)

In general all EArS reactions proceed by the same mechanism:



benzenonium ion
(a carbocation)

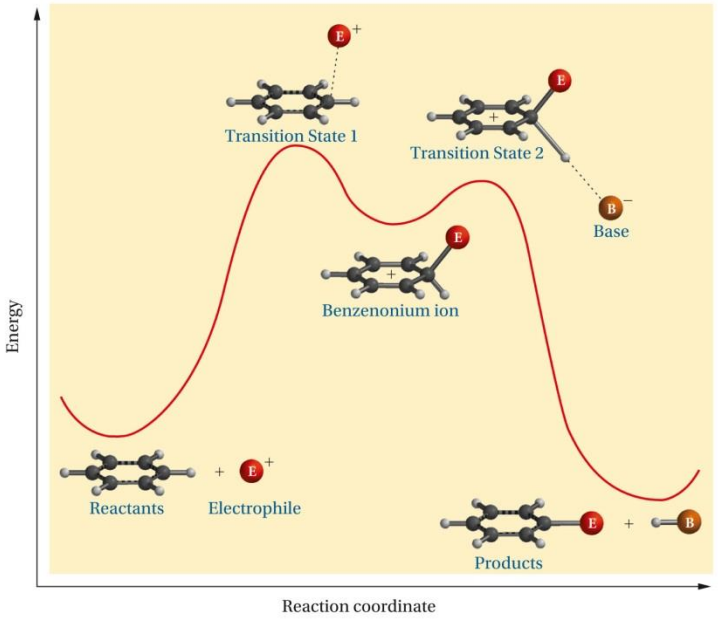


ortho para ortho

Benzenonium resonance structures

Mechanism of Electrophilic Aromatic Substitution (EArS)

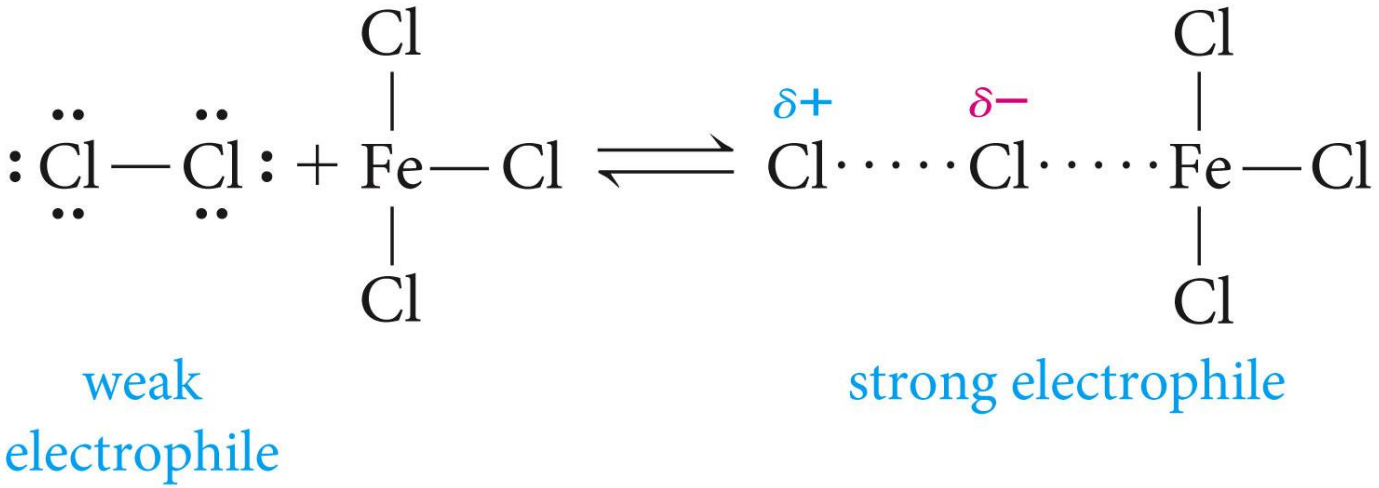
As with allenes and alkynes, the carbocation generated by the addition of the electrophilic is a stable intermediate, i.e.



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

1 EArS - Halogenation

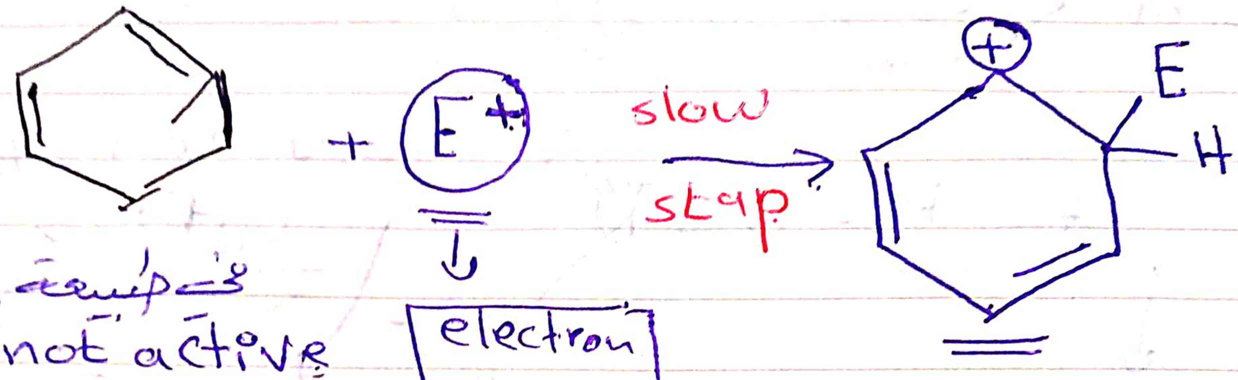
- Cl_2 and Br_2 are weak electrophiles on their own so need to be "activated" by using a Lewis acid catalyst.
- Commonly the corresponding iron trihalide is used, $FeCl_3$ or $FeBr_3$



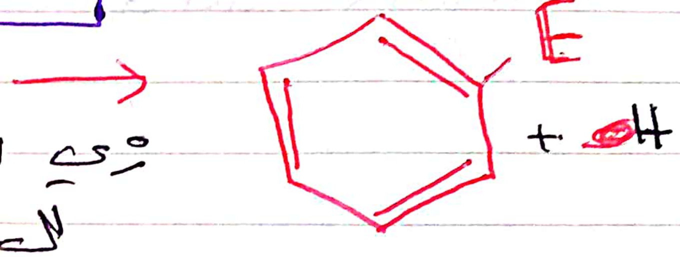
Dete: Page:

المحاضرة السادسة عشر

* general mechanism *



تحت طبيعة الحال
+ not active
more
stable



* زي اللي عملنا استبدال لل (H) بـ E^+

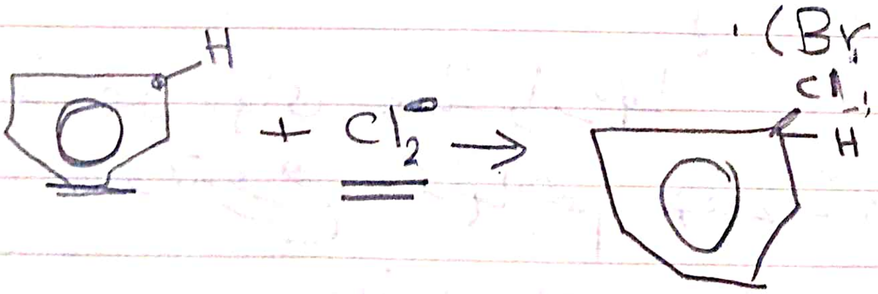
*

* يوجد نوعين من التفاعلات هما الإحلال، إضافة .
لمحاضرة هنا:

① EARs - Halogenation!

* هي عملية استبدال ال (H) بواحدة من الهالوجينات (Br / Cl)،

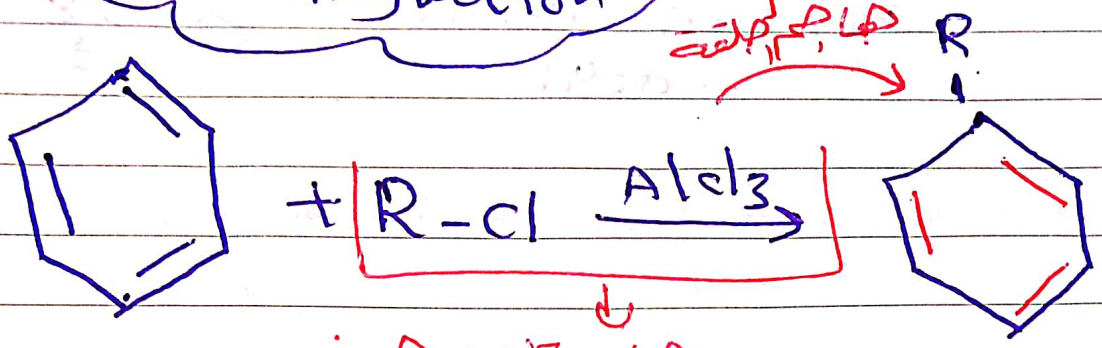
مثلا:



* ليش لضل مشكلة (H) فبنمسح هذه [H]
حتى أحقق حكي (Rowl) وهكذا...
كي يحصل على حلقة بنزين أكثر استقرار.

Dete: Page:

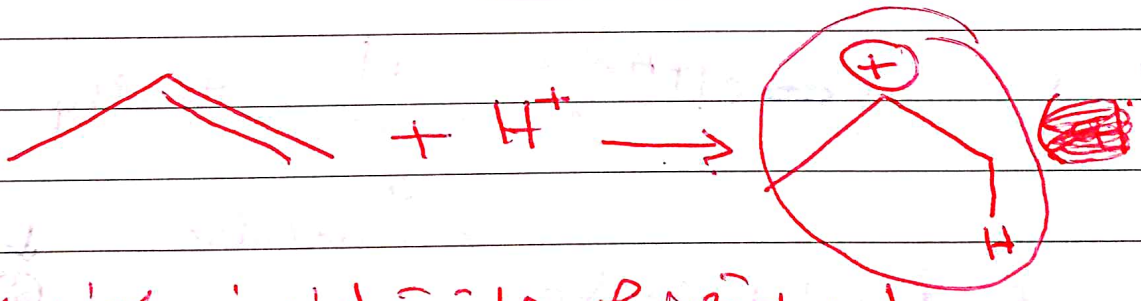
* طيب على بسريع وتشكل عام معادلة لعام لل تفاعل Freidele-Craft alkylation



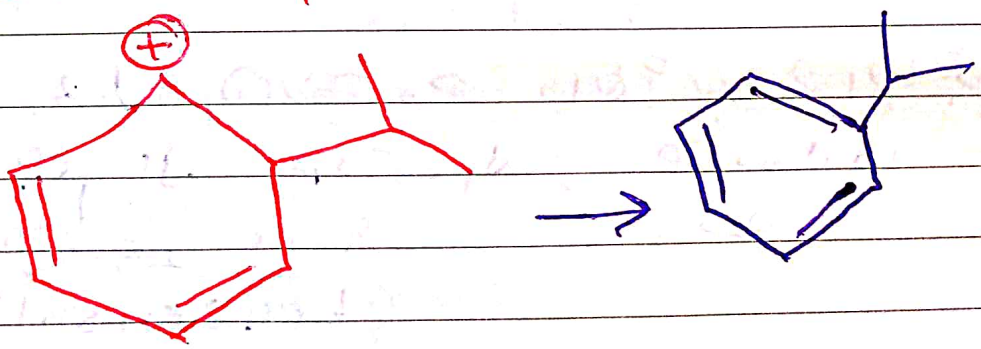
* * *

* B alkylation using an alkene and acidi-

* * alkene الفكرة هو نأمن

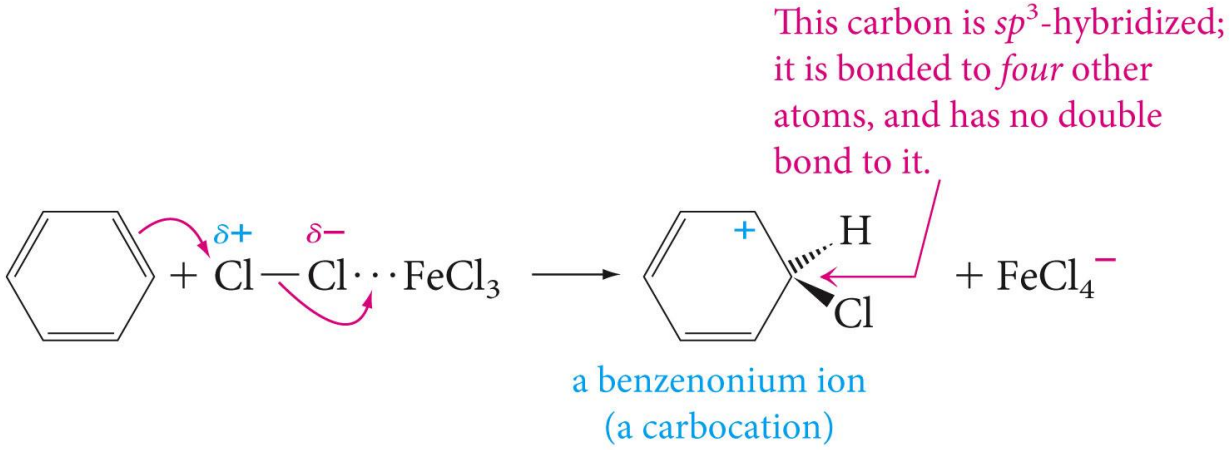


بتروح بجي حلقة البنزين وتعطي هك

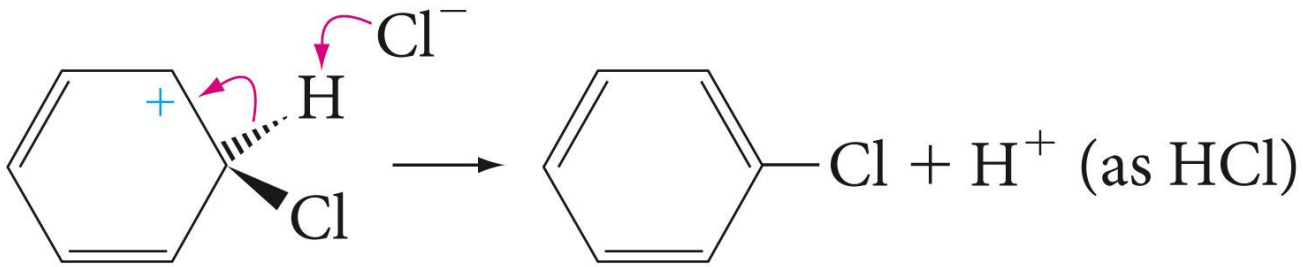


EArS - Halogenation

The rate determining step is:

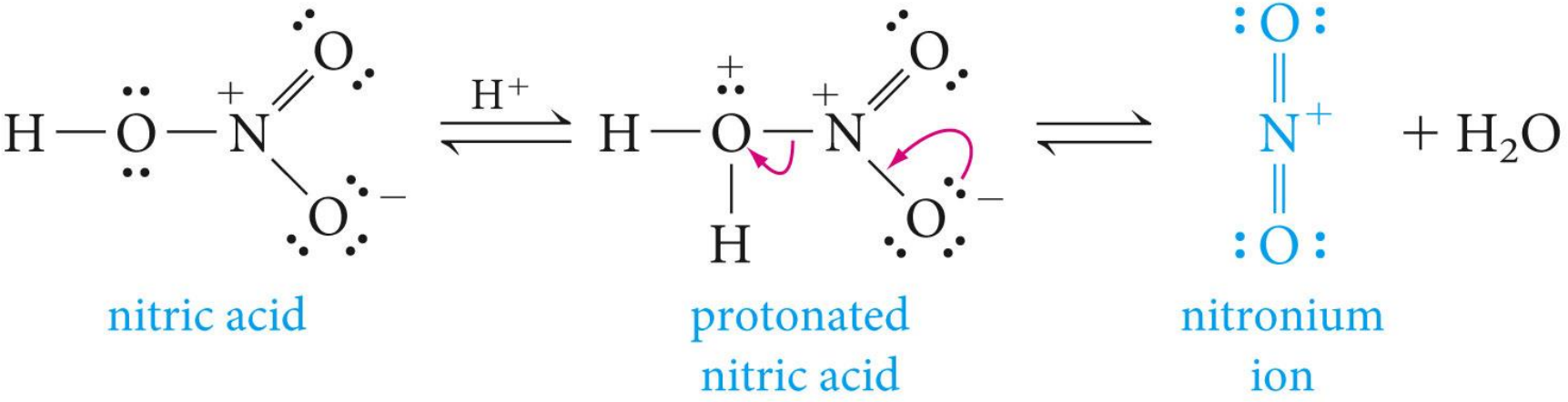


The base in this case is the chloride ion:



2 EArS - Nitration

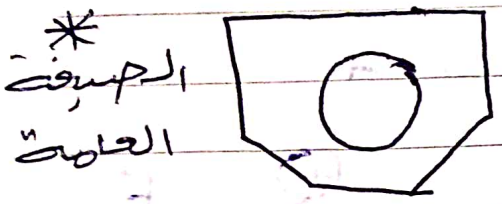
In the case of nitration, <u>sulfuric acid is used to generate a more reactivity electrophile, a nitronium ion.</u>



Dete: Page:

2 EARs - Nitration: تفاعل إضافة

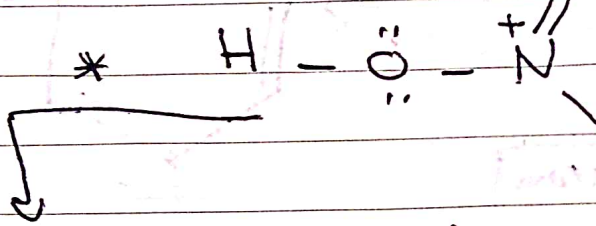
* هي عملية إضافة HNO_3 المركز إلى حلقة البنزين بوجود H_2SO_4 كعامل مساعد.



$$+ HNO_3 \xrightarrow{H_2SO_4}$$

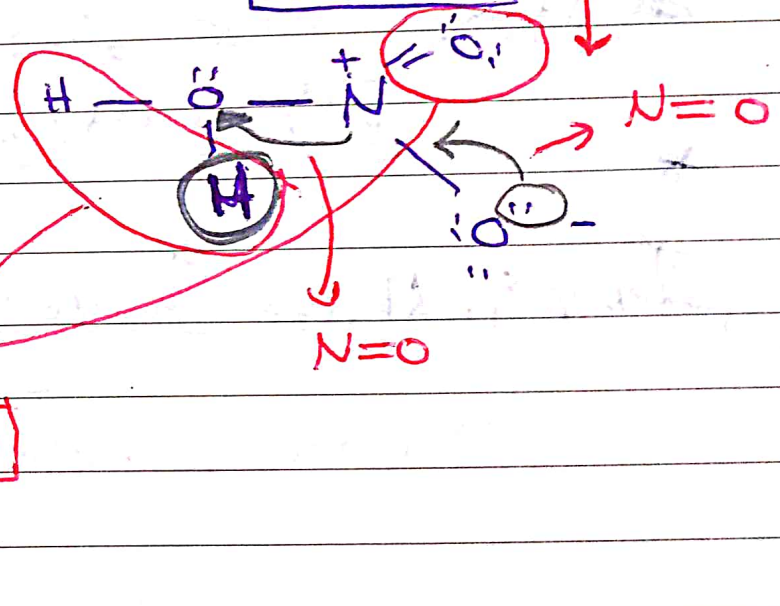
* الحمض العامل

حضير أول شيء:-

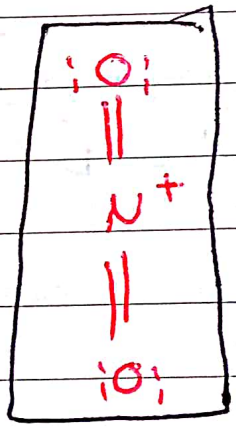


nitric acid.
(Lwies of nitric) acid

H_2SO_4 المركز



الناتج هو

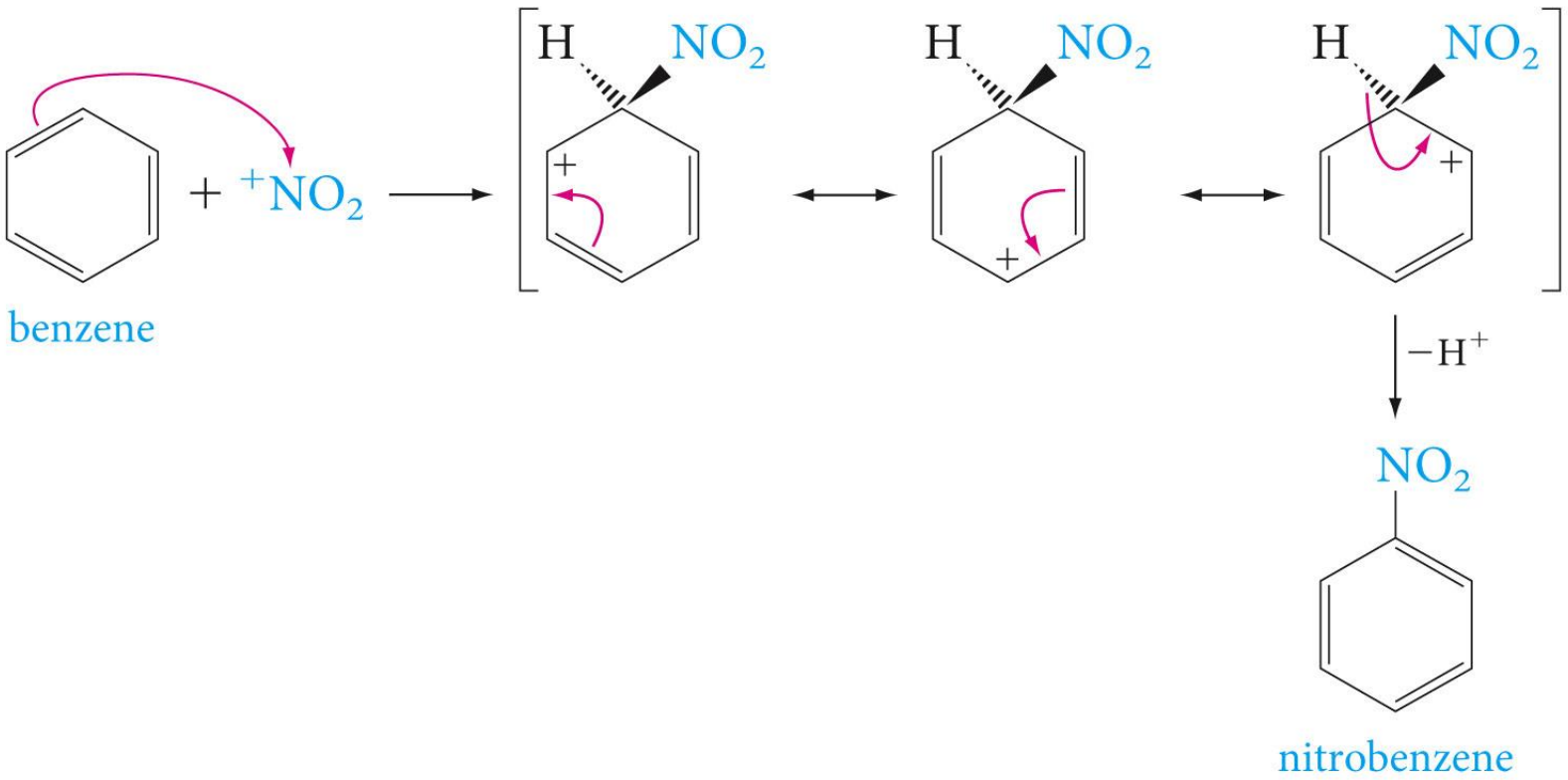


* تكمل هاي مشوارها وتروح لهالحلقة البنزين.

nitrobenzene

EArS - Nitration

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

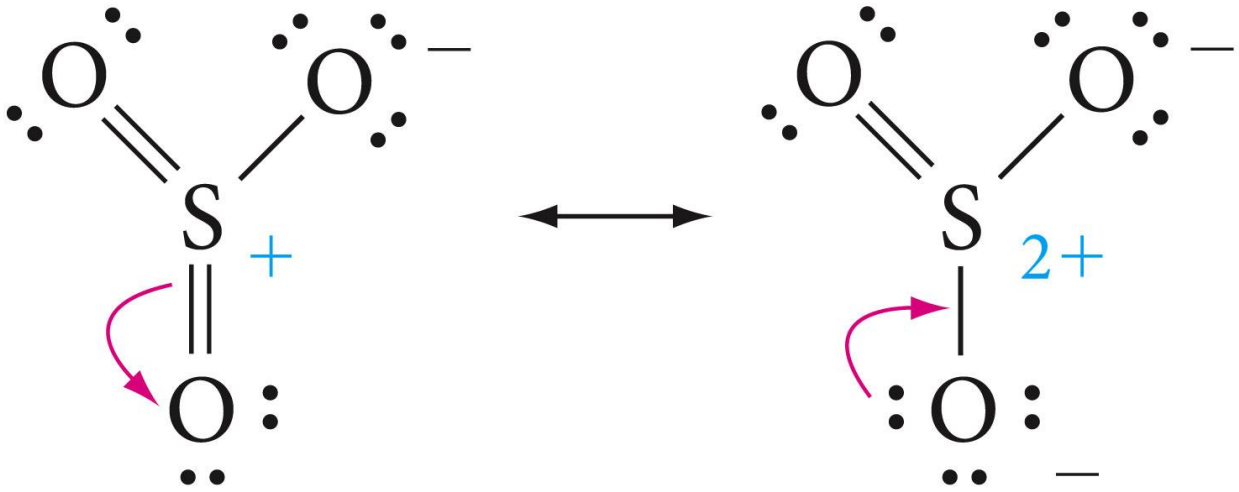


EArS - Sulfonation

3

Sulfonation will generate a benzenesulfonic acid.

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



3 ⇒ EARs - sulfonation:-

* الـ هي عملية إضافة sulfur trioxide إلى حلقة البنزين لإنتاج benzensulfonic acid.

* ملاحظة: إستبدال (H^+) هي خطوة موجودة في كل التفاعلات البنزين.

4 EARs - Alkylation:- *هذا التفاعل لديه طريقتين هما:

ⓐ Friedel - crafts alkylation,

ⓑ Alkylation using on an alkene and acid.

* ⓐ $R-Cl + AlCl_3 \rightarrow R^+ + AlCl_4$

R^+ → carbocation

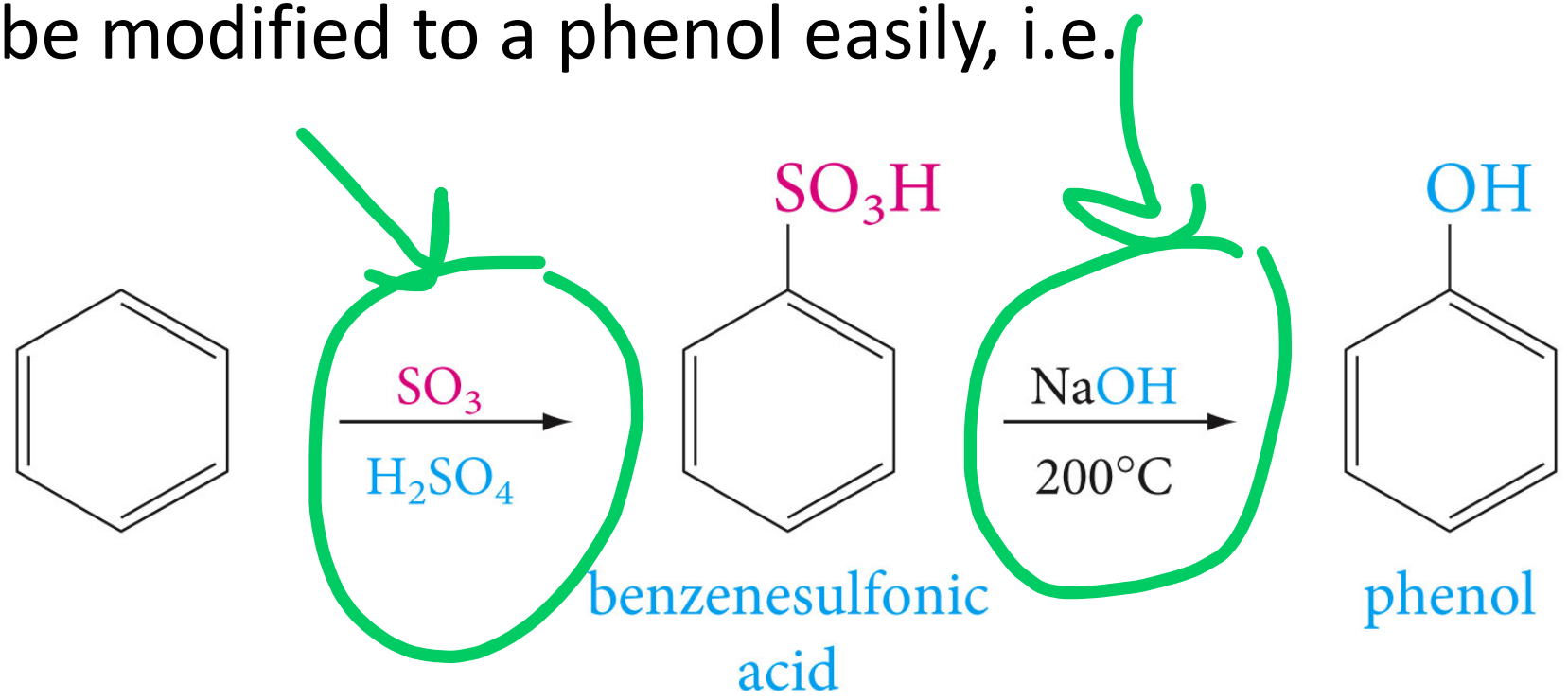
* Friedel-crafts alkylation * ⊛ فهذه هي فكرة

* وبعدين الخطوة الثانية وهي دائماً بروح الناتج منها جمع الـ حلقة البنزين ثم يحلها تتفاعل على أساس أنها

benzensulfonic acid

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.



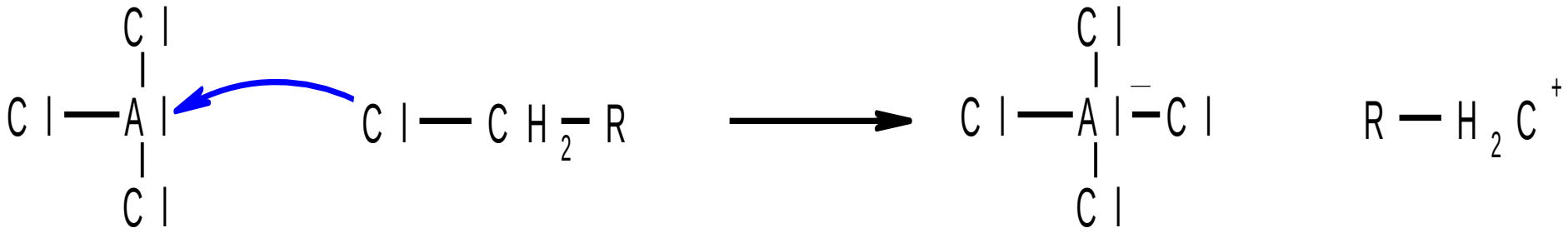
4 EArS - Alkylation

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

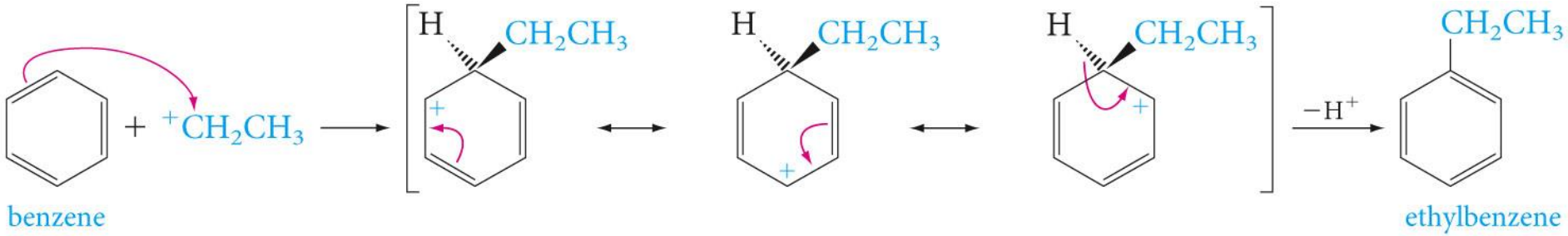
Friedel-Crafts Alkylation

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

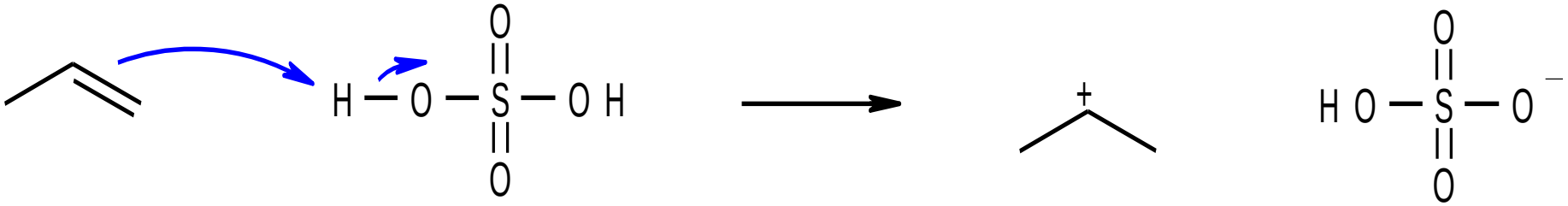
The product is an alkylbenzene, i.e.



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.

6 Alkylation from Alkenes

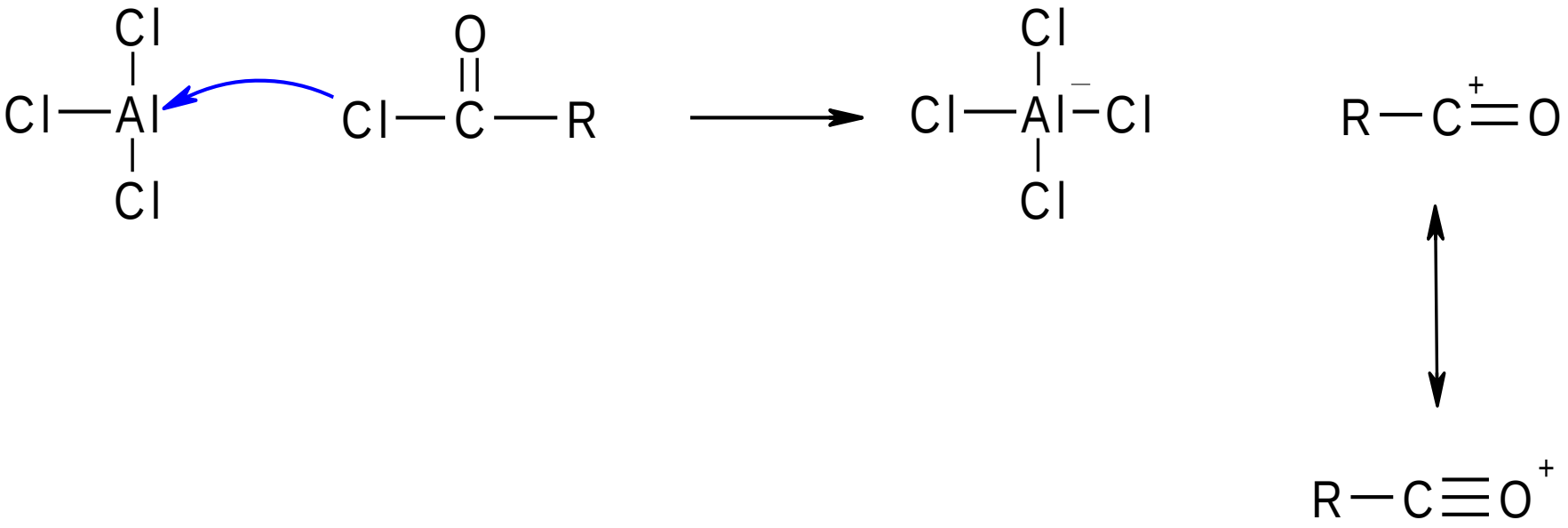
Alkylation can also be achieved by using an alkene and an acid (sulfuric as the conjugate base is a poor nucleophile), i.e.



Note: this will generate the Markovnikov carbocation!

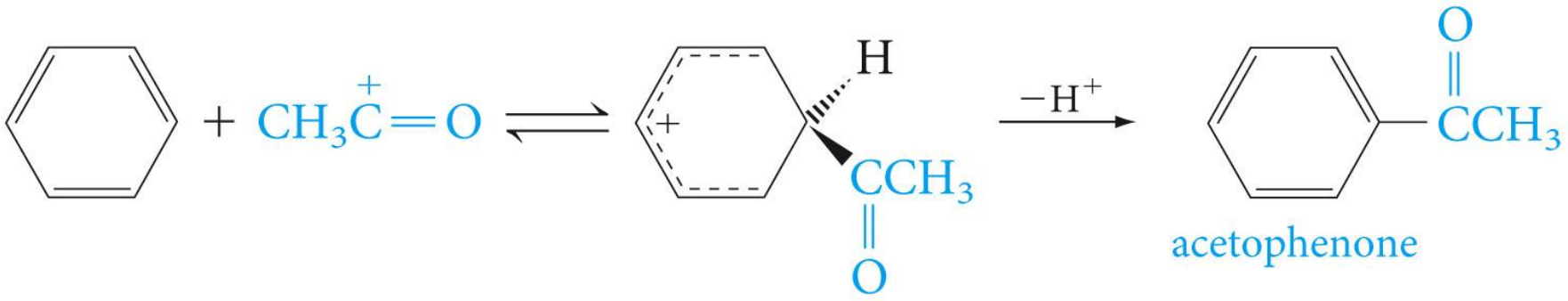
5 Friedel-Crafts Acylation

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.

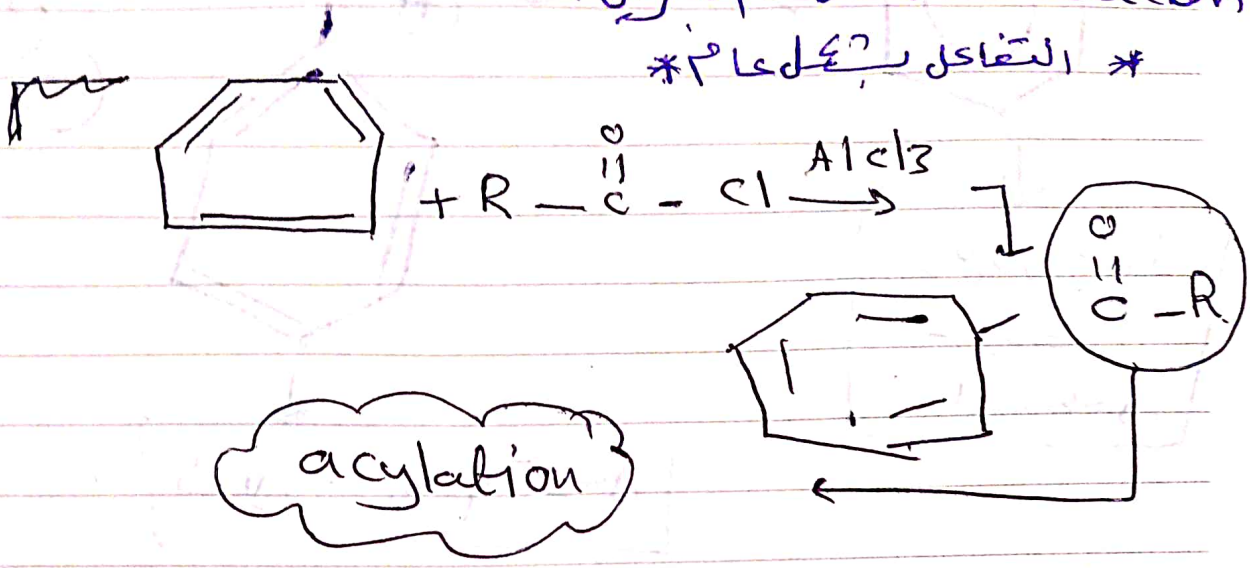


Note: the same limitations for nitro and sulfonic acid groups apply.

Date: Page:

5 ⇒ Friedel Carfts acylation:- نحصل على Phenyl Keteon مشتقة البنزين.

* التفاعل بشكل عام *



* فكرة التفاعل نفس الشيء ولكن بإضافة ذرات الأكسجين وتبعتها.

* * *

* تأثير التفرعات على التفاعل:-

① سرعة التفاعل.

② على الناتج (ممكن نطلع عنها أكثر من product)

* * *

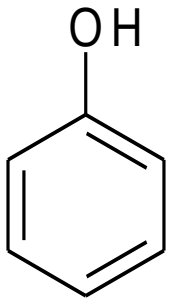
1 Reaction Rates:- some groups increase Reaction rates and other decrease the Reaction's Rate.

~~some groups~~

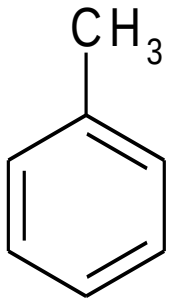
* مثال سؤال من المجموعات الكبيرة ومن المجموعات اللي تنقل.

Reaction Rates

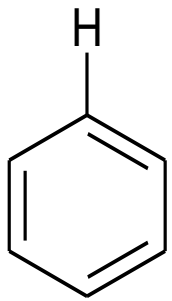
Experimentally you can observe the following relative rates of reaction:



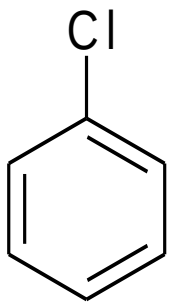
phenol
1000



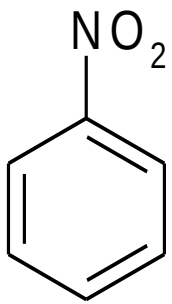
toluene
24.5



benzene
1



chlorobenzene
0.033



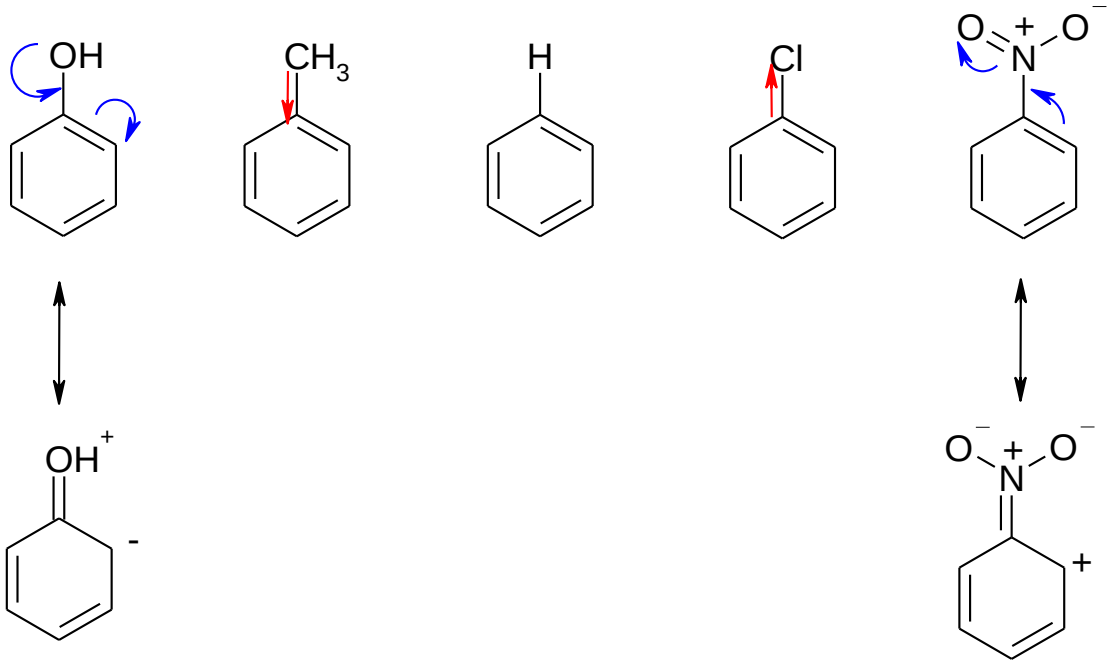
nitrobenzene
0.0000001

What is causing these differences?

بسبب اختلاف نوع المجموعه المرتبطة ادب الي اختلاف سرعه التفاعل

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.



Directing Effects

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?

تزداد
السرعه