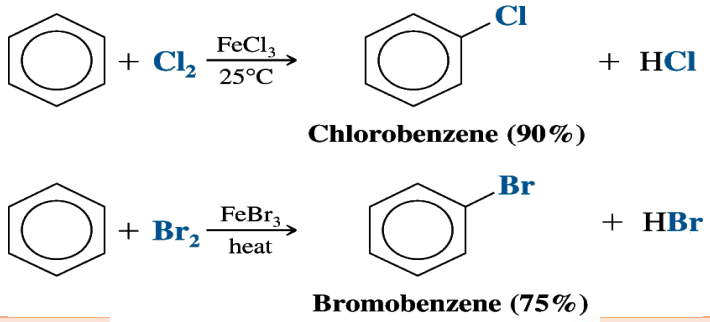
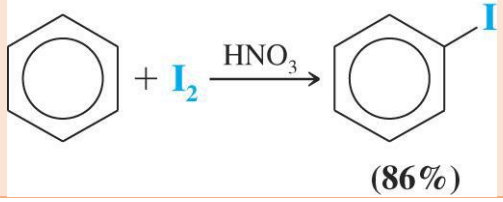
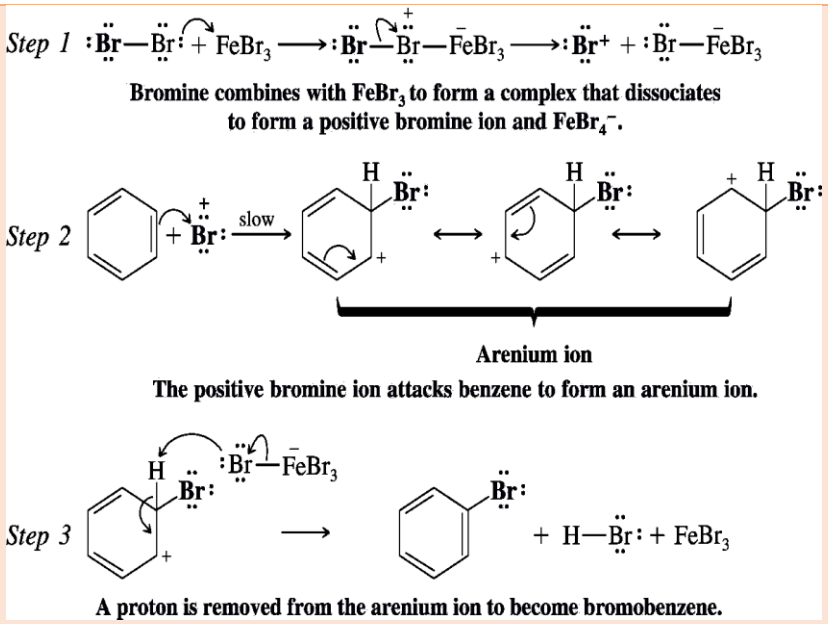
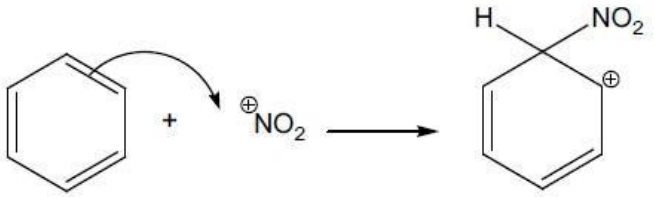
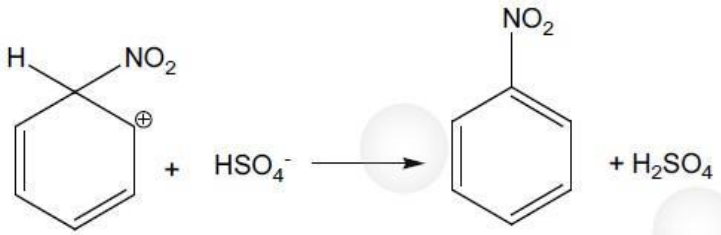
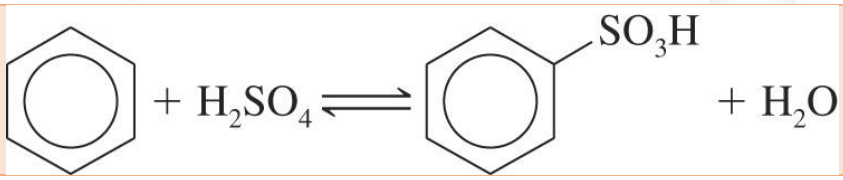
Organic chemistry2: Dr.Gehan abdelhafez.

Student: Mohamed Mokhtar

ملخص المحاضرة الثانية(كاملة)

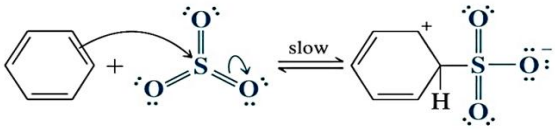
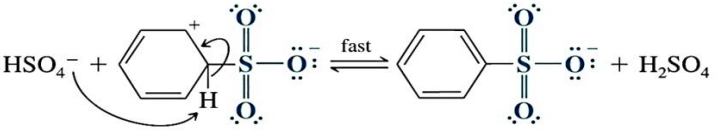
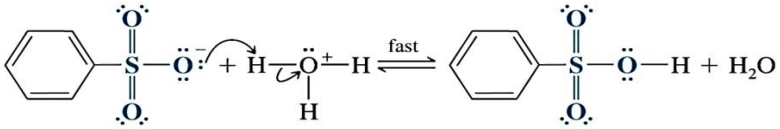
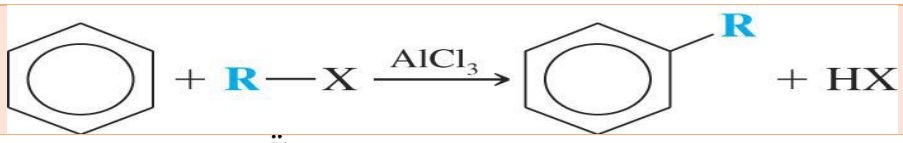
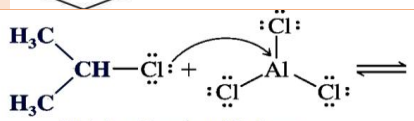
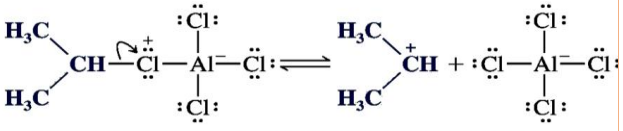
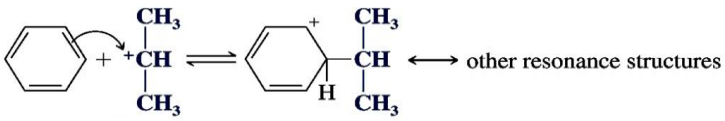
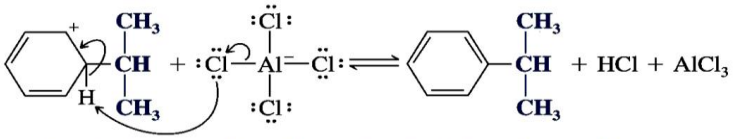
QUESTION	ANSWER
How to derive the aryl group (Ar)?	by removal of a hydrogen atom from an arene. (Ar-H)
General Mechanism for Electrophilic Aromatic Substitution	**step 1**the electrophile reacts with two pi electrons from the aromatic ring to form an arenium ion.The arenium ion is stabilized by resonance which delocalizes the charge. **step 2** a proton is removed and the aromatic system is regenerated.
Why shouldn't the Fluorination method be used?	**Because fluorination occurs so rapidly it is hard to stop at mono-fluorination of the ring.**
Example for Halogenation of Benzene by cl – br	
Example for Halogenation of Benzene by i	

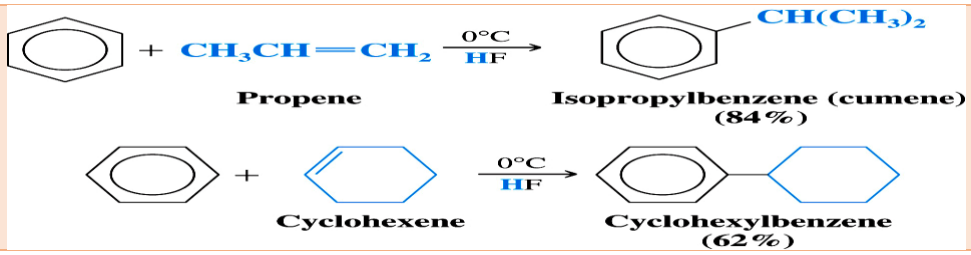
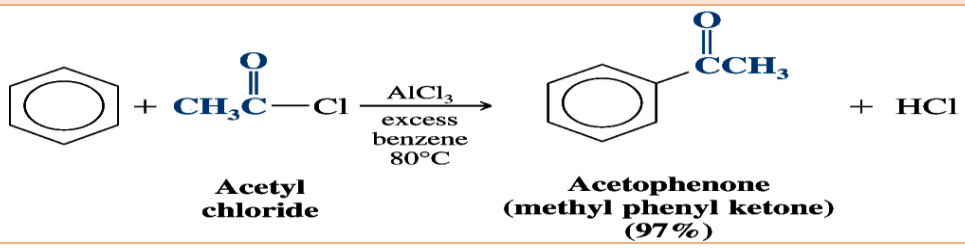
NOTES

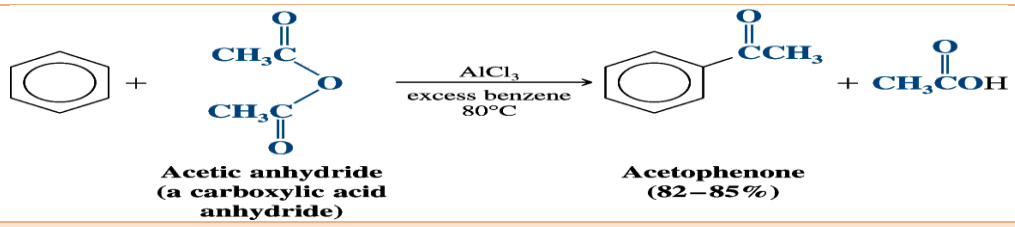
What is the of the mechanism of the hydrogenation (bromination)?	 **The FeBr3 catalyst is regenerated**
What is the of mechanism of the Nitration of Benzene?	1- Reaction of nitric acid and sulphuric acid to form nitronium ion NO_2^+. $H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + HSO_4^- + H_3O$ 2- Addition of NO_2^+ to benezene to form intermediate carbocation.  3- Deprotonation of the intermediate carbocation by the base to regenerate the benzene. 
What is the Sulfonation of Benzene?	

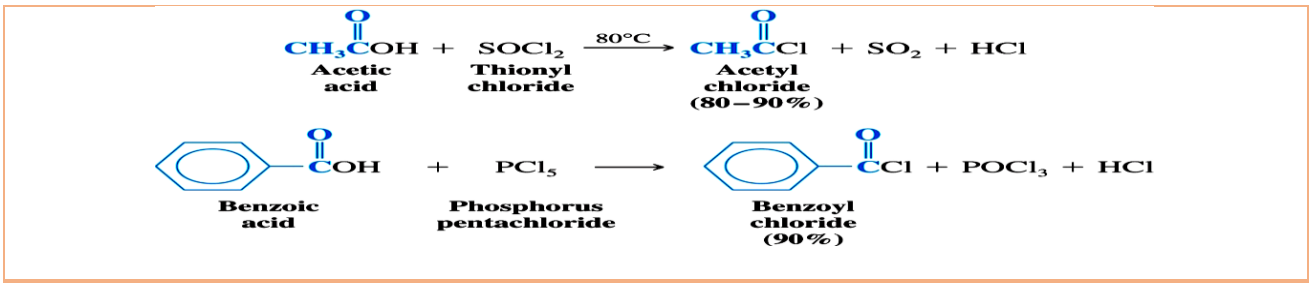
What does the Halogenation of Benzene require?	requires the presence of a Lewis acid.
What does the Nitration of Benzene require?	Nitration of benzene occurs with a mixture of concentrated nitric and sulfuric acids
What does the Sulfonation of Benzene require?	Sulfonation occurs most rapidly using **fuming sulfuric acid**. The reaction also occurs in **conc. sulfuric acid**, which generates small quantities of **SO3** (an electrophile) ,
The electrophile for Nitration of Benzene is	nitronium ion (NO2+)
The electrophile in Friedel-Crafts acylation	acylium ion (R-C+=O)
The electrophile for Halogenation of Benzene	Bromonium ion Br+
What does the Friedel-Crafts acylation require?	Friedel-Crafts acylation requires reaction of **an acid chloride** or acid anhydride **with a Lewis acid** such as aluminium chloride.
How does Desulfonation occur?	Desulfonation can be accomplished **using dilute sulfuric acid** (i.e. with a high concentration of water), or by **passing steam through the reaction** and **collecting the volatile desulfonated** compound as it distils **with the steam**

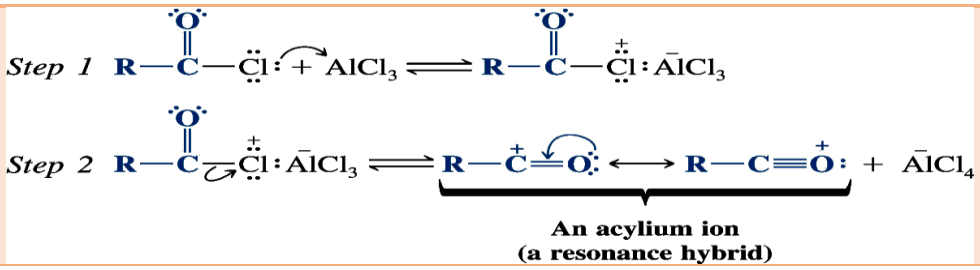
NOTES

What is the of mechanism of the Sulfonation of Benzene?	*Step 1* $2\,H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$ **This equilibrium produces SO_3 in concentrated H_2SO_4.** *Step 2*  ⟷ other resonance structures **SO_3 is the actual electrophile that reacts with benzene to form an arenium ion.** *Step 3*  + H_2SO_4 **A proton is removed from the arenium ion to form the benzenesulfonate ion.** *Step 4*  **The benzenesulfonate ion accepts a proton to become benzenesulfonic acid.**
What is (Friedel-Crafts Alkylation)?	An aromatic ring can be alkylated by an alkyl halide in the **presence of a catalytic amount of Lewis acid.**
Reaction:	
What is the of mechanism of Friedel-Crafts Alkylation?	*Step 1*  **This is a Lewis acid–base reaction (see Section 3.2B).**  **The complex dissociates to form a carbocation and $AlCl_4^-$.** *Step 2*  ⟷ other resonance structures **The carbocation, acting as an electrophile, reacts with benzene to produce an arenium ion.** *Step 3*  + HCl + $AlCl_3$ **A proton is removed from the arenium ion to form isopropylbenzene. This step also regenerates the $AlCl_3$ and liberates HCl.**

Other compounds that can form a carbocation… Two examples:	
What is the function of Lewis acid in Friedel-Crafts Alkylation?	generate a carbocation electrophile (R+)
What are the Limitations of Friedel-Crafts alkylation?	1. Powerful electron-withdrawing groups (blue colored) make an aromatic ring much less reactive toward Friedel-Crafts alkylation or acylation. 2. Aryl and vinyl halides cannot be used in Friedel-Crafts reactions as alkylating agents because they do not form carbocations readily.  3. Polyalkylation occurs frequently with Friedel-Crafts alkylation because the first alkyl group introduced activates the ring toward further substitution. 4. Rearrangement of carbocations: In Friedel-Crafts alkylation, the alkyl carbocation intermediate may rearrange to a more stable carbocation prior to alkylation.
Why rearrangement does not occur in F-C acylation?	because acylium ion is stabilized by resonance The electrophile in Friedel-Crafts acylation is an acylium ion (R-C+=O)
What is (Friedel-Crafts Acylation)?	An acyl group has a carbonyl attached to some R group
Reaction: ex.1 **ex.2**	

	
How could you prepare acid chlorides?	Acid chlorides are made from **carboxylic acids**

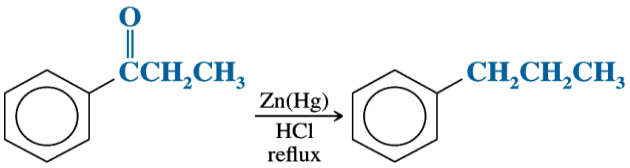


Why doesn't the polyacylation occur?	because the acyl group deactivates the aromatic ring to further substitution.
Generation of acylium ion	

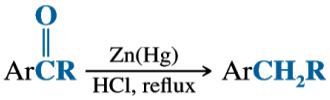
NOTES

Convert: Benzene ⟶ Propylbenzene

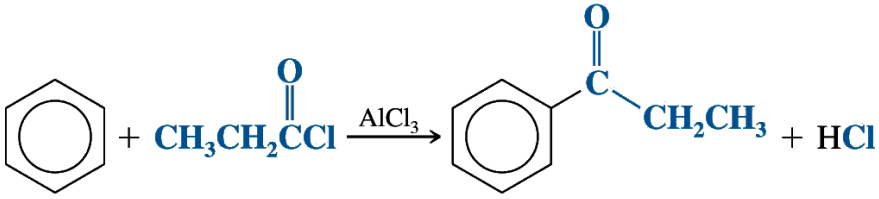
1-



Ethyl phenyl ketone — **Propylbenzene (80%)**



2-



Propanoyl chloride — **Ethyl phenyl ketone (90%)**