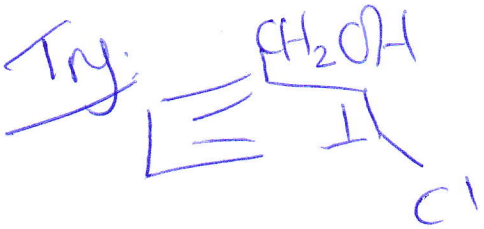
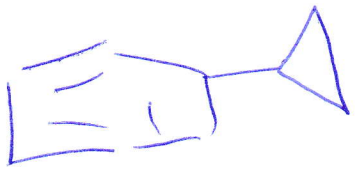
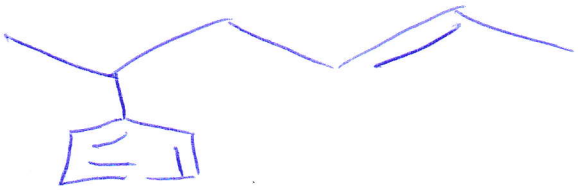
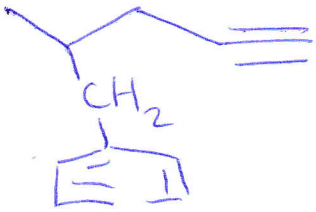
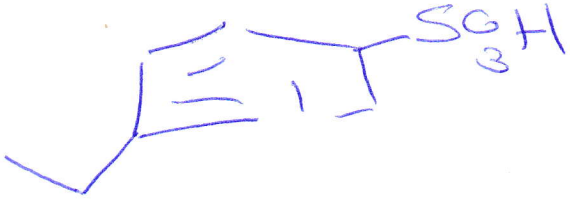
Try:

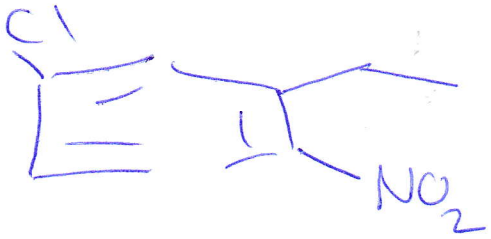


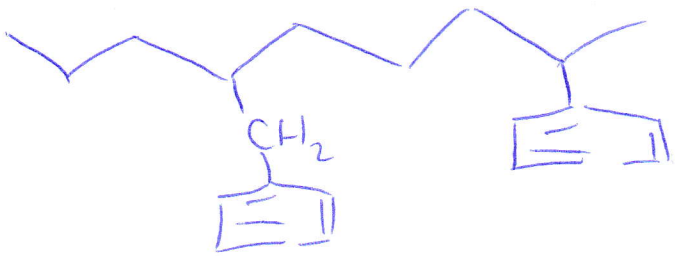








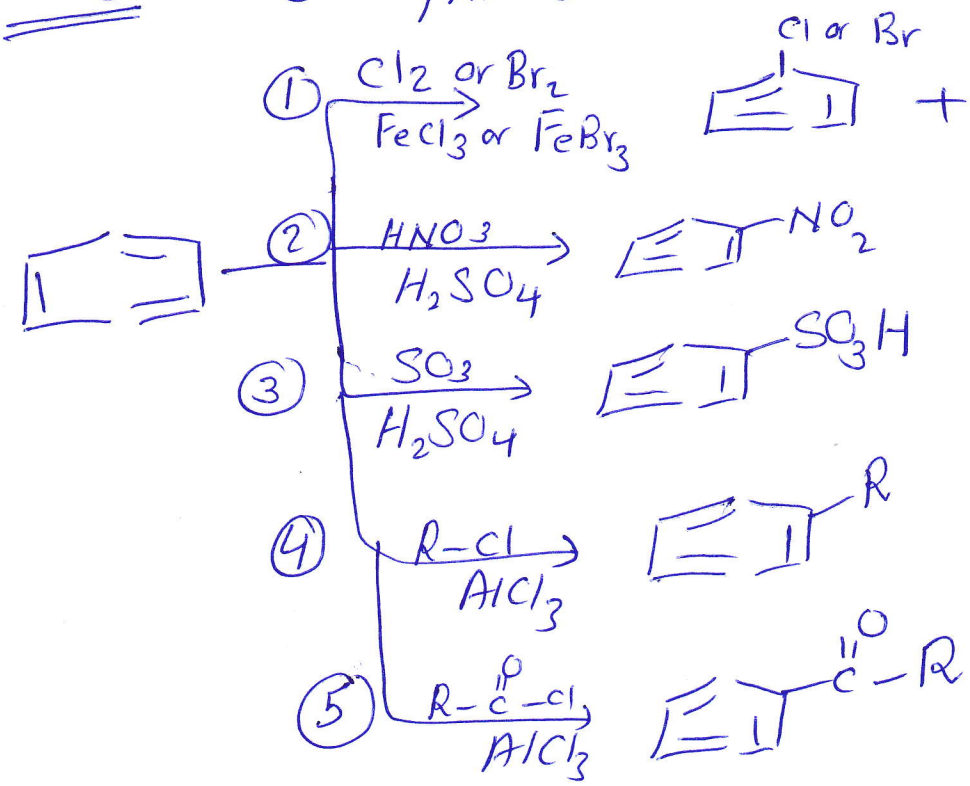




biphenyl

Cha. 4 Aromatic Compounds

4.8 Electrophilic Aromatic Substitution (EAS)



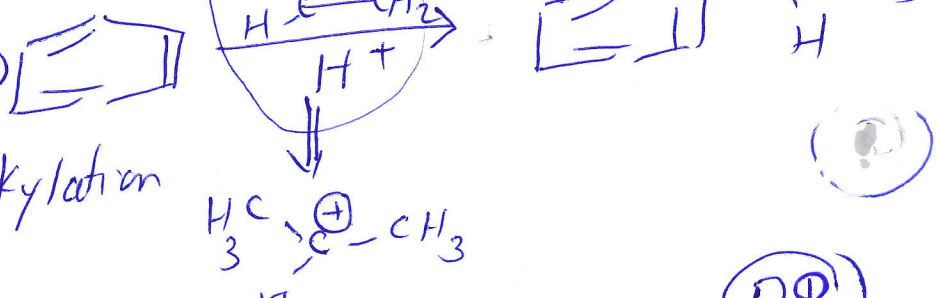
* Names of reactions:- ① halogenation (chlorination or bromination)

② nitration ③ Sulfonation ④ Friedel-Crafts alkylation

⑤ Friedel-Crafts acylation

* One hydrogen atom in benzene is replaced by (X or NO_2 or SO_3H or R or $\overset{O}{\overset{\|}{C}}-R$)

* Examples:

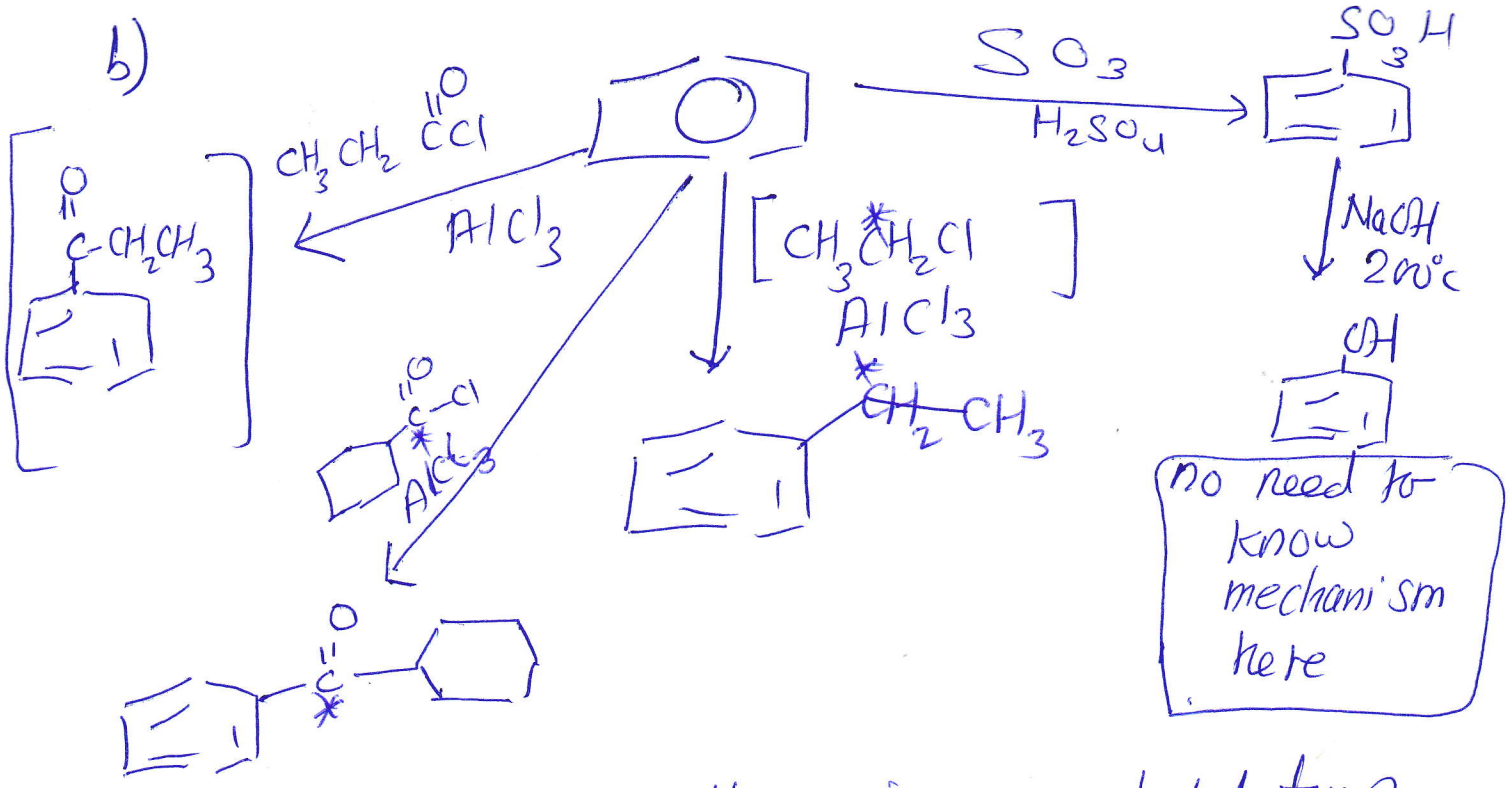
a) 

This rxn is type of alkylation

(1)

(2)

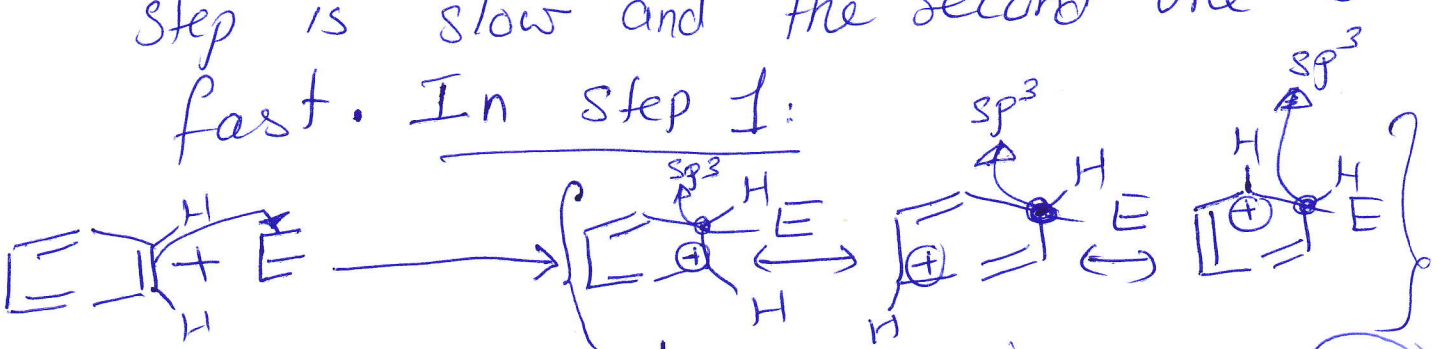
b)



In all reactions, there is a substitution not addition such as alkene (even benzene has 3 π bonds). Benzene is not an alkene.

4.9 Mechanism of electrophilic aromatic substitution

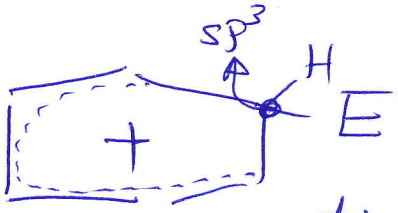
* All reactions undergo the same mechanism: it consists at 2 steps, the 1st step is slow and the second one is fast. In step 1:



electrons attack electrophile

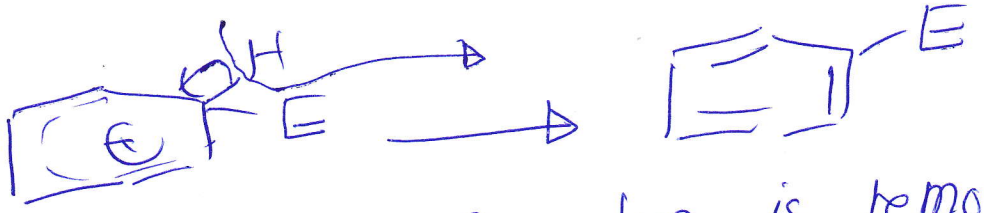
benzenonium ion
"intermediate"
"carbocation

Draw a resonance hybrid for 3 resonance structures



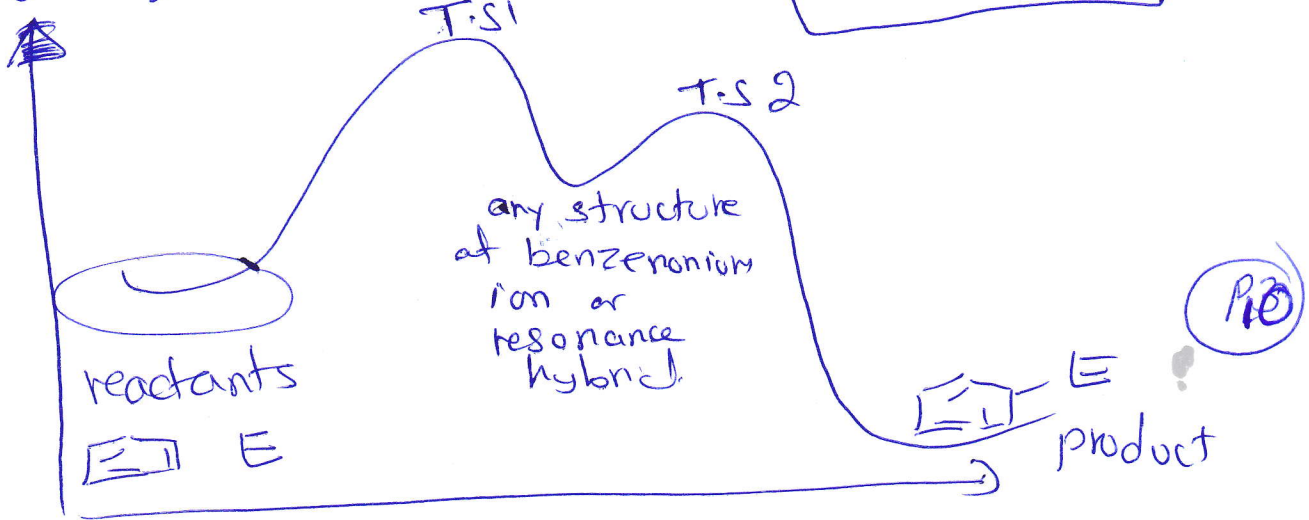
This intermediate is <u>not</u> aromatic (we have sp^3 carbon)
less stable than benzene.

Now, the second step is



* hydrogen atom at sp^3 carbon is removed, σ bond becomes a π bond, and the compound will be again aromatic
we can't remove any hydrogen except one that is attached to sp^3 carbon. This is <u>mono</u>substitution reaction. Only 1 hydrogen is substituted.

see P.125



Important question: What is the electrophile (E) in each of the following reactions?

① $X-X + FeX_3 \longrightarrow X^{\delta+} \cdots X-FeX_3^{\delta-}$

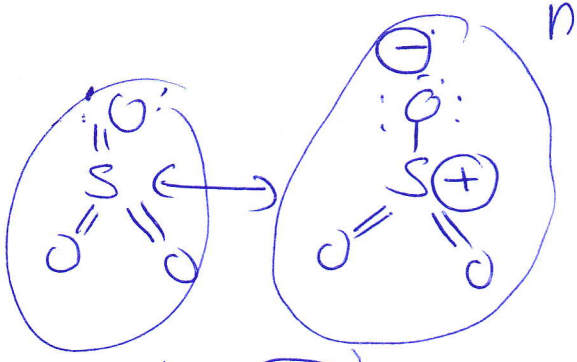
FeX_3: Catalyst, needs electron

$X^{\delta+}$: E in halogenation

② $HNO_3 + H_2SO_4 \Longrightarrow NO_2^{+}$ ($O=\overset{+}{N}=O$)

nitronium ion (E) in nitration

③ SO_3:



Same molecule

Electrophile in sulfonation

Same thing for "SO_3 in H_2SO_4" fuming sulfuric acid.

④ For Friedel-Crafts alkylation:-

$CH_3-CH_2-Cl + AlCl_3 \Longrightarrow CH_3\overset{+}{C}H_2 + AlCl_4^-$

$AlCl_3$: Catalyst, needs electron

$CH_3\overset{+}{C}H_2$: Electrophile.

⑤ For Friedel-Crafts acylation:-

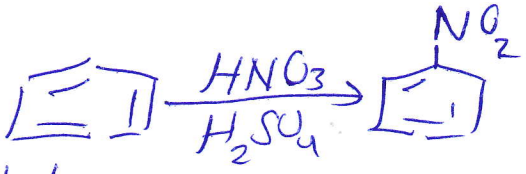
$R-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \Longrightarrow R-\overset{O}{\overset{\|}{C}}^{+} + AlCl_4^-$

$AlCl_3$: Catalyst

$R-\overset{O}{\overset{\|}{C}}^{+}$: electrophile

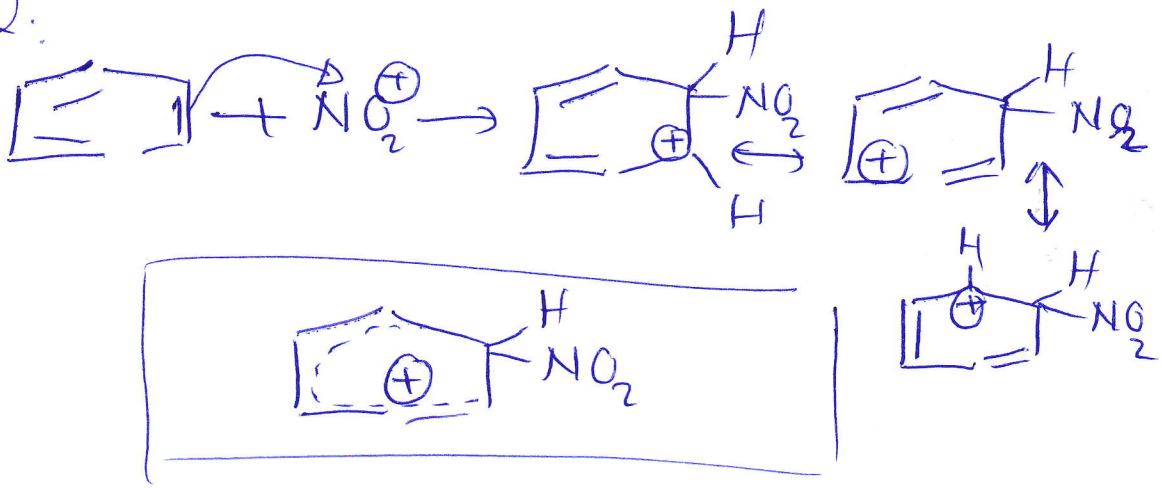
Summary; we have 5 different types of electrophile

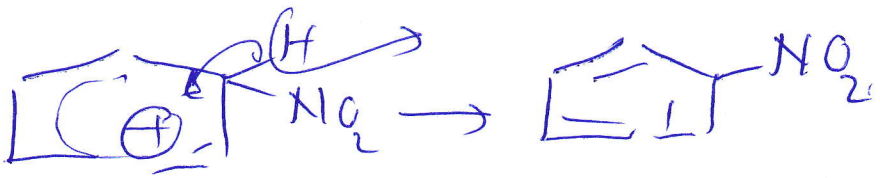
$X^{\delta+}$, $NO_2^{\oplus}$, SO_3, $R^{\oplus}$, $R-C^{\oplus}=O$.

Ex. Draw a mechanism for 

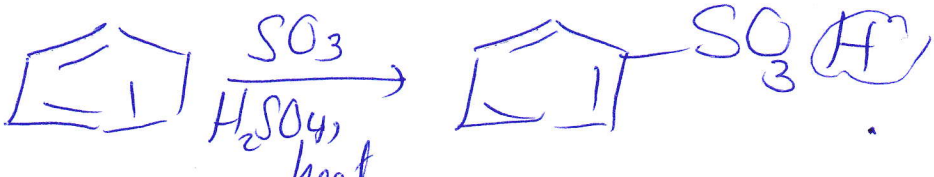
Step 1: Generating of electrophile

$HNO_3 + H_2SO_4 \longrightarrow NO_2^{\oplus}$

Step 2. 

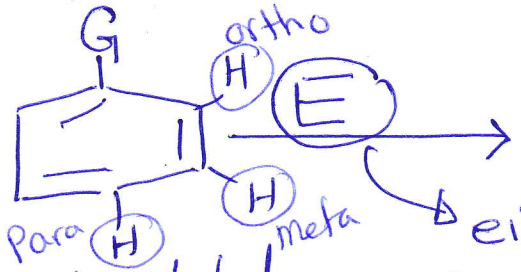
Step 3: 

* In case of sulfonation (SO_3) ⟹ there is a hydrogen in the product



4.10 Ring Activating and Deactivating Substituents.

* If we have monosubstituted benzene, and a second substitution rxn is required, such as:-



monosubstituted benzene

either halogenation, nitration, sulfonation, alkylation or acylation.

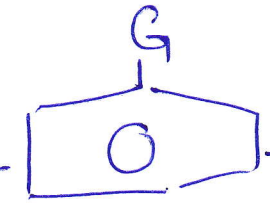
* Two concepts should be discussed.

The First one is: Reactivity (fast rxn vs slow rxn relative to benzene).

The Second Concept is: Orientation (which hydrogen in monosubstituted benzene should be replaced, ortho, meta or para?).

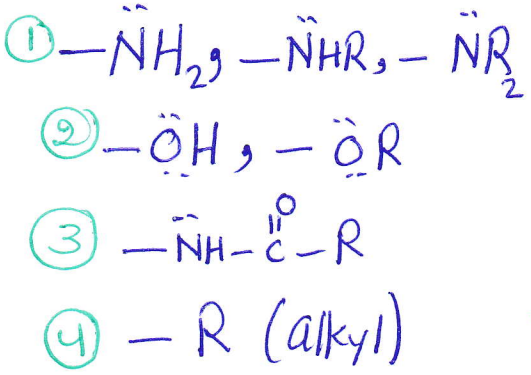
* Let's begin with **Reactivity.**

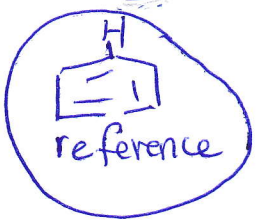
Group "G" in monosubstituted could be either:

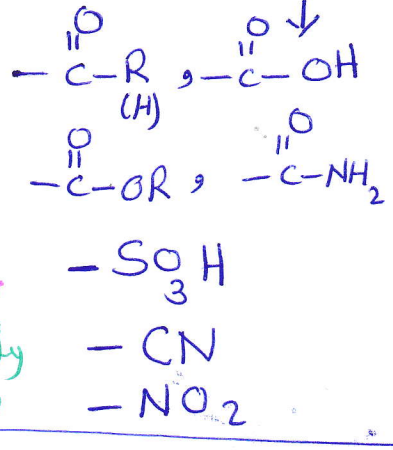


Activating

Deactivating



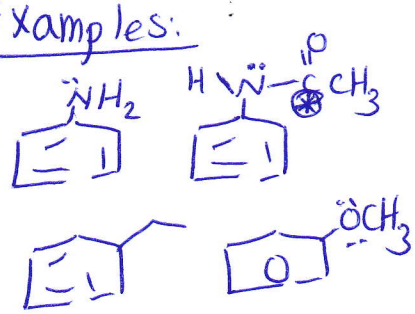




Decreases reactivity within group.

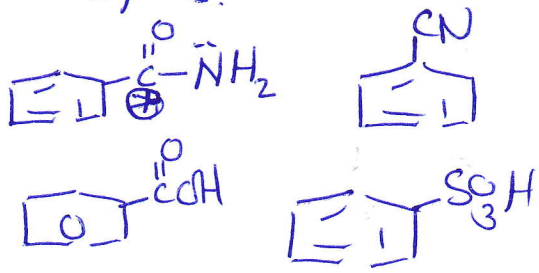
Decreases reactivity within group

Examples:



This line "–" represents the bond between G and benzene.

Examples:



*Did you observe the difference between these groups?

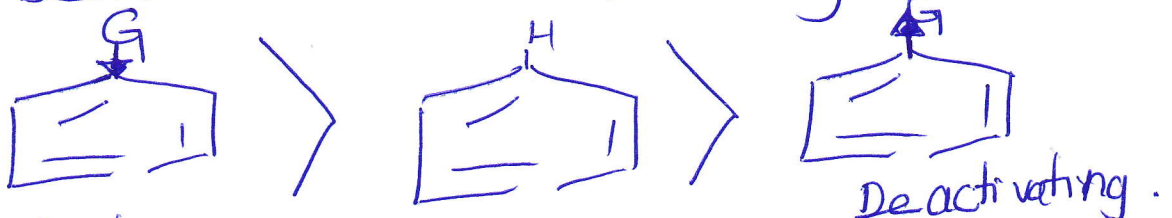
Activating groups:
"Electron-releasing"
"Electron-donating"

nitrogen and oxygen atoms (have lone pair of electrons) attached directly to benzene, or R-group. "No lone pair of electrons".

Deactivating groups:
"Electron-withdrawing"

C(=O) is attached directly to benzene on presence of SO_3H, CN, NO_2

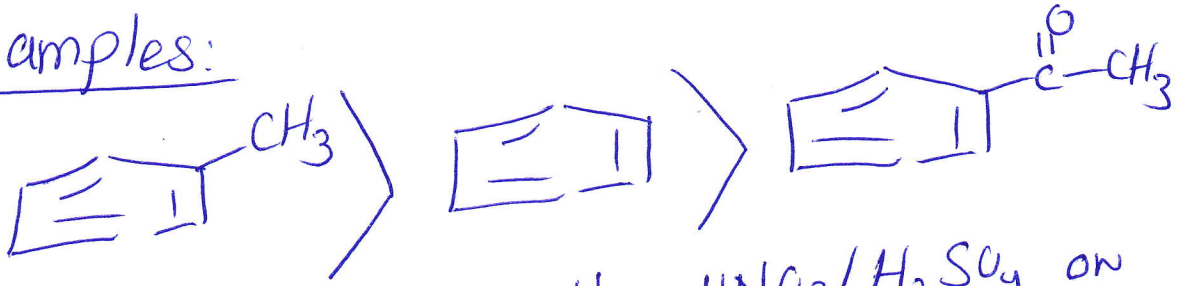
Now, reactivity of electrophilic aromatic substitution has the following order:



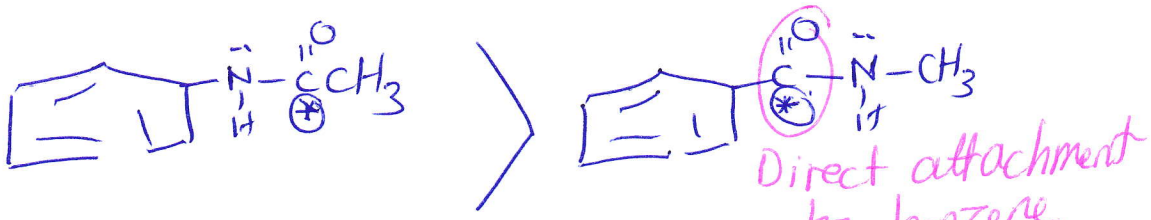
activating

Deactivating.

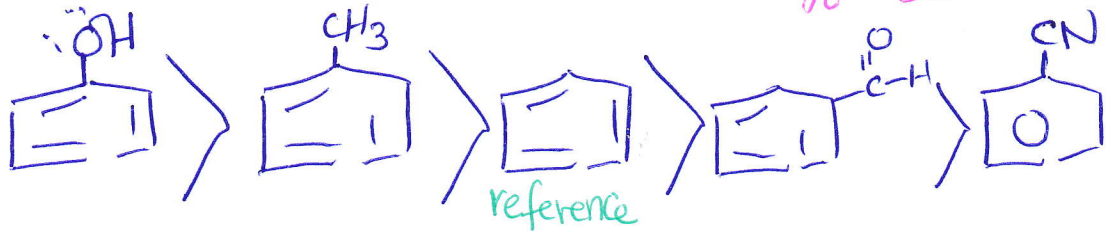
Examples:

① 

towards reaction with HNO_3/H_2SO_4 or $CH_3Cl/AlCl_3$ or $Cl_2/FeCl_3$

② 

Direct attachment to benzene

③ 

reference

Note: you have to remember all of substituents and to which groups (activating or deactivating) are they belong

Now, what is the explaination for this trend?