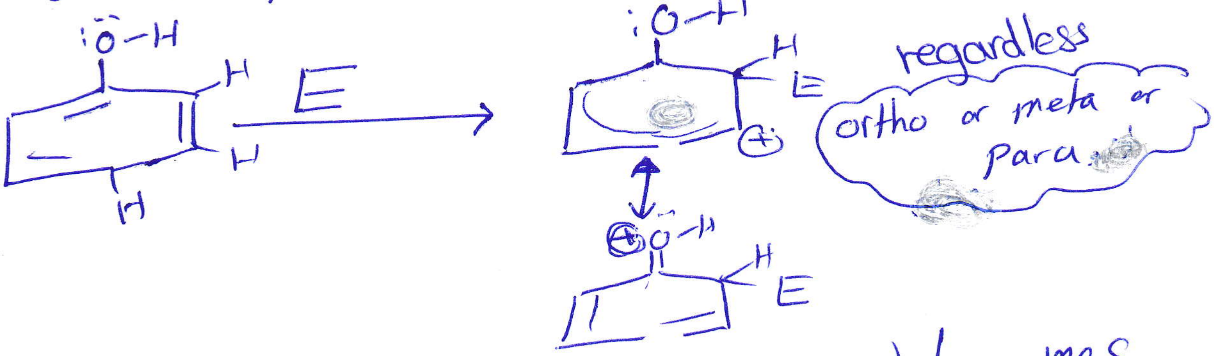
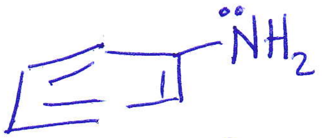
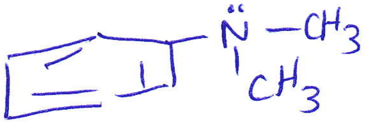
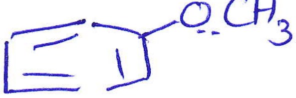
*Activating groups are electron-donating groups; it means when the <u>second</u> electrophilic aromatic substitution reaction is occured, these substituents can donate electrons (-ve charge) to benzenonium ion (electrophile, +ve charge) as shown:-

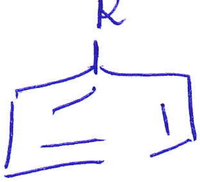


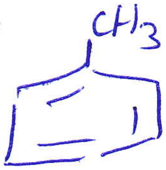
the intermediate (benzenonium ion) becomes more stable and consequently, reaction becomes faster. This is also observed if nitrogen atom is present instead of oxygen.



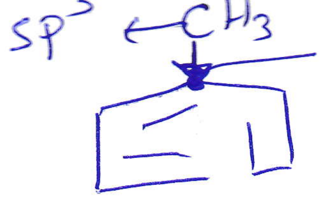




<u>Note:</u> 

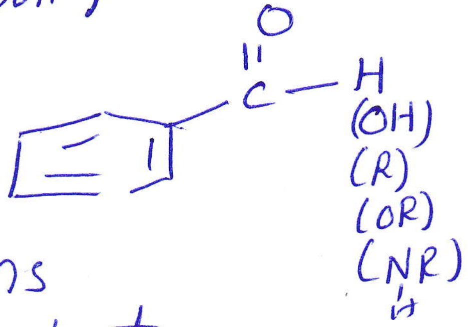
such as 

has no lone pair on the carbon atom of CH_3. Please remember due to hybridization (sp^2 is more electronegative than sp^3 carbons), R is electron-donating group.

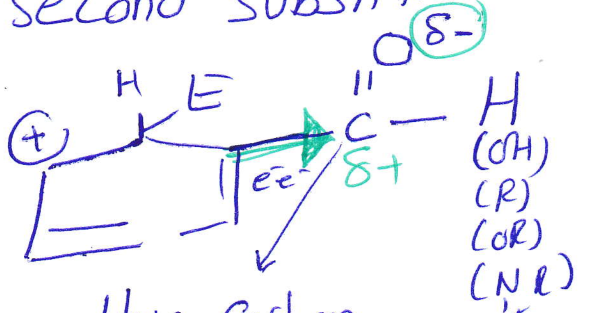


sp2 (more electronegative carbon than sp3 Carbon).

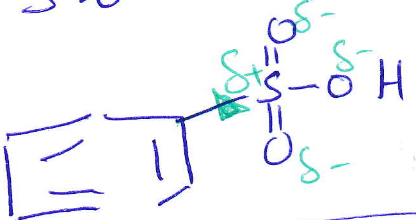
On the other hand,

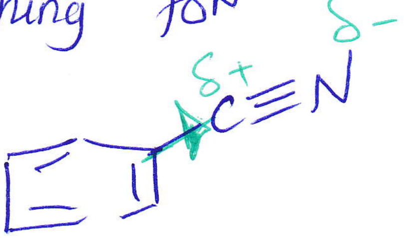


withdraws electrons from the intermediate when second substitution reaction is occured.



this Carbon withdraws electrons (-ve charge) from the ring, consequently intermediates becomes less stable and the rxn very slow. Same thing for

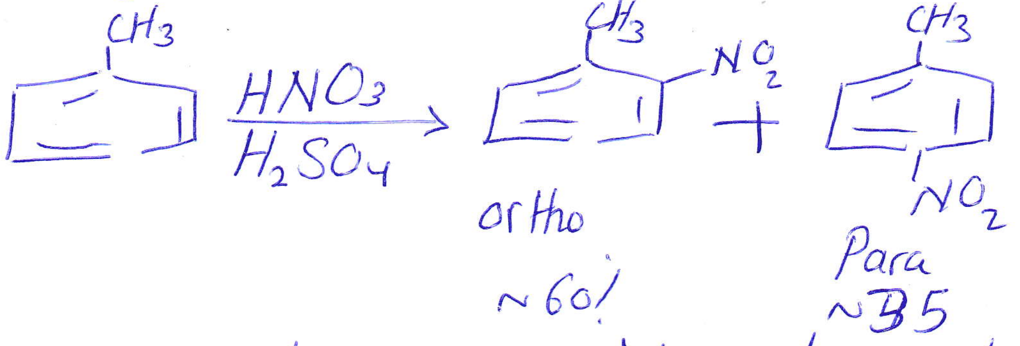




no lone pair of electrons on the nitrogen atom.

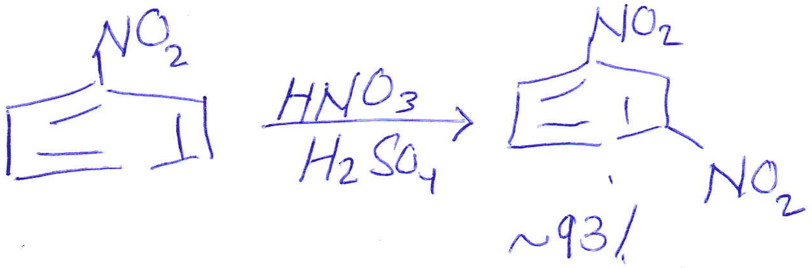
* Now, remember the first Concept was reactivity (Page 6) and a second one is orientation.

4.11 * Regarding the orientation, electron-releasing groups direct(تُوَجِّه)a second electrophile mainly (Ortho + Para) positions, Examples:



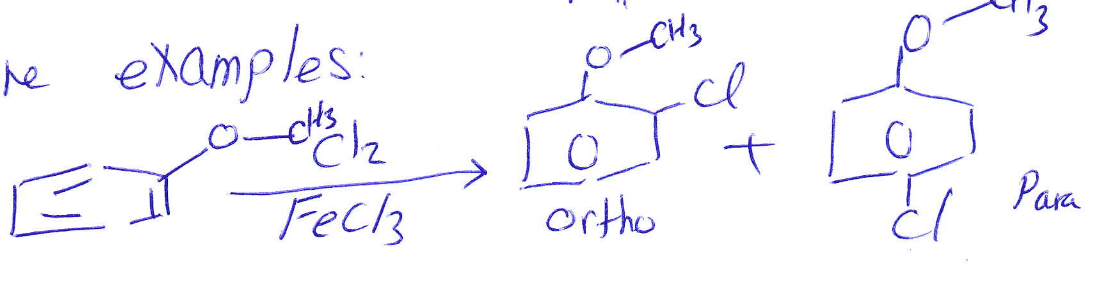
Two products are obtained mainly, very little amount of meta isomer is also produced.

On the other hand, electron-withdrawing groups direct a second substituent mainly meta position.

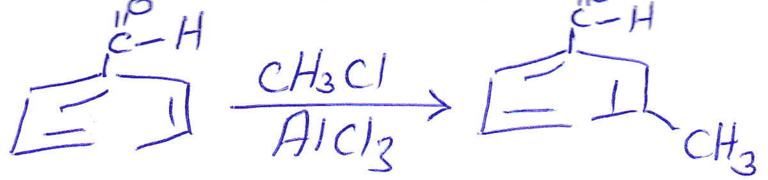


* More examples:

a)

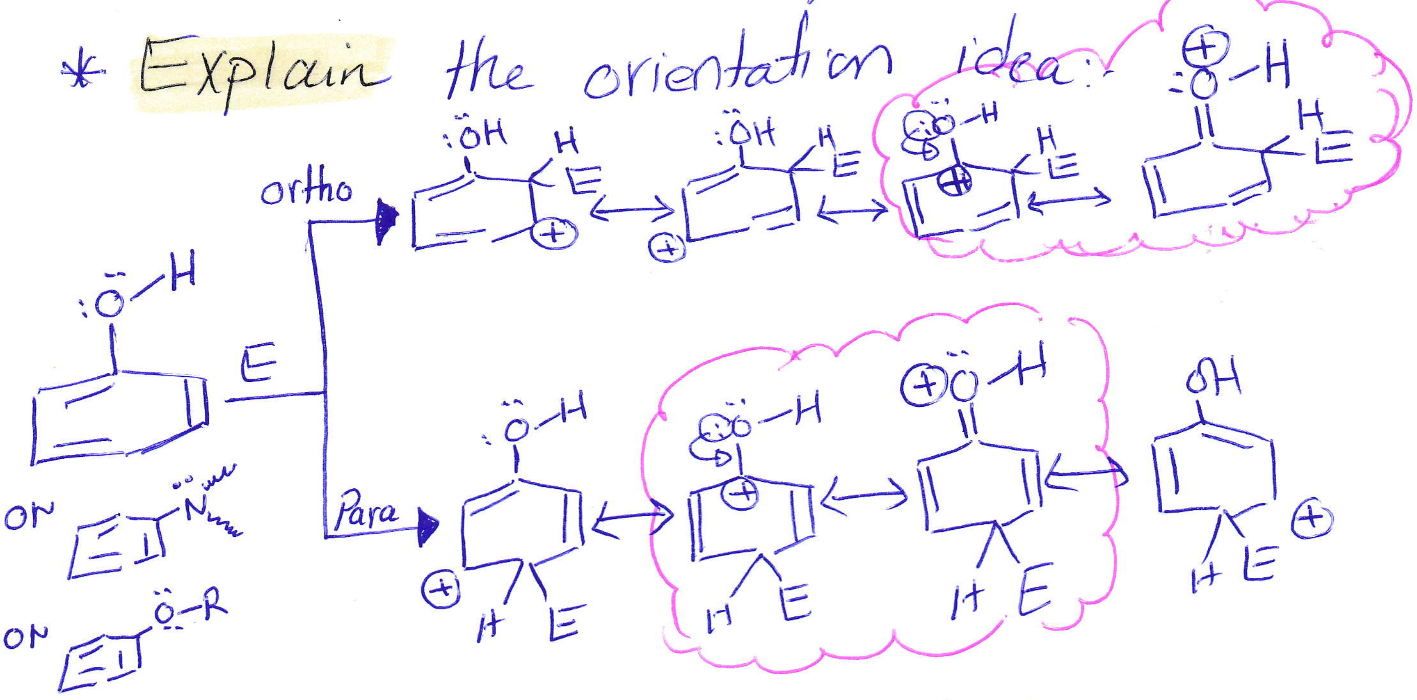


b)

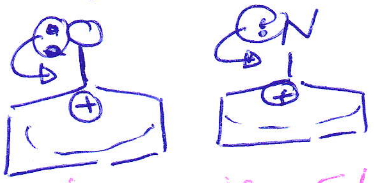


Important Note: We look on substituent on benzene $(-\overset{O}{\overset{\|}{C}}-H)$ (electron-withdrawing group) to know the direction (o+P) or (m); ignore the type of electrophile $(\overset{+}{CH_3})$, as in the above example.

* Explain the orientation idea:

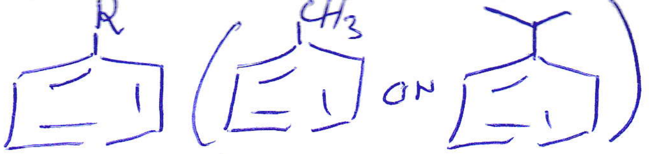


Presence of lone pair of electrons on oxygen and nitrogen atoms permits to draw 4 resonance structures, since a positive charge on carbon atom is adjacent to oxygen or nitrogen.



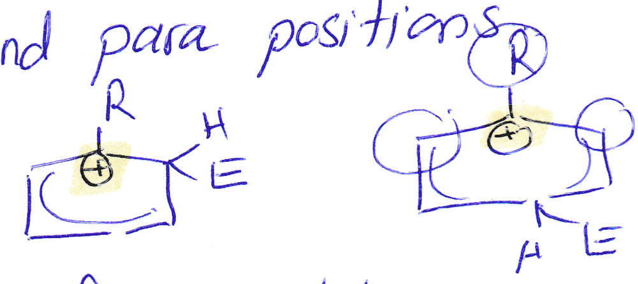
*This situation is more stable than meta position.

Important question:-



prefers ortho and para directions, in spite of no lone pair of electrons is present on methyl group (CH_3). why ?

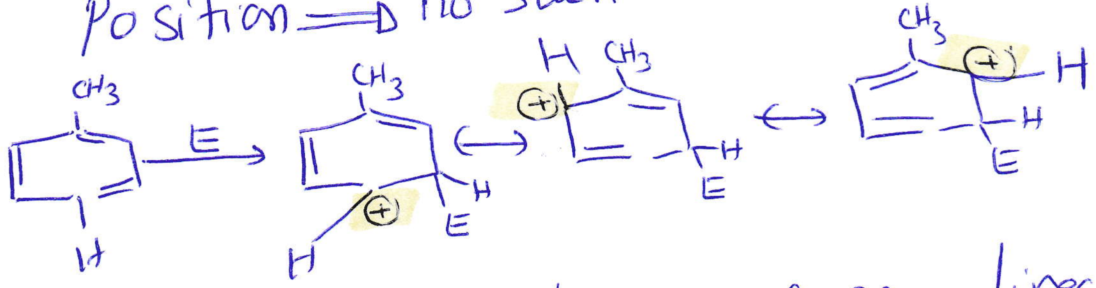
Answer is present in Page 130. In this case, we have stable intermediates at ortho and para positions.



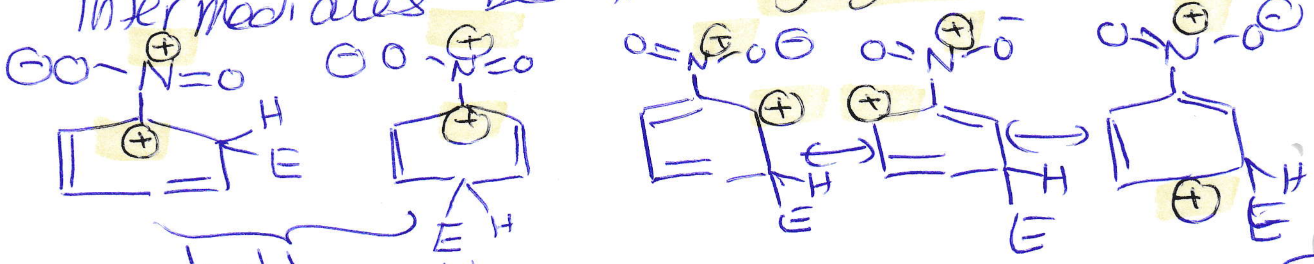
3° > 2° > 1°

Carbocation Stability (chapter 3).

but if electrophile was directed on meta position ⟹ no such carbocation is present.



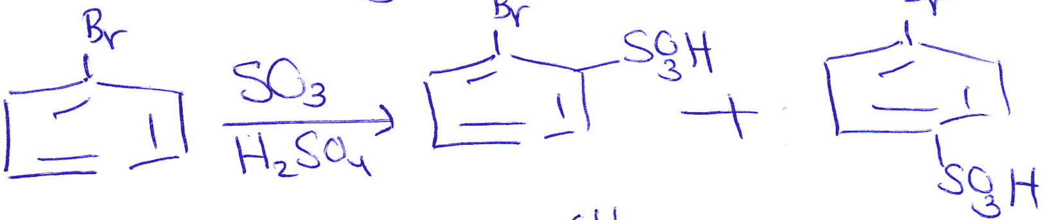
Finally, Electron-withdrawing groups direct second electrophile meta position, because if electrophile attached to ortho and para positions, the intermediates become highly unstable. (P.133)

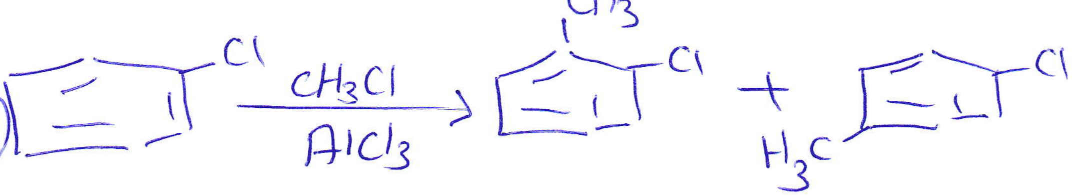


highly unstable (not formed)

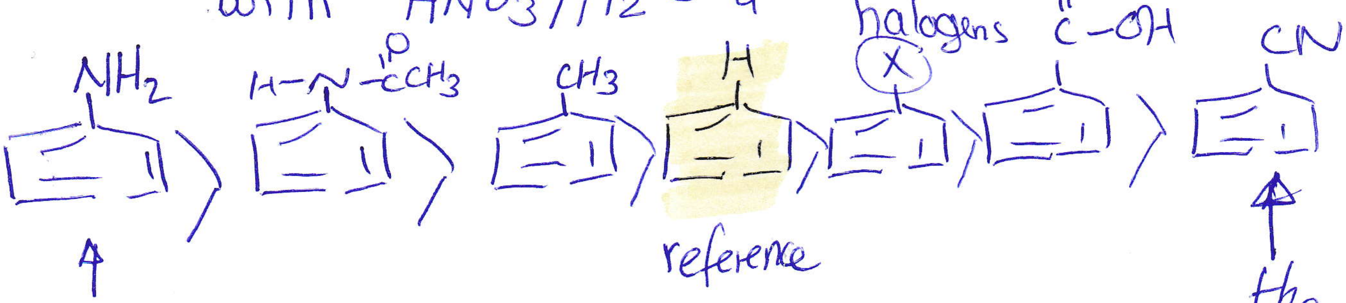
* Now, what about halogens?

Halogens direct ortho and para positions; as (electron-donating groups) BUT deactivate Electrophilic aromatic substitution as (electron-withdrawing groups).

ex1


ex2


ex3 Arrange the reactivity towards reaction with HNO_3/H_2SO_4.



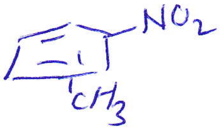
the most reactive

reference

the least reactive

4.12 Importance of Directing effect in Synthesis.

a) Prepare  from 

b) Prepare  from benzene

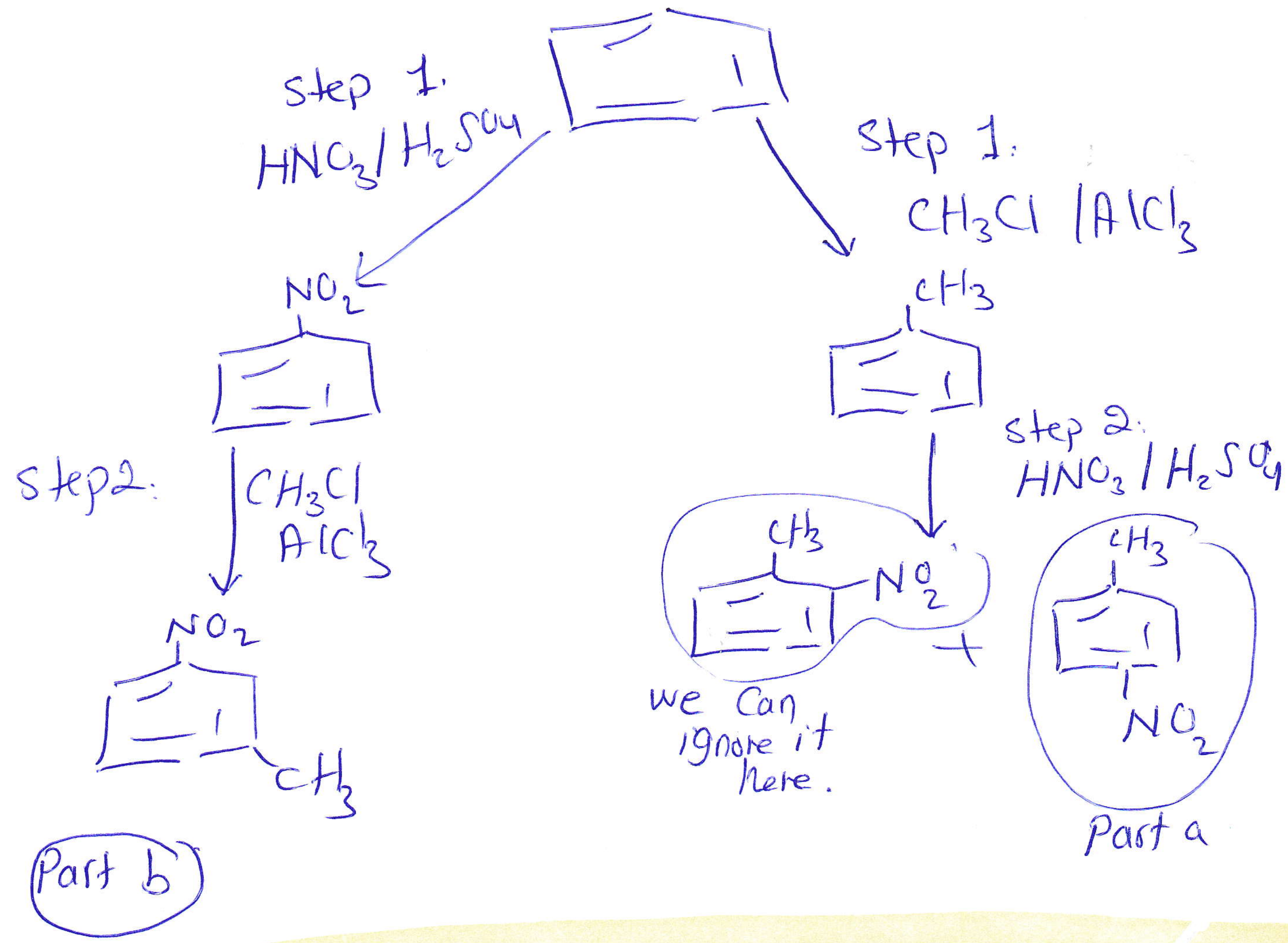
To solve such problems, first determine proper reagents. Second determine proper oder of reactions.

First: reagents used

HNO_3/H_2SO_4 for NO_2 "nitration"

$CH_3Cl/AlCl_3$ for "CH_3" Alkylation.

Second: Order of steps. Let's try:



End of chapter 4.