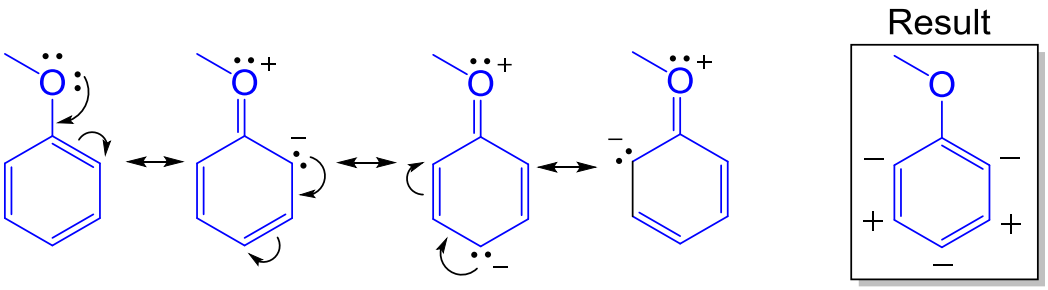
# Substituent Effects in Aromatic Systems

## Electron Donor Groups

Relative to a hydrogen substituent, we can say there are two types of groups we can place on aromatic rings: electron donors and electron withdrawers:

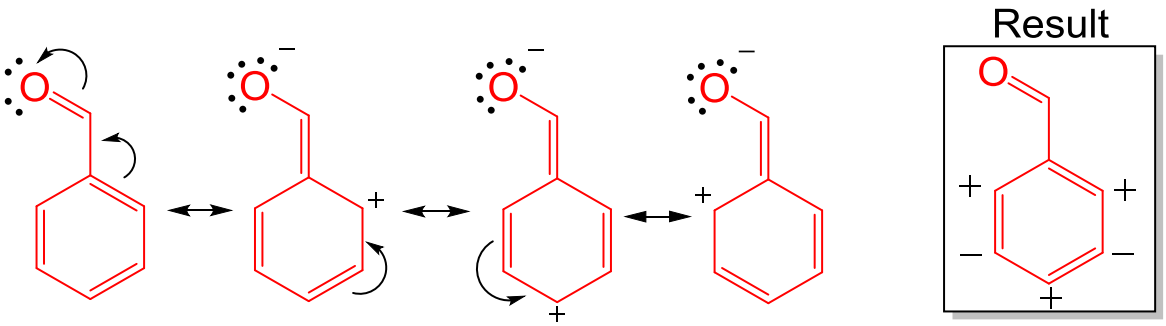
A donor is either an alkyl group OR an atom with a lone pair that has a $\delta^-$ charge on it. Typical examples are oxy groups and halogens:




Aromatic rings typically react as nucleophiles and therefore an anionic character makes the ortho/para positions more reactive. ∴ electron donor groups (EDGs) make the ring ortho/para directors.

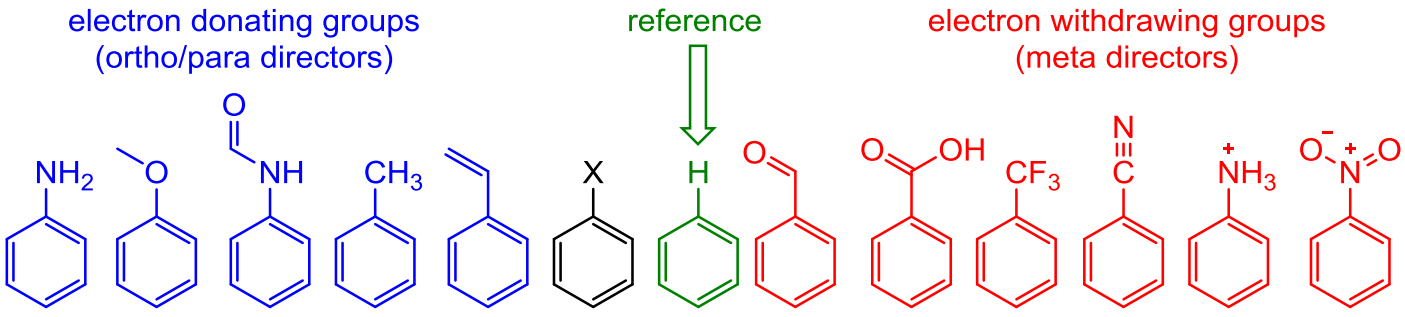
## Electron Withdrawing Groups

A withdrawer usually has a $\delta^+$ atom right next to the ring. Examples are – $CF_3$ or carbonyl groups:




Overall, the ring is deactivated (less reactive) because it is not as nucleophilic. The meta positions are not as affected by this resonance and so electron withdrawing groups (EWGs) are meta directors.

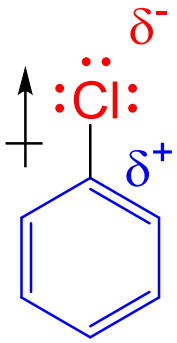
Here's a representative list of EDGs and EWGs:




halogens (X) are ortho/para directors but are deactivating/withdrawing

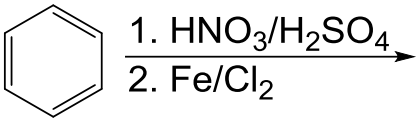
We mentioned before that a donor is either an alkyl group OR an atom with a lone pair that has a $\delta^-$ charge on it.

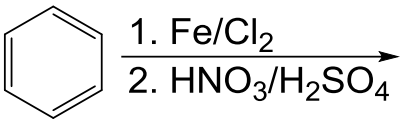
An alkyl halide fits this definition perfectly and is definitely an ortho/para director. Overall however, it deactivates the ring (makes it less reactive) because it withdraws more electron density through induction than it gives through resonance.



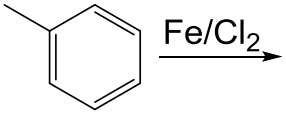

Questions to consider:

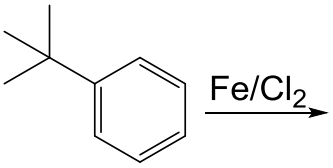
1. What is the major products of the following reactions and why?



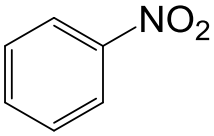

2. What is the major products of the following reactions and why?

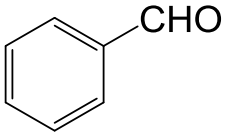


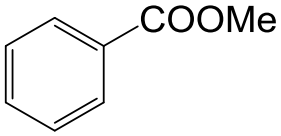




3. How will the rates of reaction with $Fe/Cl_2$ for the following reagents compare:

i ii iii

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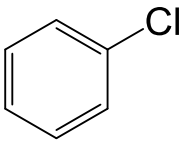
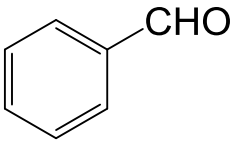
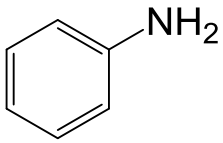
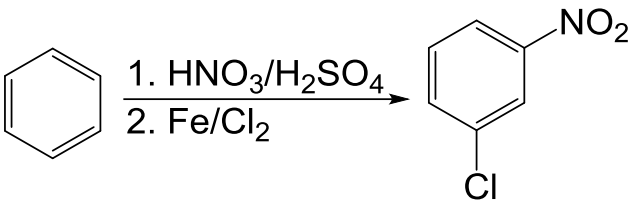


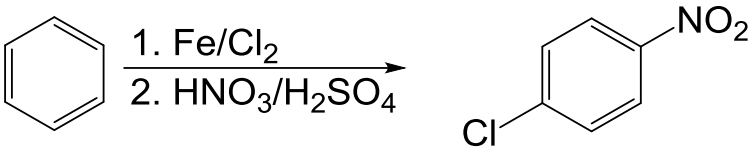



1. Answer:

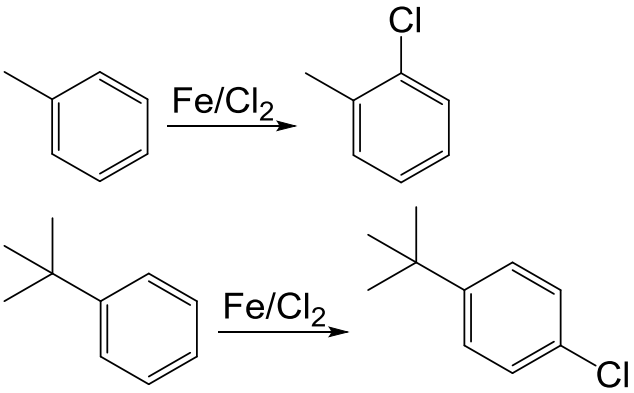



The product after step 1 is nitrobenzene. Nitro is an EWG and is a meta-director




The product after step 1 is chlorobenzene. Chlorine is an ortho/para director. Because Cl is a large atom, the para product would likely be preferred.

2. Answer:



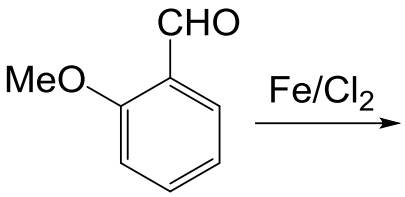

An alkyl group is ortho/para directing. The influence of an EDG is felt more by the ortho position, however, the ortho position is crowded. With toluene, the product is meta. With a t-butyl group, the product is para because it is too bulky to substitute ortho.

Note that whether the ortho/para product forms with toluene is temperature dependent but we don't think that far in this course.

3. Answer: iii>ii>i because $NO_2$ is more withdrawing than $CHO$ is more withdrawing than $COOMe$. Not only are withdrawing groups meta directors, they are also **deactivating**! Practically speaking, most literature would say nitrobenzene would not even react in electrophilic halogenation. For this class we assume it does.
   Answer: iii>i>ii The amine will be most reactive and most likely undergo side reactions. Halogens are not as deactivating as carbonyls.

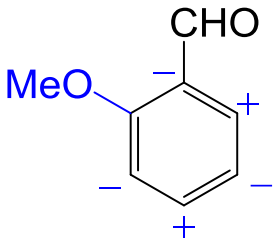
Effects of multiple substituents:

Where would the halide add in the following scenario?

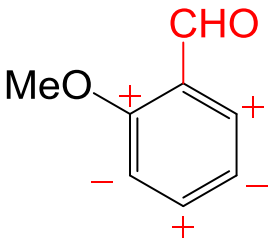



These questions are rare but not difficult to solve because the directing effects are simply cumulative. What I like to do is superimpose the effects of one group and another on the ring to see if they both activate a spot:

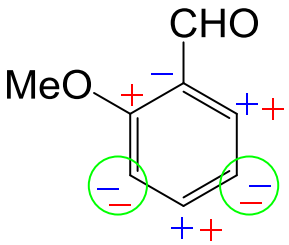
Donor Effects



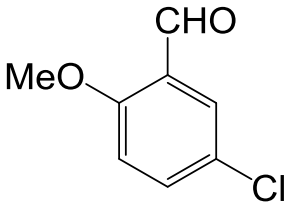

Withdrawer Effects




Result




We can see the two positions in green are both electron rich relative to the rest of the ring. We also know that OMe is relatively large so the product is most likely

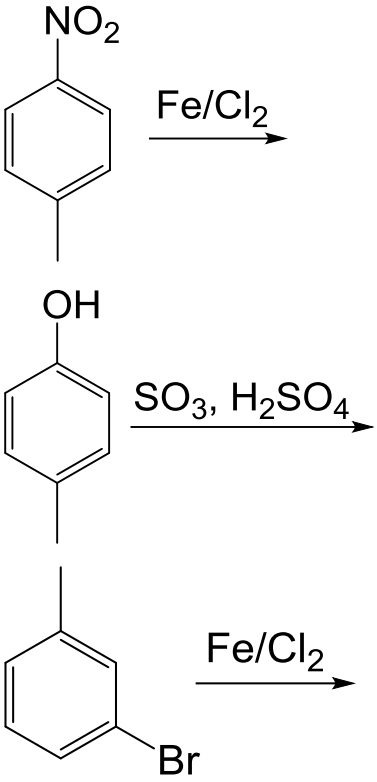



If you have two donors with opposing effects, the stronger donor is more directing.

If you have two withdrawers with opposing effects, the weaker withdrawer's positions are more reactive. Usually though, the ring is rendered unreactive by the number of deactivating groups.

If you have a donor and withdrawer with opposing effects, typically the effects of the withdrawer are stronger.

What are the products of the following reactions:



Answers: