

## 18.6: SUBSTITUENT EFFECTS ON THE EAS REACTION

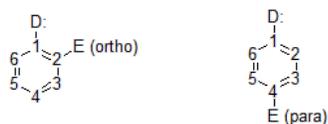
### IMPORTANT NOTE:

Recognizing substituents as Electron Donating or Withdrawing is a useful skill for evaluating reaction mechanisms. For Electrophilic Aromatic Substitution (EAS) reactions, the rate determining step is the formation of a positively charged sigma complex. In future reactions, the intermediate may have a negative charge. While the electron donating and withdrawing properties of a substituent are inherent within the substituent, their effect on the stability of an intermediate and the reaction rate depends on the charge of the intermediate.

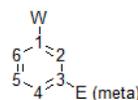
### SUBSTITUENTS AND THEIR DIRECTING EFFECTS IN EAS REACTIONS

Electron donating groups (D) direct the reaction to the ortho- or para-position, which means the electrophile substitutes for the hydrogen on carbon 2 or carbon 4 relative to the donating group. The withdrawing group directs the reaction to the meta position, which means the electrophile substitutes for the hydrogen on carbon 3 relative to the withdrawing group. The halogens are an exception to this pattern. The halogens are a deactivating group that direct ortho or para substitution.

Donating groups direct the Electrophile (E) to the ortho- and para-positions.



Withdrawing groups direct the Electrophile (E) to the meta-position.



Examples of electron donating groups in the relative order from the most activating group to the least activating:

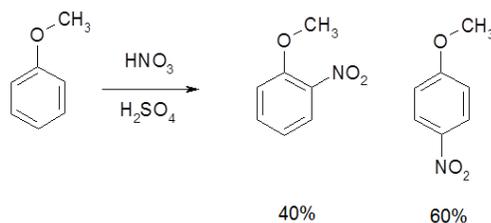
$-\text{NH}_2, -\text{NR}_2 > -\text{OH}, -\text{OR} > -\text{NHCOR} > -\text{CH}_3$  and other alkyl groups with R as alkyl groups ( $\text{C}_n\text{H}_{2n+1}$ )

Examples of electron withdrawing groups in the relative order from the most deactivating to the least deactivating:

$-\text{NO}_2, -\text{CF}_3 > -\text{COR}, -\text{CN}, -\text{CO}_2\text{R}, -\text{SO}_3\text{H} > \text{Halogens}$  with R as alkyl groups ( $\text{C}_n\text{H}_{2n+1}$ )

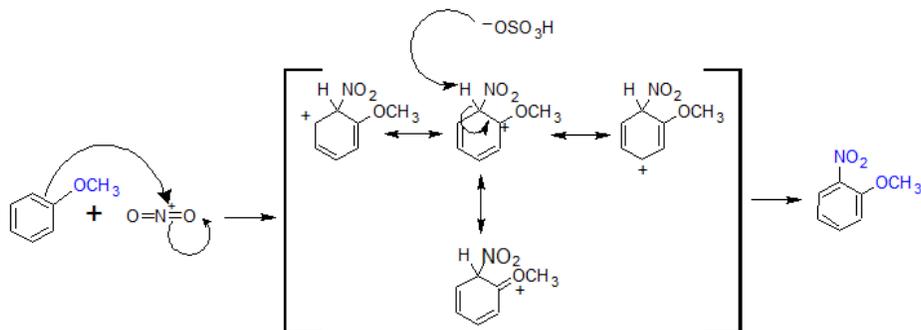
### ORTHO-, PARA-DIRECTORS VIA RESONANCE

Groups that donate electrons through resonance are ortho-, para-directors for EAS reactions. Methoxybenzene (anisole) will be used to demonstrate the ortho-, para-direction of substituents that stabilize the sigma complex through resonance. The nitronium ion ( $\text{O}=\text{N}^+=\text{O}$ ) will be used to represent the Electrophile ( $\text{E}^+$ ).

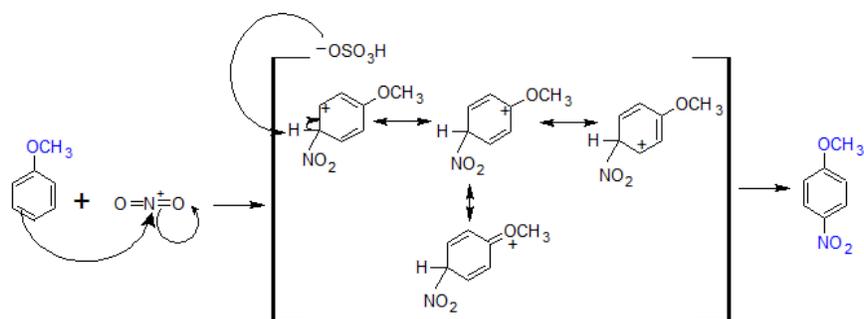


The ortho- and para-directed mechanisms for the nitration of anisole are shown below. When the nitro group adds at the ortho or para position, the stability of the sigma complex is increased by the presence of a fourth resonance form. The greater the stability of the sigma complex causes the ortho and para products to form faster than meta. Generally, the para-product is favored over the ortho-product because of steric effects even though there are two ortho-positions.

#### Mechanism for ortho-directed product formation

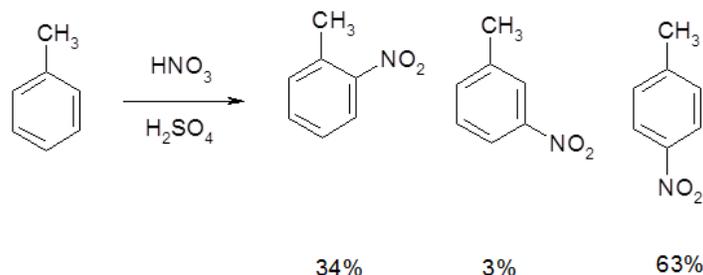


#### Mechanism for para-directed product formation



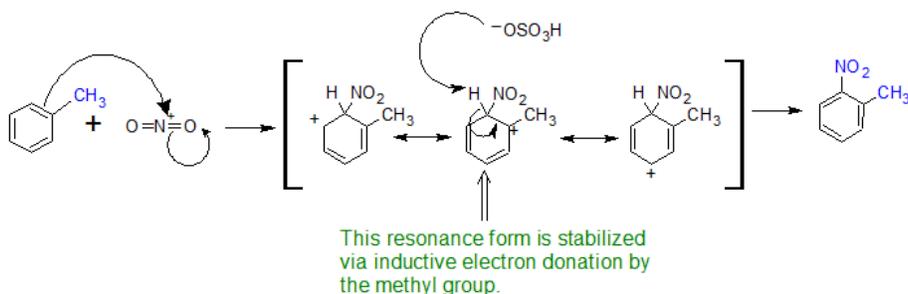
## ORTHO-, PARA-DIRECTORS VIA INDUCTION

Alkyl groups are ortho-, para-directors for EAS reactions. Toluene will be used to demonstrate the ortho-, para-direction of substituents that stabilize the sigma complex through induction. The nitronium ion ( $\text{O}=\text{N}^+=\text{O}$ ) will be used to represent the Electrophile ( $\text{E}^+$ ). Since the inductive effect is weaker than resonance, we can see that a small percentage of the meta product is also isolated.

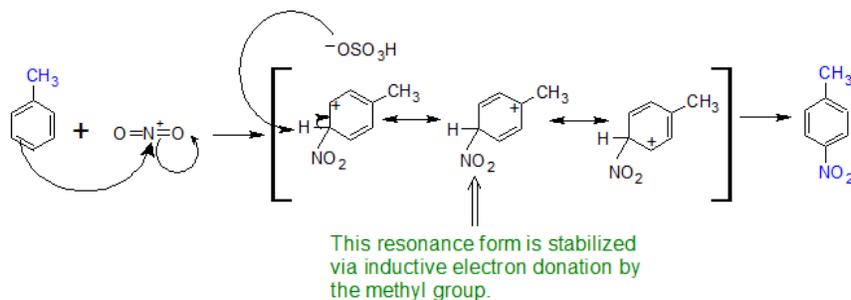


Looking at the stability of the resonance structures of the sigma complex in the reaction mechanism for nitration of toluene explains why the ortho- and para- substitutions are the major products. When the nitro group adds at the ortho or para position, the methyl group stabilizes the transition state through induction electron donation which favors the formation of the ortho- and para- products. As seen with the resonance directed products, the para product is favored because of steric effects even though there are two ortho- positions.

### Mechanism for ortho-directed product formation



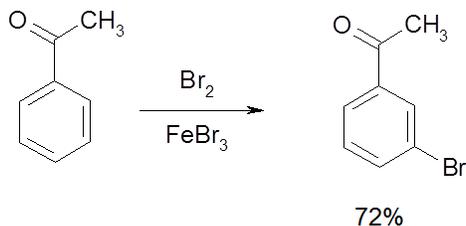
### Mechanism for para-directed product formation



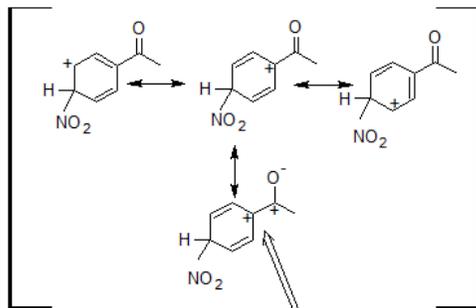
## META DIRECTORS - THE ELECTRON WITHDRAWING GROUPS

Electron withdrawing groups destabilize the sigma complex and deactivate benzene rings to EAS reactions. For electron withdrawing groups, all of the sigma complexes are destabilized. The meta-position is the least destabilized and produces the largest percentage of the reaction products.

Acetophenone will be used to demonstrate the reactivity of meta-directors using the sigma complexes below. Acyl groups are resonance deactivators.

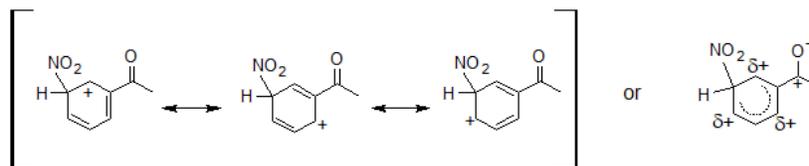


Ortho and para reactions produce a resonance structure that places the arenium cation next to an additional cation at the carbonyl carbon. This close proximity of partial positive charges destabilizes the sigma complex and slows down ortho and para reaction.



para-(shown) and ortho-directors destabilize the sigma complex by forcing two partial positive charges into close proximity.

By default the meta product forms faster because the destabilizing effects are reduced through greater physical separation of the partial positive charges.

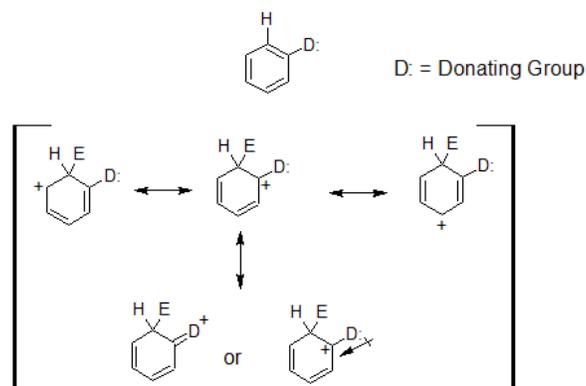


Meta-directors reduce destabilization of the sigma complex.

## SUBSTITUENTS AND ELECTROPHILIC AROMATIC SUBSTITUTION (EAS) REACTION RATES

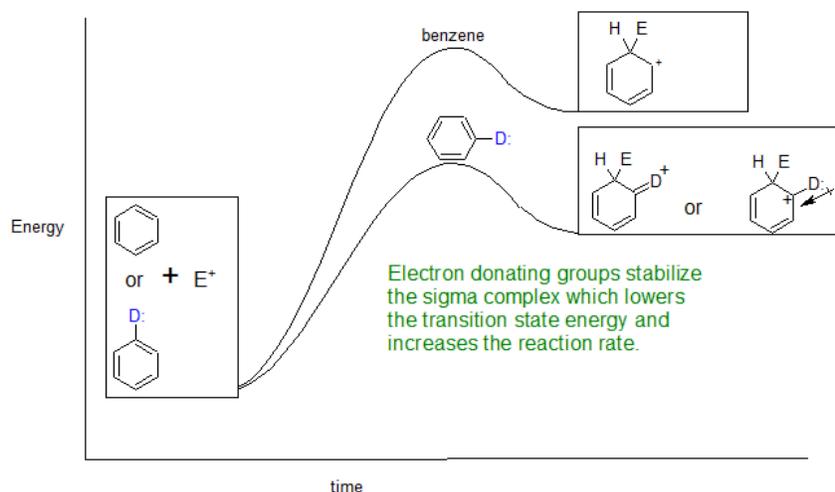
Since sigma complex formation is the rate determining step of EAS reactions, benzene derivatives are divided into two groups based on how the substituent stabilizes or destabilizes the positively charged sigma complex. The EAS reaction of a substituted ring with an activating group is faster than benzene. On the other hand, a substituted ring with a deactivated group is slower than benzene. Activating groups speed up the EAS reaction by either resonance or inductive electron donation (typically R groups). For resonance, unpaired electrons can be donated to stabilize the positive charge of the sigma complex in the transition state. Stabilizing the intermediate, speeds up the reaction by lowering the activating energy. Inductive electron donation by R groups is an analogous, yet weaker effect than resonance. Inductive electron donation helps to stabilize the sigma complex and speed up (activate) the reaction. Deactivating groups withdraw the electrons away from the carbocation of the sigma complex causing destabilization and increasing the activation energy which slows down (deactivates) the reaction.

- **Activated rings:** the substituents on the ring **donate** electrons and increase EAS reaction rates
  - Examples of electron donating groups in the relative order from the most activating group to the least activating:
    - NH<sub>2</sub>, -NR<sub>2</sub> > -OH, -OR > -NHCOR > -CH<sub>3</sub> and other alkyl groups with R as alkyl groups (C<sub>n</sub>H<sub>2n+1</sub>)



The electron donating group (D:) activates the ring with an additional resonance form or inductive donation effect to stabilize the + charge of the sigma complex.

The reaction energy diagram illustrating the substituent effect of electron donating groups (D:) on EAS reaction rates is shown below.

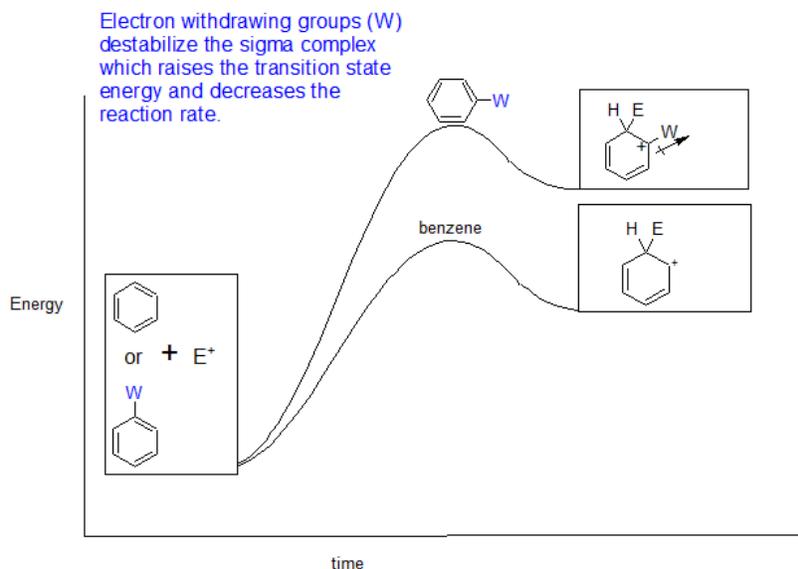


- **Deactivated rings:** the substituents on the ring **withdraw** electrons and decrease EAS reaction rates
  - Examples of electron withdrawing groups in the relative order from the most deactivating to the least deactivating:
    - NO<sub>2</sub>, -CF<sub>3</sub> > -COR, -CN, -CO<sub>2</sub>R, -SO<sub>3</sub>H > Halogens with R as alkyl groups (C<sub>n</sub>H<sub>2n+1</sub>)



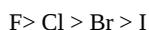
The electron withdrawing group (W) deactivates the ring by destabilizing the sigma complex. Note the proximity of the + and  $\delta^+$  charges.

The reaction energy diagram illustrating the substituent effect of electron withdrawing groups (W) on EAS reaction rate is shown below.



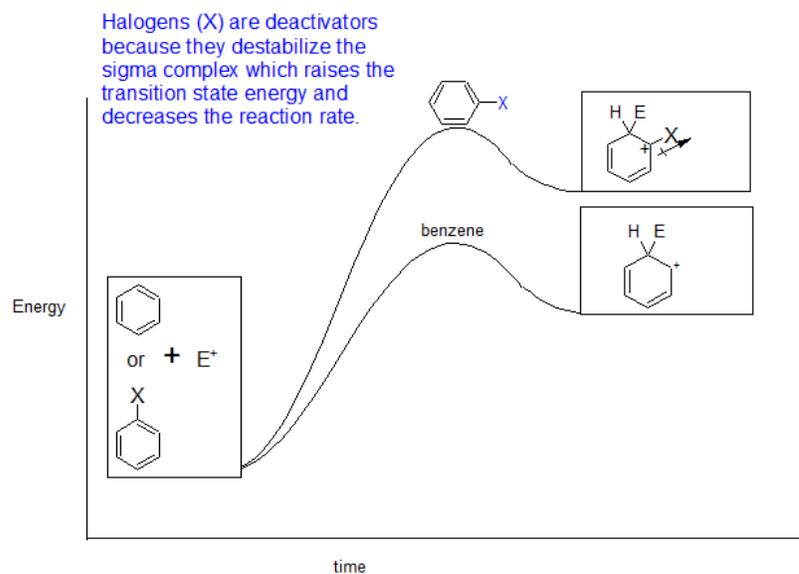
- **The Halogen Paradox: Deactivators that are ortho, para-directors**

Halogens deactivate rings to subsequent EAS reactions. The order of reactivity of the benzene rings toward the electrophilic substitution when it is substituted with a halogen groups, follows the order of electronegativity.

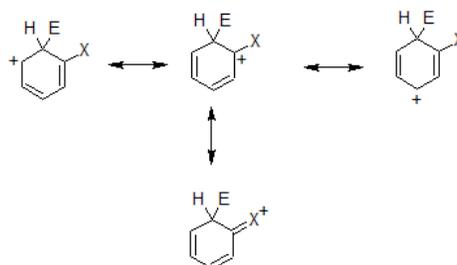


The ring that is substituted with the most electronegative halogen is the most reactive ring ( less deactivating substituent) and the ring that is substituted with the least electronegative halogen is the least reactive ring ( more deactivating substituent ). The size of the halogen also effects the reactivity of the benzene ring - as the size of the halogen increases, the reactivity of the ring decreases.

However, the lone pair electrons on the halogen atoms are still available for resonance delocalization in the sigma complex causing ortho-, para-direction of the electrophile. The reaction energy diagram below resolves these contradictory aspects of EAS reactions of halogenated benzene derivatives.



Halogens (X) are o-, p-directors because they create an additional resonance form in the sigma complex.



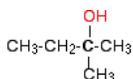
## REFERENCES

- Schore, N.E. and P.C. Vollhardt. 2007. *Organic Chemistry, structure and function*, 5th ed. New York, NY: W.H. Freeman and Company.
- Fryhle, C.B. and G. Solomons. 2008. *Organic Chemistry*, 9th ed. Danvers, MA: Wiley.

## OUTSIDE LINKS

- [http://en.Wikipedia.org/wiki/Activating\\_group](http://en.Wikipedia.org/wiki/Activating_group)
- [http://en.Wikipedia.org/wiki/Deactivating\\_group](http://en.Wikipedia.org/wiki/Deactivating_group)
- [http://www.columbia.edu/itc/chemistry/c3045/client\\_edit/ppt/PDF/12\\_12\\_14.pdf](http://www.columbia.edu/itc/chemistry/c3045/client_edit/ppt/PDF/12_12_14.pdf)

In a tertiary (3°) alcohol, the carbon atom holding the -OH group is attached directly to three alkyl groups, which may be any combination of same or different. Examples:

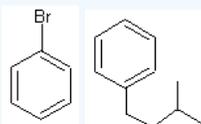


2-methylpropan-2-ol

2-methylbutan-2-ol

## Exercises

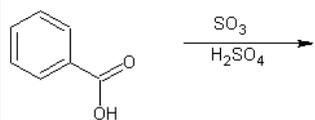
13. Predict the direction of the electrophile substitution on these rings:



14. Which nitration product is going to form faster?

nitration of aniline or nitration of nitrobenzene?

15. Predict the product of the following two sulfonation reactions:



A.

16. Classify these two groups as activating or deactivating groups:

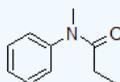
A. alcohol

B. ester

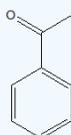
17. By which effect does trichloride effect a monosubstituted ring?

18. Trichloromethylbenzene has a strong concentration of electrons at the methyl substituent. Comparing this compound with toluene, which is more reactive toward electrophilic substitution?

19. The following compound is less reactive towards electrophilic substitution than aniline? Explain.



20. Consider the intermediates of the following molecule during an electrophilic substitution. Draw resonance structures for ortho, meta, and para reactions.

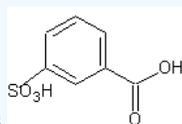


### Answer

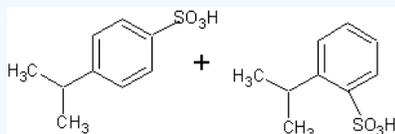
13. The first substitution is going to be ortho and/or para substitution since we have a halogen substituent. The second substitution is going to be ortho and/or para substitution also since we have an alkyl substituent.

14. The nitration of aniline is going to be faster than the nitration of nitrobenzene, since the aniline is a ring with  $\text{NH}_2$  substituent and nitrobenzene is a ring with  $\text{NO}_2$  substituent. As described above  $\text{NH}_2$  is an activating group which speeds up the reaction and  $\text{NO}_2$  is a deactivating group that slows down the reaction.

15.



A. the product is



B. the product is

16.

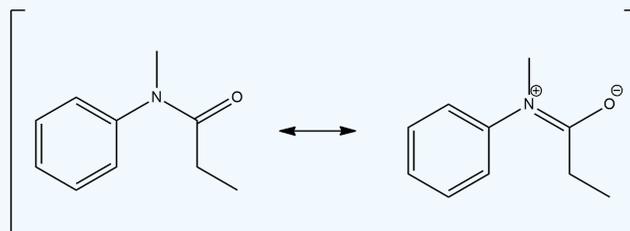
A. alcohol is an activating group.

B. ester is a deactivating group.

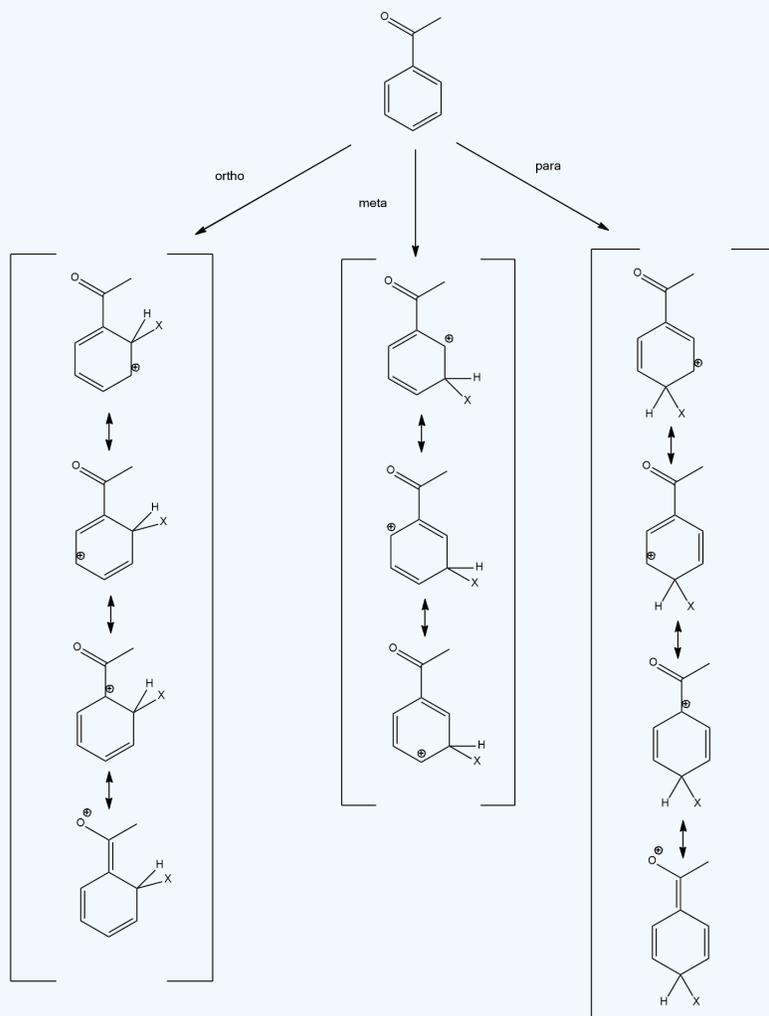
17. Trichloride deactivate a monosubstituted ring by inductive effect.

18. The trichloromethyl group is an electron donor into the benzene ring, therefore making it more stable and therefore more reactive compared to electrophilic substitution.

19. As seen in resonance the electron density is also localized off of the ring, thereby deactivating it compared to aniline.



20.



## 16.6 TRISUBSTITUTED BEN

### EXERCISES

#### QUESTIONS

##### Q16.5.1

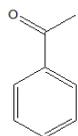
(Trichloromethyl)benzene has a strong concentration of electrons at the methyl substituent. Comparing this toluene, which is more reactive toward electrophilic substitution?

##### Q16.5.2

The following compound is less reactive towards electrophilic substitution than aniline? Explain.

##### Q16.5.3

Consider the intermediates of the following molecule during an electrophilic substitution. Draw resonance structures for ortho, meta, and para attacks.



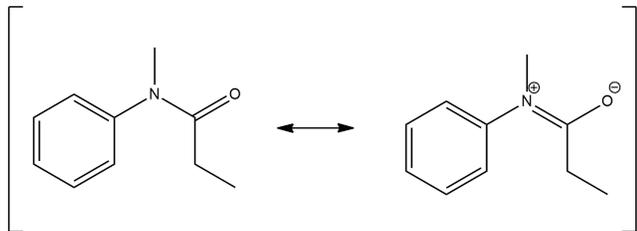
## SOLUTIONS

### S16.5.1

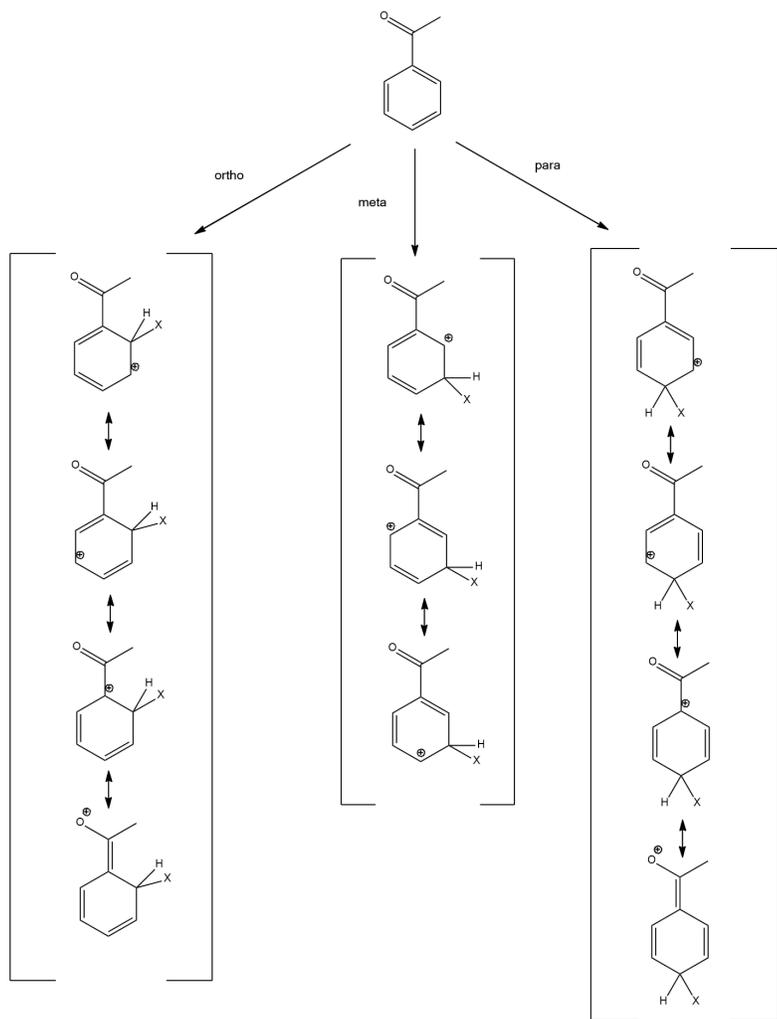
The trichloromethyl group is an electron donor into the benzene ring, therefore making it more stable and therefore more reactive compared to electrophilic substitution.

### S16.5.2

As seen in resonance the electron density is also localized off of the ring, thereby deactivating it compared to aniline.



### S16.5.3



## CONTRIBUTORS AND ATTRIBUTIONS

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- Lana Alawwad (UCD)

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