

## ORGANIC CHEMISTRY 2 LECTURE GUIDE 2019

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## Lesson IV.12. Substituent Effects on the Regiochemistry of EAS

*More stable intermediate = more product*

If there is already a substituent on a benzene ring and we then attempt to further substitute it, we need to consider what is the major product will be. If a monosubstituted arene is subjected to EAS, we can get *o*-, *m*-, and *p*- products:

A

In order to understand which product(s) are formed in highest yield, we must examine the mechanism, keeping in mind one of the ***generally applicable principles*** used in examining organic chemical transformations:

B

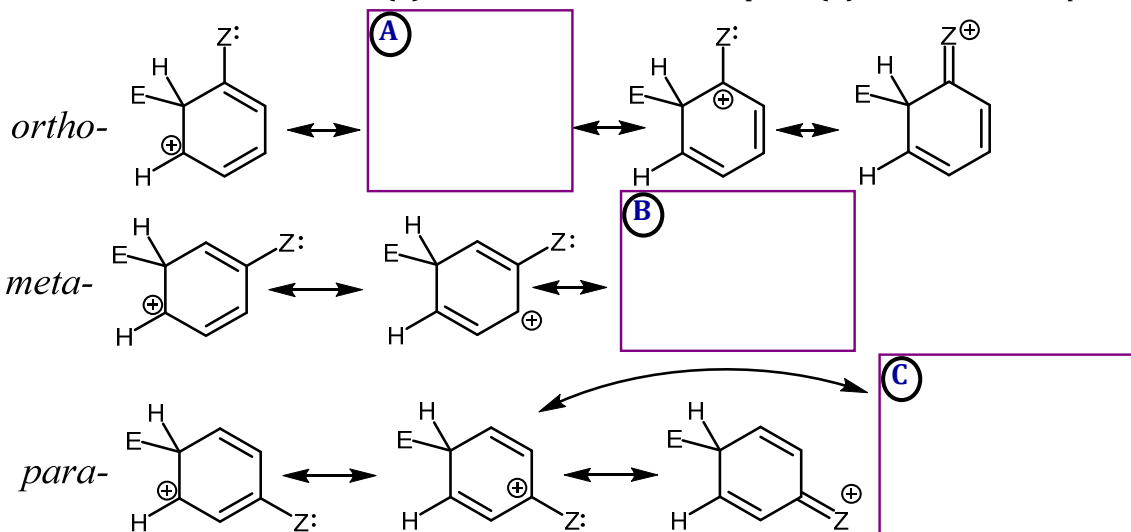
\*EAS = Electrophilic aromatic substitution

Notes

## Lesson IV.12. Substituent Effects on the Regiochemistry of EAS

### Directing ability for EAS

Consider a resonance donor (Z) substituent with electrophile (E) added *o*-, *m*- or *p*-:



Conclusion:

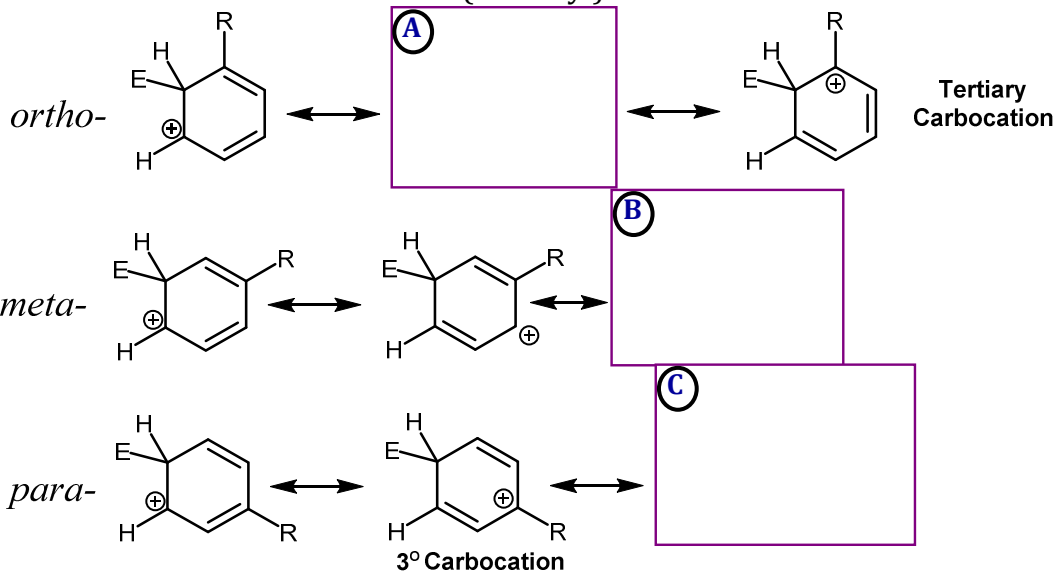
**D**

## Notes

## Lesson IV.12. Substituent Effects on the Regiochemistry of EAS

### Directing ability for EAS

Now consider an inductive donor (R = alkyl):



Conclusion:

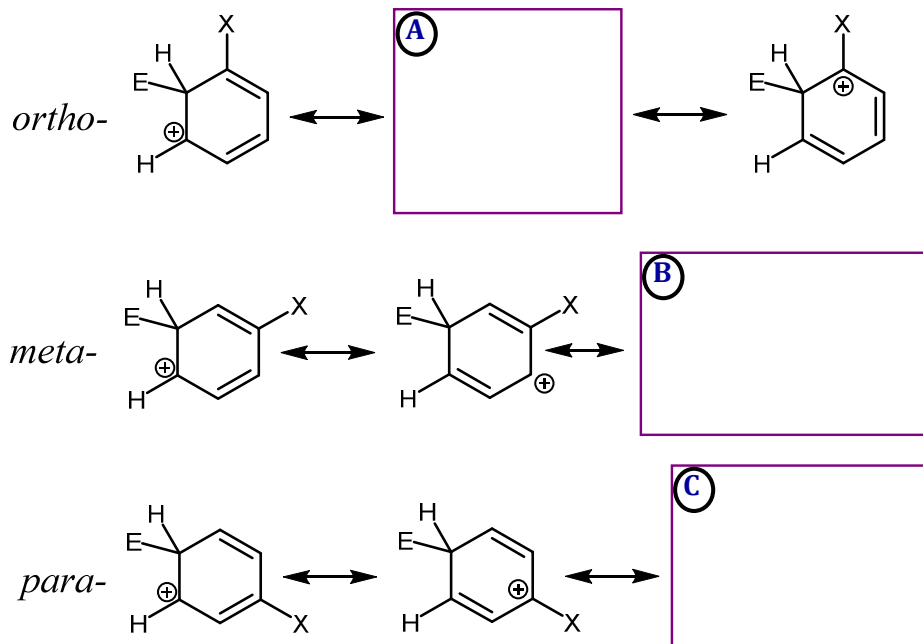
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## Notes

## Lesson IV.12. Substituent Effects on the Regiochemistry of EAS

### Directing ability for EAS

Next, a halogen (X = F, Cl, Br, I):

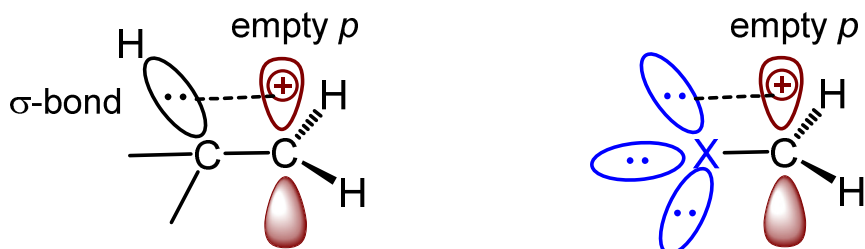


Notes

## Lesson IV.12. Substituent Effects on the Regiochemistry of EAS

### *Directing ability for EAS*

For halogens consider their interaction with an adjacent carbocation as compared to the hyperconjugation that stabilizes carbocations:



(A)

(B)

The figure above illustrates that a halogen is able to stabilize a positive charge on an adjacent C. With this knowledge and the resonance contributors on the previous page, we conclude:

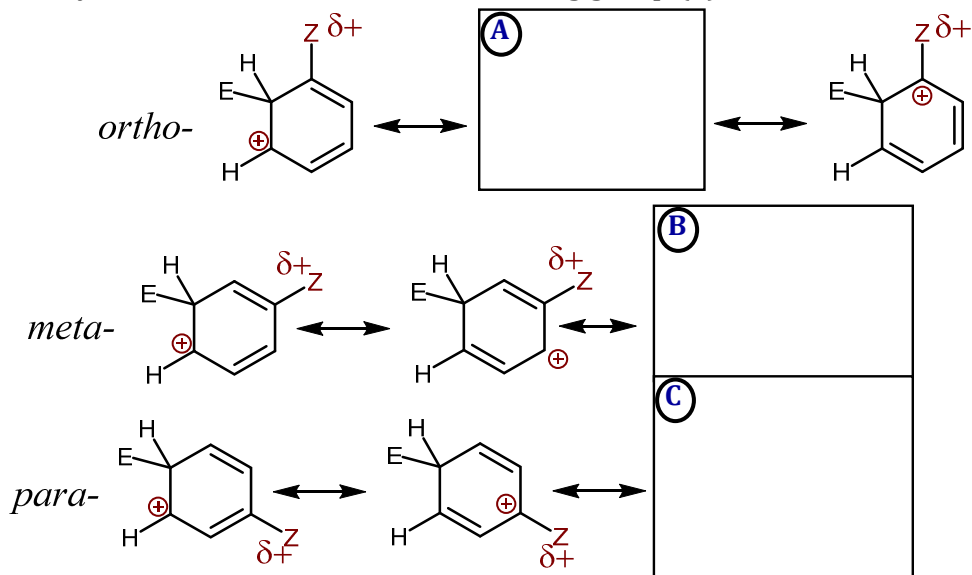
(C)

### Notes

## Lesson IV.12. Substituent Effects on the Regiochemistry of EAS

### Directing ability for EAS

Finally, consider an inductive withdrawing group (Z):



Conclusion:

**(D)**

## Notes

## Lesson IV.12. Substituent Effects on the Regiochemistry of EAS

### *Directing ability for EAS*

A general trend worth noting is that we can correlate a substituent's **EAS Reactivity Group** with its **EAS Directing Type**:

(A)

and

(B)

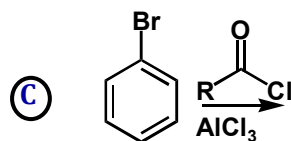
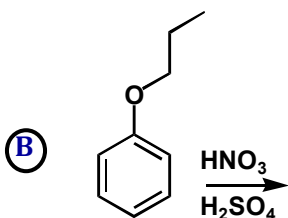
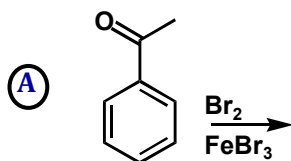
Remember that these are *general trends* to help us predict the **major** product; you typically will not get *exclusively* the favored product(s)

Notes



**Lesson IV.12. Substituent Effects on the Regiochemistry of EAS***Directing ability for EAS practice*

Example: Give the major product(s) of the following reactions using your knowledge of whether the existing substituent is *o*-/*p*- directing or *m*-directing.



Notes