ORGANIC CHEMISTRY 2 LECTURE GUIDE 2019

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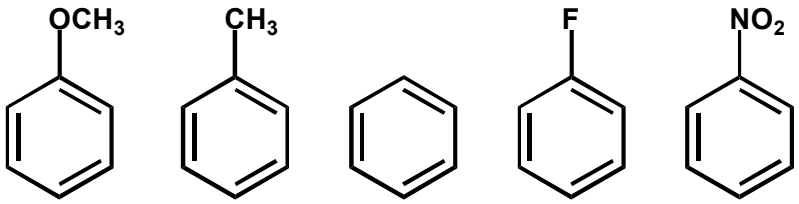
Lesson IV.11. Substituent Effects on the Rate of EAS

More stable intermediate = faster reaction



Most reactive ← **Susceptibility to electrophilic aromatic substitution** → **Least reactive**

We have a carbocation intermediate, so a more stable carbocation will lead to its more rapid formation.

If we put **electron donor groups** on the benzene ring, it is

(A) _____ than unsubstituted benzene.

If we put **electron withdrawing groups** on, the arene will be

(B) _____ than unsubstituted benzene.

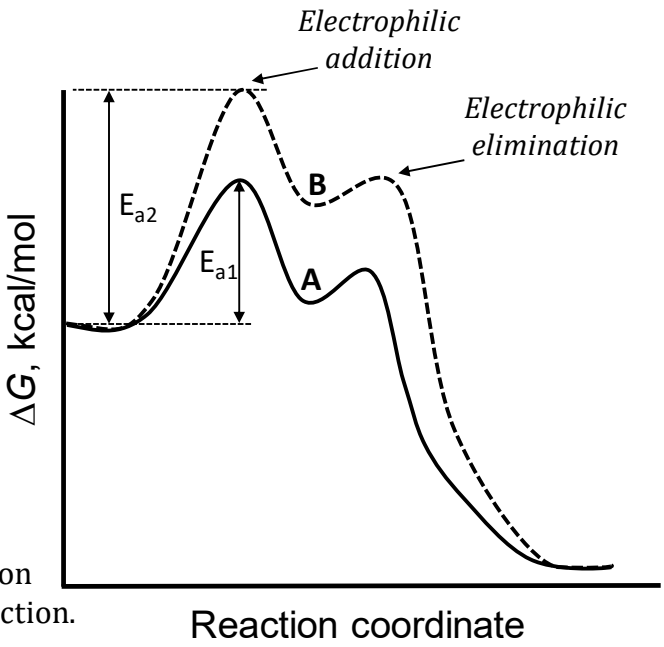
Notes

Lesson IV.11. Substituent Effects on the Rate of EAS

Reaction coordinate diagrams

The qualitative reaction coordinate diagram for two EAS reactions reminds us that:

A

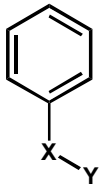


So anything that stabilizes the cation intermediate will speed up the reaction.

Notes

Lesson IV.11. Substituent Effects on the Rate of EAS

Classifying substituents



Here are some guiding principles for predicting relative activating/deactivating potential of substituents

If the element (X) **DIRECTLY** attached to the benzene ring has a **lone pair**,

A

Except **HALOGENS**:

B

2. If the substituent is a **HYDROCARBON** (i.e., alkyl, vinyl, or aryl group):

C

3. If an element (Y) **ADJACENT** to the directly attached atom is more **electronegative** than carbon or if X has a formal positive charge:

D

Notes

Lesson IV.11. Substituent Effects on the Rate of EAS

Activating and deactivating groups

So now we have seen the effect of substituents on the names **and** reactivity of aromatic compounds. Recall the trends we observed for substituents on benzene as to the reactivity of the ring in electrophilic aromatic substitution.
We can place substituents into **four general Groups**:

A
B
C
D

Notes

Lesson IV.11. Substituent Effects on the Rate of EAS

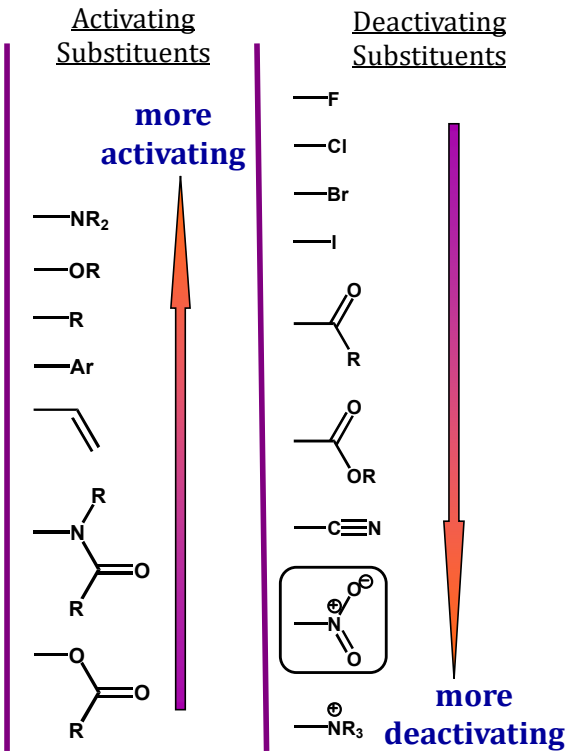
Ranking substituent activating ability for EAS

What affects the ability of an element to donate electrons to carbon?

Size – if the element is not in the same row as carbon, it is too big to effectively overlap the pi system.

Electronegativity – because fluorine is so electronegative, it does not donate electrons to the pi system enough to activate the molecule, even though it is the same size.

Combining the rules with these 2 guiding principles, we can group many substituents as activating or deactivating (relative to benzene) for cation formation.

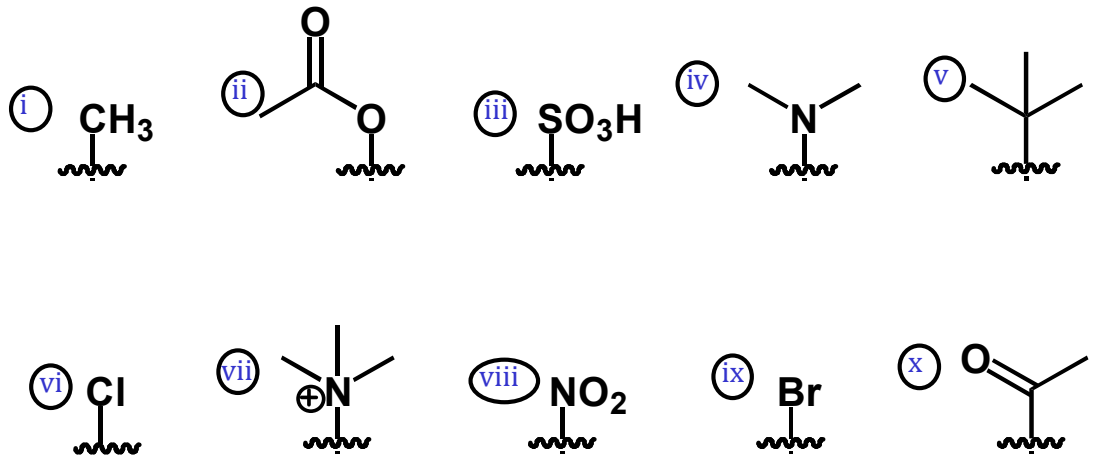


Notes

Lesson IV.11. Substituent Effects on the Rate of EAS

Ranking substituent activating ability for EAS

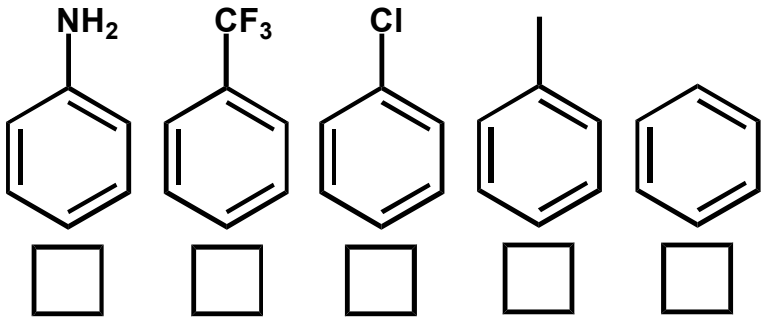
Classify each of the given substituents as being Slightly Activating (SA), Activating (A), Slightly Deactivating (SD), or Deactivating (D), relative to H (plain benzene), with respect to reactivity in Electrophilic aromatic substitution.



Notes

Lesson IV.11. Substituent Effects on the Rate of EAS
Ranking substituent activating ability for EAS

Rank these arenes from 1-5 in terms of their reactivity towards electrophilic aromatic substitution, 1 being most reactive and 5 being least reactive. Explain your selections.



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