How aromatics React (19.2)

Generally are unreactive:

\[ \text{C}_6\text{H}_5\text{Br} + \text{Br}_2 \rightarrow \text{NR} \]
\[ \text{C}_6\text{H}_5\text{Br} + \text{H-Br} \rightarrow \text{NR} \]

High energy/Reactive:

Need 'Hot' electrophile \( E^+ \)

Remind: How alkenes react \( \beta \)

\[ \text{C} = \text{C} + \text{Br}_2 \rightarrow \text{C} - \text{C} \]
\[ \text{C} = \text{C} + \text{H-Br} \rightarrow \text{C} - \text{C} - \text{Br} \]

Electrophilic Aromatic Substitution

Specific Reactions:

Catalyst needed \( \rightarrow \text{FeBr}_3 \) or \( \text{AlBr}_3 \)

1st step:

\[ \text{Br} - \text{Br} \]
\[ \text{Lewis acid} \]
\[ \text{Fe-Br} \]
\[ \text{Br-Br} \]
\[ \text{Fe-Br} \]

2nd step:

\[ \text{H-Br} \]

or \( \text{H-Br} \)

\[ \text{BH} \]
Halogenation

\[ \text{C}_2H_5 + \text{Cl}_2 \rightarrow \text{C}_2H_5 \text{Cl} \]

Nitration

\[ \text{C}_6H_5 + \text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_4\text{NO}_2 \]

Friedel-Crafts Acylation

\[ \text{C}_2H_5 + \text{R} - \text{Cl} + \text{Fe} \rightarrow \text{C}_2H_5 \text{R} \]

Friedel-Crafts Alkylation

\[ \text{C}_2H_5 + \text{R} - \text{Cl} + \text{AlCl}_3 \rightarrow \text{C}_2H_5 \text{R} \]
Electrophilic Aromatic Substitution  Chap 19.

What is the effect of the substituent on the rate and product distribution (Sec 19.14)

For benzene, look at the 'cation' produced

\[ \text{C}_6\text{H}_5^- + \text{Br}_2 \rightarrow \begin{cases} \text{C}_6\text{H}_5\text{Br}^- & \text{ortho} \\ \text{C}_6\text{H}_5\text{Br}^- & \text{meta} \\ \text{C}_6\text{H}_5\text{Br}^- & \text{para} \end{cases} \]

all are 2° carbocations

What we need to ask is due the substituent (Z) stabilize or destabilize the carbocation intermediate

- If stabilize, reaction will be faster
- If destabilize, reaction will be slower

To stabilize a carbocation, Z must: produce a better cation (3°)

To destabilize Z must: Puts a " or S+ near a + Charge

Need to ask how will the substituent (Z) effect the orientation of the electrophile E° and 0, 1, m, n to Z

Need to know where the " will show up once E° attaches

Conclusion:
- " shows up ortho & para to E°
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If \( \text{Z} \) is actuating, you want \( E^+ \) to land on the ortho, meta, or para?

\[ \text{Z} + E^+ \xrightarrow{\sigma} \text{Z} \text{ stabilized} \]

If lands ortho:

\[ Z \text{ can't help} \]

E will avoid meta

No muta product

Activating groups direct the electrophile to the ortho's para

Major products

If \( \text{Z} \) is deactivating, you want \( E \) to go

\[ Z \text{ as a deactivating} \]

destabilizes a charge

If deactivating, no \( \theta \) next to it

Poly cyclic aromatics

Actuating

To which carbons will the \( \text{OCH}_3 \) substituent direct the electrophile?

No proton

\( \text{Hot spot} \)

E yes?

E on.

(No other substituents mentioned in the image)