

Electrophilic Aromatic Substitution

January 29, 2020

- Electrophilic aromatic substitution.
 - Halogenation
 - Nitration
 - Sulfonation.
 - Friedel-Crafts Alkylation.
 - Friedel-Crafts Acylation & subsequent reduction.

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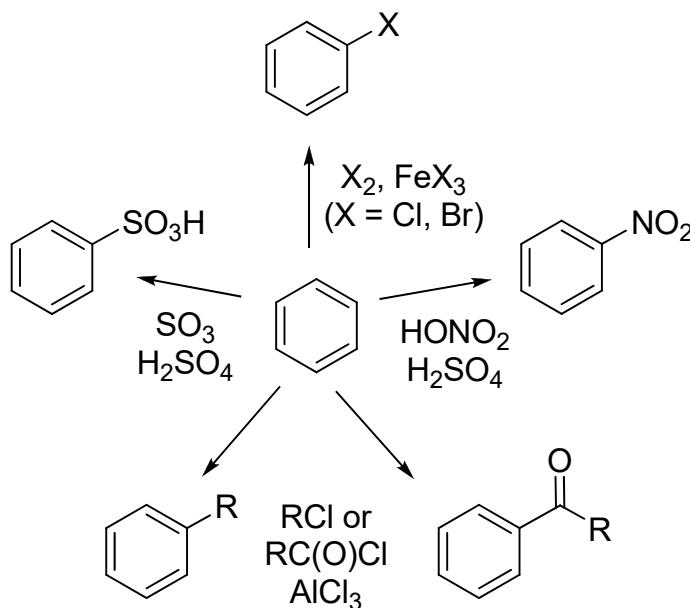
Chemistry Seminar! Prof. Arsalan Mirjafari, Florida Gulf Coast University, "(Dis)solving the World's Problems." Tuesday, January 28, 11:00 AM, Seaver North Auditorium.

O'Leary office hours: T/Th 9:00-10:00 am, SN 208.

O'Leary's evening review session: Wednesdays 7:00 PM, SN Aud. **Course website:** <http://pages.pomona.edu/~djo04747/110/>

Suggested Problems for Exam 1. 10e/11e/Chapter 14: 18, 24, 26, 27, 28, 31, 33, 35. 10e/Chapter 15: 24, 25, 27, 28, 34abc, 43, 51. 11e/Chapter 15: 22, 23, 25, 26, 32abc, 41, 49.

Electrophilic Aromatic Substitution



EAS Free-Energy Diagram

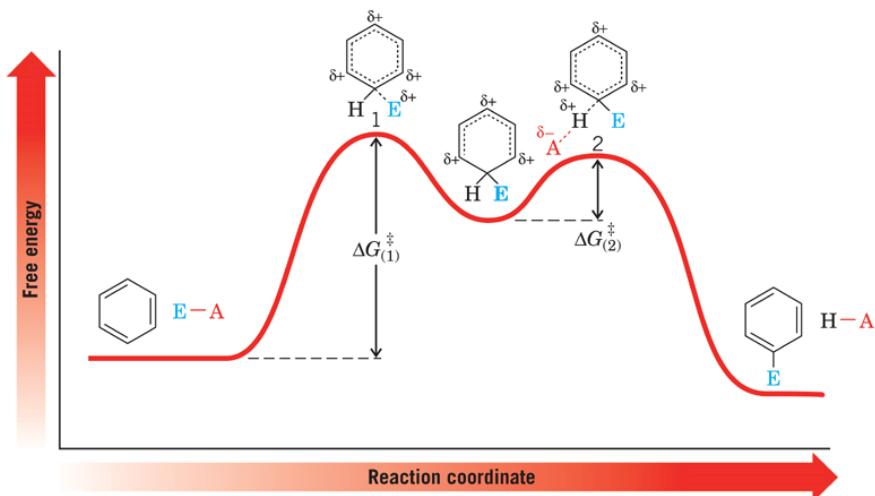
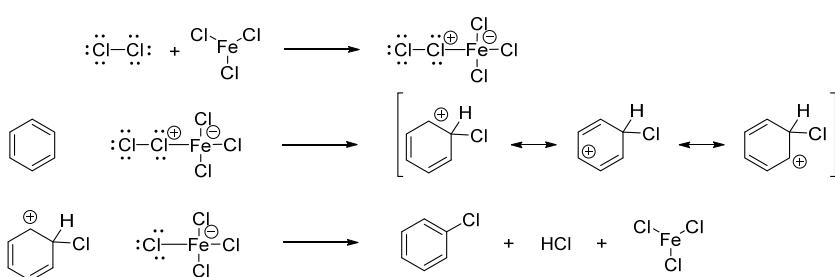
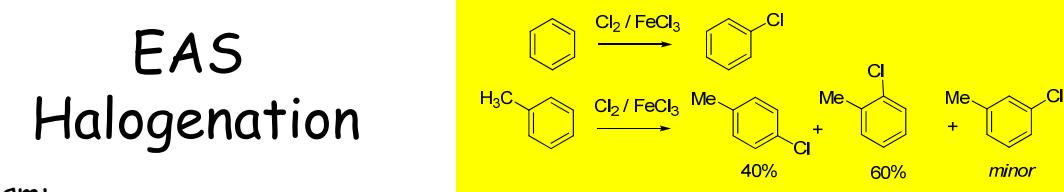


FIGURE 15.3 The free-energy diagram for an electrophilic aromatic substitution reaction. The arenium ion is a true intermediate lying between transition states 1 and 2. In transition state 1 the bond between the electrophile and one carbon atom of the benzene ring is only partially formed. In transition state 2 the bond between the same benzene carbon atom and its hydrogen atom is partially broken. The bond between the hydrogen atom and the conjugate base is partially formed.

EAS

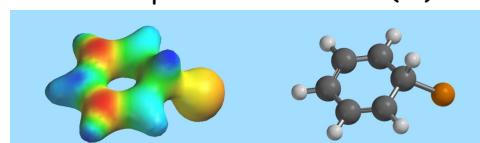
Halogenation

Mechanism:



Bromination, use $\text{Br}_2/\text{FeBr}_3$
(mechanism identical as above)

eps for arenium ion (Cl)



Iodination, use I_2/HNO_3
(forms I^+ by oxidation of I_2)

EAS Nitration

Mechanism:

The mechanism starts with the reaction of sulfuric acid ($\text{HO-SO}_2\text{O-H}$) and nitric acid ($\text{H-O-N}^+ \text{O}_2^-$). It shows the formation of a protonated nitronium ion ($\text{H-O-N}^+ \text{O}_2^-$), loss of water to form nitronium ($\text{O}=\text{N}^+$), and the formation of an arenium ion intermediate (C_6H_5^+) via resonance with the benzene ring. This intermediate then reacts with water (H_2O) to produce nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) and a hydronium ion (H_3O^+).

Yield: ~100%

3D Models: A ball-and-stick model and a space-filling model of nitrobenzene are shown.

EAS Sulfonation

Sulfonation: Benzene reacts with SO_3 and H_2SO_4 to form benzenesulfonic acid ($\text{C}_6\text{H}_5\text{SO}_3\text{H}$). Phenol ($\text{C}_6\text{H}_5\text{OH}$) reacts with SO_3 and H_2SO_4 to form two products: 4-hydroxybenzenesulfonic acid (75% yield) and 2-hydroxybenzenesulfonic acid (25% yield).

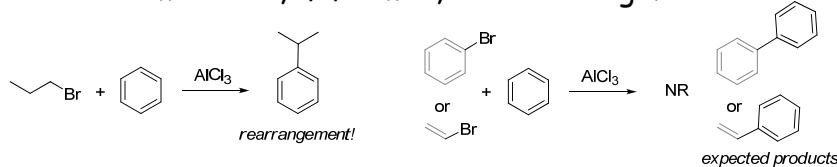
Desulfonation: Benzenesulfonic acid ($\text{C}_6\text{H}_5\text{SO}_3\text{H}$) is treated with dilute H^+ and H_2O /steam to yield benzene (C_6H_6).

Mechanism:

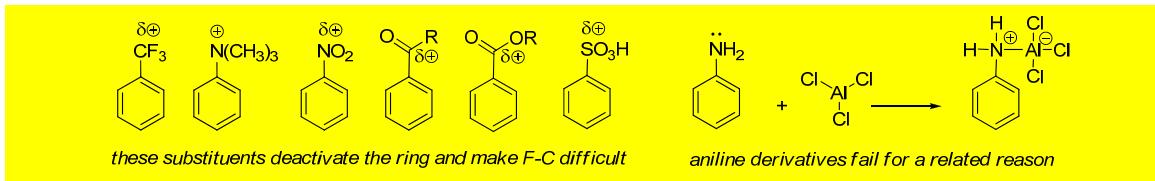
The mechanism starts with the reaction of two molecules of sulfuric acid ($\text{HO-SO}_2\text{O-H}$) to form a dimer ($\text{O=S-O-SO}_2\text{O=O}$), a hydronium ion (H_3O^+), and water (H_2O). This dimer then reacts with benzene (C_6H_6) to form a resonance-stabilized arenium ion intermediate (C_6H_5^+), which is bonded to a sulfonate group (SO_3^-). This intermediate then reacts with water (H_2O) to produce benzenesulfonic acid ($\text{C}_6\text{H}_5\text{SO}_3\text{H}$) and a hydronium ion (H_3O^+).

Friedel-Crafts: Limitations

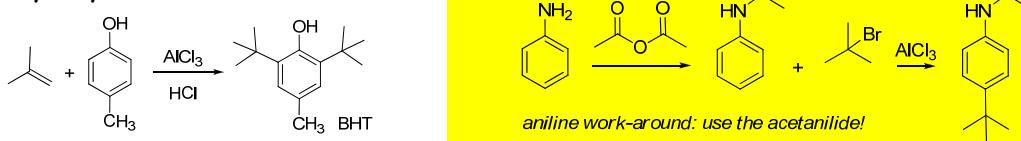
1. Carbocation intermediates, if formed, can rearrange.



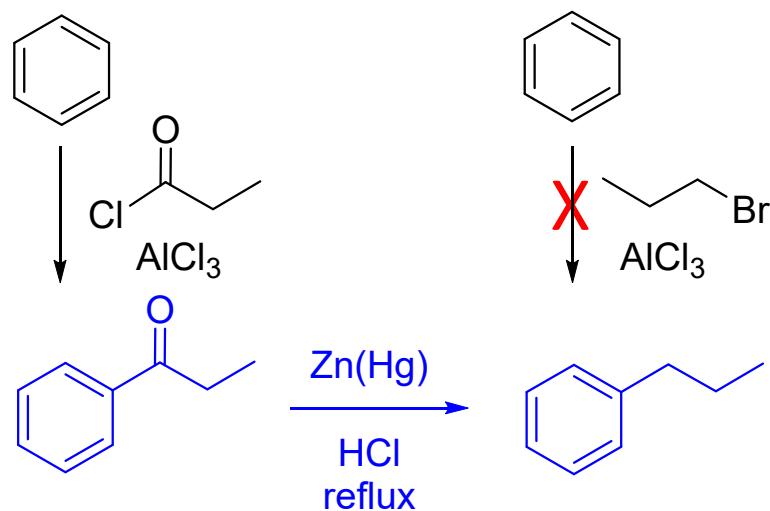
2. Electron-withdrawing groups (EWG) shut down F-C reactions.



3. Polyalkylations often occur.



Clemmensen Reduction: A Typical Application



• Mechanism of the C-R falls beyond the scope of this course.