

Electrophilic Aromatic Substitution

January 29, 2020

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

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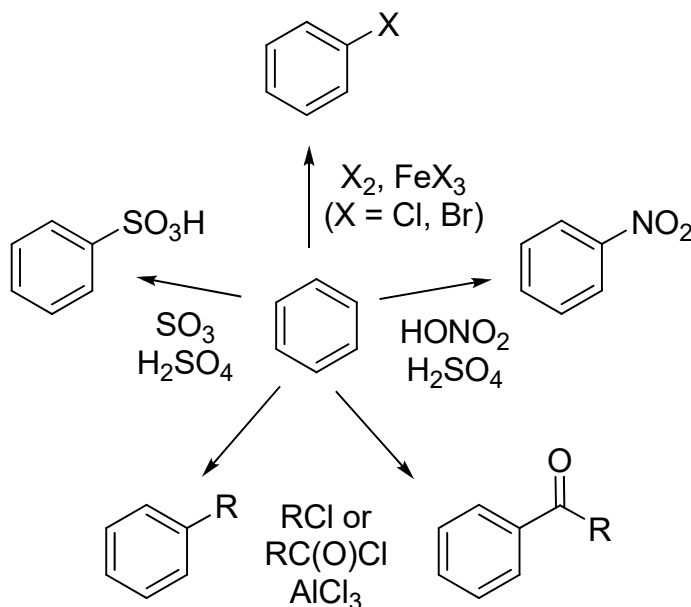
Chemistry Seminar! Prof. Arsalan Mirjafari, Florida Gulf Coast University, "(Dis)solving the World's Problems." Tuesday, January 28, 11:00 AM, Seaver North Auditorium.

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

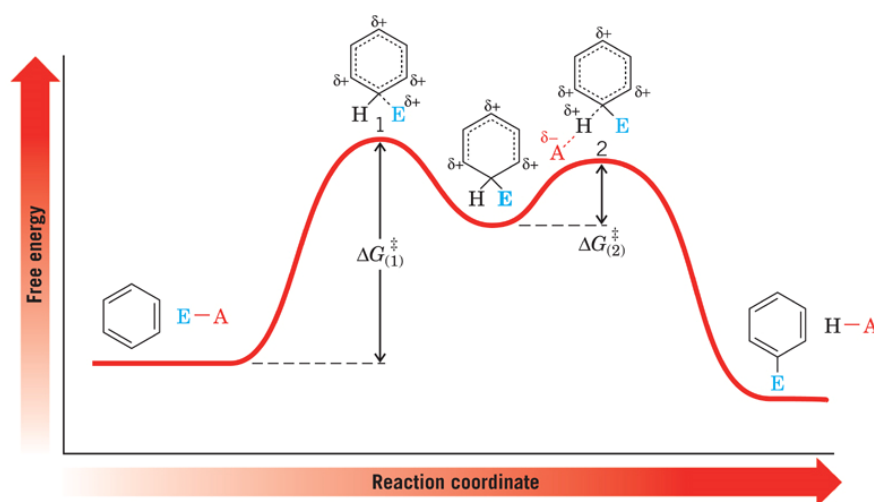
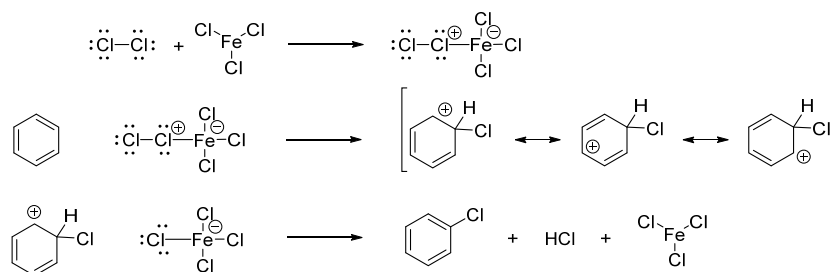


FIGURE 15.3 The free-energy diagram for an electrophilic aromatic substitution reaction. The arenium ion is a true intermediate lying between transition states 1 and 2. In transition state 1 the bond between the electrophile and one carbon atom of the benzene ring is only partially formed. In transition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

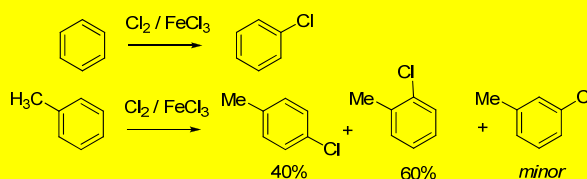
EAS Halogenation

Mechanism:

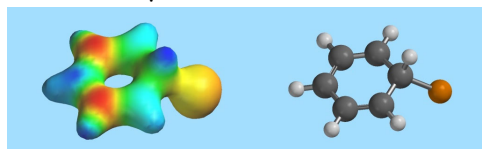


Bromination, use $\text{Br}_2/\text{FeBr}_3$
(mechanism identical as above)

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

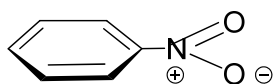
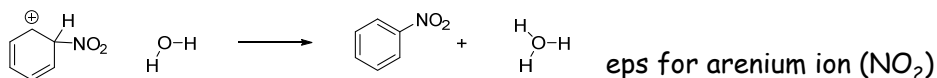
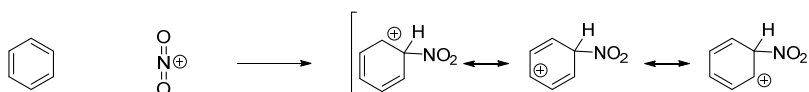
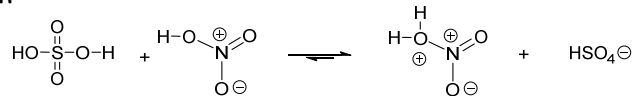


eps for arenium ion (Cl)

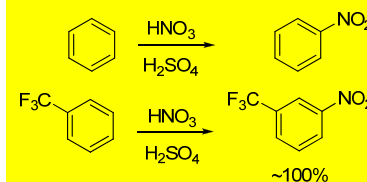


EAS Nitration

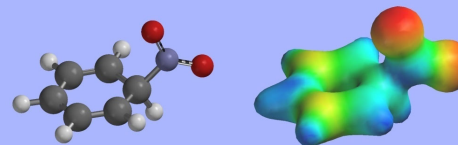
Mechanism:



nitrobenzene

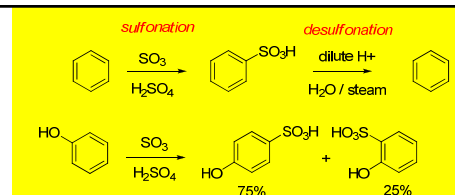
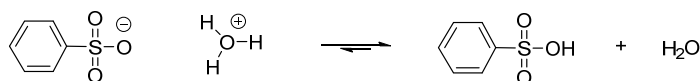
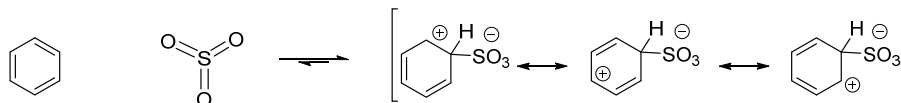
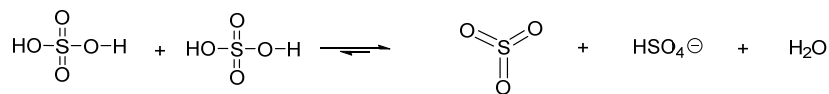


eps for arenium ion (NO₂)



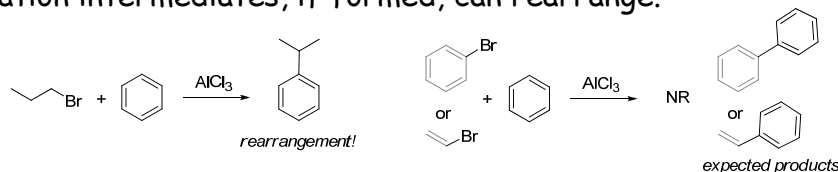
EAS Sulfonation

Mechanism:

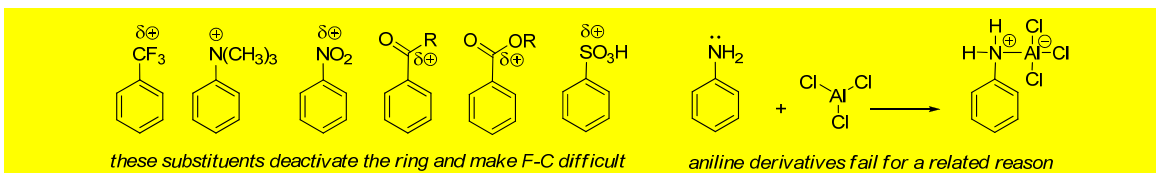


Friedel-Crafts: Limitations

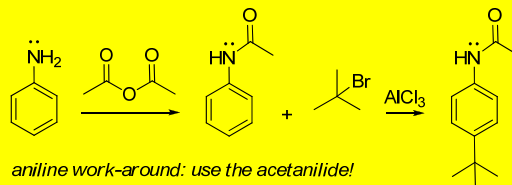
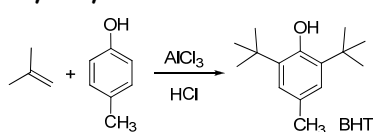
1. Carbocation intermediates, if formed, can rearrange.



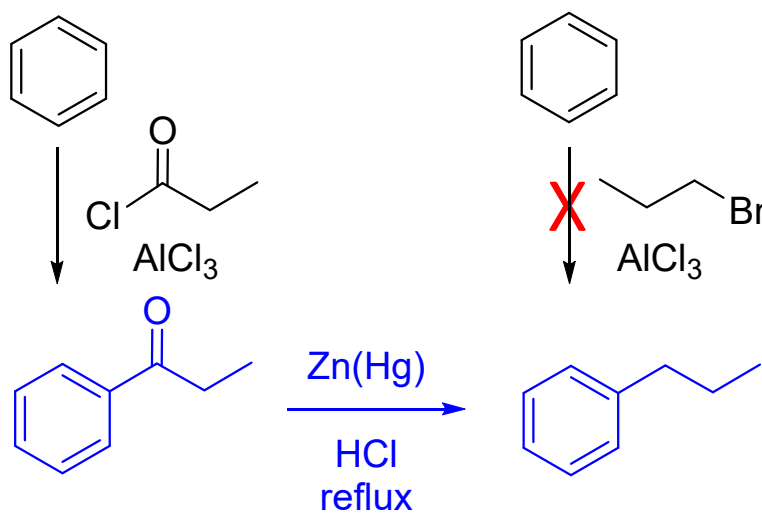
2. Electron-withdrawing groups (EWG) shut down F-C reactions.



3. Polyalkylations often occur.



Clemmenson Reduction: A Typical Application



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