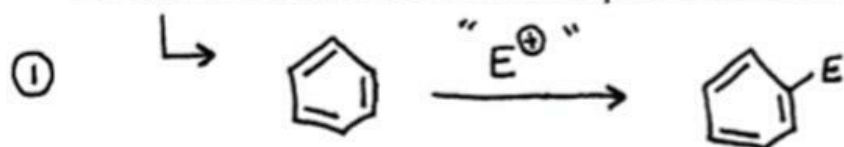
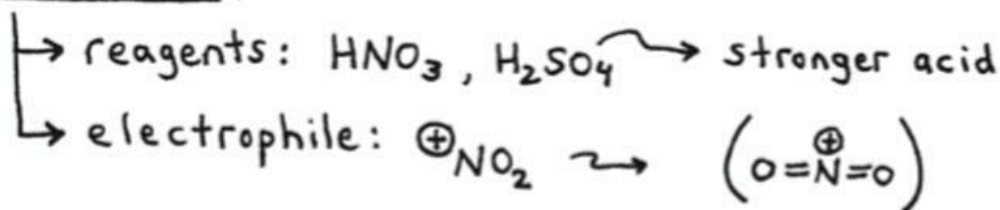


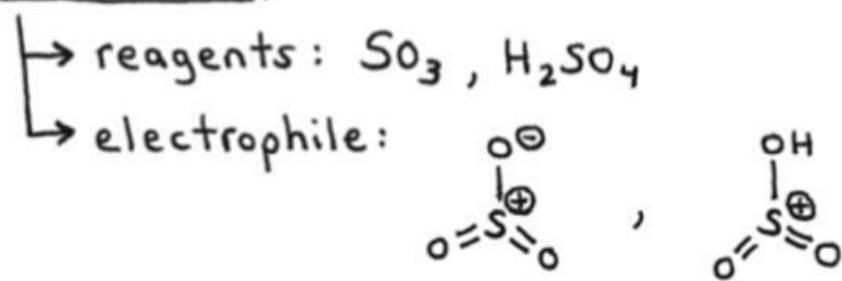
* Overview of Electrophilic Aromatic Substitutions. 15-2



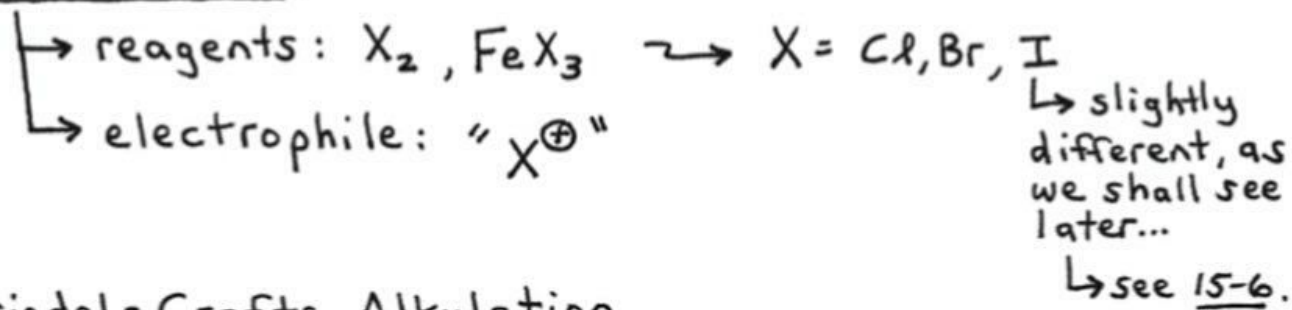
① Nitration.



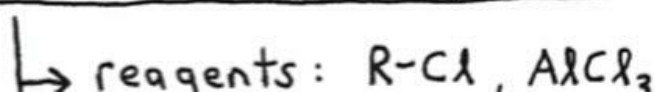
② Sulfonation.



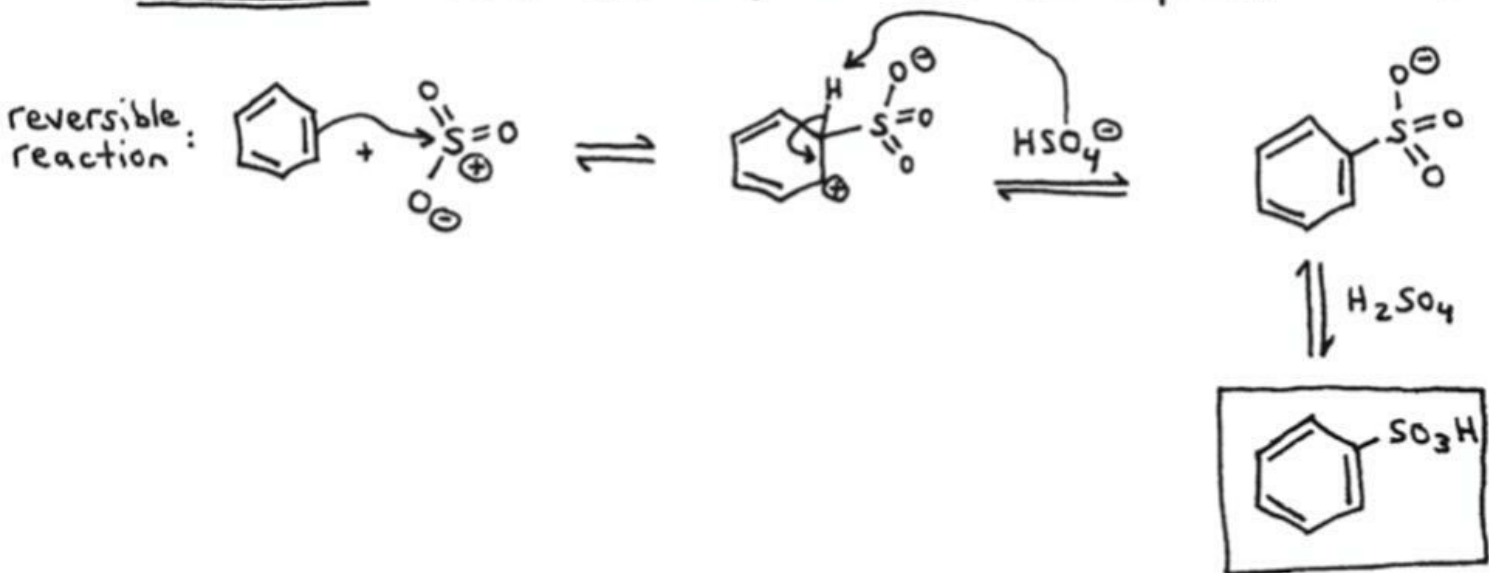
③ Halogenation.



④ Friedel-Crafts Alkylation.



mechanism: we'll use SO_3 as the electrophile. 15-4



* notes:

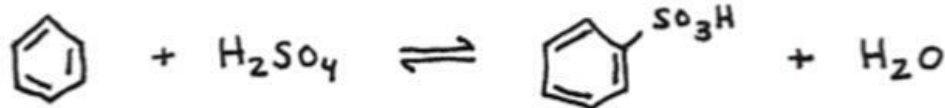
- reaction works with H_2SO_4 because:



- reaction is faster with a solution of " SO_3 in H_2SO_4 " "fuming sulfuric acid".

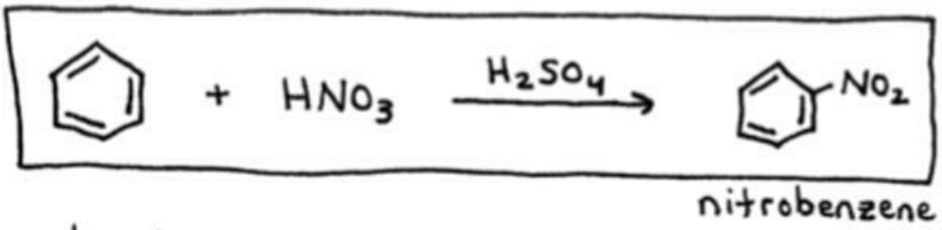
- net reaction (with H_2SO_4) prefers product with excess H_2SO_4

Le Châtelier's Principle

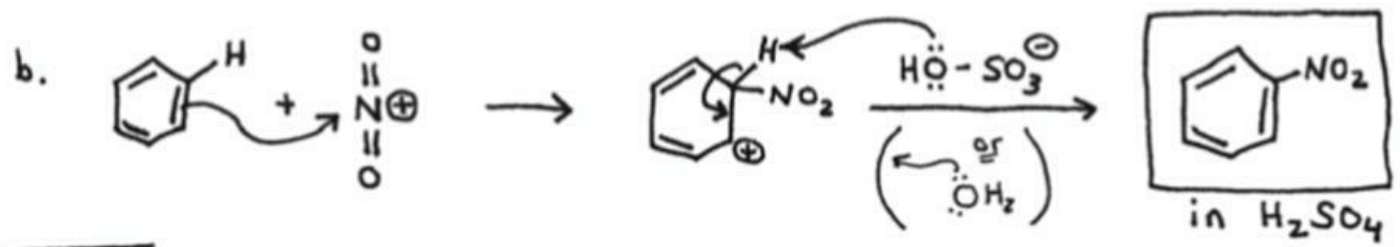
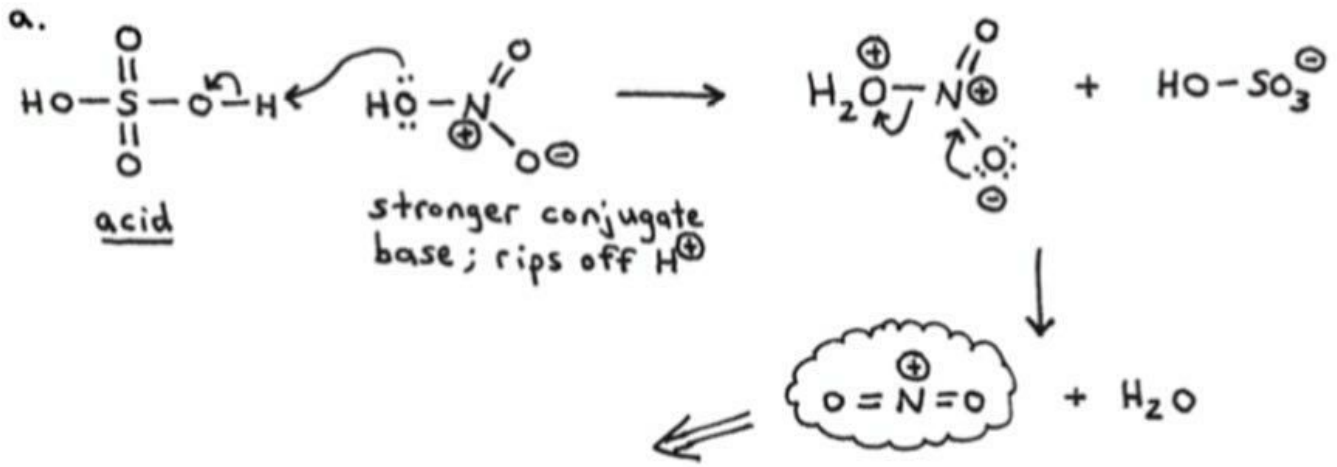


- now let's look at E.A.S. reactions ①-⑤ in detail...

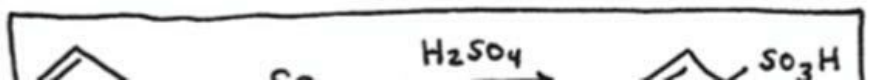
① Nitration.



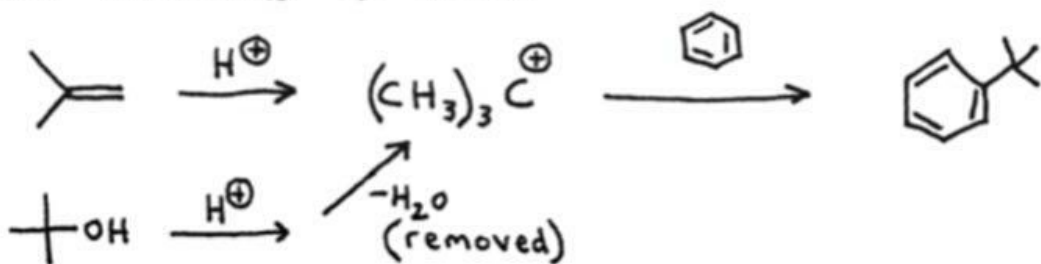
mechanism:



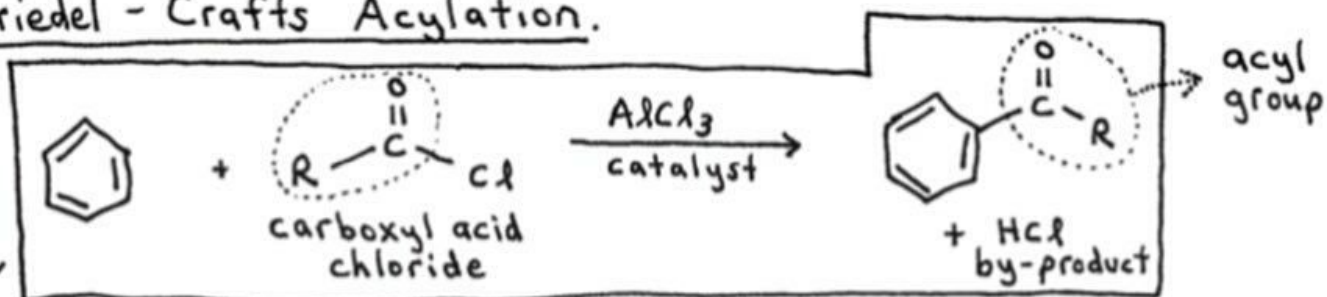
② Sulfonation.



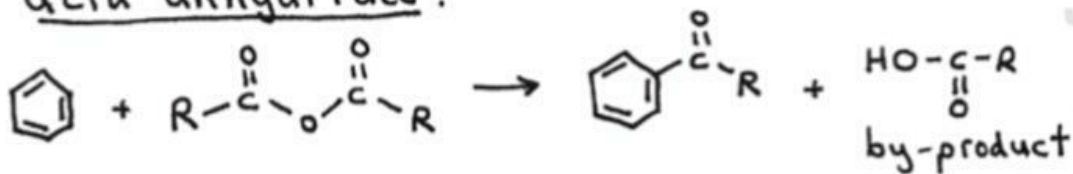
* 2° and 3° carbocations can be generated by other methods as well:



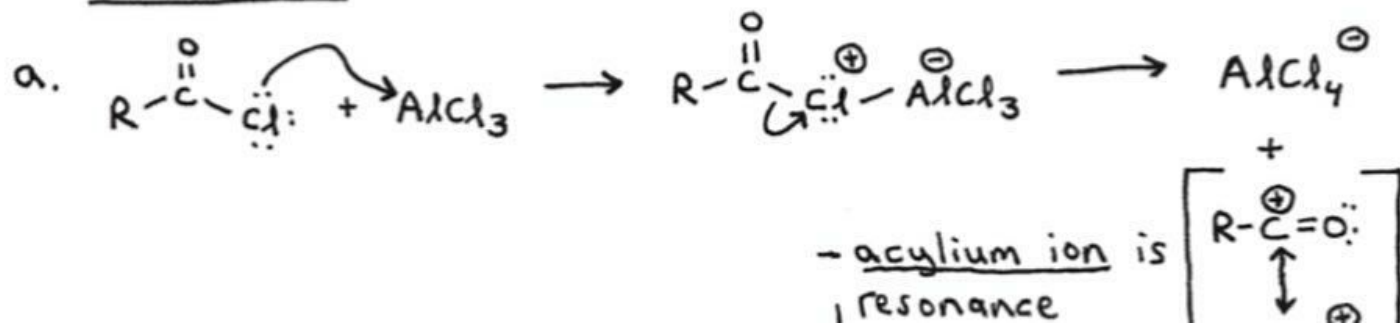
⑤ Friedel - Crafts Acylation.



* note: as a side point, it should be noted that the reaction also works with acid anhydrides.



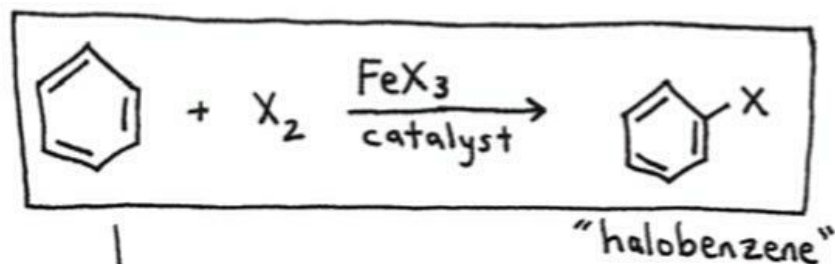
mechanism:



③ Halogenation of Aromatic Rings.

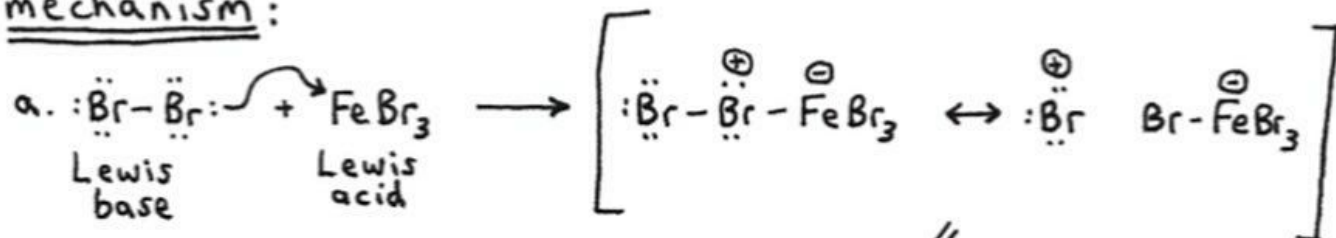
↳ replacing -H with -X ; X = Cl, Br, I

↳ slightly different process.



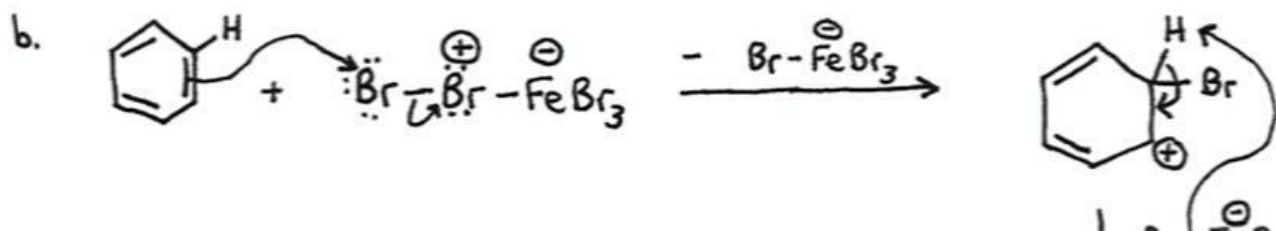
↳ the Lewis acid, FeX₃, makes X more electrophilic by polarizing X₂

mechanism:



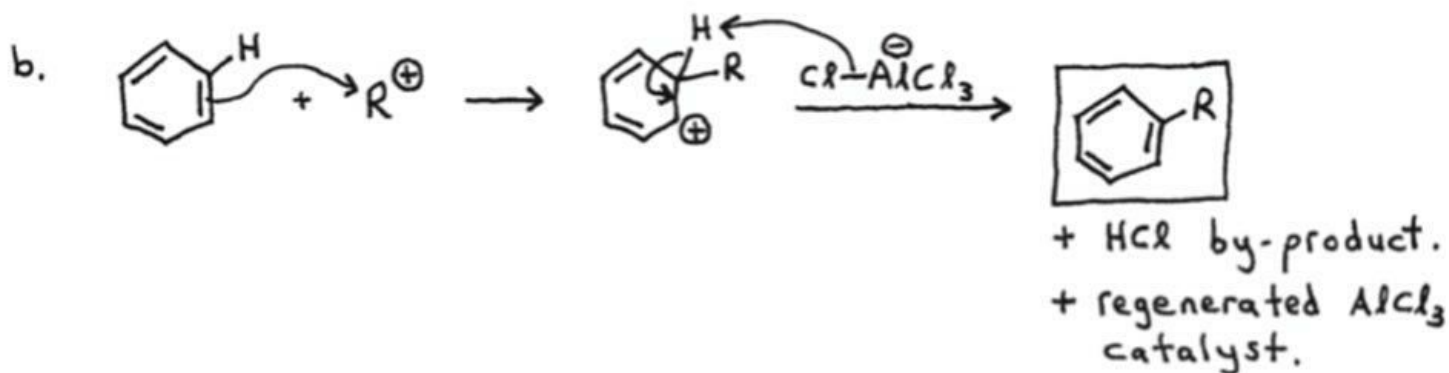
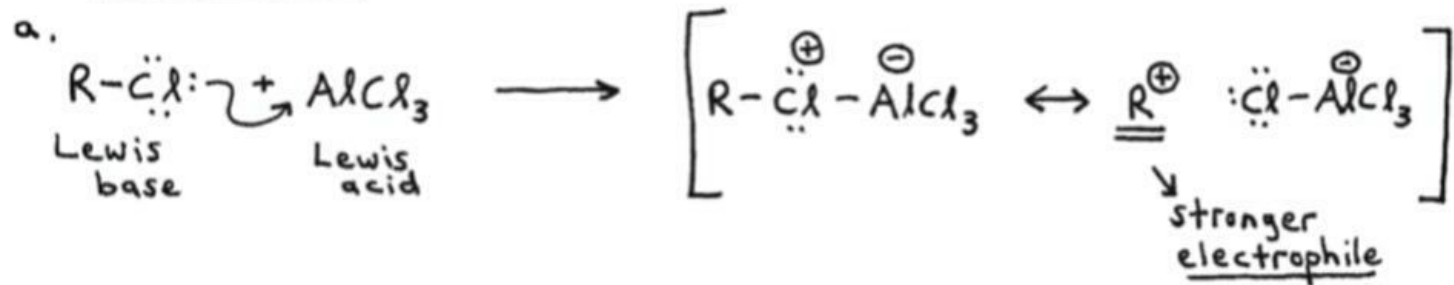
actual: $\delta^+ \quad \delta^+ \quad \ominus$
 $\text{Br} \cdots \text{Br} - \text{FeBr}_3$

↳ this one reacts as the electrophile.



mechanism:

15-7



* notes:

↳ "R" may be 3°, 2°, 1°, or methyl.

↳ rearrangement may occur, and usually does.

- ↳ proof that free carbocations are involved.
- ↳ still unclear whether free 1° and methyl carbocations are involved

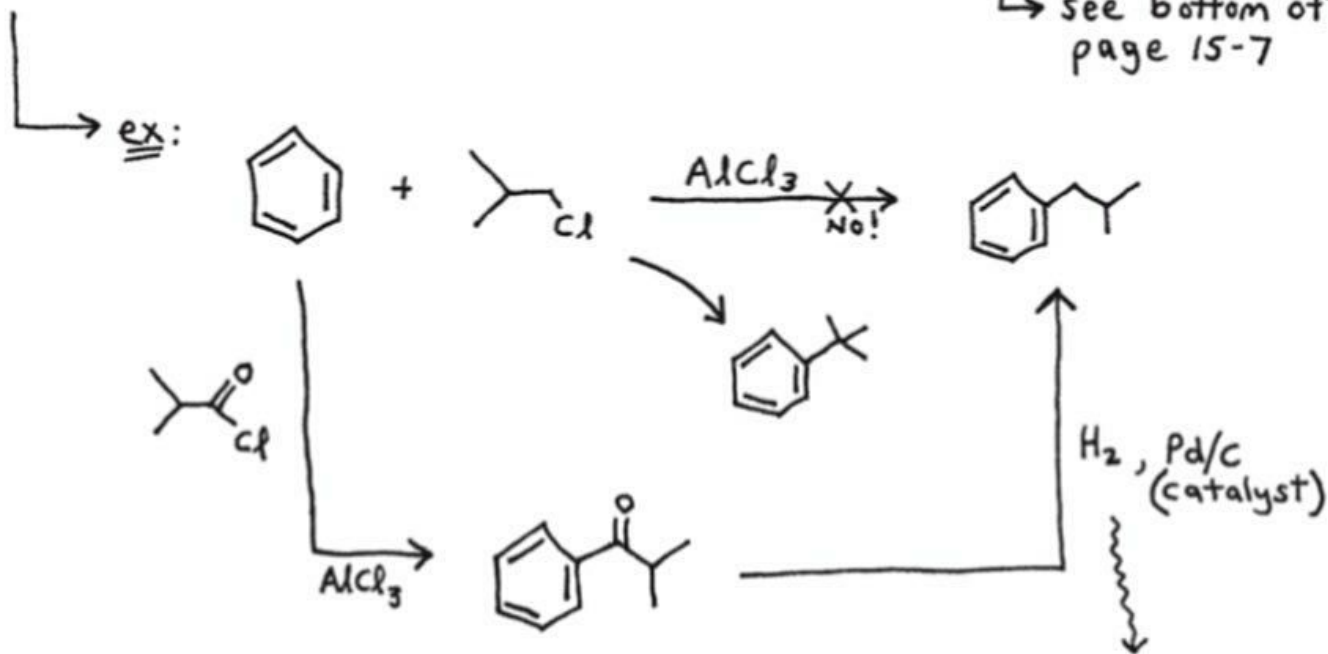
😊 don't worry about this ← (may not be "free":)

$$\text{R}-\underset{\delta^{\oplus}}{\text{CH}_2} \cdots \cdots \underset{\delta^{\oplus}}{\text{C}}\text{l}-\overset{\ominus}{\text{Al}}\text{Cl}_3$$

↙ "method" if ...

- * Friedel-Crafts Acylation is a good way to
- * introduce groups that would rearrange with
- * Friedel-Crafts Alkylation (i.e. isobutylbenzene).

↳ see bottom of page 15-7

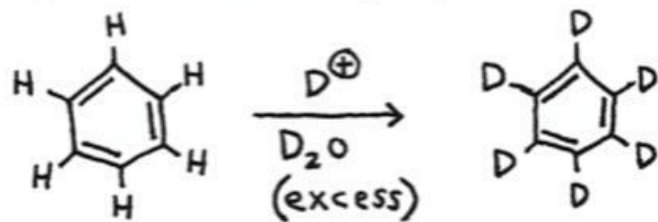


more common, but not until later in the course:

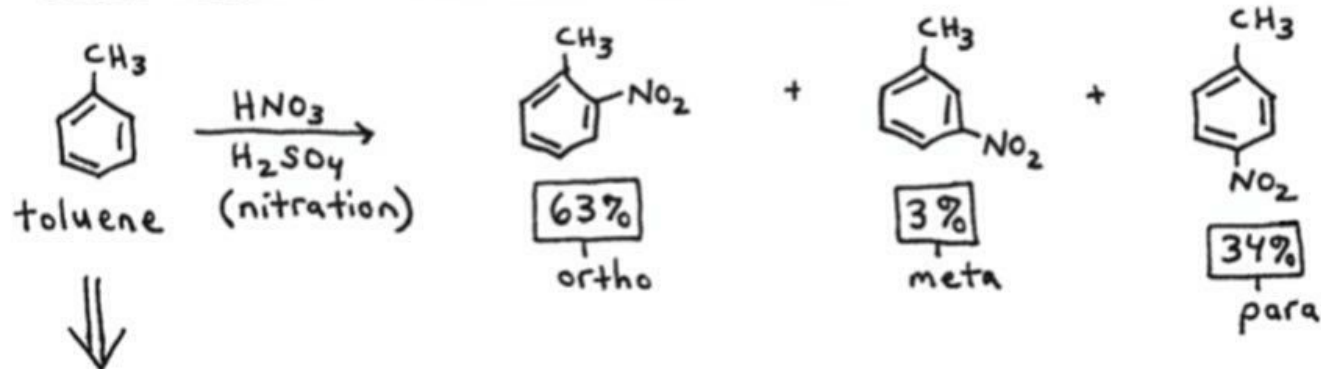
or: $\text{Zn}(\text{Hg}), \text{HCl}$

or: $\text{H}_2\text{NNH}_2, \text{OH}^\ominus, \Delta$

⑥ Use of H^\oplus (D^\oplus) as the electrophile.



* Directing Effects of Substituents.



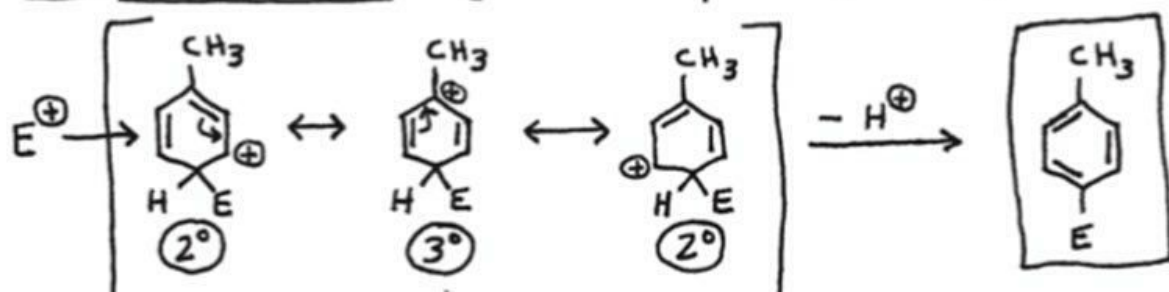
* CH_3 is an ortho, para director - it directs incoming electrophiles to o- and p- slots.

→ meta won't give a 3° carbocation like ortho and para will.

* nitration of toluene () is ~ 23 times faster than nitration of benzene (). So the " $-\text{CH}_3$ " substituent is an activator.

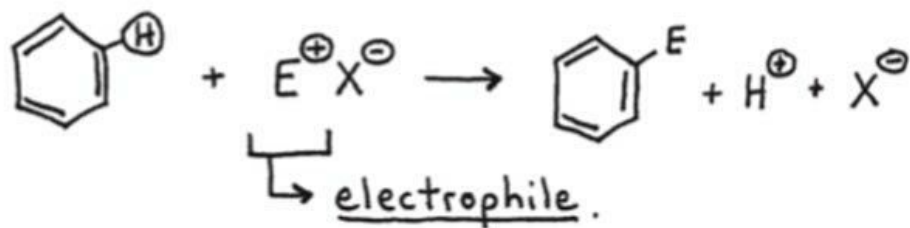
* mechanism of the above reaction: 3 mechanisms...

A. Para attack by electrophile (" E^\oplus ")



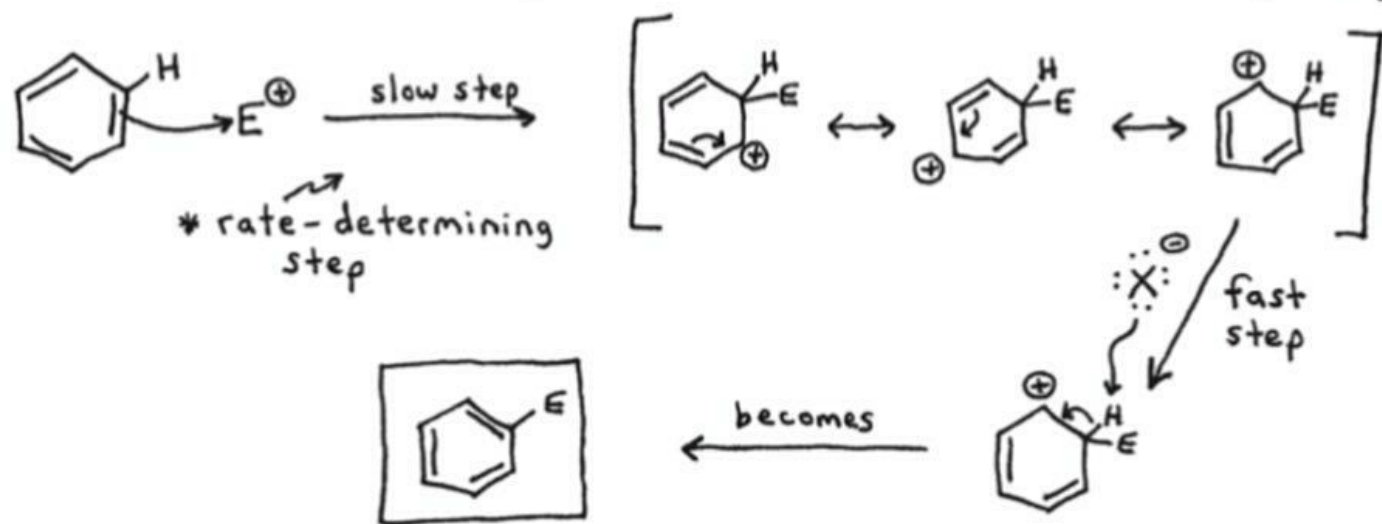
Section 15 = Electrophilic Aromatic Substitution. 15-1

↳ "The Chemistry of Benzene".

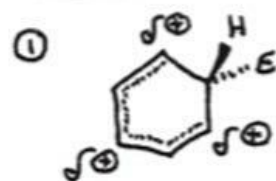


* General Mechanism.

↳ ... of electrophilic aromatic substitution (E.A.S.)



- notes :



↳ \oplus charge is delocalized to the positions ortho and para to the site of E^{\oplus} attack.