Aromatics III

Electrophilic Substitution Rxns

Ref 15: 1 – 9 (both ed^{ns})

Prob 15: 1, 3, 5, 7 (both ed^{ns})

Adv Rdg 15: 10 – 14 (both ed^{ns})

General

- π e^{-}'s dominant
- but less reactive than in alkenes

  (*b/c of aromtic stabilization*)
- **strong** electrophiles needed
- end result:

  substitution

  (*not addition*)

General Mechanism

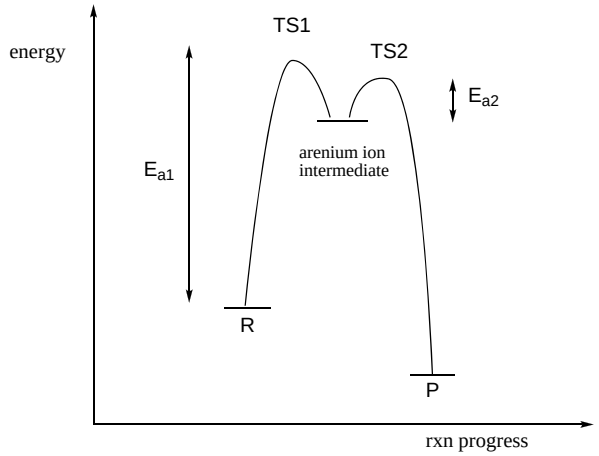
N.B. *H replaced by E*

step 1: similar to alkene rxn

step 2: restoration of aromaticity

Reaction Profile

simple 2-step energy diagram; (like S_N1, ...)



Ex. :Rxn w/ Strong Acid, C_6H_6 + HCl(aq)

5 Important Rxns

1.) Halogenation

2.) Nitration

3.) Sulfonation

4.) Alkylation

5.) Acylation

1.), 4.), 5.) know detailed mech.

2.), 3.) know reagents & products

1.) Halogenation

(w/ Cl_2, Br_2, I_2)

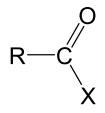
catalyst needed:

"Friedel- Crafts" = Lewis acid

common cat.: $AlCl_3$, $FeCl_3$ (*have* e^- *gap*)

Ex. Chlorination of benzene

5.) Acylation

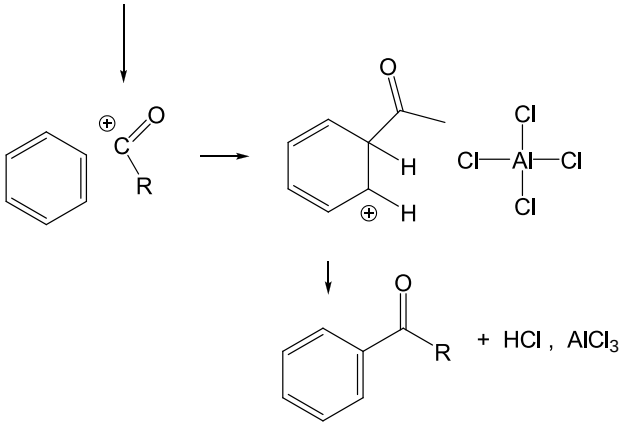


acid chloride = "acyl chloride"

& Lewis acid

Formation of "E^+":

Example:

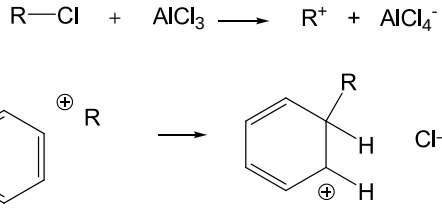


Aromatic Ketone !!

5.) Alkylation

alkyl halide & Lewis acid

Details:



Alkyl Benzene !!

Complication w/ Alkylations

1.) rearrangement of R^+ cation

can occur if more stable cation
can be formed by hydride or alkide shift

2.) multi - substitution

initial product may be more reactive
than original substrate

Ex.