CHEM 242 – Lecture 17 24/02/2014

Overheads: - Outline
Handout: EAS template

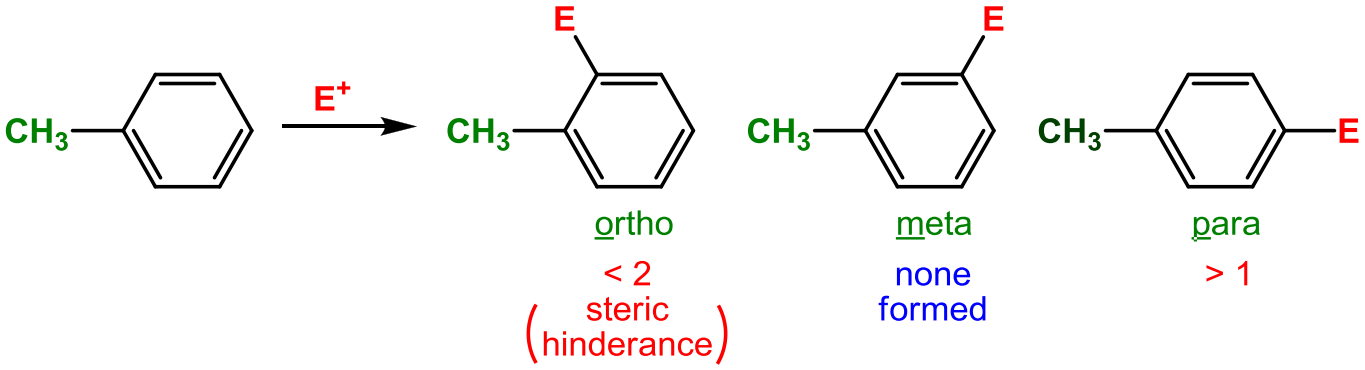
Feedback on Midterm

Recap before Break Electrophilic Aromatic Substitution

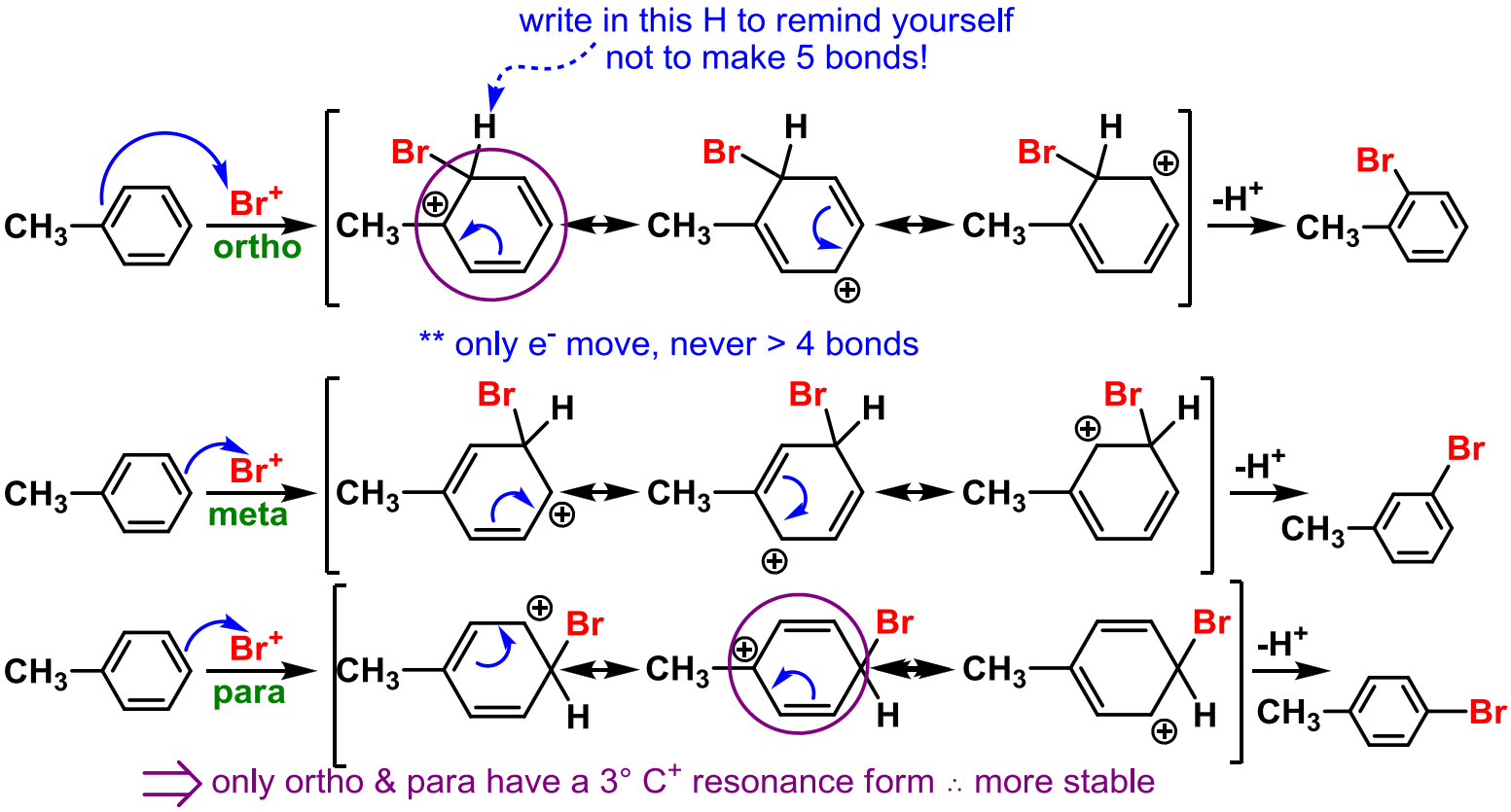
5 Types of E^+:

E^+	Reactants	Product
NO_2^+	$HNO_3 + H_2SO_4$	Ar—NO_2
Br^+ or Cl^+	$Br_2 + FeBr_3$ OR $Cl_2 + AlCl_3$	Ar—Br or Ar—Cl
SO_3H^+	$SO_3 + H_2SO_4$	Ar—SO_3H
$R-C^+=O$	i) $R-C(=O)-Cl + AlCl_3$ ii) then H_2O	$Ar-C(=O)-R$ → $Ar-CH_2-R$ (can then reduce)
R^+	$R-Cl + AlCl_3$	Ar—R

What if there is already a group on the benzene ring?



⇨ Any alkyl (R) or aryl (Ar) group on benzene ring directs E^+ to ortho and para
Why? Stabilization of C^+ intermediate
⇨ Must look at 3 resonance forms for C^+



Result: 1) R– gives only ortho and para

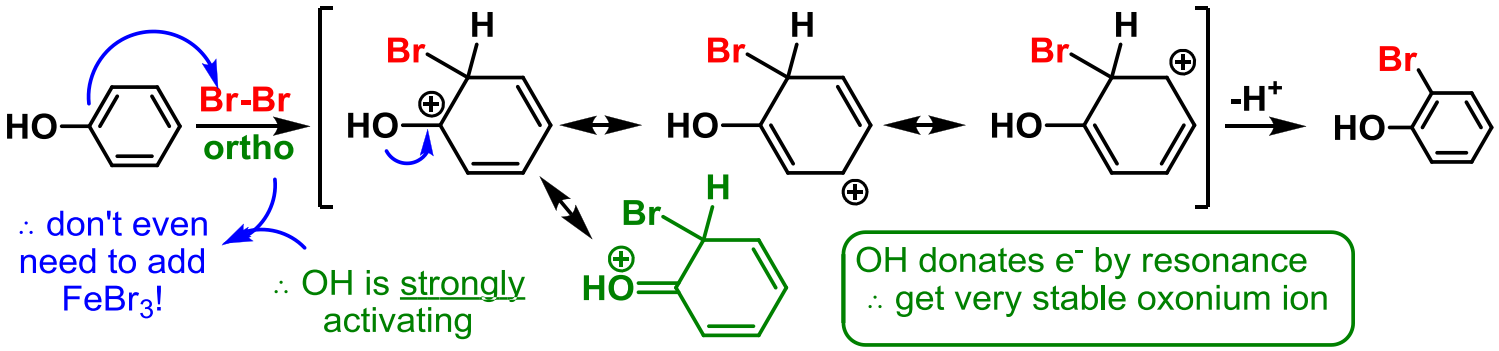
2) R– react faster than benzene (3° > 2° ∴ ~600 x faster)

⇒ R group is activating (faster) and ortho-para directing

Other Activating Groups

- all electron-donating groups can stabilize C^+
- ∴ speed up reaction and all direct o/p

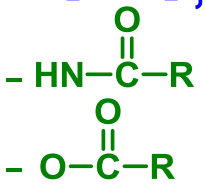
eg OH: - alcohols are strongly electron-donating
- lone pairs on O can do resonance with C^+



**Practice at home: Draw res. Forms for m & p, show only o & p have "extra" res. form

Activating Groups: Table 19.1/16.1 in old book

-OH; -OR
$-NH_2$; $-NR_2$ } strongly activating



(amide, like lab)

} moderately activating

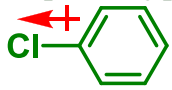
(e^- also do resonance with C=O, ∴ less to donate)

-R; -Ar - weakly activating

Electron-Withdrawing groups are deactivating:

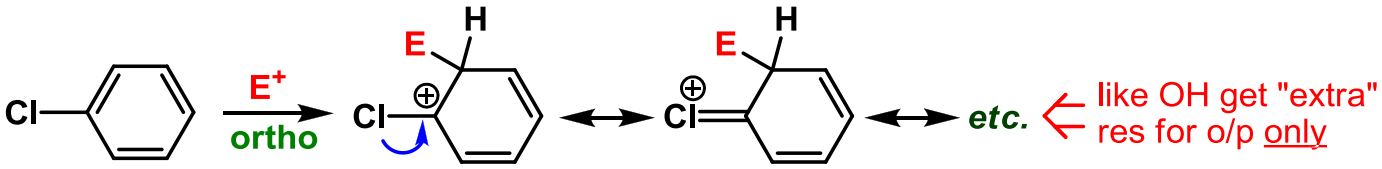
- remove e^- from ring ∴ C^+ less stable, slower reaction

Deactivating Groups: 2 types:

1) Halogens: 

ring is δ^+ ∴ reacts ~ 50x slower than benzene

BUT: lone pairs can still donate to stabilize o & p



← like OH get "extra" res for o/p only

F, Cl, Br, I are weakly deactivating; still o/p