

Overheads: - Outline

Recap Monday: Directing Effects of Substituents

Activating Groups:

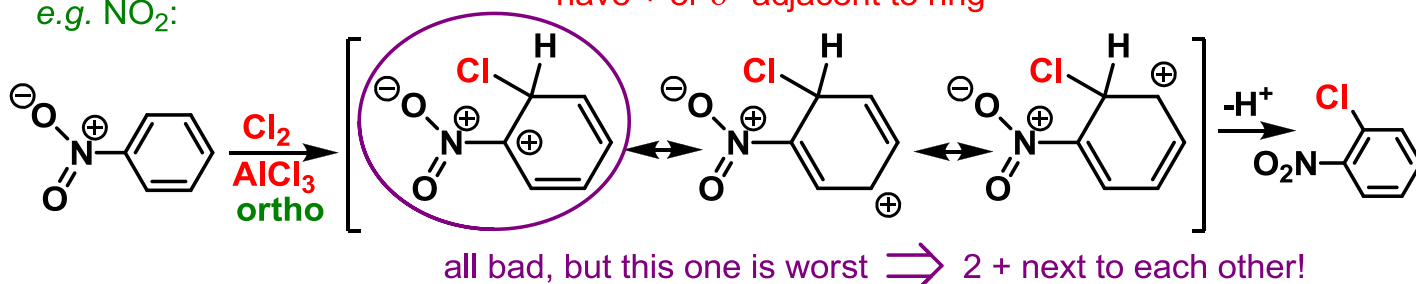
- Atoms with lone pairs directly on benzene ring (OH, OR, NR₂)
- Alkyl or aryl groups
- All stabilize C⁺ ∴ speed up reaction and direct o/p

Weakly Deactivating Groups:

- Halogens
- Slow down reaction but still direct o/p

2) More strongly deactivating groups: withdraw e- more strongly

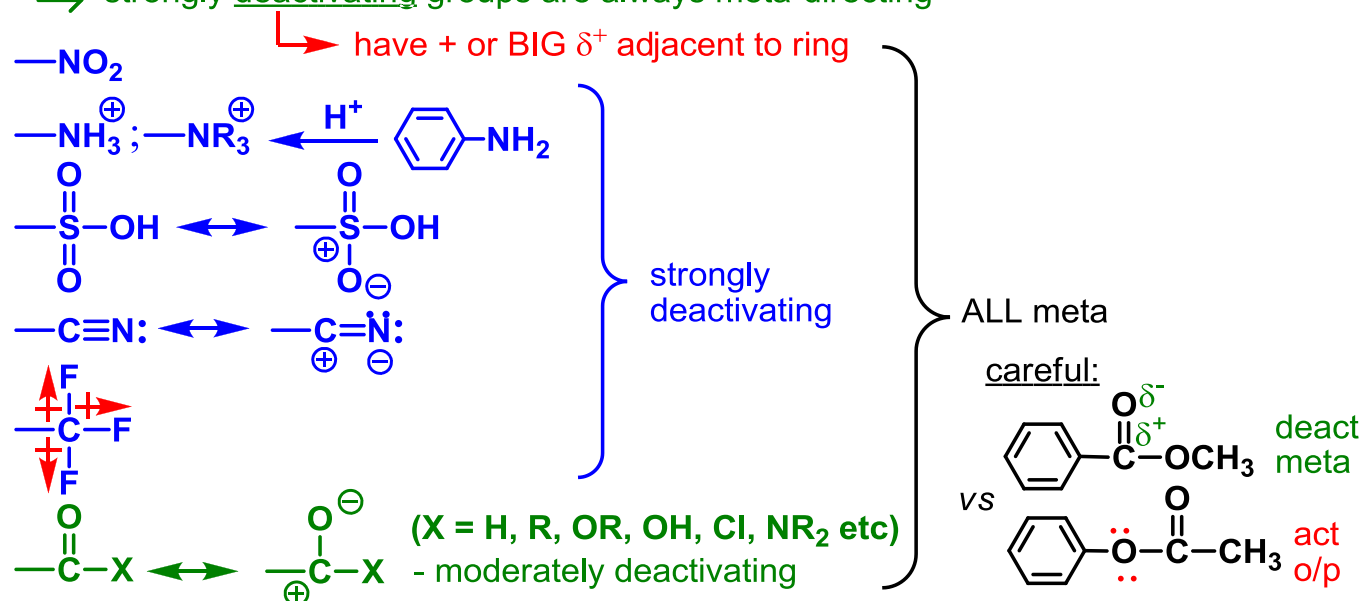
e.g. NO₂: - have + or δ⁺ adjacent to ring



Draw m & p, see that meta never has 2 adjacent +'s

∴ not as bad! ~ NO₂ is strongly deactivating and meta-directing

⇒ strongly deactivating groups are always meta-directing



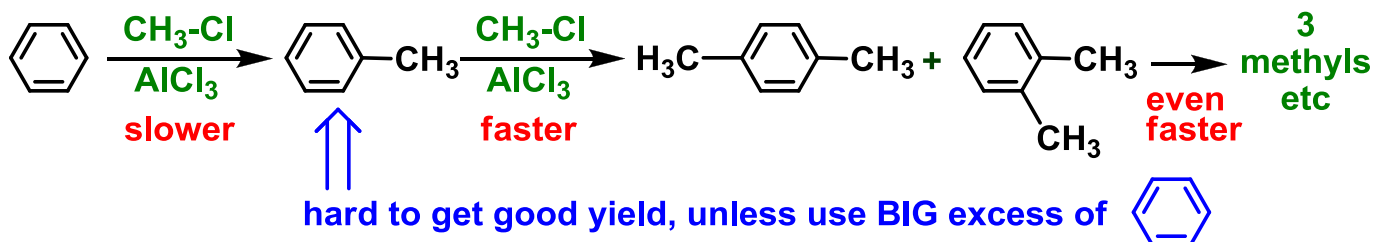
Summary:

- All Activating
 - Weakly deactivating (halogens)
 - Moderately deactivating
 - Strongly deactivating
- } o/p
} meta

⇒ Table 19.1 (16.1 in 6th ed) ⇒ LEARN IT!

Notes on Reactivity

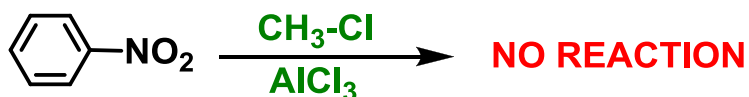
- 1) Since c1ccccc1C reacts faster than c1ccccc1, hard to add only one R group!



*** unless otherwise indicated, assume only one E⁺ adds (monosubstitution)

- 2) Friedel - Crafts Reactions are harder to do than other 3 E⁺

⇒ Friedel - Crafts does not work with strongly or moderately deactivating groups (i.e. meta directors) ⇒ too slow!

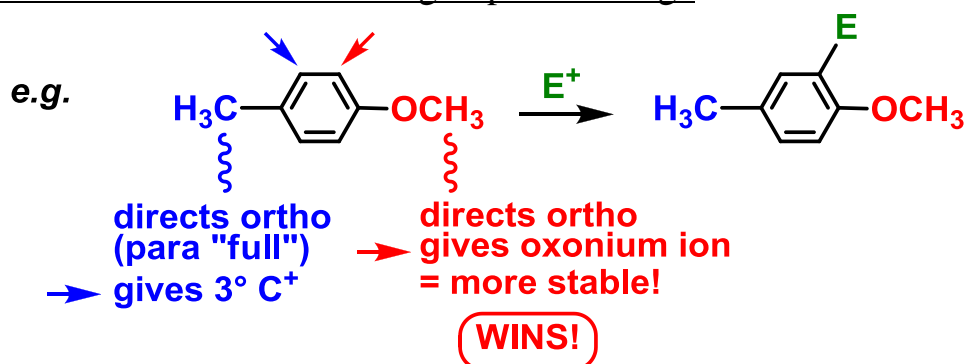


- 3) Ar-NH₂ is base:



- ⇒ can't do HNO₃ / H₂SO₄ or SO₃ / H₂SO₄
⇒ can't do FC (AlCl₃ = Lewis Acid)
⇒ ONLY Br₂ or Cl₂ work with Ar-NH₂

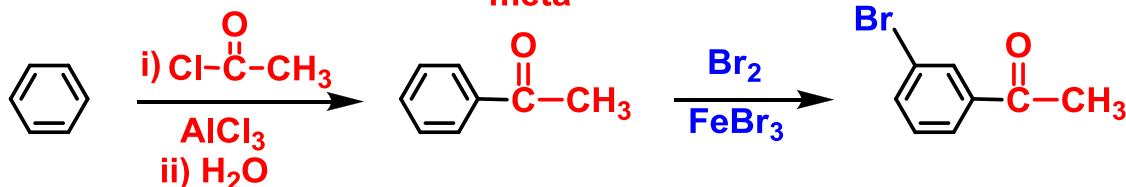
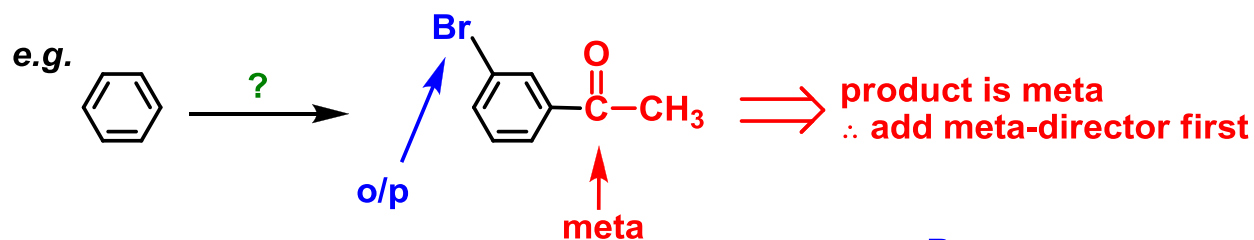
What if there is more than one group on the ring?



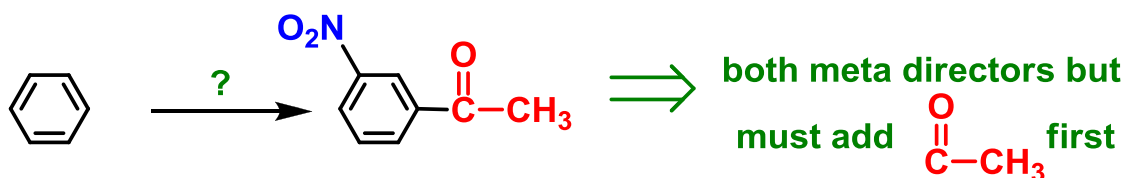
Rule: most strongly activating group “wins”

Strategy for Synthesis

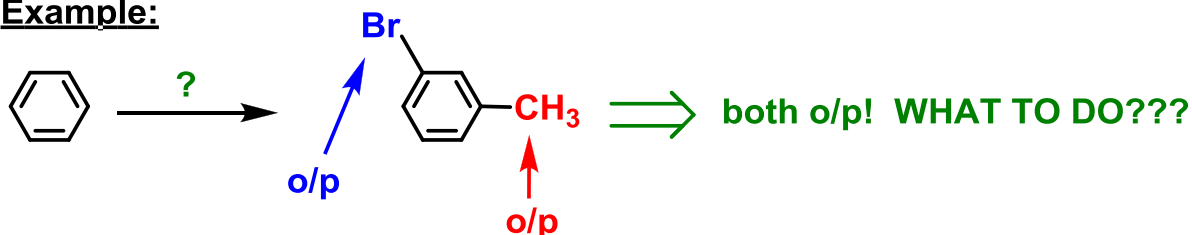
⇒ consider directing effects when deciding which to add first



** also consider reactivity: e.g. can't do FC with meta-directors

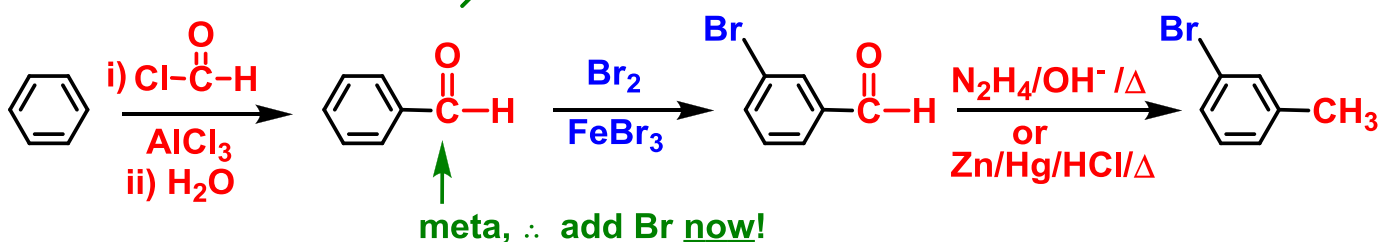


Last Example:



Is there another way to add a CH₃ group?

HINT: it is 1°! ⇒ acylation - reduction



⇒ Good trick! Put in acyl, use as meta-director, THEN reduce to alkyl