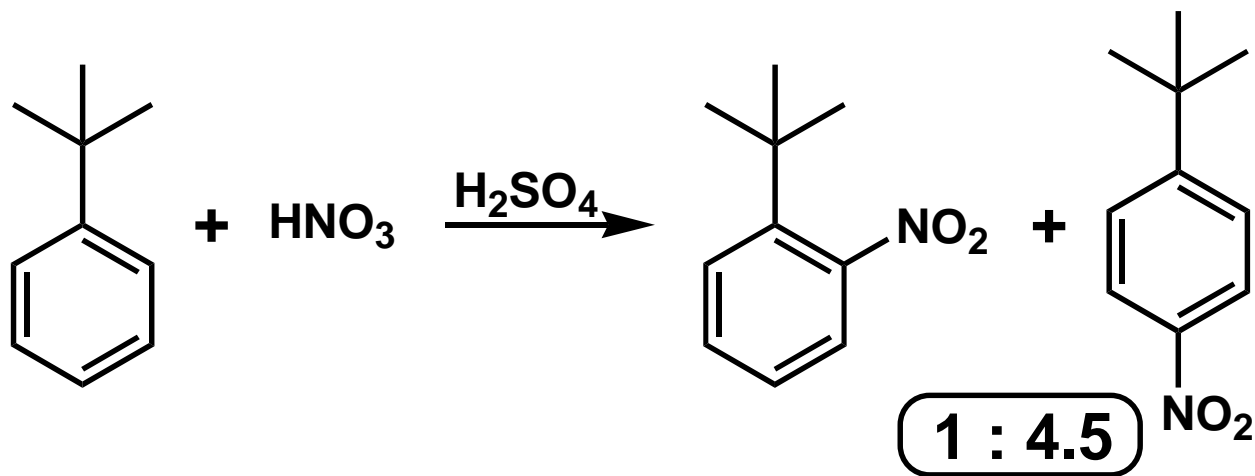
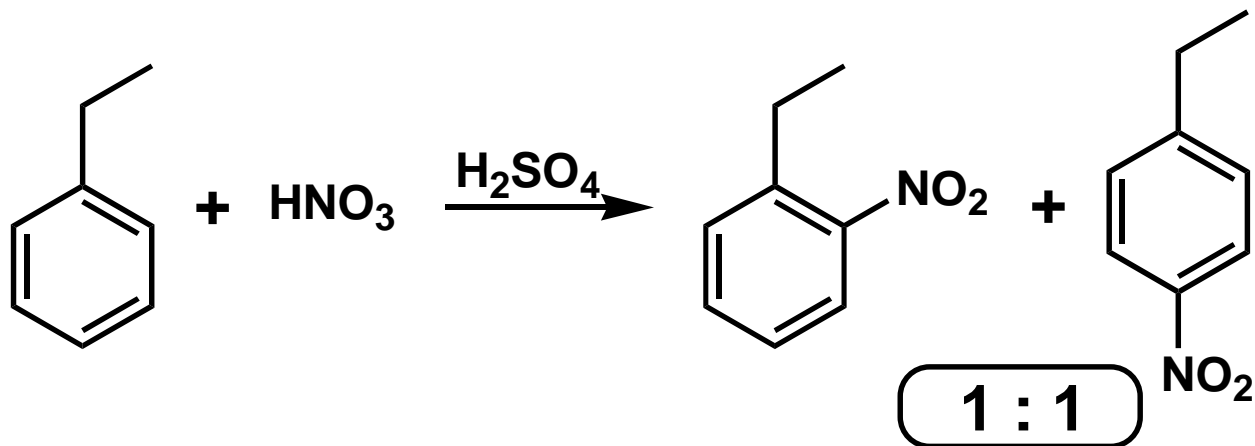


# General Considerations About Ortho vs. Para Substitution

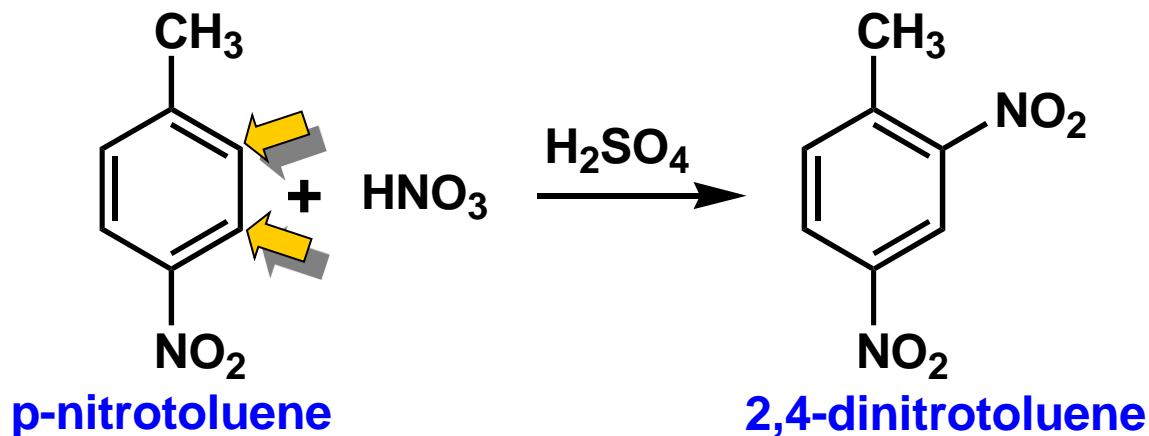


Ortho and para substitution have similar electronic considerations. Steric factors can have an influence on the ortho / para product ratio.

# Electrophile Orientation With Disubstituted Benzenes

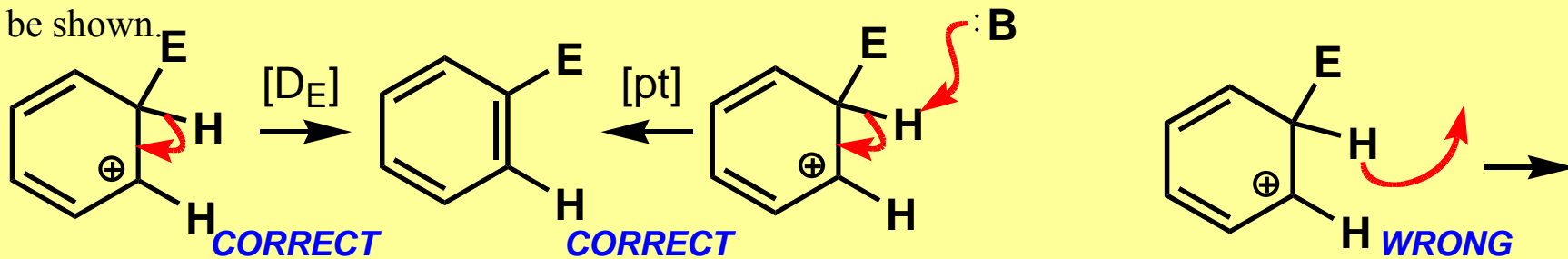
With disubstituted benzenes:

- First consider the contributions of the individual substituents and determine if they direct to a **common position** to produce a major product.
- When substituents are in competition, **strongly activating** substituents will dominate weakly activating or deactivating ones.



# Summary

- The  $\pi$  bonds in aromatic compounds behave as nucleophiles and are thus reactive toward electrophiles. In the first step of **electrophilic aromatic substitution**, the aromatic ring attacks an electrophile in an  $[A_E]$  fashion to give a delocalized carbocation intermediate.
- In the second step of **electrophilic aromatic substitution**, the carbocation undergoes  $[D_E]$  with loss of  $H^+$  from the same carbon to which the electrophile added, re-forming the benzene ring (the net result is substitution at this C).
- The electronic nature of substituents on an aromatic ring has profound effects on the rate of reactivity and the regiochemistry of electrophilic aromatic substitution reactions.
- Draw your curved arrows correctly. Arrows should not show the  $H^+$  flying off into space! If  $H^+$  loss via  $[D_E]$  bothers you, show a weak base making a new bond to hydrogen at the same time the C–H bond is cleaved (technically now a  $[pt]$  step). Often the base is assumed to be present but need not be shown.



# Summary

- Electrophiles preferentially attack ortho or para to electron-donating substituents such as (RO–, R<sub>2</sub>N–, RCONH–) and halo substituents, whereas electrophiles attack meta to electron-withdrawing groups such as carbonyl, –CN, –NO<sub>2</sub>, and –SO<sub>3</sub>H.
- The directing ability of a group is closely related to its ability to stabilize or destabilize the intermediate carbocation.