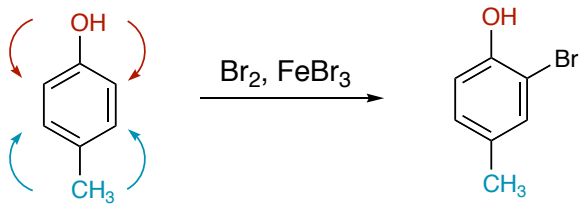
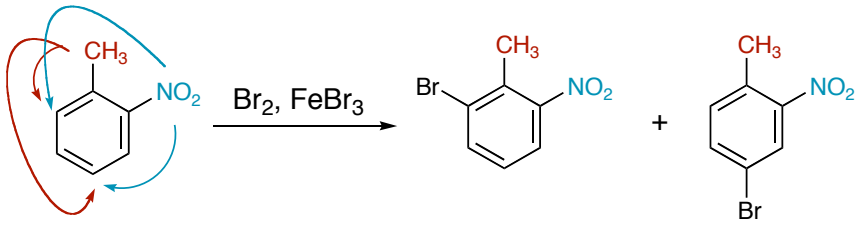
Chapter 16 - Chemistry of Benzene: Electrophilic Aromatic Substitution

More than one substituent

If more than one substituent is present on a benzene ring, they may work together or may be opposing each other for directing electrophilic addition. Electron Donating Groups (strong) usually win against Electron Withdrawing Groups. Resonance Effects are Stronger than Inductive Effects.

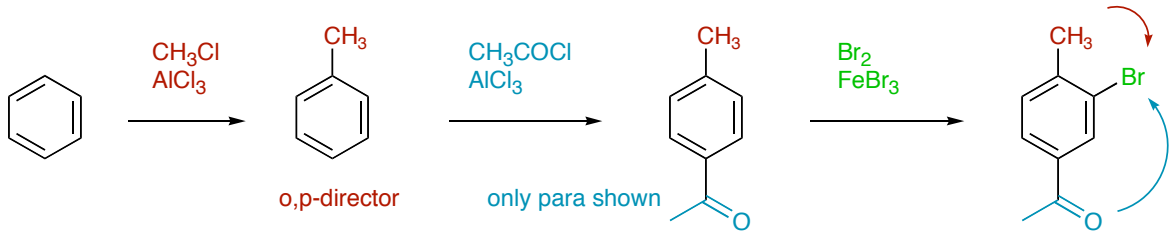


OH is the stronger director (resonance) so it will be the important director for the substitution with bromine.

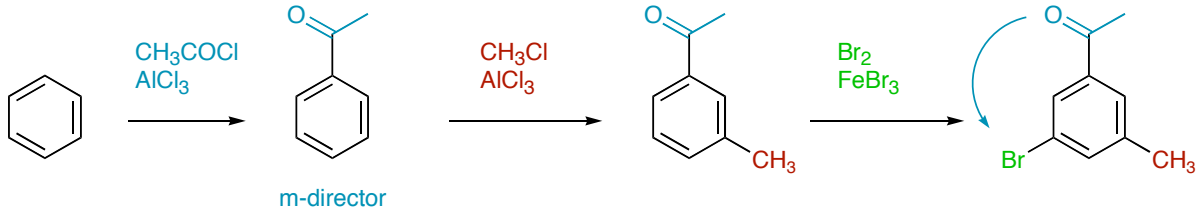


CH_3 and NO_2 are both directing to the same positions and are thus working together

Because substituents direct in different ways, the order of addition can have a large influence on the product outcome.



both groups direct to the same place



Groups fighting - probabl a mixture, but alkyl is weak - so ketone would most likely direct the Br meta to it.

Nucleophilic Aromatic Substitution

Under normal conditions, nucleophiles don't react with aromatic rings. However, if there are good electron withdrawing groups on the ring, nucleophilic substitution can take place. This does not occur by an S_N1 or S_N2 reaction. The mechanism is an addition of the nucleophile followed by loss of the leaving group. The electron withdrawing groups need to be ortho or para to the leaving group. This is where the negative charge appears in the intermediate. Thus, the more you can stabilize the negative charge, the better the reaction will be. Note, that m-nitrochlorobenzene will not undergo nucleophilic substitution, while o- or p-nitrochlorobenzene will.