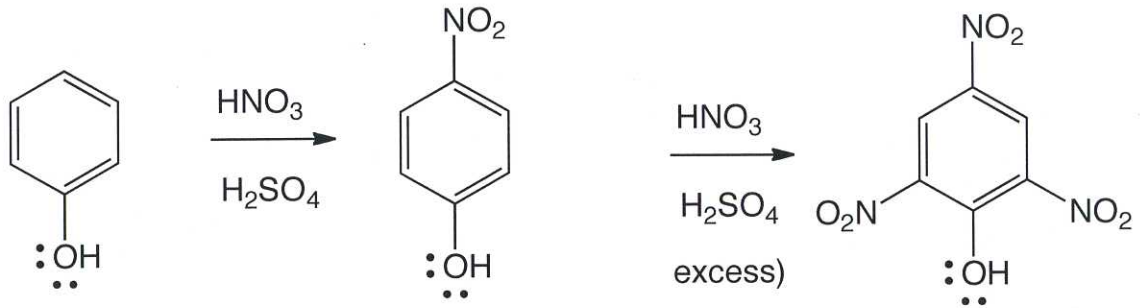
How to determine position & reactivity: Examples

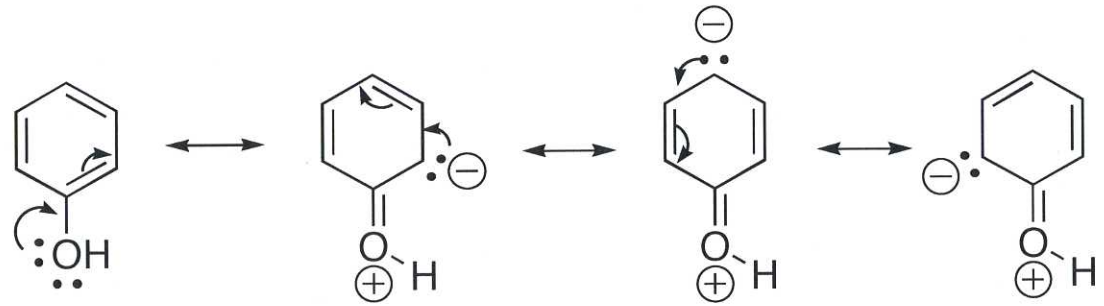
Strongest donating group wins:



para (and ortho)

2,4,6-trinitrophenol

picric acid



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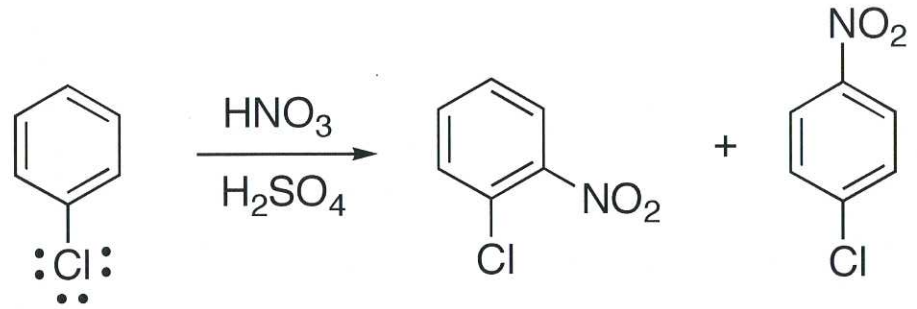
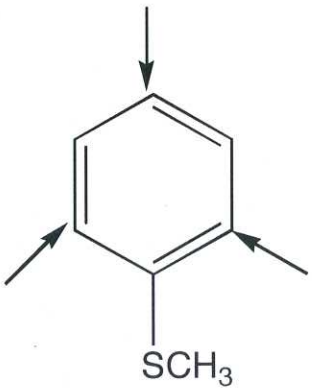


chloro group is an electron withdraw group inductively

BUT - a weak resonance donator - gives ortho, para substitution
resonance beats inductive effect



S is under O in the periodic table

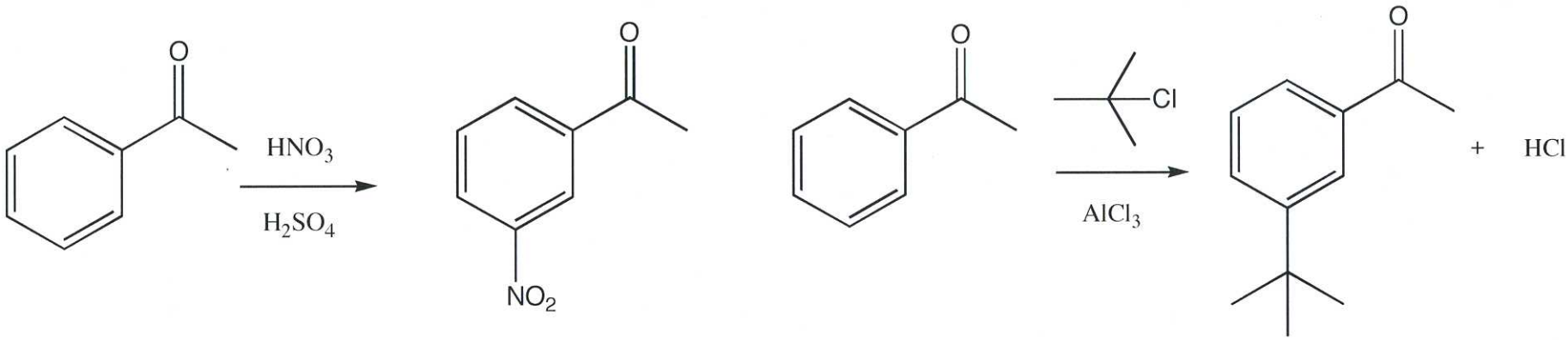
it has two lone pairs

it is resonance donating

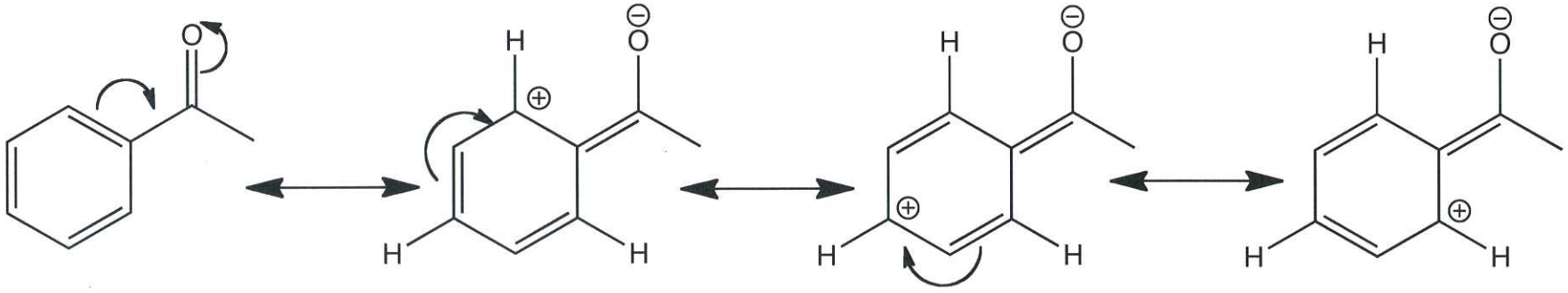
it is *ortho* and *para* directing

How to determine position & reactivity: Examples

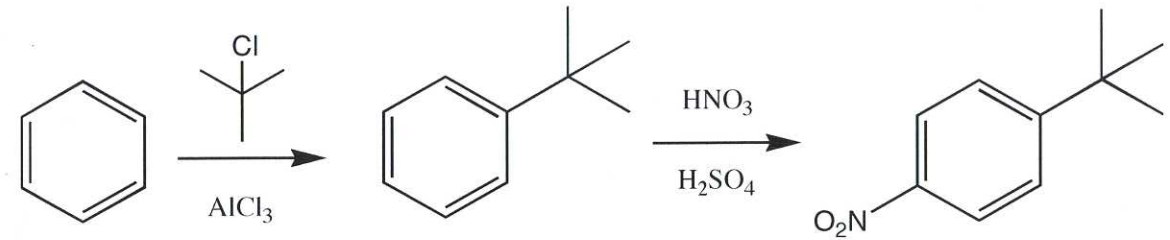
Acetophenone is *meta* directing

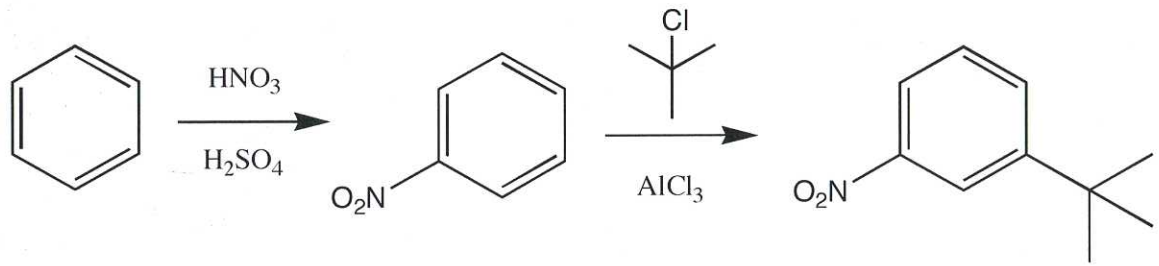


when the electrophile attacks it avoids the partial positive charges on the *ortho* and *para* positions



Notice how the order that reactions are done affects the following two examples:

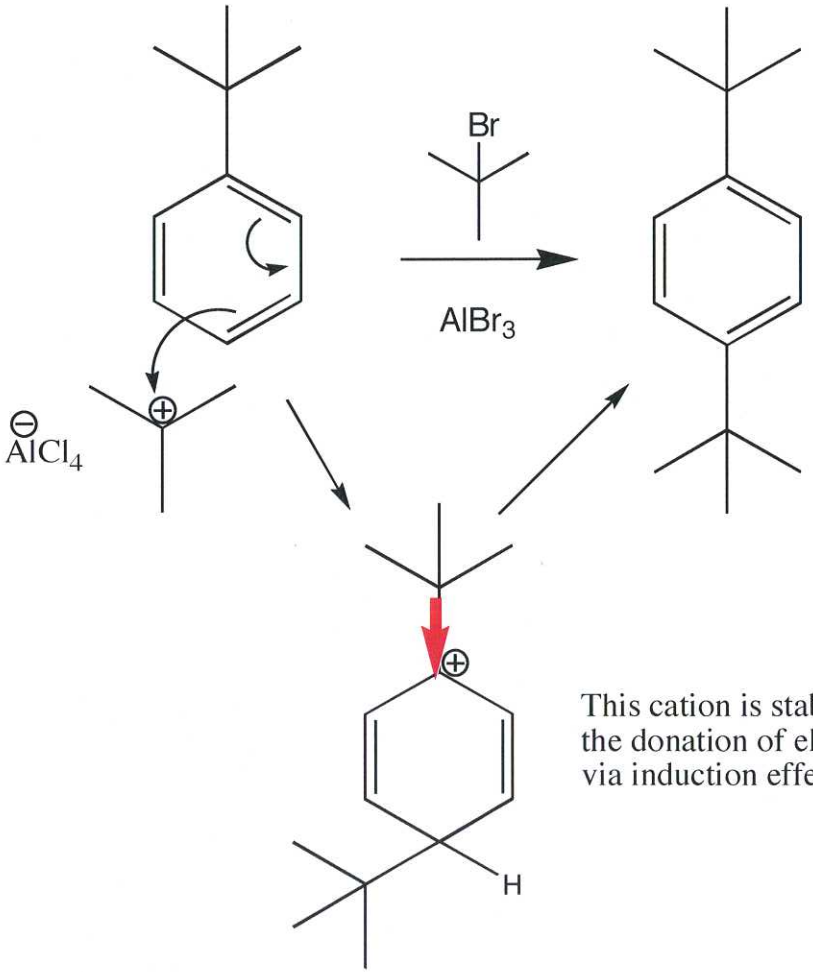




products of the above two series of reactions are structural (or constitutional) isomers

How to determine position & reactivity: Examples

Alkyl groups are inductively (weak) ortho-para directing

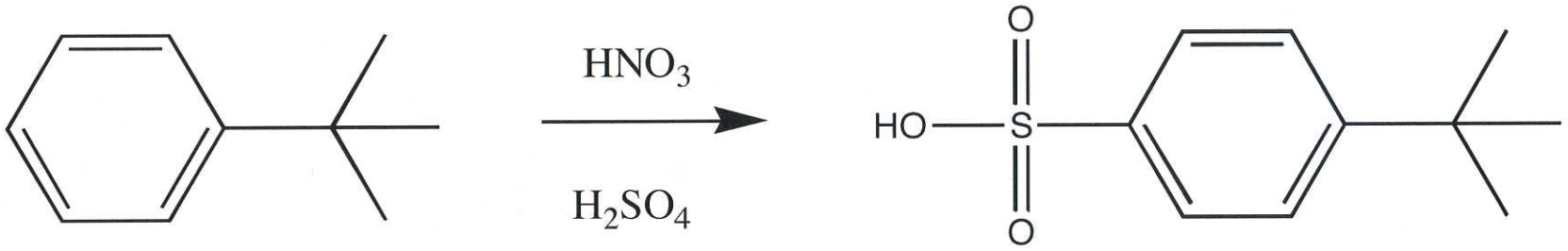


reaction occurs at the *para* position
instead of the *ortho* position due to sterics

This cation is stabilized by resonance as well as the donation of electrons from the *t*-Bu group via induction effects (shown by the red arrow)

How to determine position & reactivity: Examples

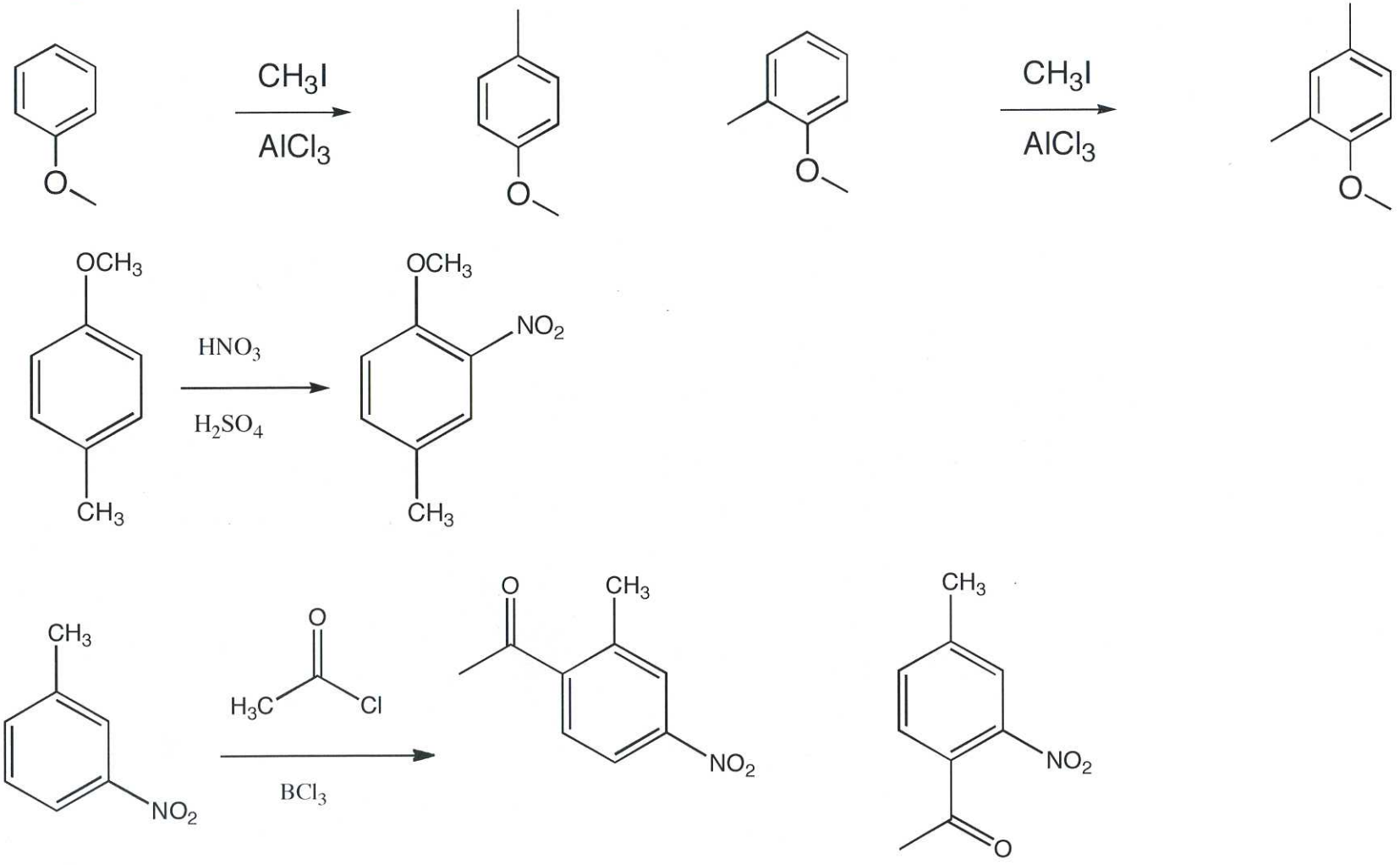
Alkyl groups are inductively (weak) ortho-para directing



reaction occurs at the *para* position
instead of the *ortho* position due to sterics

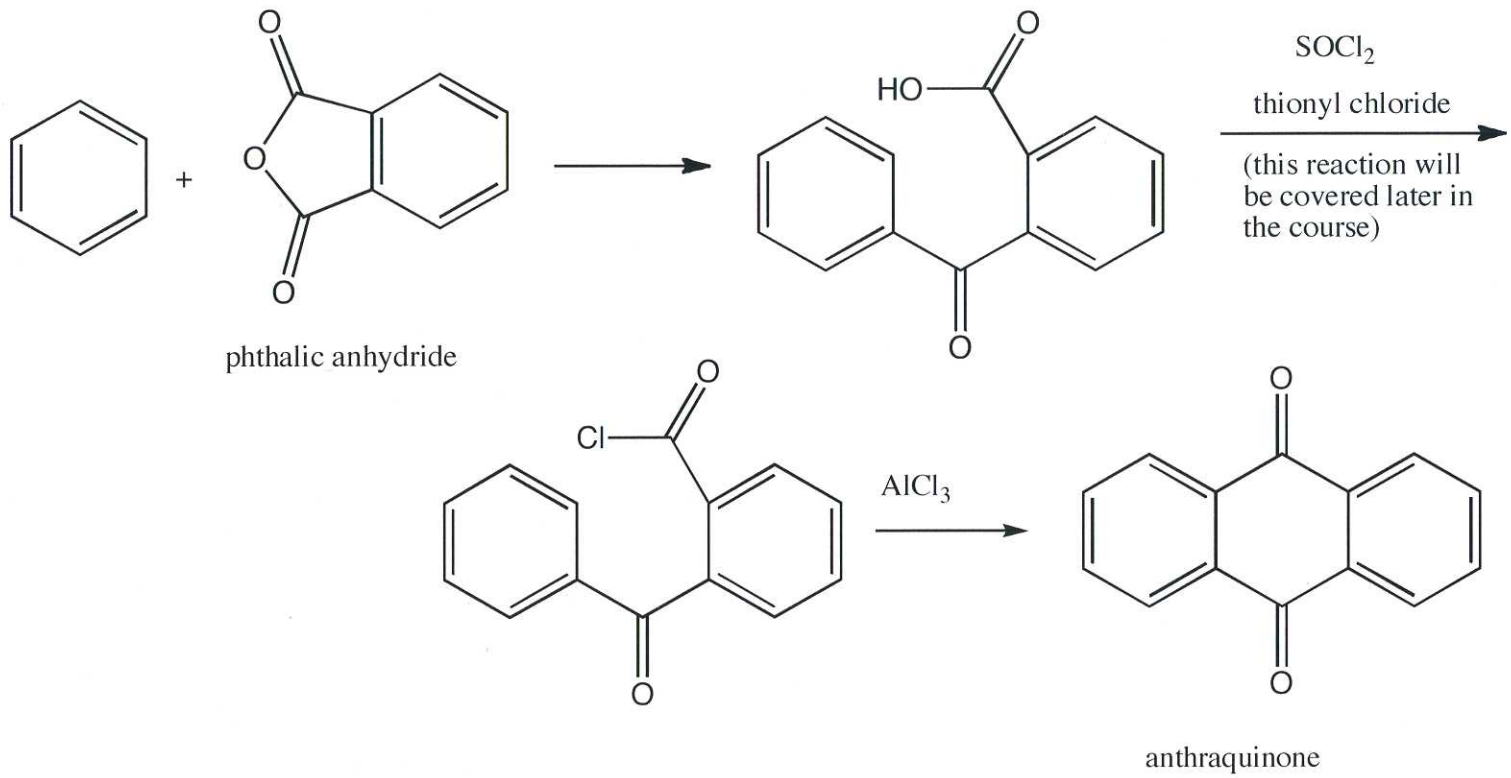
How to determine position & reactivity: Multiple Substitution

Strongest donating group wins:



position that is between meta substituents is too sterically hindered

How to determine position & reactivity: 6 & 5 rings favoured

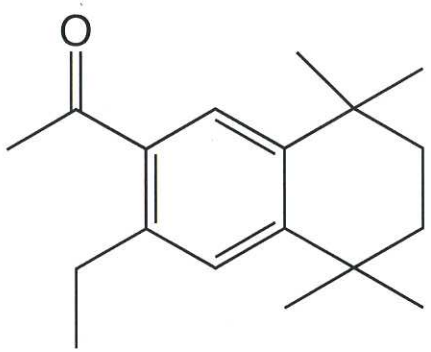


the substituent (a ketone) would normally direct the second acylation to the *meta* position as a resonance withdrawer

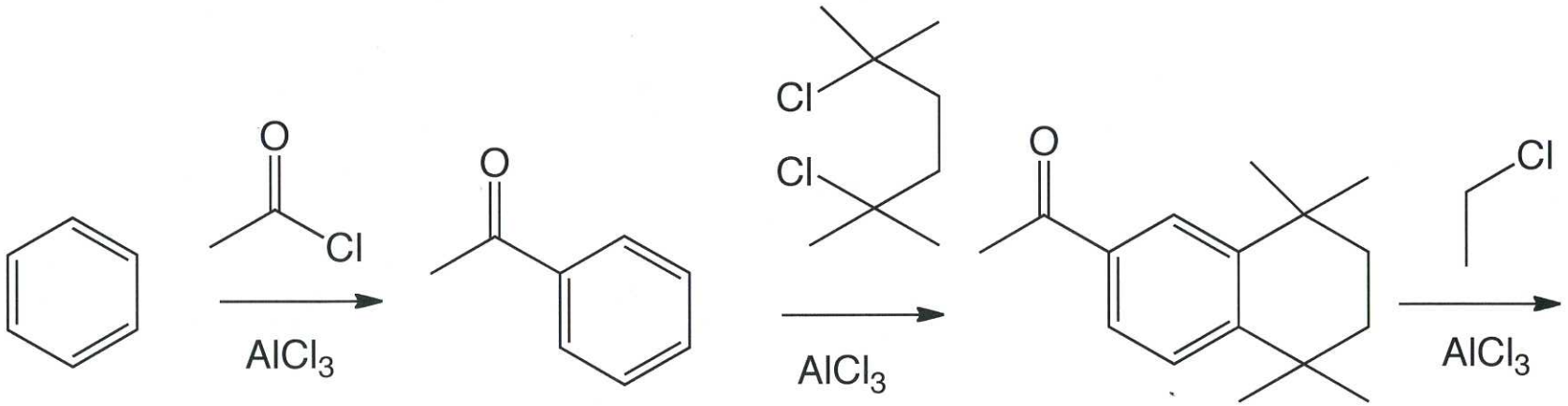
does not occur as this would produce a very strained structure

Also formation of 6 membered & 5 membered rings favoured

Synthesis Example: sequence of steps is critical

Make  from benzene

versalide



Reactions of Side Chains of Aromatic Compounds: to discuss 3 types

1. Alkyl Side Chain Oxidation Reaction

2. Clemmensen Side Chain Reduction Reaction

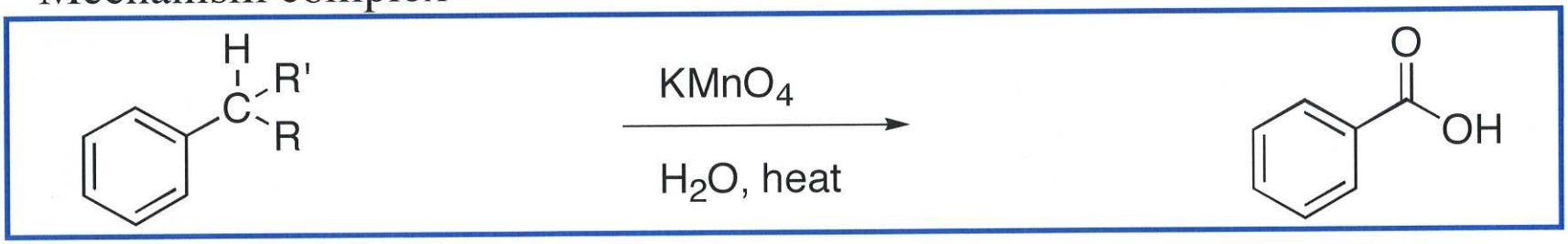
3. Nitro Reduction & Ar Amino Diazotization Reaction

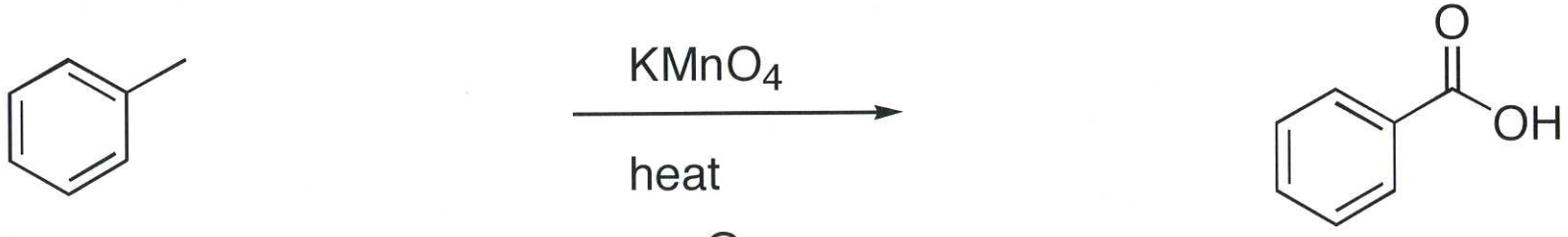
1. Alkyl Side Chain Oxidation Reaction of Aromatic Compds

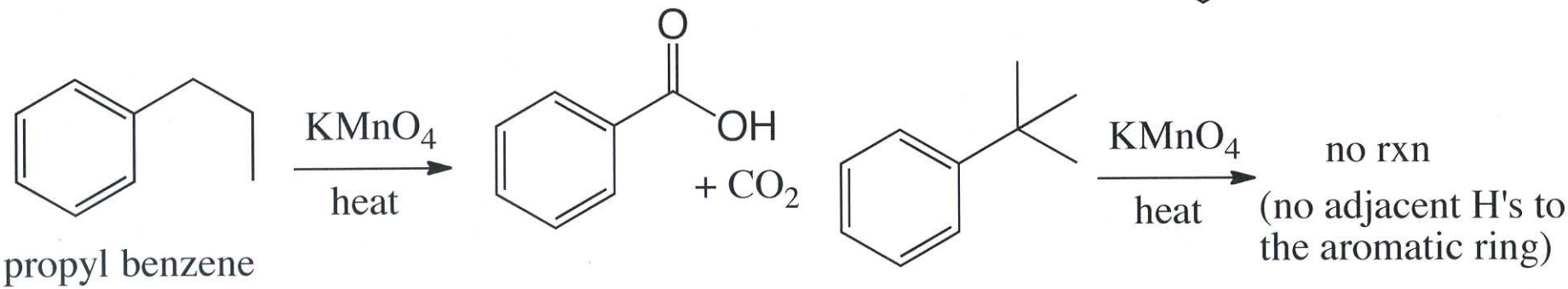
If the carbon directly attached to the aromatic ring has ≥ 1 hydrogen attached to it, it can be oxidized to corresponding carboxylic acid by $KMnO_4$

Carbon dioxide (CO_2) is typically a product + others possible

Mechanism complex

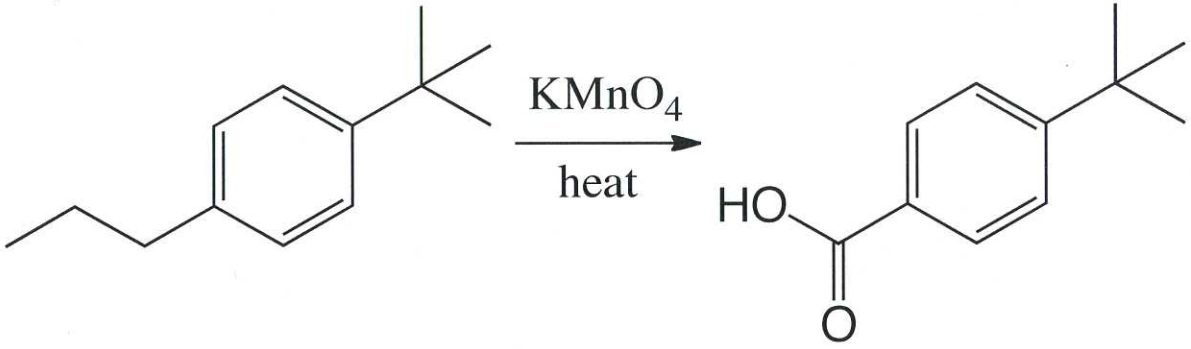


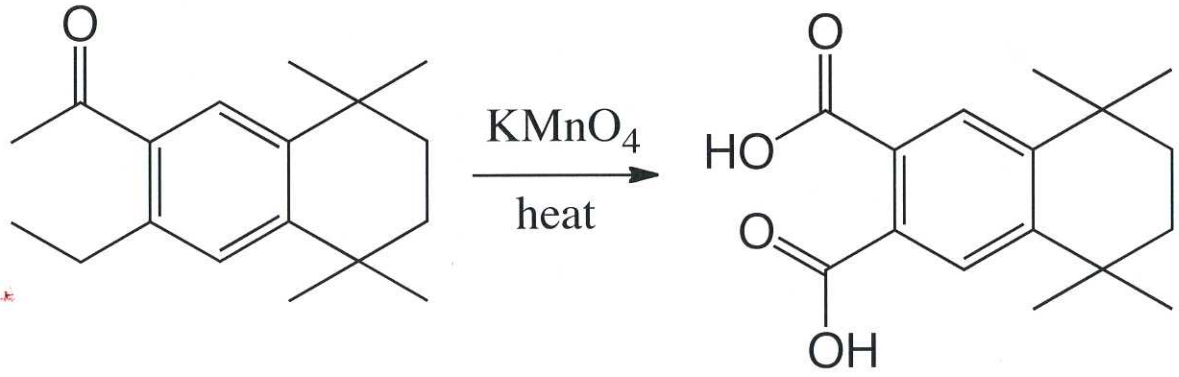


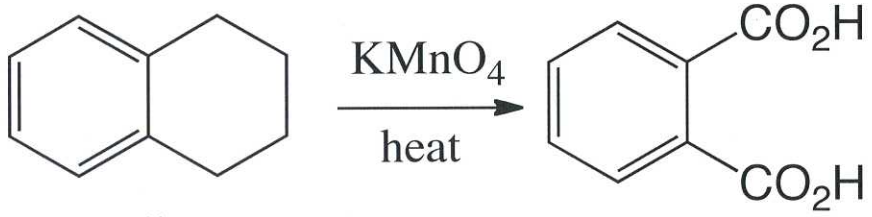


propyl benzene

1. Alkyl Side Chain Oxidation: Examples







tetralin