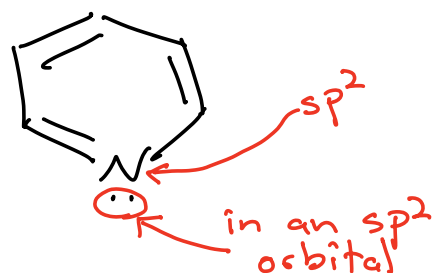


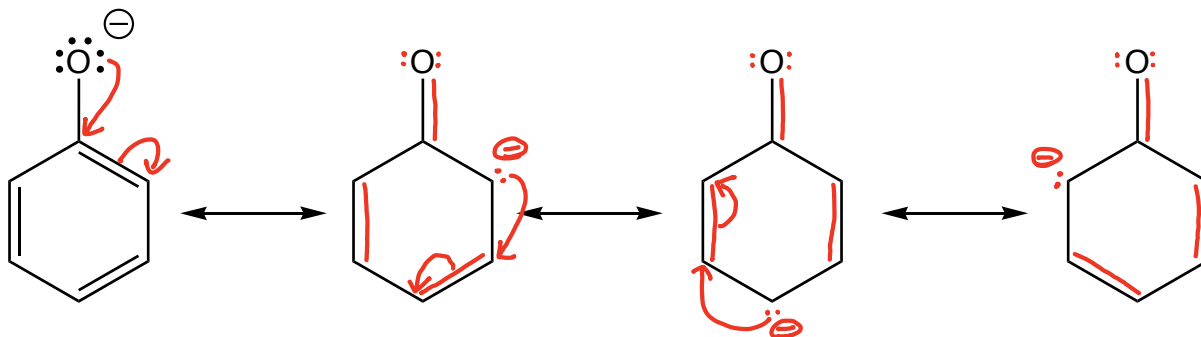
The "lone pair" on N is actually part of the 6 π electrons so they are delocalized and not able to bond to a proton



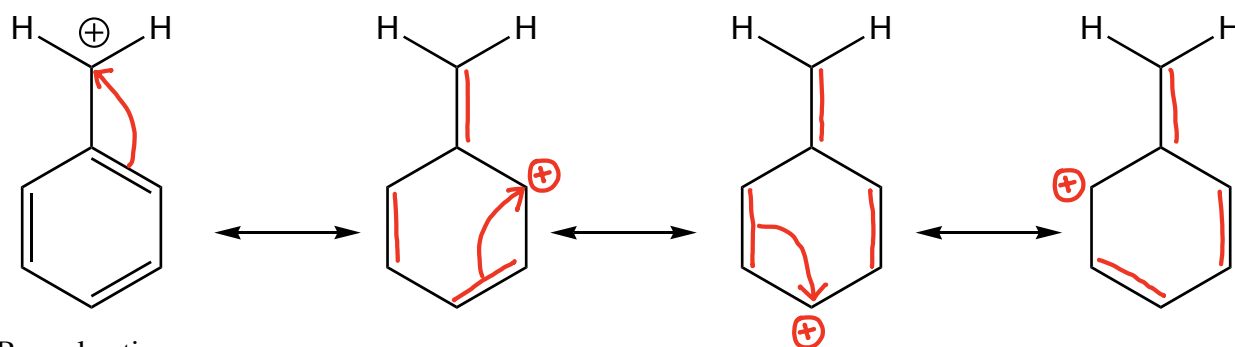
The lone pair on N is available to bond to a proton

This is the base!

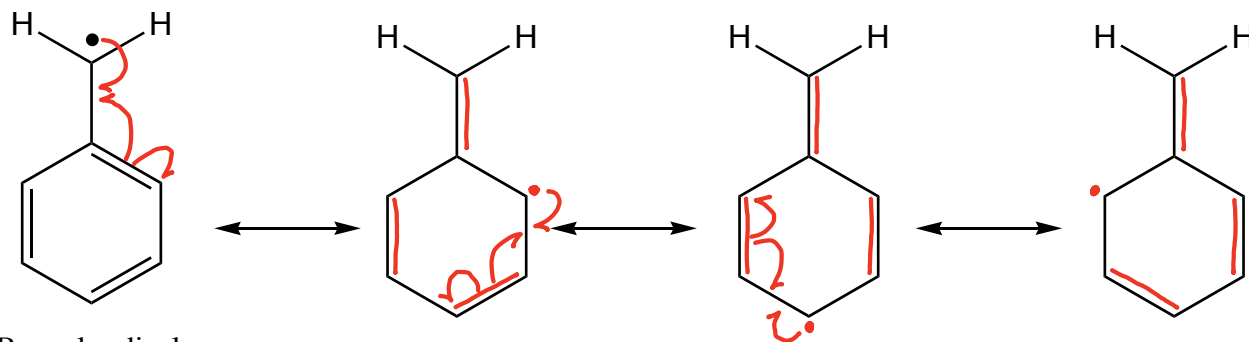
Aromatic resonance stabilization of charged species



Phenoxide anion



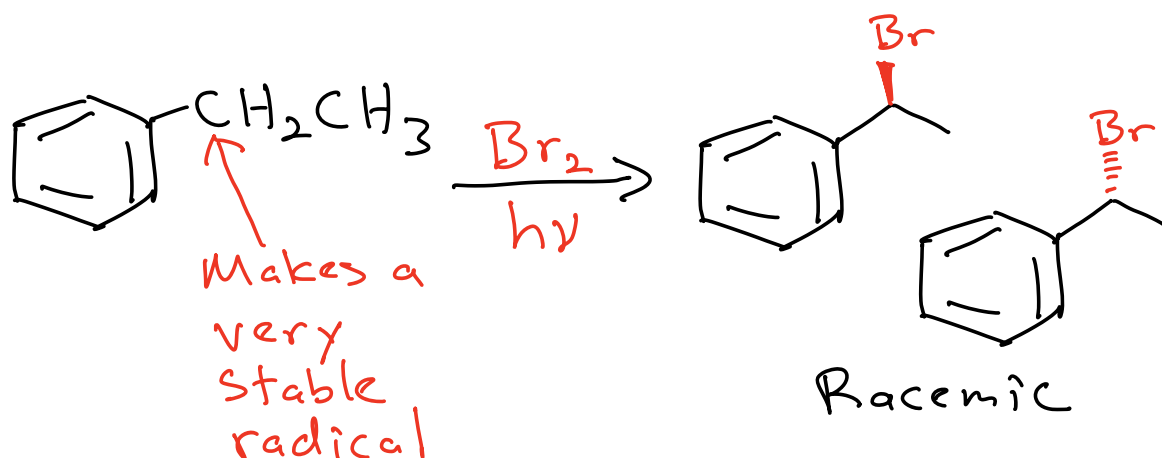
Benzyl cation



Benzyl radical

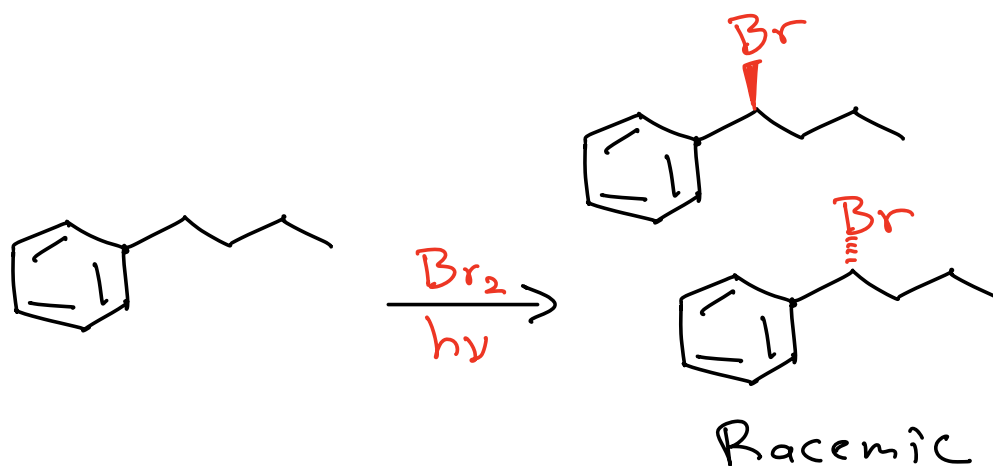
Benzene rings stabilize anions,
cations and radicals (Golden Rules
5,6 and 7)

Free radical halogenation



Radical Stability

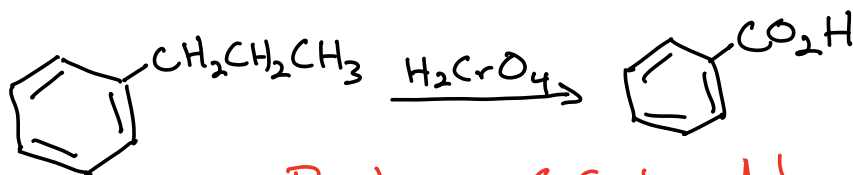
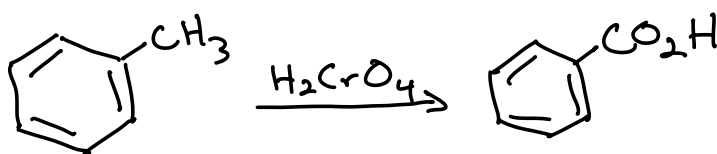
Methyl < 1° < 2° < 3° < Benzylic Radical



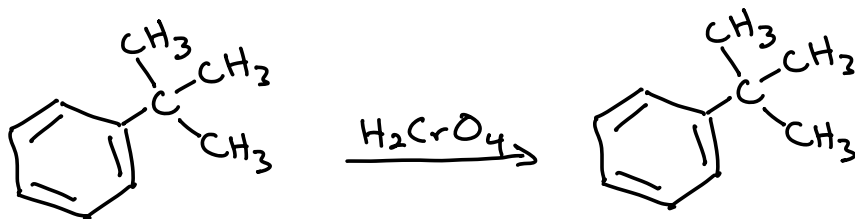
Oxidation

The benzylic carbon is easy to oxidize all the way to a carboxylic acid — even breaking C-C bonds!

The benzylic carbon needs at least one H atom for the reaction to occur



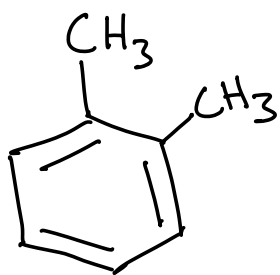
Broke a C-C bond!



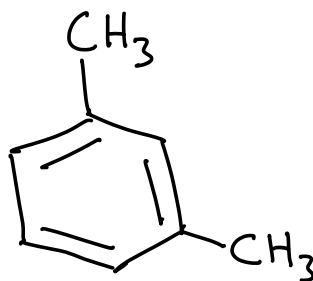
No C-H bond on benzylic C atom

(NO REACTION)

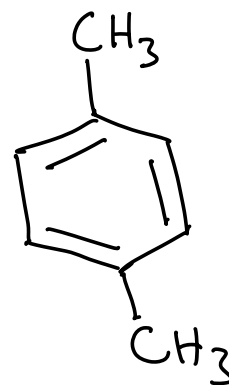
Important terms



ortho

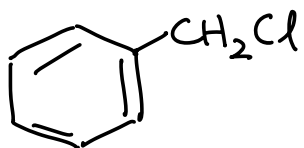


meta

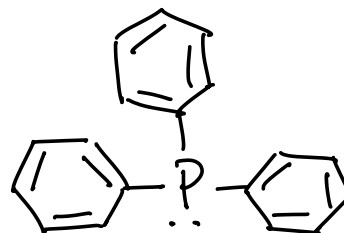


para

Benzyl vs. Phenyl

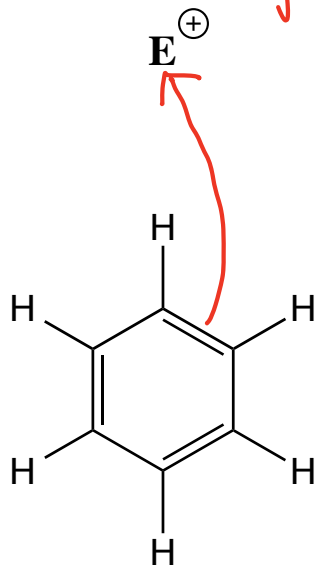


Benzyl chloride

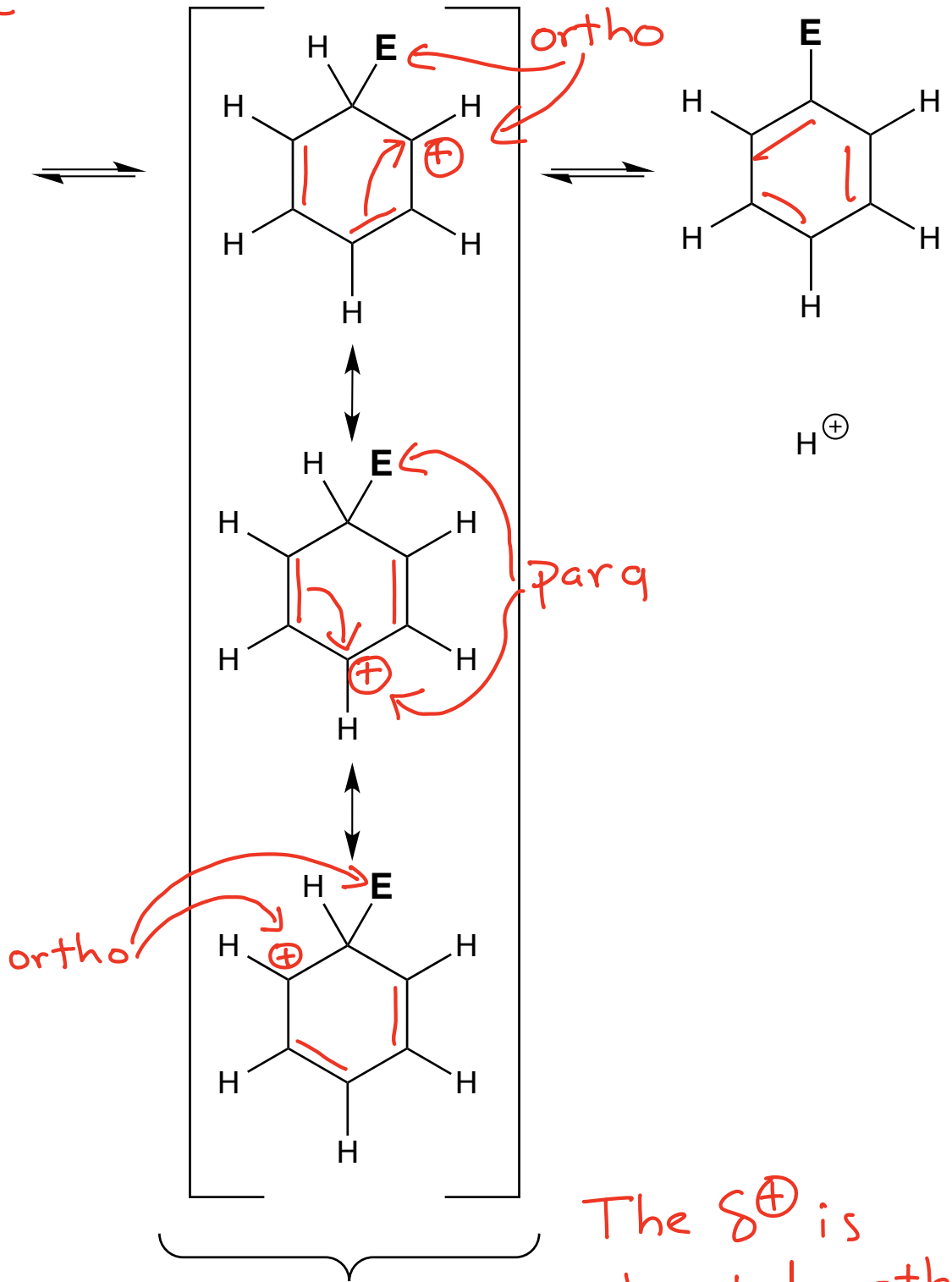
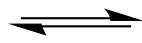


Triphenyl phosphine

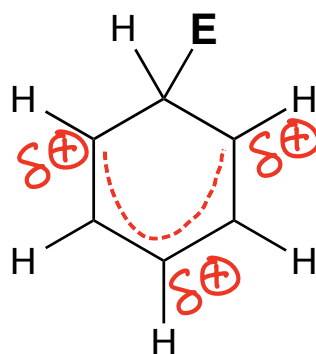
Wicked Strong Electrophile



Weak Nucleophile



Called the Arenium Ion



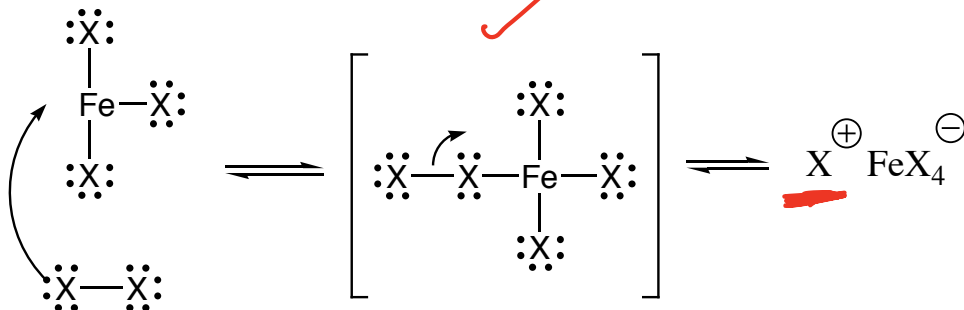
The δ^+ is located ortho and para to where the new bond to "E" is located

Summary → Wicked strong electrophile reacts with the benzene π electron density to make a resonance delocalized arenium ion intermediate that loses a proton to give a substituted benzene

The arenium ion intermediate has partial \oplus charge ortho and para to the new bond to E

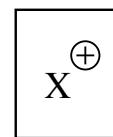
Reagents

Halogenation X_2, FeX_3

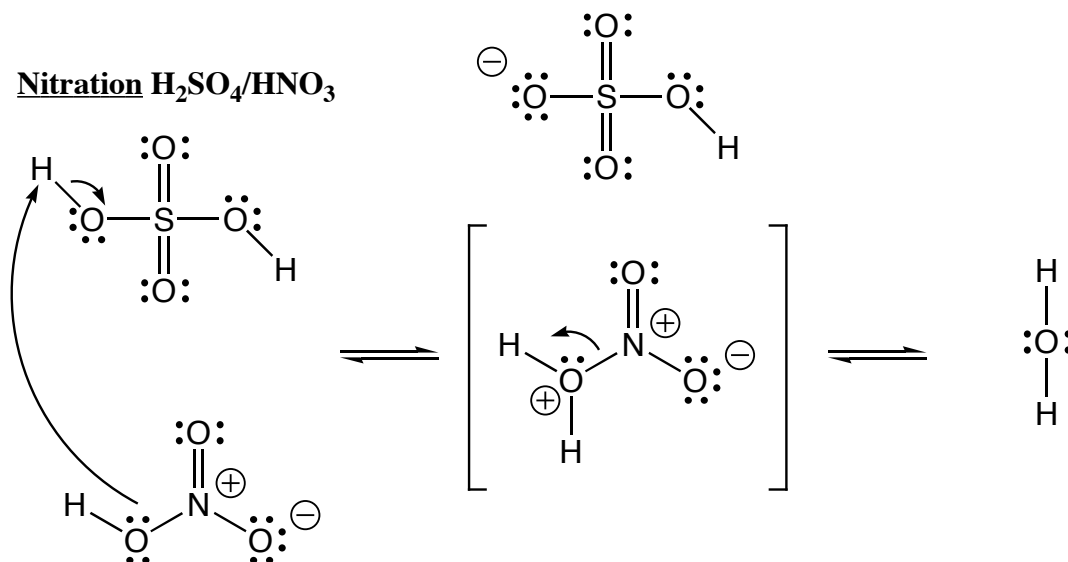


$X = Br, Cl$

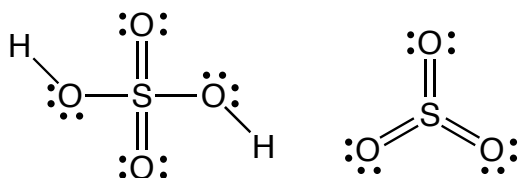
Wicked strong
electrophile



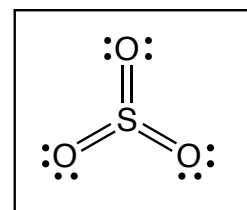
Nitration H_2SO_4/HNO_3



Sulfonation H_2SO_4/SO_3

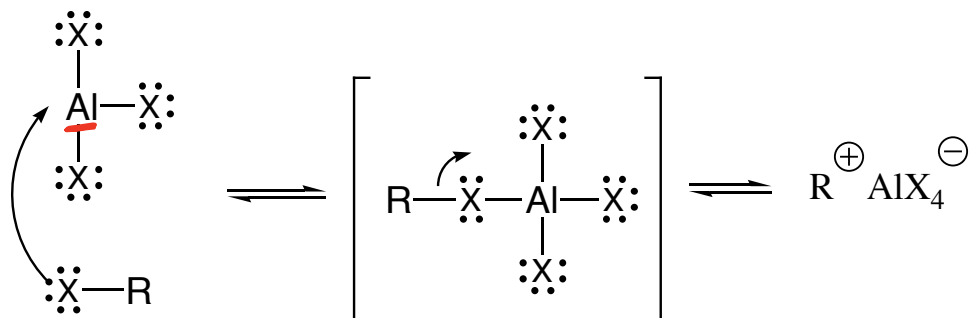


Fuming sulfuric acid
contains both of the
above reagents, the SO_3
is the important one



Reagents

Friedel-Crafts Alkylation $R-X, AlX_3$



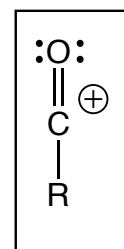
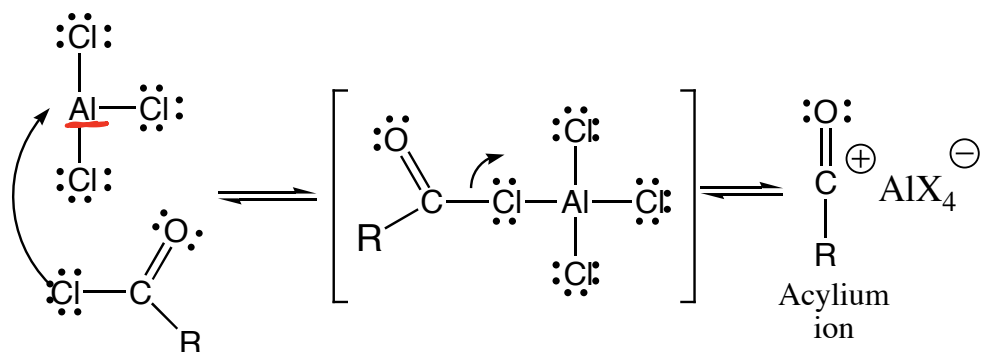
$X = Br, Cl$

Wicked strong electrophile

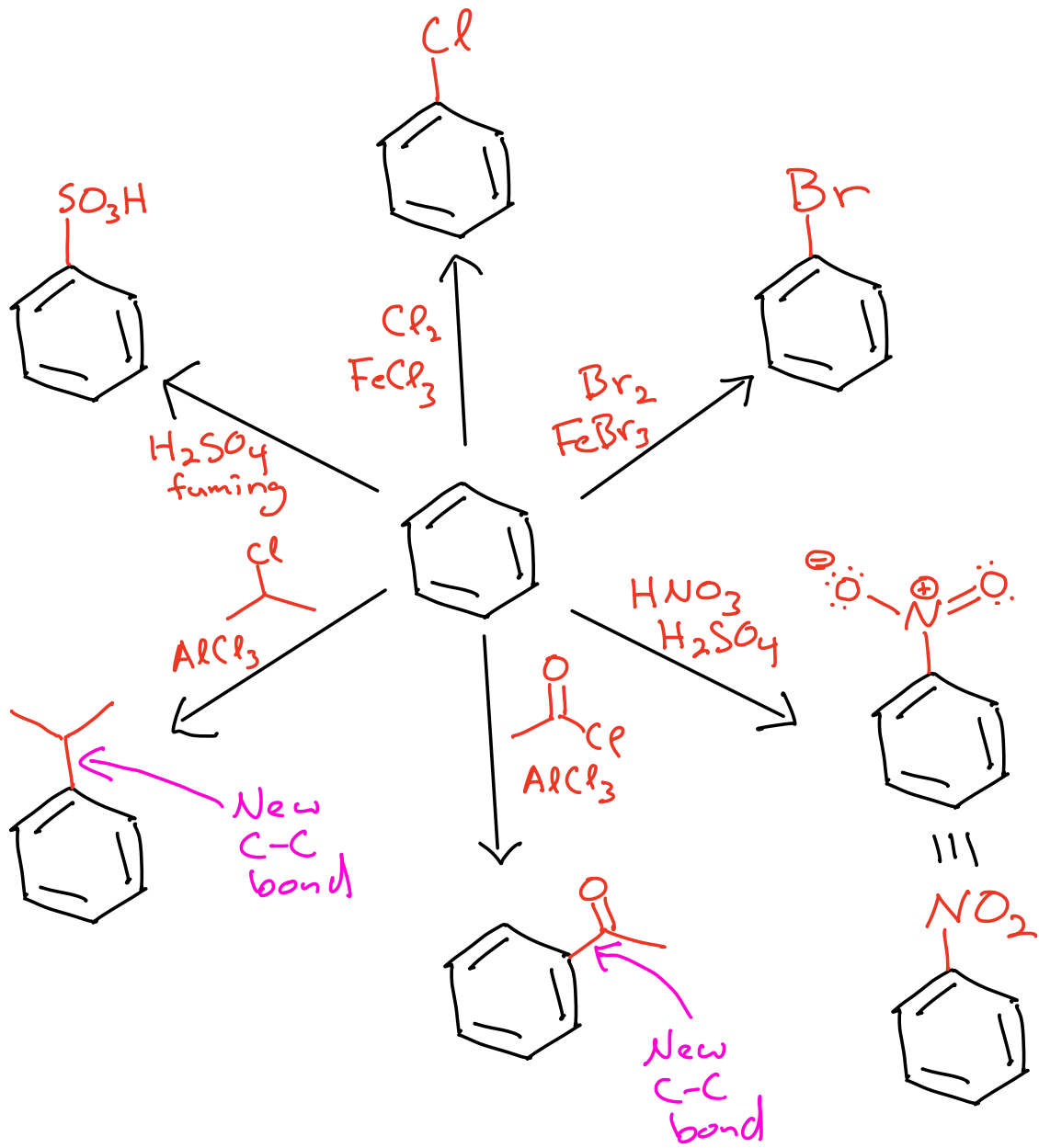


Note this is a carbocation, so it will rearrange if it is a primary or a rearrangement-prone secondary cation

Friedel-Crafts Acylation $RCOCl, AlCl_3$



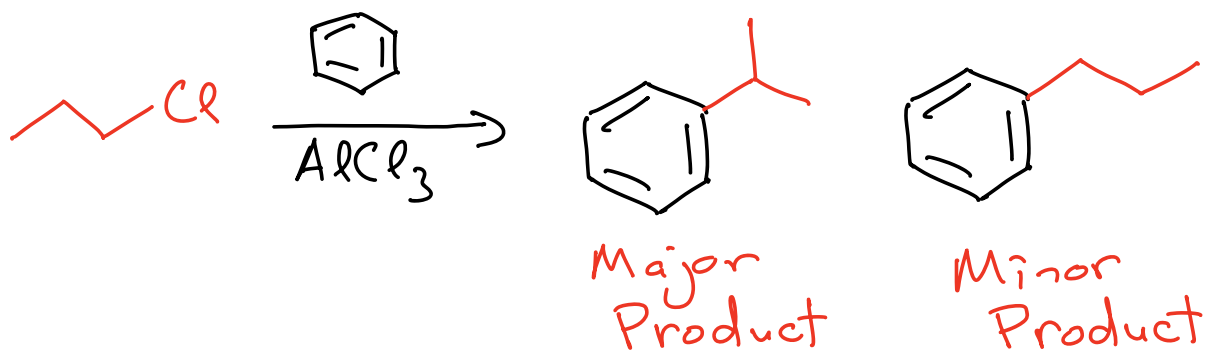
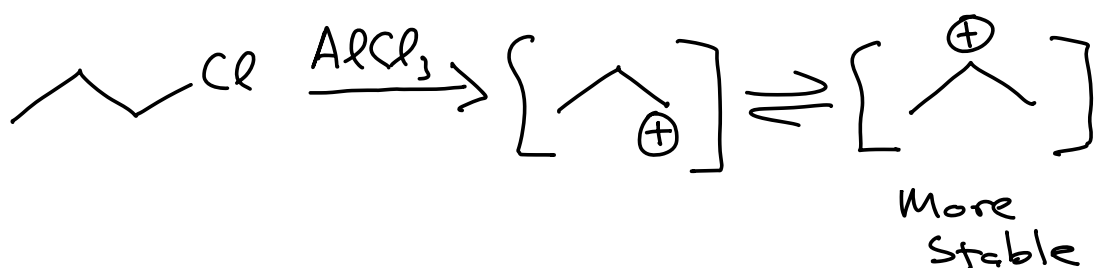
Other notes: 1) It is hard to stop the Friedel-Crafts alkylation after one alkyl group adds (because alkyl groups are "good", that is, activating), but it can be done. 2) Neither Friedel-Crafts reaction works if there is already an electron withdrawing (bad) group on the ring.



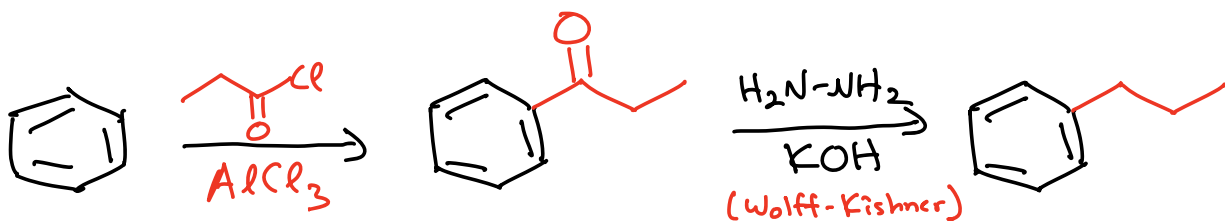
Friedel-Crafts Alkylations

Issue #1 → Carbocations rearrange!

Cannot use primary haloalkanes — they always rearrange!



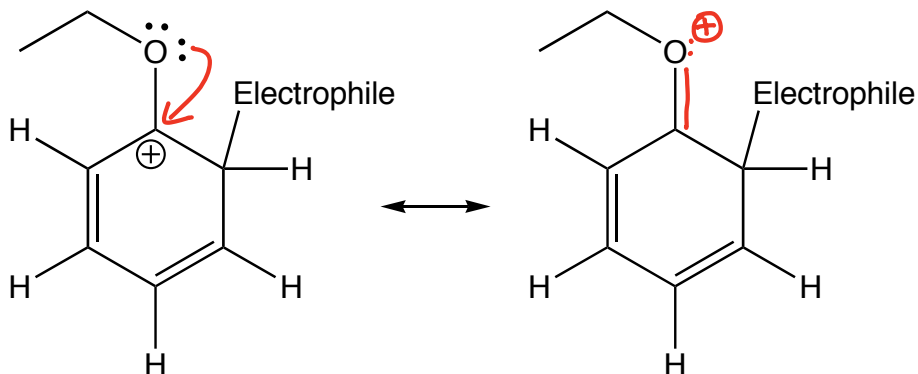
Workaround for primary alkyl group



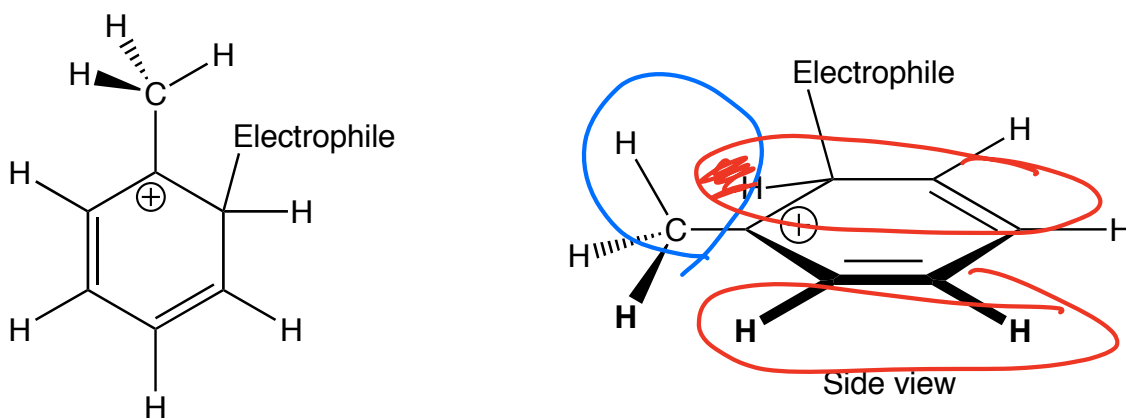
Issue #2 → Time capsule: Alkyl groups are GOOD groups, so it is difficult (but not impossible) to stop at the addition of one alkyl group.

Arenium ion *stabilizing* interactions ← GOOD

A) **Pi donation**, a resonance effect for atoms with lone pairs attached to the ring

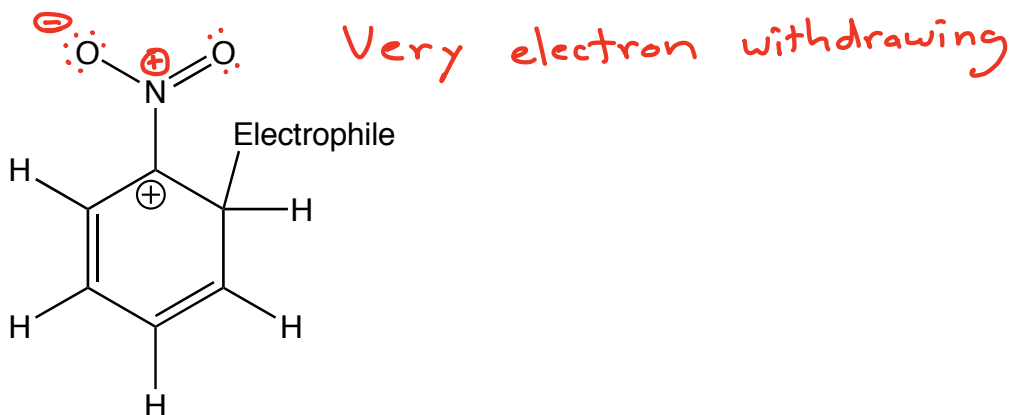


B) **Hyperconjugation** for alkyl groups attached to the ring



Arenium ion *destabilizing* interaction ← BAD

A) **Inductive effect** of electronegative atoms or groups attached to the ring



GOOD → Through π donation
or hyperconjugation
the arenium ion
is stabilized
Most effective ortho
and para

↓
Activating
Ortho-Para
Directing

Atoms attached to the ring
have a lone pair of electrons
or alkyl groups

BAD → Through the
inductive effect -
electron withdrawing
groups - the arenium
ion is destabilized
"Least bad" meta

↓
Deactivating
Meta directing

Mostly when the atom attached
to the ring has a π bond
or $-CX_3$ in which X is halogen

UGLY



Deactivating
Ortho-Para
Directing

→ Both GOOD and BAD
at the same time

→ Through pi donation
or hyperconjugation
the arenium ion
is stabilized

Most effective ortho
and para

→ Through the
inductive effect -
electron withdrawing
groups - the arenium
ion is destabilized

