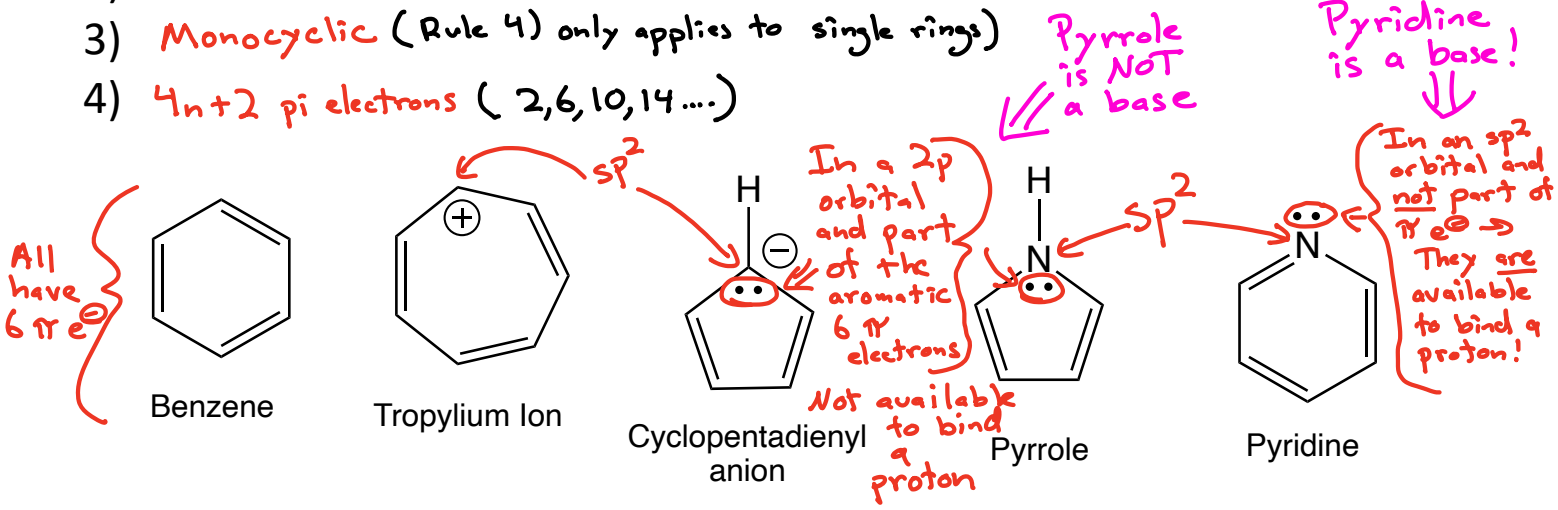
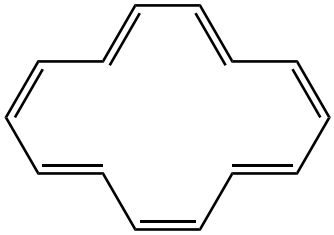
Hückel's Aromaticity Criteria

1) All ring atoms are sp^2 (they have a 2p orbital)
2) Flat (so the 2p orbitals overlap)
3) Monocyclic (Rule 4) only applies to single rings)
4) 4n+2 pi electrons (2, 6, 10, 14 ....)





Annulene

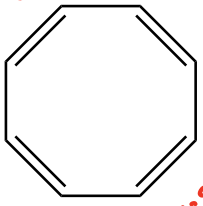
14 π electrons

4 π electrons

Not a stable molecule

Cyclobutadiene

8 π electrons



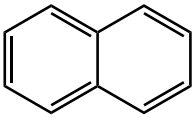
Folds so 2p orbitals do not overlap and avoids antiaromaticity

Cyclooctatetraene

Antiaromatic → These are much less stable than predicted as simple alkenes

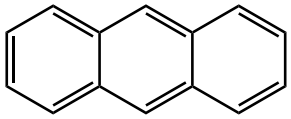
All fused benzene compounds are aromatic no matter the number of π electrons → Not monocyclic so Hückel's 4n+2 rule does not apply!

10 π electrons



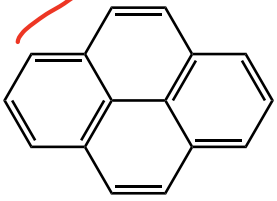
Naphtalene

14 π electrons



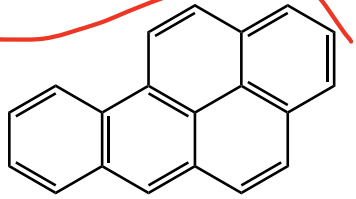
Anthracene

Still aromatic!



Pyrene

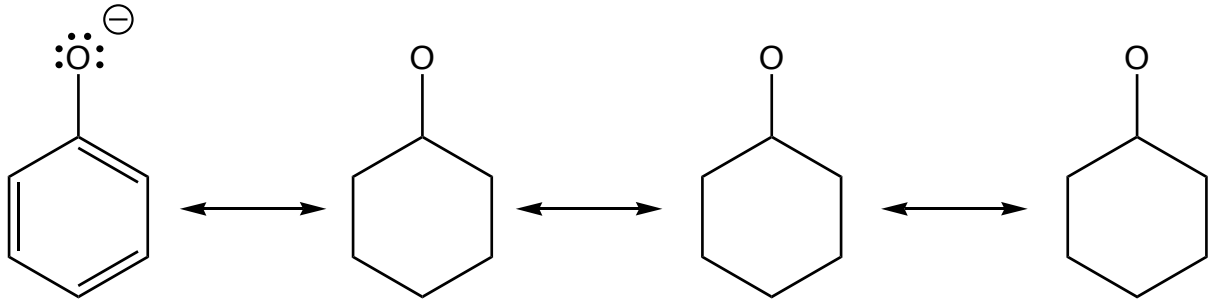
16 π electrons!



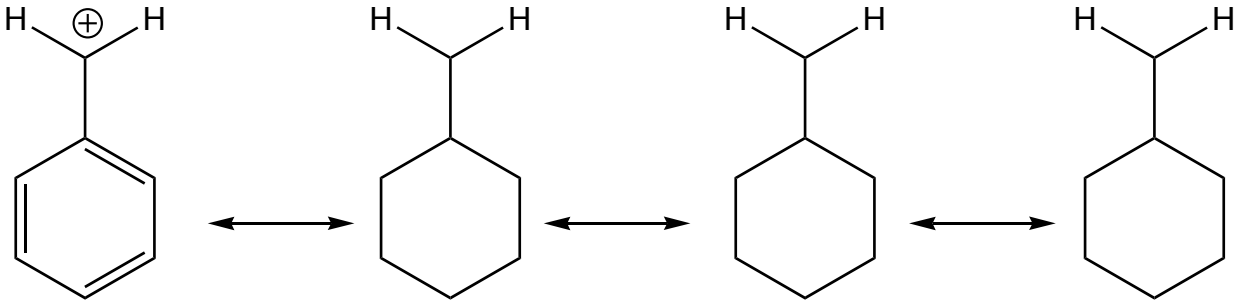
Benzo[α]pyrene

20 π electrons

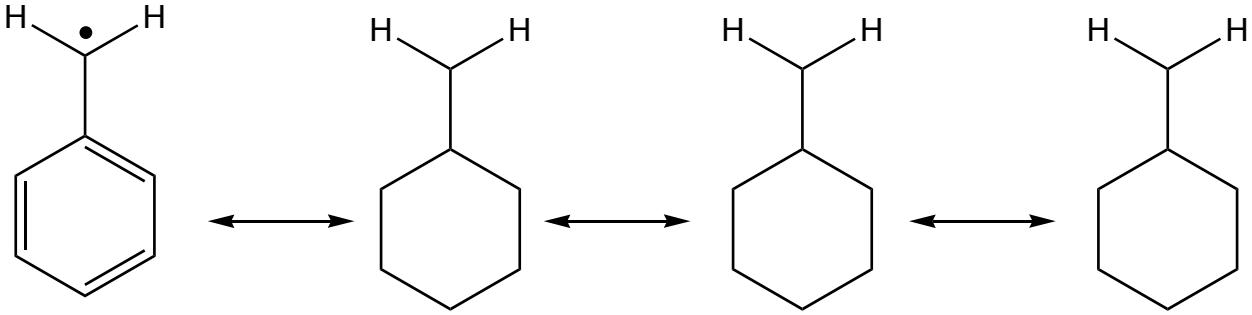
Aromatic resonance stabilization of charged species



Phenoxide anion



Benzyl cation



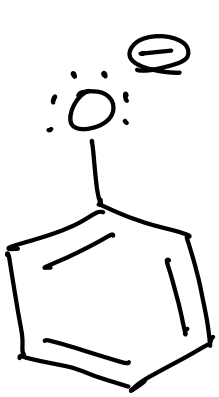
Benzyl radical

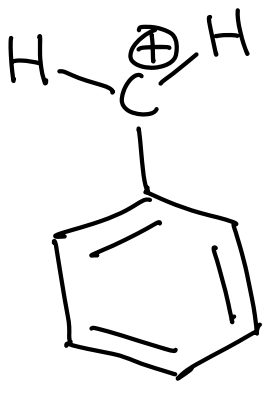
Important takeaways from the contributing structures

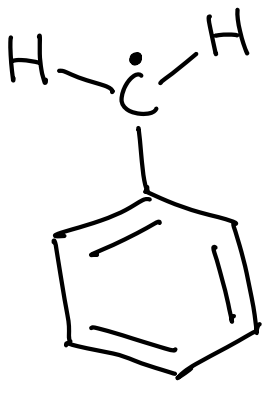
1) Benzene rings stabilize anions, cations and radicals

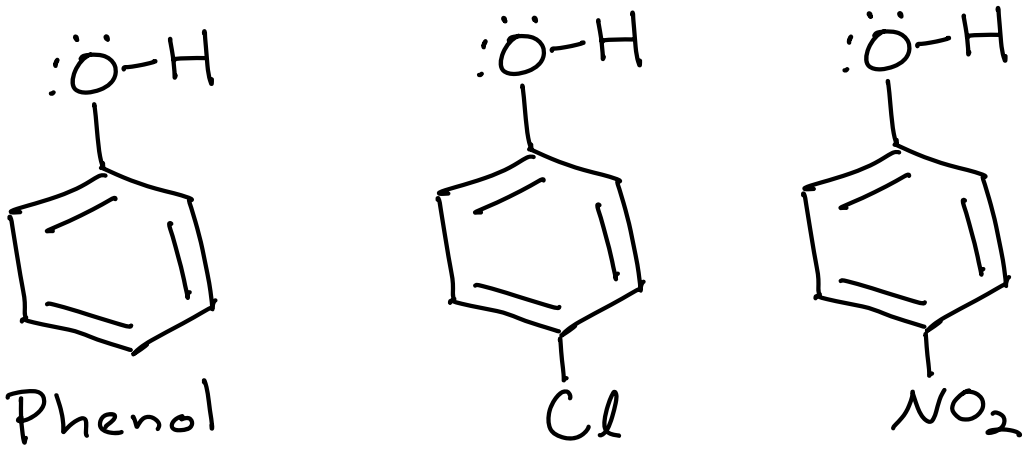
2) Molecules can have electrons on an atom outside the ring delocalized into the π system and the "extra" electrons do not count against the $4n+2$ number of π electrons

Summary →



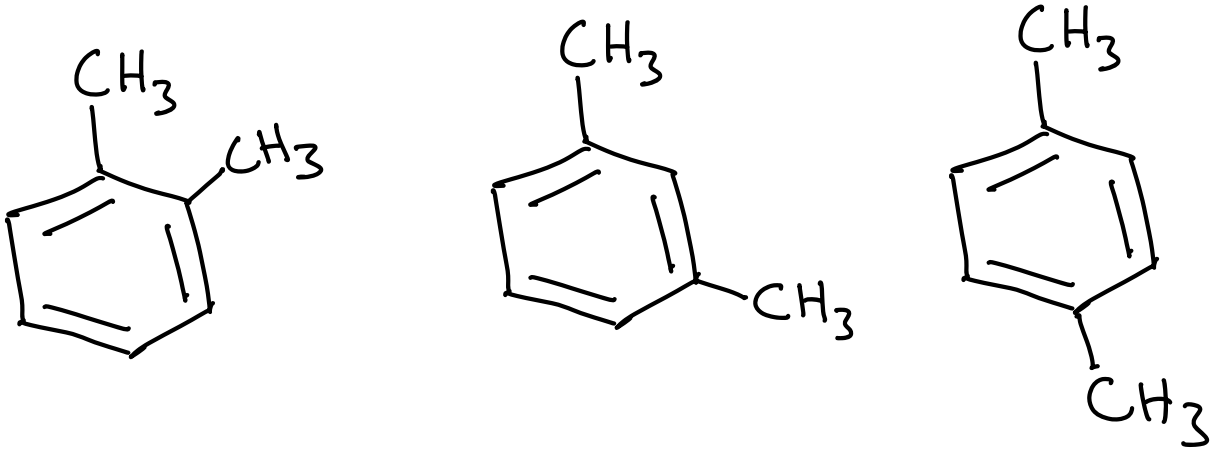




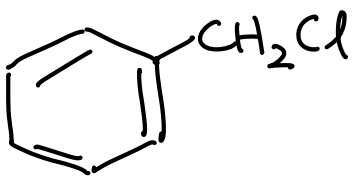


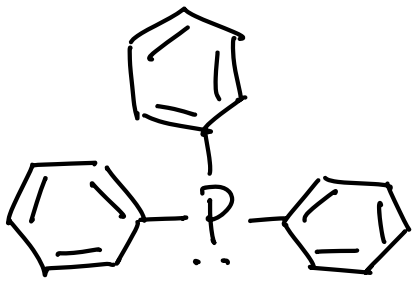
Electron withdrawing groups on the ring stabilize the deprotonated anion, making an OH group more acidic (Inductive effect)

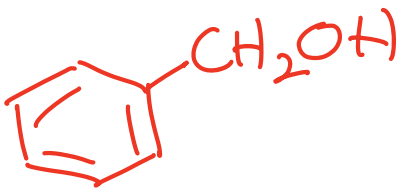
Important terms

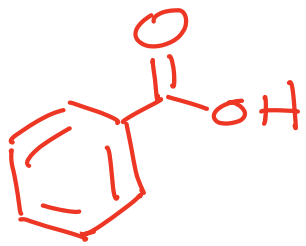


Benzyl vs. Phenyl

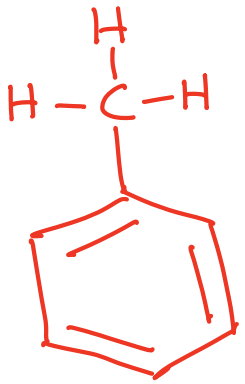




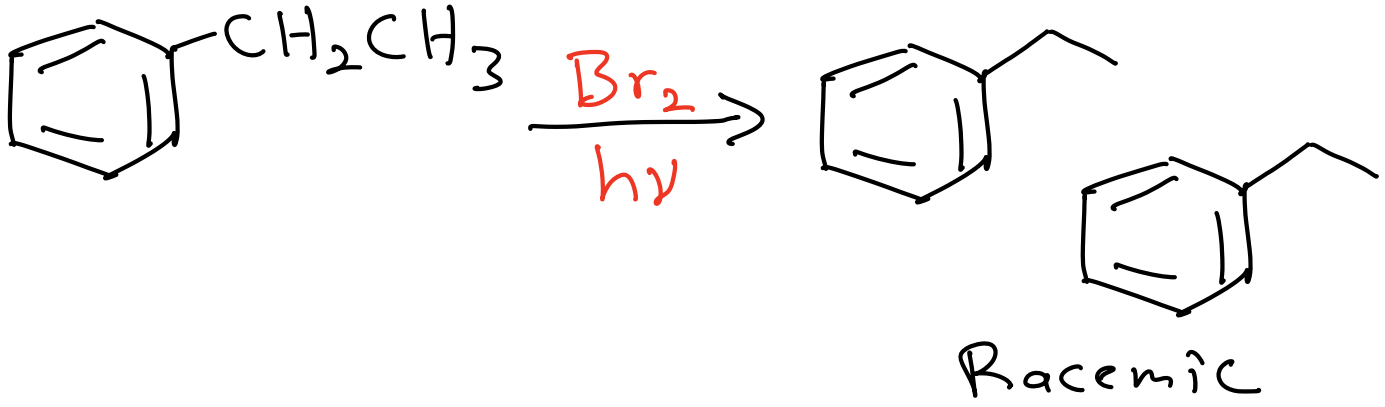




A carbon attached to a benzene ring has special reactivity so it has a special name — the benzyl carbon



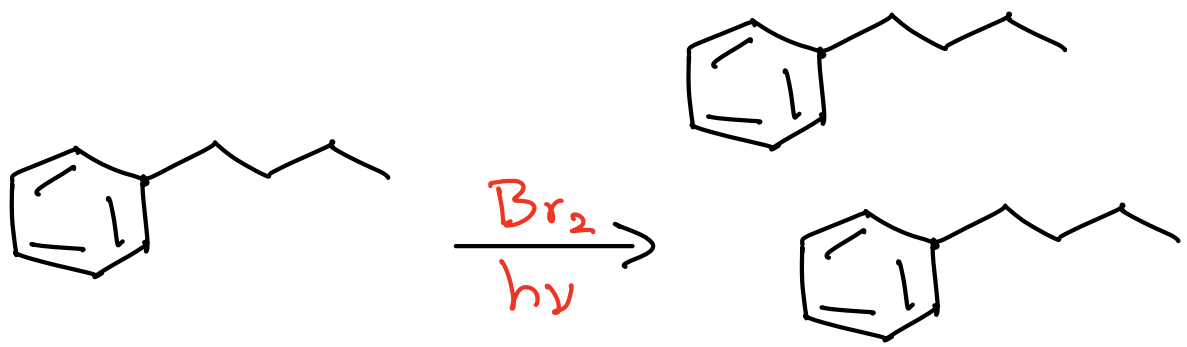
Free radical halogenation



Racemic

Radical Stability

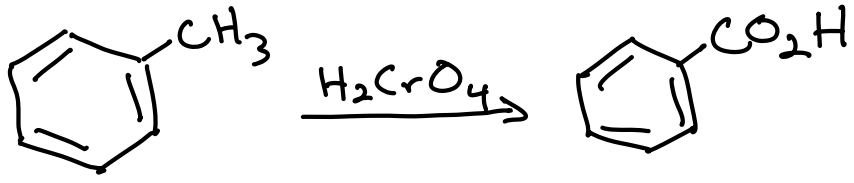
Methyl < 1° < 2° < 3° < Benzyl Radical

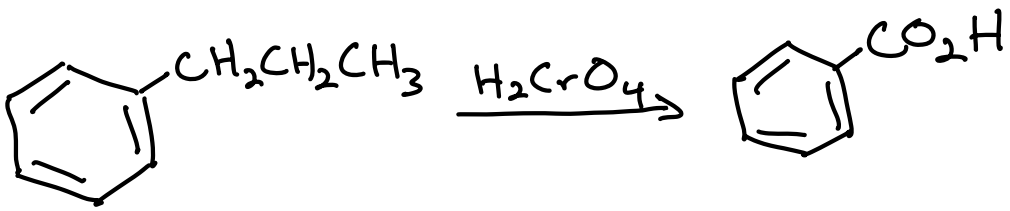


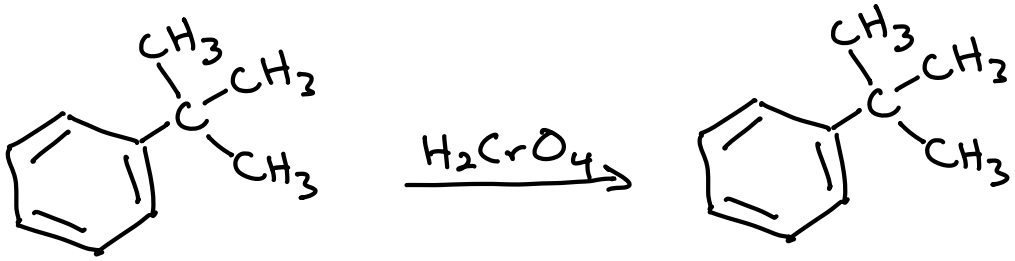
Racemic

Oxidation

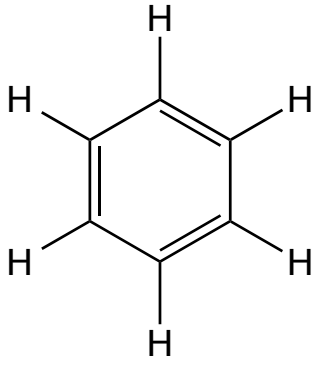
The benzylic carbon is easy to oxidize all the way to a carboxylic acid —



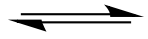


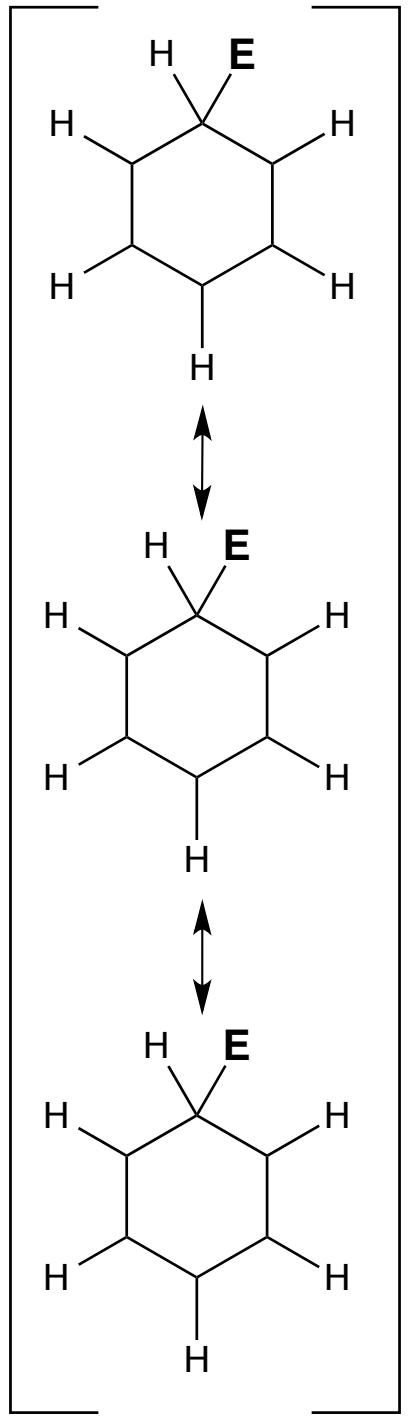


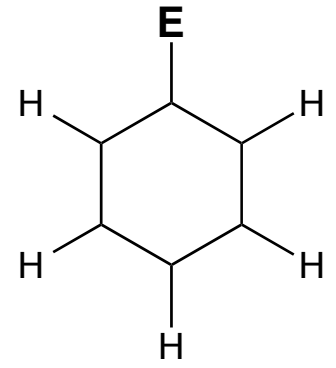
Wicked Strong Electrophile



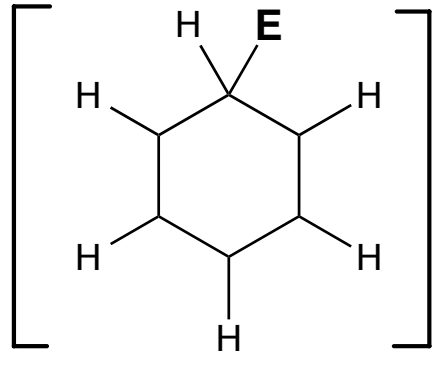
Weak Nucleophile







Called the Arenium Ion



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

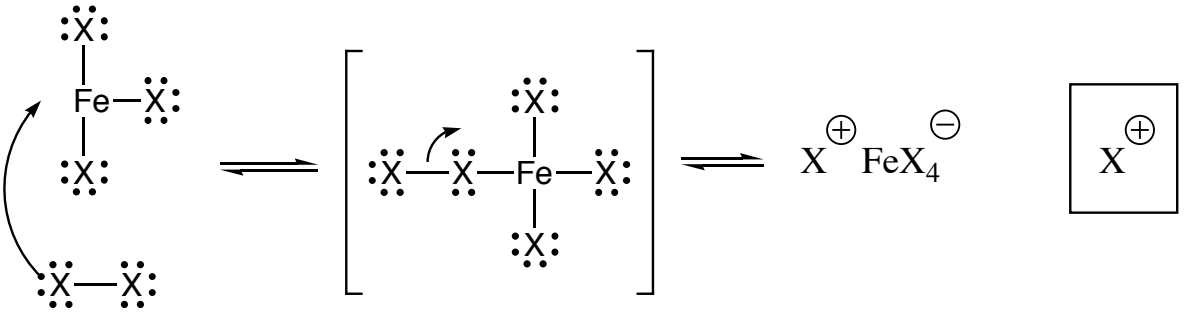
This reaction is called "Electrophilic Aromatic Substitution (EAS)"

Reagents

Wicked strong electrophile

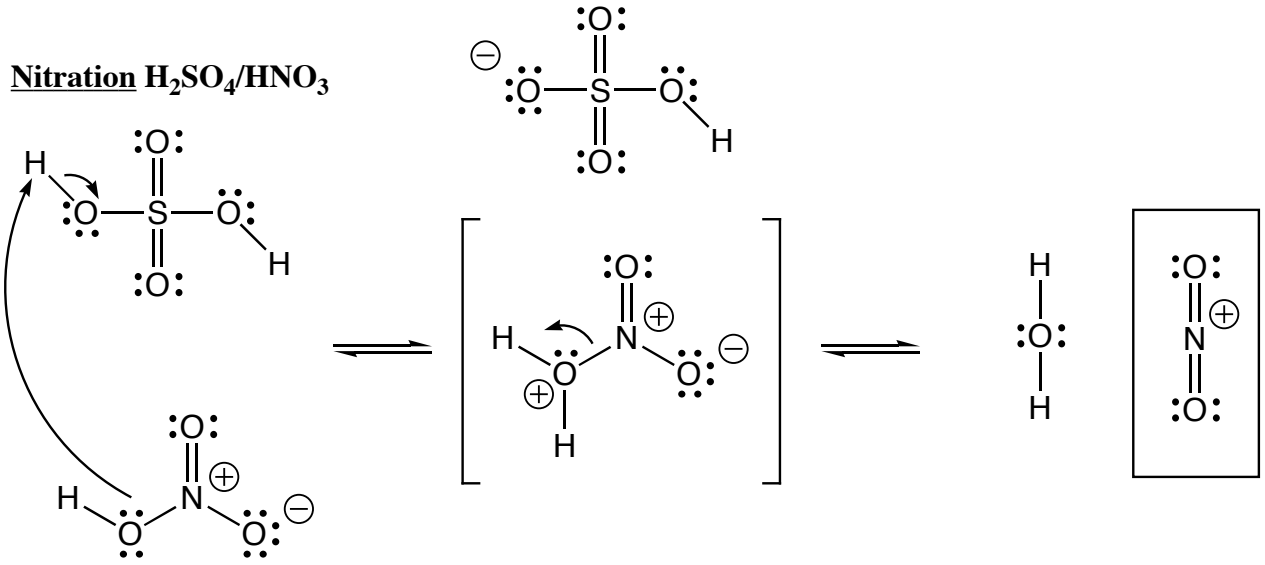
$\mathbf{E^{\oplus}}$

Halogenation $\mathbf{X_2, FeX_3}$



X = Br, Cl

Nitration $\mathbf{H_2SO_4/HNO_3}$



Sulfonation $\mathbf{H_2SO_4/SO_3}$

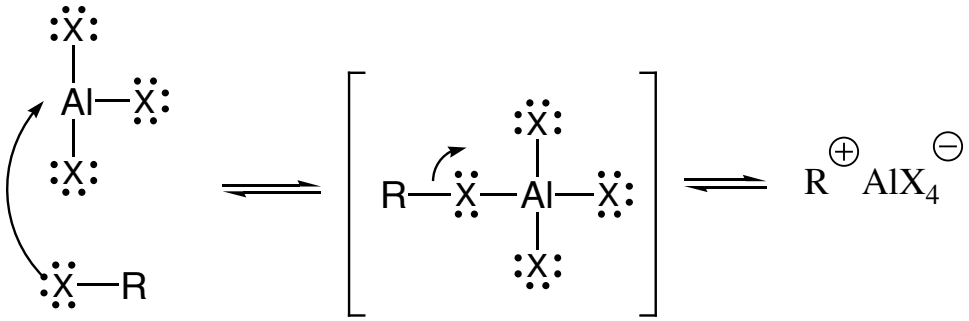
Fuming sulfuric acid contains both of the above reagents, the SO_3 is the important one

Reagents

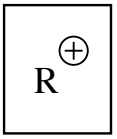
Wicked strong electrophile

$\underline{\mathbf{E}^{\oplus}}$

Friedel-Crafts Alkylation **R-X, AlX_3**

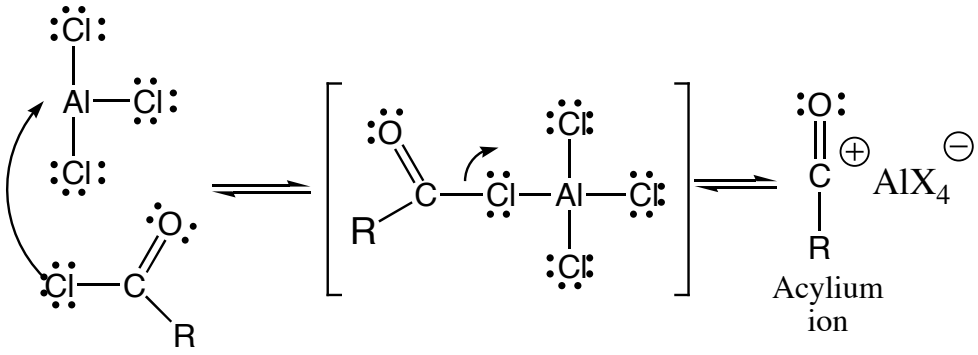


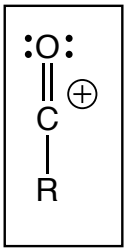
X = Br, Cl



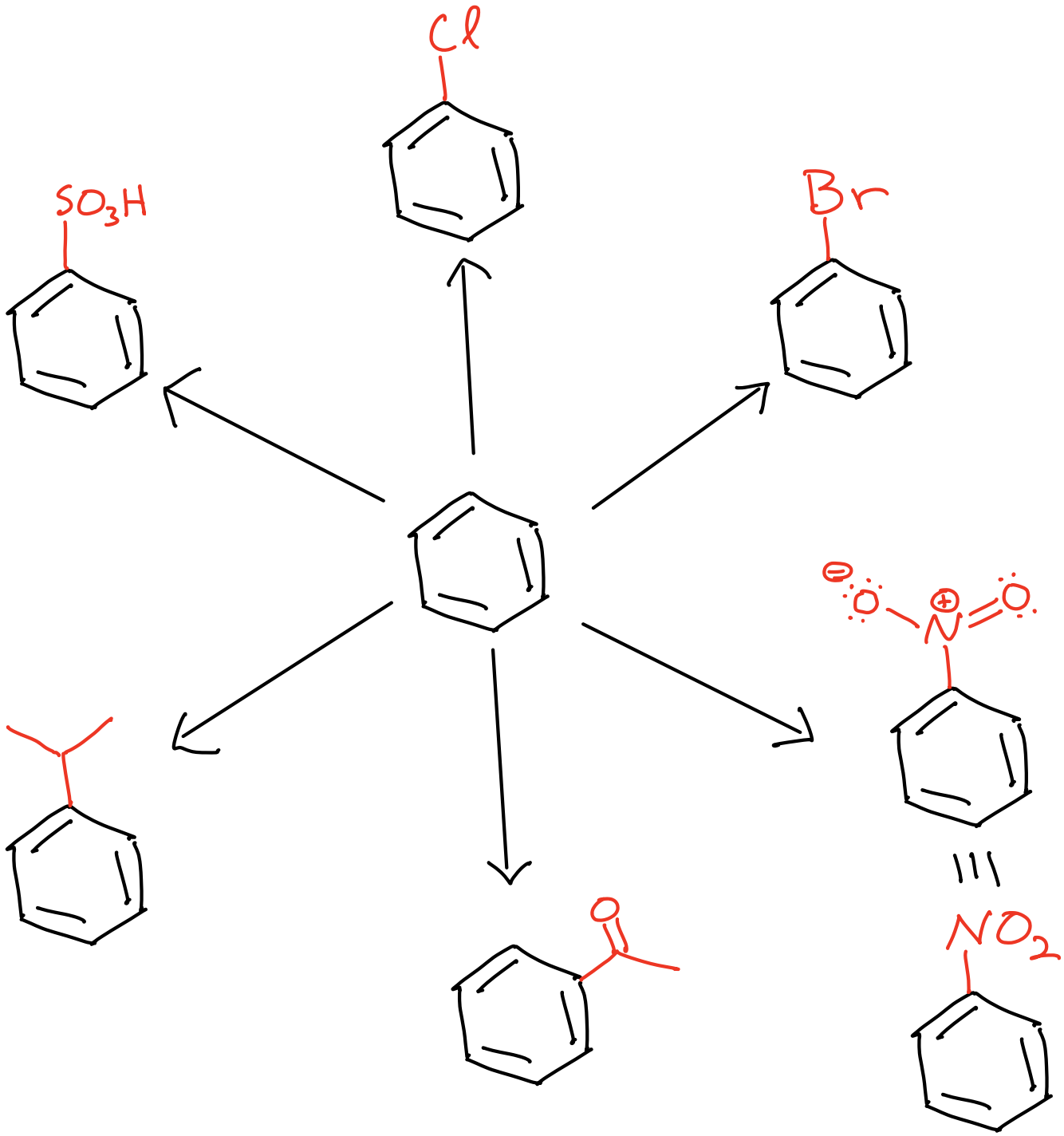
Note this is a carbocation, so it will rearrange if it is a primary or a rearrangment-prone secondary cation

Friedel-Crafts Acylation **RCOCl, $AlCl_3$**





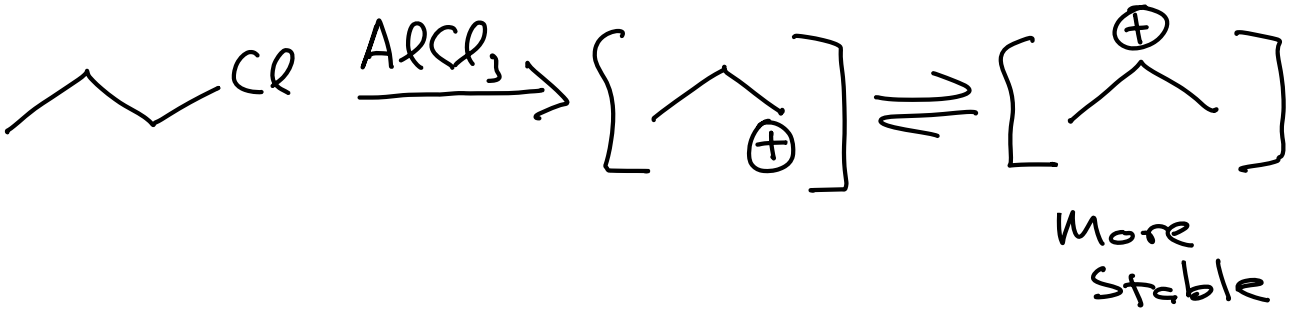
Other notes: 1) It is hard to stop the Friedel-Crafts alkylation after one alkyl group adds (because alkyl groups are "good", that is, activating), but it can be done. 2) Neither Friedel-Crafts reaction works if there is already an electron withdrawing (bad) group on the ring.

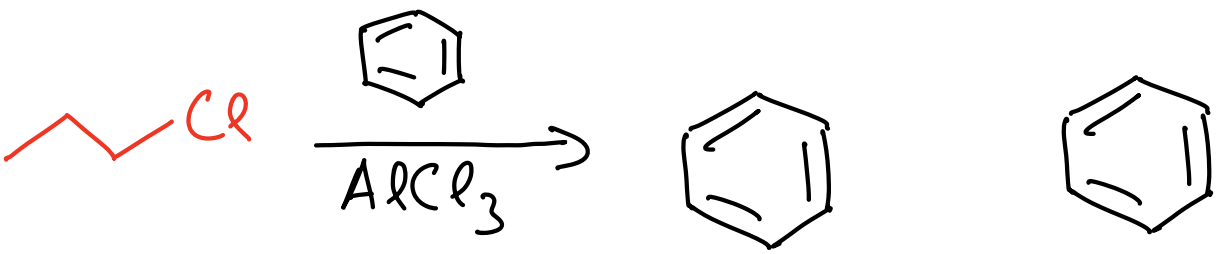

Cl
SO3H
Br
NO2

Friedel-Crafts Alkylations

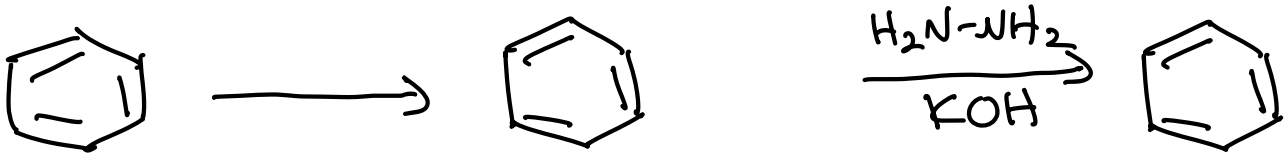
Issue #1 →

Cannot use primary haloalkanes —





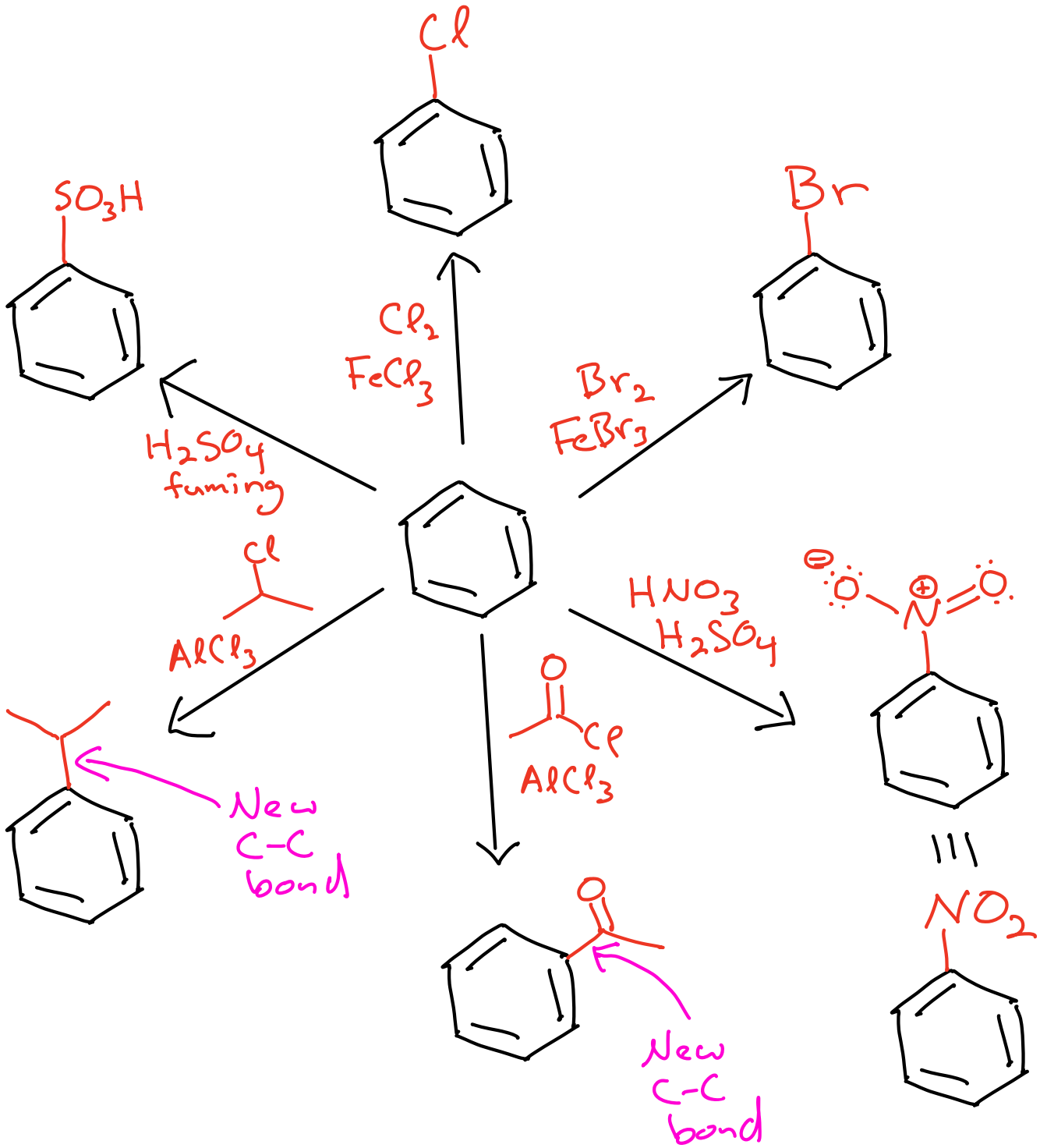
Workaround for primary alkyl group

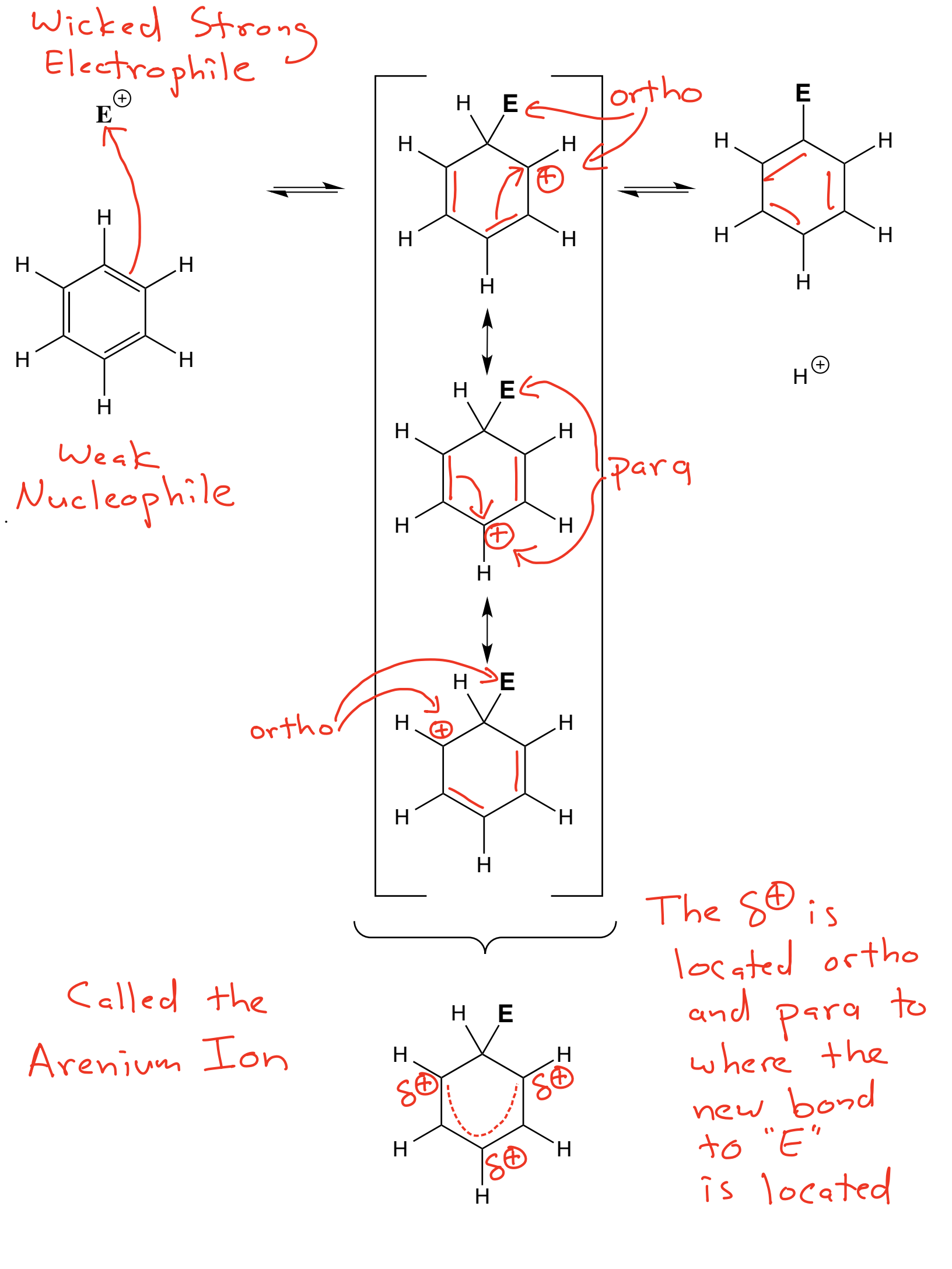


* Acylium ions do NOT rearrange!

Issue #2 → Time capsule: Alkyl groups are GOOD groups,

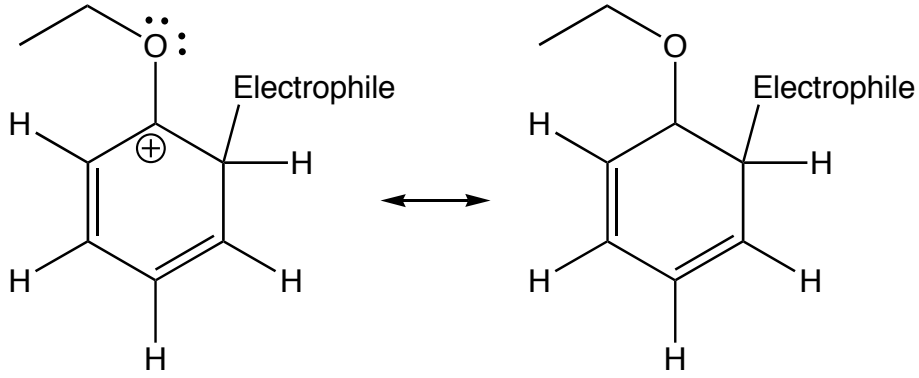
Issue #3 → Time capsule: Neither the Friedel-Crafts alkylation or acylation will work if


Cl
Cl_2
$FeCl_3$
SO_3H
H_2SO_4
fuming
Br
Br_2
$FeBr_3$
Cl
$AlCl_3$
HNO_3
H_2SO_4
O
Cl
$AlCl_3$
New
C-C
bond
O
New
C-C
bond
NO_2

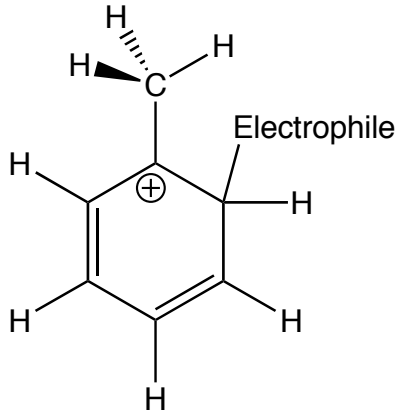

Wicked Strong Electrophile
E⊕
Weak Nucleophile
ortho
para
ortho
H⊕
Called the Arenium Ion
δ⊕
The δ⊕ is located ortho and para to where the new bond to "E" is located

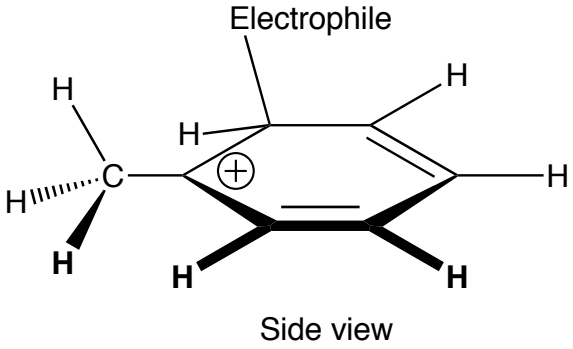
Arenium ion ***stabilizing*** interactions

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



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

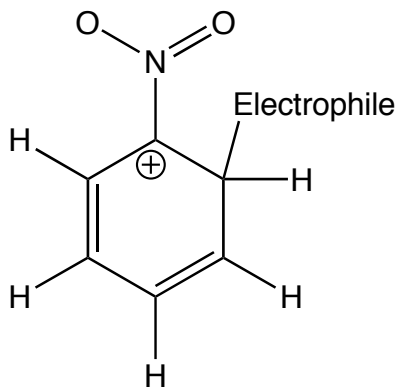




Side view

Arenium ion ***destabilizing*** interaction

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

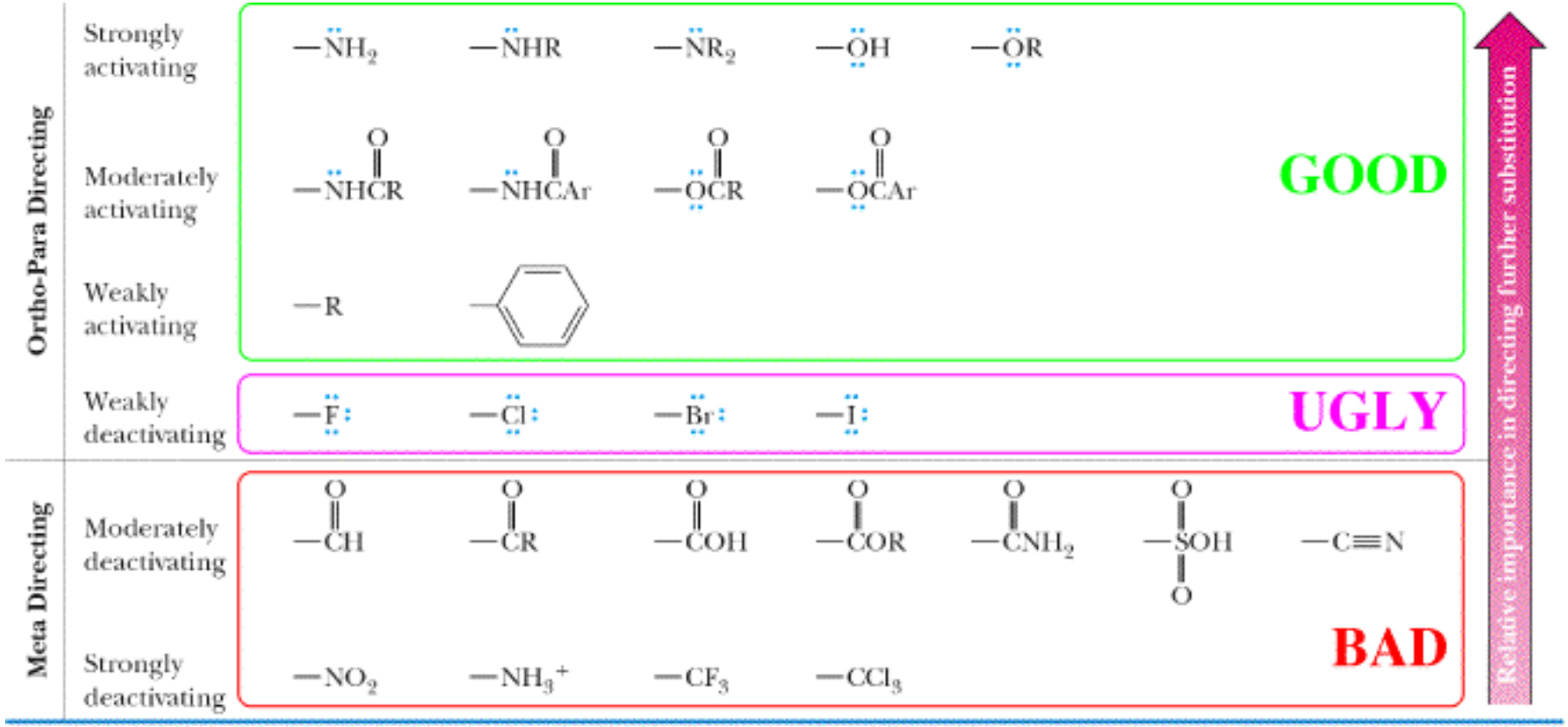


GOOD → Through pi donation or hyperconjugation the arenium ion is stabilized

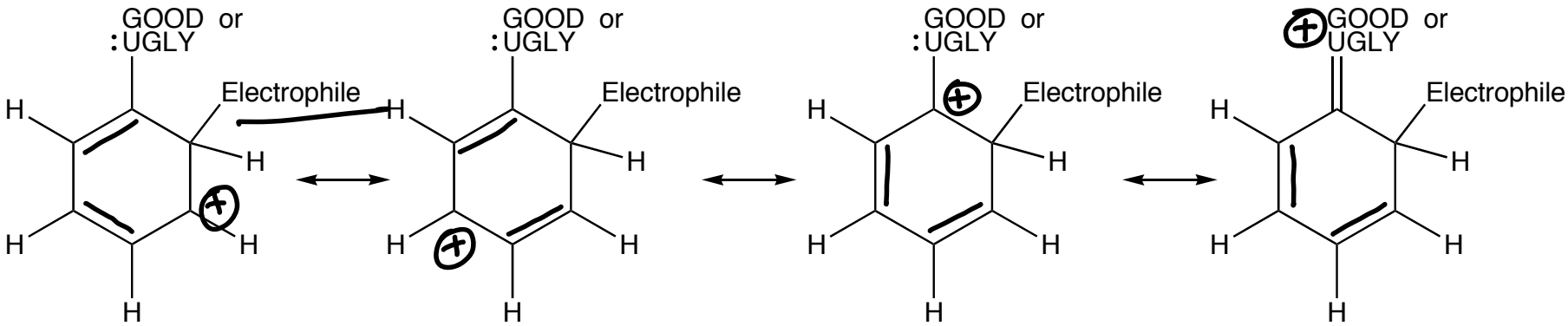
BAD ⟶ Through the inductive effect - electron withdrawing groups - the arenium ion is destabilized

UGLY

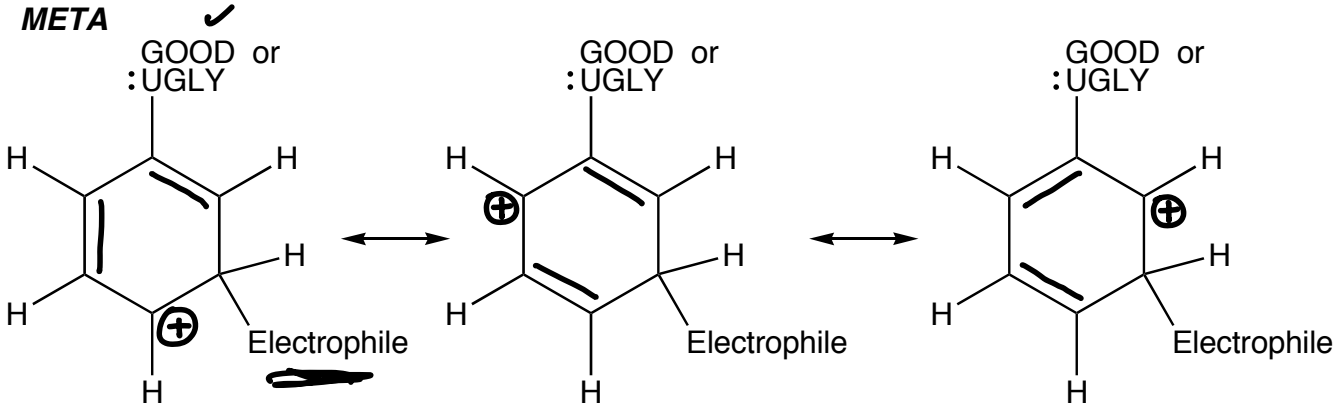
- Both GOOD and BAD at the same time
- Through pi donation or hyperconjugation the arenium ion is stabilized
- Through the inductive effect- electron withdrawing groups- the arenium ion is destabilized


Ortho-Para Directing
Meta Directing
Strongly activating
Moderately activating
Weakly activating
Weakly deactivating
Moderately deactivating
Strongly deactivating
—NH2
—NHR
—NR2
—OH
—OR
—NHCR
—NHCAr
—OCR
—OCAr
—R
—F:
—Cl:
—Br:
—I:
—CH
—CR
—COH
—COR
—CNH2
—SOH
—C≡N
—NO2
—NH3+
—CF3
—CCl3
GOOD
UGLY
BAD
Relative importance in directing further substitution

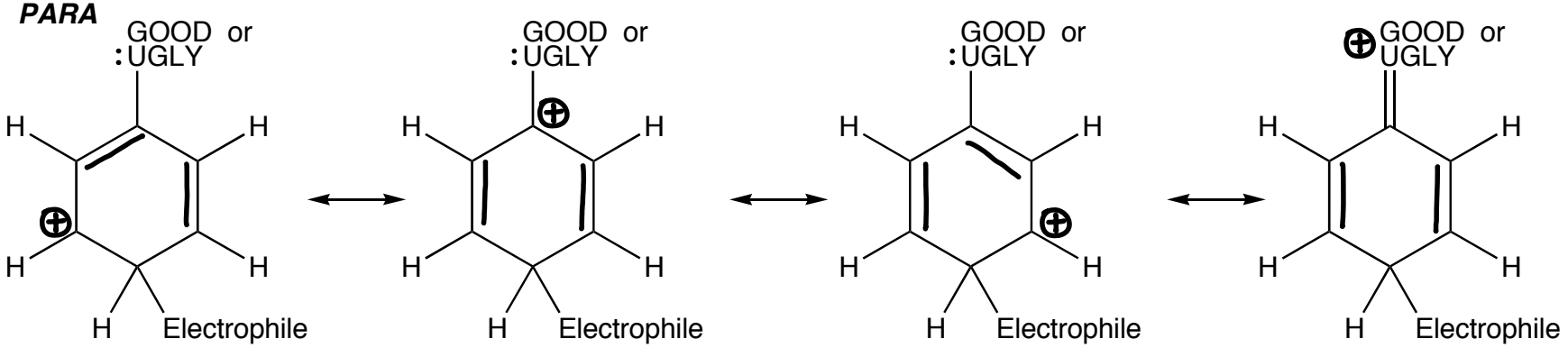
ORTHO



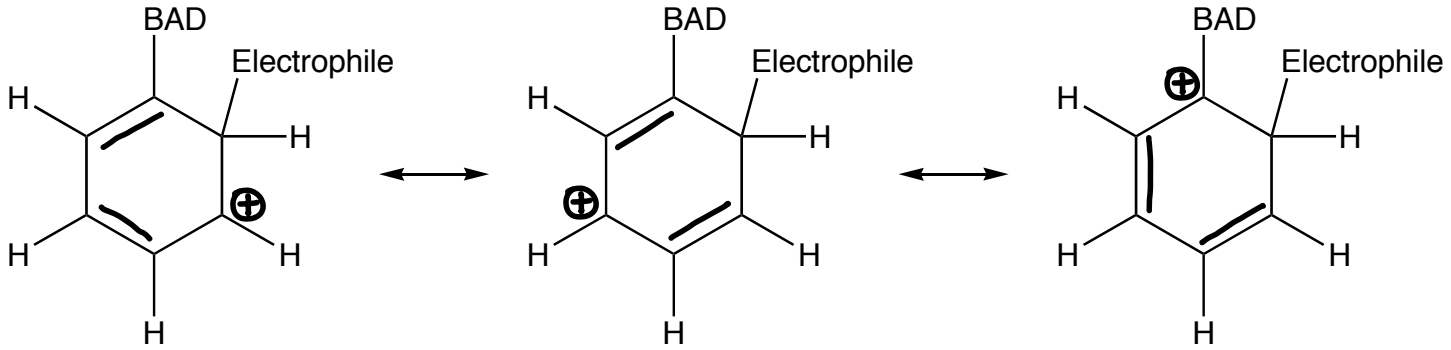
META



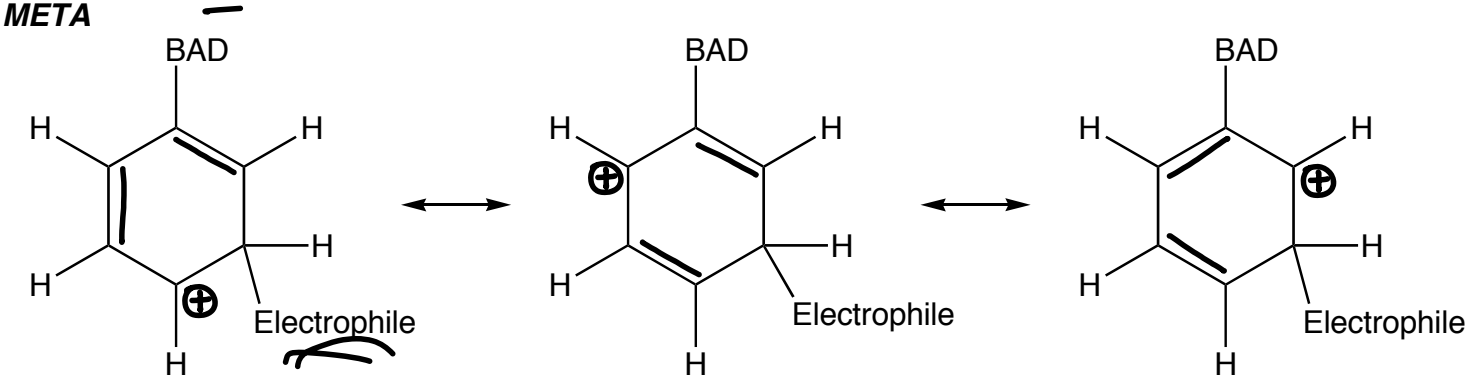
PARA



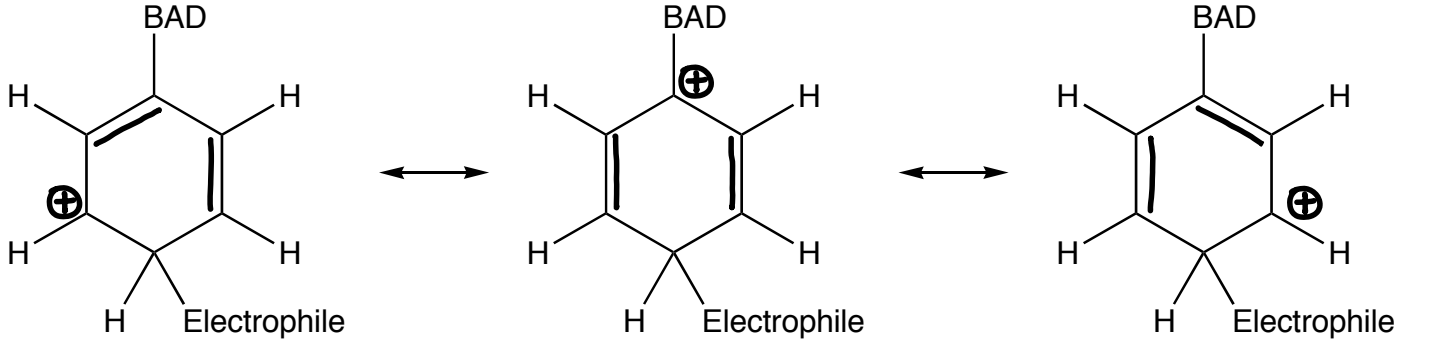
ORTHO

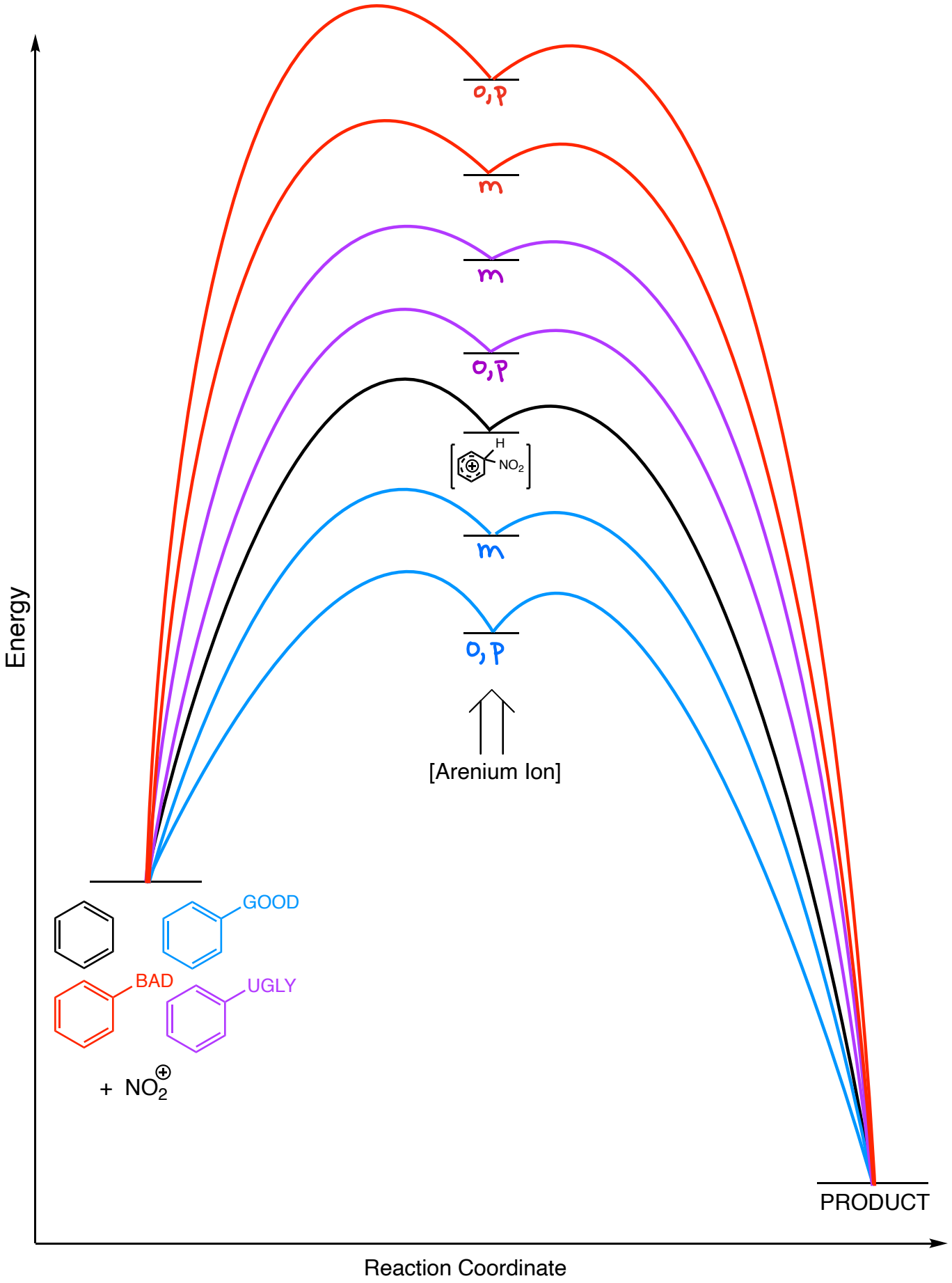


META

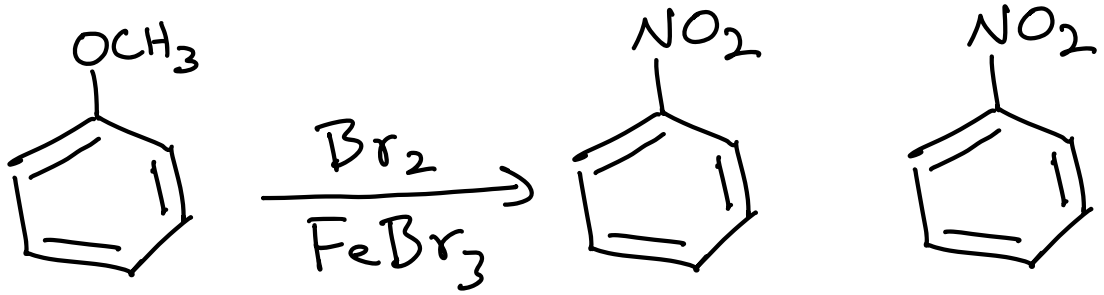


PARA

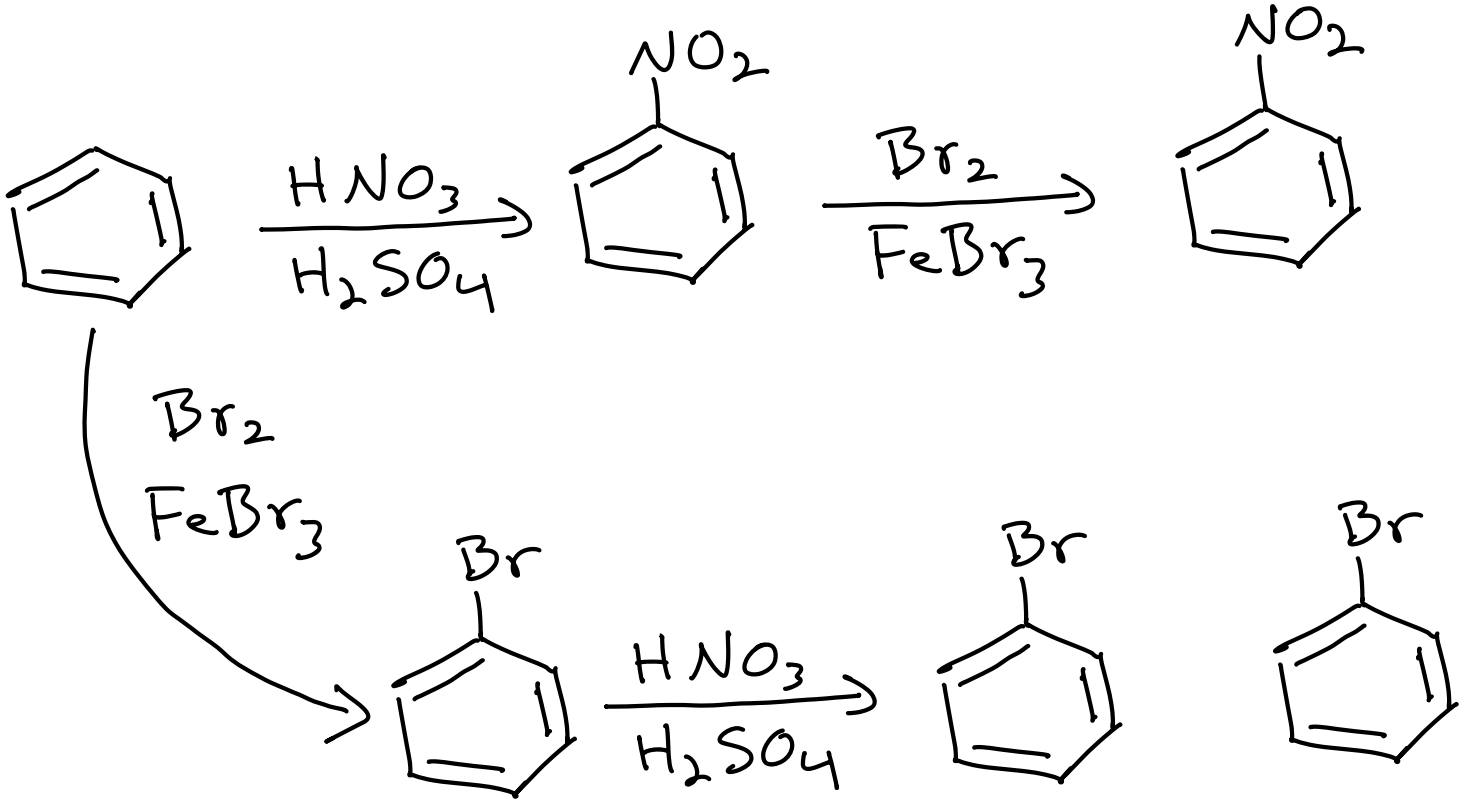



o,p
m
m
o,p
H
NO2
m
o,p
[Arenium Ion]
GOOD
BAD
UGLY
+ NO2⊕
PRODUCT
Energy
Reaction Coordinate

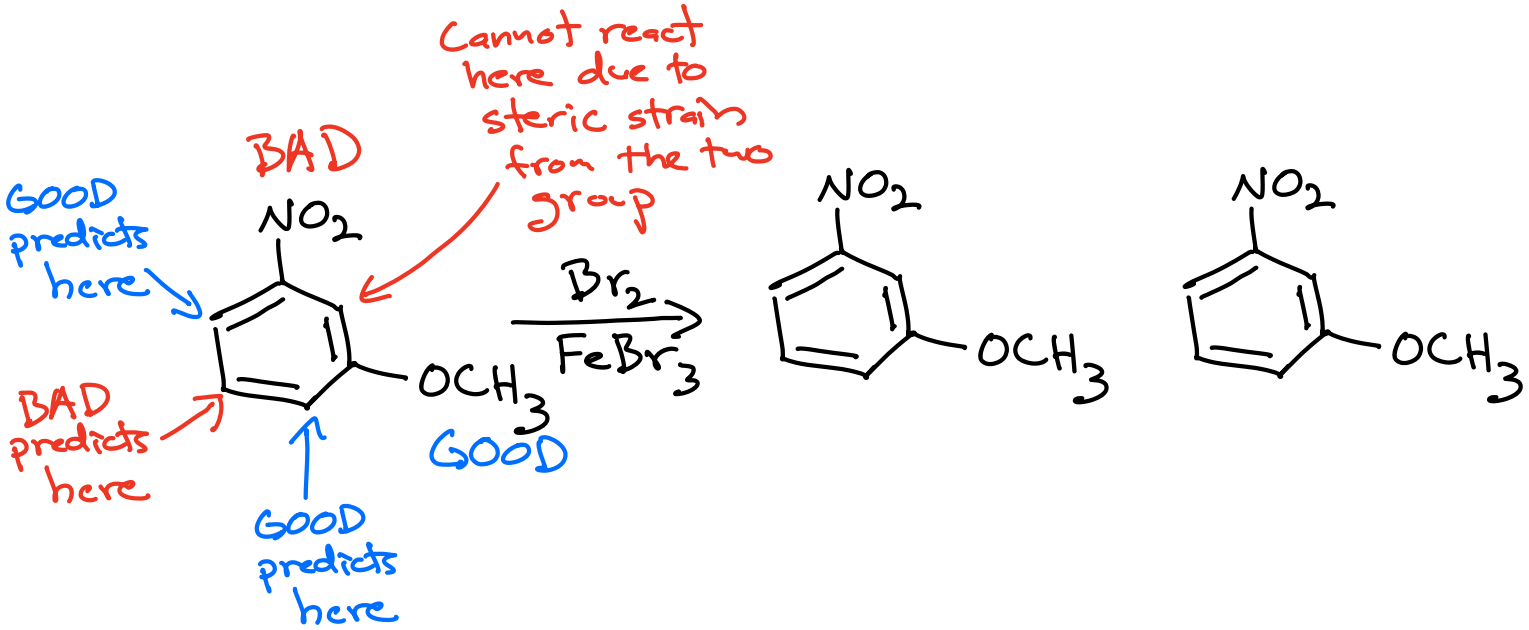
Examples

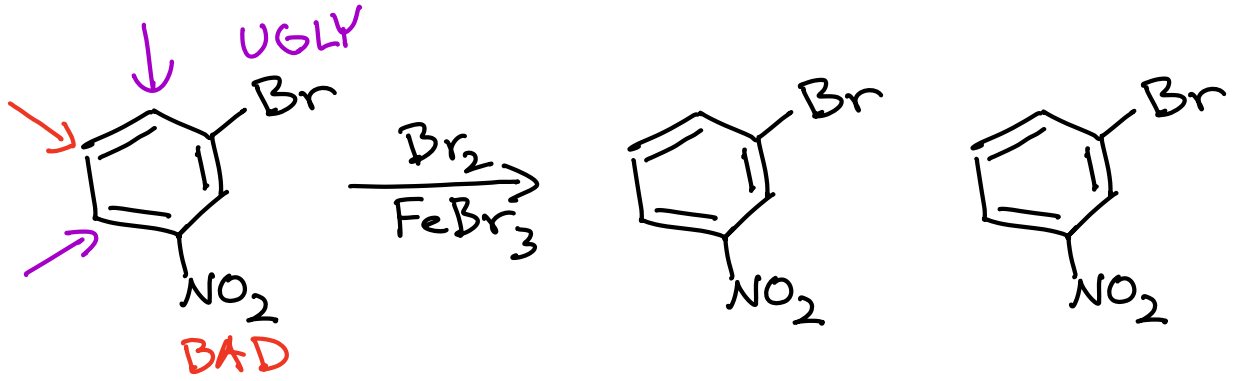


The order in which you add groups matters!

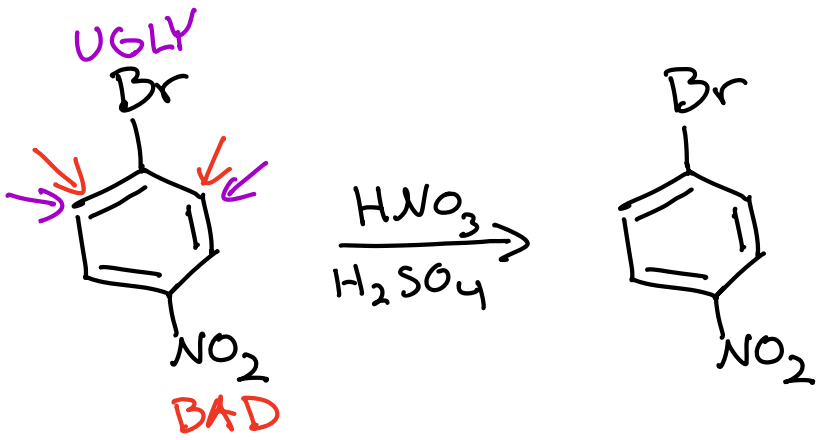


What if there are two groups already on the ring and they predict different products? It is a duel → the movie got it right!





Sometimes two groups will predict the same outcome



Classic Question