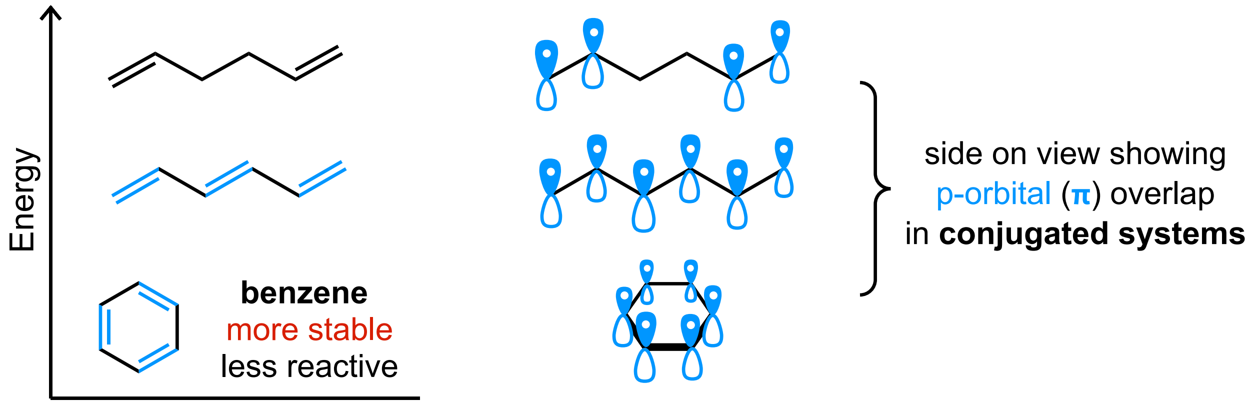
Aromaticity and Benzene Reactivity

This page will connect the concept of aromaticity to ideas you have already seen related to resonance, stability, and reactivity.



The bottom Lewis structures show alternating C-C and C=C bonds, referred to as a **conjugated π system** (**π** electrons are delocalized).

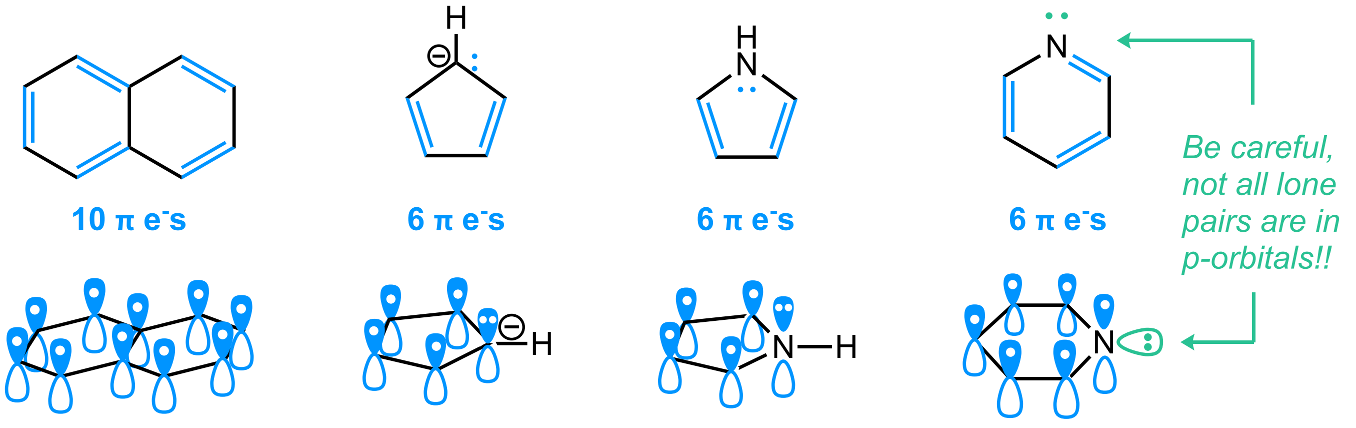
Benzene though, is ***more stable*** than its open chain counterpart. This enhanced stability is referred to as ***aromaticity***.

Aromatic systems can be identified by the criteria shown below:

- **cyclic** system
- continuous overlapping p-orbitals; requires planar (flat) shape
- Huckel's Rule: 4n + 2 = **π e^-s** (must solve n with a whole number)

What qualifies as a **π e^-**? ***Delocalized e^- that exists in a p-orbital***

Examples of aromatic systems

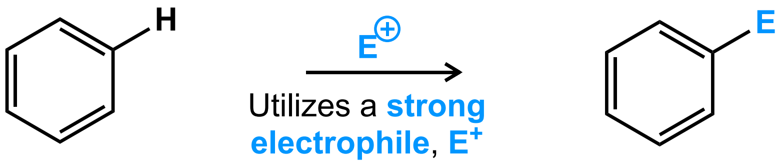


In general, although aromatic systems *have* **π** e^-s, their increased stability prevents them from undergoing addition reactions. **Many aromatic systems instead undergo unique substitution reactions, instead of addition reactions.** The reactivity of aromatic systems (focused on benzene) is detailed on the following pages.

EAS Reactions

Electrophilic Aromatic Substitution

Net EAS reaction: E^+ substitutes for H



nucleophile

Utilizes a **strong electrophile**, E^+ (formed using Lewis or Brønsted acid catalyst)

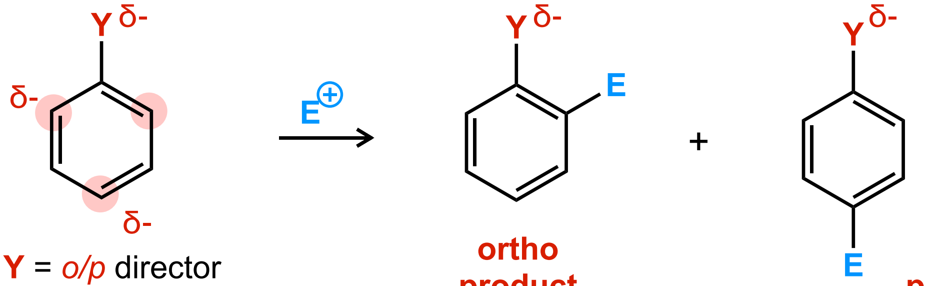
EAS proceeds through an addition-elimination process to yield a net substitution reaction

EAS is strongly impacted by the directing effects of existing groups on ring

A. Summary of **directing effects** in **EAS** reactions (an example of **regioselectivity**)

Common *o/p* directors - (typically an EDG)

1. Alkyl groups (R)
2. groups with a lone-pair bearing atom connected to the benzene ring



Y = *o/p* director

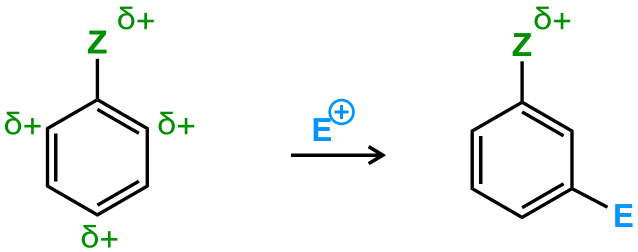
ortho product

para product

para product is generally preferred

Common *m* directors (typically an EWG)

1. Groups with a positive charge (full or partial) on the atom directly attached to benzene ring

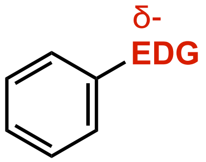


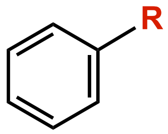
Z = *m*-director

meta product

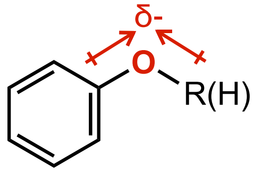
B. Summary of **rate effects** in **EAS** reactions (activating / deactivating)

Electron donating groups (**EDG**) activate **EAS** reactions; increase rate
common examples:

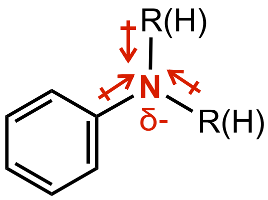




alkyl groups

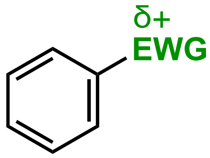


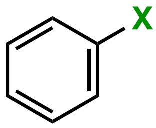
alcohols and ethers



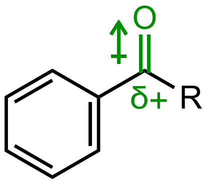
amines

Electron withdrawing groups (**EWG**) ***de*activate** **EAS** reactions; decrease rate
common examples:

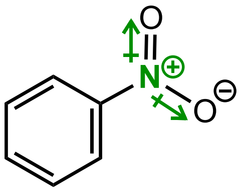




halogens



carbonyls

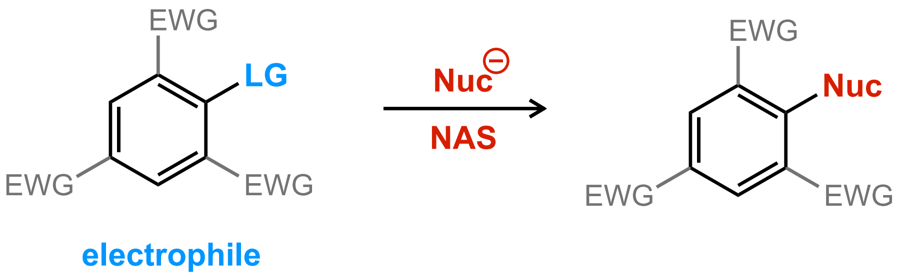


nitro

NAS (S_NAr) Reactions

Nucleophilic Aromatic Substitution

Net NAS reaction: **Nuc** substitutes for **LG**
where **LG** ability (F > Cl > Br > I)



NAS typically through an addition-elimination process to yield a net substitution reaction

Works best for: benzene with EWGs *o*- or *p*- to the LG

Note that this effect is the reverse of **EAS** reactions because the benzene ring acts as an **electrophile** in an **NAS** reaction and therefore prefers **EWG**s (like NO_2 or CF_3).

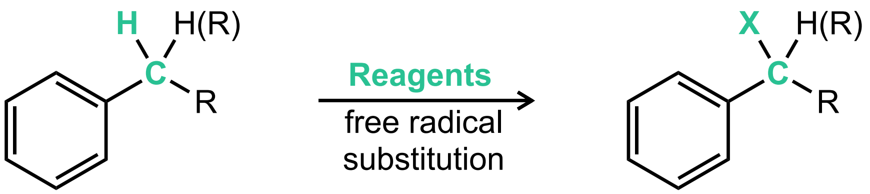
Benzylic Reactions

Benzene rings also enhance the rate of reaction at **benzylic** positions = C(sp^3) adjacent to the benzene ring.

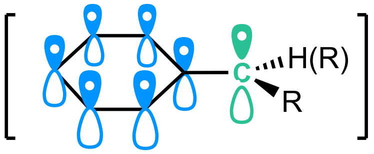
Commonly, **benzylic C—H bonds can be oxidized or reacted in a free radical substitution reaction.**

The presence of the benzylic C—H bond is key to the success of these reactions.

Benzylic Halogenation



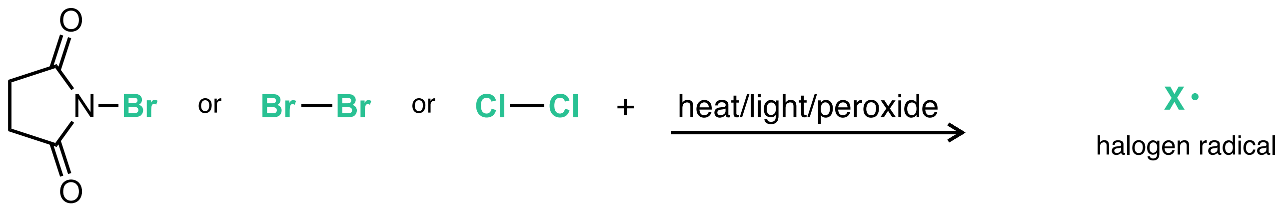
X = Br or Cl



Radical intermediate stabilized through resonance

Reagents for benzylic halogenation

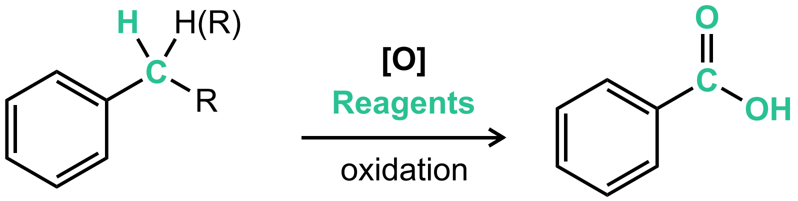
Radical halogenation can be conducted using either NBS, Br_2, or Cl_2 in the presence of heat, light, and/or peroxide to initiate the formation of a halogen radical



NBS

Benzylic Oxidation

Creates a carboxylic acid regardless of the R group, as long as at least 1 benzylic C—H is present



Reagents for benzylic oxidation

$KMnO_4$ or Na_2CrO_7, H_2SO_4