

a halogen on carbon sets up a leaving group, and everything else follows from how well it leaves

Haloalkane vs haloarene

Haloalkane (alkyl halide)

- halogen on an sp^3 carbon, e.g. $\text{CH}_3\text{CH}_2\text{Cl}$
- C-X bond is a normal sigma bond, halogen lone pairs not delocalised
- undergoes nucleophilic substitution readily

Haloarene (aryl halide)

- halogen on an sp^2 aromatic carbon, e.g. chlorobenzene
- halogen lone pair conjugates into the ring, C-X gets partial double-bond character
- resists nucleophilic substitution under ordinary conditions, needs forcing conditions

the same halogen behaves completely differently depending on whether the carbon it sits on is sp^3 or aromatic sp^2

Classification and nomenclature *

- primary (1°): halogen carbon attached to one other carbon; secondary (2°): two; tertiary (3°): three
- allylic halide: halogen on the carbon next to a $\text{C}=\text{C}$ double bond; benzylic halide: halogen on the carbon next to an aromatic ring
- IUPAC name treats halogen as a substituent prefix: chloro, bromo, iodo, fluoro, cited alphabetically with other substituents
- vinyl halide: halogen directly ON a double-bond carbon ($\text{C}=\text{C}-\text{X}$); like aryl halides, this C-X also resists substitution

Common preparation routes *

from an alcohol, SOCl_2 (best: only gases as byproducts)



from an alkene, HX addition (Markovnikov)



from an alkane, free-radical halogenation under UV light



SOCl_2 is preferred over $\text{PCl}_5/\text{PCl}_3$ because the only side products, SO_2 and HCl , are gases and leave the mixture cleanly

sp^3 carbon lets the halogen leave, sp^2 carbon won't let go. that one distinction decides almost every reaction in this chapter

