

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

## Haloalkane vs Haloarene

### Haloalkane

- halogen on an  $sp^3$  carbon, e.g.  $CH_3CH_2Cl$
- C-X is a normal, moderately polar sigma bond
- undergoes nucleophilic substitution readily

### Haloarene

- halogen directly on an  $sp^2$  aromatic carbon
- lone pair conjugates into the ring: C-X gets partial double-bond character
- SHORTER and stronger than a haloalkane's: 169 pm vs 178 pm for C-Cl
- resists nucleophilic substitution unless an activating group is present

haloalkene and haloalkyne also exist, halogen on an  $sp^2$  (vinylic) or  $sp$  (alkynyl) carbon of an open chain, and both resist substitution for the same reason as a haloarene

## Classifying Monohalogen Compounds

- by hydrocarbon skeleton: haloalkane, haloalkene, haloalkyne, haloarene. by halogen count: mono, di, tri or polyhalogen
- primary/secondary/tertiary ( $1^\circ/2^\circ/3^\circ$ ): halide carbon attached to one, two or three other carbons
- allylic halide: halogen on  $sp^3$  carbon next to a C=C double bond
- benzylic halide: halogen on  $sp^3$  carbon next to an aromatic ring
- vinylic halide: halogen ON the  $sp^2$  double-bond carbon itself

## Nomenclature \*

- common names: alkyl group name + halide, e.g. ethyl bromide, isopropyl chloride, tert-butyl bromide
- IUPAC treats halogen as substituent prefix (chloro-, bromo-, iodo-, fluoro-), cited alphabetically
- e.g.  $CH_3CH_2Br$  is bromoethane,  $CH_2=CHCl$  is 1-chloroethene
- dihalobenzenes: common names use o-/m-/p-, IUPAC uses locants 1,2-/1,3-/1,4-

## Preparing Alkyl Halides from Alcohols

halogen acid, reactivity order  $3^\circ > 2^\circ > 1^\circ$  alcohol;  $ZnCl_2$  (Lucas reagent) needed for  $1^\circ/2^\circ$  but not  $3^\circ$



phosphorus trihalide,  $PBr_3/PI_3$  generated in situ from red P +  $Br_2/I_2$



$PCl_5$  on an alcohol



thionyl chloride, byproducts are BOTH gases, so no separation needed: the preferred route for straight-chain  $1^\circ$  alcohols



phosphorus halides avoid the rearrangement that HX addition can trigger, so straight-chain primary alcohols give unrearranged alkyl halides with  $PX_3$

