

### 13. Halogenoalkenes

- Discrepancies between number of electrons and electron cloud size exist, i.e.  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  have similar number of electrons, but electron cloud size of heptane, which has 23 atoms is much larger, therefore  $\text{I-d}$  is greater and boiling point is higher.
- Bromo/Iodo/Polychloroalkanes are denser than water
- Monochloroalkanes are less dense than water
- A carbocation with a benzene ring attached to the C with positive charge is stabilised by charge dispersal. (resonance effect) The empty p-orbital of the positively charged C atom overlaps with the p-orbital of the C in the benzene ring so that **pi electrons in the benzene ring can delocalise** to the C with positive charge and thus **disperse the positive charge**.
- Halogenoarenes are less reactive towards nucleophilic substitution because of the **partial double bond character** of the C-X bond (p-orbital of the halogen overlaps with the pi electron cloud of the benzene ring, lone pair of electrons in the p-orbital of the halogen can delocalise into the benzene ring, resulting in the partial double bond character in the C-X bond, and thus more energy required to break the C-X bond. Furthermore, the electron-rich ring causes electron repulsion between electrons in the benzene ring and the approaching electron-rich nucleophile)
- NOTE THE ABOVE ^^ is usually tested when asking which route will give a greater yield.
- In testing for a specific halogen (Br, I or Cl)
  - Heat with NaOH (aq) for hydrolysis of the C-X bond to form X-
  - Cool the mixture (prevent decomposition of  $\text{AgNO}_3$  added later)
  - Acidify with  $\text{HNO}_3$  (neutralised excess NaOH or  $\text{Ag}^+$  may react with  $\text{OH}^-$  to form brown ppt of  $\text{Ag}_2\text{O}$ )
  - Add  $\text{AgNO}_3$
  - $\text{AgCl}$  is white
  - $\text{AgBr}$  is cream
  - $\text{AgI}$  is yellow