CHEM 261 Oct 27, 2014

Addition of X2 to alkenes (Halogenation)

$$\begin{matrix} I-CI \\ \emptyset & \Diamond \end{matrix} \qquad \text{lodine monochloride}$$

$$\begin{array}{c|c} & ICI & \\ \hline \end{array}$$

E.g 1)
$$\xrightarrow{Br_2}$$
 \xrightarrow{Br} \xrightarrow{Br}

E.g 2
$$\xrightarrow{\text{Br}_2/\text{H}_2\text{O}}$$
 $\xrightarrow{\text{OH}}$

Mechanism:

E.g 3
$$\xrightarrow{\text{H}_2\text{O}/\text{Br}_2}$$
 $\xrightarrow{\text{P}}$ $\xrightarrow{\text{$

Alkyl groups donate electrons and stabilize positive charge.

- The more substituents, the more stable the carbocation.

Reaction of alkenes with halogen and water/alcohol

General reaction

$$C=C$$
 X_2 $C-C$ RO X

$$X = CI, Br, F R = alkyl/H$$

Eg 1.

Eg. 3

For A-B addition: most positive end adds to least substituted end of C=C (to give most stable carbocation).

Eg. 1

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

eg.
$$\frac{Br_2}{CH_3 OH} \xrightarrow{OCH_3}$$

eg.
$$\xrightarrow{Br_2}$$
 \xrightarrow{OH} \xrightarrow{Br} \xrightarrow{OH} \xrightarrow{Br}

eg.
$$Br_2$$
 Br_2

eg.
$$\bigcap_{OH}$$
 \bigcap_{O}

Hydrogen Halide Addition (HX)

General reaction

$$C=C$$
 + HX \longrightarrow $-C-C-$ - Usually syn

Electrophile- substance that seeks negative charge

Eg.

Markovnikov rule in Addition reactions

- positive species adds to the least substituted end of C=C
- negative species adds to the more substituted end of C=C (stabilized positive charge)

Carbocation Stability:

$$\stackrel{\cdot}{3} > \stackrel{\cdot}{2} > 1 > CH_3$$

$$C \xrightarrow{C} C \xrightarrow{H} C \xrightarrow{H} C \xrightarrow{H} C \xrightarrow{H_3}$$

Hydration and Ether formation

General Reactions:

$$C=C$$
 + HOH \longrightarrow No reaction

$$C=C + HOH \xrightarrow{\frac{\Theta}{\text{eg) HBr, HCl}}} \begin{array}{c} \overset{\oplus}{\text{Hoh}} & \overset{\downarrow}{\text{-C-C-}} \\ \overset{\downarrow}{\text{-Hoh}} & \overset{\downarrow}{\text{-C-C-}} \\ \overset{\downarrow}{\text{-Hoh}} & \overset{\downarrow}{\text{-Hoh}} & \overset{\downarrow}{\text{-Syn and Anti}} \\ & & & & & & \\ \hline C=C + HOR & \overset{\oplus}{\text{-Hoh}} & \overset{\downarrow}{\text{-C-C-}} \\ & & & & & & \\ \hline R=\text{alkyl} & & & & & \\ \hline \end{array}$$