## Recall:

Alkane Reactions:

-Combustion, Radical Substitution, Nucleophilic Substitution

$$R-H \xrightarrow{O_2} CO_2 + H_2O$$

$$R-H \xrightarrow{X_2} R-X + H-X$$
Alkyl halide

$$R-X \xrightarrow{\stackrel{\oplus}{\longrightarrow} Nu}{}^{\oplus} R-Nu + \stackrel{\oplus}{M} \stackrel{\odot}{X} S_N^2 \text{ occurs on } 1^{\circ}/2^{\circ} \text{ subtrates}$$

Alkyl halide

Alkene/Alkyne Reactions: -Addition, Oxidation



Generating an Acetylide anion:



The resulting acetylide anion can be used in the synthesis of other acetylenes by substitution reactions.

#### Example:



#### **Elimination Reactions:**

2 Types of Mechanisms: E1 and E2



Base vs. Nucleophile:



Base

Nucleophile

#### Elimination ( $E_1$ and $E_2$ )

Substitution ( $S_N$ 1 and  $S_N$ 2)

#### **Types of Elimination Reactions:**

- 1) Dehydrogenation with transition metals: possible, but not selective, so people don't bother
- 2) Dehalogenation (Removal of X<sub>2</sub>) Always E<sub>2</sub>



 Dehydrohalogenation (Removal of HX); Fluorine F<sup>-</sup> is not desirable substrate Can be E<sub>1</sub> or E<sub>2</sub>. E<sub>2</sub> is favored by sterically hindered bases like tBuOK; E<sub>1</sub> requires heat and tertiary halide



$$- \begin{array}{c} OR \\ -C-C \\ H \end{array} \xrightarrow{R = H, Alkyl} \\ H_2SO_4 \end{array} \xrightarrow{C=C} + H-OR$$

- $E_1 \text{ Or } E_2$
- **<u>E2 Reaction</u>** (E=Elimination):
  - Rate depends on two concentrations
  - Stereospecific
  - Concerted (bonds being formed and broken at the same time)
    - No intermediate
  - Anti-periplanar geometry





tBuOK

Goes fast as substituents are in favorable anti-periplanar geometry



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Goes slow as because there is no anti-periplanar geometry with adjacent hydrogen and ring flip is unfavorable

Need hydrogen on adjacent carbon and anti-periplanar geometry for the loss of HBr **Example #5: small nucleophiles/bases favour substitution** 

KOH + OH minor E<sub>2</sub> major S<sub>N</sub>2 Br





**Example 8: Start with different sterochemistry get different product stereochemistry** (a diasteromer)



H and Br need to be in "Anti" configuration (anti-periplanar)



- Zinc mechanism always proceeds via E2



# **<u>E<sub>1</sub> Reaction</u>:**

- Rate depends on one concentraion
- Not concerted (carbocation intermediate)
- Not stereospecific
- Favoured with leaving group being 3°

X must be a good leaving group (no  $OH^{-}/RO^{-}$ ). However, addition of an acid can protonate hydroxyls and ethers. Water molecule  $H_2O$  or an alcohol ROH are good leaving groups and elimination can proceed.







Nucleophile has to be present for substitution to predominate

### Example #4:

How to make it? There are multiple ways to perform that synthesis



**Best route:** 





Here an elimination at 1-bromopropane can happen with the formation of propene:







Following Zaitsev rule 1-methyl-1-cyclohexene is formed as a more substituted alkene **Example #2:** 



Due to mechanism of Zn, the double bond is stuck at less substituted end.

Double bond can go to more substituted if it is left in acid via cation:



# Example #4: bulky nucleophiles/bases favour elimination



A little