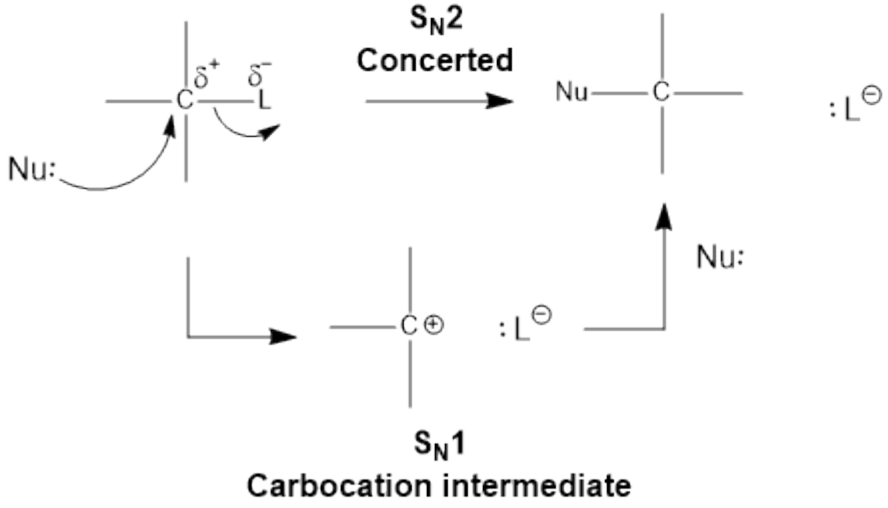
CHEM 261 **Nov 2, 2015**

Review

Summary of Substitution Reactions:

S_N2	S_N1
Bimolecular	Unimolecular
Concerted	Step-wise (Carbocation intermediate)
Stereospecific (conversion)	Not stereospecific
Best if primary carbon	Best if tertiary carbon
Never if tertiary carbon	Never if primary carbon
Never on C=C	Never on C=C



Nu: Nucleoplile

L: Leaving group

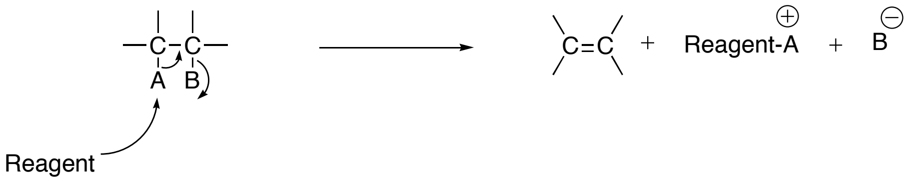
C^{δ^+} : Electrophilic carbon

Electrophile: Seeks a pair of e^-
(or negative charge)

Elimination Reactions

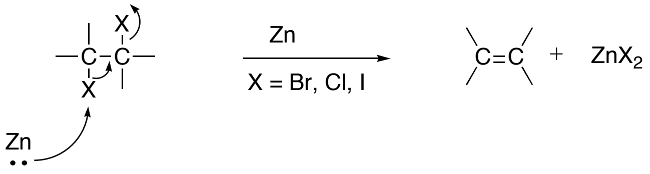
Synthesis of Alkenes and Alkynes

General



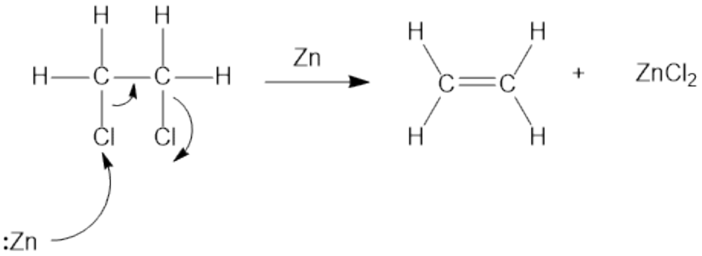
Three examples/types:

1) Dehalogenation - Always E_2



Examples:

1.



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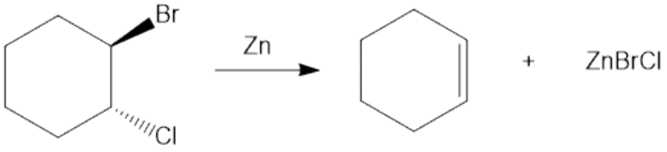

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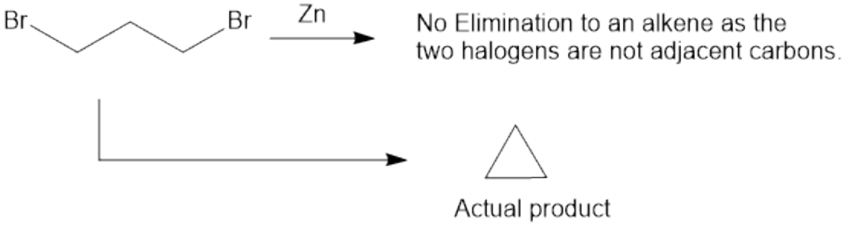
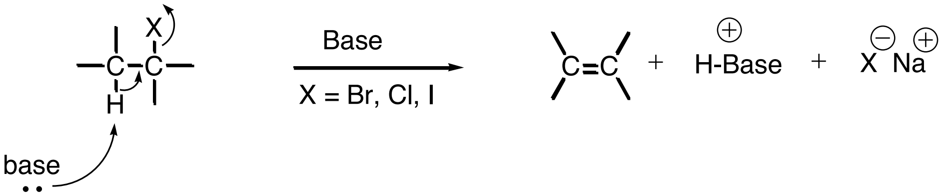
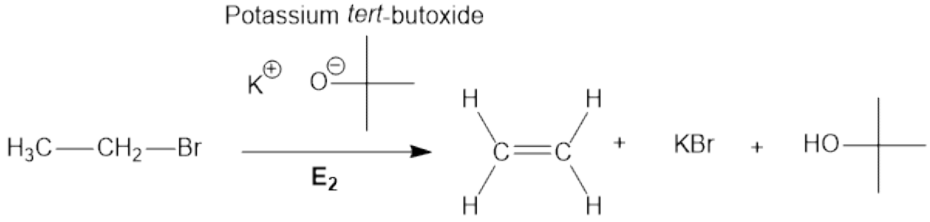


2) Dehydrohalogenation - Generally requires base (e.g. R-O$^-$ Na$^+$). Can be E_1 or E_2.

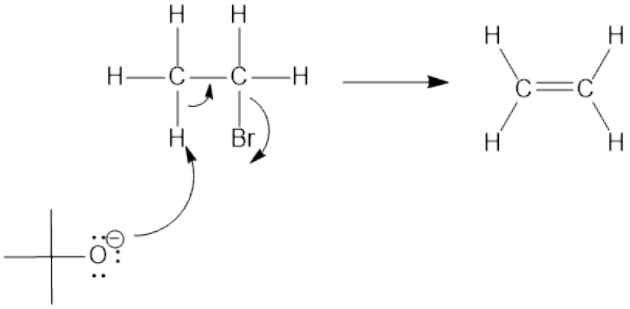


Examples:

1.



Mechanism



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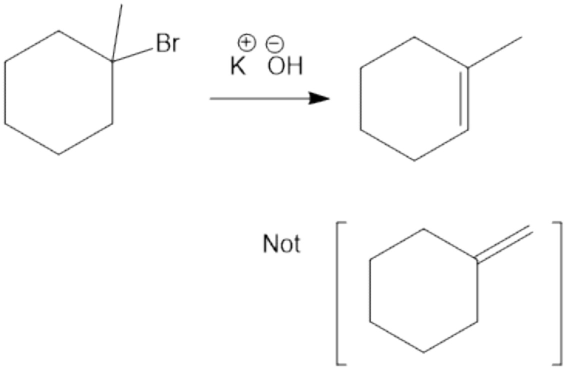
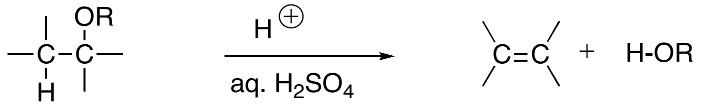


Elimination reactions are favored in basic media.

Zaitsev Rule – Formation of the most substituted double bond is favoured in elimination reactions.

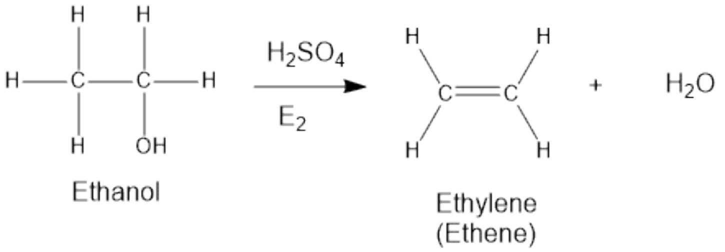
3) Dehydration / Ether Cleavage – In general requires acid



R= H or Alkyl

Examples:

1.



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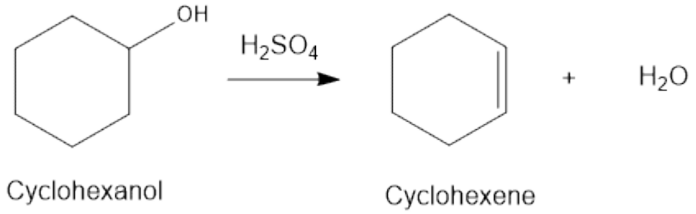

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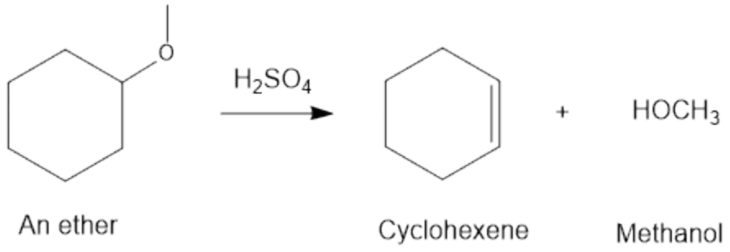

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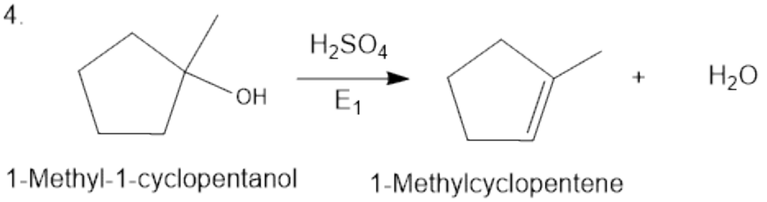
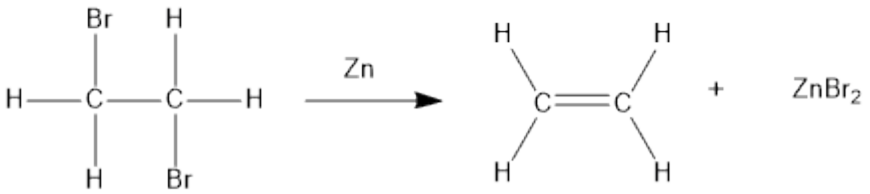


Summary of Elimination Reactions

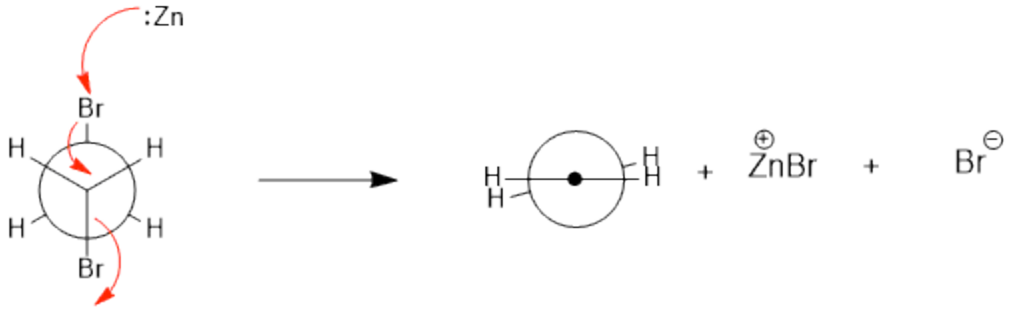
E_2	**E_1**
Bimolecular	Unimolecular
Concerted	Step-wise (Carbocation intermediate)
Stereospecific (Antiperiplanar)	Not stereospecific
Best if primary carbon	Best if tertiary carbon, never primary

Mechanism of E2 Eliminations

Example: E_2 Dehalogenation.



Newman projection of 1,2-dibromoethane



The staggered anti-periplanar conformation (most stable) in 1,2-dibromoethane favors an E_2 reaction. This conformation allows the optimal geometry within the molecule for a concerted mechanism (bonds being broken and formed simultaneously).