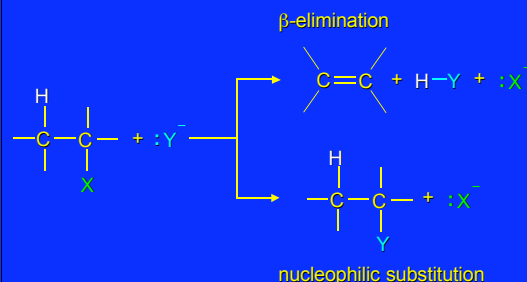


Substitution and Elimination
Competing Reactions
 S_N1 & S_N2 vs. E1 and E2
Formation of Alkenes

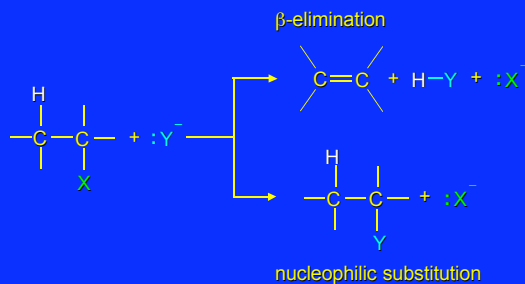
Two Reaction Types

Alkyl halides can react with Lewis bases in two different ways; nucleophilic substitution or elimination.



Two Reaction Types

How can we tell which reaction pathway is followed for a particular alkyl halide?



Elimination versus Substitution

A systematic approach is to choose as a reference point the reaction followed by a typical alkyl halide (secondary) with a typical Lewis base (an alkoxide ion).

The major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism.

Example

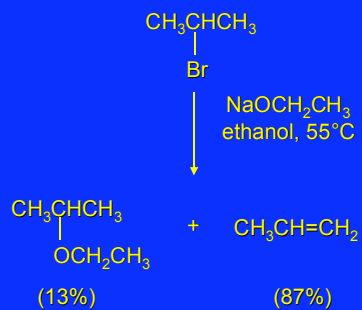
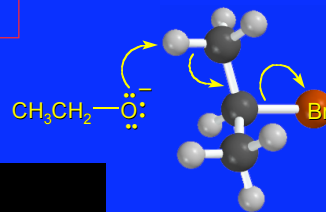


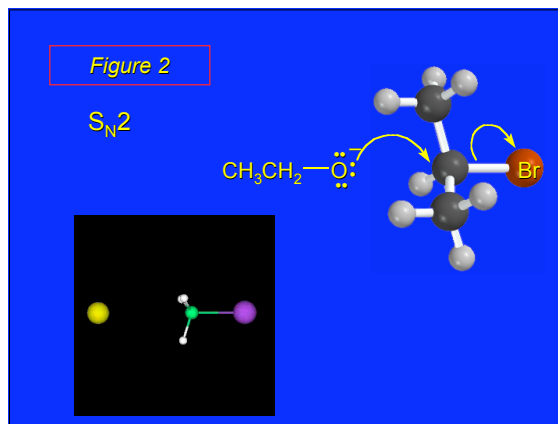
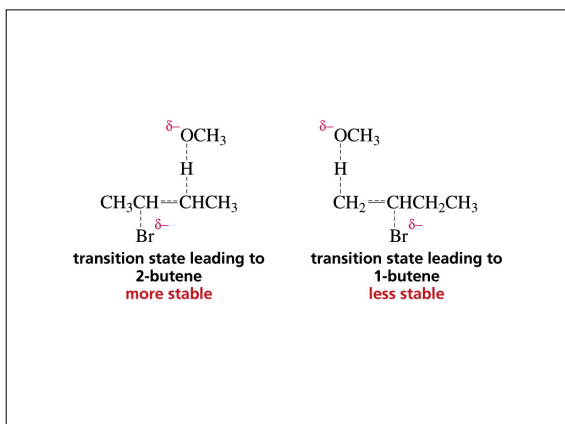
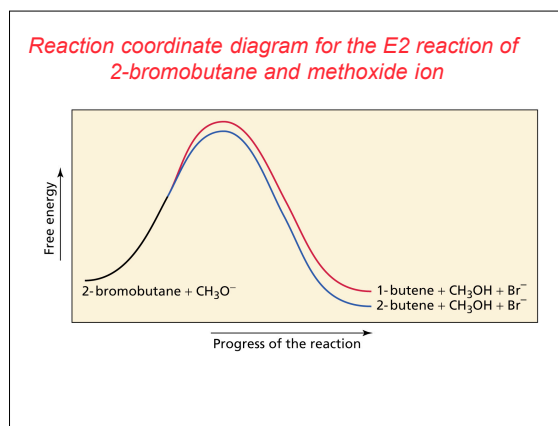
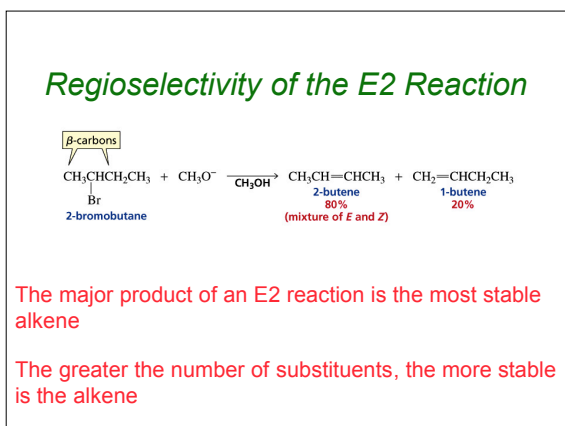
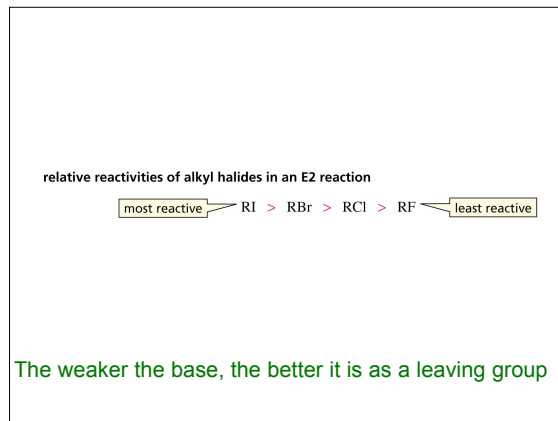
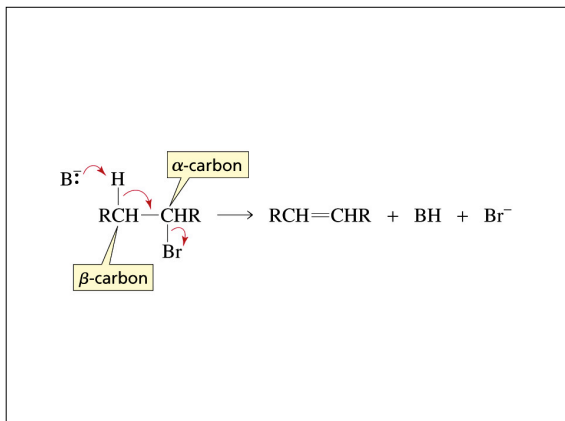
Figure 1

E2



6a

The E2 Mechanism



When is substitution favored?

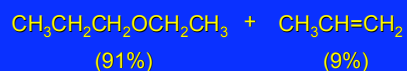
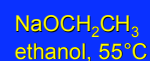
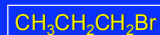
Given that the major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism, we can expect the proportion of substitution to increase with:

- 1) decreased crowding at the carbon that bears the leaving group

Uncrowded Alkyl Halides

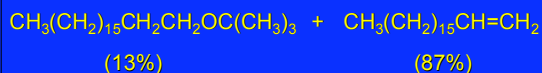
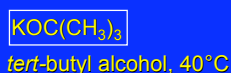
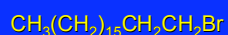
Decreased crowding at carbon that bears the leaving group increases substitution relative to elimination.

primary alkyl halide



But a crowded alkoxide base can favor elimination even with a primary alkyl halide.

primary alkyl halide + bulky base



When is substitution favored?

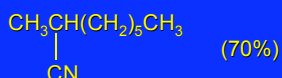
Given that the major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism, we can expect the proportion of substitution to increase with:

- 1) decreased crowding at the carbon that bears the leaving group
- 2) decreased basicity of the nucleophile

Weakly Basic Nucleophile

Weakly basic nucleophile increases substitution relative to elimination

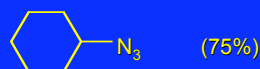
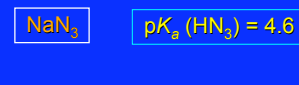
secondary alkyl halide + weakly basic nucleophile



Weakly Basic Nucleophile

Weakly basic nucleophile increases substitution relative to elimination

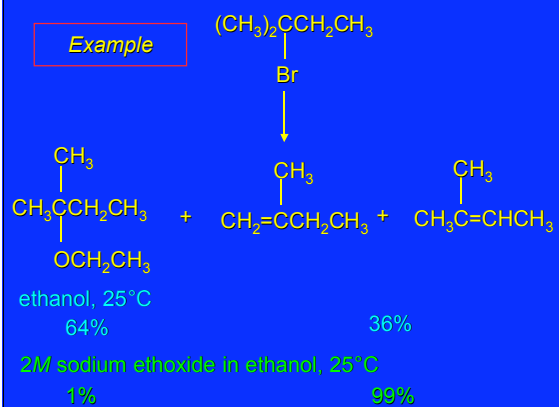
secondary alkyl halide + weakly basic nucleophile



Tertiary Alkyl Halides

Tertiary alkyl halides are so sterically hindered that elimination is the major reaction with all anionic nucleophiles. Only in solvolysis reactions does substitution predominate over elimination with tertiary alkyl halides.

Example



Putting things together: Elimination vs. Substitution

🎯 Click all alkyl halides that can effectively undergo an E2 reaction.

1° Alkyl Halide	2° Alkyl Halide	3° Alkyl Halide
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Done