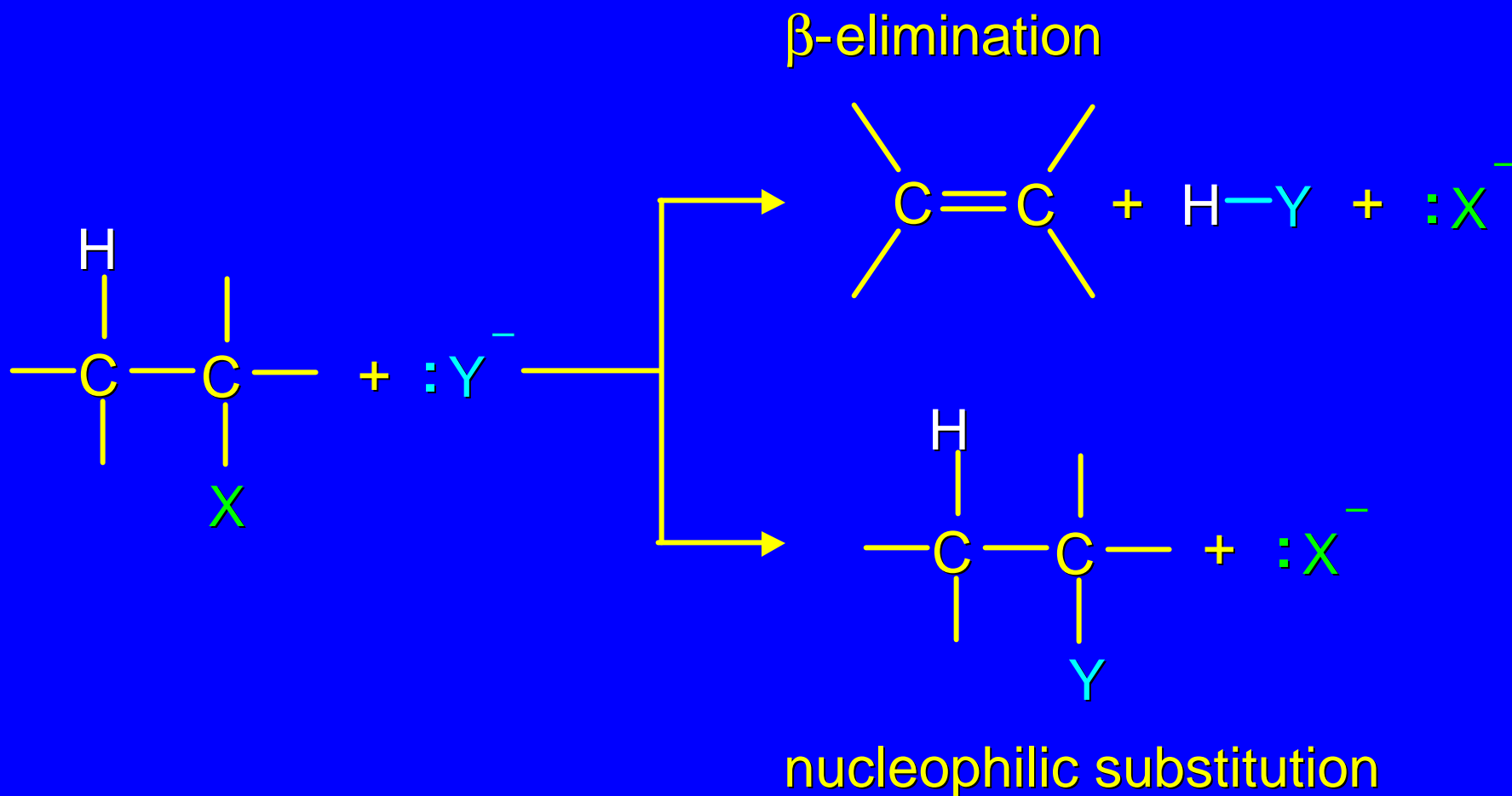


8.13

Substitution and Elimination
as Competing Reactions

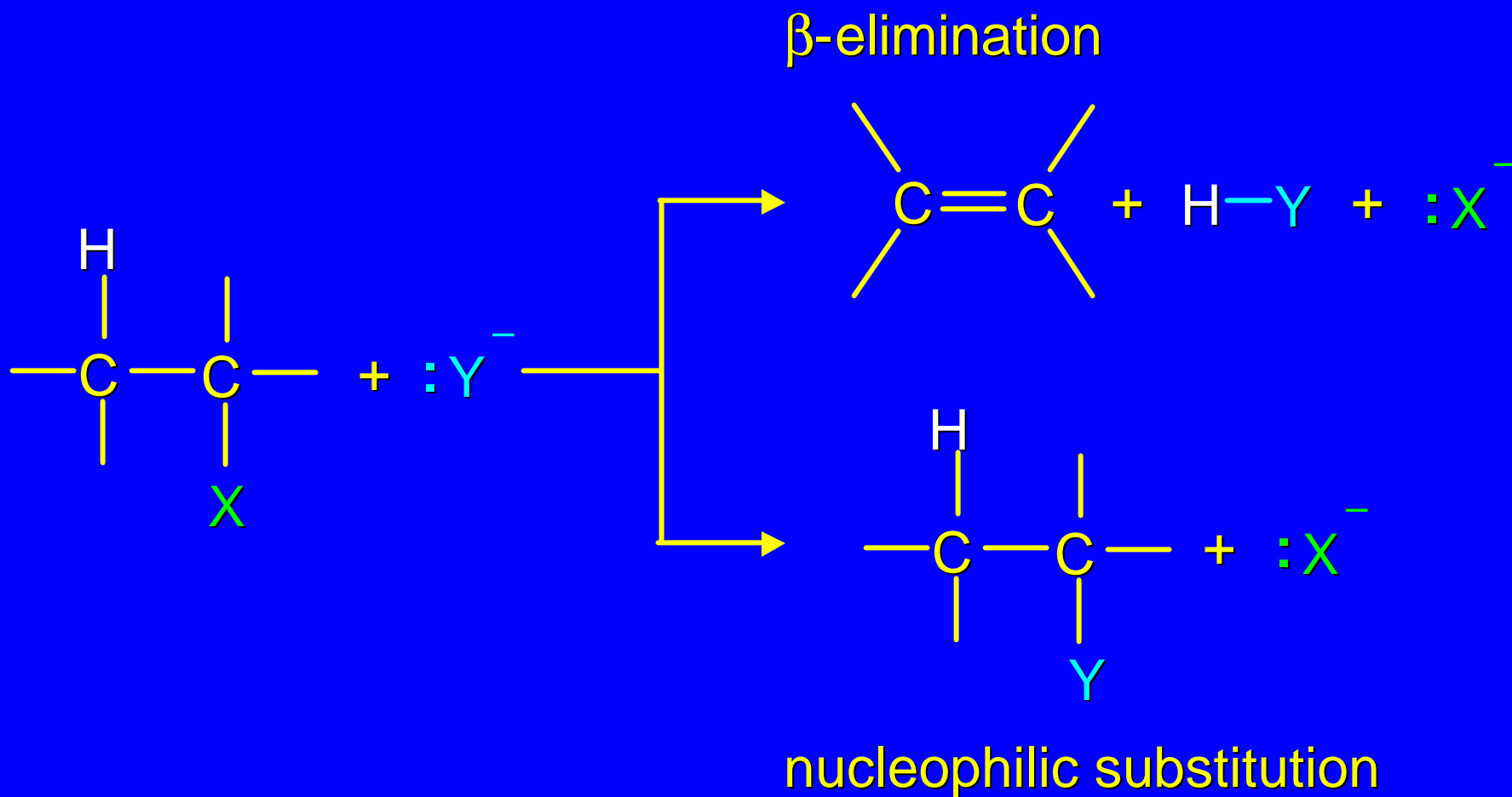
Two Reaction Types

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?

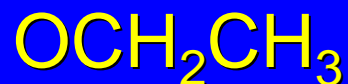
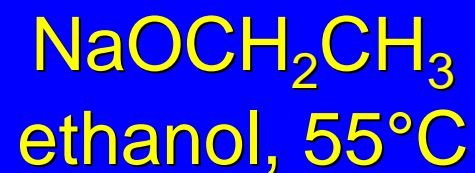


Elimination versus Substitution

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



(13%)

+



(87%)

Figure 8.11

E2

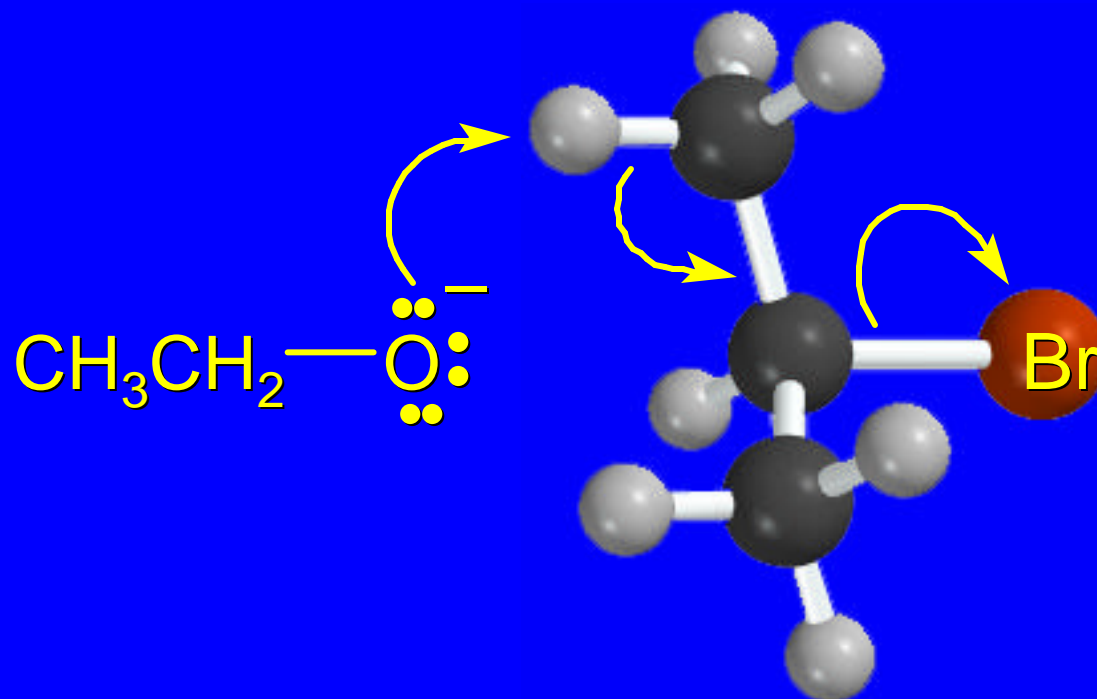
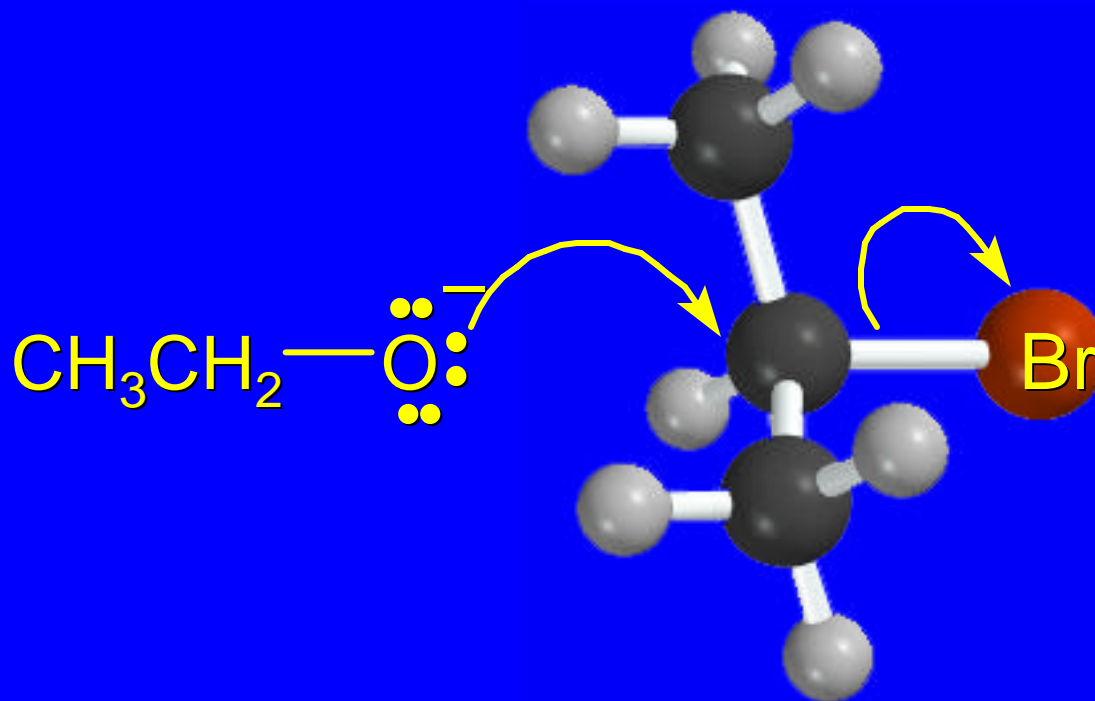


Figure 8.11

S_N2



When is substitution favored?

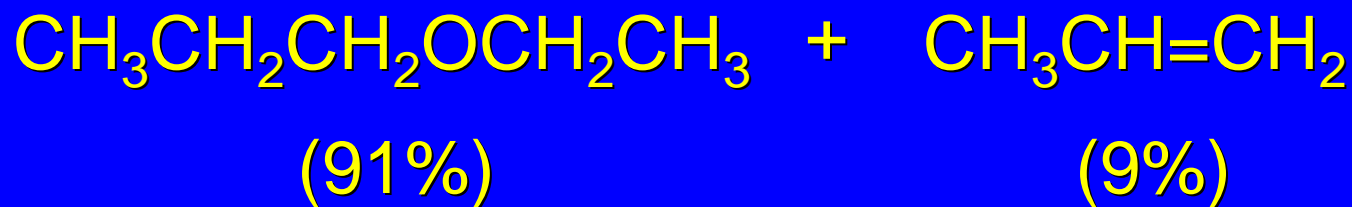
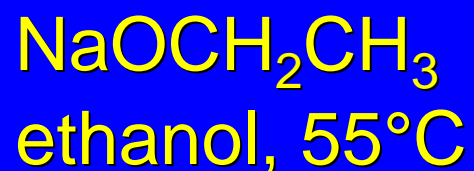
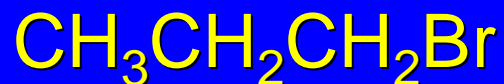
Given that the major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism, we can expect the proportion of substitution to increase with:

- 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

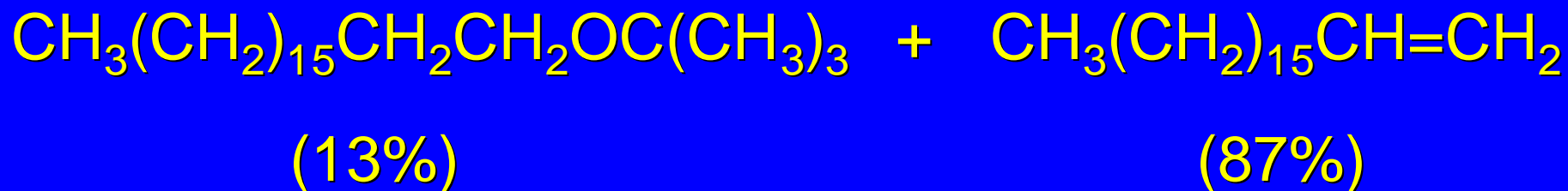


But a crowded alkoxide base can favor elimination even with a primary alkyl halide.

primary alkyl halide + bulky base



tert-butyl alcohol, 40°C



When is substitution favored?

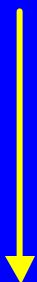
Given that the major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism, we can expect the proportion of substitution to increase with:

- 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



KCN

DMSO

$\text{p}K_a(\text{HCN}) = 9.1$

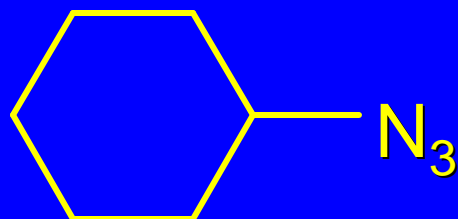
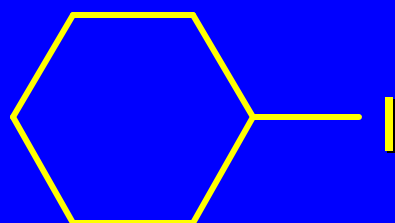


(70%)

Weakly Basic Nucleophile

Weakly basic nucleophile increases substitution relative to elimination

secondary alkyl halide + weakly basic nucleophile



(75%)

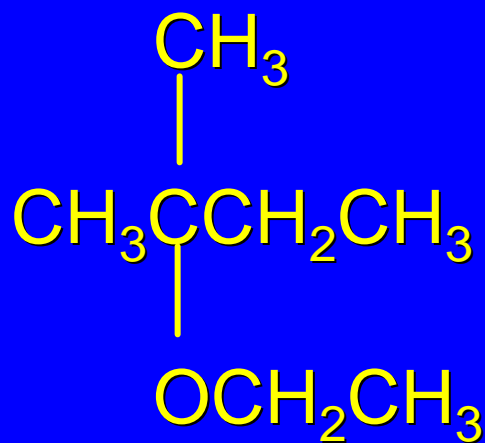
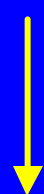
Tertiary Alkyl Halides

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



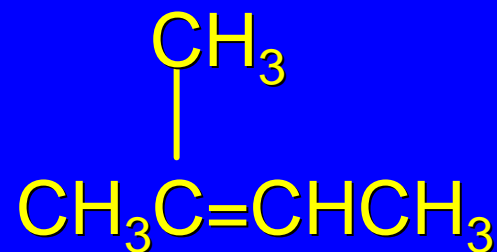
Br



+



+



ethanol, 25°C

64%

36%

2M sodium ethoxide in ethanol, 25°C

1%

99%