

Chapter 7 End:

Competition Between Elimination and Substitution

- SN1 vs. SN2
- E1 vs. E2
- SN2 vs E2/ SN1 vs. E1

SN2 vs. SN1

Substitution Nucleophilic *Bimolecular*

SN2

Substitution Nucleophilic *Unimolecular*

SN1

Experimental Evidence

SN2

1. The rate of the reaction is dependent on the concentration of the alkyl halides and the nucleophile

SN1

1. The rate of the reaction depends only on the concentration of the alkyl halide

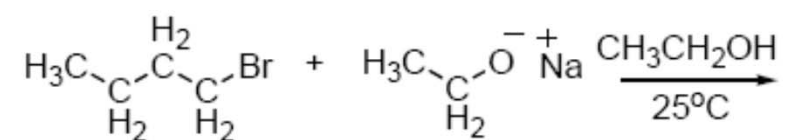
E2 vs. E1

E2 - Elimination *Bimolecular*

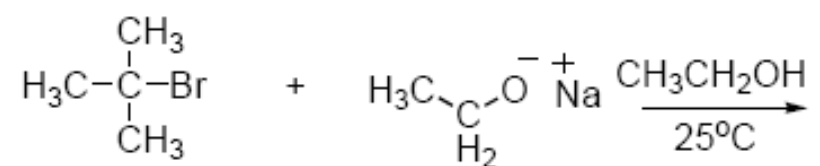
E1 - Elimination *Unimolecular*

Some experimental data:

1. Primary alkyl halide as starting material (SM); base as “nucleophile”



3. Tertiary alkyl halide as starting material (SM); base as “nucleophile”



Competition Between Substitution and Elimination

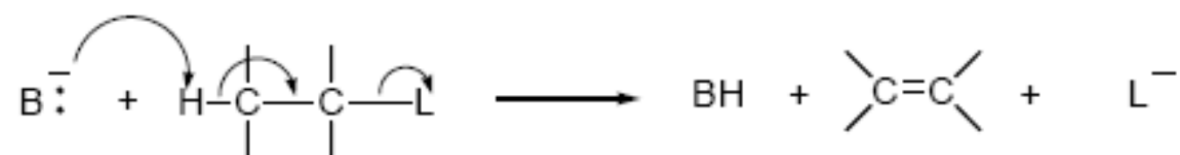
Alkyl halides can undergo S_N2 , S_N1 , E2 and E1

1) decide whether the reaction conditions favor S_N2 /E2 or S_N1 /E1

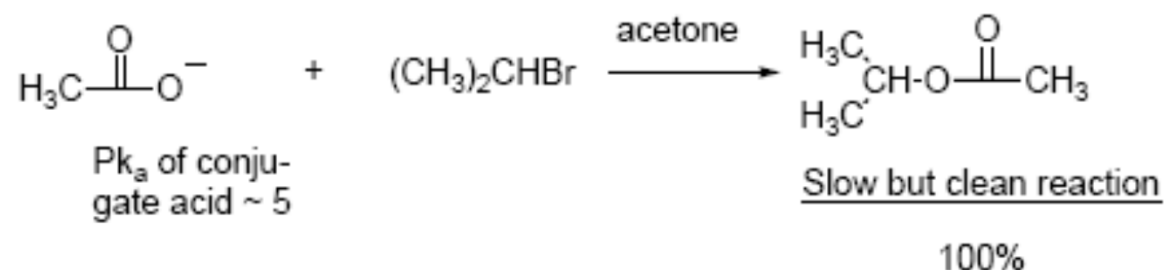
2) decide how much of the product will be the substitution product and how much of the product will be the elimination product

List of Factors/Concepts:

Steric effects: slows SN_2 , helps E_2

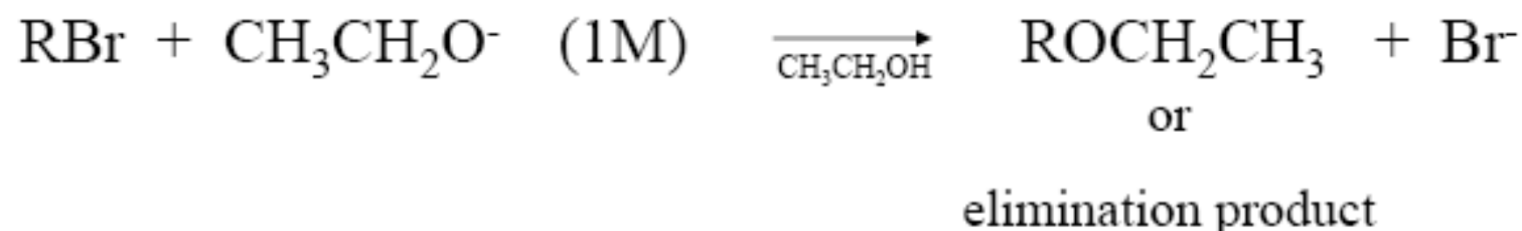


Driving force is protonation of strong base and formation of weaker one. L^-



- 2) Steric hindrance at α or β carbons. We know that for 2° and 3° carbon centers S_N2 reaction is slowed. This allows E_2 to become *relatively* faster and we see more elimination product.

Illustration showing effect of branching at α or β carbons:



	% Subst.	%Elimin.
CH_3Br	99+	~ 0
CH_3CH_2Br	99	1
$CH_3CH_2CH_2CH_2Br$	90	10
$(CH_3)_2CHCH_2Br$	40	60
$(CH_3)_2CHBr$	20	80
$(CH_3CH_2)_2CHBr$	12	88

When is substitution favored?

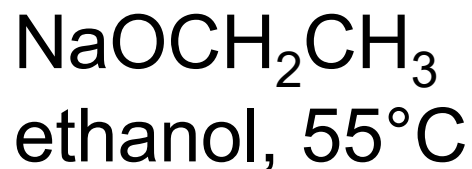
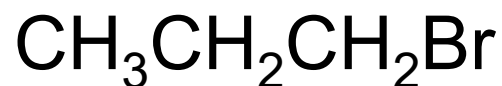
Given that the major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism, we can expect the proportion of substitution to increase with:

1)

Uncrowded Alkyl Halides

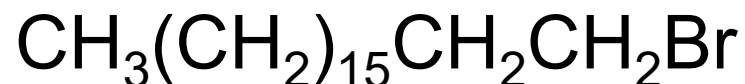
Decreased crowding at carbon that bears the leaving group increases substitution relative to elimination.

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



Weakly Basic Nucleophile

Weakly basic nucleophile increases
substitution relative to elimination

secondary alkyl halide + weakly basic nucleophile



KCN

DMSO

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

For Next Time....

Suggested Homework Problems Chapter 7

#1,14,21,26, 31, 36,38,41,44,50,52,53,59,64,65

Exam#2 → Wednesday OCTOBER 25th!