

Learning Guide for Chapter 10 - Alkyl Halides II

I. Elimination Reactions of Alkyl Halides

Introduction

Mechanisms

Beta hydrogens, constitutional isomers, and stereoisomers

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Strong and Weak Bases

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Solvents

Eliminations of Aryl and Vinyl Halides

II. Substitution vs Elimination

III. Using Elimination for Synthesis

I. Elimination Reactions of Alkyl Halides

Introduction

Describe the result of a substitution reaction. Give an example.

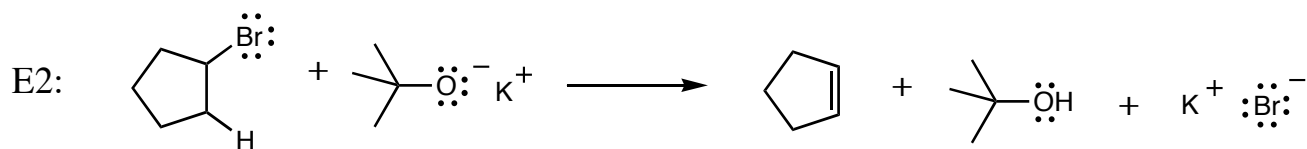
How is an elimination reaction different? Give an example.

What does it mean to say that substitution and elimination reactions are competing reactions?

Mechanisms

What are the two mechanisms by which elimination may occur?

Consider the following mechanisms:



Draw in the arrows to show how this reaction occurred.

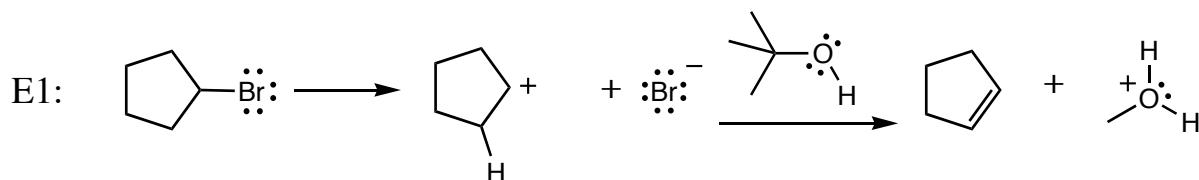
What type of Lewis acid/base reaction is this?

How could this mechanism be described?

Identify the acid and the base.

Why can the alkyl halide behave as an acid?

Why is the alkoxide a good base?



Draw in the arrows to show how this reaction occurred.

What types of Lewis acid/base reactions occur?

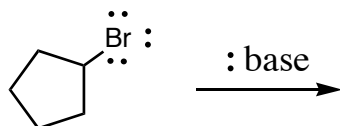
How could this mechanism be described?

Identify the acid and the base.

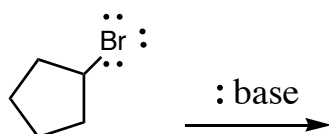
Why can the carbocation behave as an acid?

Beta hydrogens, constitutional isomers, and stereoisomers

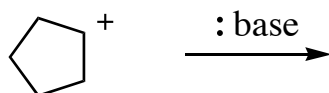
What is the relationship between the halogen and the H that is removed? Why?



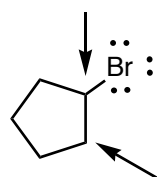
Why can't the H on the same carbon as the halogen be removed?



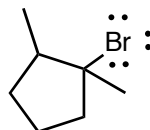
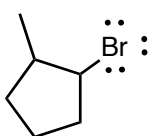
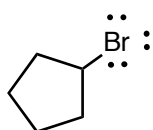
What is the relationship between the carbocation and the H that is removed?



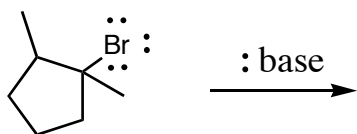
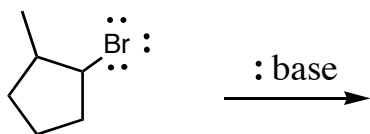
What is this relationship called?



Is it possible for there to be more than one set of beta hydrogens?

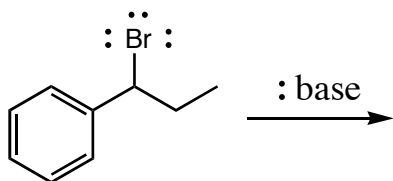


What two elimination products could be formed from the following compounds?
What is their relationship?



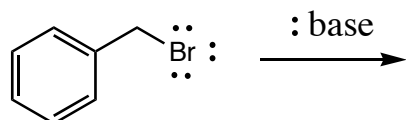
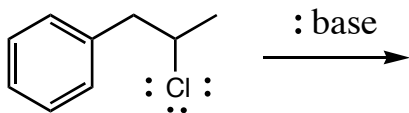
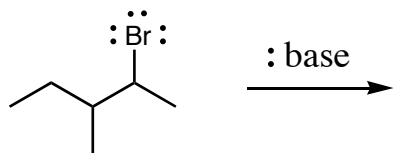
Not all isomers will be formed in equal amounts. Which are favored?

What two elimination products could be formed from the following compounds?
What is their relationship?



Which isomer will be favored?

Give all products of the following reactions. Indicate which is favored.



E2 vs. E1

How are the E2 and E1 reactions the same?

What are the two bases used in the examples? Which do you think is stronger, and why?

E2

E1

What are the two acids used in the examples? Which do you think is stronger, and why?

E2

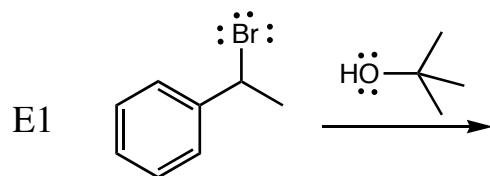
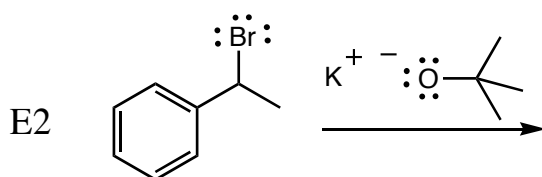
E1

How do the strengths of the acid and base go together?

Scenario A: strong base added to alkyl halide

Scenario B: weak base added to alkyl halide

Following the pattern of the reactions given previously, draw the mechanisms for the following reactions:



Strong and Weak Bases

What do nucleophiles and bases have in common?

What is the difference between how the base attacks and how the nucleophile attacks?

Could one molecule act as both a nucleophile and a base?

What do S_N2 and E2 have in common?

What do S_N1 and E1 have in common?

What factors make a nucleophile stronger?

NaOH vs H_2O

$HC\equiv CNa$ vs NaOH

NaSH vs NaOH

CH_3CH_2ONa vs $(CH_3)_3COK$

How do these same factors affect the strength of bases?

NaOH vs H_2O

$HC\equiv CNa$ vs NaOH

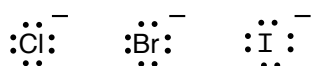
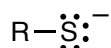
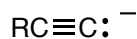
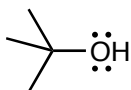
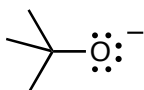
NaSH vs NaOH

CH_3CH_2ONa vs $(CH_3)_3COK$

Which reactions will the following molecules participate in?

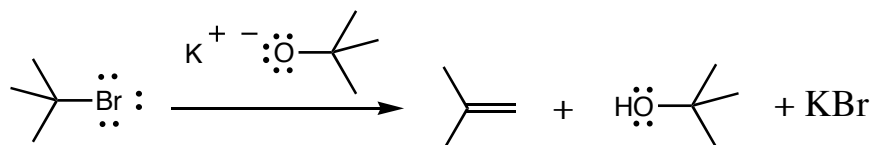
NaOH

H_2O



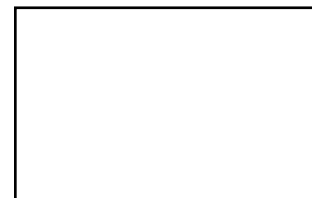
Rate laws

Consider the following E2 reaction.



Draw the energy diagram for this reaction.

What is the rate-limiting step? What reagents are involved?



Draw the structure of the transition state.

What would happen to the rate of the reaction if you

doubled the concentration of the alkyl halide?

doubled the concentration of the base?

What is the order of the alkyl halide? the base? the reaction?

Write the rate law:

What does E2 stand for?

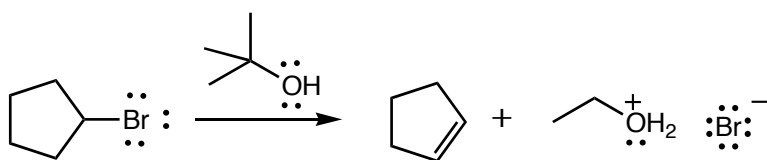
How does the halogen affect the reaction rate?



How does the structure of the alkyl halide affect the rate?



Consider the following E1 reaction.



Draw the energy diagram for this reaction.

Which is the rate limiting step?



Which reagents are involved in the rate limiting step?

Draw the structure of the transition state for this step.

What would happen to the reaction rate if you

doubled the concentration of the alkyl halide?

doubled the concentration of the nucleophile or base?

What order is the alkyl halide? the base? the reaction?

Write the rate law:

What does E1 stand for?

How does the halogen affect the reaction rate?



How does the structure of the alkyl halide affect the rate?



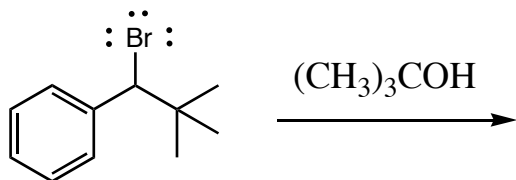
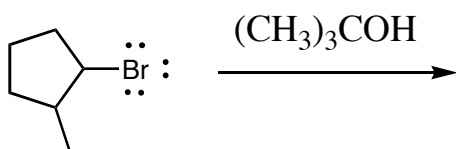
Rearrangements

Which elimination reaction has the possibility of rearrangements?

Which alkyl halides are most likely to rearrange?

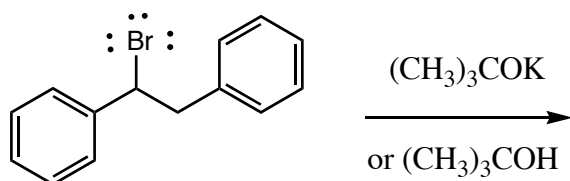
What kinds of rearrangements can occur?

What rearrangement will occur in the following reactions? Draw the carbocation and the elimination products.



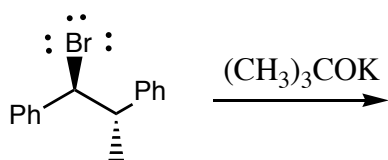
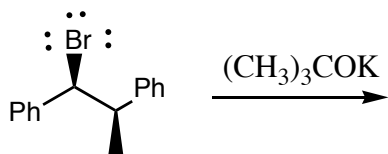
Stereochemistry

What types of stereoisomers can be formed in an elimination reaction?

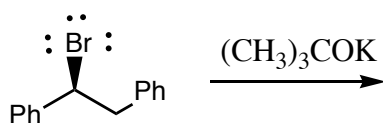


What orientation is required in order for an E2 reaction to occur?

Which stereoisomer will be formed from the following alkyl halides?

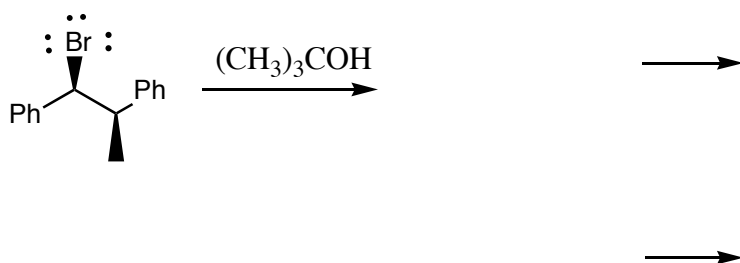


What would happen with the following alkyl halide?

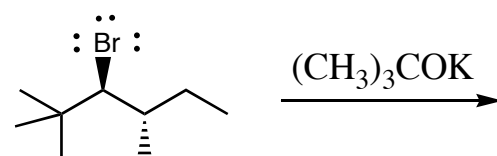
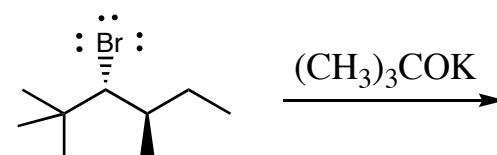
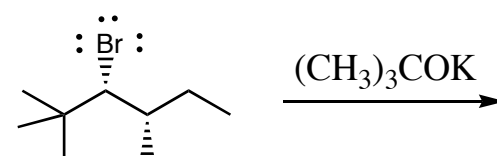
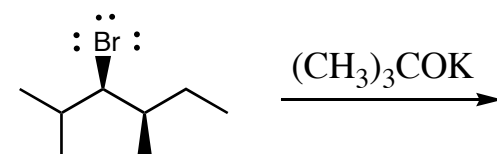
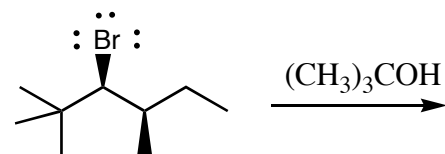
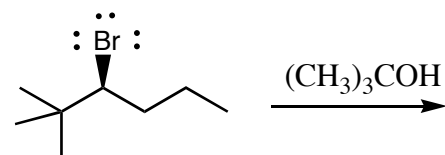
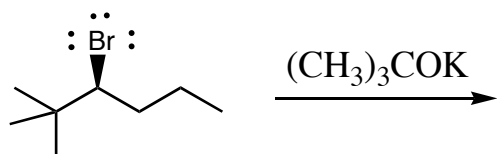


Under what conditions will an E2 reaction give only one stereoisomer?

What orientation is required for an E1 reaction to occur?



How many stereoisomers will result from the following reactions?



Solvents

What kinds of solvents were best for S_N2 reactions?

Why?

What kinds of solvents were best for S_N1 reactions?

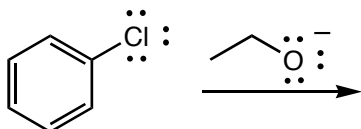
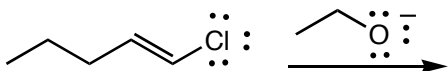
Why?

Which of these is E2 most like? What kind of solvents would be best?

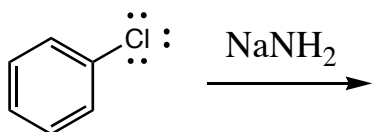
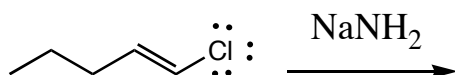
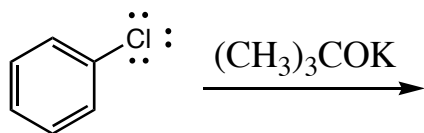
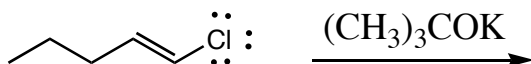
Which of these is E1 most like? What kind of solvents would be best?

Eliminations of aryl and vinyl halides

Can aryl and vinyl halides undergo S_N2 or S_N1 reactions?



Can aryl and vinyl halides undergo elimination?



Summary of Elimination Reactions

E2 reactions:

result:

mechanism:

reagent:

stereochemistry:

rate law:

alkyl halides:

rearrangements?

solvent:

E1 reactions:

result:

mechanism:

reagent:

stereochemistry:

rate law:

alkyl halides:

rearrangements?

solvent:

II. Elimination vs Substitution

What does it mean to say that elimination and substitution are competing reactions?

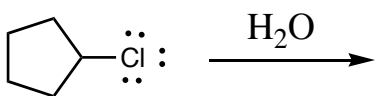
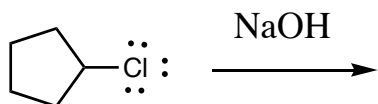
What reagents does substitution require?

What reagents does elimination require?

Can some molecules act as nucleophiles or bases?

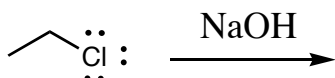
The following criteria can help us decide:

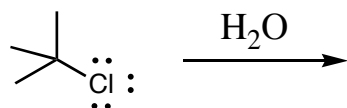
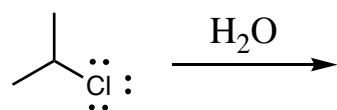
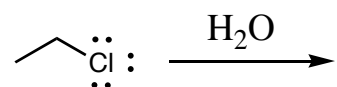
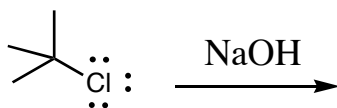
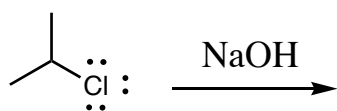
1) How can we choose between 1st and 2nd order reactions?



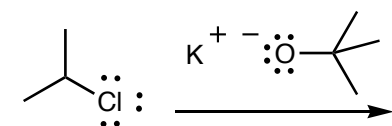
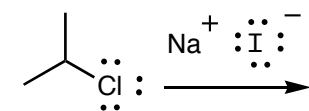
2) How can we choose between substitution and elimination reactions?

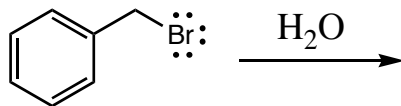
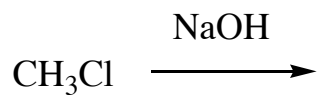
A) use reaction rates





B) Watch out for special cases





Would it be possible to have a reaction in which no product was formed?

Summary:

strong Nu

weak Nu

1° RX

2° RX

3° RX

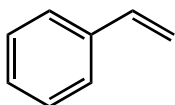
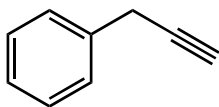
exceptions:

III. Synthesis Using Elimination

What kinds of functional groups can be made using substitution reactions?

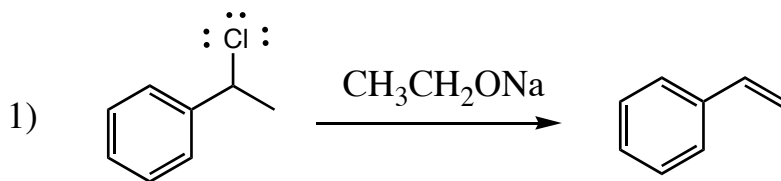
What kinds of functional groups can be made using elimination reactions?

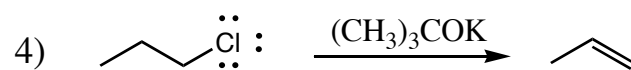
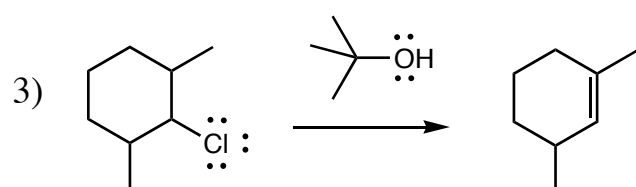
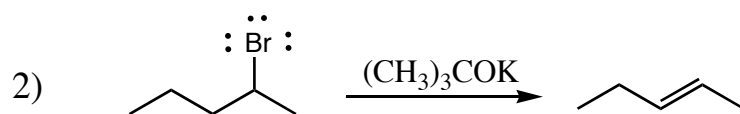
What starting materials and reagents could be used to make the following compounds?



In order to have a good synthesis, what must be true?

What will go wrong in the following examples? What can be done about it? Rewrite the reaction so that it will work (if possible).





Write a good synthesis for the following compounds, or explain why you can't.

