

Learning Guide for Chapter 9 - Alkyl Halides I

I. Introduction to alkyl halides

types of organic halides, where alkyl halides are found, preparation, spectroscopy, reactivity, nomenclature

II. Substitution reactions of alkyl halides

Introduction

Mechanisms

Which substitution reaction?

Strong vs Weak Nucleophiles

Products

Stereochemistry

Rate Laws

Rearrangements

Solvents

Exclusion of aryl halides, vinyl halides, and acid chlorides

Summary of Substitution Reactions

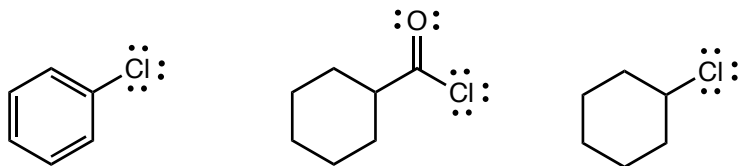
III. Synthesis Using Substitution Reactions

I. Introduction to alkyl halides

Types of organic halides

What is the purpose of categorizing organic halides into different groups?

Label the following compounds as alkyl halides, aryl halides, and acid halides.

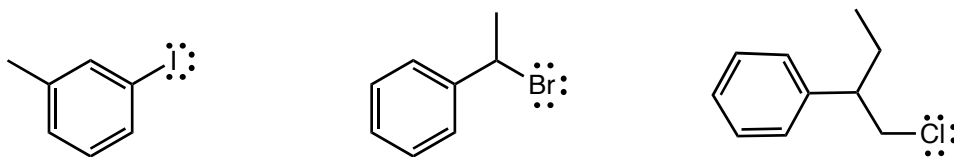


This chapter will focus on:

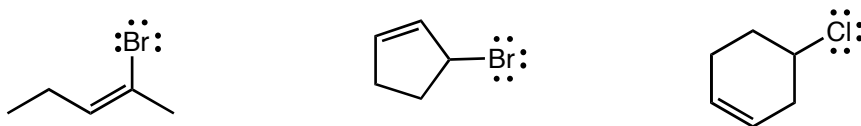
Compounds with more than one halide can be classified by how close together the halides are. Which of these is a geminal dihalide, and which is a vicinal dihalide?



Not all compounds that contain a benzene ring are aryl halides. Classify the following. What category do they all belong to?



Organic halides may also contain a C=C. Classify the following. What category do they all belong to?

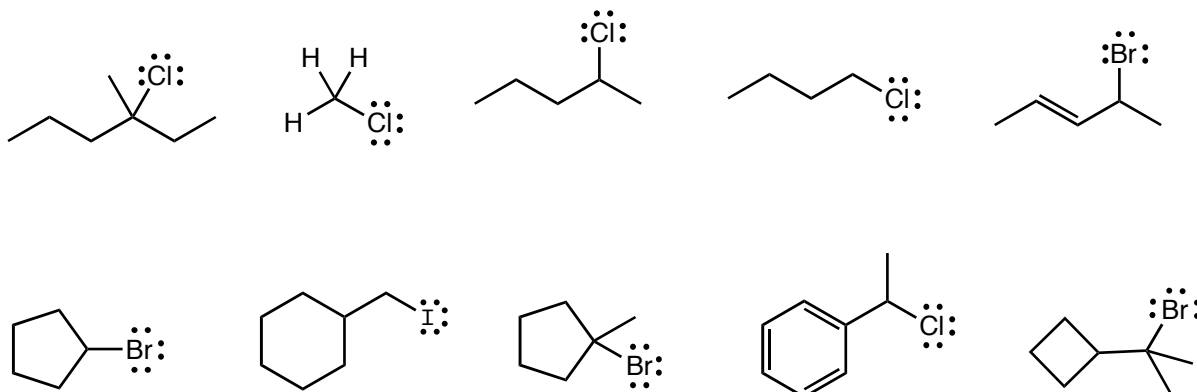


Some aromatic halides and some unsaturated halides react like alkyl halides, and some do not. The important factor is the hybridization of the C the halogen is attached to.

sp^3 carbon

sp^2 carbon

Label the following as methyl, 1° , 2° , 3° , allyl, and benzyl.



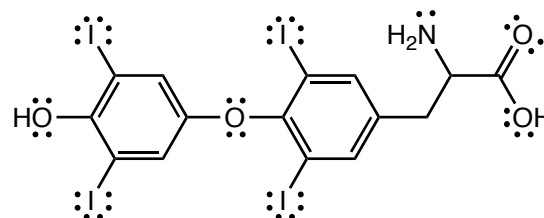
Where organic halides are found

Are organic halides common in nature?

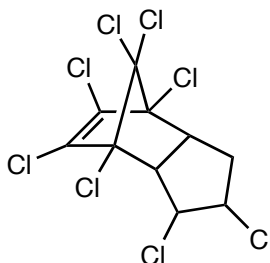
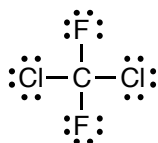
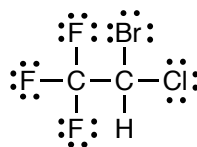
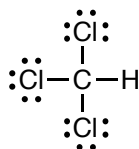
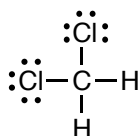
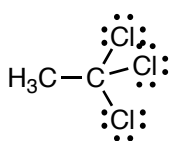
Why is iodine necessary in the human diet?

Where do we get it?

What happens if you don't?



How are alkyl halides used in industrial, commercial, and medical applications?



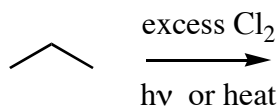
Preparation of alkyl halides

How can alkyl halides be synthesized from alkanes?

What difficulty does this reaction have?

What kind of intermediate is formed in this reaction?

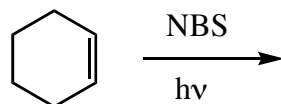
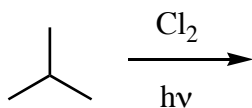
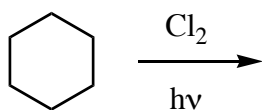
What would the products of the following reaction be?



What reagent can be used in place of Br₂?

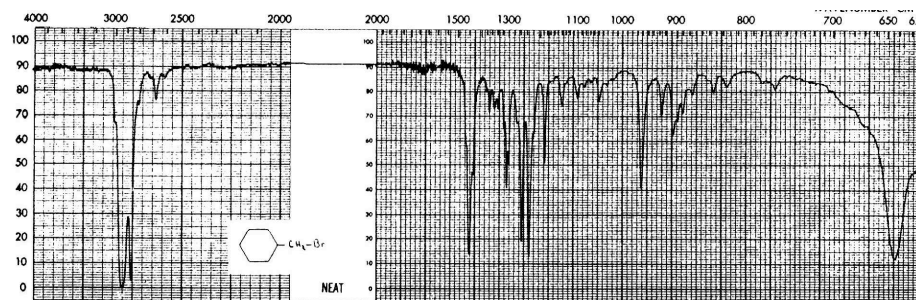
What stabilizes radical intermediates?

Why are the following reactions successful at forming only one major product?



Spectroscopy of alkyl halides

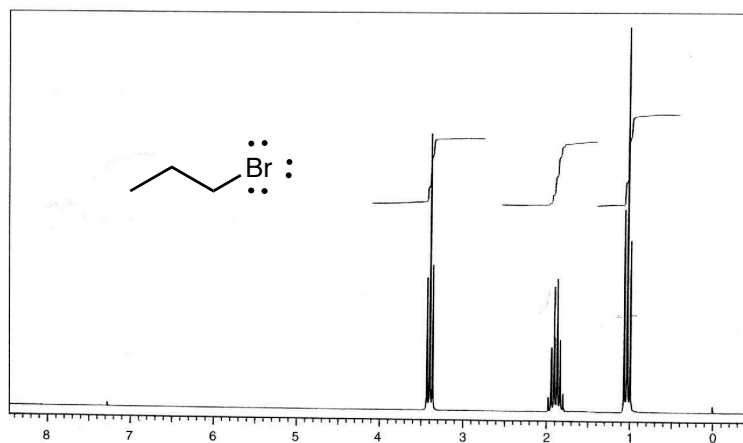
What IR bands does this alkyl halide spectrum have?



Is IR a good way to identify alkyl halides?

How can you locate the H's on a C with a halogen attached?

Assign the H's on the following spectrum.



Reactivity of alkyl halides

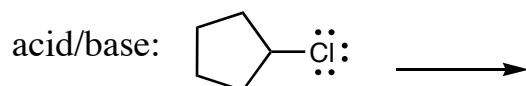
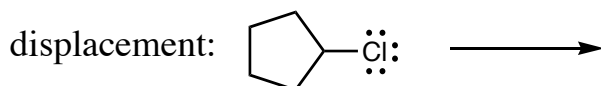
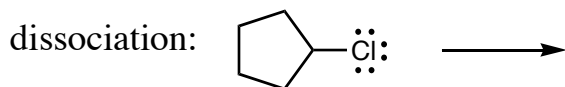
Give the order of electronegativity of halogens atoms:

Give the order of size of the halogen atoms:

Give the order of bond strength of C-X:

Show the polarity of the carbon-halogen bond: 

Show how an alkyl halide can react in each of the following ways:



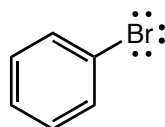
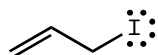
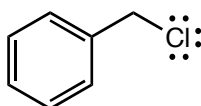
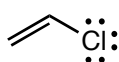
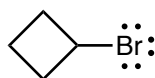
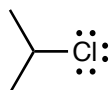
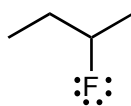
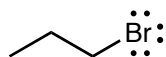
What do all of these reactions have in common?

Nomenclature of alkyl halides

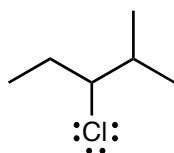
What are the two ways to name alkyl halides?

How do you construct a common name?

Give the common names for the following compounds.

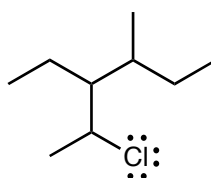
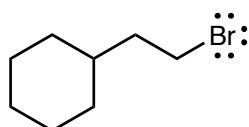
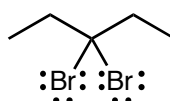
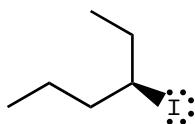
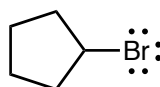
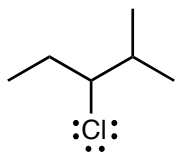


Why can't you write a common name for the following compound?



Review the steps for naming a compound using IUPAC rules.

Give names for the following compounds.

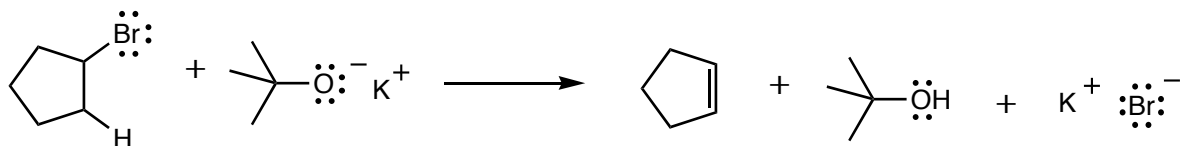
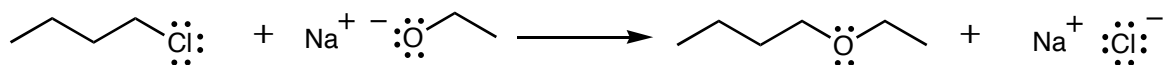


II. Substitution reactions of alkyl halides

Introduction

What are the two types of reactions that alkyl halides can do?

Which of the reactions represented below is a substitution reaction? Which is an elimination reaction? Why?

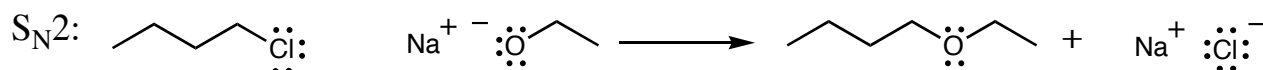


Which of these will we study in this chapter? In the next?

Mechanisms

What is a mechanism?

How many ways can a substitution occur? What are the mechanisms called?



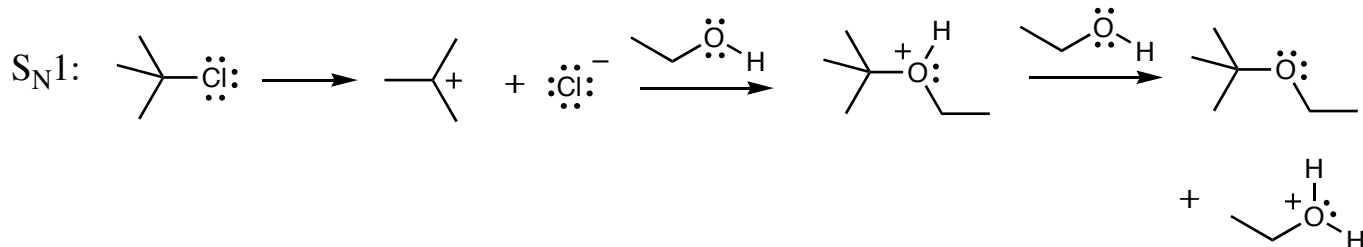
What type of Lewis acid/base reaction is this?

How could this mechanism be described?

Where is the nucleophile, and where is the electrophile?

Why is the alkyl halide a good electrophile?

Why is the alkoxide a good nucleophile?



What type of reaction is this?

How could this mechanism be described?

Where are the nucleophile, electrophile, acid, and base?

Why can alkyl halides dissociate?

Why is the carbocation a good electrophile?

Which substitution reaction?

How are the S_N1 and S_N2 reactions the same?

Which are the two electrophiles used in the examples? Which do you think is more reactive? Why?

S_N2

S_N1

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

S_N2

S_N1

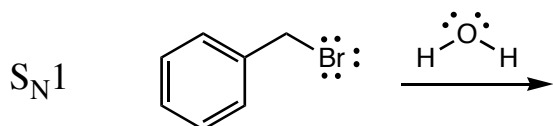
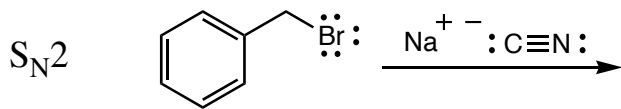
How do the strength of the nucleophile and electrophile fit together?

Scenario A: strong Nu added to alkyl halide

Scenario B: weak Nu added to alkyl halide

What determines whether an S_N1 or and S_N2 reaction will occur?

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



Nucleophiles in Substitution Reactions

The following are nucleophiles commonly used in substitution reactions, listed in order of nucleophilicity:

alkyne anions

cyanide

thiolates

hydroxide

alkoxides

exception:

tert-butoxide

halides

water

alcohols

exception:

tert-butyl alcohol

What is the cut off point between nucleophiles that follow S_N2 vs. S_N1 mechanisms?

Why are alcohols weak nucleophiles while alkoxides are strong nucleophiles?

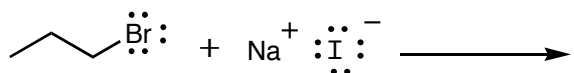
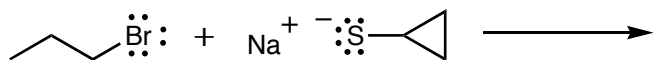
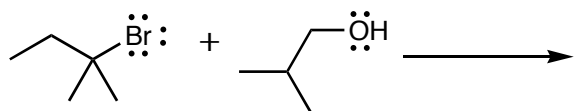
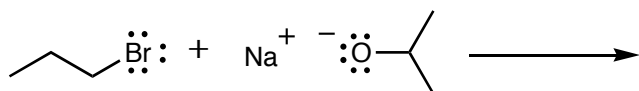
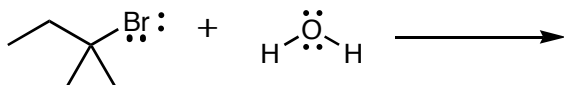
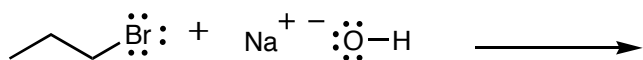
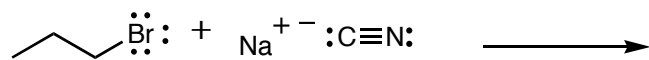
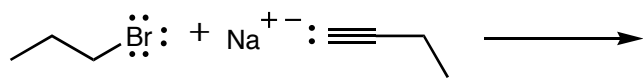
Why won't tert-butoxide and tert-butyl alcohol work as nucleophiles?

Why are alkyne anions the best nucleophiles?

Which of the halides is the best nucleophile? Why are they all poor nucleophiles?

Products

Give the products of the following reactions. Then note what nucleophile produced what product. Which mechanism will each follow?

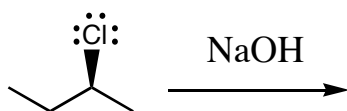


Stereochemistry

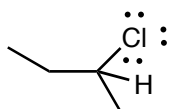
Can a substitution reaction involve a carbon that is a stereocenter?

Can a substitution reaction create a new stereocenter?

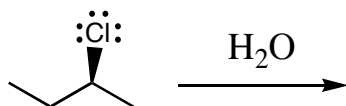
What happens to a stereocenter involved in an S_N2 reaction?



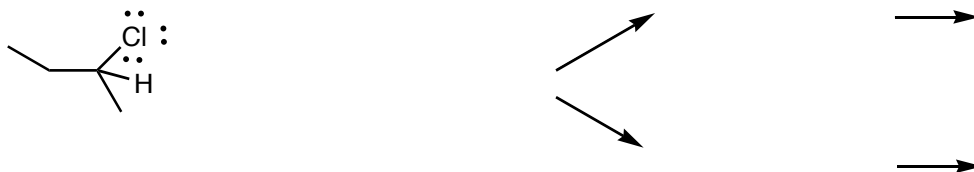
How does this happen?



What happens to a stereocenter involved in an S_N1 reaction?



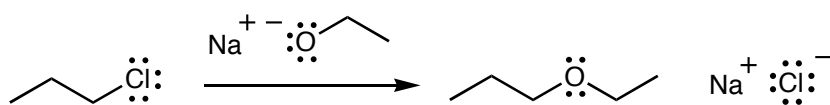
How does this happen?



The actual ratio isn't 1 to 1 - it's more like 2 to 3. Why?

Rate laws

Consider the following S_N2 reaction.



Draw the energy diagram for this reaction.

Which reagents are involved in the rate limiting step?

Draw the structure of the transition state.

What would happen if you

doubled the concentration of the alkyl halide?

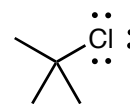
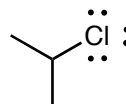
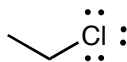
doubled the concentration of the nucleophile?

What is the order of the alkyl halide? the nucleophile?

Write the rate law:

What does S_N2 stand for?

What happens to the rate of S_N2 reactions as the substitution increases?

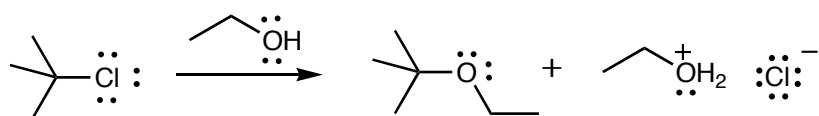


steric
hindrance

activation
energy

rate of
reaction

Consider the following S_N1 reaction.



Draw the energy diagram for this reaction.

Which is the rate limiting step?



Draw the structure of the transition state for this step.

Which reagents are involved in the rate limiting step?

What would happen if you

doubled the concentration of the alkyl halide?

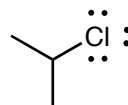
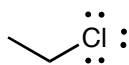
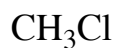
doubled the concentration of the nucleophile or base?

What order is the alkyl halide? the nucleophile or base?

Write the rate law:

What does S_N1 stand for?

What happens to the rate of S_N1 reactions as the substitution increases?



carbocation
stability

activation
energy

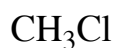
rate of
reaction

How does the identity of the halogen atom affect the rate of substitution reactions?

two possible explanations:

longer bonds break more easily

more EN, more stable afterwards



Will this be true for both $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$ reactions?

Rearrangements

In which substitution reaction do carbocations form?

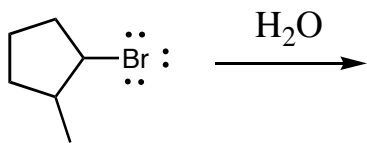
Why do carbocations undergo rearrangements?

Which carbocations are mostly likely to rearrange?

What are the two ways in which a carbocation can rearrange?

Which carbocation will give the product?

Give the substitution products in the following reaction.



Solvents

Why is a solvent useful when running a reaction?

What are the important issues when considering solvents for substitution and elimination reactions?

What kind of solvent do S_N2 reactions require?

high polarity solvent - to dissolve charged reagents

What kind of solvent do S_N1 reactions require?

What solvents are in the following categories?

nonpolar

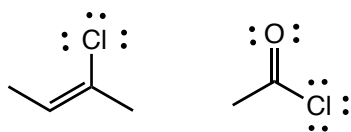
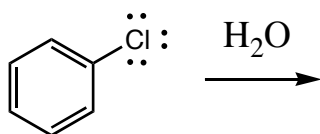
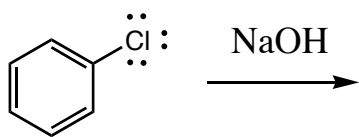
moderately polar

highly polar, aprotic

highly polar, protic

Exclusion of aryl halides, vinyl halides, and acid chlorides

Why can't aryl halides undergo substitution reactions?



Summary of Substitution Reactions

S_N2 reactions:

result:

mechanism:

reagent:

stereochemistry:

rate law:

alkyl halides:

rearrangements?

solvent:

S_N1 reactions:

result:

mechanism:

reagent:

stereochemistry:

rate law:

alkyl halides:

rearrangements?

solvent:

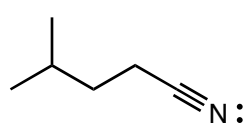
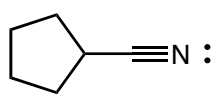
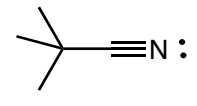
III. Synthesis Using Substitution Reactions

What is synthesis?

What steps should you go through?

- 1) look at the compound to decide what nucleophiles you could use
- 2) decide what alkyl halides you could use
- 3) decide if the reaction will be favorable

Consider the following target molecules:

	nucleophile	alkyl halide	rxn	favorable?
				
				
				
				

nucleophile

alkyl halide

rxn

favorable?

