

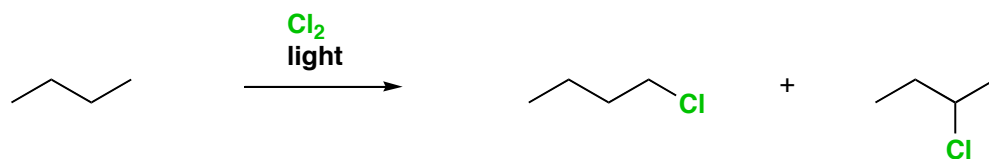
Chem 341 • Organic Chemistry I

Lecture Summary 28 • October 31, 2007

Chapter 10 - Alkyl Halides

Preparation of Alkyl Halides - free radical halogenation

Free radical halogenation of alkanes will produce alkyl halides, however, the reaction usually produces a mixture of products. Note that the reaction proceeds via carbon radical intermediates and similar to carbocations, a carbon radical is more stable if it is more substituted. Thus, tertiary hydrogens are more reactive than secondary hydrogens, which are more reactive than primary hydrogens in this process.



expected statistical ratio from six 1° H's and four 2° H's

6 : 4

actual ratio observed

30 : 70

=> secondary H's are 3.5 times more reactive than primary H's for radical chlorination



expected statistical ratio from nine 1° H's and one 2° H

9 : 1

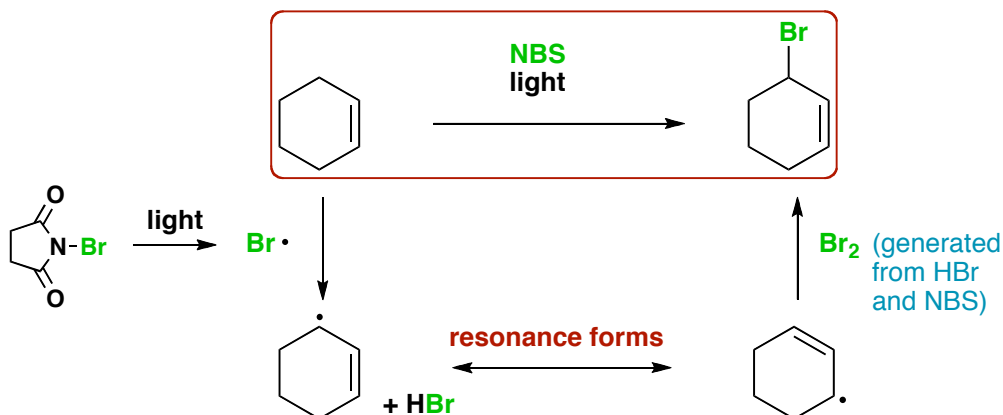
actual ratio observed

65 : 35

=> tertiary H's are 5 times more reactive than primary H's for radical chlorination

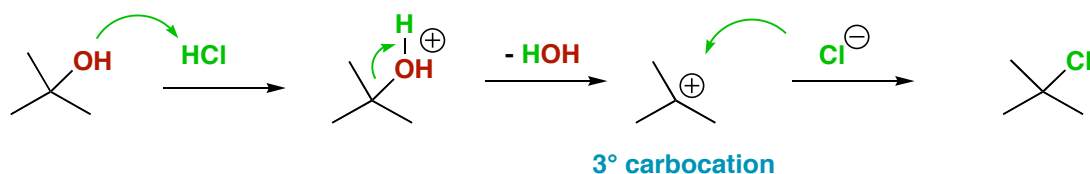
Allylic Bromination - free radical

Allylic radicals are strongly stabilized by resonance. Thus, radical halogenation of molecules with an alkene will selectively substitute one of the allylic hydrogens. For example, bromine radicals, generated by the photolysis of NBS, will generate allylic bromides.

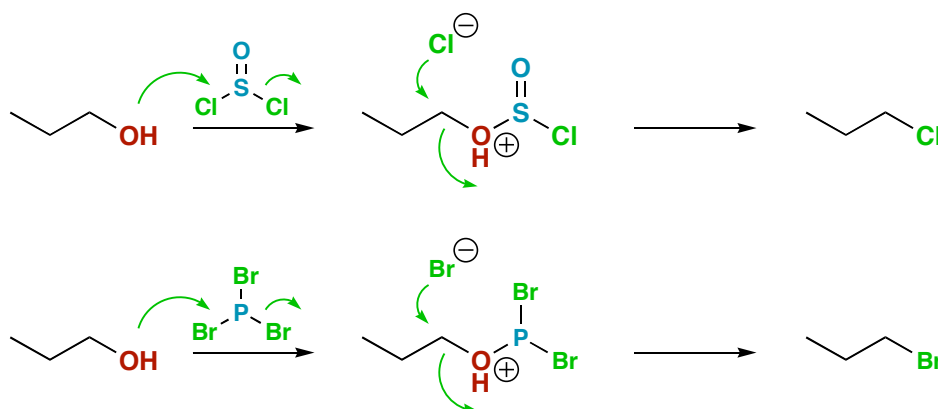


Preparation of Alkyl Halides - substitution of alcohols

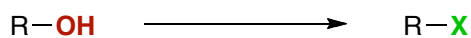
The substitution of an alcohol functional group with a halogen can be carried out on tertiary alcohols with mineral acids. This reaction only works with 3° alcohols as the mechanism involves the loss of water to form a carbocation and subsequent addition of halide.



Primary and secondary alcohols often undergo competing processes under acidic conditions such as eliminations and carbocation rearrangements. Thus, it is not practical to do the substitution reaction on these alcohols with HCl or HBr. However, bromides can be prepared by reaction with PBr_3 and chlorides with SOCl_2 . These reagents provide a dual role of activating the OH group to make it a good leaving group (polarize the C-O bond more) and supplying the X^- for the substitution reaction.

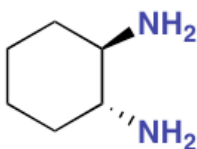
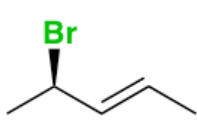
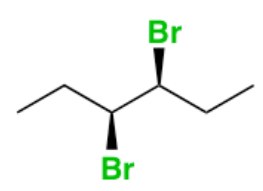
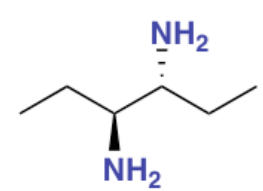


The conditions for substitution of an alcohol functional group with a halogen depends on the degree of alkyl substitution on the alcohol.



Alcohol	Chloride	Bromide
tertiary (3°)	HCl	HBr
primary (1°) or secondary (2°)	SOCl_2	PBr_3

Quiz of the day

Q: Which of the following compounds is NOT chiral? <i>Happy Halloween!</i>	<input type="checkbox"/> 1:	 A cyclohexane ring with an amino group (NH ₂) on a wedge at the top position and another amino group (NH ₂) on a dash at the adjacent position.
	<input type="checkbox"/> 2:	 A skeletal structure of 3-bromo-1-butene with a bromine atom (Br) on a wedge at the third carbon of a four-carbon chain that has a double bond between carbons 1 and 2.
	<input type="checkbox"/> 3:	 A skeletal structure of 2,3-dibromopentane with bromine atoms (Br) on wedges at the second and third carbons of a five-carbon chain.
	<input checked="" type="checkbox"/> 4:	 A skeletal structure of trans-2,3-diaminopentane with an amino group (NH ₂) on a wedge at the second carbon and another amino group (NH ₂) on a dash at the third carbon of a five-carbon chain.