

7.3: PREPARATION OF ALKYL HALIDES

Learning Objective

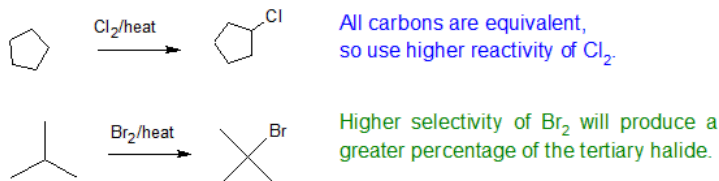
- specify the reagents for the most efficient synthesis of alkyl halides using free-radical halogenation of alkanes (Chapter 5) or allylic halogenation of alkenes with NBS

FREE RADICAL HALOGENATION OF ALKANES

Free radical halogenation of alkanes is the substitution of a single hydrogen on the alkane for a single halogen to form a haloalkane. Light is required to initiate the radical formation and is a good example of a photochemical reaction. The simplest example is shown below for methane reacting with chlorine in the presence of light to form chloromethane and hydrogen chloride gas.

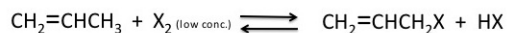


Free radical halogenation of alkanes has been thoroughly explained in chapter 5. The structure of the alkane is evaluated to choose between the high reactivity of chlorine (Cl_2) and the high selectivity of bromine (Br_2).



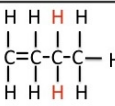
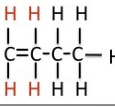
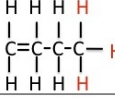
ALLYLIC BROMINATION

When halogens are in the presence of unsaturated molecules such as alkenes, the expected reaction is addition to the double bond carbons resulting in a vicinal dihalide (halogens on adjacent carbons). The reaction is studied in a later chapter. To avoid halogen reactions at the alkene the halogen concentration is kept low enough that a substitution reaction occurs at the allylic position rather than addition at the double bond. The product is an allylic halide (halogen on carbon next to double bond carbons), which is acquired through a radical chain mechanism.



WHY SUBSTITUTION OF ALLYLIC HYDROGENS?

As the table below shows, the dissociation energy for the allylic C-H bond is lower than the dissociation energies for the C-H bonds at the vinylic and alkylic positions. This is because the radical formed when the allylic hydrogen is removed is resonance-stabilized. Hence, given that the halogen concentration is low, substitution at the allylic position is favored over competing reactions. However, when the halogen concentration is high, addition at the double bond is favored because a polar reaction out competes the radical chain reaction.

Type of Hydrogen	Dissociation Energy (DH°)
allylic 	88 kcal/mol
vinylic 	106 kcal/mol
alkylic 	98 kcal/mol

RADICAL ALLYLIC BROMINATION USING NBS AND LIGHT

PREPARATION OF BROMINE (LOW CONCENTRATION)

NBS (N-bromosuccinimide) is the most commonly used reagent to produce low concentrations of bromine. When suspended in tetrachloride (CCl_4), NBS reacts with trace amounts of HBr to produce a low enough concentration of bromine to facilitate the allylic

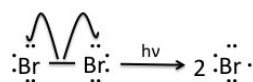
bromination reaction.



ALLYLIC BROMINATION MECHANISM

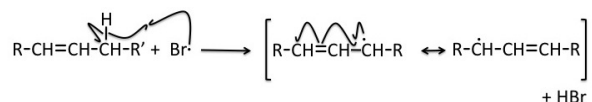
STEP 1: INITIATION

Once the pre-initiation step involving NBS produces small quantities of Br_2 , the bromine molecules are homolytically cleaved by light to produce bromine radicals.

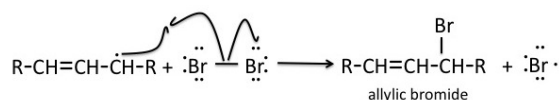


STEP 2: PROPAGATION

One bromine radical produced by homolytic cleavage in the initiation step removes an allylic hydrogen of the alkene molecule. A radical intermediate is generated, which is stabilized by resonance. The stability provided by **delocalization** of the radical in the alkene intermediate is the reason that substitution at the allylic position is favored over competing reactions such as addition at the double bond.

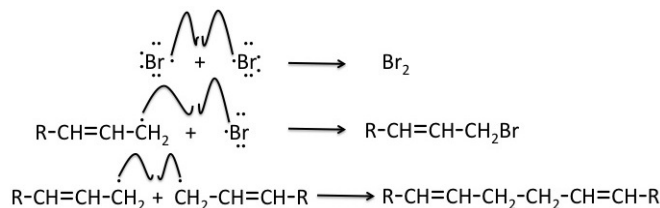


The intermediate radical then reacts with a Br_2 molecule to generate the allylic bromide product and regenerate the bromine radical, which continues the radical chain mechanism. If the alkene reactant is asymmetric, two distinct product isomers are formed.



STEP 3: TERMINATION

The radical chain mechanism of allylic bromination can be terminated by any of the possible steps shown below.

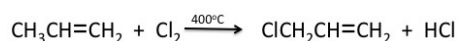


RADICAL ALLYLIC CHLORINATION

Like bromination, chlorination at the allylic position of an alkene is achieved when low concentrations of Cl_2 are present. The reaction is run at high temperatures to achieve the desired results.

INDUSTRIAL USES

Allylic chlorination has important practical applications in industry. Since chlorine is inexpensive, allylic chlorinations of alkenes have been used in the industrial production of valuable products. For example, 3-chloropropene, which is necessary for the synthesis of products such as epoxy resin, is acquired through radical allylic chlorination (shown below).

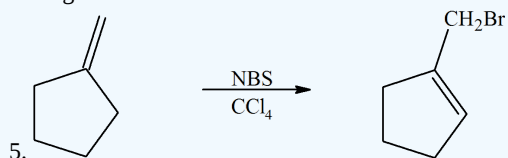


EXERCISES

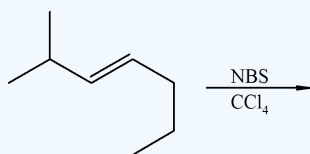
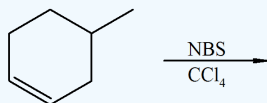
Exercises

1. Predict the two products of the allylic chlorination reaction of 1-heptene.
2. What conditions are required for allylic halogenation to occur? Why does this reaction outcompete other possible reactions such as addition when these conditions are met?

- Predict the product of the allylic bromination reaction of 2-phenylheptane. (Hint: How are benzylic hydrogens similar to allylic hydrogens?)
- The reactant 5-methyl-1-hexene generates the products 3-bromo-5-methyl-1-hexene and 1-bromo-5-methyl-2-hexene. What reagents were used in this reaction?

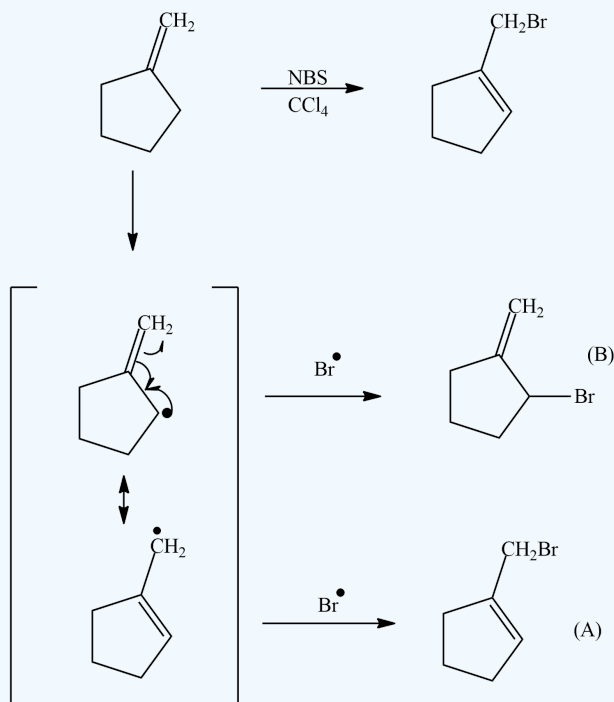


6. Predict the products of the following reactions:

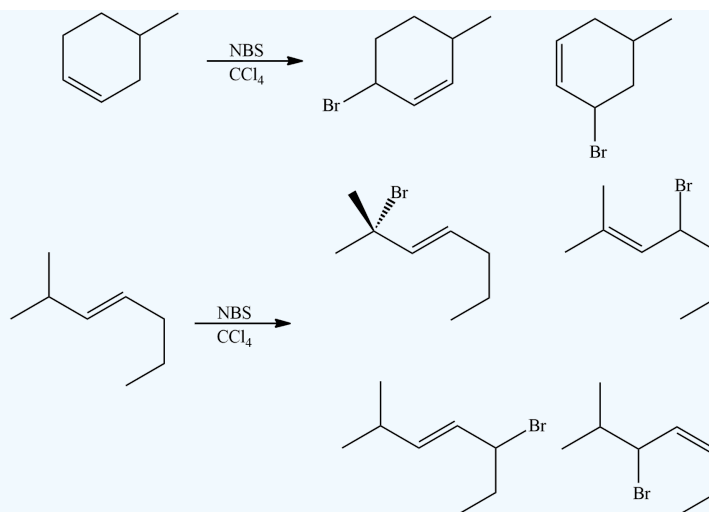


Solutions

- 3-chloro-1-heptene and 1-chloro-2-heptene
- A low concentration of halide radical is sufficient for reaction at the allylic carbon without creating a reactivity environment for the pi bond of the alkene.
- 2-bromo-2-phenylheptane
- NBS with light
- The product (A) is a 1° halogen which is more stable product even though the (B) had a better transition state with a 2° radical.



6.



REFERENCES

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CONTRIBUTORS AND ATTRIBUTIONS

- Sharon Wei (UCD), Liza Chu (UCD)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))

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