

10.3: PREPARING ALKYL HALIDES FROM ALKENES - ALLYLIC BROMINATION

OBJECTIVES

After completing this section, you should be able to

1. write the equation for the bromination of a symmetrical alkene using N-bromosuccinimide.
2. predict the product formed when a given symmetrical alkene is treated with N-bromosuccinimide.
3. identify the reagent, the symmetrical alkene, or both, needed to produce a given allyl halide by allylic bromination.
4. list the following radicals in order of increasing or decreasing stability: allyl, vinyl, primary alkyl, secondary alkyl, tertiary alkyl, methyl.
5. explain the ease of forming an allyl radical, and the difficulty of forming a vinyl radical, in terms of relative C-H bond dissociation energies.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

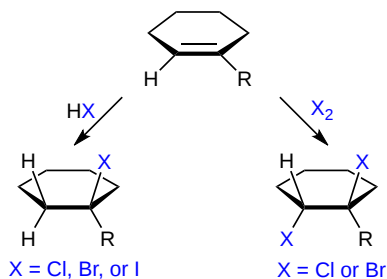
- allylic carbon

STUDY NOTES

We have discussed the electrophilic addition of X_2 and HX to alkenes as a route to forming alkyl halides (Sections 7.8 and 8.2). In this section we introduce bromination at the allylic position with N-bromosuccinimide (NBS). Notice that at the moment we are restricting our studies to the allylic bromination of symmetrical alkenes, such as cyclohexene. When we introduce an element of asymmetry, we find that more than one allyl radical can be formed; therefore, we must assess the relative stability of each radical when trying to predict which product will predominate. The method of doing this assessment is described in the next section.

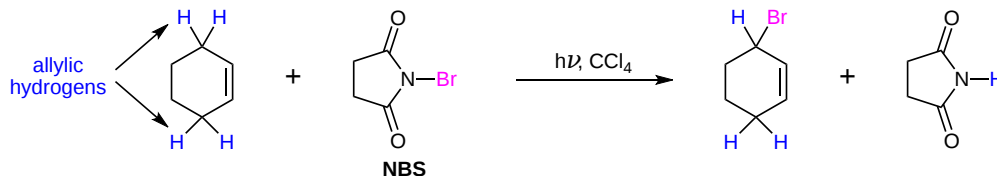
ALLYLIC BROMINATION

Previously, alkyl halides have been produced through reactions with alkenes. Hydrogen halides (HCl , HBr , and HI) react with alkenes in an electrophilic addition reaction discussed in Section 7-8 to yield alkyl halides as products. Also, Bromine (Br_2) and chlorine (Cl_2) can react with alkenes to provide dihalogenated products as discussed in Section 8-2.



Another method for preparing alkyl halides from alkenes is with **N-bromosuccinimide (NBS)** in carbon tetrachloride (CCl_4) solution with the presence of light. The reaction specifically causes the substitution of bromine with a hydrogen attached to a carbon adjacent to the double bond - the allylic position.

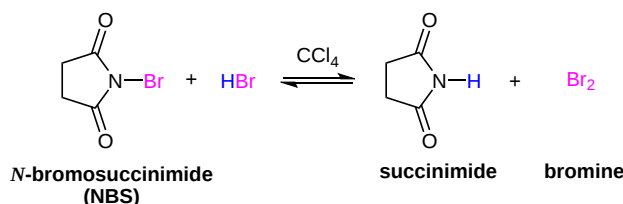
GENERAL REACTION



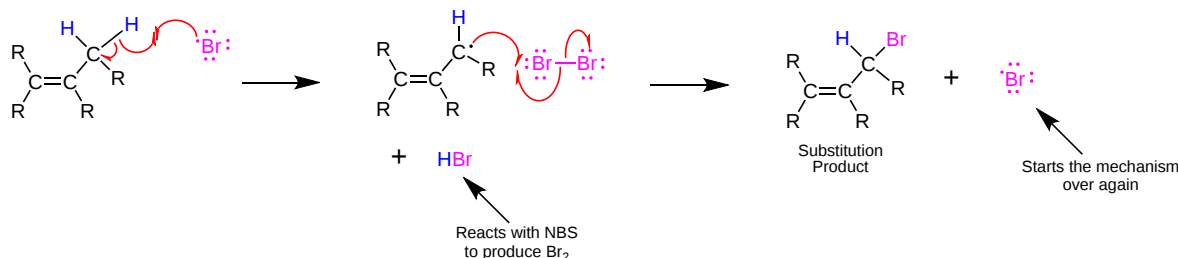
MECHANISM

The allylic bromination with NBS is analogous to the alkane halogenation reaction (Section 10.2) since it also occurs as a radical chain reaction. NBS is the most commonly used reagent to produce low concentrations of bromine. When suspended in tetrachloride (CCl_4), NBS

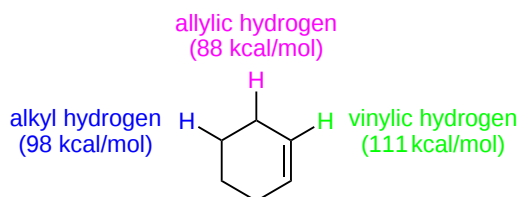
reacts very rapidly with the HBr formed during the reaction mechanism to provide bromine (Br_2) which is required for the reaction to continue. Under the correct conditions, NBS provides a constant but very low concentration of Br_2 in the reaction mixture. The low concentration of Br_2 helps to prevent the formation of unwanted side-products.



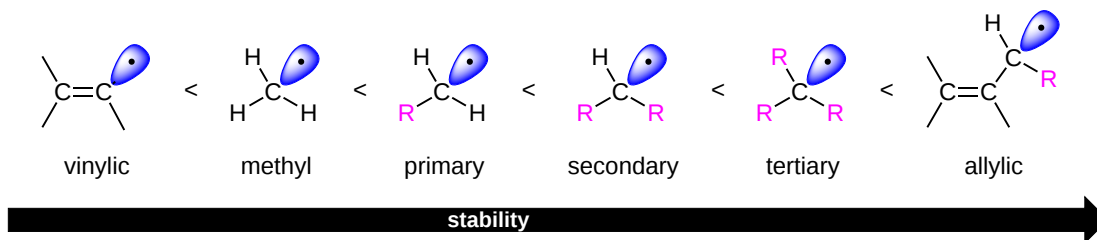
The mechanism starts with the formation of a small amount of bromine radical which then abstracts an allylic hydrogen to form an allylic radical and HBr. The HBr can then react with NBS to form the Br_2 required for the reaction. The allylic radical then abstracts a bromine atom from Br_2 to form the allyl halide product and a bromine radical. The bromine radical produced allows the reaction to continue.



The predominance of allylic substitution over other positions is based on bond dissociation energies. An allylic C-H bond has a strength of about 88 kcal/mol which is much weaker than a typical alkyl C-H bond (98 kcal/mol) or vinylic C-H bond (111 kcal/mol). Therefore, an allylic C-H bond is most likely to form a free radical and react.



Because an allylic C-H bond requires less energy to undergo homolytic cleavage than even a tertiary C-H bond, it can be inferred that an allylic radical is more stable than a tertiary radical. The ordering of stability in radicals can be expanded to include vinylic and allylic radicals. The enhanced stability of allyl radicals can be attributed to resonance stabilization which will be discussed in the next section.



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