

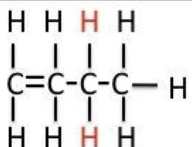
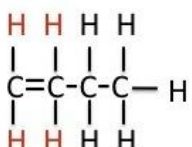
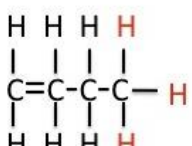
M.SC-Sem-II, CC-VIII , Organic Chemistry II
UNIT - I Free Radical Reactions Allylic halogenations(NBS)

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). However, when the halogen concentration is low enough, alkenes containing allylic hydrogens undergo substitution 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?

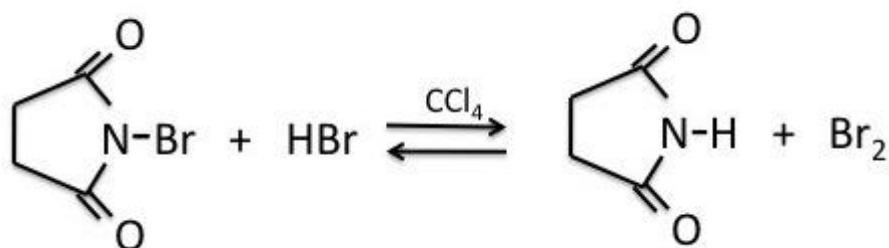
As the table below shows, the dissociation energy for the allylic C-H bond is lower than the dissociation energies for the C-H bonds at the vinylic and alkylic positions. This is because the radical formed when the allylic hydrogen is removed is **resonance**-stabilized. Hence, given that the halogen 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 outcompetes 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 (Wohl-Ziegler Reaction)

Preparation of Bromine (low concentration)

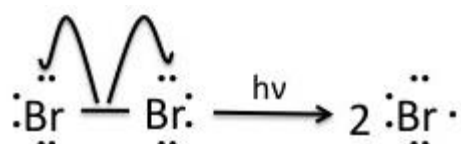
NBS (N-bromosuccinimide) is the most commonly used reagent to produce low concentrations of bromine. When suspended in tetrachloride (CCl₄), NBS reacts with trace amounts of HBr to produce a low enough concentration of bromine to facilitate the allylic bromination reaction.



Allylic Bromination Mechanism

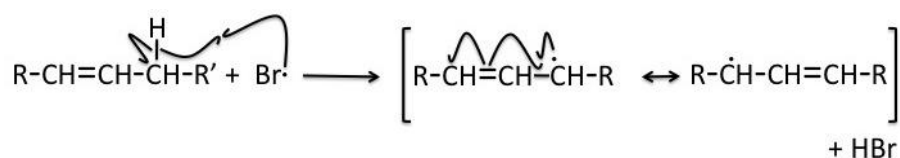
Step 1: Initiation

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.

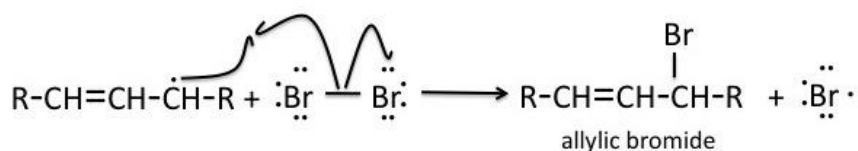


Step 2: Propagation

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.

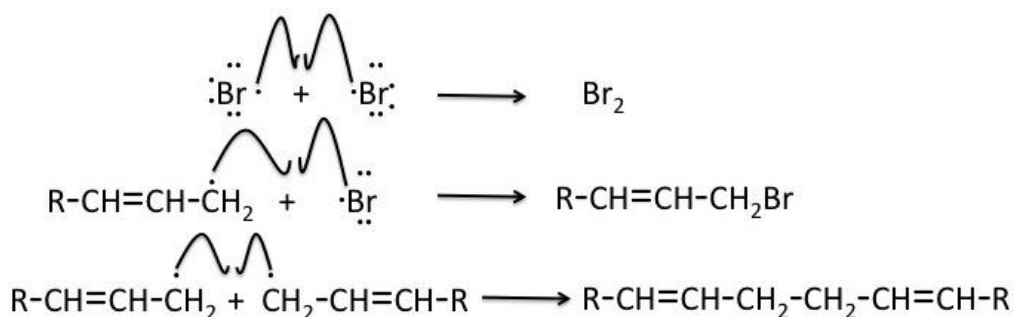


The intermediate radical then reacts with a Br_2 molecule to generate the allylic bromide product and regenerate the bromine radical, which continues the radical chain mechanism. If the alkene reactant is asymmetric, two distinct product isomers are formed.



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).

