

Carbon-carbon double bond as substituents

Free Radical Halogenation of Alkenes

- Free radical halogenation of alkenes is a fundamental organic transformation that involves the substitution of a hydrogen atom by a halogen atom (usually chlorine or bromine) through a free radical mechanism.
- This reaction can occur at allylic positions (the carbon atoms adjacent to the double bond), as direct halogenation of the double bond typically leads to addition rather than substitution.
- Therefore, free radical halogenation of alkenes is particularly important when discussing allylic halogenation.

Reaction Conditions and Halogenation Reagents

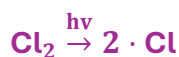
- Common halogens used:** Chlorine (Cl_2) or Bromine (Br_2).
- Initiation method:** Usually requires heat or light ($h\nu$) or a radical initiator like AIBN (azobisisobutyronitrile) or benzoyl peroxide.
- Solvent:** Typically carried out in non-polar solvents like CCl_4 or inert gases to prevent unwanted side reactions.
- Reactivity of halogens:**
 - Chlorine** is more reactive but less selective.
 - Bromine** is less reactive but more selective, making it preferable for controlled reactions.

Mechanism

The process occurs via a chain mechanism involving three main steps:

1. Initiation

- The halogen molecule undergoes homolytic cleavage when exposed to heat or light, generating two halogen radicals:



2. Propagation

- The halogen radical abstracts an allylic hydrogen (a hydrogen attached to a carbon adjacent to the $\text{C}=\text{C}$ bond), producing an allyl radical:



- This allylic radical then reacts with another halogen molecule to form the allyl halide and regenerate the halogen radical:



- This regenerates the chain-carrying radical and continues the chain process.

3. Termination

- Two radicals combine to terminate the reaction, though this is relatively rare compared to the propagation steps.

Selectivity and Stability

- Allylic positions are favored because the resulting allylic radical is resonance-stabilized.
- The stability of the intermediate radical determines the site of halogenation.
- The reaction is regioselective — it selectively occurs at positions that lead to the most stable intermediate radical.

Limitations and Issues

- **Over-halogenation:** Excess halogen can lead to multiple substitutions.
- **Competing reactions:** Halogenation across the double bond (addition) can compete under certain conditions, especially in the absence of radical initiators.
- **Stereochemical considerations:** Since the allyl radical is planar and symmetric, it can lead to mixtures of stereoisomers if not controlled.

Example

- Allylic bromination of propene with NBS (N-Bromosuccinimide) in the presence of light:



- This is a preferred method because NBS provides a low steady-state concentration of Br_2 , favoring allylic substitution over addition.

Comparison of Free Radical Substitution with Free Radical Addition

- Understanding the difference between free radical substitution and free radical addition is essential for predicting product outcomes, especially when dealing with alkenes and alkynes.
- These two reaction types operate via radical pathways but differ significantly in their mechanism, substrates, intermediates, and products.

Free Radical Substitution

Definition

- In this type of reaction, a radical replaces an atom or group (typically hydrogen or halogen) on a molecule. It's a substitution because one group is replaced by another.

Common Example

- Allylic bromination of alkenes using NBS is a classic example. Another is the halogenation of alkanes.

Mechanism Outline

- **Initiation:** Generation of free radicals.
- **Propagation:** Radical abstracts a hydrogen or group, forms a new radical.
- **Termination:** Two radicals recombine.

Requirements

- Requires a radical initiator (heat/light/AIBN).
- Preferential at **allylic or benzylic** positions due to resonance stabilization.
- The substrate should have easily abstractable hydrogens.

Product

- A hydrogen (or another atom) is replaced by a halogen or another radical-bearing group.

Free Radical Addition

Definition

- This reaction involves the addition of radicals across a double or triple bond, forming new sigma bonds and eliminating the pi bond.

Common Example

- Anti-Markovnikov addition of HBr to alkenes in the presence of peroxides is a classical example.

Mechanism Outline

- Initiation: Peroxide decomposes into alkoxy radicals which initiate the chain.
- Propagation: Radical adds to the double bond forming a new carbon radical, which then abstracts a halogen.
- Termination: Radical recombination.

Requirements

- Needs a source of radicals (often peroxides).
- Works best with electron-rich alkenes.
- Usually involves electrophilic radicals adding to nucleophilic alkenes.

Regioselectivity

- In contrast to ionic addition, radical addition often follows Anti-Markovnikov orientation due to the stability of the carbon radicals formed.
- **For example:**



Key Differences

Feature	Radical Substitution	Radical Addition
Type of reaction	Replacement of atom/group	Addition across a multiple bond
Substrate type	Usually alkanes or allylic alkenes	Alkenes or alkynes
Site of reactivity	Allylic, benzylic, tertiary hydrogens	Double or triple bonds
Radical intermediate	Formed by H-abstraction	Formed by radical addition to pi bond
Orientation	Depends on radical stability	Often Anti-Markovnikov
Control methods	Light, heat, radical initiators	Peroxides and heat
Products	Haloalkanes (e.g., allyl halide)	Addition products (e.g., haloalkanes)

Free Radical Substitution In Alkenes

Fundamental Concepts

- Free radical substitution in alkenes primarily refers to the replacement of a hydrogen atom at an allylic position (adjacent to a C=C double bond) with a halogen or another group via a radical mechanism.
- This is in contrast to electrophilic addition reactions, which target the double bond itself.
- The allylic position in an alkene is particularly reactive in radical substitution due to the resonance stabilization of the resulting allyl radical.

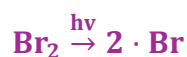
Mechanism Overview

- The substitution process generally follows a radical chain mechanism consisting of **initiation**, **propagation**, and **termination** steps.

These are discussed in detail below.

1. Initiation

- A halogen source (Cl_2 or Br_2) or halogen donor (e.g., NBS) is homolytically cleaved under the influence of light or heat to generate halogen radicals.



- Or, using NBS (N-Bromosuccinimide):



2. Propagation

- A halogen radical abstracts a hydrogen atom from the allylic position of the alkene, forming an **allyl radical**, which is resonance-stabilized.



- The resulting allyl radical reacts with a Br₂ molecule (or similar halogen donor), yielding the **allylic halide** product and regenerating a halogen radical.



- This maintains the chain propagation.

3. Termination

- This occurs when two radicals combine, ending the chain process:



- Or other radical-radical combinations.

Regioselectivity and Resonance

- Allylic radicals are resonance stabilized, which means they have delocalized electrons across the π-system:



- This delocalization allows for multiple sites of substitution, potentially leading to isomeric products if the substrate has more than one allylic position. For example:



- Here, substitution can occur at either end of the resonance-stabilized allylic radical.

Role of NBS

- NBS is a key reagent for selective allylic bromination. It acts as a slow, steady source of Br₂ in low concentration, which minimizes side reactions like addition to the double bond.
- NBS is particularly favored for its:
 - Selectivity
 - Efficiency in forming mono-brominated products
 - Clean reaction profiles

Substrate Scope

- Radical substitution in alkenes is typically limited to:
 - Allylic and benzylic hydrogens
 - Tertiary hydrogens (due to high radical stability)
 - Not favored for primary non-allylic alkenes or unactivated alkanes

Synthetic Applications

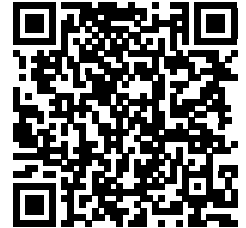


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