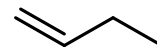


## CONCEPT: REACTIONS AT THE ALLYLIC POSITION

Allylic Position

- **Recall:** The allylic position is the C atom adjacent to a \_\_\_\_\_ bond.

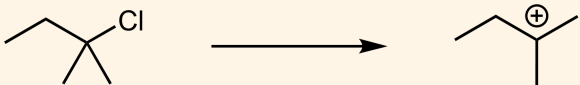
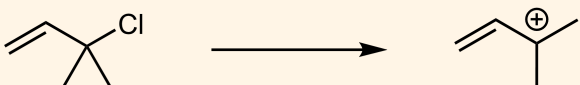
□ Allylic compounds react differently than alkenes.



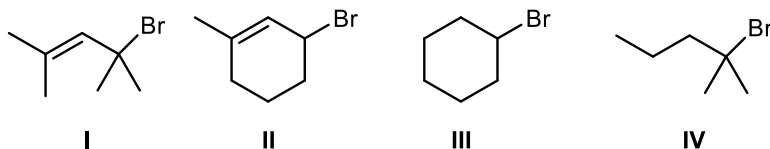
- 1) **S<sub>N</sub>1/E1 reactions:** allylic compounds react \_\_\_\_\_ than their alkyl counterparts.
- 2) **S<sub>N</sub>2/E2 reactions:** allylic halides react faster than alkyl halides.
- 3) **Radical reactions:** \_\_\_\_\_ takes place at the allylic position.
- 4) **Allylic Anions:** rapidly \_\_\_\_\_ due to resonance.

### 1) S<sub>N</sub>1/E1 Reactions of Allylic Compounds

- **Recall:** Step \_\_\_\_ is the rate-determining step in S<sub>N</sub>1 and E1 reactions.
  - Allylic carbocations form faster than similarly substituted alkyl carbocations due to their \_\_\_\_\_.
- **Alkyl C<sup>+</sup>:** stabilized by \_\_\_\_\_. □ **Allylic C<sup>+</sup>:** Stabilized by \_\_\_\_\_.

Carbocation Formation		
Reaction		Relative Rate
		_____
		_____

**EXAMPLE:** Arrange the following alkyl halides in decreasing order of their relative reaction rates under S<sub>N</sub>1 conditions.



a) III > IV > I > II

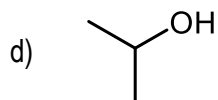
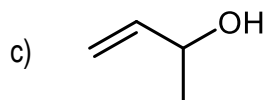
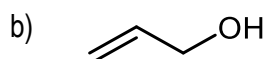
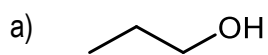
b) I > II > IV > III

c) IV > I > II > III

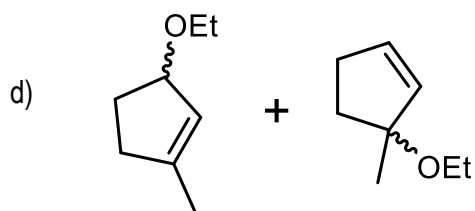
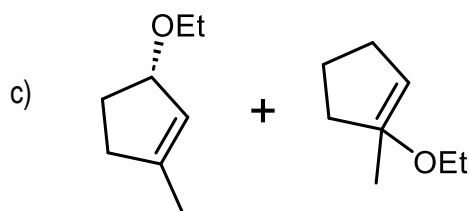
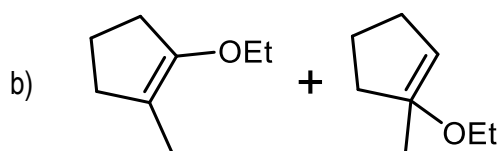
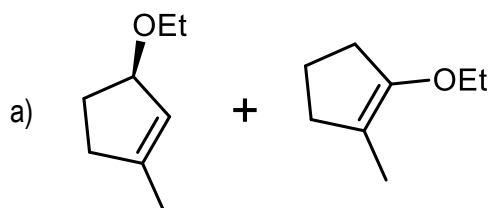
d) I > II > III > IV

**CONCEPT: REACTIONS AT THE ALLYLIC POSITION**

**PRACTICE:** Which of the following alcohols will undergo acid-catalyzed dehydration at the fastest rate?



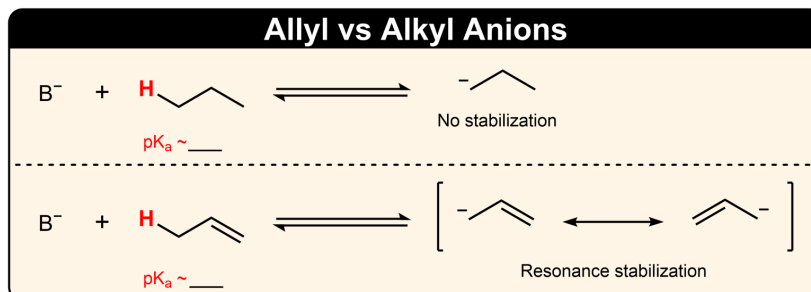
**PRACTICE:** What are the substitution products of the following reaction?



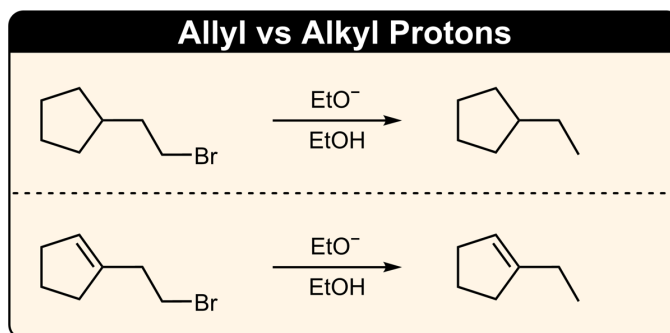
## CONCEPT: REACTIONS AT THE ALLYLIC POSITION

### 2) E2 Reactions Involving Allylic Protons

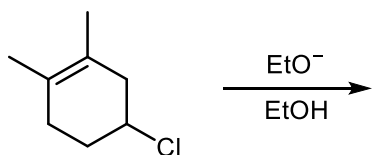
- Allylic anions are \_\_\_\_\_ acidic than alkyl protons because of a more stable \_\_\_\_\_ base.



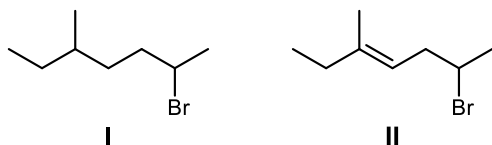
- Enhanced acidity of the allylic protons results in a \_\_\_\_ ratio of elimination products.
  - Alkene products of such eliminations are stabilized by \_\_\_\_\_.



**EXAMPLE:** Provide the mechanism and draw the structure of the major elimination product for the following reaction.



**PRACTICE:** Which of the following compounds will undergo E2 elimination at the fastest rate?

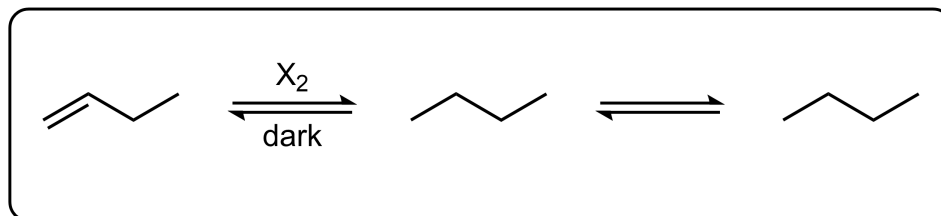


- a) I
- b) II
- c) Both will proceed at equal rates.

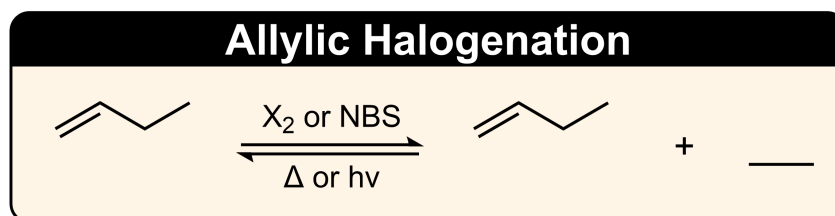
## CONCEPT: REACTIONS AT THE ALLYLIC POSITION

### 3) Radical Reactions of Allylic Compounds

- **Recall:** Halogens add to double bonds through a \_\_\_\_\_ ion intermediate.

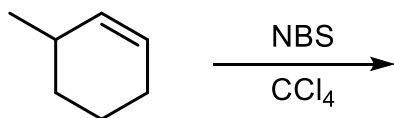


- The reaction site changes in the presence of a *radical initiator*, and substitution products are formed.

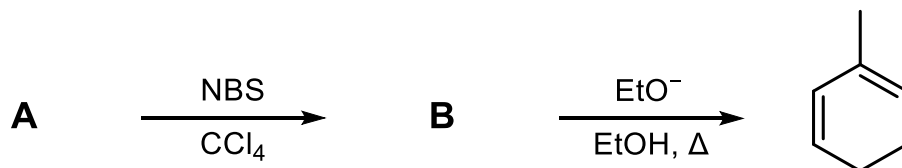


- Radical initiators can be  $\Delta$ ,  $h\nu$ , or \_\_\_\_\_.

**EXAMPLE:** Draw the structure of the major product for the following reaction.



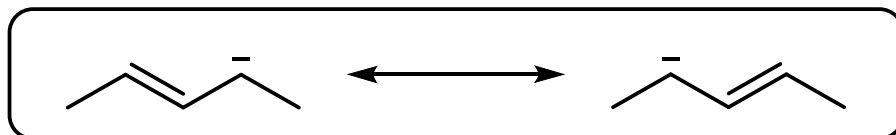
**PRACTICE:** Draw the structures of the compounds A and B for the following synthesis.



## CONCEPT: REACTIONS AT THE ALLYLIC POSITION

### 4) Allylic Anion Rearrangements

- Allylic anions are more stable than alkyl anions due to resonance.

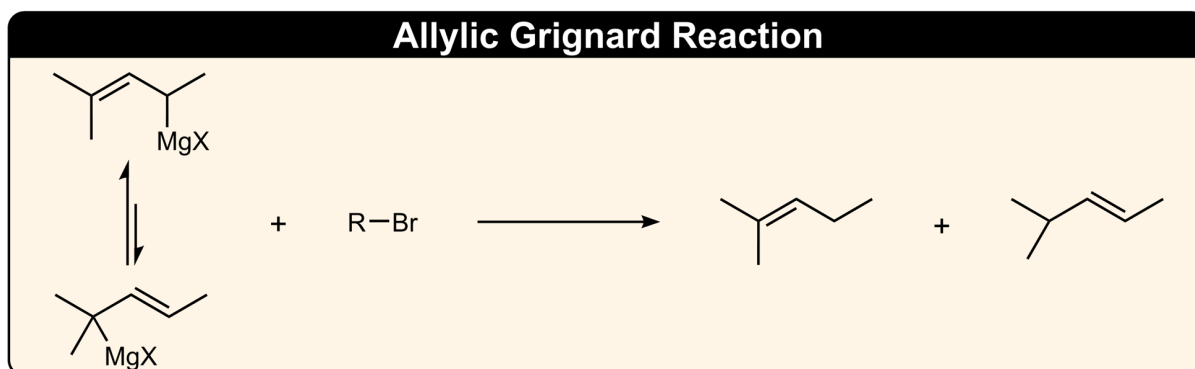


- Resonance in allylic Grignard reagents can result in two \_\_\_\_\_ anions in equilibrium.

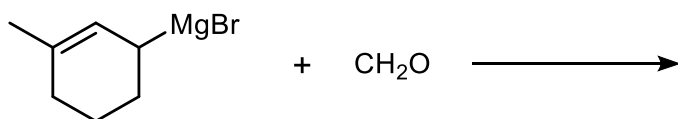


- ☐ **Recall:** alkene stability is determined by \_\_\_\_\_ rule.

- Each of the two isomers produces a \_\_\_\_\_ product with an electrophile.



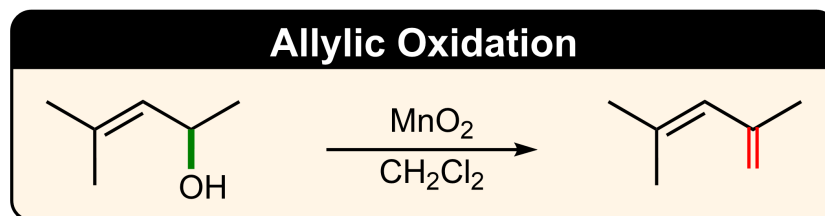
**EXAMPLE:** Draw products for the following reaction.



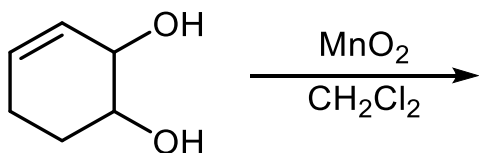
## CONCEPT: REACTIONS AT THE ALLYLIC POSITION

### Allylic Oxidation

- A weak oxidation where  $\text{MnO}_2/\text{CH}_2\text{Cl}_2$  oxidizes the allylic  $-\text{OH}$  group.
  - The alkene double bond remains unchanged.



**EXAMPLE:** Draw the product of the following oxidation reaction.



**PRACTICE:** Draw the structures of products A and B for the given reactions.

