

## Chapter 7: Radical Reactions

Radical reactions are very different than polar reactions and comprise only a small number of reactions that will be used in a typical organic chemistry course.

Here is a summary of polar and radical reactions:

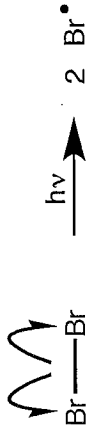
	Radical Reactions	Polar Reactions
Electron Movement	Move an odd number of electrons	Move an even number of electrons
Catalyst	Reaction requires the use of a catalyst like light, high heat or peroxides to initiate the reaction	A catalyst may or may not be required
Mechanism Arrows	A single-headed arrow is used to denote movement of an unpaired, <b>single</b> electron	A double-headed arrow is used to indicate movement of a <b>pair</b> of electrons
Nucleophiles/Electrophiles	This classification is <i>not</i> generally used for radical reactions	This classification <b>is</b> used for polar reactions
Intermediates	Radical	Carbocation, Carbanion, Carbene, or none
Reaction Steps	3 distinct steps: <ul style="list-style-type: none"> <li>• Initiation</li> <li>• Propagation</li> <li>• Termination</li> </ul>	Reactions may be concerted or stepwise. No polar reaction follows this radical 3-step protocol.

## Radical Mechanism Steps

Please keep in mind that each of the three steps below happen concurrently once a small amount of the radical is formed.

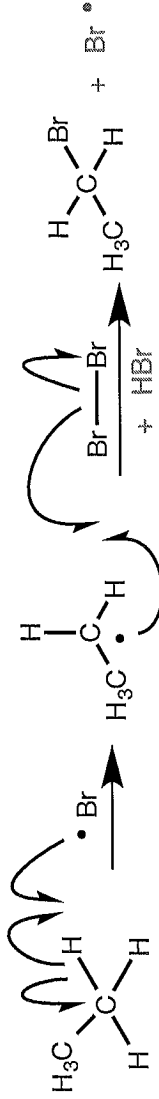
**NOTICE:** In a radical reaction mechanism, two arrows can originate from the same bond (initiation step), this is not allowed in polar reaction mechanisms. Also notice that the head of two arrows can come together to indicate formation of a new bond. This is also not allowed for polar reaction mechanisms.

**Initiation Step:** This is the first step of the mechanism when radicals are formed by the action of light ( $h\nu$ ), high heat ( $\Delta$ ) or peroxides.



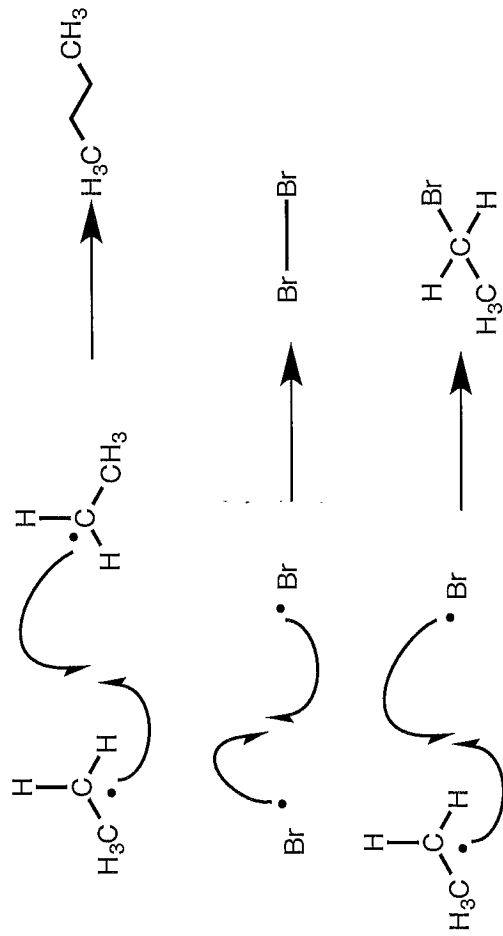
Notice that one electron from the Br-Br bond goes to each bromine as the bond breaks. This type of bond breaking is called homolytic cleavage - each atom gets an equal number of electrons upon dissociation. Also notice that two arrows originate from the same sigma bond - this is rarely seen in polar reactions.

**Propagation Step:** This is the second step of the mechanism when the initial radical reacts with a non-radical species to make a new radical. The radical is consumed and regenerated in this step.



Notice that a radical bromine is reacting with a non-radical C-H bond to form H-Br and a radical carbon. The radical carbon then reacts with non-radical  $\text{Br}_2$  to form the desired C-Br bond and regenerate the bromine radical in the process. (Recall that each step is happening concurrently after we form just a small amount of bromine radical, so there is still  $\text{Br}_2$  floating around from the initiation step. You will also see that  $\text{Br}_2$  is generated in the termination step.)

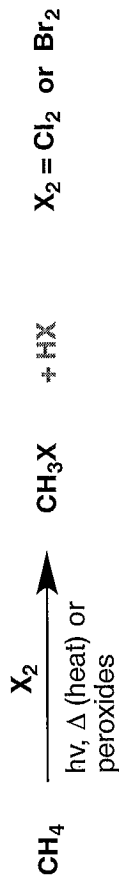
**Termination Step:** This is the last step of the mechanism when all remaining radicals are consumed. This step often leads to generation of desired products and undesired byproducts as well as regeneration of reagents.



Notice that there are two radicals on the left side of the arrow, and zero radicals on the right hand side of the arrow. Each termination step involves a net destruction of radicals.

## Radical Halogenation of Alkanes

General Reaction:

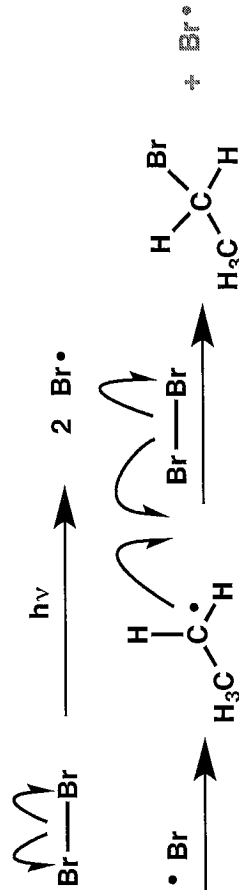


### Mechanism Basics Box:

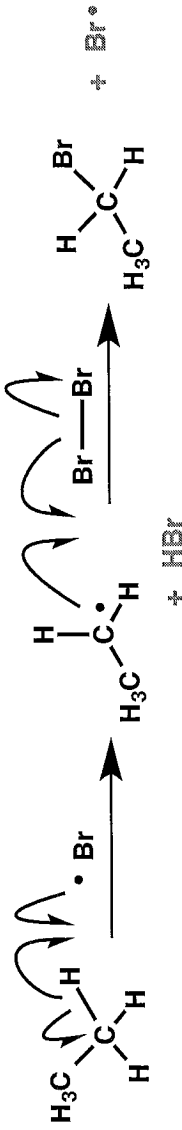
- Radical intermediates are formed by the action of light (hv), high heat or peroxides
- Radical reactions have three distinct steps: initiation, propagation, and termination
- There is a difference in reactivity between chlorine and bromine; bromine is highly selective for the more stable radical intermediate (tertiary > secondary >> primary)

### General Mechanism:

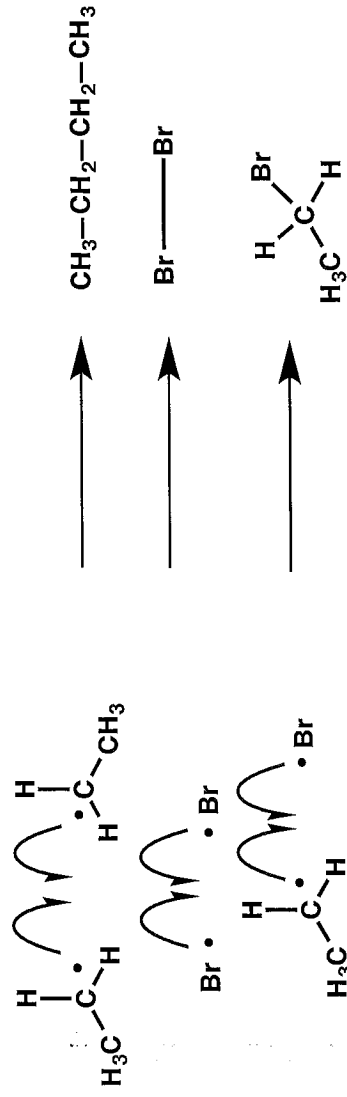
Initiation [net increase in # of radicals]



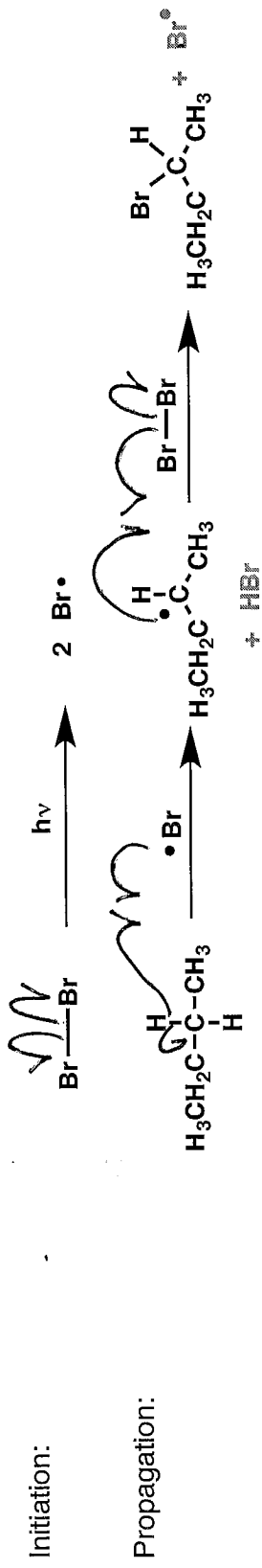
Propagation [no net change in # of free radicals]



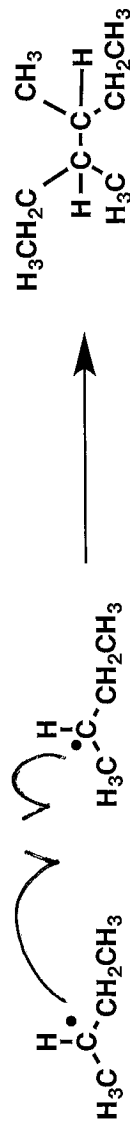
Termination [net decrease in # of free radicals]



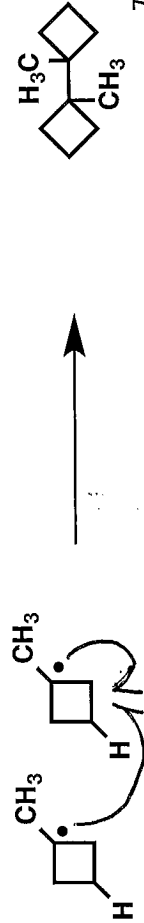
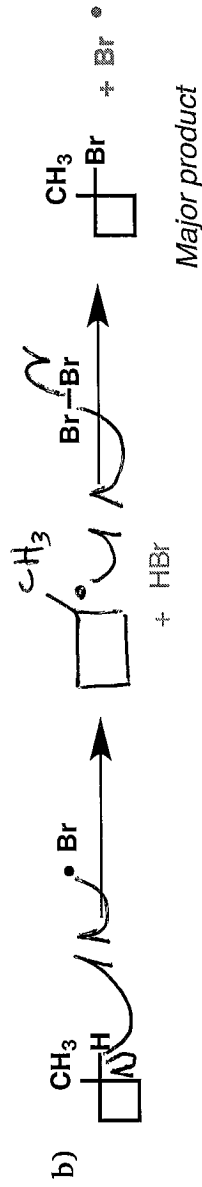
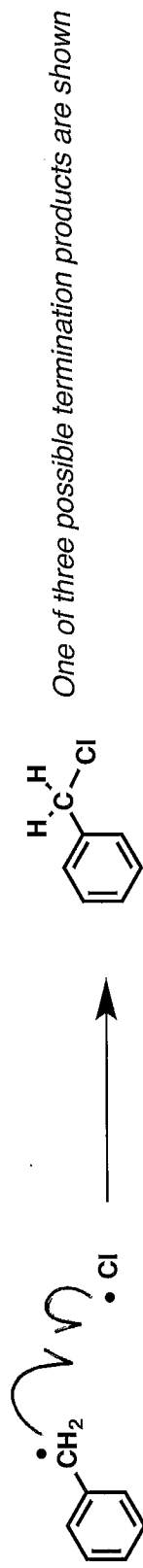
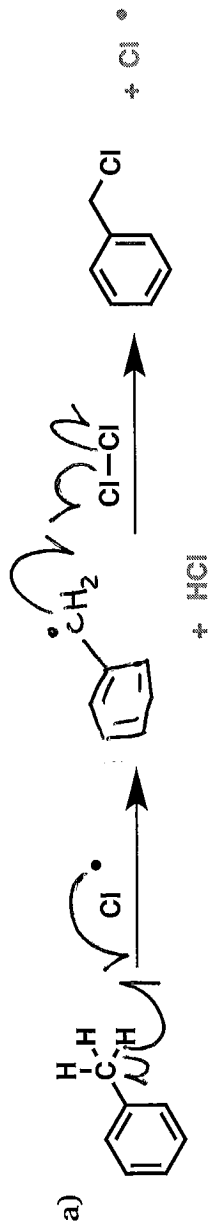
Fill in the missing arrows.



Termination:



Provide missing arrows and intermediates for the propagation and termination steps shown.



Two of three possible termination products are shown



Complete the mechanism by following the pattern (draw arrows and intermediate)

a) Propagation:

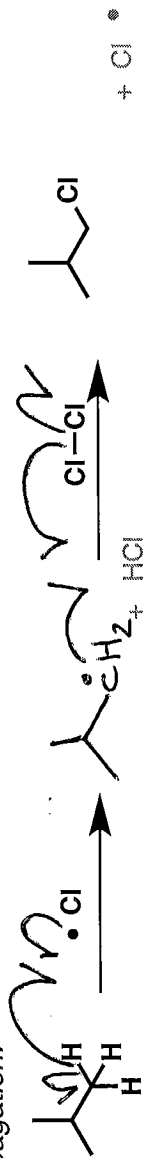


Termination:

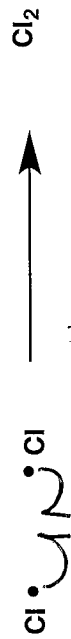


One of three possible termination products are shown

b) Propagation:



Termination:

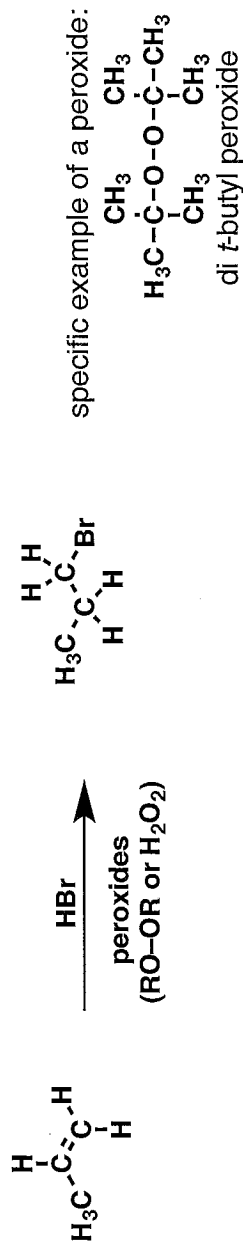


Two of three possible termination products are shown



## Radical Addition of Hydrogen Bromide to Alkenes

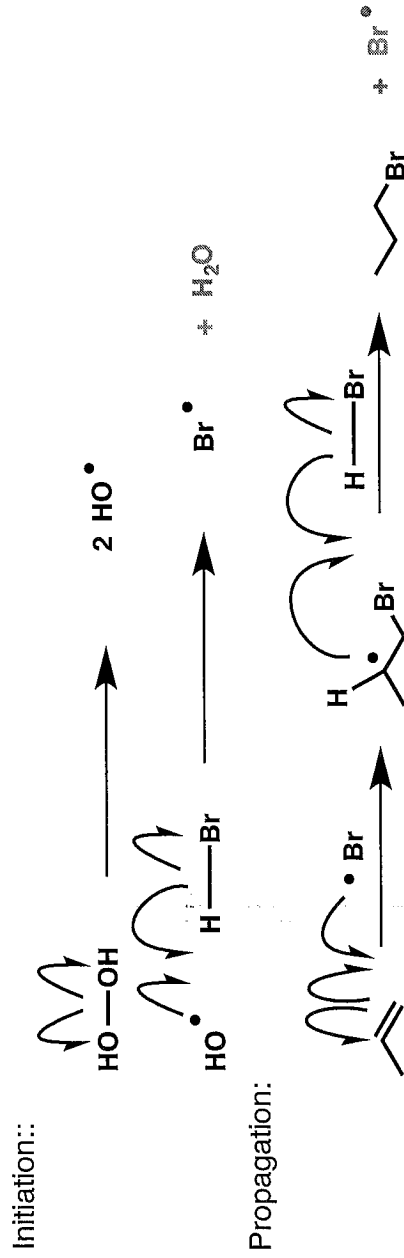
General Reaction:



### Mechanism Basics Box:

- Addition proceeds to yield the more stable radical. The reaction has “anti-Markovnikov” selectivity because the initial addition of bromine radical takes place at the least substituted carbon on the alkene
- The reaction does not proceed with HF, HCl, or HI.
- The use of non-polar solvents such as  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$  promote radical addition, which limits the amount of “Markovnikov” addition to the alkene as a competing reaction

### General Mechanism:

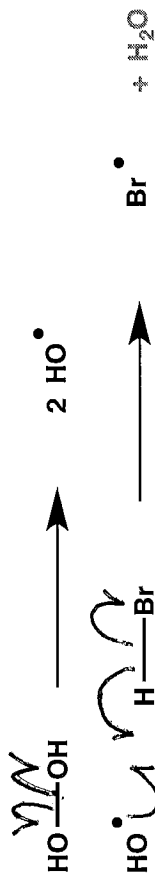


Termination: See “Radical Addition To Alkanes”

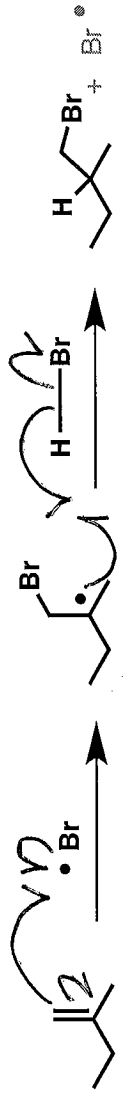


Fill in the missing arrows.

a) *Initiation:*

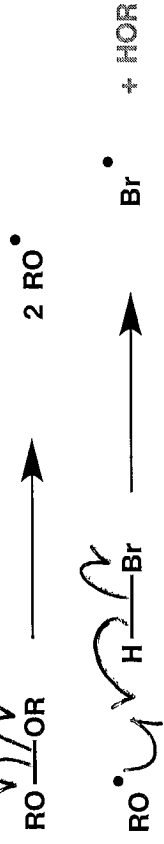


*Propagation:*



Complete the mechanism by following the pattern (draw arrows and intermediate)

b) *Initiation:*

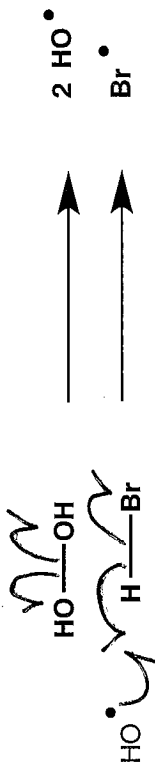


*Propagation:*



Complete the mechanism by following the pattern (draw arrows and intermediate)

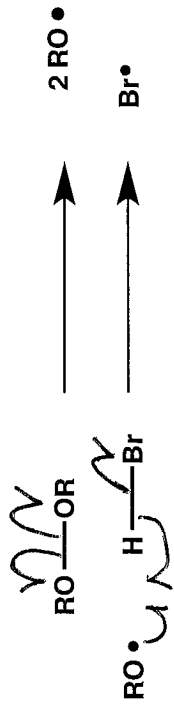
a) *Initiation:*



*Propagation:*



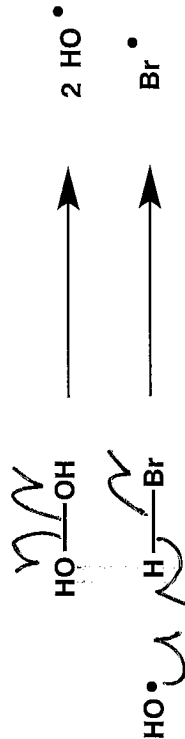
b) *Initiation:*



*Propagation:*



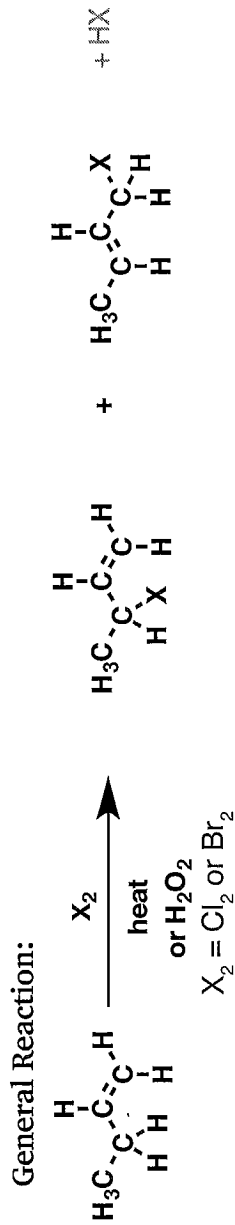
c) *Initiation:*



*Propagation:*



## Allylic Halogenation of Alkenes

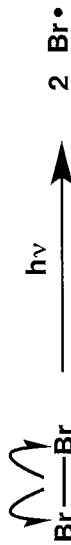


### Mechanism Basics Box:

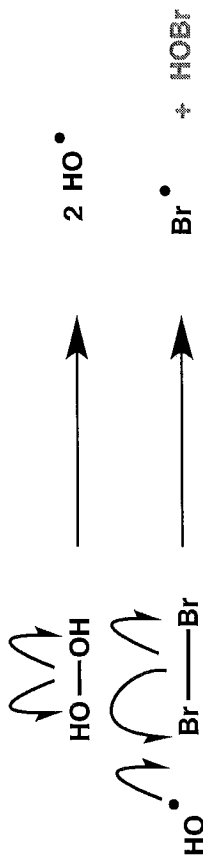
- This reaction requires a low concentration of halogen ( $\text{X}_2$ ) and heat, or the presence of a radical initiator. With high concentrations of halogen and log temperatures, addition to the alkene is favored.
- Allylic radicals have several resonance forms which may lead to multiple products
- N-bromo succinimide (NBS) can also be used as a source of low-concentration  $\text{X}_2$  to produce an allylic bromide

### General Mechanism:

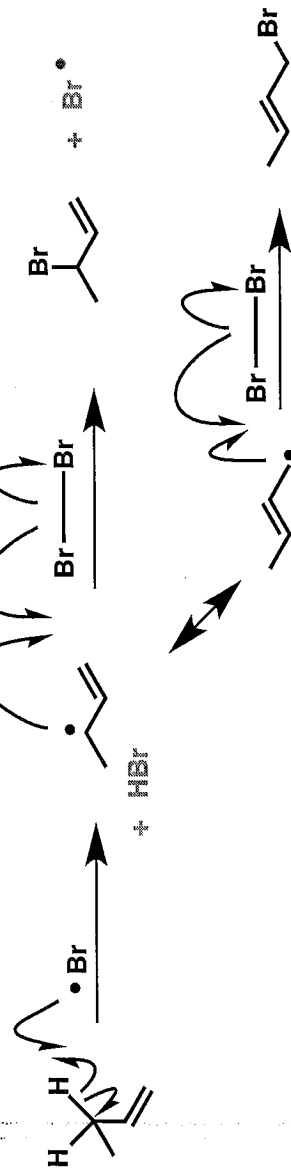
Initiation with high heat



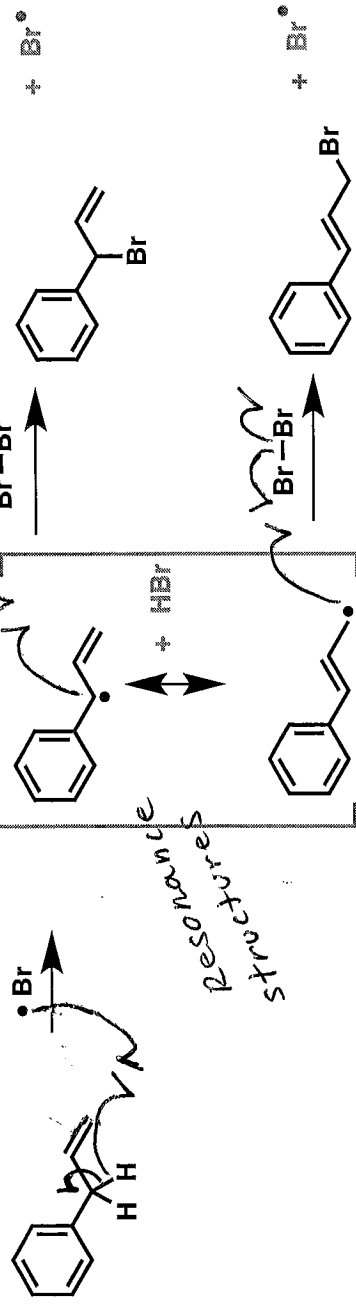
Initiation with peroxides



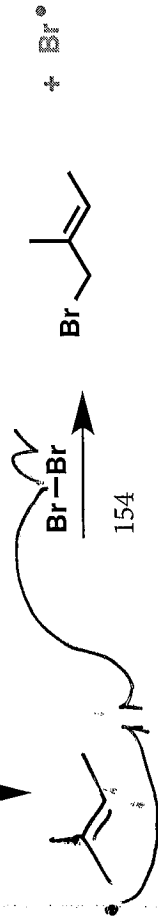
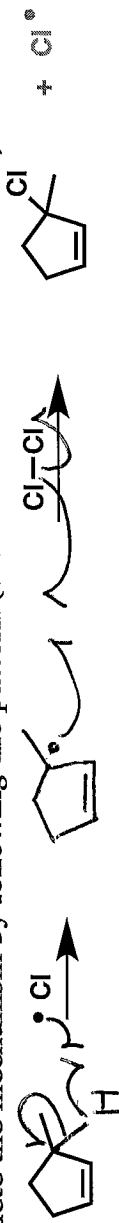
Propagation



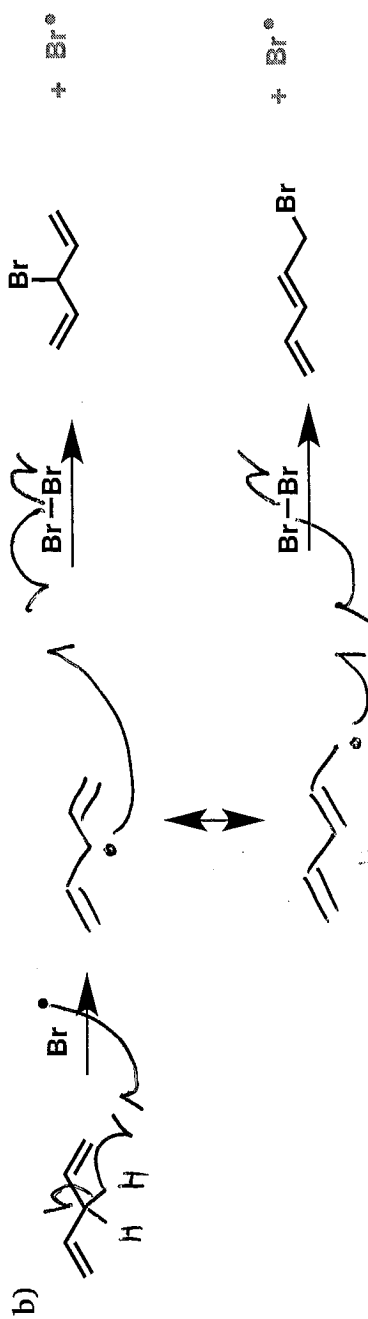
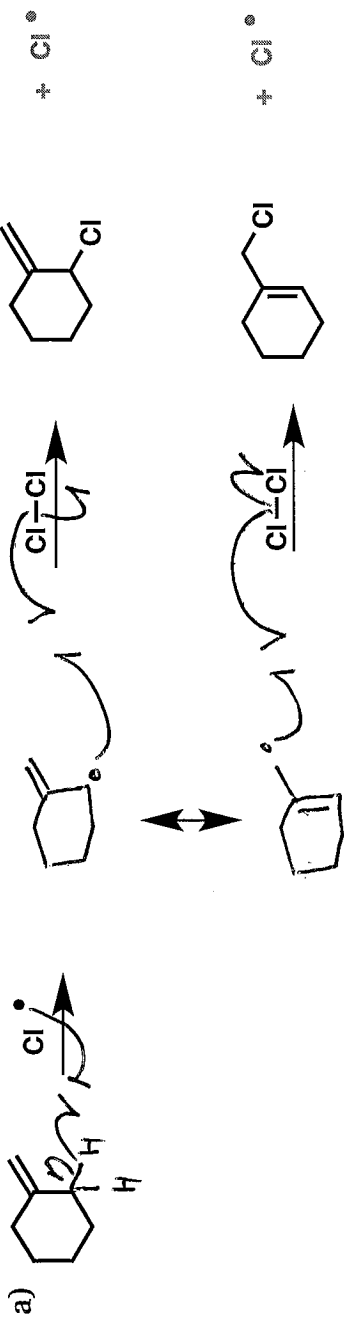
Draw in the missing mechanism arrows.



a) Complete the mechanism by following the pattern (draw arrows and intermediates).



Complete the mechanism by following the pattern (draw arrows and intermediates).

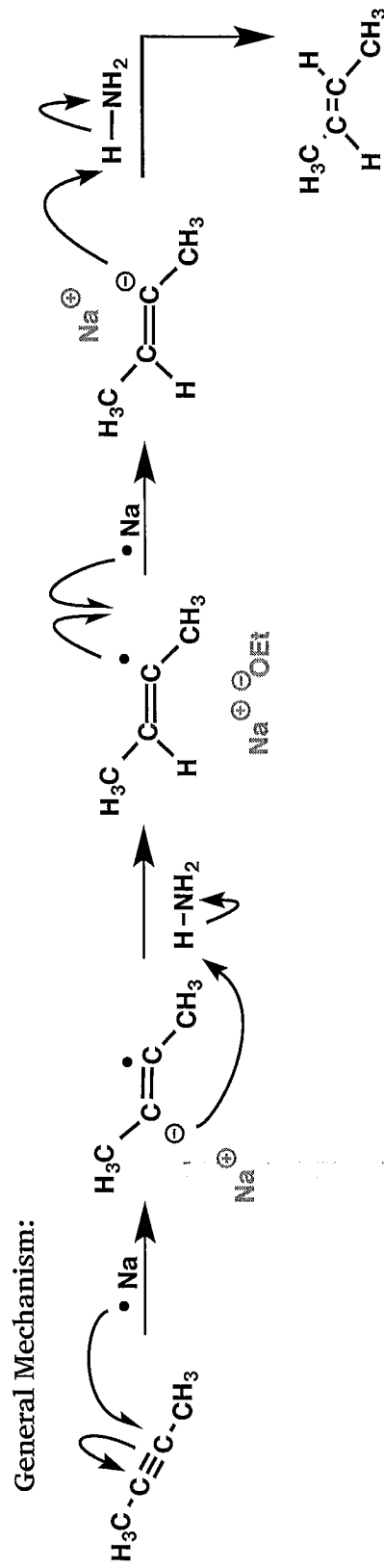


## Dissolving Metal Reductions of Alkynes

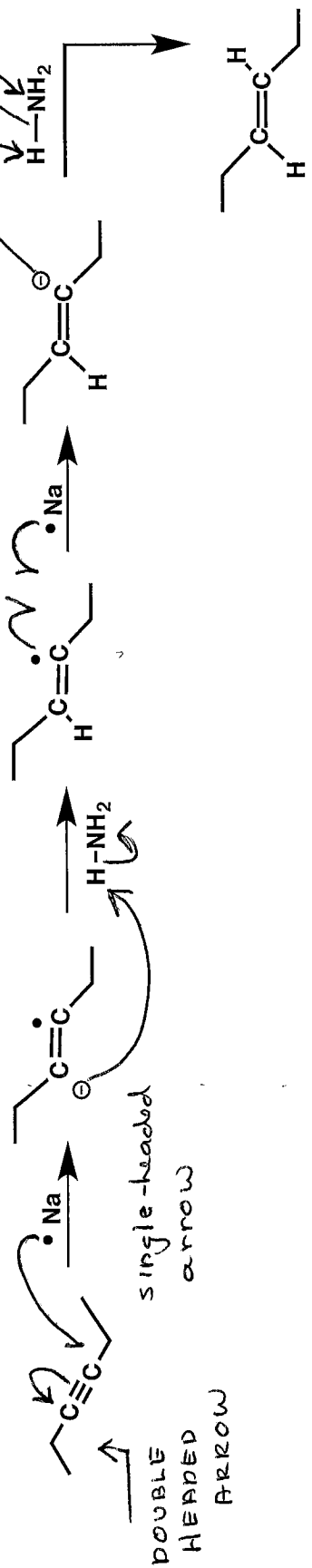


### Mechanism Basics Box:

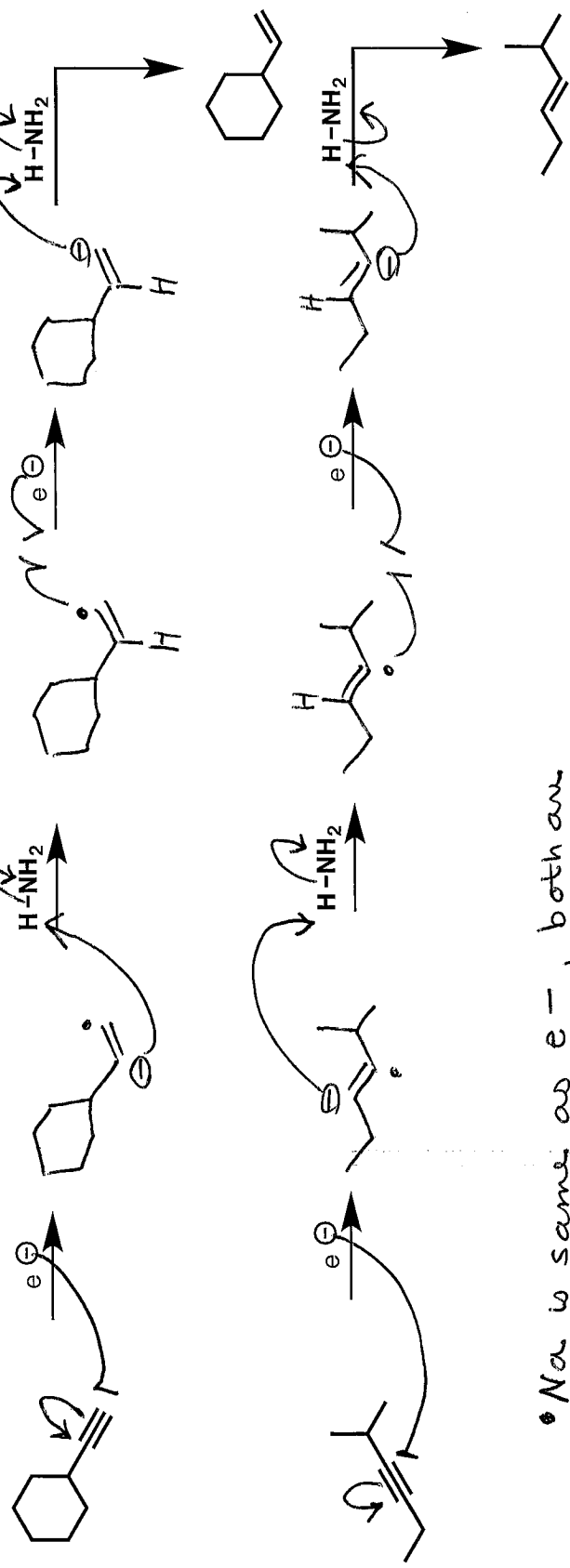
- Initial electron transfer in step 1 results in a radical anion that is “anti”
- Evidence indicates that step 2 (the first proton transfer) is the rate determining step
- A *trans* vinylic anion is preferentially formed in step 3 because it is more stable than a *cis* vinylic anion. This is the origin for the *trans* alkene which is formed.



Fill in the missing arrows.

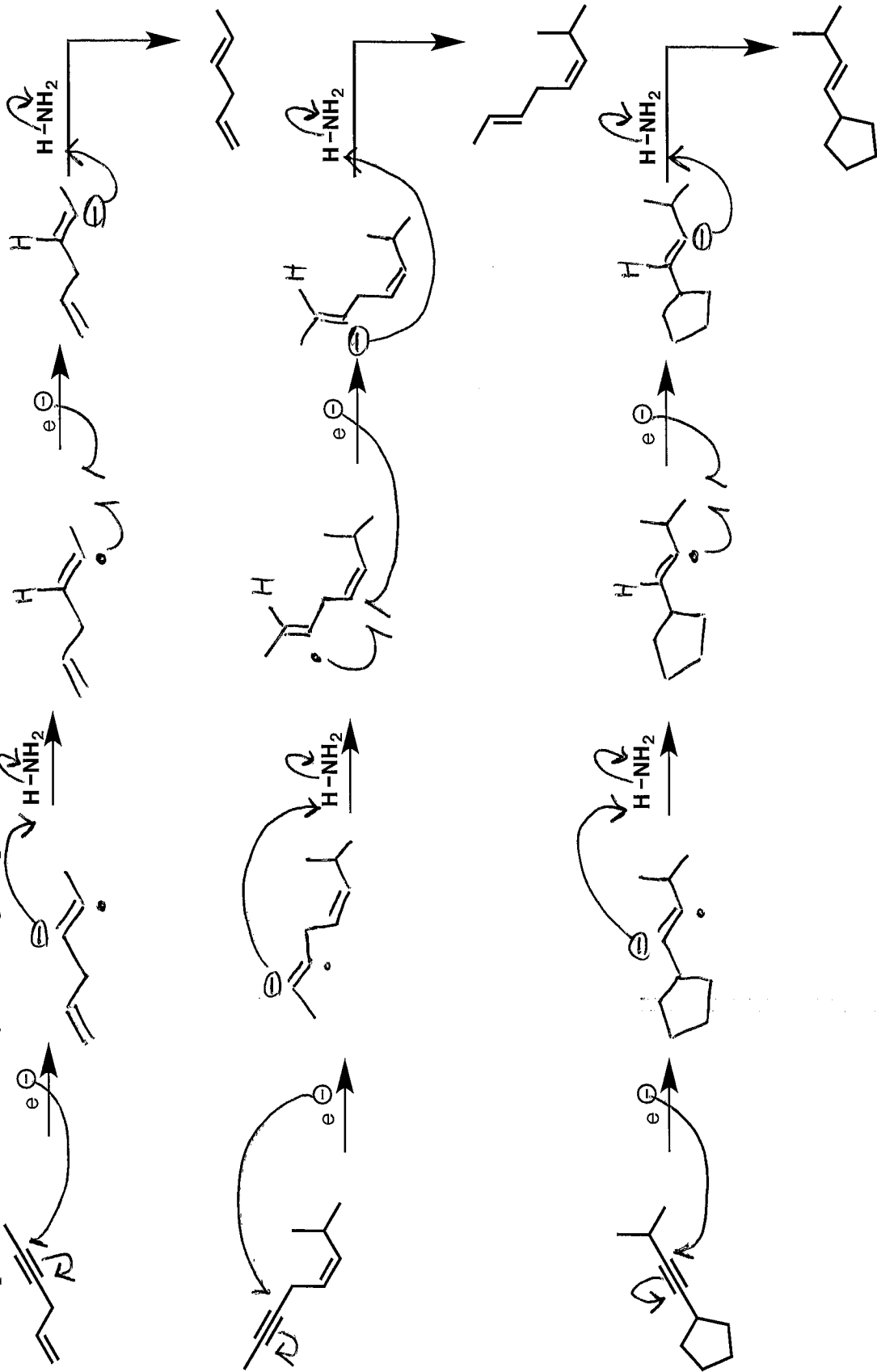


Complete the mechanism by following the pattern (draw arrows and intermediates).



• Na is same as e<sup>-</sup>, both are electron sources.

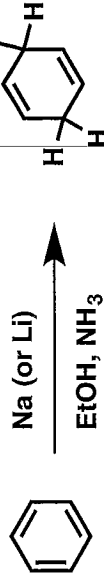
Complete the mechanism by following the pattern (draw arrows and intermediates).





## Birch Reduction of Benzene

### General Reaction:

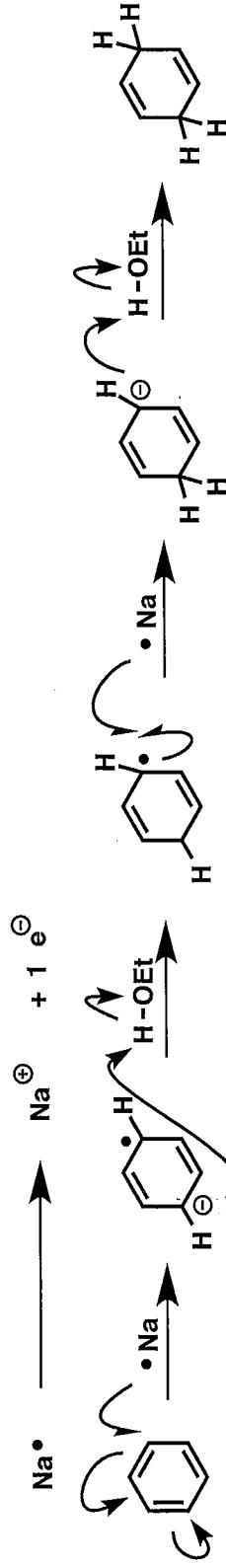


Can also use other alcohol solvents such as *i*-PrOH and *t*-BuOH

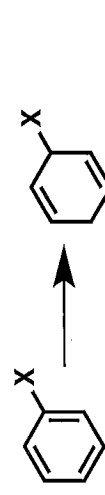
### Mechanism Basics Box:

- This mechanism is very similar to the dissolving metal reduction of alkynes. Unlike with alkynes, however, the proton source for this reaction is the alcohol solvent, not the NH<sub>3</sub>.
- A non-conjugated 1-4 diene is selectively produced

### General Mechanism:

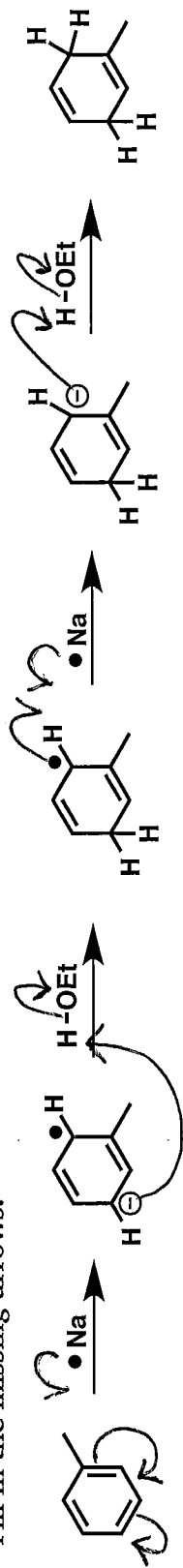


X = activator (such as alkyl groups, -OR, -NR<sub>2</sub>, etc.)

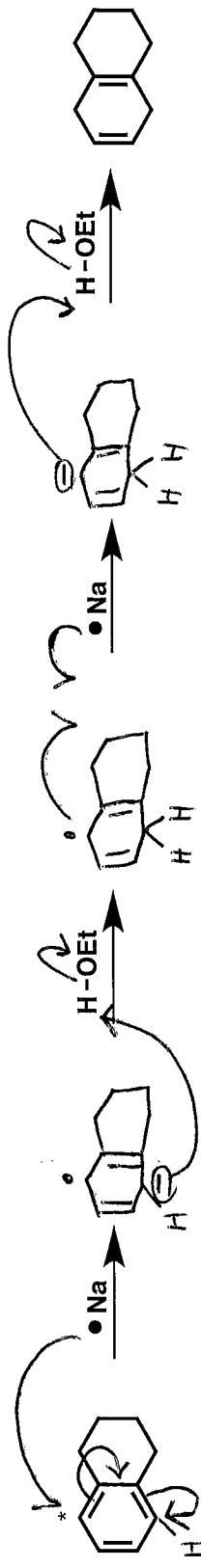


X = deactivator (such as NO<sub>2</sub>, SO<sub>3</sub>R, CN, CF<sub>3</sub>, etc.)

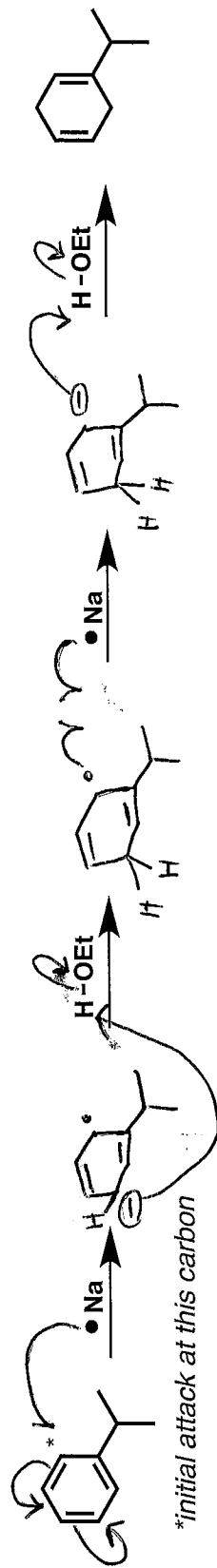
Fill in the missing arrows.



Complete the mechanism by following the pattern (draw arrows and intermediates).



\*initial attack at this carbon



\*initial attack at this carbon

Complete the mechanism by following the pattern (draw arrows and intermediates)

