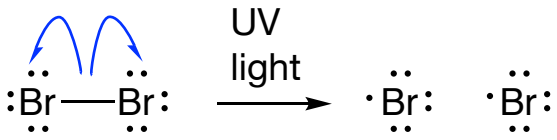
Radicals are single-electron species. Since electrons are almost always paired in stable molecules, there is a driving force for a radical to pair up with another electron.

Most radical reaction mechanisms have three stages: 1) initiation; 2) propagation; and 3) termination.

1) *Initiation.* Radicals are formed under heat or light conditions.

   Homolysis: Very weak bonds can sometimes cleave in half spontaneously at room temperature or with heat or light.



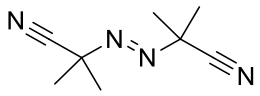
- Given the following average bond strengths (in kcal/mol), **rank** the top five bonds most likely to undergo homolysis.

bond	Cl-Cl	O-O	C-N	C-O	Br-Br	H-H	C-I	C-C	N-N
BDE	58	35	73	86	46	104	51	85	39

Hydrogen peroxide (below) is often used as a radical initiator. It is added to a reaction to provide a source of radicals**.**

- Show, with arrows, how this happens.

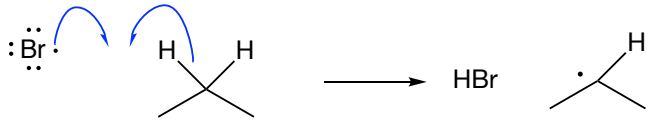
- Challenge: AIBN (below) is another common radical initiator, driven by N_2 formation.
- Show, with arrows, how AIBN can cleave to form resonance-stabilized radicals and a dinitrogen molecule.



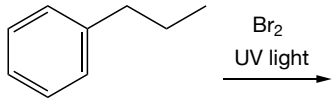
2*) Radical Propagation*

Radicals react with other species to produce new radical intermediates.

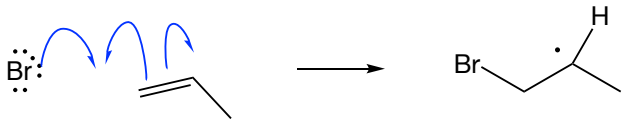
There are a number of ways for radicals to propagate. The radical may act by *atom abstraction*, stealing an atom (usually a hydrogen) and its electron from another molecule.



- Draw the initiation and propagation for the reaction shown below. Be sure to choose the most stable radical product for the propagation step.

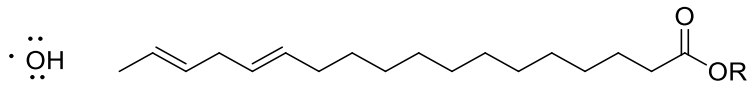


It may also react with an alkene.



- Explain why the bromine was added to the terminal end of this alkene.

- Show, with arrows, how a hydroxyl radical can abstract a hydrogen atom from a fatty acid.
- Draw the most stable radical product and explain your choice.

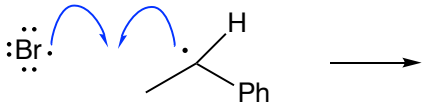


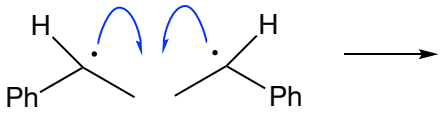
3*) Radical Termination*

A termination step is any step in which radicals are destroyed, and no new radicals are produced.

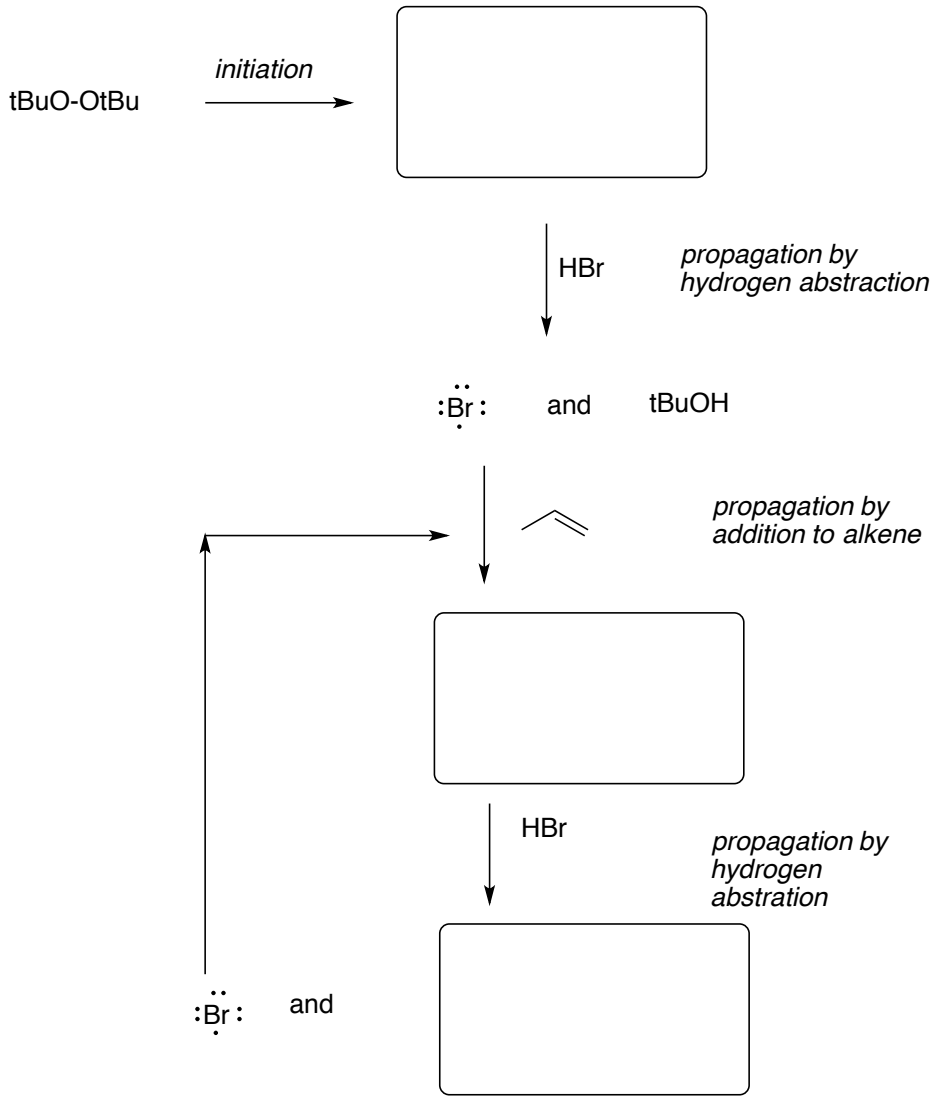
Different pathways are possible. For example, two radicals may simply combine and pair up electrons together.

- Draw the products of the termination steps shown below:





Radical Bromination (put all 3 stages together)



- Suggest a step that will cause termination of the chain reaction.

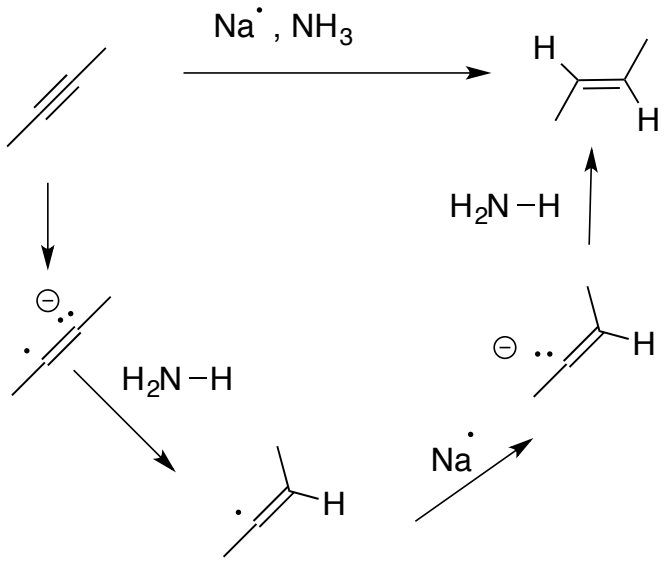
- Explain why only a "catalytic" amount of initiator is needed in a radical chain reaction.

Radical reductions of alkynes

Radical reduction of alkynes is a stereospecific method for preparing trans alkenes.

- Why is sodium metal a good source of a single electron?

- Draw the arrows for this mechanism.



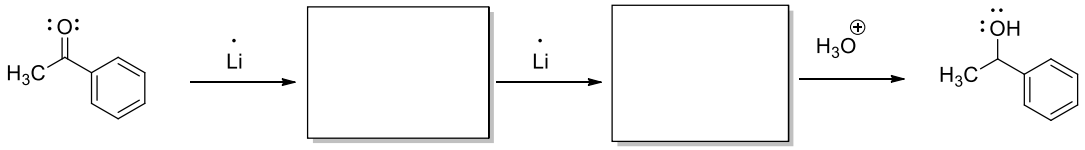
- Provide a reason for why this reaction gives only the trans product.

- *Review:* How do you form the cis alkene from an alkyne?

Single Electron Transfer in Organic Redox Reactions

In lithium reductions of carbonyls, a single electron is transferred from the lithium atom.

- Show the intermediates generated in the following reaction.
- Add arrows to show electron movement.



Compare the reactant on the left and product on the right.

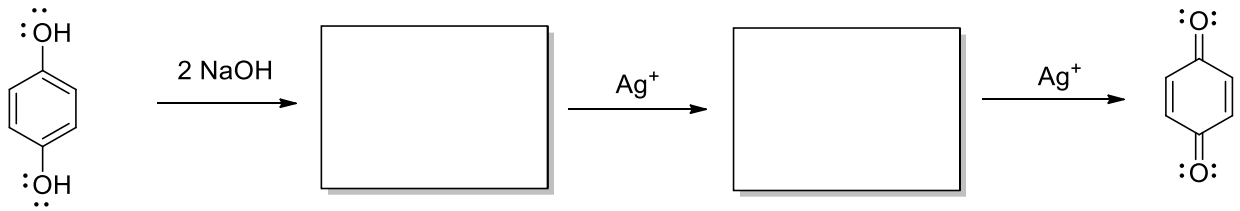
- What is the difference in terms of number of electrons and protons in each compound?

- Why is an electron easily transferred from the lithium atom?

- Why is it so easy to transfer an electron to a carbonyl?

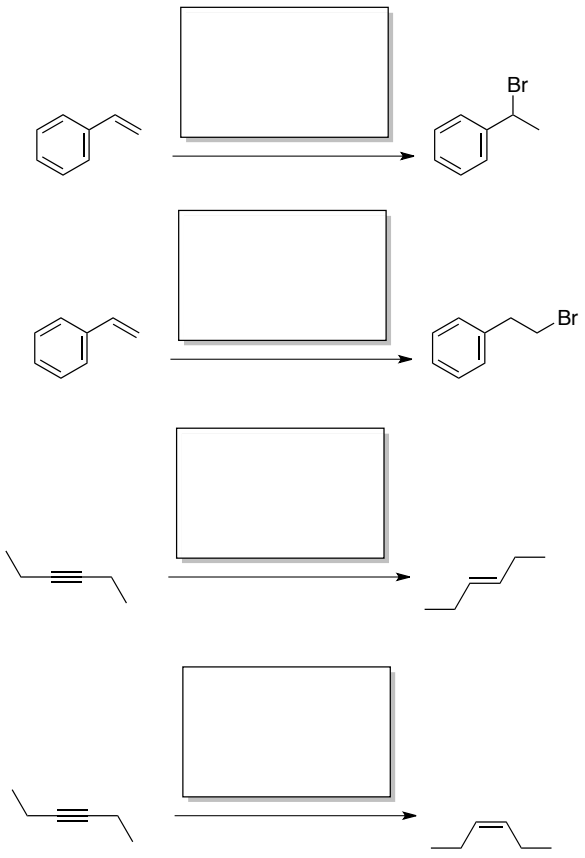
In black and white photography, reduction of silver salts (to silver metal) is used to produce a picture.

- Show the intermediates generated in the following reaction.
- Add arrows to show electron movement.

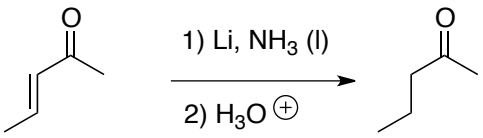


Practice Radical Questions

1. Provide the reagents or products for the following transformations:

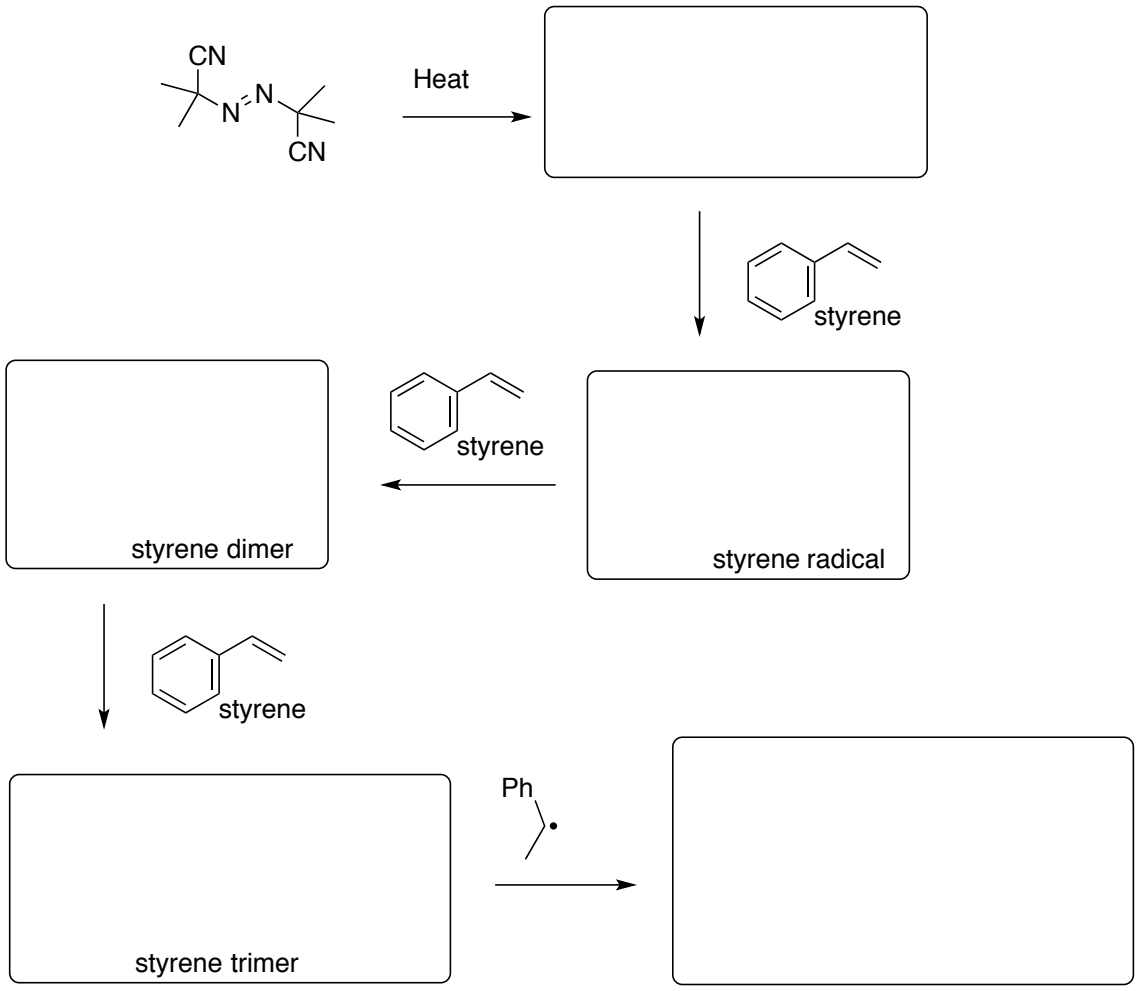


2. Challenge: Provide a mechanism for the following reaction:



Radical Polymerization Reactions

- Provide a mechanism for the following radical polymerization reaction:



- Suggest a step that will cause termination of the polymerization reaction.

- In doing an alkene halogenation with Br_2, radical polymerization could be a side product. Propose conditions that might deter this unwanted reaction.