Objective 14: Apply reactivity principles to radical reactions: identify radical reaction conditions, describe mechanism, use curved arrows for common radical steps to predict products.

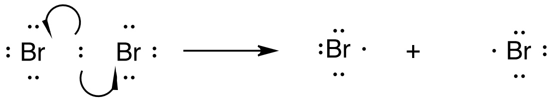
Quiz Practice problems

Key ideas:

So far, we have looked at polar reactions – an electron pair (bonding pair or lone pair) breaks or forms a bond, which we represent with a curved arrow.

In a radical reaction, a bonding pair of electrons breaks to form unpaired electrons. A substance with unpaired electrons is called a radical.

Example: Br_2 splits into 2 Br radicals when exposed to light.



A radical reaction mechanism consists of three steps:

1. initiation: a non-radical forms two radicals. See Br_2 forming 2 Br radicals in the presence of light.
2. propagation: a non-radical reacts with a radical to form a new non-radical and new radical.

There are usually two or more propagation steps.

3. termination: two radicals form a non-radical.

This step stops the reaction. You don't want a termination step to occur because the reaction yield will be low.

We will look at the following radical reactions:

Alkane halogenation: R-H + X-X --> R-X + H-X

Alkene hydrohalogenation (non-Markovnikov addition): alkene + HBr – peroxides --> R-Br

Allylic bromination: alkene + Br_2/light or NBS --> alkene with Br substituted in allylic carbon.

Radical polymerization: alkene + peroxide --> polymer

Skills:

Given reactants, use curved arrows (half arrows) to describe radical reaction mechanism (initiation, propagation, termination).

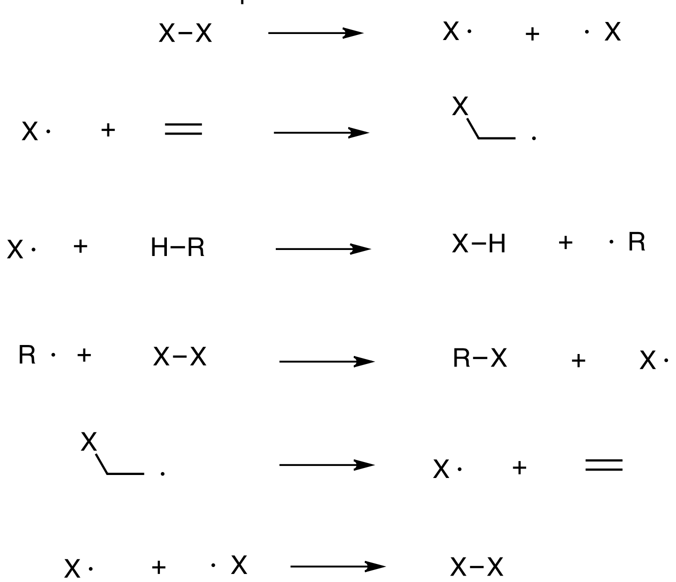
Given alkane and halogen, draw the structure of the products. Identify the major product. Give reasons.

Given alkene and HX, draw the structure of the products. Identify the major product. Give reasons.

Given alkene and Br_2/light or NBS, draw the structure of the products. Identify the major product. Give reasons.

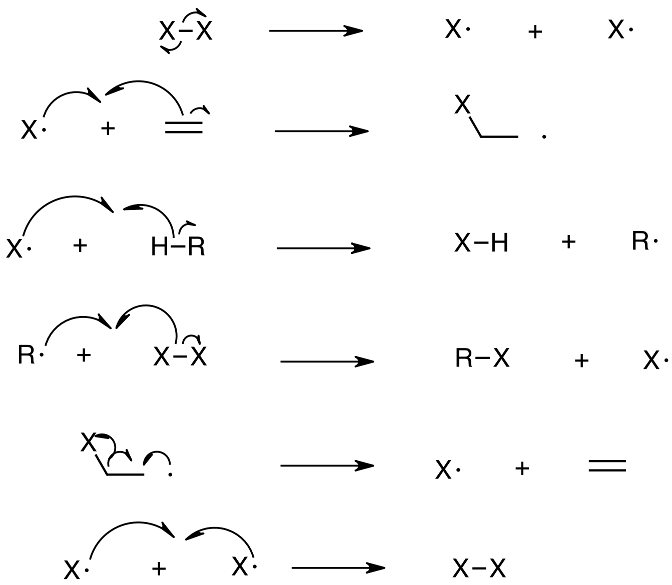
Given alkene and peroxide, draw the structure of the polymer.

0. Radical Reaction patterns. Use curved arrows to show how each product forms.

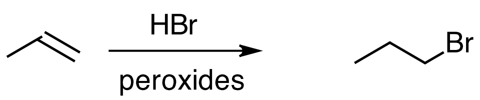


Answers:

Remember each single bond (sigma or pi bond) is an electron pair. Use a half arrow for one electron. You used a full arrow for an electron pair.



1. We looked at the non-Markovnikov addition of HBr to an alkene in the presence of peroxides. This is a radical reaction. Example:

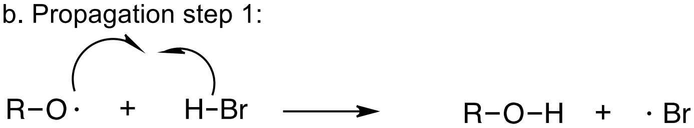


a. Initiation step: (organic peroxide = ROOR)

RO−OR ⟶ 2 R−O·

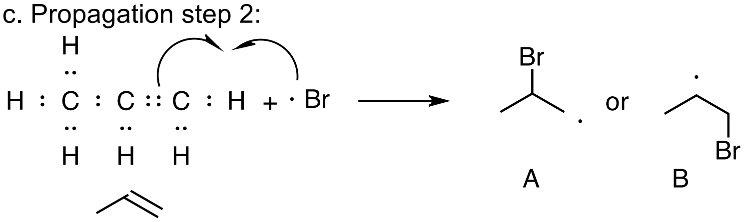
Use curved arrows to show how reactants form products.
Note: a O-O single bond is a weak bond compared to a C-H, C-C, or O-H bond – it does not take much energy to break this bond.

b. Propagation step 1:



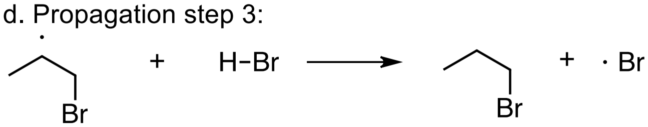
One curved arrow is missing. Draw in the curved arrow to show how reactants form products.

c. Propagation step 2:



(i) One curved arrow is missing. Draw in the curved arrow to show how reactants form products.
(ii) Which product, A or B, forms? Hint: the stability of radicals is the same as the stability of carbocations.

d. Propagation step 3:



Use curved arrows to show how reactants form products.

Once the non-Markovnikov addition product forms and Br radical, Propagation steps 2 and 3 occur many times.

e. Termination step:

Suggest a termination step. Show reactants and products. Use curved arrows to show how reactants form products.

Answers:

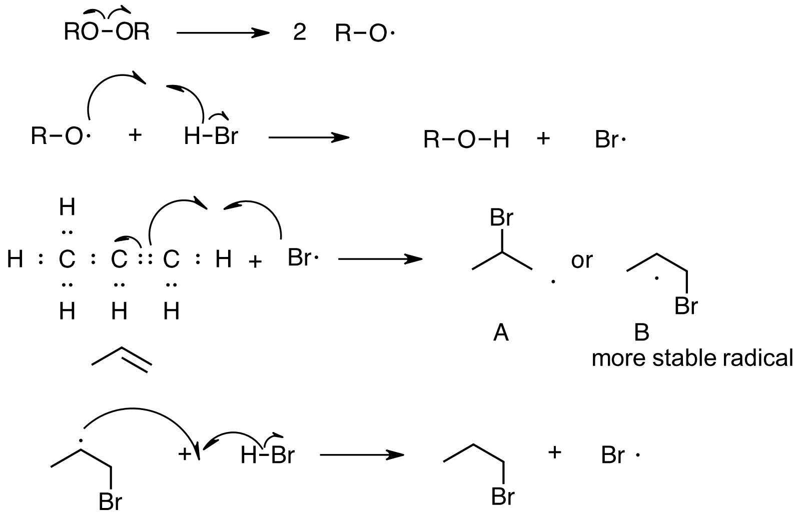
a-e.

In the termination step, a radical reacts with another radical.

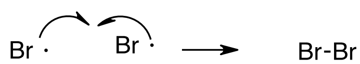
Choose any two radicals from intermediates.

If an organic radical reacts with another radical, the reaction yield will decrease so you want the reaction conditions to have a low concentration of radicals.

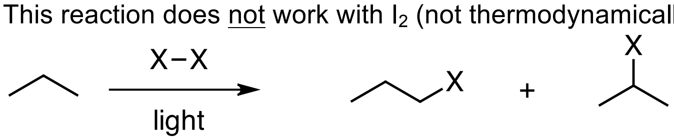
Low concentration of radicals ==> non-radical reacts with a radical ==> many propagation steps.



possible termination step:

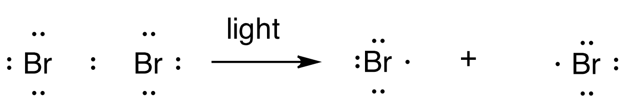


2. The addition of HBr to an alkene is one way to make an alkyl halide.
Another way to make an alkyl halide is by radical halogenation of alkane. X = halogen = Cl or Br.
This reaction does <u>not</u> work with I_2 (not thermodynamically favored). F_2 is too reactive.



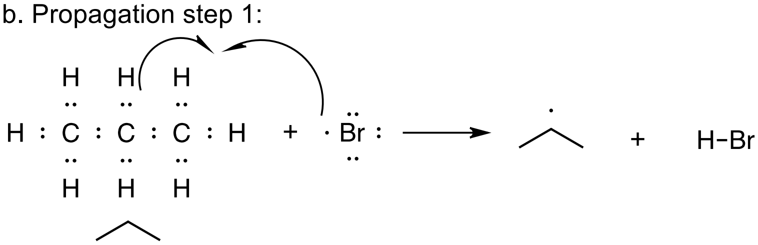
The product depends on X. If X = Cl, the product distribution is random. If X = Br, the more substituted RBr is produced.

a. Initiation step:



Use curved arrows to show how reactants form products.

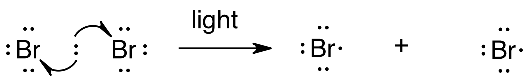
b. Propagation step 1:



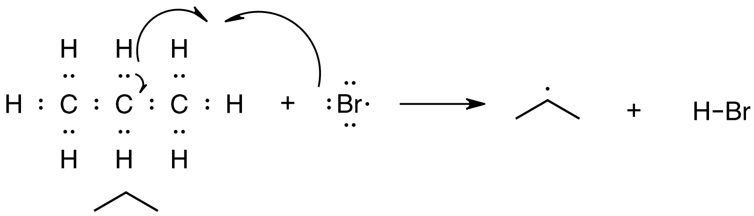
(i) One curved arrow is missing. Draw in the curved arrow to show how reactants form products.
(ii) This reaction shows a 2^{o} radical forming. A 1^{o} radical can form. Use curved arrows to show how this 1^{o} radical forms.
(iii) Which radical most likely forms? Why?

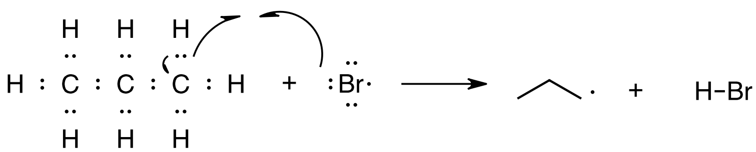
c. Propagation step 2:
The radical in the previous step reacts with Br_2 to form the alkyl halide product and a Br radical.
Use curved arrows to show how reactants form products.

d. More Br radical formed in the previous step. What Propagation step happens next?
e. Termination step:
Suggest a termination step. Show reactants and products. Use curved arrows to show how reactants form products.
Answers:
a.

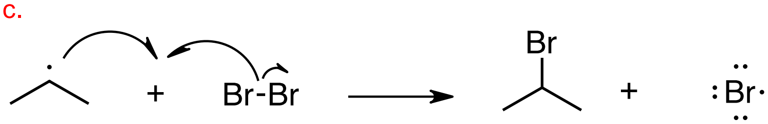


b.

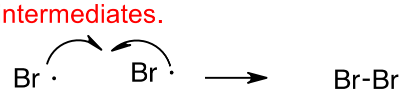




The C-H bond that reacts with the Br radical depends on stability.
2^o radical is more stable than a 1^o radical so the 2^o radical forms.
c.

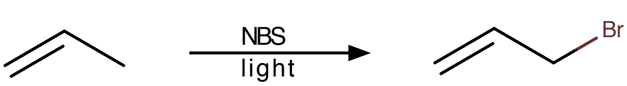


This propagation step forms the product.
d. The next step in the mechanism is Propagation step 1 to make more propyl radical.
e. In the termination step, a radical reacts with another radical.
Choose any two radicals from intermediates.

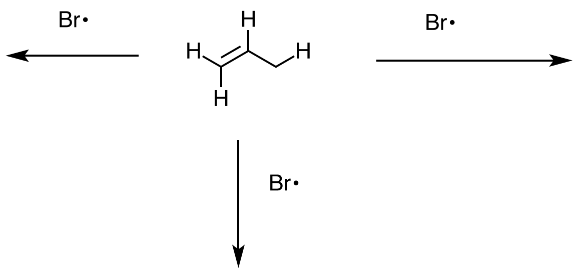
possible termination step: 

If an organic radical reacts with another radical, the reaction yield will decrease so you want the reaction conditions to have a low concentration of radicals.
Low concentration of radicals ==> non-radical reacts with a radical ==> many propagation steps.

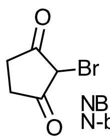
3. Allylic bromination. The allylic carbon is the carbon adjacent to the vinylic carbon in an alkene.



In the initiation step of the radical mechanism, a Br radical is formed from Br_2/light or NBS.
Once Br radical forms, it reacts with propylene (or other alkene with allylic carbon). The Br radical can react with at least three different bonds.
a. Draw the product(s) of each reaction.
b. Which bond does Br radical most likely react with? Give reasons.
c. In the next propagation step, which product reacts with _____ to make the ***allylic bromide***?

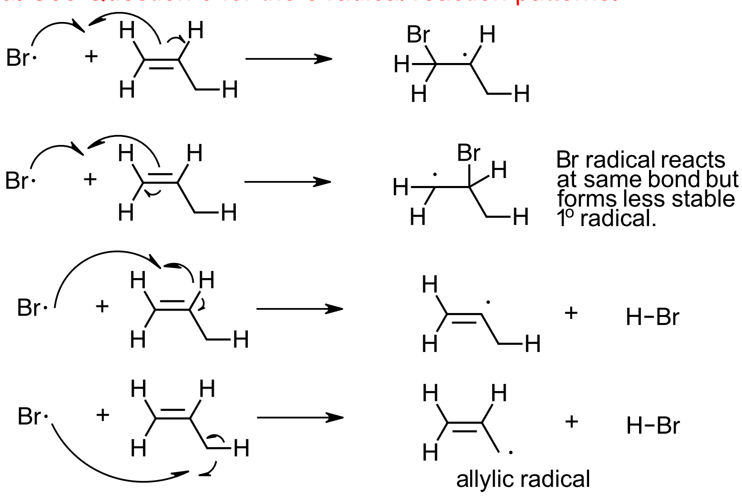


Answers:



NBS =
N-bromosuccinimide

a. See Question 0 for the 6 radical reaction patterns.



b. The Br radical reacts with the allylic C-H bond to form an allylic radical. The allylic C-H bond is weaker than an alkane C-H bond. Note: this reaction forms a 1° allylic radical, which is more stable than a 1° radical.

c. In the next propagation step, the allylic radical reacts with NBS or Br_2 to make the ***allylic bromide*** product and another radical (either the radical that forms when the C-Br bond breaks in NBS or Br radical).
You do not want the allylic radical to react with a Br radical because this will terminate the reaction.

4. Plastics are polymers. Polymers are long chains of repeating units called monomers. Many polymers are made by a radical reaction.

a. Ethylene (C_2H_4) is used to make polyethylene plastic (used in plastic bags and plastic wrap).

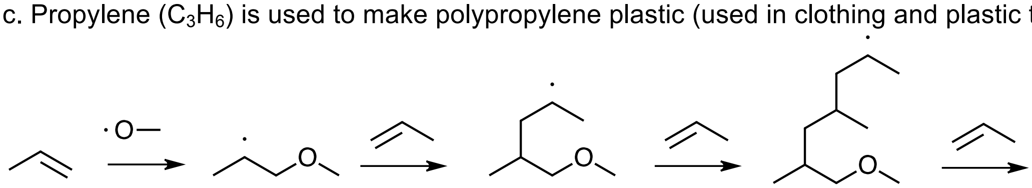
Initiation: RO-OR ⟶ 2 • OR

Propagation: = + • OR ⟶

Draw the structure of the produce of the propagation step. Use curved arrows to show how this product forms.

b. This propagation steps occurs many times to "grow" the polymer chain. Show how the product of the first propagation step in Question 3a reacts with an ethylene molecule to form a six carbon compound. Use curved arrows to show how this product forms.

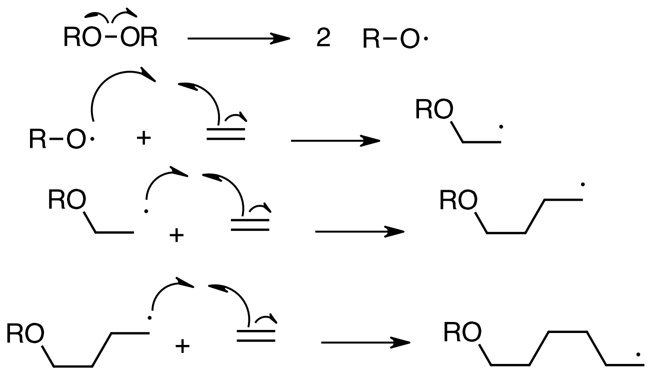
c. Propylene (C_3H_6) is used to make polypropylene plastic (used in clothing and plastic toys).



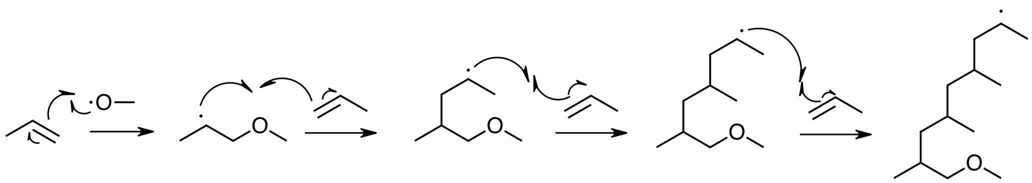
Use curved arrows to show how each compound forms.

Answers:

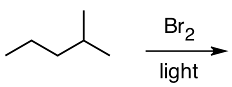
a and b.

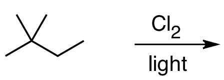


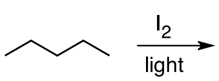
c.

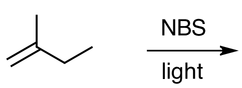


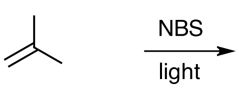
5. (i) For each reactant, identify each carbon as 1^{o}, 2^{o}, or 3^{o}.
(ii) For each reactant, circle the allylic carbon.
(iii) Predict the product of each reaction.

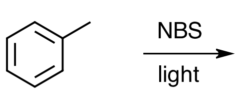




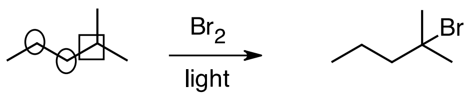


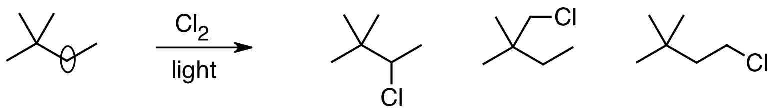


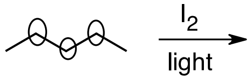




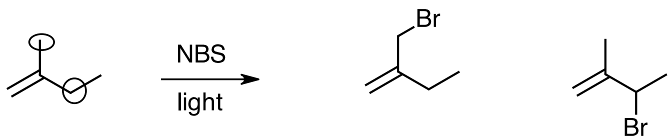
Answers:
(i) For 1^{st} three reactions, 2^{o} carbons are circled, 3^{o} carbons are boxed. 1^{o} and 4^{o} (quaternary) carbons are not labeled.
(ii) For last three reactions, allylic carbons are circled.
(iii) Radical bromination – Br substitutes at most substituted C.
Radical chlorination – Cl substitutes at random C.
Radical iodination – no reaction.

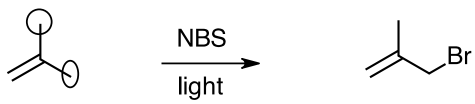


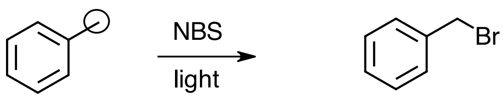




no reaction - not thermodynamically favored







6. 1-bromopropane is used as a solvent for adhesives, in asphalt production and synthetic fiber production, to degrease plastics, optics, and metal surfaces, and to remove soldering residues from electronic circuit boards (https://en.wikipedia.org/wiki/1-Bromopropane).
Consider the two reactions:
(i) Propene + HBr/peroxides --->
(ii) Propane + Br_2/light --->
Which method would you use to make 1-bromopropane? Give reasons.
Answers:
Use Method (i). Method (ii) produces 2-bromopropane. In radical bromination, Br substitutes at most substituted C.