Objective 12: Apply reactivity principles to Electrophilic Addition reactions 1: alkenes – identify structural features (pi bond) and electrophiles, use curved arrows to predict product.

Quiz Practice problems

Key ideas:

In an addition reaction, a carbon-carbon pi bond (nucleophile) reacts with an electrophile, which adds (forms a sigma bond) to each C in the double bond (vinylic carbon).

Structural features: C=C pi bond, electrophile

In general, a carbocation intermediate forms. Stability of carbocations: $3^o > 2^o > 1^o$

The stability of the carbocation intermediate determines the product. See Markovnikov addition.

An addition reaction is the reverse of an elimination reaction.

Skills:

Identify C=C pi bond in a compound.

Identify electrophile in addition reaction.

Given reactants, use curved arrows to show how nucleophile (C=C pi bond) reacts with electrophile to form addition product(s).

Identify the major product if more than one addition product forms.

Identify reaction conditions for Markovnikov addition.

Identify reaction conditions for non-Markovnikov addition.

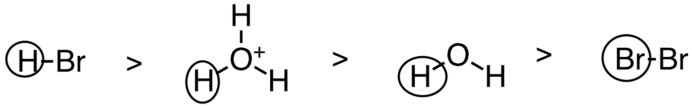
1. a. Is a C=C bond a strong or weak nucleophile

b. The following compounds are electrophiles: HBr, Br_2, H_2O, H_3O^+. Circle the electrophilic atom in each compound. Rank these electrophiles from strongest to weakest.

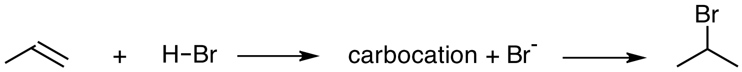
Answers:

a. C=C pi bond is a weak nucleophile.

b.



2. Hydrohalogenation: Propylene reacts with HBr to form 2-bromopropane.



a. Use curved arrows to show how the reactant forms a carbocation. Draw the structure of the carbocation.

b. Show how the carbocation reacts with Br^- to form 2-bromopropane.

c. Why does 2-bromopropane form (Markovnikov addition) and not 1-bromopropane (non-Markovnikov addition – see part h)?

d. The carbocation does not react with HCl. Explain why.

e. The carbocation reacts with water. Use curved arrows to show how the carbocation reacts with water to form a product. Draw the structure of the product.

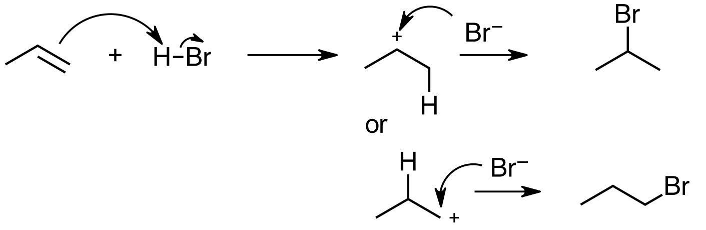
f. The carbocation reacts with propylene. Use curved arrows to show how the carbocation reacts with propylene to form a product. Draw the structure of the product.

g. Name another substance the carbocation can react with. Use curved arrows to show how the carbocation reacts with this substance to form a product. Draw the structure of the product.

h. Propylene reacts with HBr in the presence of peroxides to form 1-bromopropane (non-Markovnikov addition). This reaction involves a radical reaction mechanism, which we will look at in Objective 14.

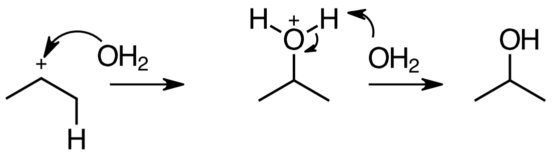
Answers:

a, b, and c. 2-bromopropane forms because the 2^o carbocation is more stable and forms faster than the 1^o carbocation (which has not been observed experimentally).

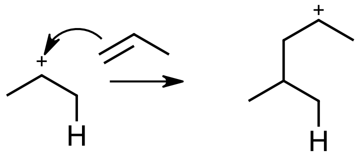


d. The carbocation does not react with HCl because both substances are electrophiles.

e.



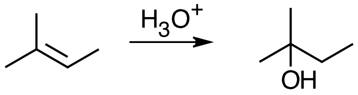
f. Note: a new 2° carbocation forms. This 2° carbocation can react with another propylene to form a bigger 2° carbocation, which reacts with another propylene to form a bigger 2° carbocation. This is an example of a polymerization reaction. A 1° carbocation does not form – very unstable.



g. The carbocation is an electrophile so it reacts with a nucleophile, e.g., CH_3O^-.

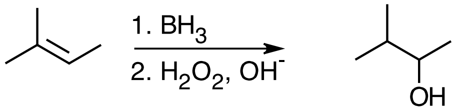
3. Hydration: 2-methyl-2-butene reacts with H_3O^+ to form 2-methyl-2-butanol.

a. Use curved arrows to show how the reactant forms products.



b. If water is used instead of H_3O^+, this reaction will not occur. Explain why. (Hint: see Question 1.)

c. Hydration: non-Markovnikov. An alkene reacts with BH_3 followed by H_2O_2/OH^- to form 3-methyl-2-butanol.



The B in BH_3 is an electrophile. Draw the structure of BH_3 and explain why the B is an electrophile.

You want to know the reactants and products of the hydroboration reaction but you will not be responsible for knowing the hydroboration mechanism.

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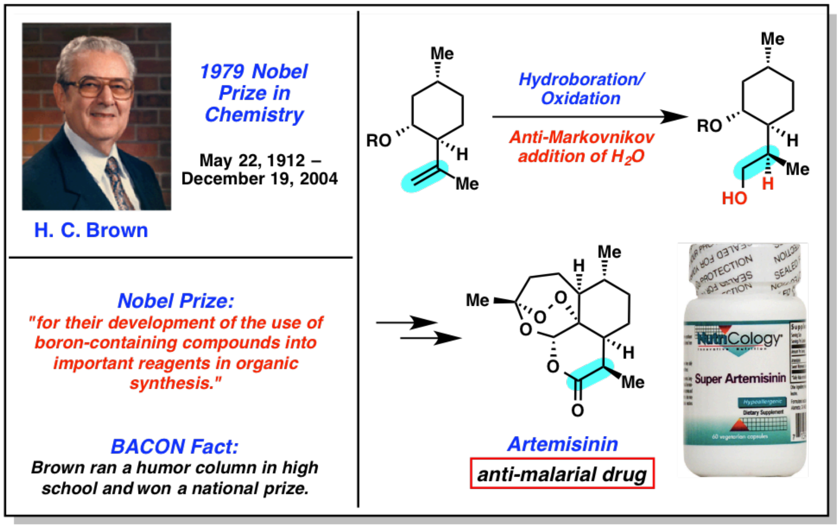


1979 Nobel Prize in Chemistry

May 22, 1912 – December 19, 2004

H. C. Brown

Nobel Prize:

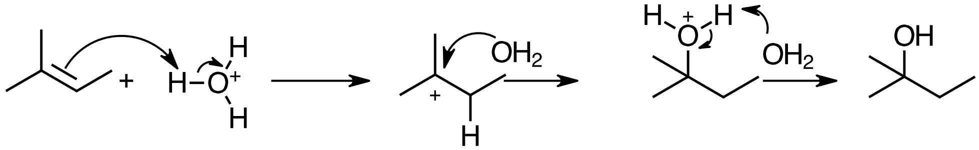
"for their development of the use of boron-containing compounds into important reagents in organic synthesis."

BACON Fact:

Brown ran a humor column in high school and won a national prize.

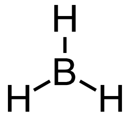
Answers:

a.

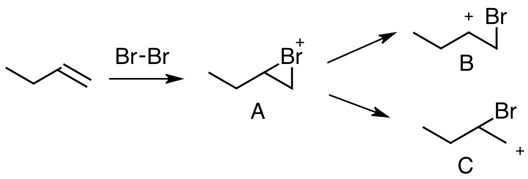


b. Water is not a strong enough nucleophile to react with the weakly nucleophilic C=C pi bond.

c. In BH_3, the B has only 6 electrons around it ==> electron deficient ==> electrophile.

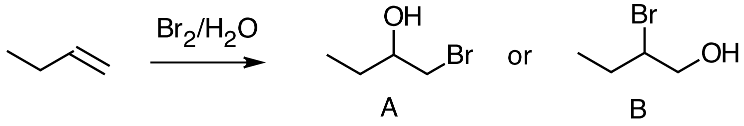


4. Halogenation: 1-butene reacts with Br_2 to form 1,2-dibromobutane. Although Br_2 is non-polar, it considered an electrophile. Electrons move around each Br nucleus.
At one instance of time, more electrons are around 1st Br than the second so 1st Br has a partial (-) charge and the 2nd Br has a partial (+) charge. $\overset{\delta-}{Br}\text{-}\overset{\delta+}{Br}$
At another instance of time, more electrons are around the 2nd Br than the 1st so 1st Br has a partial (+) charge and the other Br has a partial (-) charge. $\overset{\delta+}{Br}\text{-}\overset{\delta-}{Br}$
The Br with the (+) charge is the electrophile.
a. When an alkene reacts with Br_2, a bromonium ion intermediate (Structure A) forms. Use curved arrows to show how 1-butene reacts with Br_2 to form Structure A.

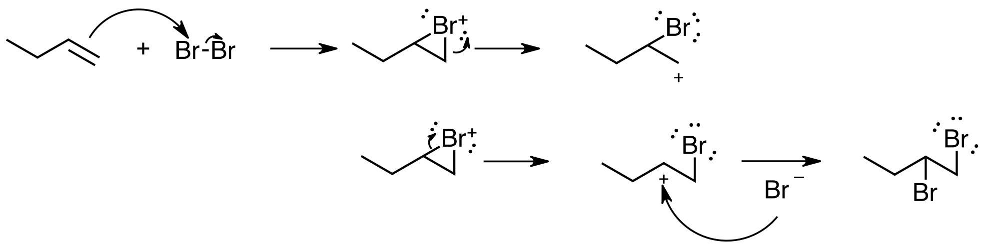


b. Once Structure A forms, a C-Br bond can break to form Structure B or Structure C. Which structure, B or C, forms? Give reasons. Use curved arrows to show bonds breaking and forming.
c. Show how Structure B or Structure C reacts with Br^- to form 1,2-dibromobutane. Use curved arrows to show bonds breaking and forming.

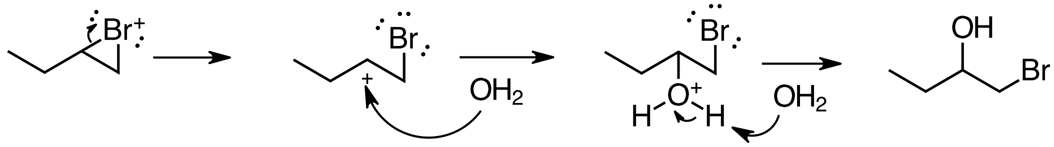
d. Bromohydrin formation: Does Product A or Product B form? Use curved arrows to show bonds breaking and forming. Hint: the bromonium ion intermediate forms like in part a. Which substance, Br^- or H_2O, is the better nucleophile?



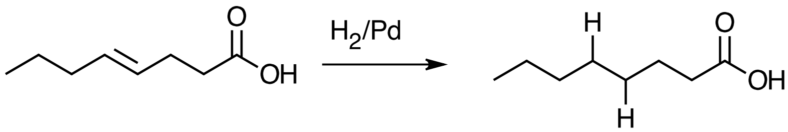
Answers:
a and b. The 2° carbocation forms (B) because it is more stable than the 1° carbocation (C).
c.



d. Product A forms.
H_2O is the better nucleophile than Br^-.
We will see Compound A in Chem 12B. It is used to make an epoxide, which are found in biomolecules and a very useful in organic synthesis.



5. Hydrogenation: an alkene reacts with H_2 with a Ni or Pd or Pt catalyst to make an alkane. This is how the unsaturated fats are converted to saturated fats. You want to know the reactants and products of the hydrogenation reaction but you will not be responsible for knowing the hydrogenation mechanism.



The hydrogenation reaction is also considered a reduction reaction.

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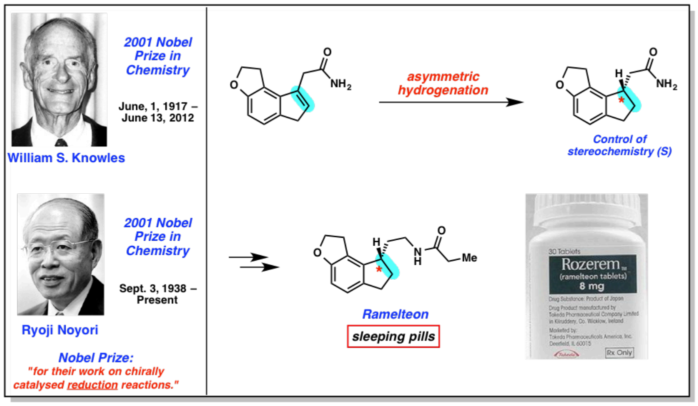


2001 Nobel Prize in Chemistry

June, 1, 1917 – June 13, 2012

William S. Knowles

Control of stereochemistry (S)

2001 Nobel Prize in Chemistry

Sept. 3, 1938 – Present

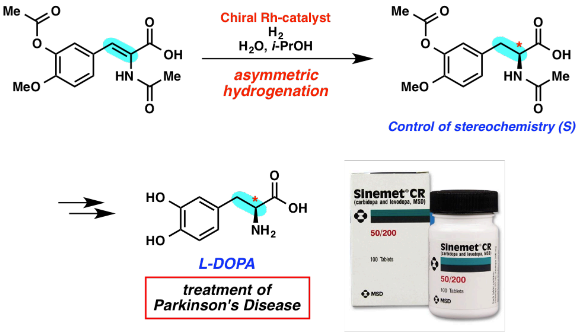
Ryoji Noyori

Nobel Prize: "for their work on chirally catalysed reduction reactions."

sleeping pills

Anti-depressants: Synthesis of L-dopa (a precursor to adrenaline):

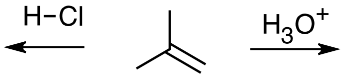
Industrial synthesis of L-DOPA using Asymmetric Hydrogenation

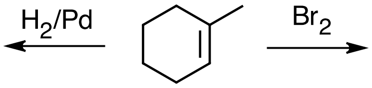


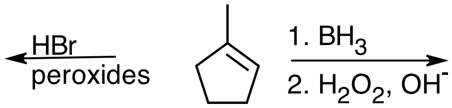
Control of stereochemistry (S)

treatment of Parkinson's Disease

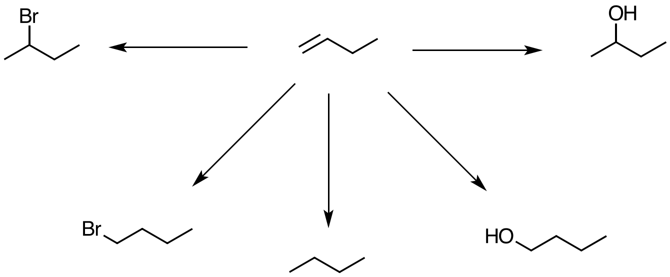
6. a. Predict the product(s) of each reaction. Use curved arrows to show how each reaction occurs.





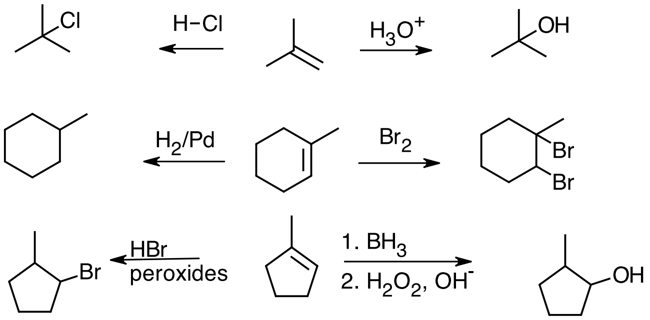


b. How would you synthesis each compound from 1-butene? Determine the reaction conditions for each reaction:

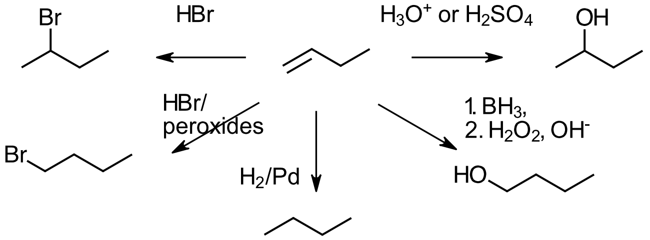


Answers:

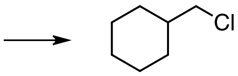
a.

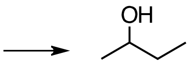


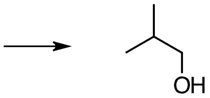
b.

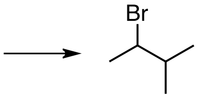


7. a. Draw the structure of the reactants and identify the reaction conditions to make the following compounds. Use curved arrows to show how each reaction occurs.

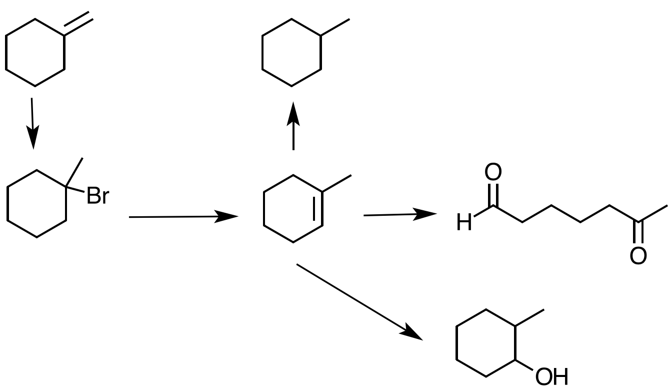




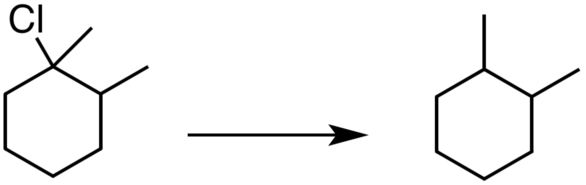




b. Identify the reagents you would use for each transformation.

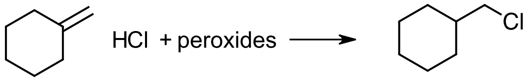


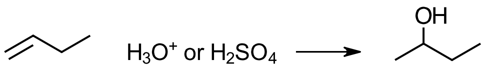
c. Suggest an efficient synthesis for the following transformation:

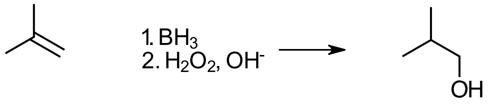


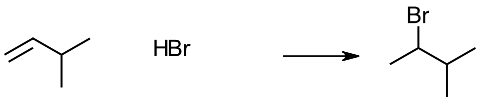
Answers:

a.

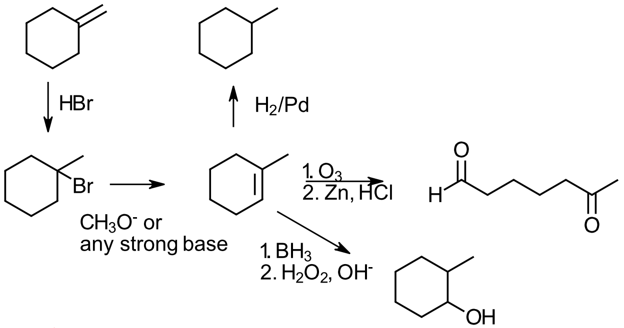






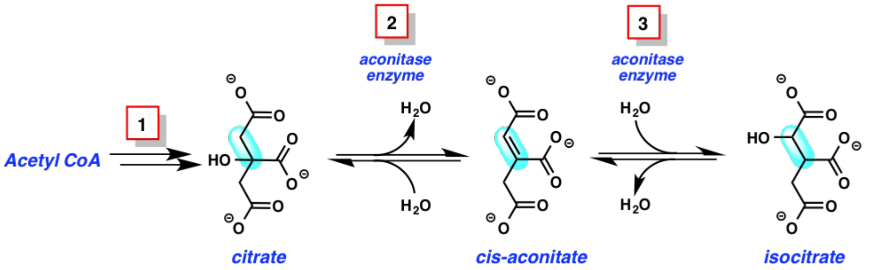


b.

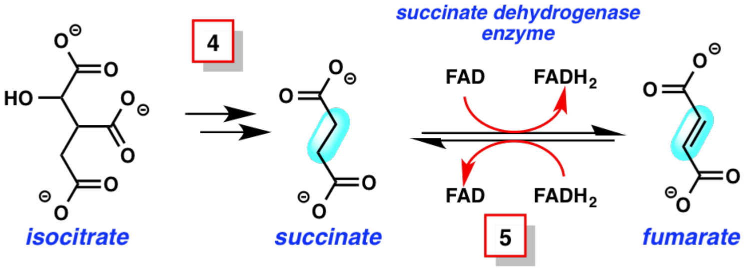


c. 1st step: Want to remove or eliminate Cl so do an elimination reaction with Cl as leaving group and a C=C bond forms.
Use a strong base, e.g., CH_3O^-.
2nd step: Convert the C=C bond to C-C bond with a hydrogenation reaction.
Use H_2/Pd.

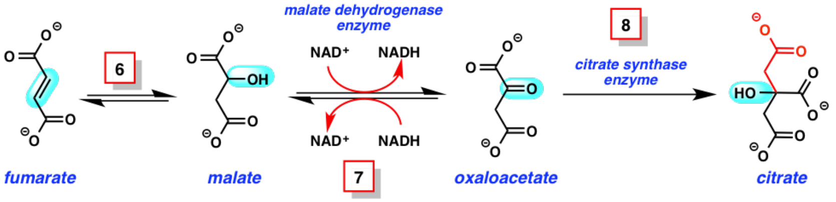
8. From LearnBacon.com
a. Kreb's cycle: how would you classify Step 3? (Markovnikov or anti-Markovnikov addition?)



b. How would you classify Step 5 of Kreb’s cycle? (oxidation reaction)



c. Kreb’s cycle Steps 6-8:



Beautiful Mind movie: dehydration prevents the Kreb’s cycle from functioning effectively after a night-out (hangover). Which step is the dehydration reaction?

Answers:

a. Step 3 is an anti-Markovnikov hydration. In lab, use 1. BH_3 followed by 2. H_2O_2/OH^-.

b. Step 5 is an oxidation reaction. The reverse of Step 5 is an alkene hydrogenation reaction using H_2/Pd.

FAD is a biological oxidizing agent. $FADH_2$ is a biological reducing agent.

c. The dehydration reaction is the reverse of Step 6 (ROH --> alkene is an elimination reaction).