Assignment 4 Task 1

Due: 11:59pm on Friday, October 5, 2018

You will receive no credit for items you complete after the assignment is due. Grading Policy

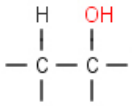
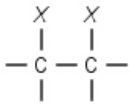
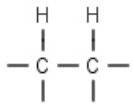
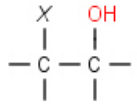
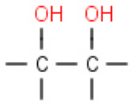
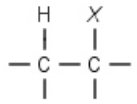
Introduction to Addition Reactions

Different organic compounds undergo similar reactions because they have similar structural or functional characteristics. For example, the reaction between ethanol and hydrochloric acid is similar to the reaction between propanol and hydrochloric acid. Understanding the characteristic reaction of a functional group allows us to predict how other compounds with that same functional group will react. The characteristic reactions of alkenes are electrophilic addition reactions.

Addition reactions

Addition reactions occur when compounds are added to an organic compound containing a carbon-carbon \(\texttip{\pi }{pi}\) bond. The \(\texttip{\pi }{pi}\) bond between two carbons acts as a nucleophile due to the high electron density between the two atoms. Molecules with a partial positive charge or an incomplete octet, known as *electrophiles*, start the electrophilic addition reaction by forming a new sigma bond with the electrons of the π bond.

There are many types of addition reactions, as shown in the table for addition reaction of alkenes.

Reaction type	Molecule added	General structure	Reaction type	Molecule added	General structure
hydration	\(\rm H_2O\)		**halogenation**	\(\rm X_2\)	
hydrogenation	\(\rm H_2\)		**halohydrin formation**	\(\rm HOX\)	
hydroxylation	\(\rm HOOH\)		**HX addition**	\(\rm HX\)	

Part A

The following species are part of an \(\rm HX\) addition reaction. Sort each one by its role in the reaction.

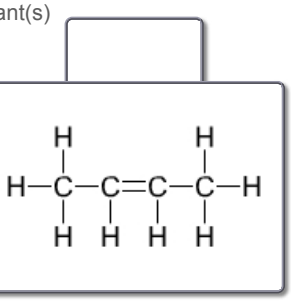
Hint 1. Formation of a carbocation in addition reactions

During an addition reaction, a partially positive atom from a polar compound will attach to an alkene through an electron-pair in a \(\rm C\!=\!C\) double bond. The resulting intermediate has a positive charge on one of the carbon atoms that was previously in the double bond. This positively charged intermediate is called a carbocation and is highly reactive.

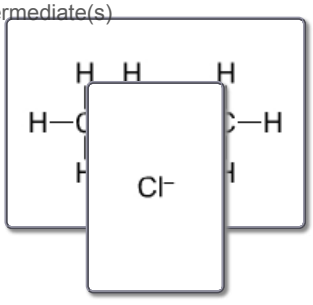
ANSWER:

Reset Help

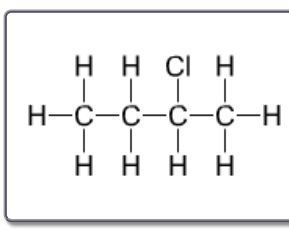
reactant(s)



intermediate(s)



product(s)



Correct

Part B

Draw the product for the hydroxylation of a mixture of *cis*- and *trans*-3-methyl-2-hexene.

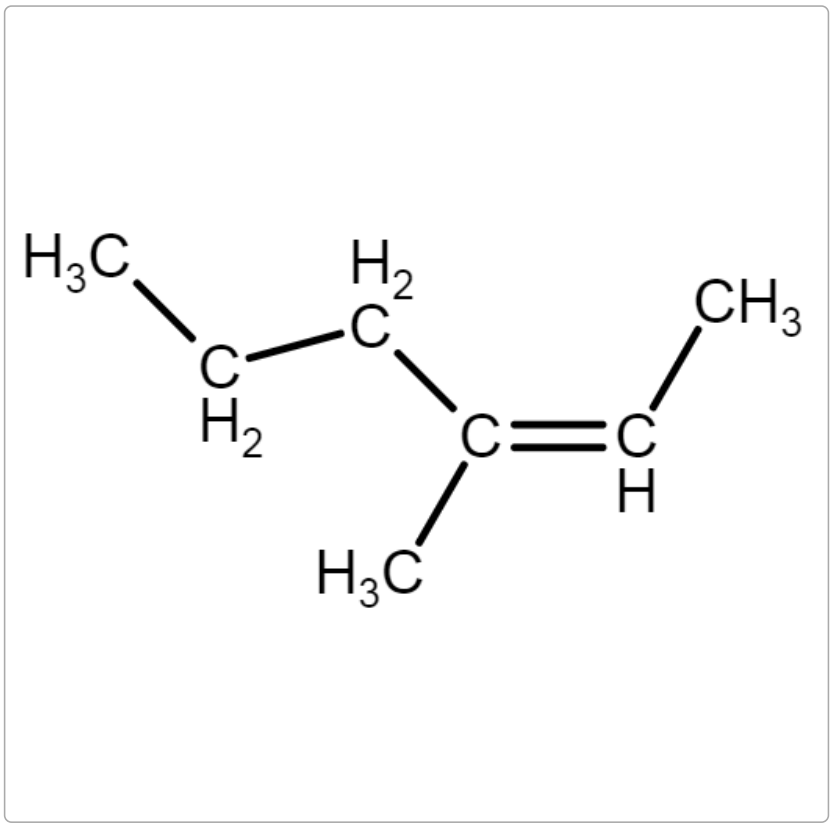
Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.

Hint 1. Draw 3-methyl-2-hexene

Draw the structure for *cis*- or *trans*- 3-methyl-2-hexene.

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.

ANSWER:



Hint 2. What groups are added during an hydroxylation

Select the atoms or groups of atoms that are added during an hydroxylation

Check all that apply.

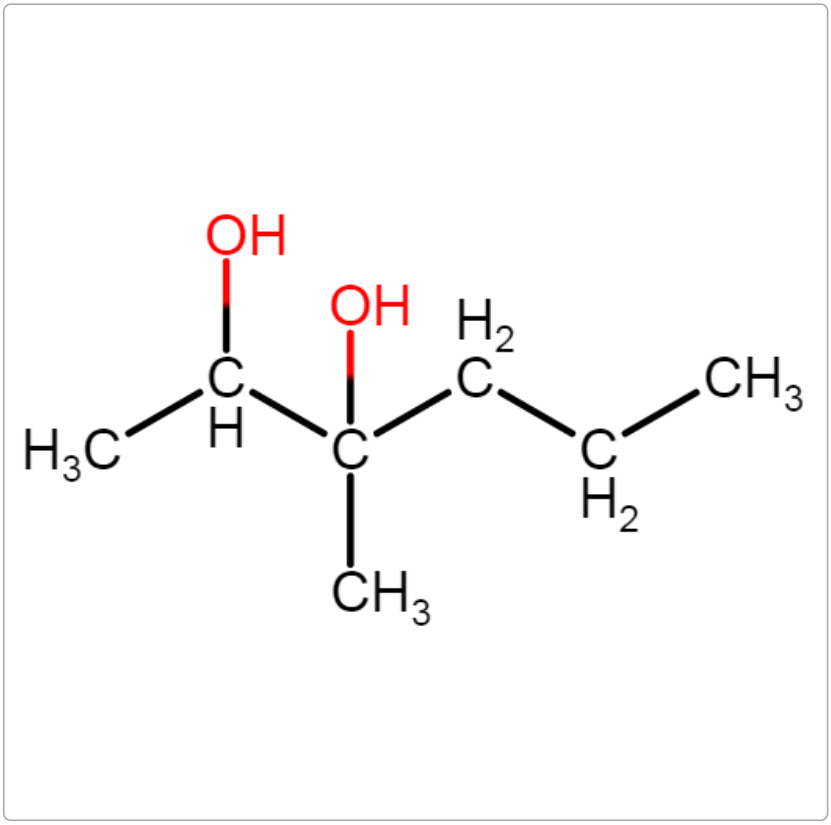
ANSWER:

- [ ] only a hydrogen atom
- [ ] a halogen atom
- [x] an \(\rm OH\) group

Correct

Two \(\rm OH\) groups are added during hydroxylation.

ANSWER:



Correct

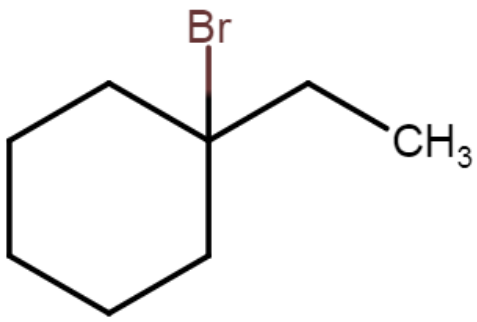
Although in this reaction there was only one product, when there is asymmetric addition of groups, such as in hydration, there are two possible products. The major product will then be the one derived from the most stable intermediate.

Alkene: Determine the alkene from its bromination product

Part A

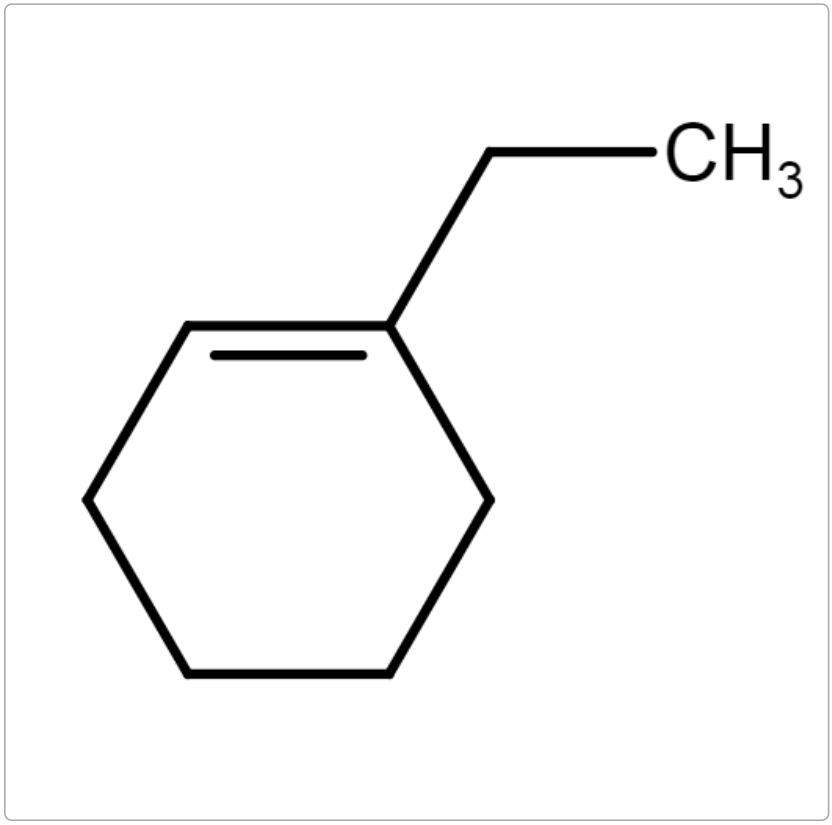
Which alkene should be used to synthesize the following alkyl bromide? (There is more than one correct answer.)

Interactive 3D display mode



Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.

ANSWER:



Correct

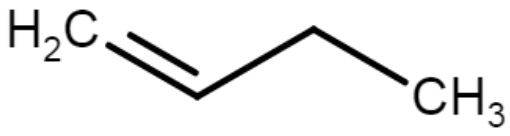
Markovnikov addition of HBr across this alkene puts the Br on the more substituted C atom to give the target.

Alkene: Reaction of 1-butene with HCl

Part A

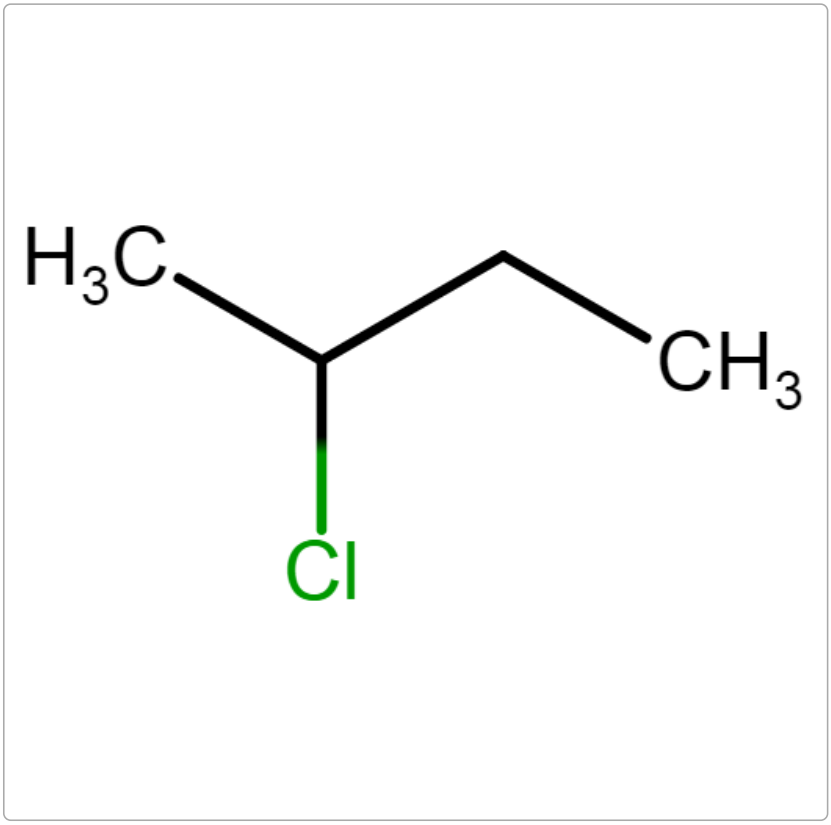
Draw the structure of the product that is formed when the compound shown below undergoes a reaction with HCl in CH_2Cl_2.

Interactive 3D display mode



Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.

ANSWER:



Correct

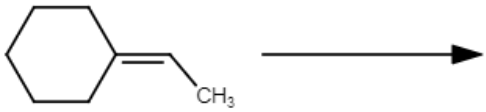
Markovnikov addition of HCl across the C=C π bond occurs.

Alkenes: Reaction of ethylidenecyclohexane and HBr, ROOR

Part A

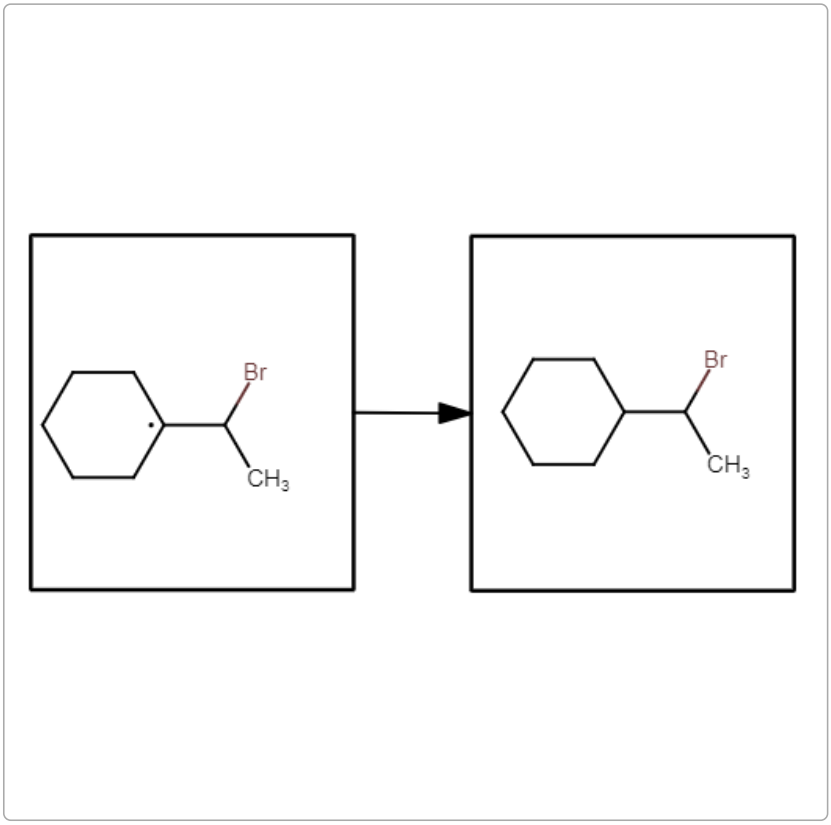
Draw the organic intermediate (in the first box) of the reaction shown below, then draw the expected product (in the second box).

Interactive 3D display mode



Draw the species on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. Include all free radicals by right-clicking on an atom on the canvas and then using the Atom properties to select the monovalent radical.

ANSWER:



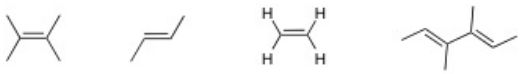
Correct

The Br atom adds to the double bond leaving the more substituted radical. This radical abstracts hydrogen from HBr to give the final product.

Chapter 8 Reading Quiz Question 1

Part A

Which of the following alkenes will generate the most stable carbocation when it reacts with a proton?



Hint 1. Protonation of alkenes

Remember that the pi bond of an alkene represents a relatively loosely held pair of electrons that can serve as a base under highly acidic conditions. Notice that the conjugate acid of an alkene is a carbocation. See 8-3.

ANSWER:

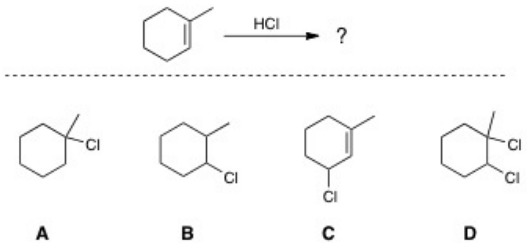
- (•) A
- ( ) B
- ( ) C
- ( ) D

Correct

Chapter 8 Reading Quiz Question 2

Part A

Which compound would be the major product of the following reaction?



Hint 1. Addition of hydrogen halides to alkenes

Recall that in general, hydrohalic acids (with the exception of HF) add to alkenes through an ionic mechanism in which the pi electrons of the alkene are protonated to give a carbocation, which is subsequently captured by the halide nucleophile. See 8-3.

ANSWER:

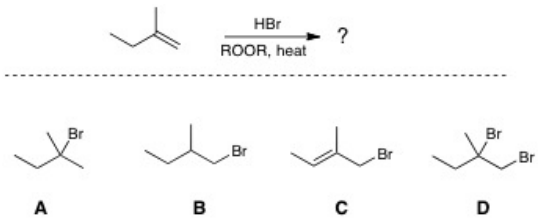
- (•) A
- ( ) B
- ( ) C
- ( ) D

Correct

Chapter 8 Reading Quiz Question 3

Part A

Which compound would be the major product of the following reaction?



Hint 1. Free radical addition of HBr

Recall that depending on the reaction conditions, HBr can add to alkenes through two different mechanisms: In the presence of radical initiators, a homolytic mechanism operates; in their absence, the standard ionic mechanism occurs. Although both mechanisms involve the formation of the most stable possible reactive intermediates, they lead to opposite regioselectivities (anti-Markovnikov or Markovnikov, respectively). See 8-3.

ANSWER:

- ( ) D
- ( ) A
- (•) B
- ( ) C

Correct

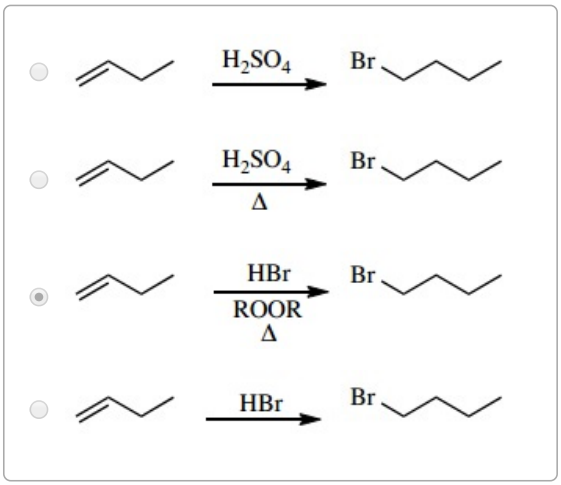
Problem 8-4

Show how you would accomplish the following synthetic conversions.

Part A

but-1-ene \(\rightarrow\) 1-bromobutane

ANSWER:

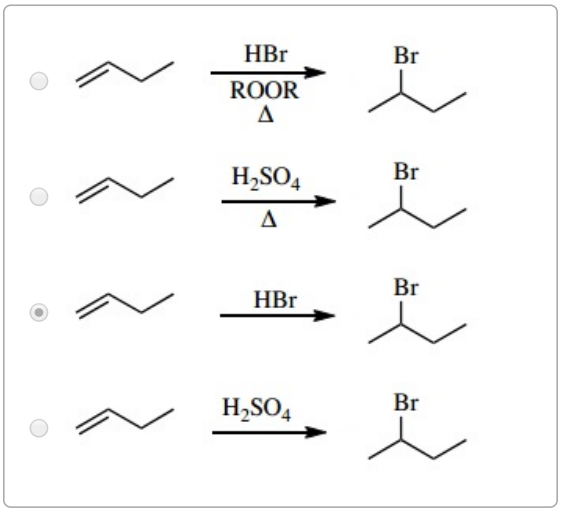


Correct

Part B

but-1-ene \(\rightarrow\) 2-bromobutane

ANSWER:

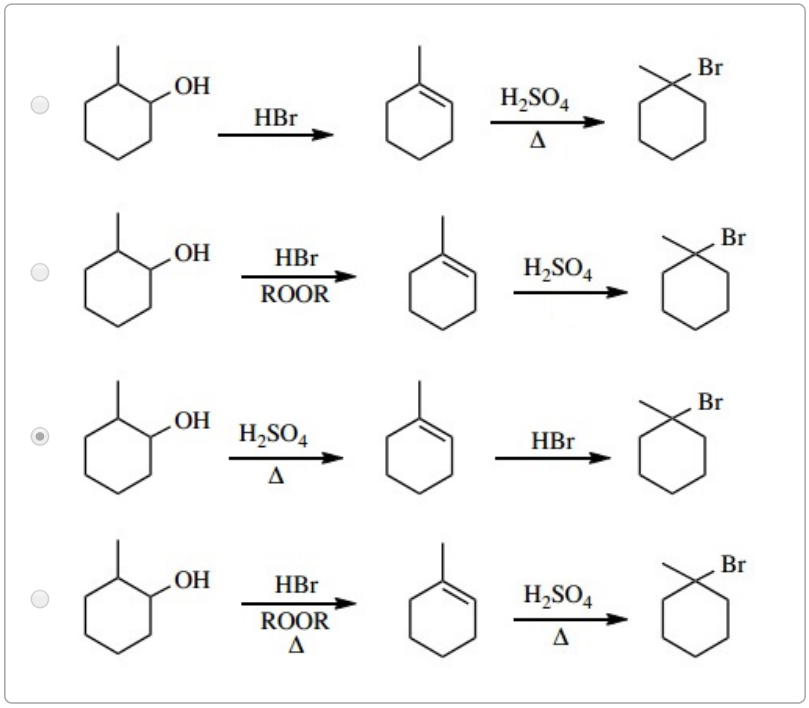


Correct

Part C

2-methylcyclohexanol \(\rm rightarrow\) 1-bromo-1-methylcyclohexane

ANSWER:

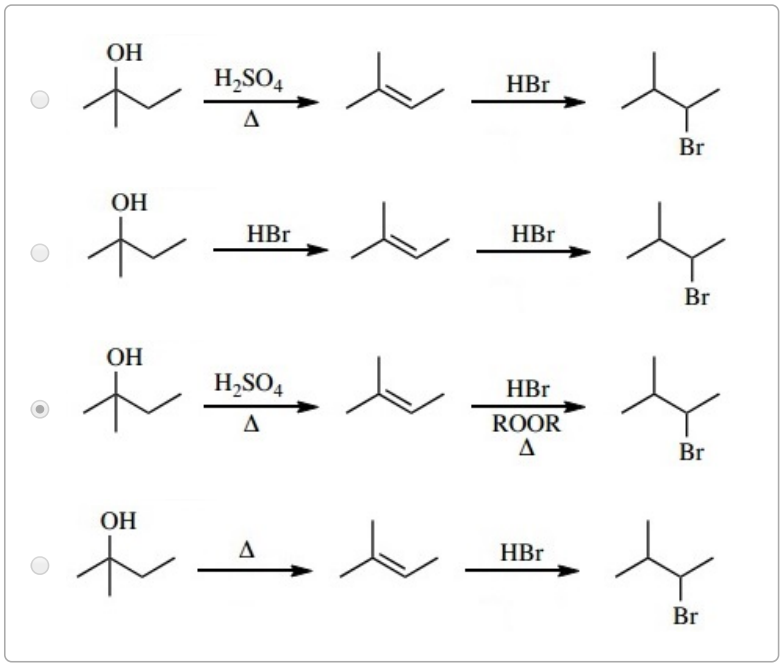


Correct

Part D

2-methylbutan-2-ol \(\rightarrow\) 2-bromo-3-methylbutane

ANSWER:



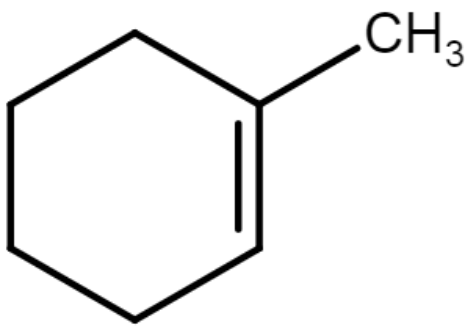
Correct

Alkenes: Hydration of 1-methylcyclohex-1-ene

Part A

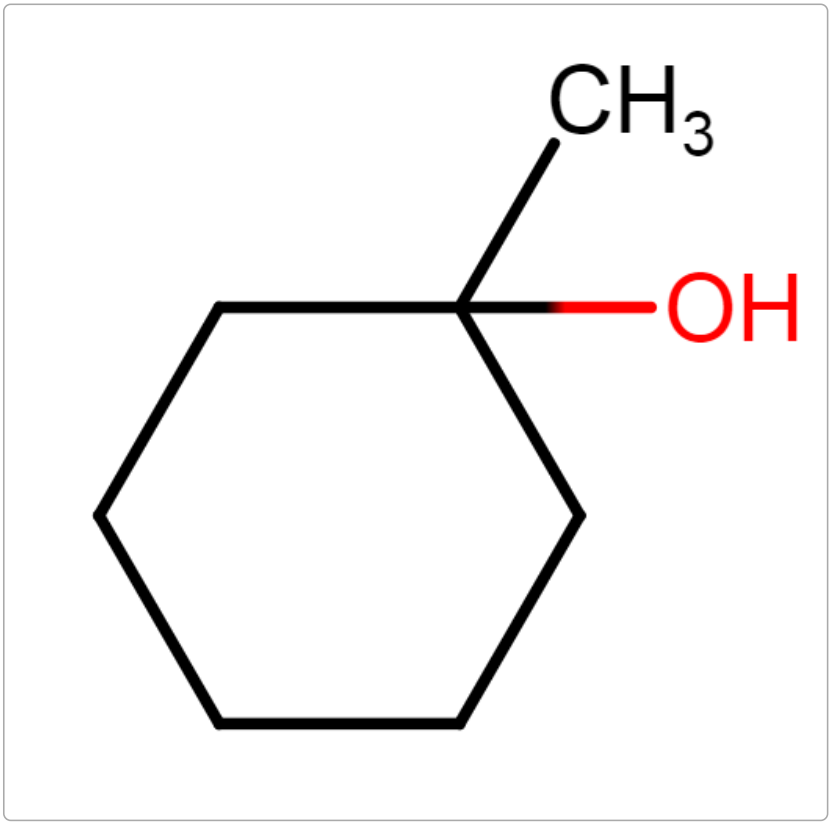
Draw the product formed when the structure shown below undergoes a reaction with diluted water solution of H_2SO_4.

Interactive 3D display mode



Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.

ANSWER:



Correct

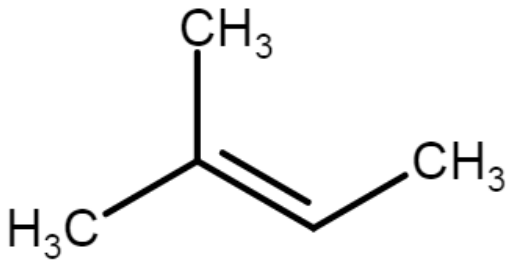
Markovnikov addition of H_2O across the C=C π bond puts the OH group on the more substituted C atom of the alkene.

Alkenes: Alkoxymercuration-demercuration of 2-methylbut-2-ene (2)

Part A

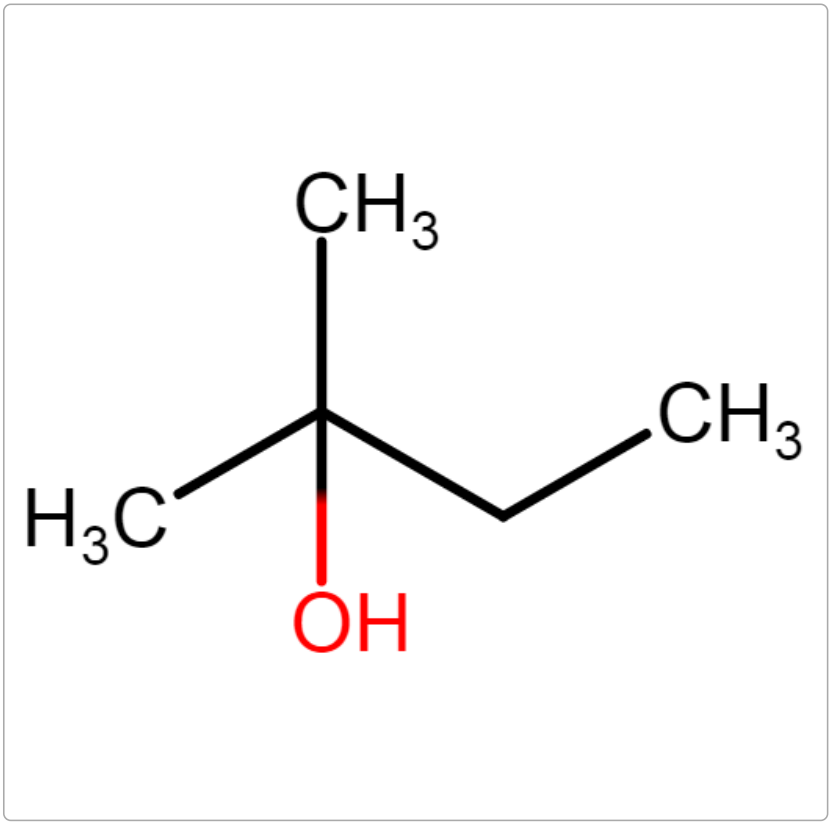
Draw the structure of the product that is formed when the compound shown below is treated with the following reagents:
1) $Hg(OAc)_2$, H_2O; 2) $NaBH_4$, HO^-.

Interactive 3D display mode



Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.

ANSWER:



Correct

The reaction sequence results in Markovnikov addition of H-OH across the C=C bond.

Alkenes: Addition Reactions

Part A

Choose the reagent(s) required to synthesize the following alcohol from 3-methyl-1-butene.

ANSWER:

- 1. \({\rm Hg(OAc)_2}\), \({\rm H_2O}\) / 2. \({\rm NaBH_4}\)
- mCPBA
- \({\rm H_2O}\) / acid
- \({\rm H_2}\), \(\rm Pd/C\)
- 1. \({\rm BH_3}\) / 2. \({\rm HO^-}\), \({\rm H_2O_2}\), \({\rm H_2O}\)

Correct

Use of \(\rm BH_3\) followed by basic hydrogen peroxide results in the anti-Markovnikov product of 2-methylpentanol.

Alkenes: Addition Reactions

Part A

Choose one reagent A, and one reagent B that when combined would give the following alcohol.

Check all that apply.

ANSWER:

- Reagent A:
- Reagent A:
- Reagent A:
- Reagent B: \({\rm BH_3}\), followed by \({\rm HO^-}\), \({\rm H_2O_2}\), and \({\rm H_2O}\)
- Reagent B: a peroxyacid
- Reagent B: \({\rm H_2O}\), \({\rm H^+}\)

Correct

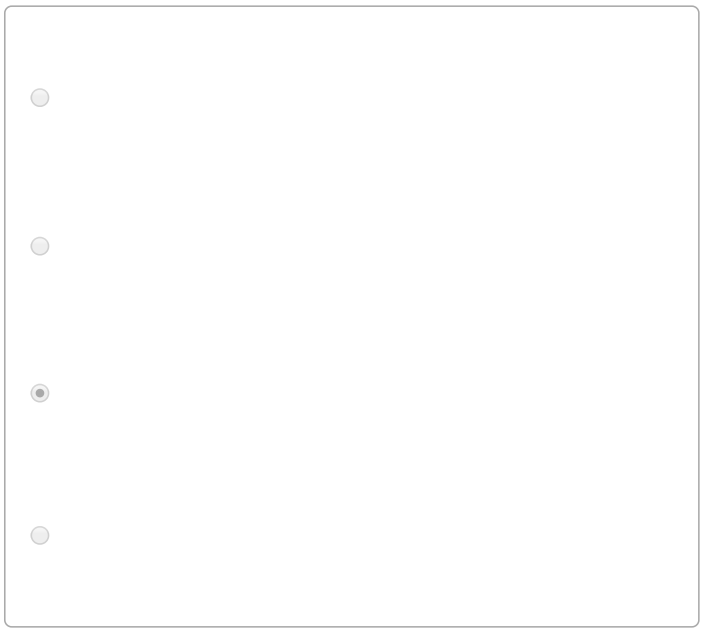
Combining methylidenecyclohexane and \(\rm BH_3\) followed by basic hydrogen peroxide results in the anti-Markovnikov product of cyclohexylmethanol.

Problem 8-15

Show how you would accomplish the following transformations.

Part A

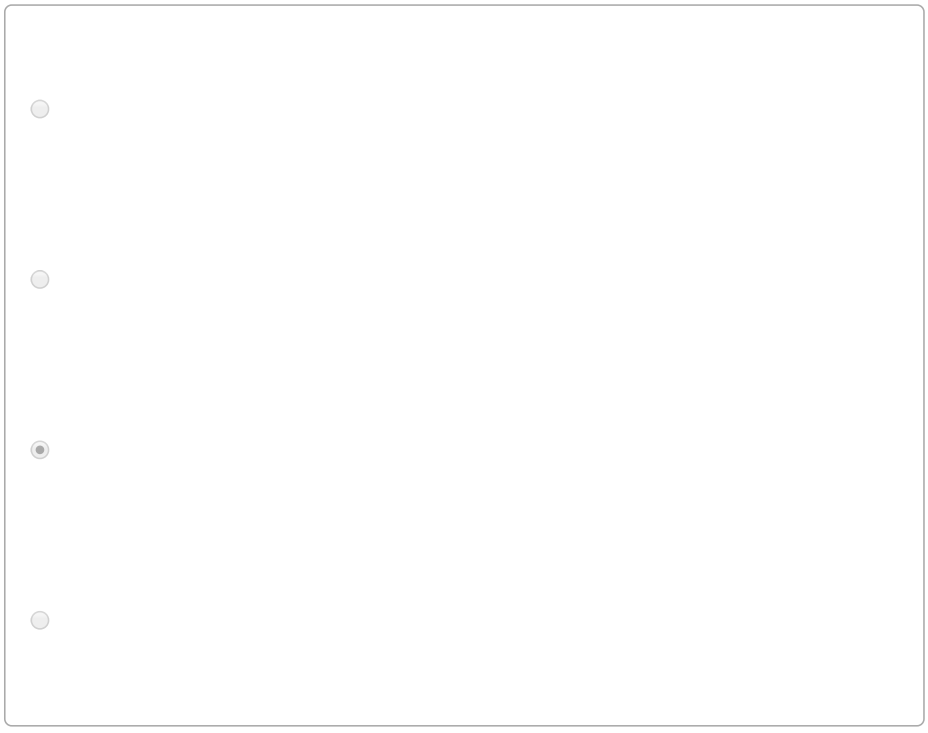
ANSWER:



Correct

Part B

ANSWER:

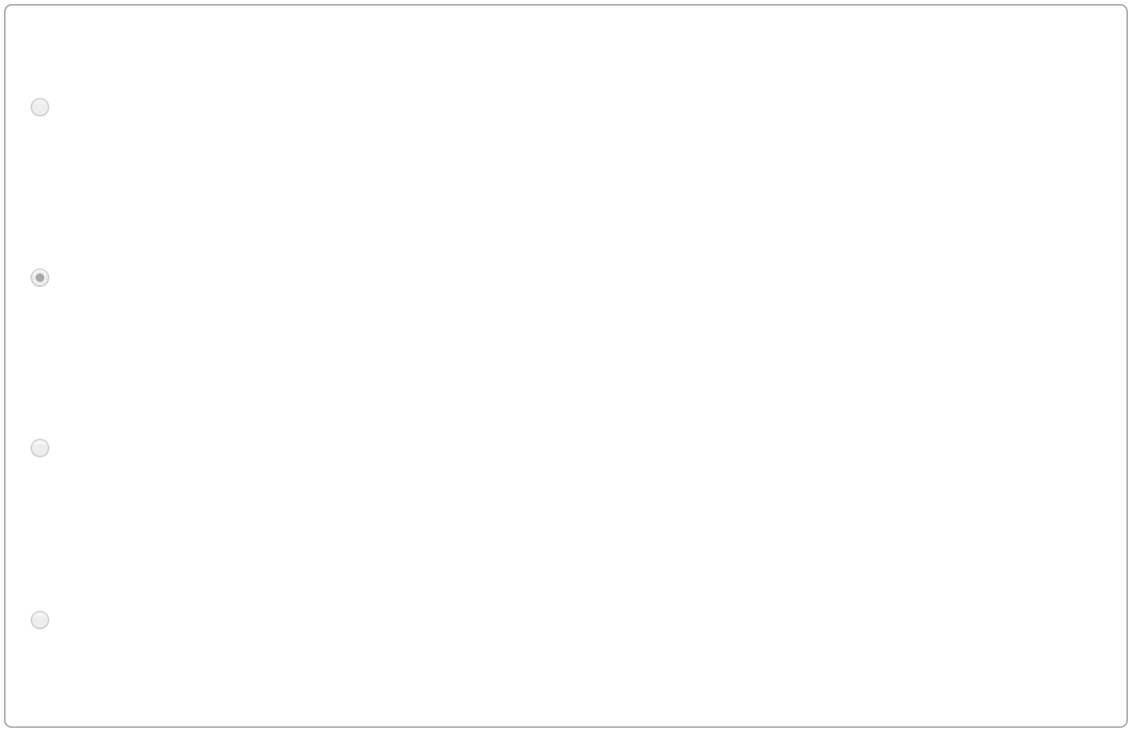


Correct

Part C

1-methylcycloheptanol \(\to\) 2-methylcycloheptanol

ANSWER:



Correct

Alkene: Addition Reactions

Part A

Choose the reagents that would be required to carry out the following synthesis:

ANSWER:

- HBr
- \({\rm Br_2}\), \({\rm H_2O}\)
- \({\rm Br_2}\), \({\rm CH_2Cl_2}\)
- \({\rm H_2}\), \(\rm Pd/C\)
- mCPBA

Correct

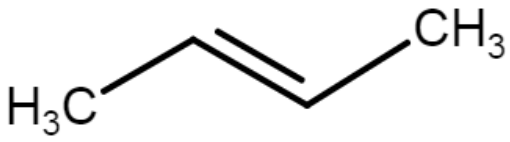
Addition of halogens onto both carbon atoms involved in a double bond can be accomplished by using the diatomic molecule and an inert solvent (in this case methylene chloride \(\rm CH_2Cl_2\)) that will not react with the halogen.

Alkenes: Reaction of (2E)-but-2-ene with Br2 in CH2Cl2

Part A

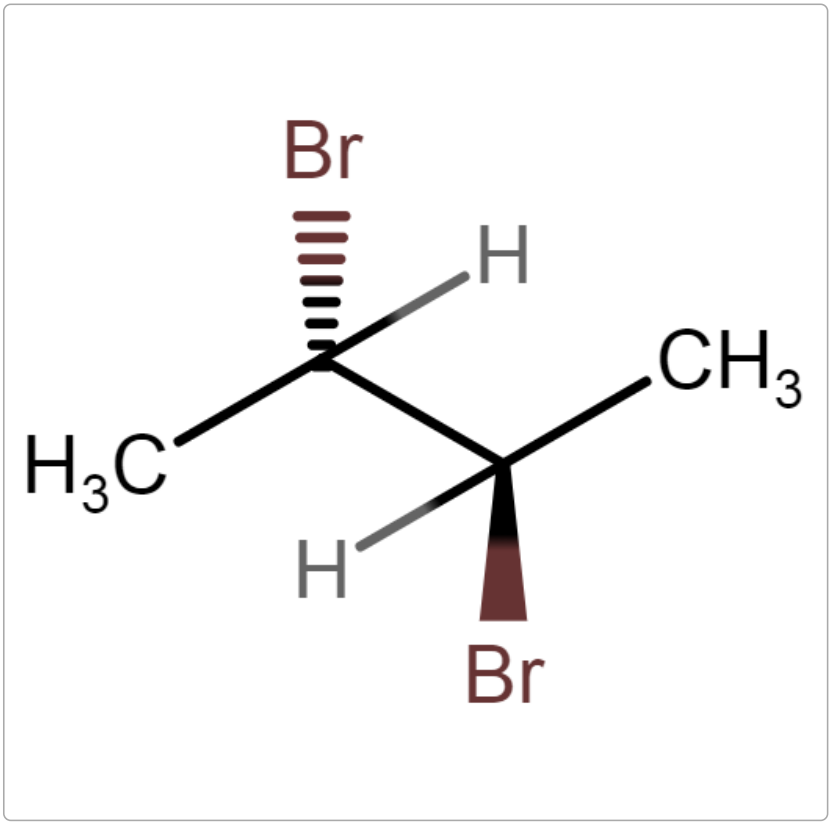
Draw the product formed when the compound shown below undergoes a reaction with Br_2 in CH_2Cl_2.

Interactive 3D display mode



Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default. Show the appropriate stereochemistry by choosing the dashed or wedged buttons and then clicking a bond on the canvas.

ANSWER:



Correct

Anti addition of Br-Br across the double bond occurs.

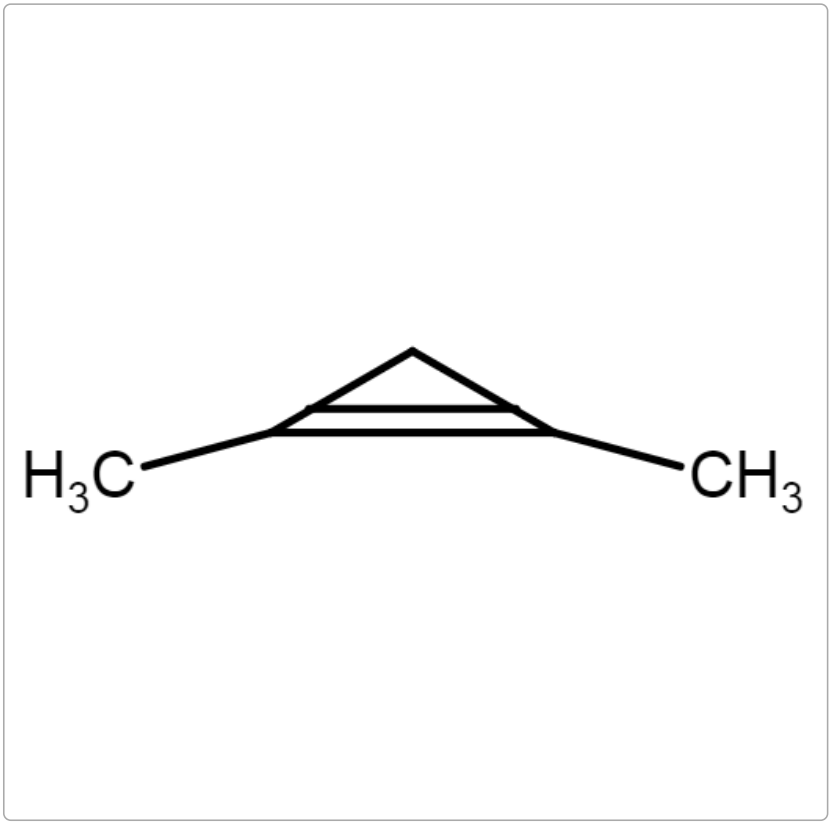
Alkenes: Determine the Alkene from the product of Reduction with H2 and Pd/C

Part A

A compound gives *cis*-1,2-dimethylcyclopropane when it is reduced with H_2 and Pd/C. The ^{1}H NMR spectrum of the compound shows only two singlets. What is the structure of the compound?

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.

ANSWER:



Correct

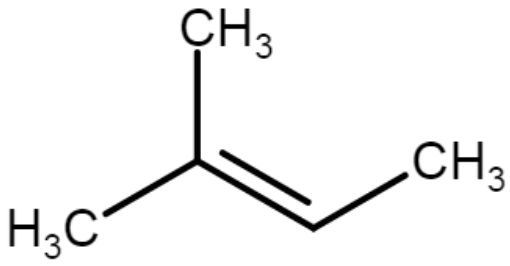
Excellent! This compound shows only two ^{1}H NMR resonances. Upon hydrogenation, the H atoms are added to the same face of the double bond to give the cis product.

Alkenes: Catalytic Hydrogenation of 2-methylbut-2-ene

Part A

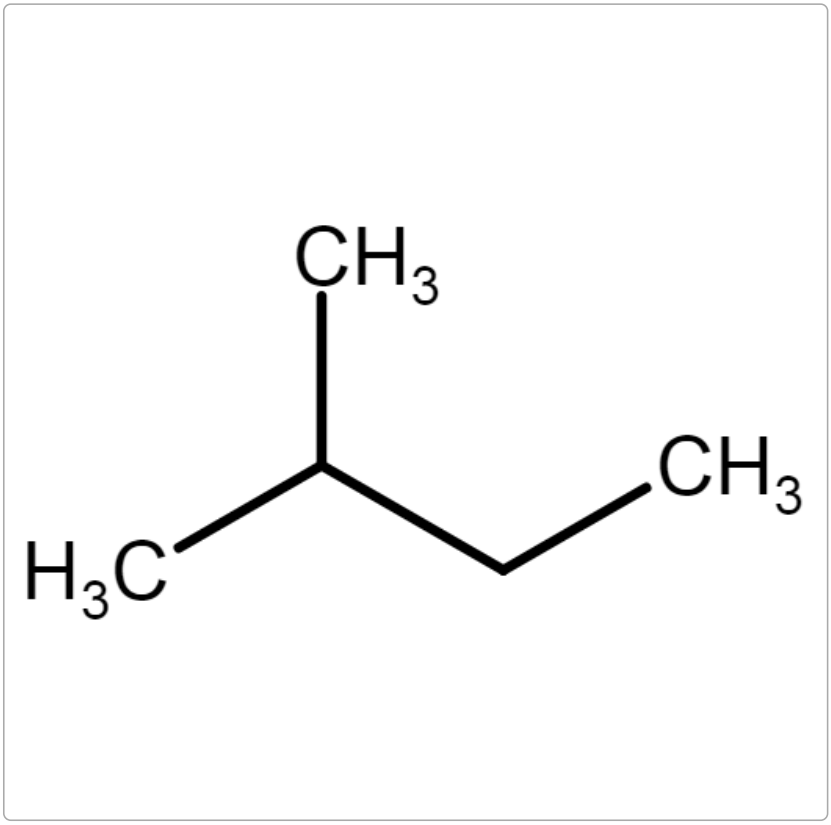
Draw the product that is formed when the compound shown below is treated with an excess of hydrogen gas and a palladium catalyst.

Interactive 3D display mode



Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.

ANSWER:



Correct

That's right! Addition of H-H across the C=C bond is catalyzed by Pd.

Score Summary:

Your score on this assignment is 97.0%.
You received 16.49 out of a possible total of 17 points.