ASSIGNMENT 2: TASK 3

Due: 11:59pm on Monday, September 17, 2018

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

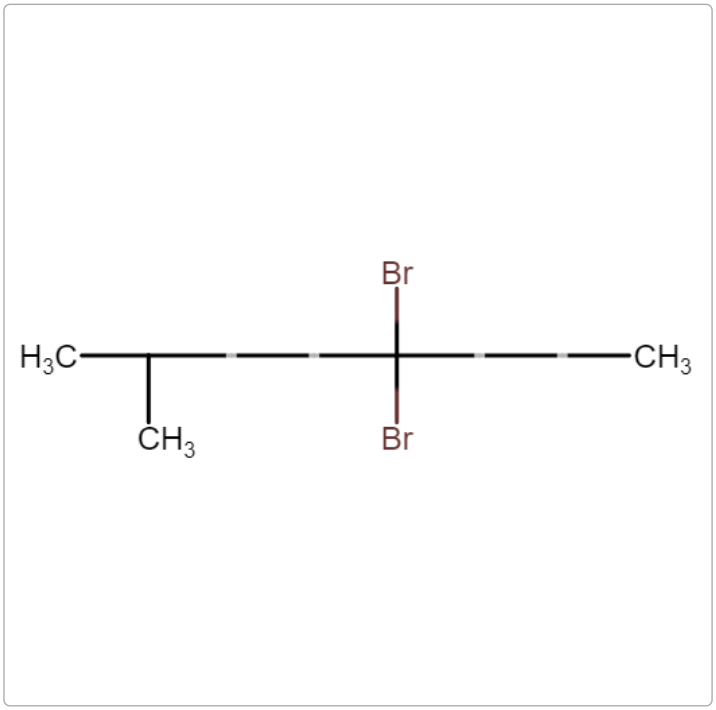
Alkyl Halides: Structure of 5,5-dibromo-2-methyloctane

Part A

Draw the structural formula of 5,5-dibromo-2-methyloctane.

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

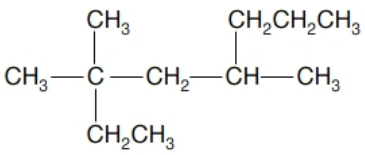
Naming Alkanes with Substituents

Alkanes can contain side groups called substituents. To name an alkane with substituents, start by determining the longest continuous chain of carbon atoms. The longest continuous carbon chain is named as a continuous chain alkane.
Next, number the longest continuous chain of carbon atoms, starting with the end nearest to a substituent. Each substituent should be labeled by its location in the chain and named either as an alkyl group (carbon branch) or a halo group (halogen atom), with a hyphen between the number and the name. For example, if a CH_3 group is attached to the third carbon atom, the substituent would have the following name: 3-methyl.

If an alkane has more than one substituent, the substituents should be alphabetized, with hyphens placed between the substituents. The substituent names are then placed in front of the name of the longest chain to complete the name of the alkane.

Part A

What is the IUPAC name for the following compound?



Enter the name of the molecule.

Hint 1. Select the longest continuous carbon chain

Select the atoms of the longest continuous carbon chain.

Identify the longest continuous carbon chain by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom Properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

ANSWER:

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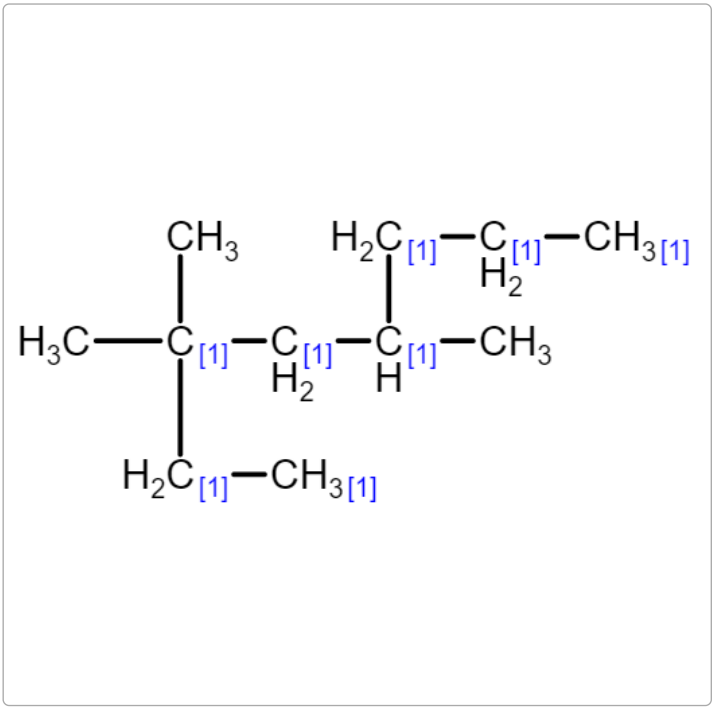


Correct

"Octane" will appear in the name of this molecule because the longest carbon chain contains eight carbon atoms.

Hint 2. Select the substituents

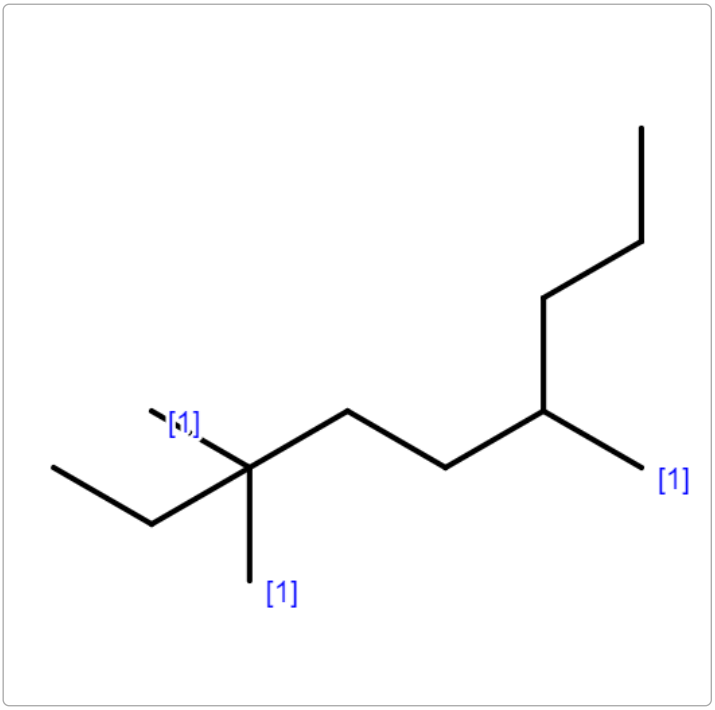
Select the atoms of the substituents.

Identify the appropriate group of atoms by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom Properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. Substituents

A *substituent* in an alkane is any atom or group of atoms that is not a part of the longest continuous carbon chain (or parent chain). Hydrogen atoms directly attached to a carbon atom in the longest continuous carbon chain are not substituents.

ANSWER:



Correct

Hint 3. Determine the name of the substituent shown

What is the name for the substituent shown?

CH_3-

Enter the name of the substituent.

ANSWER:

methyl

Correct

"Trimethyl" will appear in the name of this molecule because there are three methyl group substituents.

ANSWER:

3,3,5-trimethyloctane

All attempts used; correct answer displayed

When you look at a hydrocarbon, the longest carbon chain is not necessarily in a straight line. In this molecule, the straight chain has only five carbon atoms, but the longest carbon chain has eight carbon atoms.

Part B

Sort each of the molecules shown into the bin with the appropriate IUPAC nomenclature for the molecule.

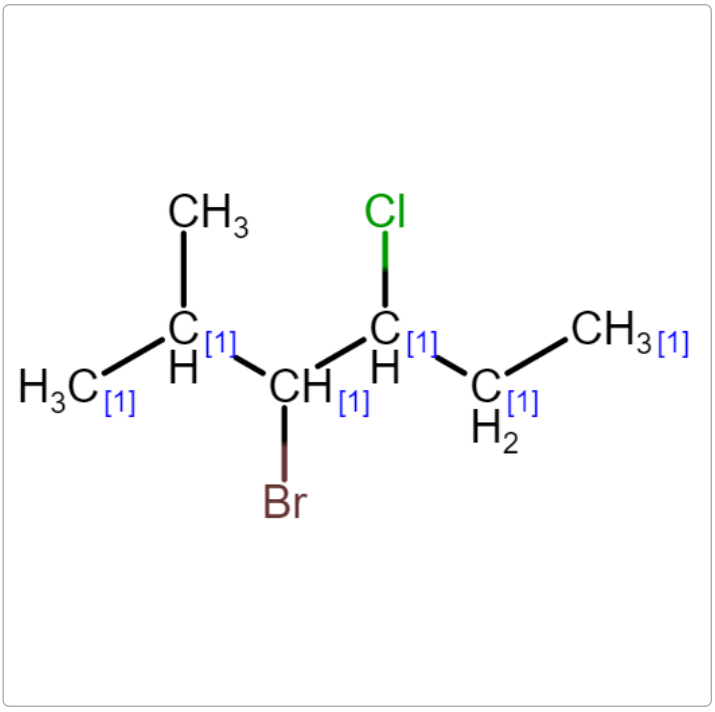
Sort each molecule into the bin with the correct IUPAC nomenclature.

Hint 1. Select the longest continuous carbon chain

Select the longest continuous carbon chain of the carbon skeleton shown.

Identify the longest continuous carbon chain by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom Properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

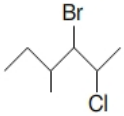
ANSWER:



Hint 2. Number the substituents of the molecule shown

A *substituent* in an alkane is any atom or group of atoms that is not a part of the longest continuous carbon chain (or parent chain). Hydrogen atoms directly attached to a carbon atom in the longest continuous carbon chain are not substituents. Keep in mind that the longest continuous carbon chain should be numbered in whatever "direction" (left to right, right to left) that gives the lowest numbers for the substituents.

For the molecule shown, list the location of each substituent, starting with the lowest numbered substituent.



Enter the number location for each substituent starting with the lowest number, separated by commas. For example, if the substituents are located at positions 2 and 3, enter 2,3.

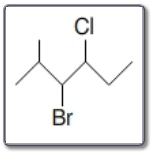
ANSWER:

2,3,4

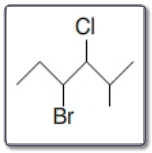
ANSWER:

Reset Help

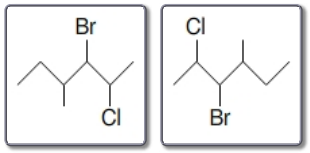
3-Bromo-4-chloro-2-methylhexane



4-Bromo-3-chloro-2-methylhexane



3-Bromo-2-chloro-4-methylhexane



Correct

Problem 6-3

For each of the following compounds give the IUPAC name. Then classify the compound as a methyl, primary, secondary, or tertiary halide.

Part A

$(CH_3)_2CHCH_2Cl$

Enter the correct IUPAC nomenclature.

ANSWER:

1-chloro-2-methylpropane

Correct

Part B

$(CH_3)_3CBr$

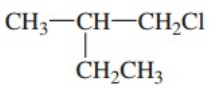
Enter the correct IUPAC nomenclature.

ANSWER:

2-bromo-2-methylpropane

Correct

Part C



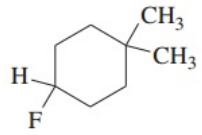
Enter the correct IUPAC nomenclature.

ANSWER:

1-chloro-2-methylbutane

Correct

Part D



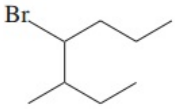
Enter the correct IUPAC nomenclature.

ANSWER:

4-fluoro-1,1-dimethylcyclohexane

Correct

Part E



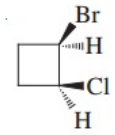
Enter the correct IUPAC nomenclature.

ANSWER:

4-bromo-3-methylheptane

Correct

Part F



Enter the correct IUPAC nomenclature.

ANSWER:

cis-1-bromo-2-chlorocyclobutane

Correct

Part G

Classify the compound as a methyl, primary, secondary, or tertiary halide.

Drag the appropriate items to their respective bins.

ANSWER:

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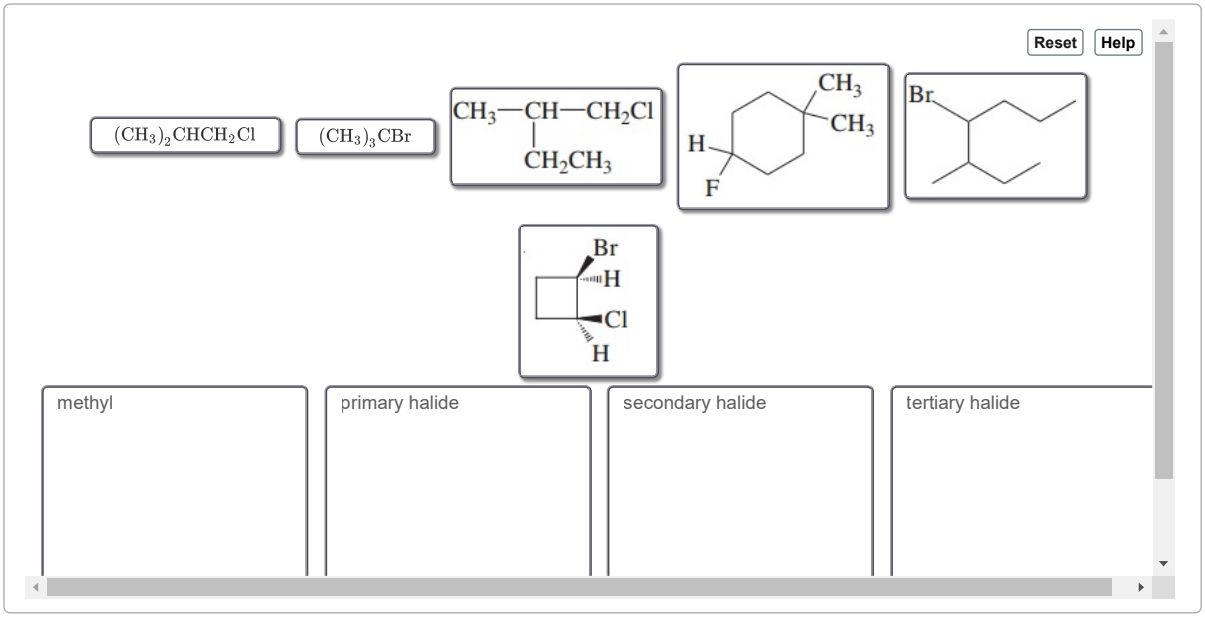


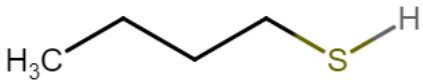
Correct

Alkyl Halides: Draw the nucleophile that would react with 1-bromobutane to give butanethiol

Part A

Draw the nucleophile needed to convert 1-bromobutane to the following substance.

Interactive 3D display mode



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

ANSWER:

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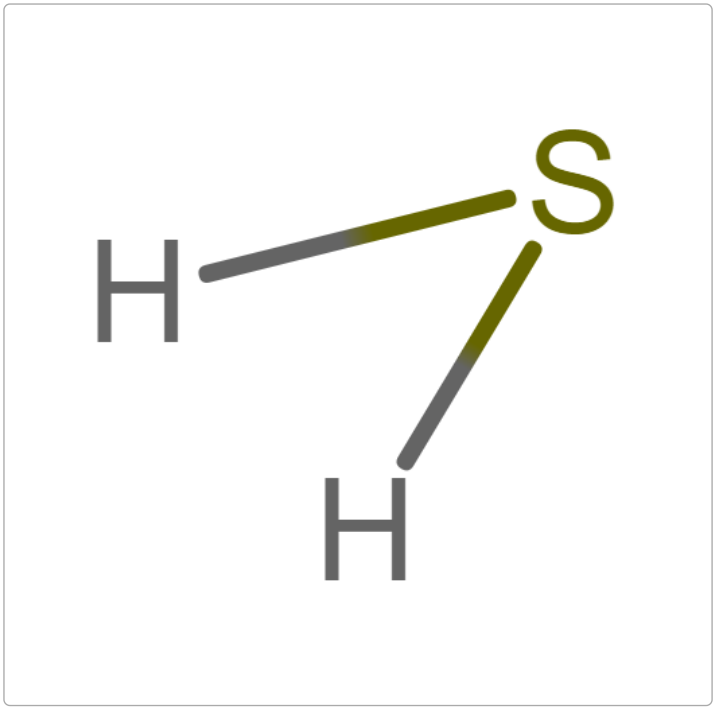


Correct

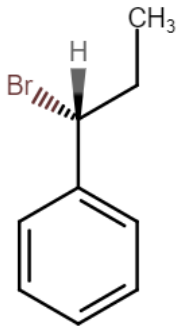
The HS^- displaces the Br atom to form the product.

Alkyl Halides: Reaction of (1R)-1-bromo-1-phenylpropane and the hydroxide ion

Part A

Draw the product formed when the structure shown below undergoes substitution with OH^-.

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:

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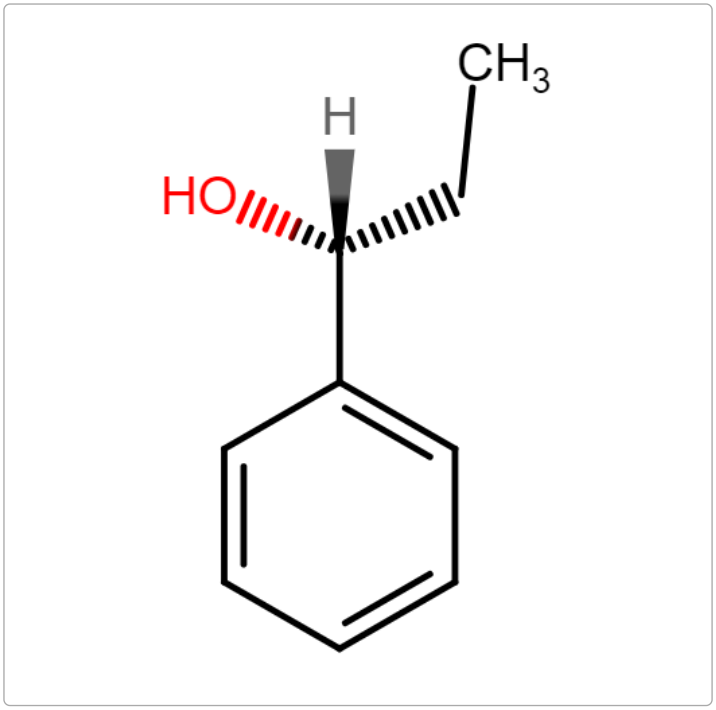


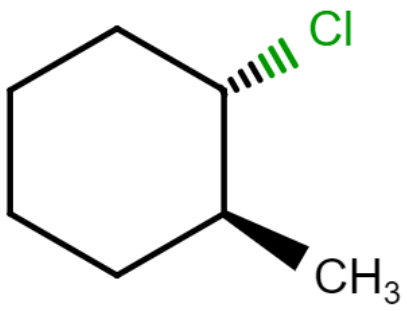
Incorrect; One attempt remaining; Try Again

Alkyl Halides: Reaction of (1S,2R)-1-chloro-2-methylcyclohexane and MeO-

Part A

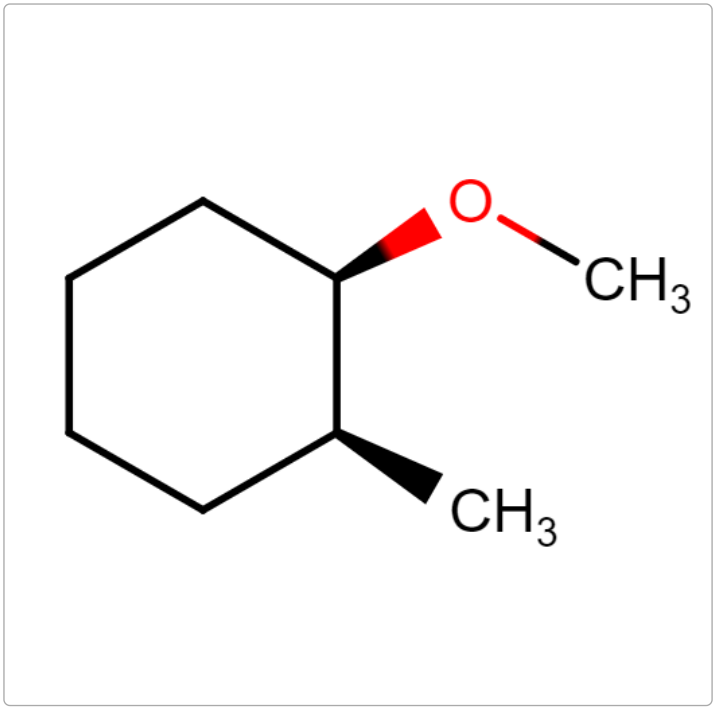
Draw the product formed when the structure shown below undergoes a S_N2 reaction with $NaOCH_3$.

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:



All attempts used; correct answer displayed

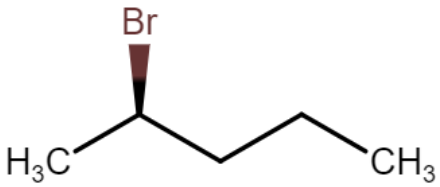
Only the electrophilic stereocenter inverts. The one that is not involved in the reaction remains unchanged.

Alkyl Halides: Substitution reaction of (2R)-2-bromopentane and CH3O-

Part A

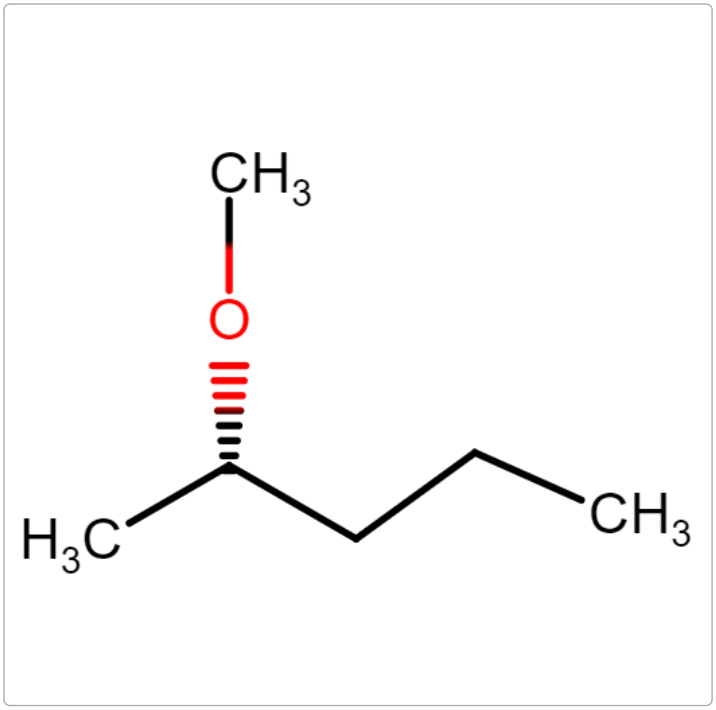
Draw the product formed when the structure shown below undergoes substitution with $NaOCH_3$.

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. To change the bond type, select the Insert menu and change the Bond setting. Show the appropriate stereochemistry by choosing the dashed or wedged buttons and then clicking a bond on the canvas.

ANSWER:



Correct

The major substitution product has undergone inversion of configuration at the electrophilic C in this S_N2 reaction under basic conditions. (In fact, elimination will predominate over substitution under these conditions.)

Problem 6-14

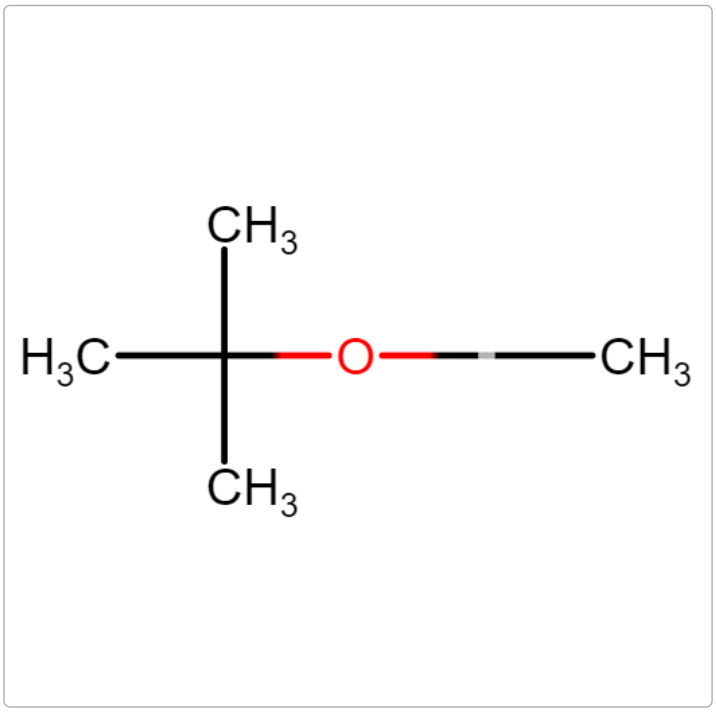
Predict the major organic products of the following substitutions.

Part A

CH_3CH_2Br (ethyl bromide) + $(CH_3)_3CO^- K^+$ (potassium *tert*-butoxide) $\longrightarrow$

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds and charges), Atoms, and Templates toolbars.

ANSWER:



Correct

Part B

$HC{\equiv}C:^- Na^+ + CH_3CH_2CH_2CH_2Cl \longrightarrow$

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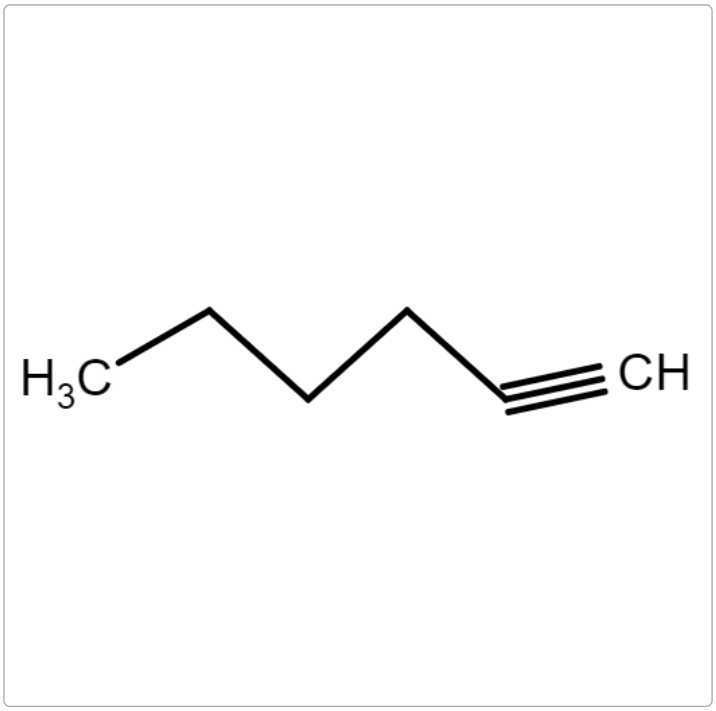
Draw the molecule on the canvas by choosing buttons from the Tools (for bonds and charges), Atoms, and Templates toolbars.

ANSWER:



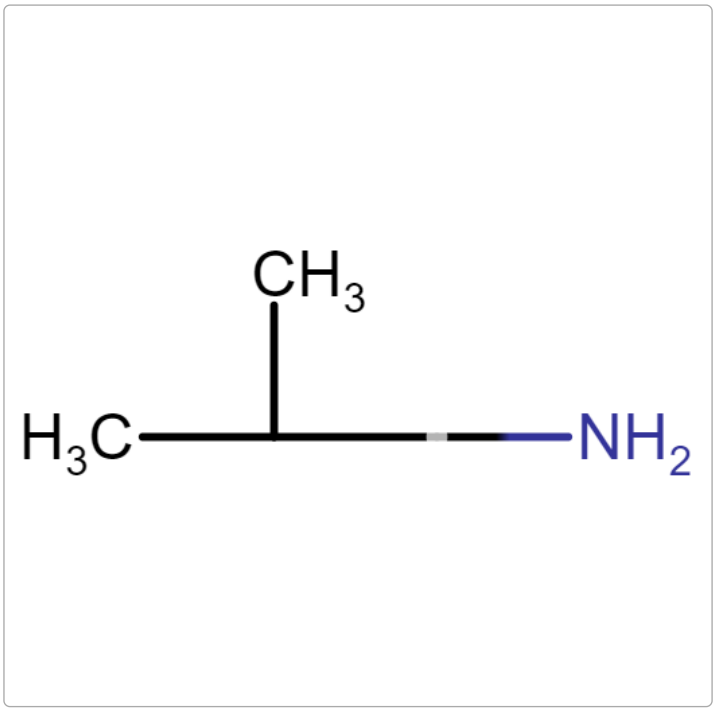
Correct

Part C

$(CH_3)_2CHCH_2Br$ + excess NH_3 $\rightarrow$

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds and charges), Atoms, and Templates toolbars.

ANSWER:



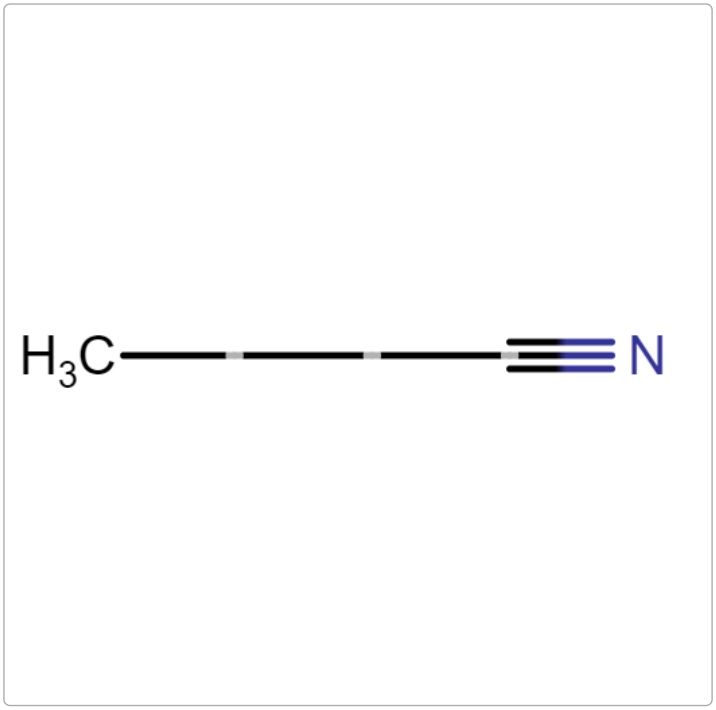
Correct

Part D

$CH_3CH_2CH_2I$ + $NaCN$ $\rightarrow$

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds and charges), Atoms, and Templates toolbars.

ANSWER:



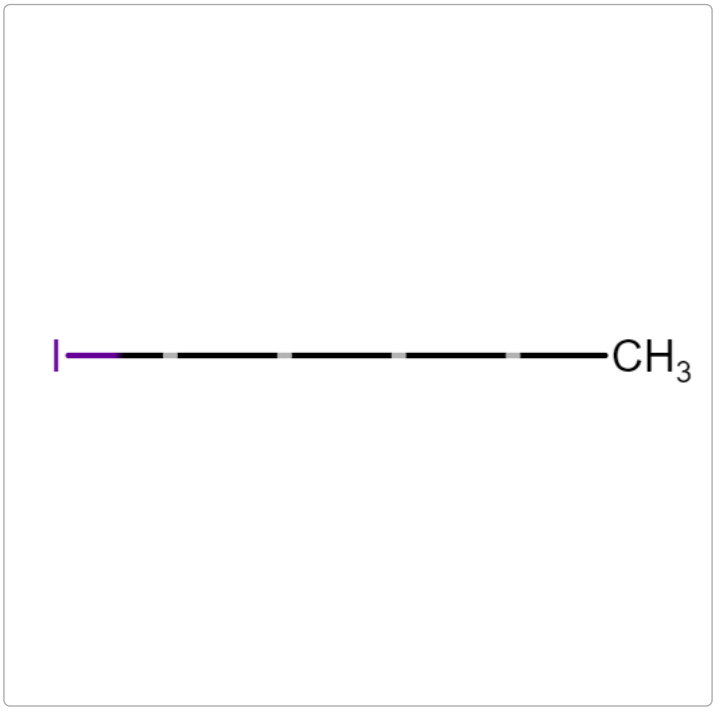
Correct

Part E

1-chloropentane + $\mathrm{NaI} \rightarrow$

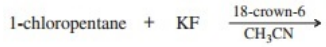
Draw the molecule on the canvas by choosing buttons from the Tools (for bonds and charges), Atoms, and Templates toolbars.

ANSWER:



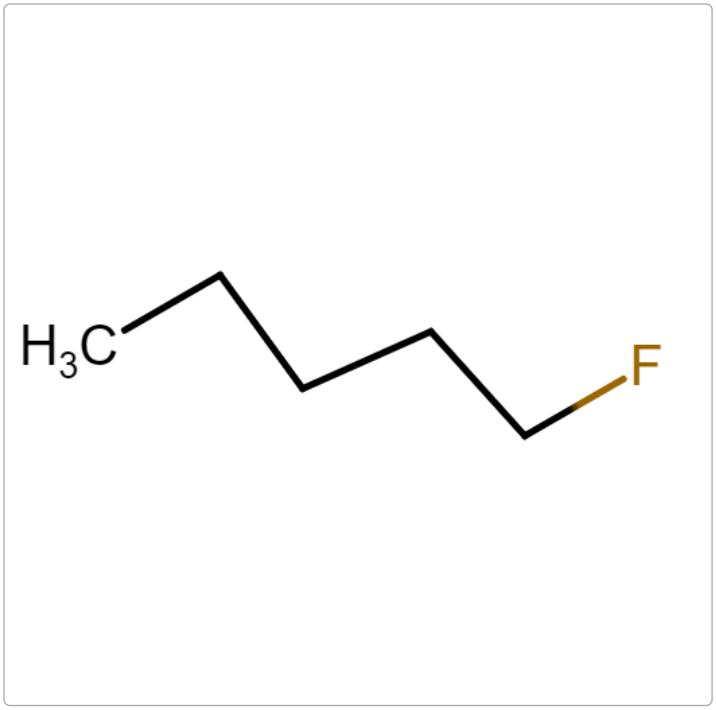
Correct

Part F



Draw the molecule on the canvas by choosing buttons from the Tools (for bonds and charges), Atoms, and Templates toolbars.

ANSWER:



Correct

Problem 6-15

Part A

Label the S_N2 reaction using 1-chlorobutane as the starting material.

Drag the appropriate labels to their respective targets.

ANSWER:

Correct

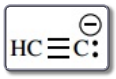
Part B

Show which nucleophile you might use in a S_N2 reaction to convert 1-chlorobutane into the following compounds.

Drag the appropriate items to their respective bins.

ANSWER:

Reset Help

HO^- | ^-CN | $^-OCH_2CH_3$ | F^- from KF/18-crown-6 | I^- |  | excess NH_3

butan-1-ol	1-fluorobutane	1-iodobutane	$CH_3(CH_2)_3CN$	$CH_3(CH_2)_3C{\equiv}CH$	$CH_3CH_2O(CH_2)_3-CH_3$	$CH_3(CH_2)_3NH_2$

Correct

Basicity and Nucleophilicity

An atom or a group of atoms that contains at least one lone pair of electrons is called a *nucleophile*. A nucleophile will donate this pair of electrons to another molecule that is electron deficient. *The nucleophilicity of the nucleophile is determined by the rate at which it attacks the nucleus of the substrate that is electron deficient*. Solvent and steric factors play an important role in determining nucleophilicity.

Nucleophilicity is a kinetic property, whereas basicity is a thermodynamic property. Nucleophilicity depends on electronegativity, the size of the electron donor atom, and the hybridization of an atom bearing a lone pair. It also depends on interactions between the nucleophile and solvent molecules, steric factors, and the nature of the electrophile.
When an electron-rich species donates its electron pair to an electron-deficient atom, the electron-rich species is called a nucleophile. The electron-deficient species is often a carbon atom. When the affinity of the electron-rich species is closer to a proton, it then acts as a base. The tendency of an electron-rich species to behave as a nucleophile or base determines whether the reaction will be a substitution or elimination reaction.

A substitution reaction is characterized by a reaction in which a functional group in a particular chemical compound is replaced by another group, whereas an elimination reaction results in the removal of two substituents from a molecule in either a one- or two-step mechanism. The fate of the reaction depends on the nature of the nucleophile, electrophile, and solvent.

Part A

Strong, moderate, and weak nucleophiles can be categorized as follows:

- A strong nucleophile contains more unsaturation, such as a double bond or triple bond, or it may be a cyclic structure. Strong nucleophiles may contain atoms with higher electronegativity, or atoms having loosely bound electron pairs. Each of these characteristics make the species more electron rich, which makes it more effective in attacking an electrophilic carbon atom.
- Moderate nucleophiles are those that increase the availability of an electron pair, usually through an electron-donating effect, but are not as good as strong nucleophiles at attacking an eletrophilic atom.
- In weak nucleophiles delocalization of an electron pair makes the electron pair less accessible. This delocalization can take place because of the presence of a carbonyl group adjacent to a nucleophilic atom, such as N or O. Neutral molecules are also poor nucleophiles and are less able to attack electrophilic atoms.

Sort the following nucleophiles as excellent, good, or poor.

Drag the appropriate nucleophiles to their respective bins.

Hint 1. The factors affecting nucleophilicity

The sorting of nucleophiles is done using the following simple factors for aprotic solvents. Consider the nature of the nucleophilic atom to decide the nature of the nucleophile.

1. A nucleophile with a negative charge is a stronger nucleophile than its conjugate acid.
   For example, an NH_2^- anion is a stronger nucleophile than NH_3 because a negatively charged nucleophile will react faster than an uncharged nucleophile or partially charged nucleophile.
2. As the electronegativity of an atom carrying an electron pair increases, the nucleophilicity decreases.
   For example, an NH_2^- anion is a stronger nucleophile than an OH^- anion, because the more electronegative O atom will hold electrons more strongly.
3. Charge delocalization decreases nucleophilicity.
   For example, in an $HCOO^-$ anion the electron cloud is delocalized over two oxygen atoms, whereas in an OH^- anion the electron cloud is available with one oxygen atom. Therefore, OH^- is a stronger nucleophile than $HCOO^-$.
4. The electron-donating group attached to an atom carrying a negative charge increases nucleophilicity.
   For example, CH_3O^- is a stronger nucleophile than OH^-, the methyl group attached to the oxygen atom is an electron-donating group. This increases the electron cloud on the oxygen atom and makes it a stronger nucleophile.
5. As the size of an atom increases, the electron cloud is more distorted toward the partially positive charge and increases its nucleophilicity. This is the reason why HS^- is a stronger nucleophile than HO^-.
6. The crowding of groups or the steric factor decreases the nucleophilicity.

The structures that show a combination of more than one factor will be the best in the set and can be termed as excellent nucleophiles.

Hint 2. Determine the effect of delocalization on nucleophilicity

The sharing of electrons by the electron-donating atom, either with another atom in a bond forming a neutral molecule or through delocalization, decreases nucleophilicity. When electrons are delocalized over a molecule, then the nucleophilicity of the electron-donating atom decreases relative to a molecule without delocalization.

Arrange the following groups based on the sharing of atoms by the electron-donating atom.

Rank from highest to lowest. To rank items as equivalent, overlap them.

ANSWER:

Reset Help

Highest Lowest

CH_3O^- CH_3COO^- CH_3OH

The correct ranking cannot be determined.

Hint 3. Arrange the nucleophiles according to their size

Rank the following nucleophiles according to the size of the atom bearing the negative charge.

Rank from largest to smallest. To rank items as equivalent, overlap them.

ANSWER:

Reset Help

Largest Smallest

I^- Br^- HO^-

The correct ranking cannot be determined.

ANSWER:

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Strong

CN^- HS^- I^- CH_3O^-

Moderate

NH_3 Br^-

Weak

CH_3OH HCOOH

Correct

Nucleophilicity is the property of an atom or group of atoms containing at least one lone pair of electrons. All factors such as inductive effects, unsaturation, and larger atomic size that make electron pairs more available will increase the nucleophilicity.

Part B

Nucleophilicity is a kinetic property. A higher nucleophilicity indicates that the nucleophile will easily donate its electrons to the electrophile and that the reaction will occur at the faster rate. The reaction rate also depends on the nature of the electrophile and solvent.
Rank the following reactions from fastest to slowest based on the nucleophilicity of the nucleophile.

Rank from fastest to slowest. To rank items as equivalent, overlap them.

Hint 1. How to approach the problem

Identify the nucleophile and determine whether there is any substituent attached to it. If substituents are electron donating, then they increase the nucleophilicity; this enhances the rate of the reaction. The more electron-donating groups attached to the atom bearing the negative charge in a nucleophile the more nucleophilic it behaves and the faster the reaction proceeds.

Hint 2. Identify the best nucleophile

Which of the following is the best nucleophile?

ANSWER:

- $(CH_3)_2N^-$
- H_2N^-
- CH_3NH^-

ANSWER:

Reset Help

Fastest Slowest

$(CH_3)_2N^- + CH_3-Br \longrightarrow (CH_3)_2NCH_3 + Br^-$

$CH_3NH^- + CH_3-Br \longrightarrow CH_3NHCH_3 + Br^-$

$H_2N^- + CH_3-Br \longrightarrow CH_3NH_2 + Br^-$

The correct ranking cannot be determined.

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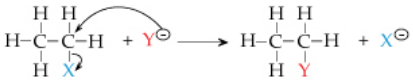
Correct

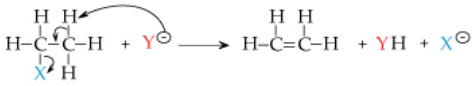
The greater the nucleophilicity of the nucleophile, the faster the rate of the reaction. The polarizability of the bond breaking in the electrophile depends on the inductive effect of the groups present in the substrate.

Nucleophilicity and basicity

An electron-rich species can behave both as a nucleophile as well as a base. Nucleophilicity is the affinity of an electron-rich species to the electron-deficient center (an electrophile), and basicity is the measure of affinity toward a proton. Nucleophilicity and basicity compete with each other in organic reactions. As the steric hindrance of the electron-rich species increases, its nucleophilicity decreases and basicity increases, leading to an elimination reaction rather than a substitution reaction, whereas strong nucleophiles give substitution reactions rather than elimination reactions. The nature of the substrate and the solvent plays an important role in deciding the course of the reactions.
When Y^- acts as a nucleophile, a substitution reaction occurs:

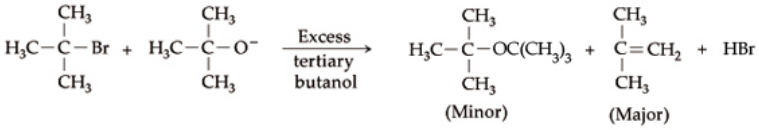


When Y^- acts as a base, an elimination reaction occurs:



Part C

The following is a representative reaction illustrating the strength of a base and a nucleophile:



Observe carefully the course of the reaction. Which of the following statements best describe the processes that occur in the reaction?

Check all that apply.

Hint 1. How to determine the course of a reaction

Find the nature of the reactant and the reagent given in the reaction. Then determine the nature of the solvent. Note that the solvent given is in excess. Think of the interaction between the solvent and the attacking reagent and its effect on the basicity and nucleophilicity of the reactive species that are formed in the reaction.

Hint 2. Determine the nature of *t*-butyl bromide

ANSWER:

The reactant \rm (CH_3)_3CBr is a
- tertiary
- secondary
- primary

alkyl halide.

Hint 3. Determine the nature of *t*-butoxide

ANSWER:

The reagent \rm (CH_3)_3CO^- is a strong
- acid
- electrophile
- base
- nucleophile

.

Hint 4. Determine the interaction between the solvent and the reagent

The reagent \rm (CH_3)_3CO^- and the solvent molecules [*t*-butanol and \rm (CH_3)_3COH] interact by _____ in solvolysis.

ANSWER:

- the masking of the reagent by the solvent
- the removal of an electron pair from a solvent molecule
- the removal of a proton from a solvent molecule

ANSWER:

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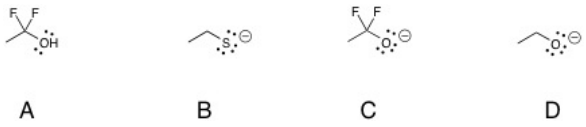
- [x] *t*-Butoxide acts as a base in this reaction.
- [ ] The formation of the carbocation is the fastest step.
- [x] Tertiary alkyl halides form stable carbocations.
- [x] Elimination is favored rather than a substitution reaction.
- [ ] The formation of the double bond is the slowest step.

Correct

Chapter 6 Reading Quiz Question 5

Part A

Rank the following species in order of decreasing nucleophilicity (list the strongest nucleophile first).



A B C D

Hint 1. Nucleophilicity

Nucleophilicity refers to the *rate* at which a species donates a pair of electrons to form a bond to C; *basicity* refers to the *equilibrium constant* for the reaction in which a species donates a pair of electrons to form a bond to H. Because of this relationship, parallels exist between nucleophilicity and basicity; however, it is important to be aware of the exceptions. See 6-10.

ANSWER:

- (•) B > D > C > A
- ( ) A > C > B > D
- ( ) B > C > D > A
- ( ) D > C > B > A

Correct

Alkyl Halides: Reaction of 1-bromo-4-methylcyclohexane with NaOH and DMSO

Part A

Draw the product formed when the structure shown below undergoes a S_N2 reaction with NaOH in DMSO. (Use a wavy bond (Single Up or Down) if you need to indicate a mixture of configurations at a particular stereocenter.) DMSO is a polar, aprotic solvent.

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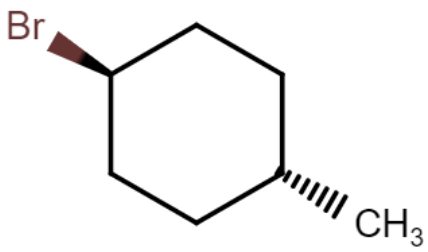

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default. Show the appropriate stereochemistry by choosing the dashed or wedged buttons and then clicking a bond on the canvas.

ANSWER:

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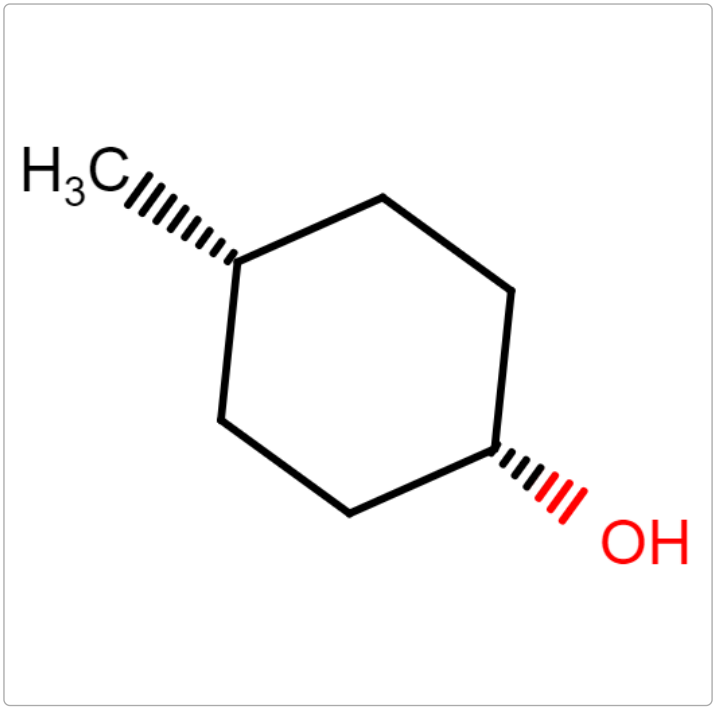


Correct

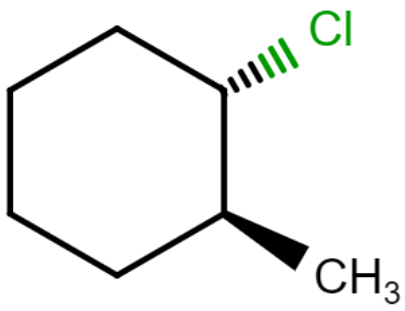
Only the electrophilic stereocenter inverts. The one that is not involved in the reaction remains unchanged.

Alkyl Halides: Substitution reaction with (1S,2S)-1-chloro-2-methylcyclohexane with conc. CH3O-

Part A

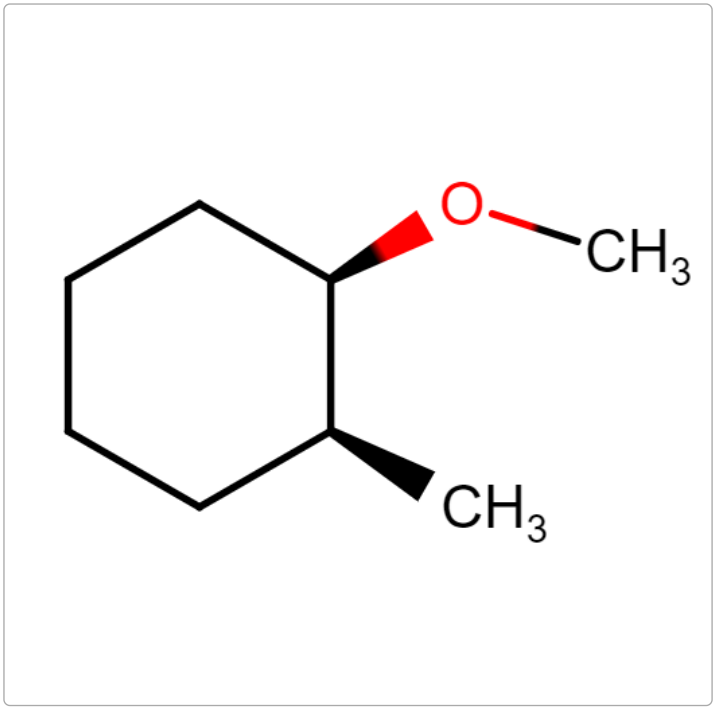
Draw the product formed when the structure shown below undergoes a substitution with $NaOCH_3$.

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

Excellent! The reaction occurs through the S_N2 mechanism, and only one enantiomer is formed.

Problem 6-21

Under appropriate conditions, (S)-1-bromo-1-fluoroethane reacts with sodium methoxide to give pure (S)-1-fluoro-1-methoxyethane.

$$\underset{(S)}{CH_3CHBrF} + NaOCH_3 \longrightarrow \underset{(S)}{CH_3CHFOCH_3} + NaBr$$

Part A

Why is bromide rather than fluoride replaced?

Select all that apply.

ANSWER:

- [x] Bromide is many orders of magnitude better than fluoride in leaving group ability.
- [ ] Fluoride is many orders of magnitude better than bromide in leaving group ability.
- [x] Fluoride is moderately basic, by far the most basic of the halides. It is a terrible leaving group.
- [x] Bromide ion is so weak it is not considered at all basic; it is an excellent leaving group.

Correct

Part B

Draw perspective structures for the starting material and the product.

Edit the reaction by drawing all steps in the appropriate boxes and connecting them with reaction arrows. Add charges where needed. Electron flow arrows should start on an atom or a bond and should end on an atom, bond, or location where a new bond should be created.

ANSWER:

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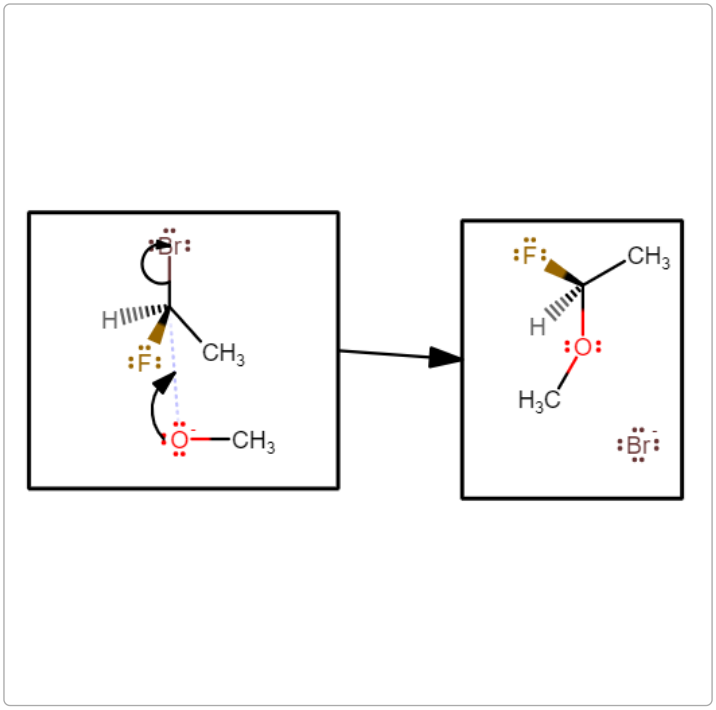


Correct

Part C

Does the product show retention or inversion of configuration?

ANSWER:

- Retention of configuration
- Inversion of configuration

Correct

Part D

Is this result consistent with reaction by the \rm S_{\rm N}2 mechanism?

ANSWER:

- No
- Yes

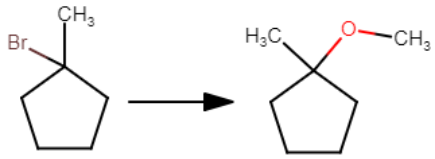
Correct

Alkyl Halides: Draw the second intermediate of solvolysis of bromomethylcyclopentane in methanol

Part A

Solvolysis of 1-bromo-1-methylcyclopentane in methanol yields an initial intermediate, a second intermediate, and then the product (1-methoxy-1-methylcyclopentane) shown. Draw the structure of the *second* intermediate.

Interactive 3D display mode



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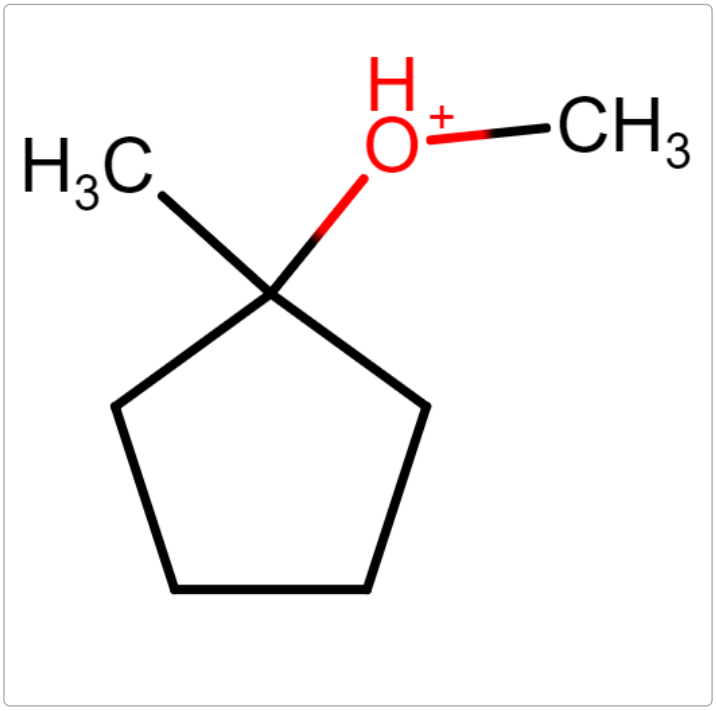
Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars, including charges where needed. The single bond is active by default.

ANSWER:



Correct

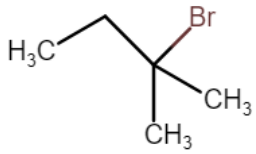
Initially a 3° cation forms, which reacts through solvolysis to form the second intermediate you have drawn. An S_N1 reaction gives the product 1-methoxy-1-methylcyclopentane after deprotonation of the second intermediate.

Alkyl Halides: Nucleophilic Substitution: Draw the intermediate in solvolysis of the 2-bromo-2-methylbutane

Part A

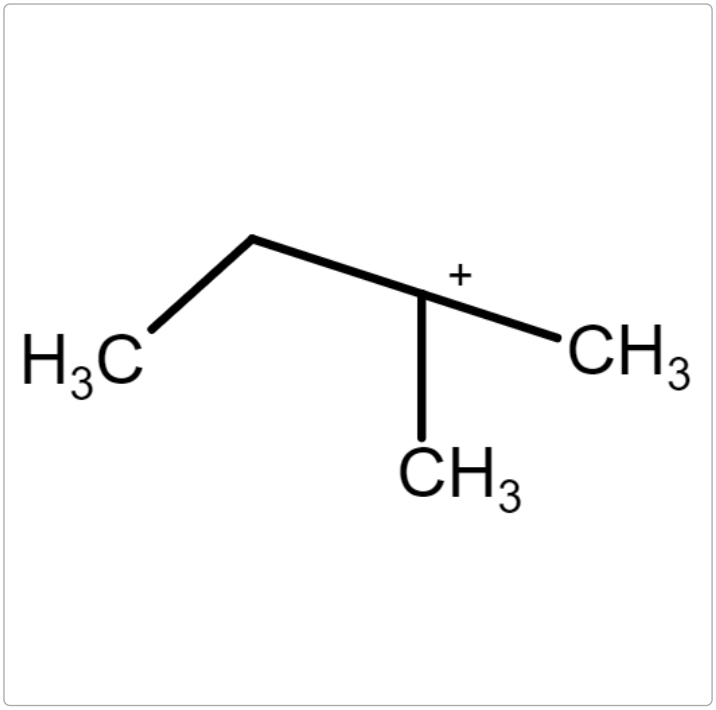
Draw the intermediate in solvolysis of the compound shown below.

Interactive 3D display mode



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

ANSWER:



Correct

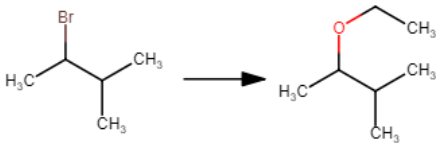
Well done. The halogen leaves and a positive charge takes its place.

Alkyl Halides: Nucleophilic Substitution: Draw the intermediate of solvolysis of 2-bromo-3-methylbutane with ethanol that leads to the unexpected product

Part A

The solvolysis product of 2-bromo-3-methylbutane with ethanol forms several products. The expected product shown below is formed by addition of ethanol to the initially formed intermediate. Draw the intermediate that leads to the unexpected product.

Interactive 3D display mode



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

ANSWER:

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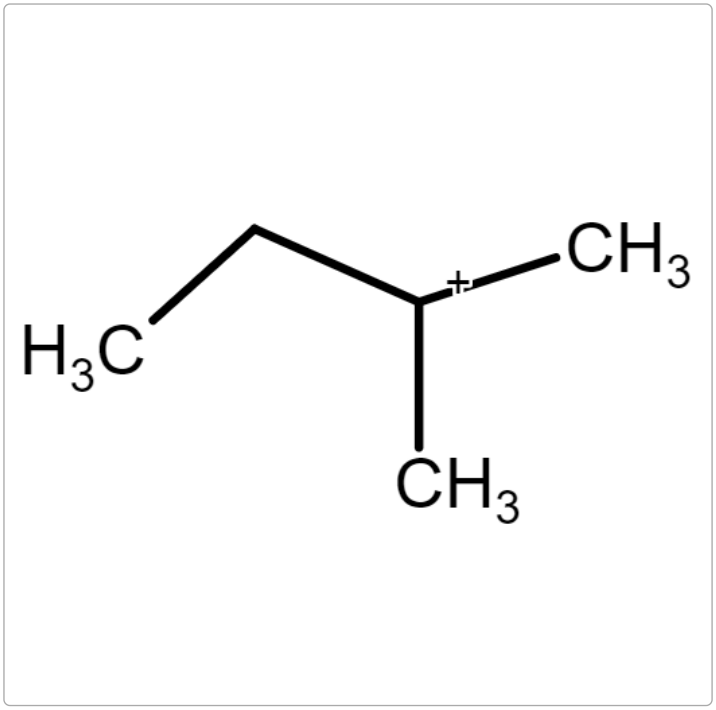


Correct

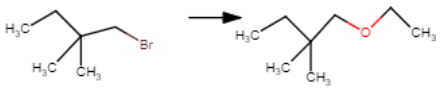
Well done. A hydride shifts from the 3° C to carbon-2, which contains the positive charge. The result is a 3° cation, which is lower in energy.

Alkyl Halides: Nucleophilic Substitution: Draw the rearranged cation of solvolysis of 1-bromo-2,2-dimethylbutane with ethanol that will eventually lead to the product

Part A

The solvolysis product of 1-bromo-2,2-dimethylbutane with ethanol initially forms the expected cation but does not give any of the expected 1-ethoxy-2,2-dimethylbutane. Draw the rearranged cation that will eventually lead to the product.

Interactive 3D display mode



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

ANSWER:

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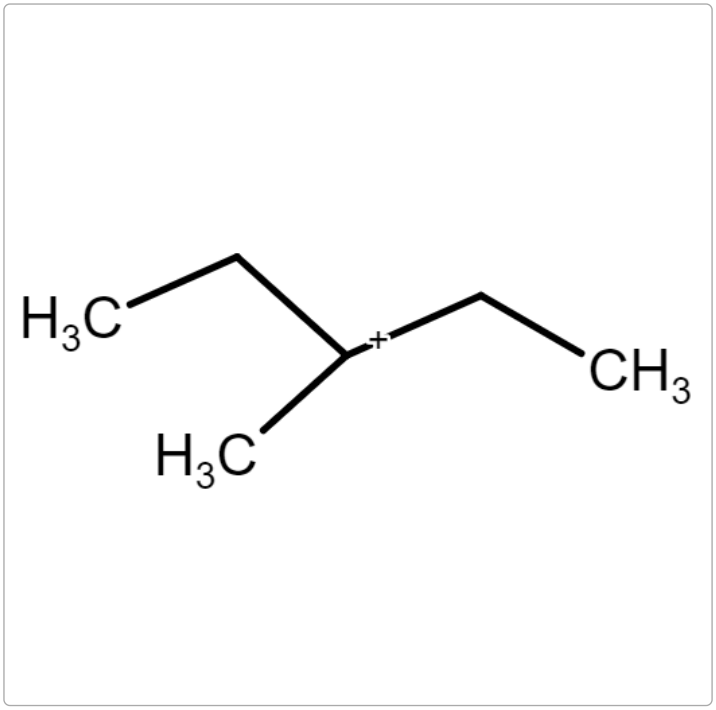


Correct

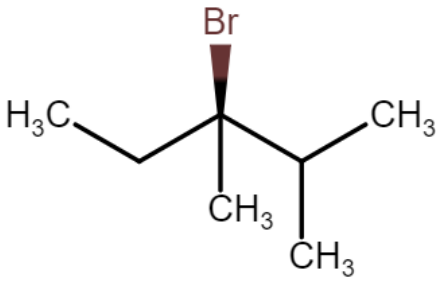
The initial formed cation is 1° and is high energy. A methide shifts from the 4° C to carbon-1, which contains the positive charge. The result is a 3° cation, which is much lower in energy.

Alkyl Halides: Reaction of (3S)-3-bromo-2,3-dimethylpentane with EtOH and heat

Part A

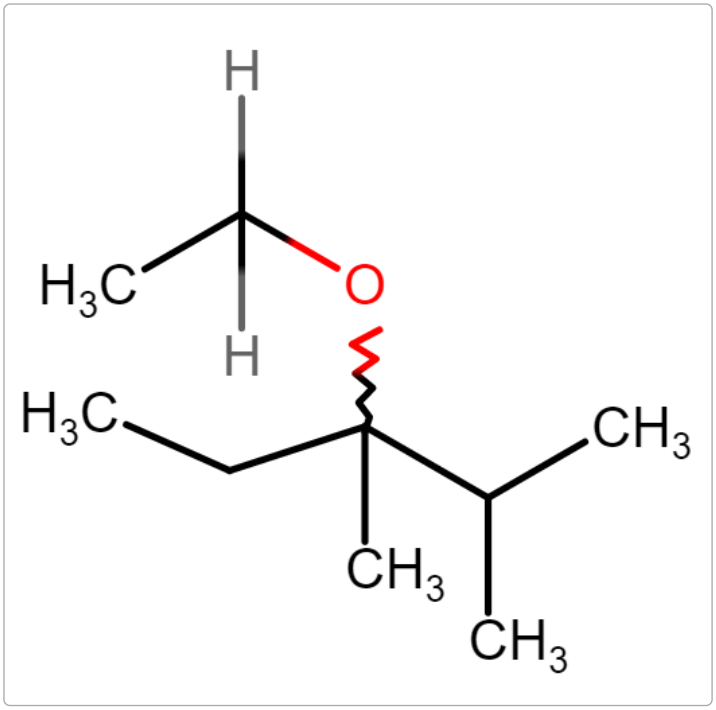
Draw the major product formed when the structure shown below undergoes substitution in CH_3CH_2OH with heat. (Use a wavy bond (Single Up or Down) if you need to indicate a mixture of configurations at a particular stereocenter.)

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. To change the bond type, select the Insert menu and change the Bond setting. Show the appropriate stereochemistry by choosing the dashed or wedged buttons and then clicking a bond on the canvas.

ANSWER:



Correct

A tertiary halide in an alcohol solvent in the absence of base will undergo substitution by the S_N1 mechanism ("stealth acidic" conditions). The electrophilic stereocenter racemizes.

Carbocations: Rank 1-bromo-3-methyl-2-butene, 2-bromo-2,3,3-trimethylbutane, and 2-bromo-2-methoxypropane by the ease with which they ionize

Part A

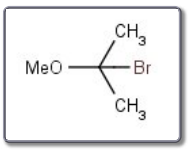
Rank the compounds by the ease with which they ionize under {\rm S_N1} conditions.

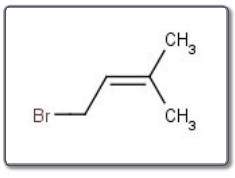
Rank the compounds from easiest to hardest. To rank items as equivalent, overlap them.

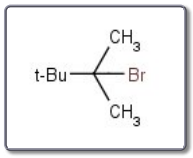
ANSWER:

Reset Help

easiest hardest







Correct

The carbocation stabilized by resonance with the \rm O atom's lone pair is lowest in energy, followed by the carbocation stabilized by resonance with the \rm C\!=\!C \pi bond.

Carbocations: Rank 2-fluoro-2-methylbutane, 2-chloro-2-methylbutane and 2-iodo-2-methylbutane by the ease with which they ionize

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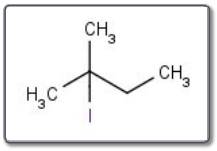
Rank the compounds by the ease with which they ionize under acidic conditions.

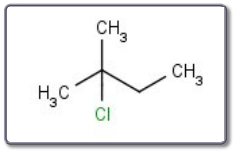
Rank the compounds from easiest to hardest. To rank items as equivalent, overlap them.

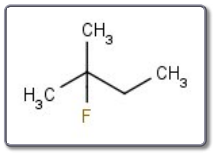
ANSWER:

Reset Help

easiest hardest







☐ The correct ranking cannot be determined.

Correct

The bigger the halogen, the worse its overlap with the \rm C(\it sp^{ 3}) orbital, and the better its leaving group ability.

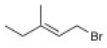
Chapter 6 Reading Quiz Question 7

Part A

Rank the following substrates in order of decreasing reactivity toward S_N1 substitution by solvolysis in ethanol solvent (list the most reactive substrate first).

A

B



C

D

Hint 1. Substrate reactivity

The reactivity of a substrate towards nucleophilic substitution depends upon the mechanism involved, which is influenced by the structure of the substrate (both the alkyl and leaving groups), as well as the nature of the nucleophile and the solvent. For S_N1 reactions, the stability of the intermediate carbocation is the primary concern. See 6-13.

ANSWER:

- ○ D > C > A > B
- ◉ C > A > B > D
- ○ A > B > C > D
- ○ C > B > D > A

Correct

Chapter 6 Reading Quiz Question 9

Part A

Consider the solvolysis of *tert*-butyl chloride in different solvents.

In which solvent is the solvolysis rate the greatest?

Hint 1. Solvent effect on solvolysis reactions

Solvolysis reactions are normally S_N1 reactions. What type of solvents are the most suitable for S_N1 reactions? See 6-13.

ANSWER:

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- 100% methanol
- 80% methanol in water
- 60% methanol in water
- 50% methanol in water

Correct

Problem 6-23

Choose the member of each pair that will react faster by the S_{\rm N}1 mechanism.

Part A

1-bromopropane or 2-bromopropane

ANSWER:

- 2-bromopropane
- 1-bromopropane

Correct

Part B

2-bromo-2-methylbutane or 2-bromo-3-methylbutane

ANSWER:

- 2-bromo-2-methylbutane
- 2-bromo-3-methylbutane

Correct

Part C

n-propyl-bromide or allyl bromide

ANSWER:

- allyl bromide
- *n*-propyl-bromide

Correct

Part D

1-bromo-2,2-dimethylpropane or 2-bromopropane

ANSWER:

- 1-bromo-2,2-dimethylpropane
- 2-bromopropane

Correct

Part E

2-iodo-2-methylbutane or *tert*-butyl chloride

ANSWER:

- 2-iodo-2-methylbutane
- *tert*-butyl chloride

Correct

Part F

2-bromo-2-methylbutane or ethyl iodide

ANSWER:

- ethyl iodide
- 2-bromo-2-methylbutane

Correct

Problem 6-24

3-Bromocyclohexene is a secondary halide, and benzyl bromide is a primary halide. Both halides undergo S_{\rm N}1 substitution about as fast as most tertiary halides.

3-bromocyclohexene benzyl bromide

Part A

Use resonance structures to explain this enhanced reactivity.

ANSWER:

- Ionization is the rate-determining step in S_{\rm N}2. Anything that destabilizes the carbocation intermediate will speed the reaction. Both of these compounds form resonance-stabilized intermediates.
- Ionization is the rate-determining step in S_{\rm N}1. Anything that stabilizes the carbocation intermediate will speed the reaction. Both of these compounds form resonance-stabilized intermediates.
- Ionization is the rate-determining step in S_{\rm N}1. Anything that destabilizes the carbocation intermediate will speed the reaction. Neither of these compounds form resonance-stabilized intermediates.
- Ionization is the rate-determining step in S_{\rm N}2. Anything that stabilizes the carbocation intermediate will speed the reaction. Neither of these compounds form resonance-stabilized intermediates.

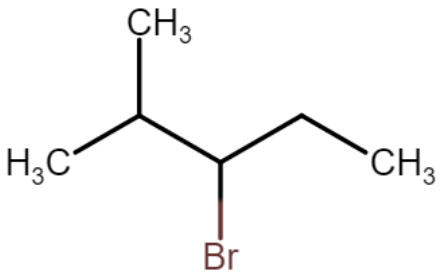
Correct

Alkyl Halides: Substitution reaction of 3-bromo-2-methylpentane and CH3OH

Part A

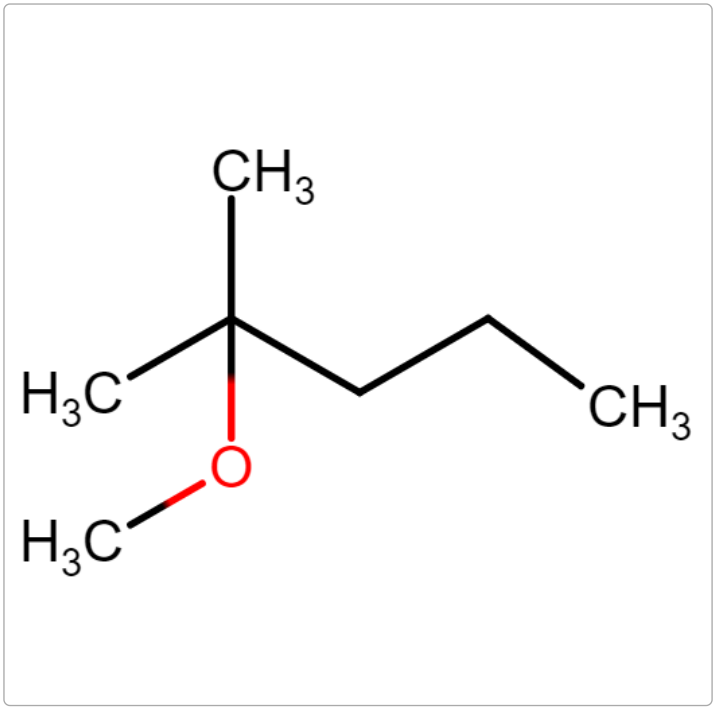
Draw the product formed when the structure shown below undergoes solvolysis in CH_3OH.

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:



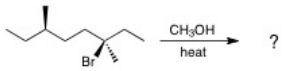
Correct

Under these "stealth acidic" conditions, S_N1 substitution occurs. The Br^- leaves to give a secondary carbocation, which undergoes a 1,2-hydride shift to give a lower-energy tertiary carbocation. CH_3OH then adds to give the ether.

Chapter 6 Reading Quiz Question 8

Part A

Which of the following best describes the product of the S_N1 reaction of (3*R*,6*R*)-3-bromo-3,6-dimethyloctane in methanol?



Hint 1. Stereochemistry of the SN1 reaction

S_N1 reactions involve the intermediacy of carbocations, which have a trigonal planar geometry at the C atom bearing the positive charge and can react with nucleophiles at either face of the trigonal plane. Be sure to understand the stereochemical consequences of this situation. See 6-14.

ANSWER:

- A mixture of enantiomers
- A single enantiomer
- A *meso* compound
- A mixture of diastereomers

Correct

Problem 6-25

Part A

Give the S_{\rm N}1 mechanism for the formation of 2-ethoxy-3-methylbutane, the unrearranged product in this reaction.

Edit the reaction by drawing all steps in the appropriate boxes and connecting them with reaction arrows. Add charges where needed. Electron flow arrows should start on an atom or a bond and should end on an atom, bond, or location where a new bond should be created.

ANSWER:

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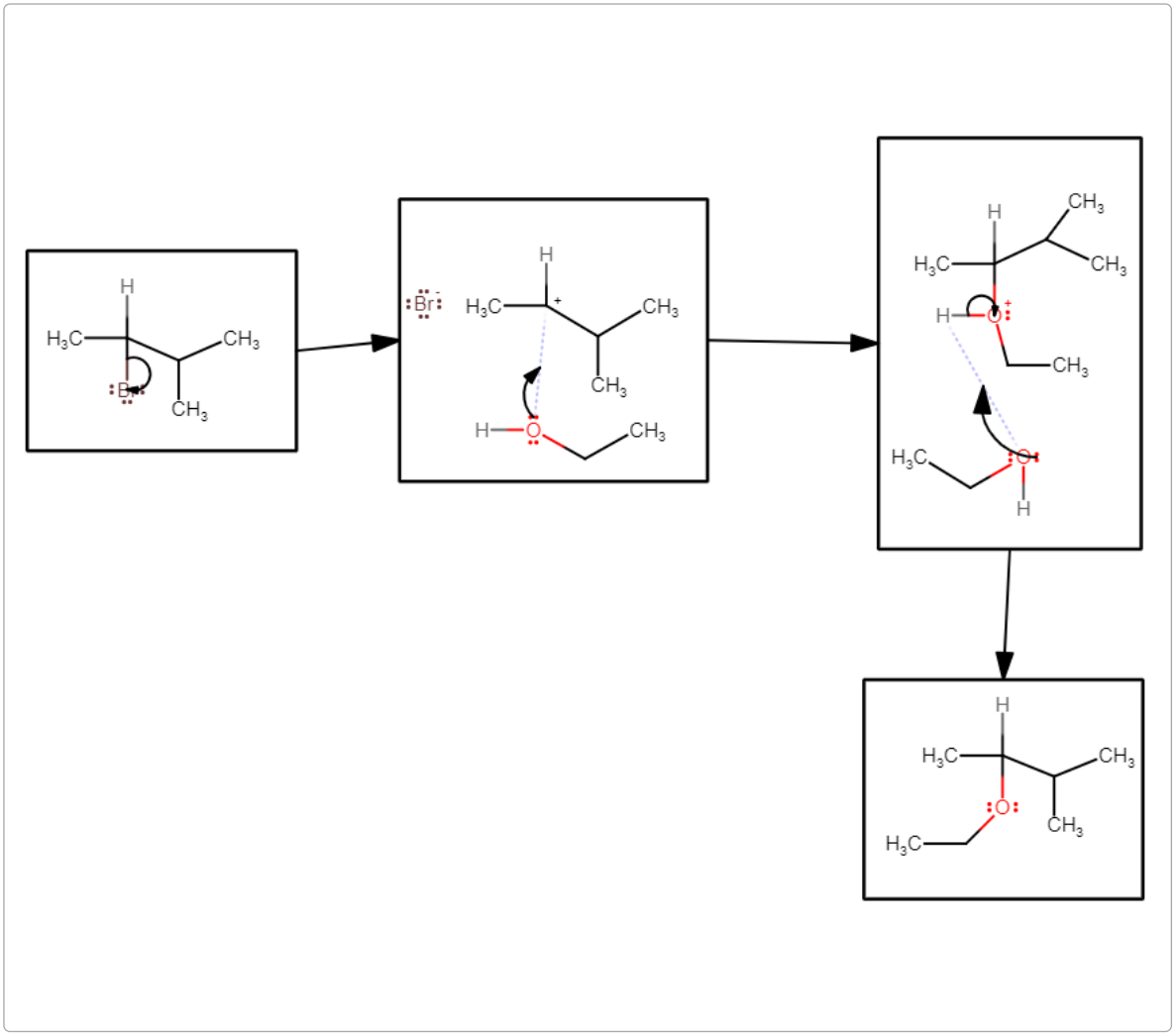
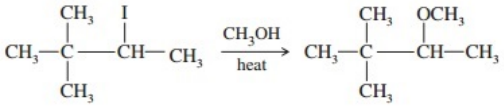


All attempts used; correct answer displayed

Problem 6-26 (a)

Propose a mechanism involving a hydride shift or an alkyl shift for each solvolysis reaction.

Part A



Edit the reaction by drawing all steps in the appropriate boxes and connecting them with reaction arrows. Add charges where needed. Electron flow arrows should start on an atom or a bond and should end on an atom, bond, or location where a new bond should be created.

ANSWER:

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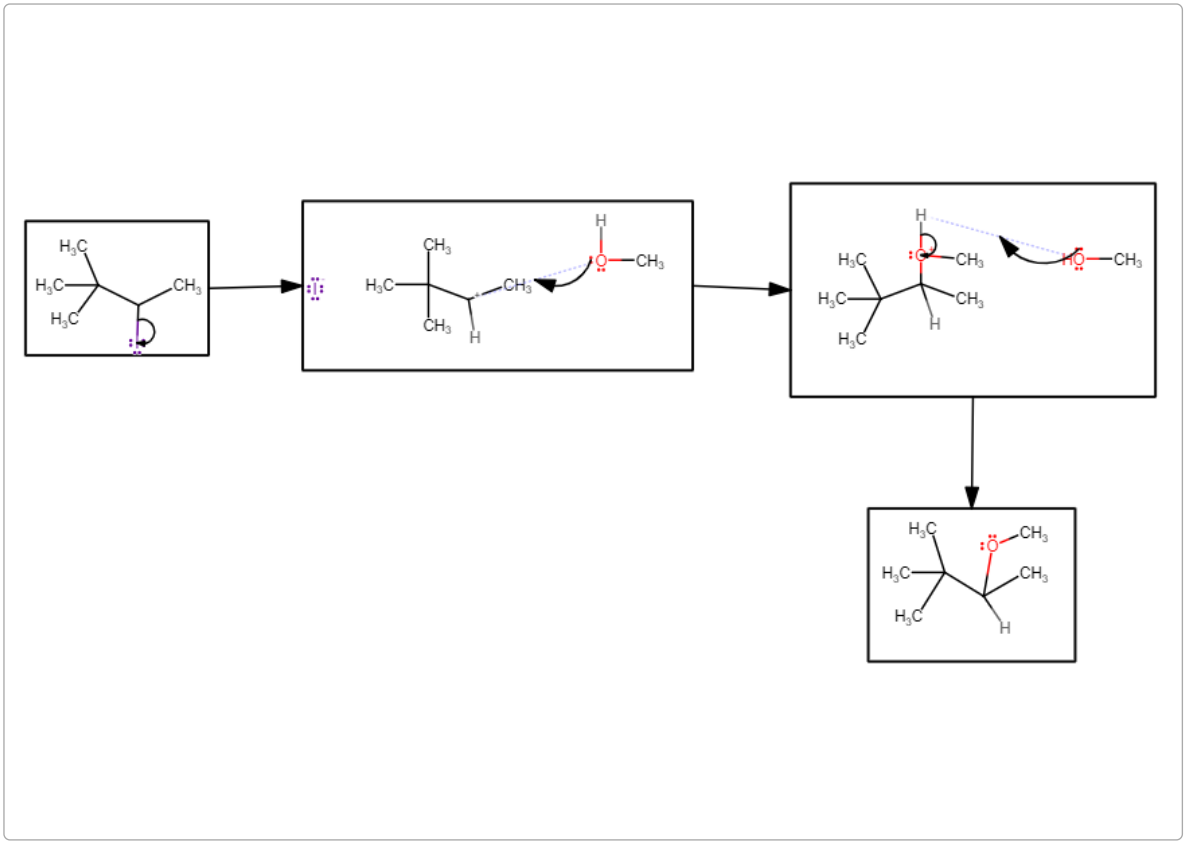
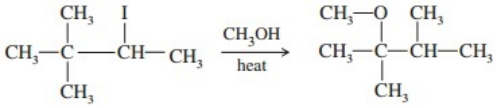


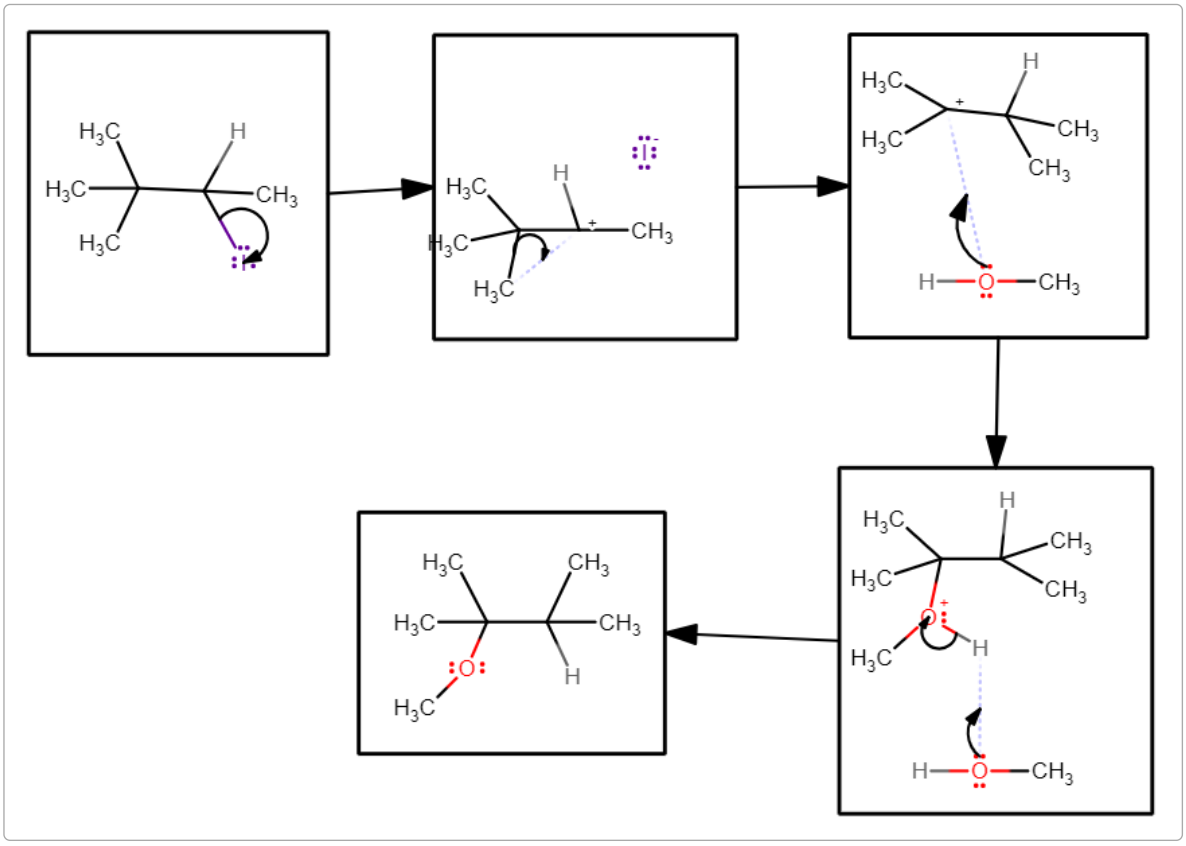
All attempts used; correct answer displayed

Part B



Edit the reaction by drawing all steps in the appropriate boxes and connecting them with reaction arrows. Add charges where needed. Electron flow arrows should start on an atom or a bond and should end on an atom, bond, or location where a new bond should be created.

ANSWER:



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Correct

Part C

Explain how each rearrangement forms a more stable intermediate.

ANSWER:

- Methyl shift to the 2^{\circ} carbocation forms a more stable 1^{\circ} carbocation.
- Methyl shift to the 1^{\circ} carbocation forms a more stable 3^{\circ} carbocation.
- Methyl shift to the 3^{\circ} carbocation forms a more stable 2^{\circ} carbocation.
- Methyl shift to the 2^{\circ} carbocation forms a more stable 3^{\circ} carbocation.

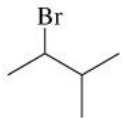
Correct

Problem 6-40 (c-d) - Enhanced - with Feedback

You may want to reference (Page) Section 6.15 while completing this problem.

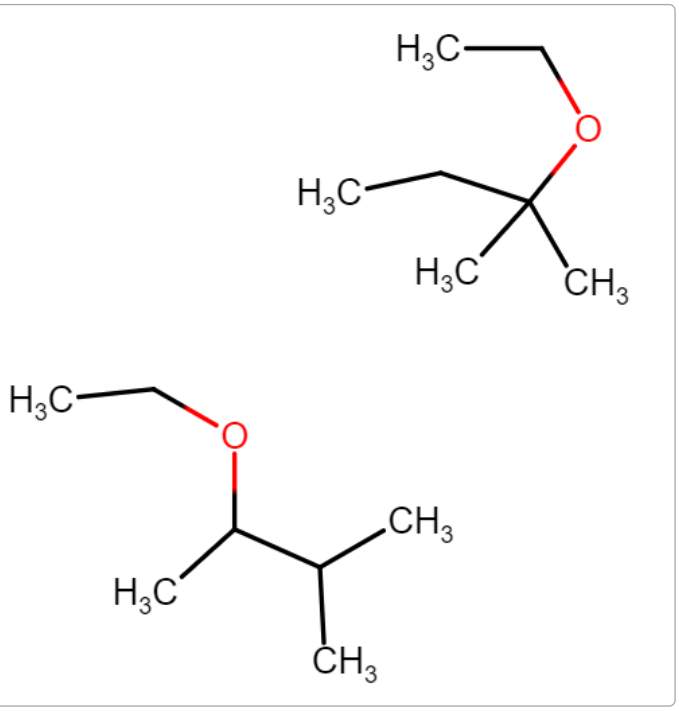
Part A

Give the solvolysis \rm (S_N1) products expected when the following compound is heated in ethanol:



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

ANSWER:



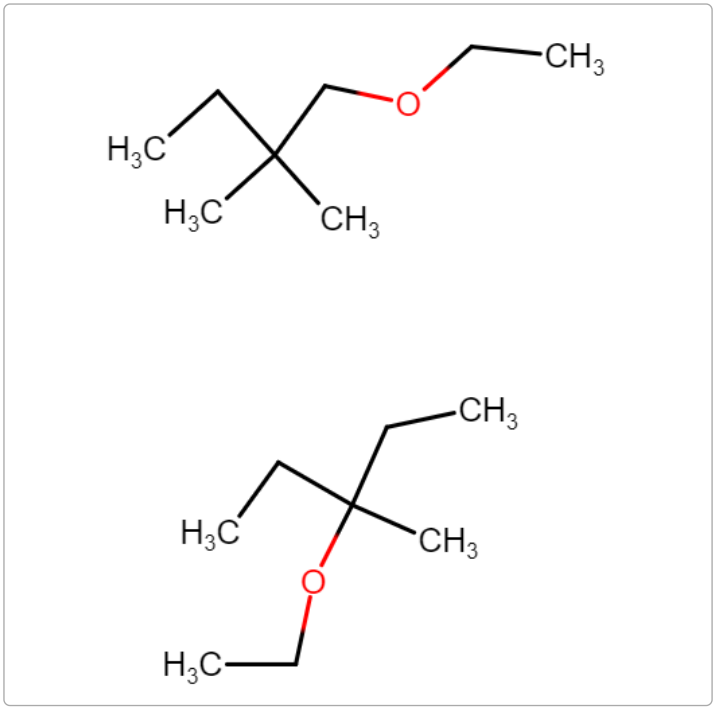
Correct

Since this is an \rm S_N1 reaction, there is a possibility of two products: the predicted nonrearranged product and the rearranged product resulting from a hydride shift to form a more stable carbocation intermediate.

Part B

Give the solvolysis \rm (S_N1) products expected when the following compound is heated in ethanol:

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



Correct

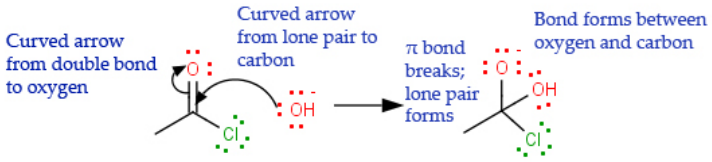
Since this is an \rm S_N1 reaction, there is a possibility of two products: the predicted nonrearranged product and the rearranged product resulting from a methyl shift to form a more stable carbocation intermediate.

An Exercise in Drawing Curved Arrows: Interpreting Electron Movement

Learning Goal:

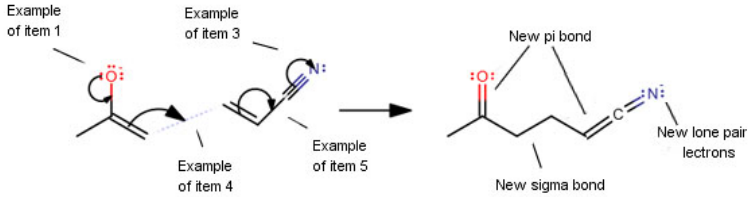
To understand and be able to interpret reaction arrows to predict products using reaction mechanisms, and then determine which curved arrows in a given mechanism are inaccurate.

Curved reaction arrows can be thought of as a set of instructions that dictate the structures that the reactants are turning into. The drawing of a curved electron flow arrow with two barbs on the arrowhead indicates that two electrons are flowing. A curved arrow drawn from a lone pair of electrons on one atom to a second atom or to the space between two atoms means that a bond will form between those two atoms. This bond will be present in the products. The drawing of an electron arrow from a double bond to an atom or to the space between two atoms means that the double bond will break and one of the two atoms of the double bond will now be bonded to that atom. This new bond will be present in the products and the \pi bond of the original double bond will be absent in the products. Alternatively, the curved arrow from a \texttip{\pi }{pi} bond may end on an atom participating in that bond, indicating the breaking of the \texttip{\pi }{pi} bond and the formation of a lone pair of electrons.



Several bond making and bond breaking scenarios are shown below using lone pairs and various types of bonds. One thing to keep in mind when using these guidelines is that the atoms carbon, oxygen, and nitrogen like to maintain complete octets of electrons. If an atom has an octet of electrons and a curved electron arrow points to that atom then that atom will have to lose two electrons to accommodate the two electrons being brought in by the curved electron arrow. The loss of the two electrons will itself be represented by a new curved electron arrow. Curved arrows will not originate on atoms with incomplete octets of electrons.

1. For two atoms that are already bonded, a curved electron arrow from a lone pair of electrons on one atom to a position between the two atoms will create a new \texttip{\pi }{pi} bond.
2. For two atoms that are not already bonded, a curved electron arrow from a lone pair of electrons on one atom to the second atom will create a new \sigma bond between those atoms.
3. A curved electron arrow from a bond to one of the two atoms of that bond means that a lone pair of electrons will reside on the atom indicated by the arrowheard.
4. A curved electron arrow from a bond to an atom that does not participate in the bond means that a new bond will form between one of the two atoms of original bond and the second atom. In Mastering, you should see a dotted line connecting the atoms forming a new bond
5. A curved electron arrow from a bond to a position between two adjacent atoms means that a bond will form between those two atoms and the electrons of the original bond will be used to make the new bond.
6. In general a two barbed arrowhead drawn to anything else (i.e. any atom or a position between two atoms) will result in either a new bond or a new lone pair of electrons.
7. In all cases, a curved electron arrow drawn from a bond to anything else (i.e. an atom of that bond, a second atom, or a position between two atoms) means that the source bond will break.



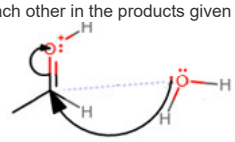
Part A

Use the curved electron flow arrows to determine where electrons move from and move to in the reaction shown. Then, draw the structure of the product based on those electron

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

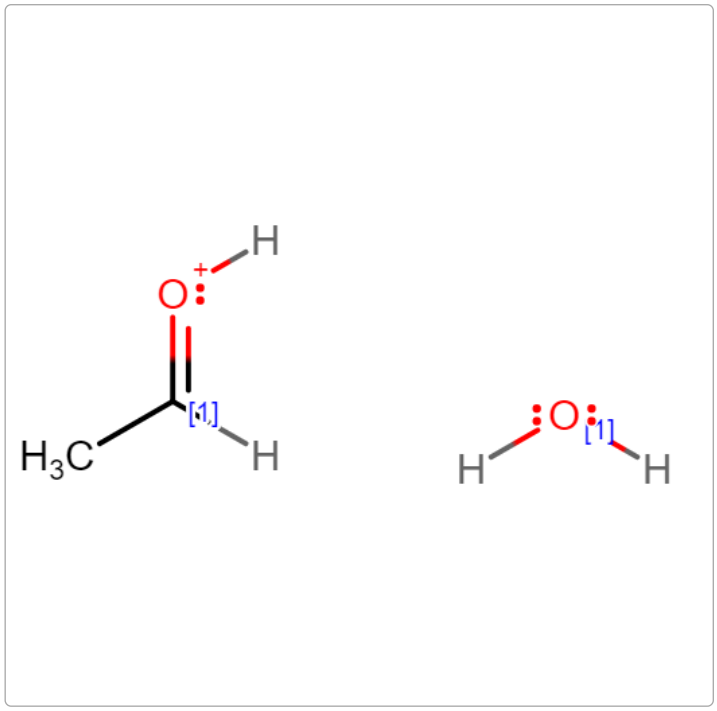
Hint 1. Identify the bond to be formed

Select the two atoms in the reactants that will be covalently bonded to each other in the products given the curved arrows shown.



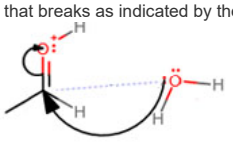
Identify the appropriate group of atoms by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-click.) Then, clear the check mark to enable the Map field before entering a value.

ANSWER:



Hint 2. Identify the bond to be broken

Select the two atoms in the reactants that participate in the covalent bond that breaks as indicated by the curved electron arrows.



Identify the appropriate bond by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms of the bond are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-click.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to identify a bond that breaks

A curved electron arrow leading away from a bond indicates that that bond will break. This bond will not be present in the products. Remember a double bond is made up of a \sigma and \pi bond, and the \pi bond can be broken leaving the \sigma bond intact.

ANSWER:

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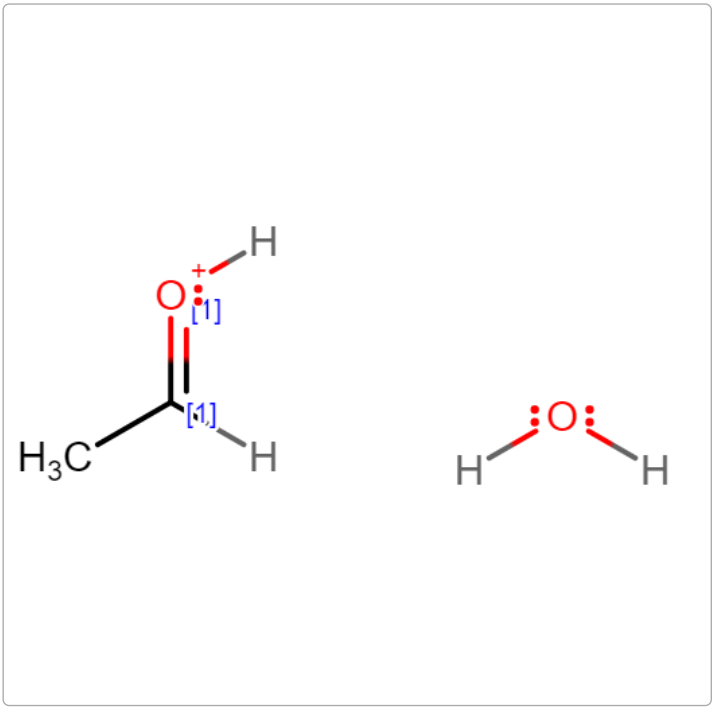
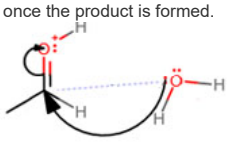


Hint 3. Identify the location of a new lone pair of electrons

Select the atom in the reactants that will host a new lone pair of electrons once the product is formed.

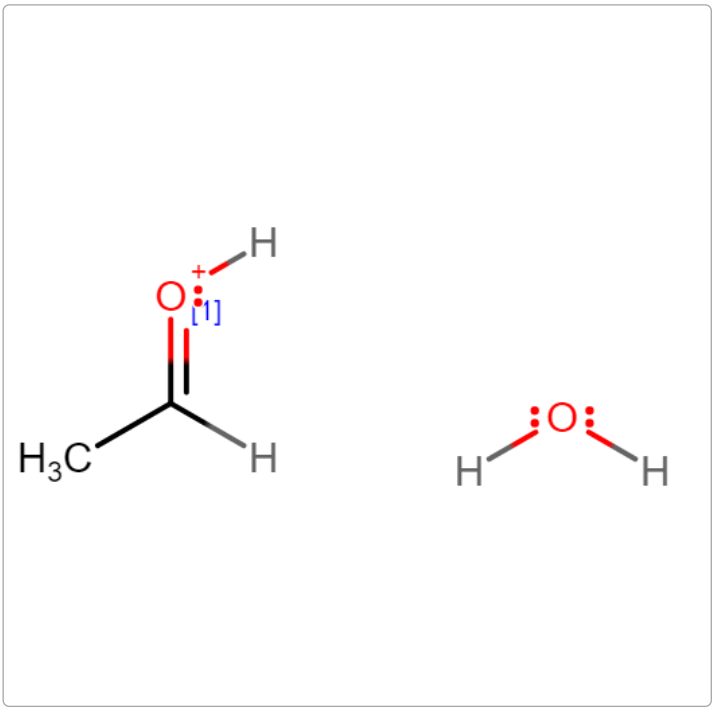


Identify the location of the new lone pair of electrons by selecting the atom and assigning it a map number of 1. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to identify a bond that will form as the result of breaking another bond

An electron arrow drawn from a bond to a specific atom that participated in that bond indicates that a new lone pair of electrons will form on that atom. Look for the start of a curved electron arrow on a bond and pointing to one of the two atoms of that bond. Remember a double bond is composed of a strong \texttip{\sigma }{sigma} bond, and a weak \pi bond. The weak \pi bond is often a starting point for curved arrows. When a \texttip{\pi }{pi} bond in broken the \texttip{\sigma }{sigma} bond will remains intact.

ANSWER:



ANSWER:

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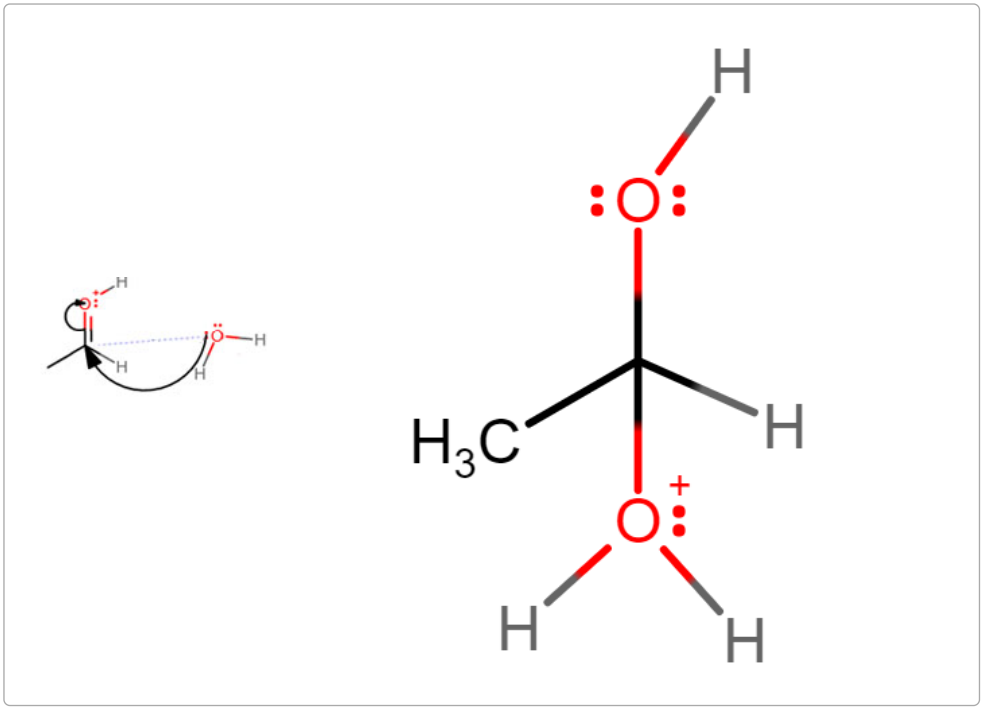


Correct

The curved electron arrows will tell you where bonds will form and which bonds will break. The arrows will start at the location where the electrons originate, and end at the location where the electrons will eventually reside. After interpreting the arrows, you can check your answer by making sure that both sides of the reaction arrow have the same number of atoms and electrons, and that the total electrical charge is the same on both sides of the reaction arrow.

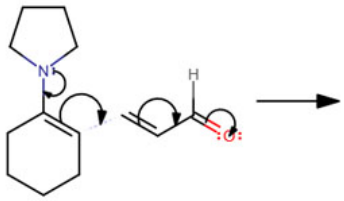
Part B

Use the curved electron flow arrows to determine where electrons move from and move to in the reaction shown. Then, draw the structure of the product based on those electron flow arrows.

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

Hint 1. Identify multiple new bonds to be formed

Three new bonds will form. Select the six atoms, two atoms for each bond, which will be involved in the formation of these new covalent bonds.



Identify the appropriate group of atoms by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

ANSWER:

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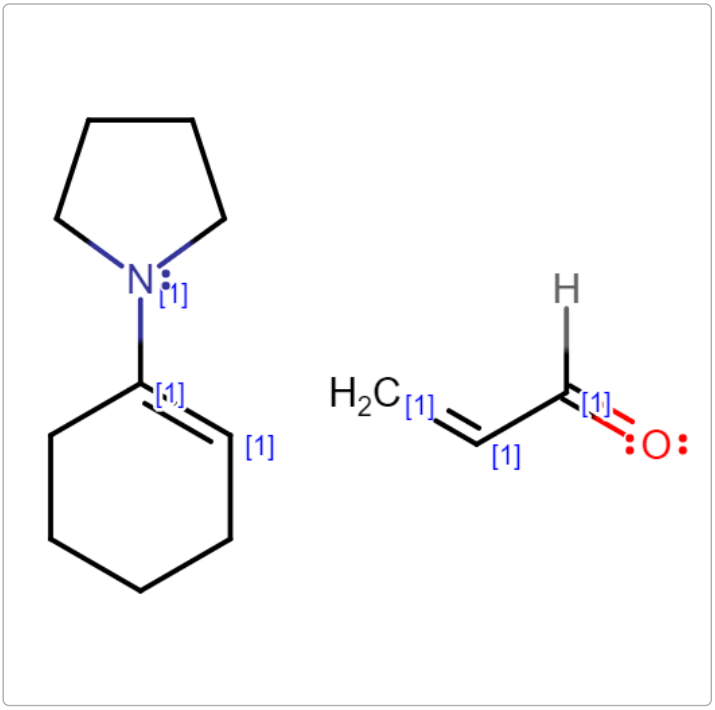
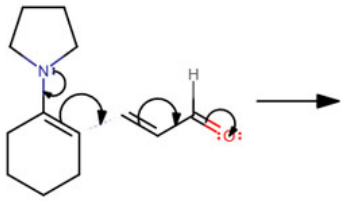


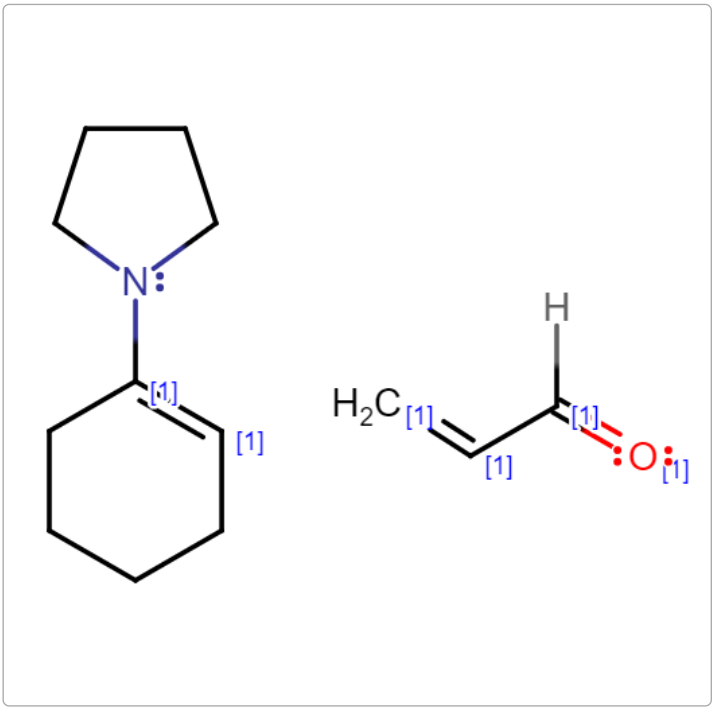
Hint 2. Identify multiple bonds to be broken

Three covalent bonds break during the reaction. Select the six atoms, two for each bond, that participate in covalent bonds in the reactants that will break according to the curved electron arrows.



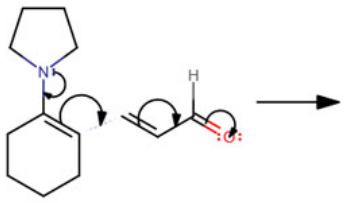
Identify the appropriate group of atoms by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

ANSWER:

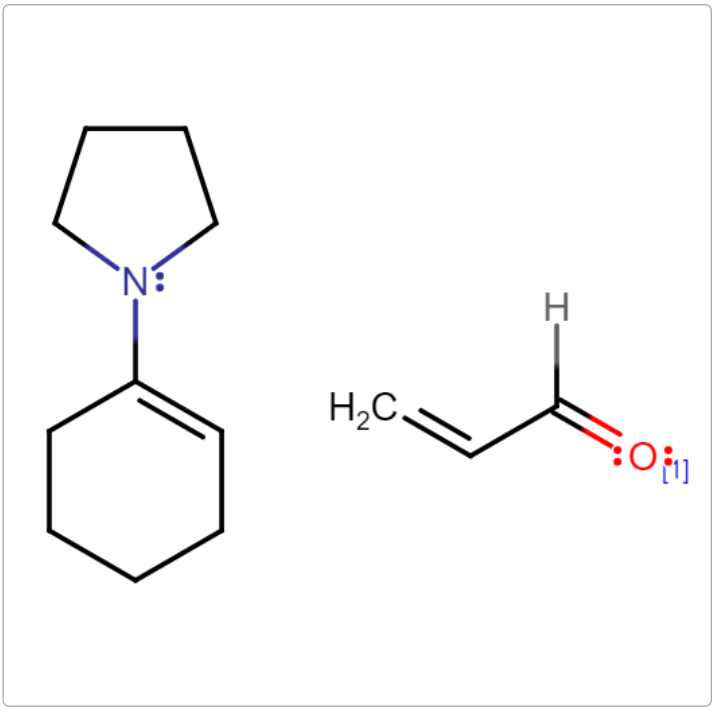


Hint 3. Identify the locations of new lone pairs of electrons in a complex system

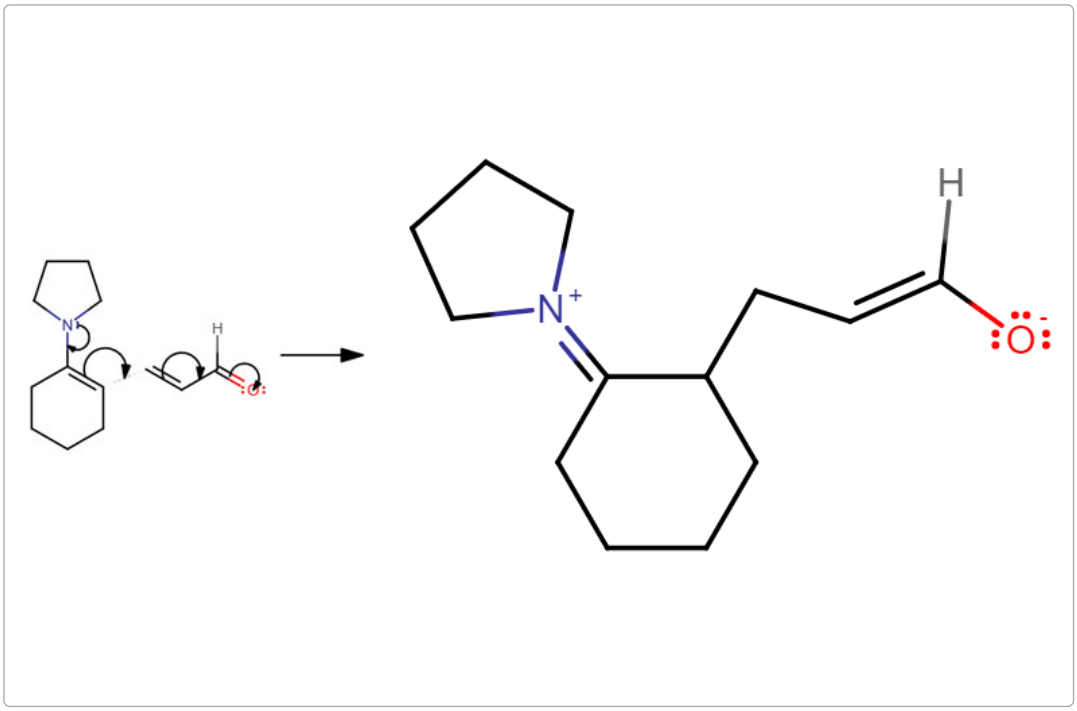
Indicate which atom or atoms in the reactants will have a new lone pair of electrons associated with it in the product structure.



ANSWER:



ANSWER:



Correct

The curved electron arrows will tell you where bonds will form and which bonds will break. The number of curved arrows is unimportant. Start at the beginning of the first electron arrow in the 'train' of electron arrows. The head of the first electron arrow on a bond or an atom then 'forces' the next arrow which in turn forces the next and so on. Atoms such as carbon, oxygen, and nitrogen prefer to have complete octets of electrons. If a curved arrow brings to electrons to an atom with a complete octet then two electrons will have to move away from that atom. This movement away is represented with a second curved arrow.

Part C

Below is a three step mechanism for the reaction of acetophenone with benzaldehyde to produce the alpha-hydroxy ketone product under basic conditions. Mechanisms differ from reaction equations by introducing reagents at the step in the mechanism in which that reagent undergoes a change and not at the beginning as with reaction equations. *All of the* Loading Web-Font TeX/Main/Italic ome of the electron arrows are incorrect.

Mark with the green check to indicate that the given direction of electron flow in the following set of molecules using curved arrows notation is correct and with the red X label to indicate when incorrect.

Drag the appropriate items onto their respective targets.

Hint 1. Identify erroneous curved arrows

Shown below are two examples of curved arrow mistakes. Curved electron flow arrows can be thought of as instructions relating how many electrons to bring to a specific atom or how many electrons to take way from a specific atom.

Indicate how many electrons will be on the atom of interest based on the curved electrons flow arrows.

Drag the appropriate items onto their respective targets.

ANSWER:

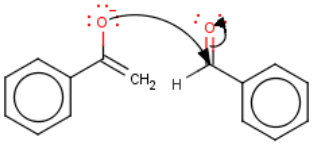
Reset Help

4 electrons
6 electrons
8 electrons
10 electrons

10 electrons
6 electrons

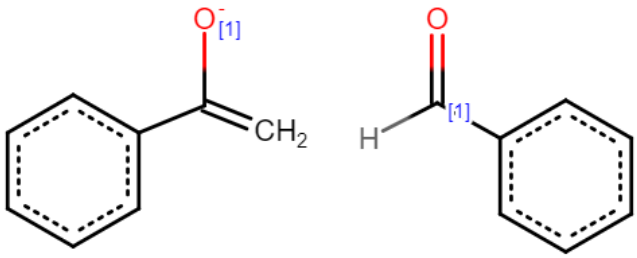
Hint 2. Identify a new bond from erroneous curved arrows

The second step of the presented mechanism is shown below. Assuming the electron arrows are correct, select the two atoms that will be covalently bonded to each other in the products that are not bonded to each other in the reactants.



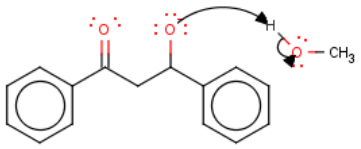
Identify the appropriate group of atoms by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

ANSWER:



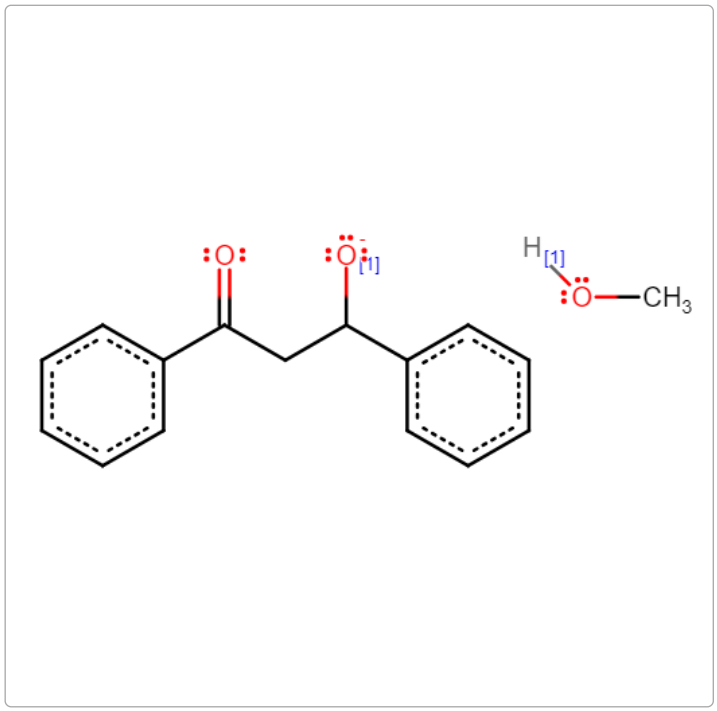
Loading Web-Font TeX/Main/Italic bond from the correct curved arrows

The third step of the presented mechanism is shown below. Assuming the electron arrows are correct, select the two atoms in the reactants that will be covalently bonded to each other in the products



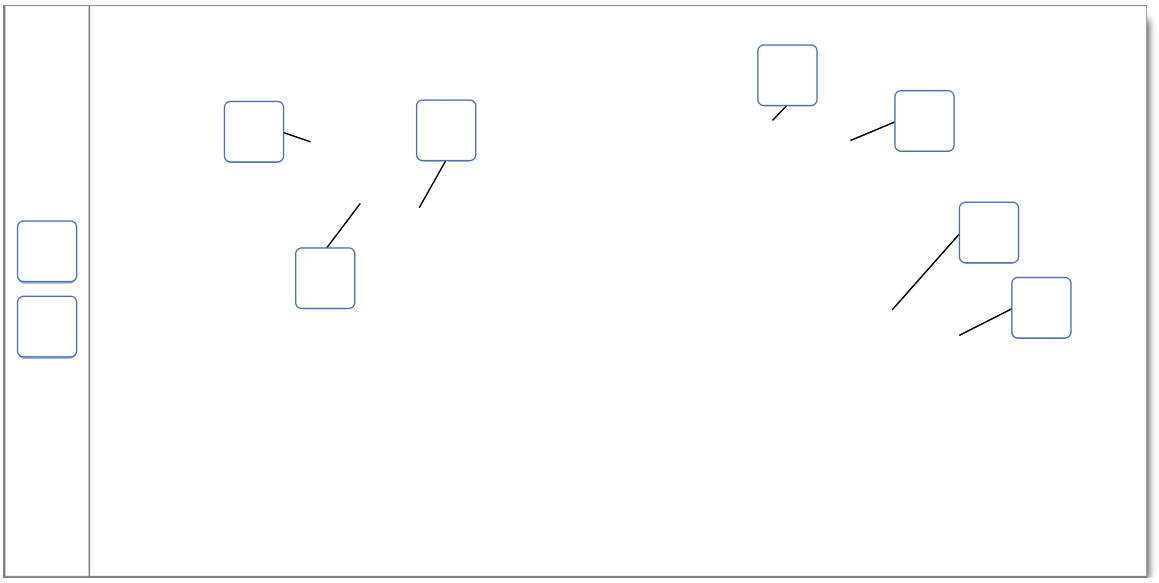
Identify the two atoms by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

ANSWER:



ANSWER:

Reset Help



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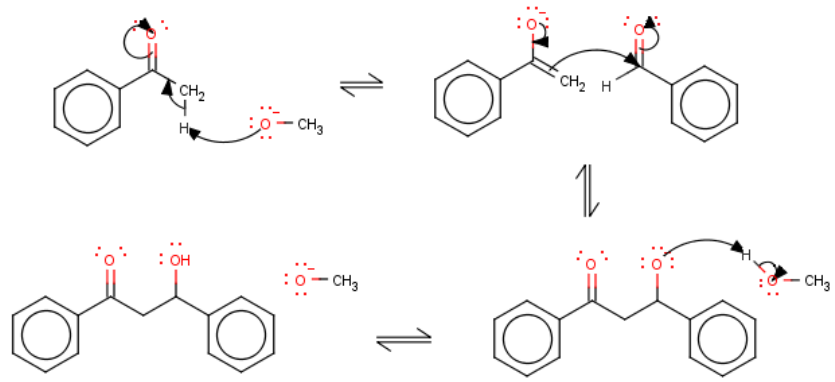
Correct

The presentation of curved arrows in a mechanism gives much more information about the system than knowing the structures of the intermediates. The intermediates in a mechanism tell you what was formed and curved arrows tell you how it was formed. The correct mechanism for the reaction is given below. See if you can follow the curved arrows leading one structure into the next.



An Exercise in Drawing Curved Arrows: Pushing Electrons

Learning Goal:

To understand and be able to use reaction arrows to explain organic reactions and reaction mechanisms.

Chemists use chemical reactions to keep track of the number and kind of reactants and the number and kinds of products produced in a chemical system. Stoichiometric coefficients are used to indicate the number of each species and structures are used to represent the kinds of reactants and products. Sometimes additional information is provided in the form of 'curved' arrows, also called electron arrows. These arrows provide information about the electrons in the system. These curved arrows indicate which covalent bonds will break and which covalent bonds and lone pairs of electrons will form during the reaction. The tail of an electron arrow is placed on either a bond or a lone pair of electrons in one of the reagents. The head of the arrow points to an atom to which a new covalent bond will form, or to which a lone pair of electrons will form. It may also point between two atoms forming a bond. The atom to which the head of an electron arrow points may be in the same reagent in which the electron arrow originated or it may be in a second reagent. If the atom to which the head of the arrow points already has a complete octet of electrons, then electrons will need to be shown migrate away for that atom. A second electron arrow will be needed to keep track of the electrons migrating away from that atom.

The electron arrow notation system is used as a book keeping system to keep track of electrons. A 'full-headed' or 'two-headed' arrow represents two electrons. A 'half-headed' of 'fish-hook' arrow represents one electron. The direction of the arrow does not necessarily correspond with the real motion of the electrons during the reaction but in many cases it does. The use of the curved arrow is strictly reserved for electrons, never atoms. While in a chemical system an atom "A" may move towards the electrons of atom "B" in the electron arrow notation system the electrons of atom "B" will be shown to move to atom "A". This rule has been universally accepted. Electron arrows never indicate the motion of atoms. Keeping track of the electrons leads to better understanding of a reaction's mechanism and gives a more complete description of how the reactant(s) are turned into product.

Guidelines for drawing curved arrows:

1. A full-headed arrow represents two electrons
2. The tail of the arrow is placed on either a lone pair of electrons or a covalent bond.
3. If an electron arrow starts on a bond, that bond will break during the reaction.
4. The head of the arrow will point to an atom or between two atoms. When pointing to an atom, a new bond will form to that atom or a lone pair of electrons will form on that atom. When pointing between two atoms, a new bond will form between the atoms.
    1. If that atom already has a complete octet of electrons then two electrons will need to be shown migrating away from that atom. A second arrow will be needed.

Part A

Use curved arrows to keep track of the electrons shown in the following reaction.

1-iodomethylcyclohexane \rightarrow tertiary cation + iodide anion

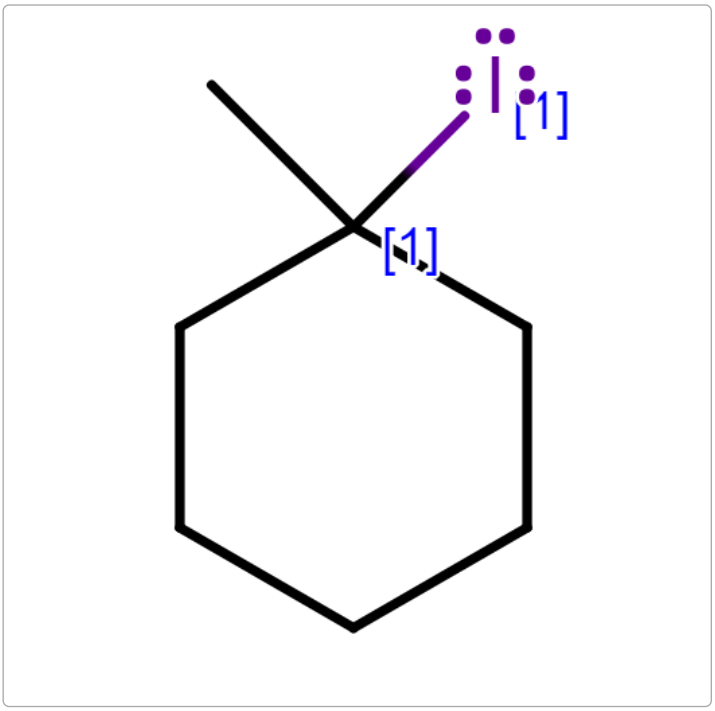
Edit the reaction by drawing all steps in the appropriate boxes and connecting them with reaction arrows. Add charges where needed. Electron flow arrows should start on an atom or a bond and should end on an atom, bond, or location where a new bond should be created.

Hint 1. Determine which bond will break

Select the two atoms in the starting material that compose the bond that will break during the reaction.

Identify the appropriate bond(s) by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms of the bond are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

ANSWER:



Hint 2. Determine which atom will receive the electrons

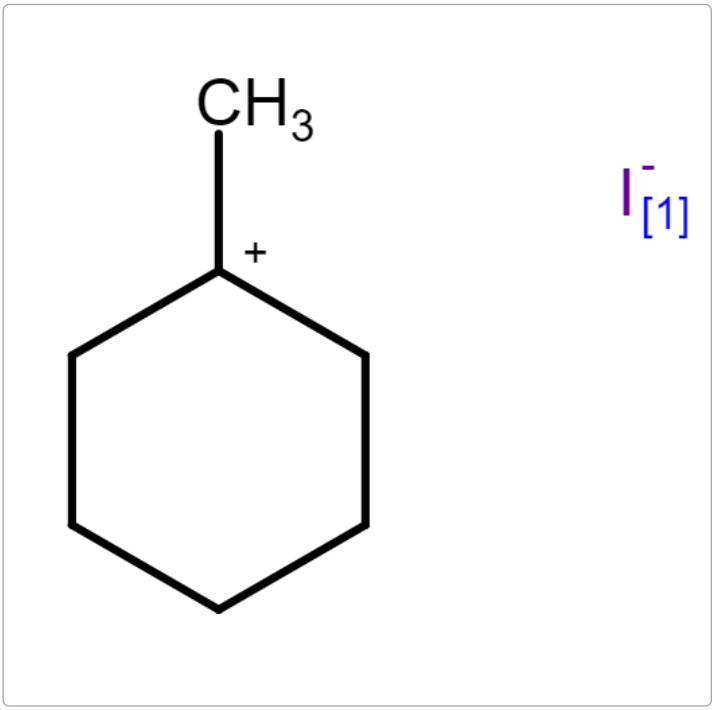
Select the atom or ion in the products that will be the final location of the electrons from the broken bond.

Identify the final location of the electrons by selecting the atom and assigning it a map number of 1. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to determine where the electrons go

Start by comparing the reactants and the products. You will notice that the products contain one less \texttip{\sigma }{sigma} bond (a single bond in this reaction) compared to the reactants. These electrons had to move to an atom, or between two atoms to form another bond. To determine where the electrons from this bond went, look for areas in the product that have a negative charge, or that have a new bond.

ANSWER:



ANSWER:

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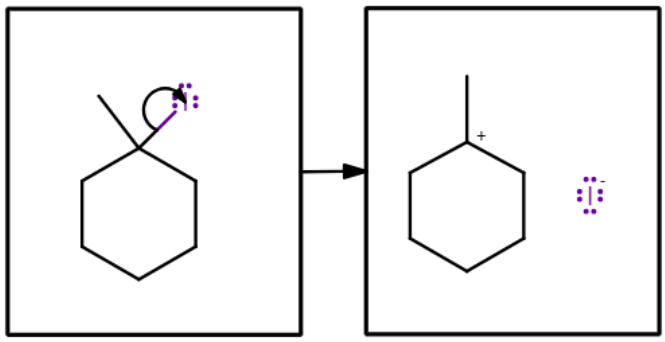
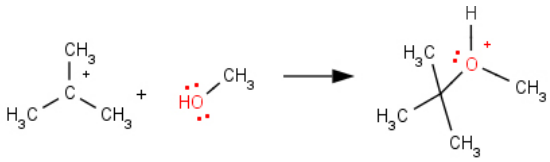


Correct

An electron arrow can be thought of a set of instructions. The tail of the arrow indicates which bond is to be broken to obtain two electrons and the head of the arrow dictates to which atom the two electrons are to go. Remember that when a bond is broken the formal charges on the atoms that made up the bond will change.

Part B

Use curved arrows on the reactant side to keep track of the electrons used to form the new covalent bond shown on the product side.



Edit the reaction by drawing all steps in the appropriate boxes and connecting them with reaction arrows. Add charges where needed. Electron flow arrows should start on an atom or a bond and should end on an atom, bond, or location where a new bond should be created.

Hint 1. Determine which bond will form

Select the two atoms which form a new covalent bond in the product.

Identify the two atoms by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to determine which atoms will form new bonds

The bond that forms will not be present on the reactant side because it hasn't come into existence yet. Look for connectivity between two atoms on the product side that is absent on the reactant side.

ANSWER:

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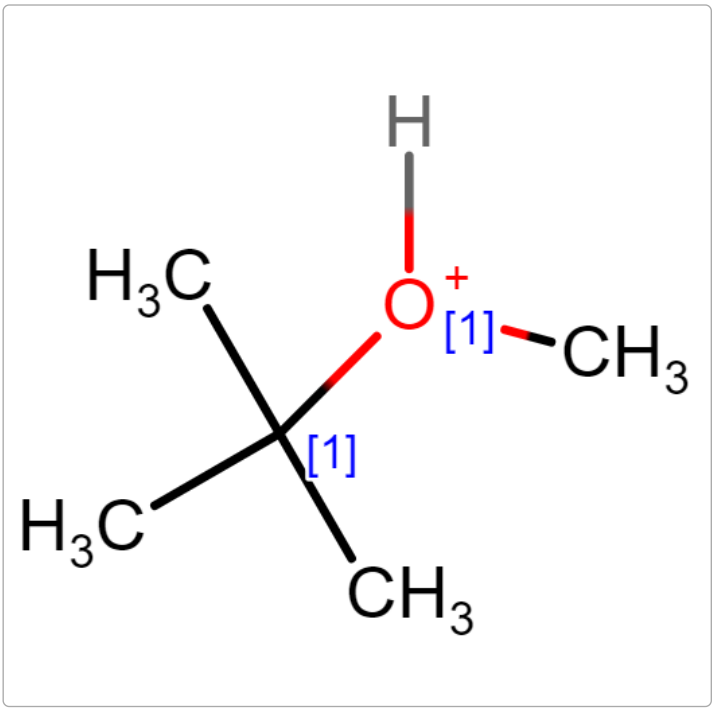


Hint 2. Determine which atom the bonding electrons came from

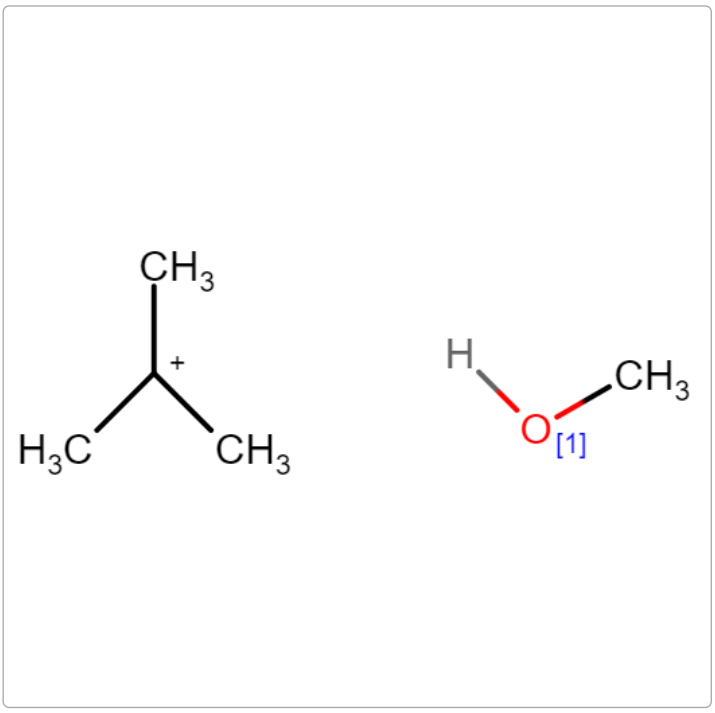
Select the atom that contributed the two electrons to the new carbon-oxygen bond shown on the product side.

Identify the atom by selecting the atom and assigning it a map number of 1. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to determine where the electrons came from

Start by looking for lone pairs of electrons or for bonds that may break. Areas of higher electron density can be sources of electrons. Then look to see if atoms associated with the lone pair or bond participate in the new carbon-oxygen bond in the products.

ANSWER:



ANSWER:

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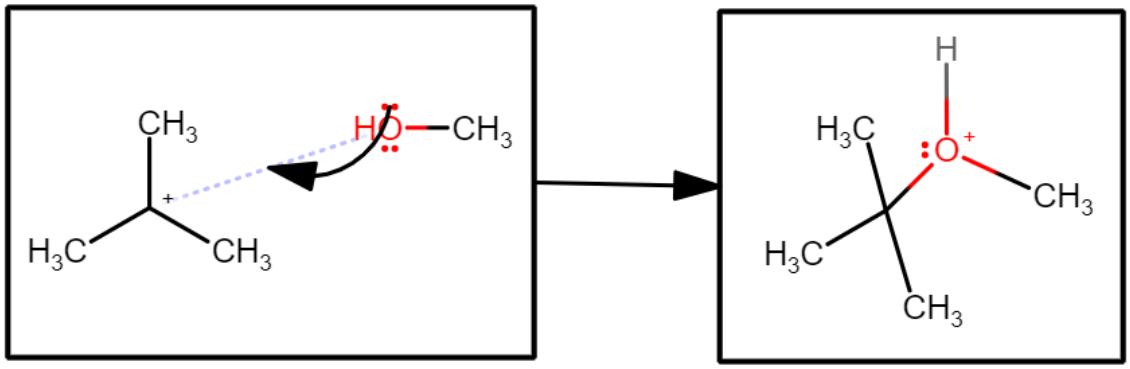
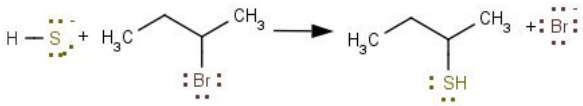


Correct

An electron arrow can be thought of a set of instructions. In this reaction, the tail of the arrow indicates which electrons from a specific atom are to be used in the formation of a new covalent bond. When these electrons come from a lone pair of electrons of an atom, that atom will be a part of the newly formed covalent bond. The head of the arrow will point to an atom that will be a part of the new bond, or between two atoms that will form the new bond.

Part C

Use curved arrows to keep track of the electron flow between the reactants and the products.



Edit the reaction by drawing all steps in the appropriate boxes and connecting them with reaction arrows. Add charges where needed. Electron flow arrows should start on an atom or a bond and should end on an atom, bond, or location where a new bond should be created.

Hint 1. Determine which bond will form

Select the two atoms in the product that are now covalently bonded to each other which were not bonded together in the reactants.

Identify the appropriate bond(s) by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms of the bond are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to determine which atoms will form a new bond

The bond that forms will not be present on the reactant side because it hasn't come into existence yet. Look for connectivity between two atoms on the product side that is absent on the reactant side.

ANSWER:

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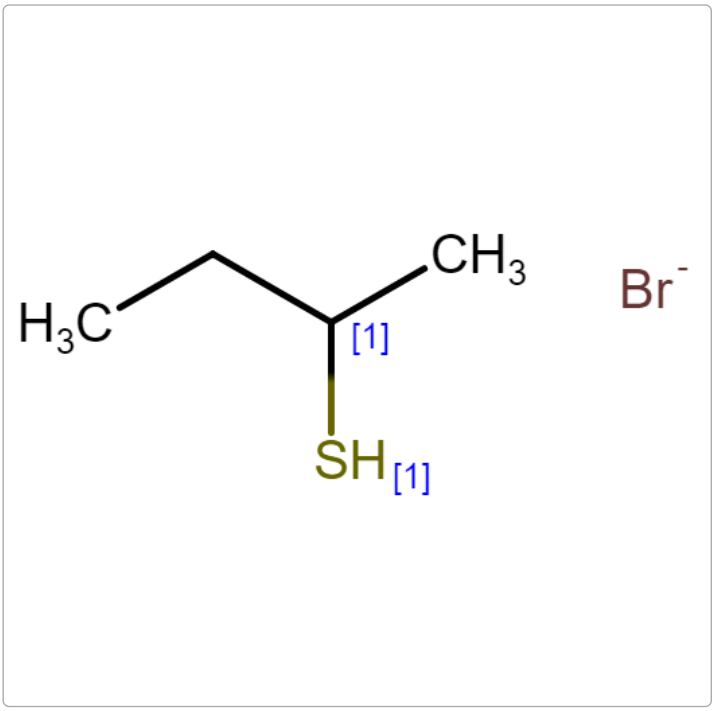


Hint 2. Determine which atom provides the electron for the new bond

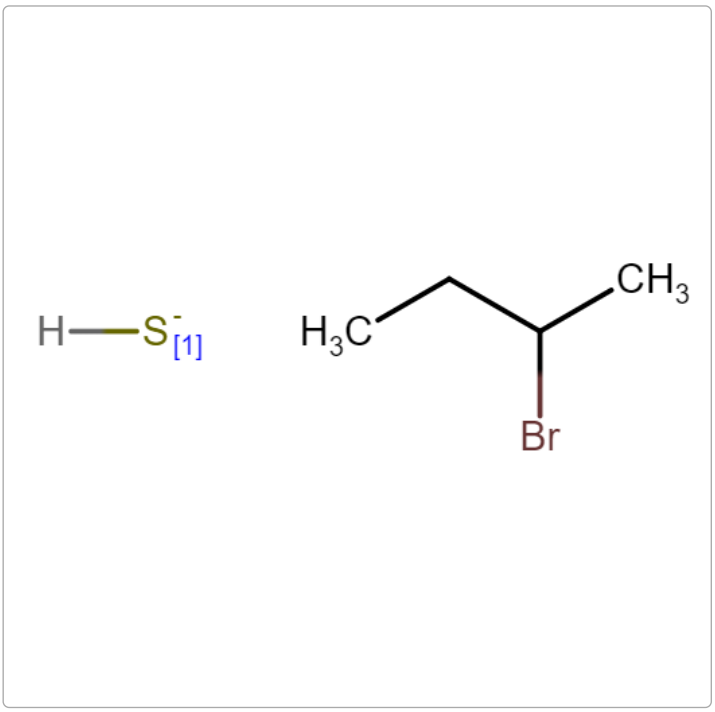
Indicate the source of the two electrons that make up the carbon-sulfur bond shown on the product side of the reaction equation by selecting a single atom, or by selecting a pair of atoms that make up a bond.

Identify the appropriate atom(s) by selecting each atom and assigning it a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. Where the electrons that are used to make bonds come from

Electrons used to make new bonds come from either lone pairs of electrons or from bonds that break. An electron arrow should start on one of these. You can determine which atom contributed the electrons by starting with the new bond. One of the two atoms in this new bond contributed the electrons. Next, determine which atom in this bond had lone pairs of electrons to contribute.

ANSWER:



Hint 3. Determine which bond will break

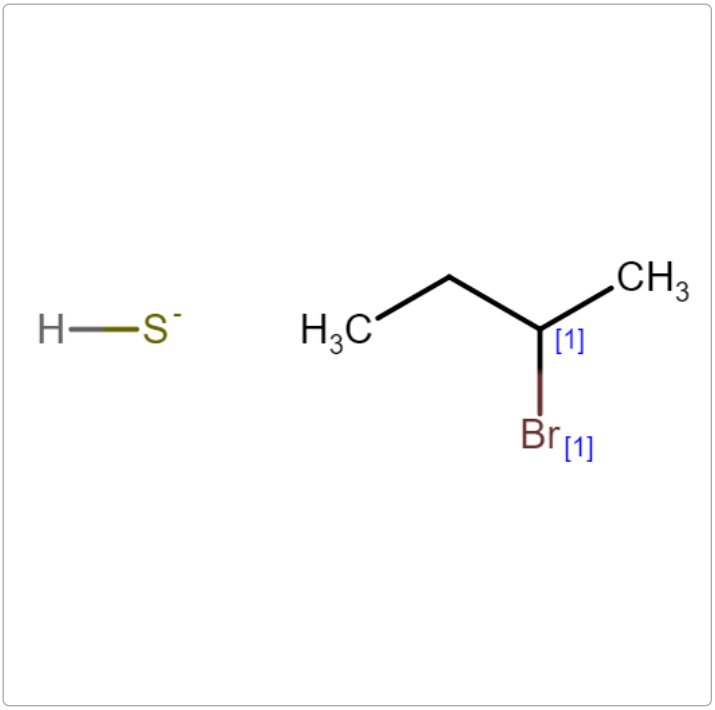
Select the two atoms in the reactants that have a covalent bond that will break during the reaction.

Identify the two atoms by selecting each atom and assigning it a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to determine which bond will break

The bond that breaks will be the source of electrons used to form the new lone pair of electrons in the products. Look for connectivity between two atoms on the reactant side that is absent on the product side.

ANSWER:



Hint 4. Determine which atom will receive the electrons

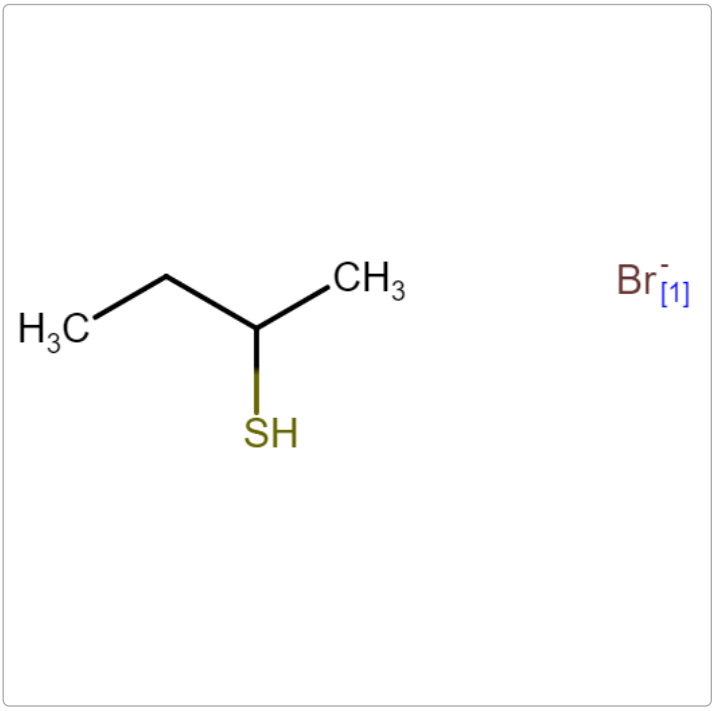
Select the atom or ion in the products that will be the final location of the electrons from the broken carbon-bromine bond.

Identify the final location of the electrons by selecting each atom and assigning it a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to determine where the electrons of the broken bond migrate to

Start by identifying the two atoms that made up the bond that broke in the reactants. Since the bond is breaking, one atom in the pair will end up with the electrons. Next, identify which of the two atoms has a new lone pair of electrons.

ANSWER:



ANSWER:

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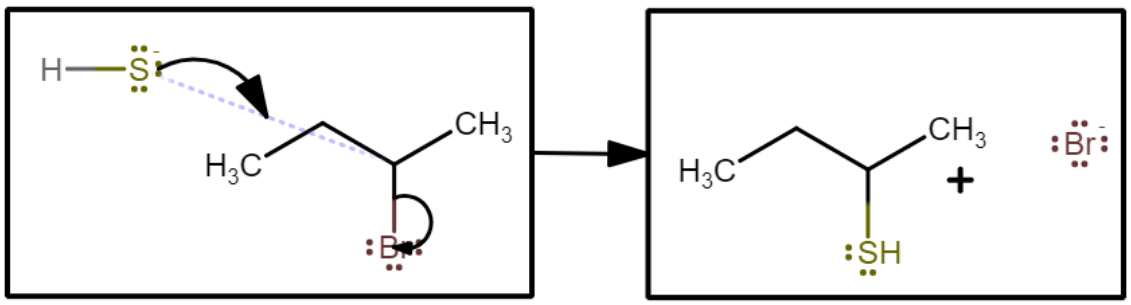
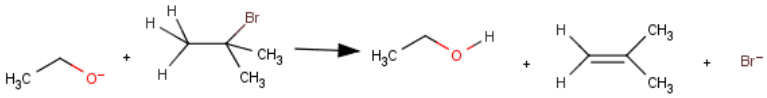


Correct

An electron arrow can be thought of a set of instructions. The origin of the arrow indicates a source of electrons such as a lone pair of electrons or a bond that breaks. In this example two curved electron flow arrows are presented. Each arrow has a different kind of electron source. The heads of the arrows point to atoms. An arrow pointing to an atom indicates that a bond to that atom will form or a lone pair of electrons on that atom will form. In this example both kinds of results are demonstrated.

Part D

Use curved arrows to keep track of electron flow between the reactants and the products.



Edit the reaction by drawing all steps in the appropriate boxes and connecting them with reaction arrows. Add charges where needed. Electron flow arrows should start on an atom or a bond and should end on an atom, bond, or location where a new bond should be created.

Hint 1. Determine which bonds will form

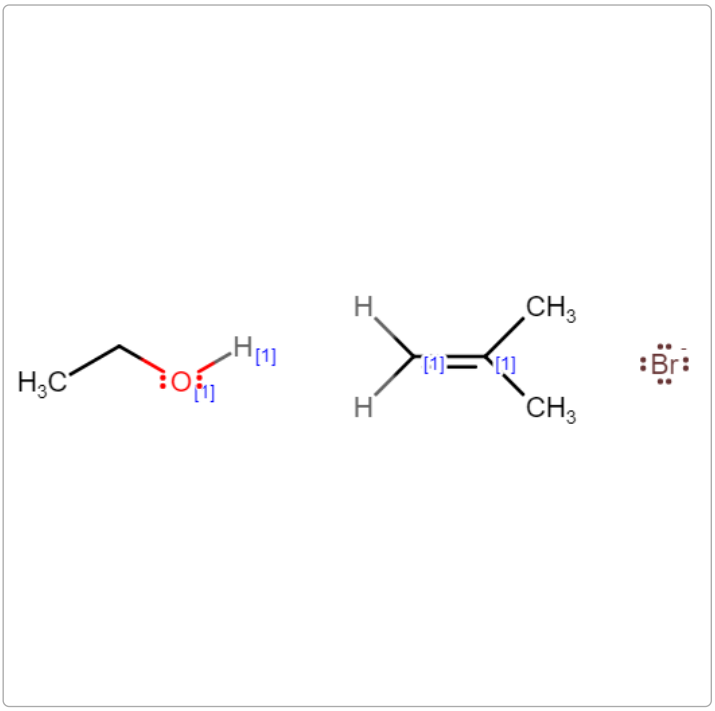
Two new bonds will form. Select the four atoms in the products that now participate in new covalent bonds.

Identify the appropriate group of atoms by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to determine which atoms are involved with new bonds

Look for covalent bond present in the products that are not present in the reactants. The atoms of those bonds are the atoms that are involved in new bond formation.

ANSWER:



Hint 2. Determine which bonds will break

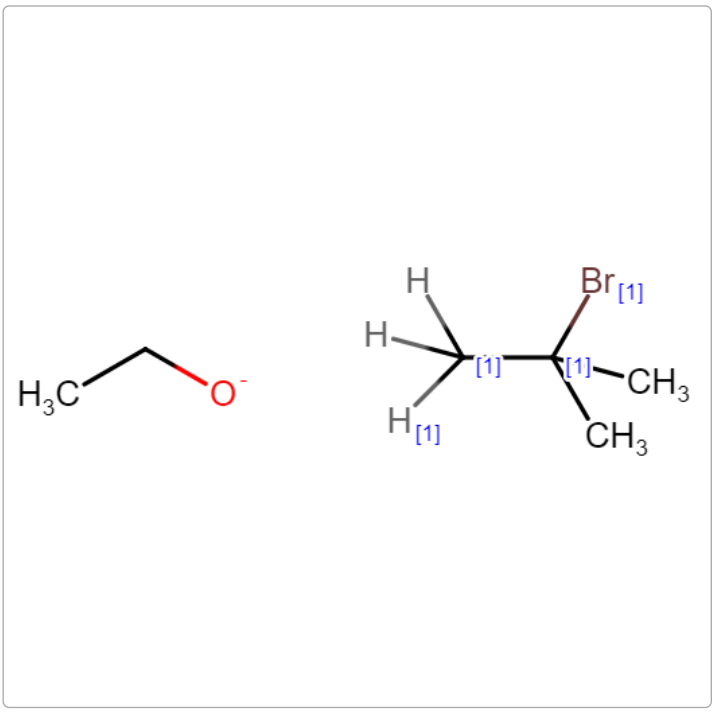
Please note the four atoms in the reactants which have a covalent bond that will break during the reaction.

Identify the appropriate group of atoms by selecting each atom individually on the canvas and assigning them a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to determine which atoms are involved in bonds that break

Look for covalent bond present in the reactants that are not present in the products. The atoms of those bonds are the atoms that are involved in bond breakage.

ANSWER:

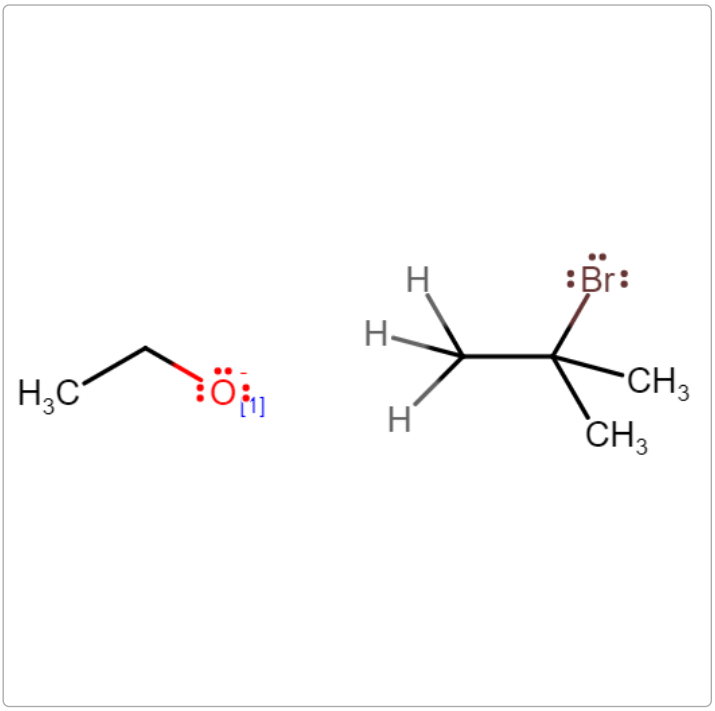


Hint 3. Determine which atom provides the electrons for the new bond

Indicate the source of the two electrons that make up the hydrogen-oxygen bond shown on the product side of the reaction equation by selecting a single atom, or by selecting a pair of atoms that make up a bond.

Identify the appropriate atom(s) by selecting each atom and assigning it a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

ANSWER:



Hint 4. Determine where the electrons of the \pi bond came from

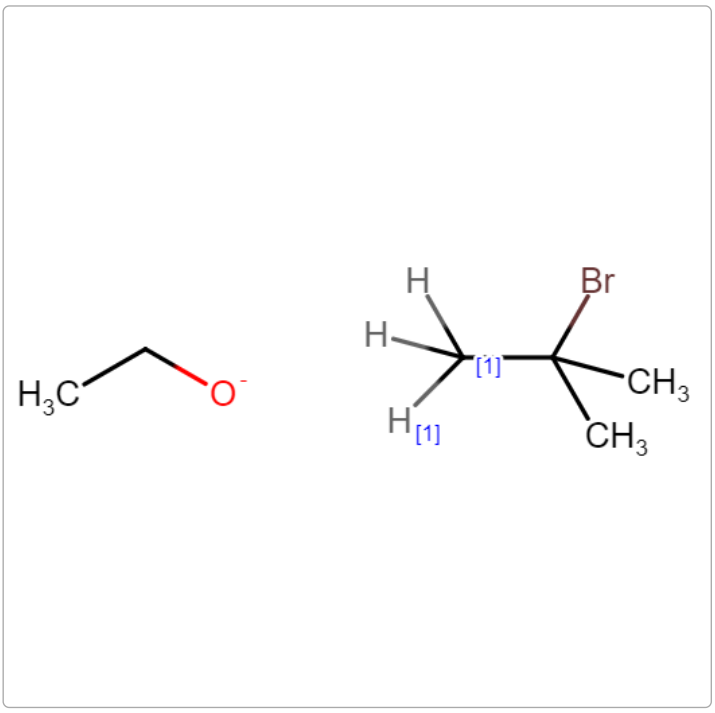
Select the two atoms involved in the bond, which upon breaking provides the electrons necessary to form the \pi bond of the carbon-carbon double bond found in isobutylene.

Identify the two atoms by selecting each atom and assigning it a map number of 1 until all atoms are mapped. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

Hint 1. How to determine where the electrons of the \pi bond came from

One of the two bonds that break during the reaction will be the source of the electrons of the \pi bond. One of the two atoms involved in the bond that breaks will be involved in the bond that forms.

ANSWER:



Hint 5. Determine which atom will receive the electrons

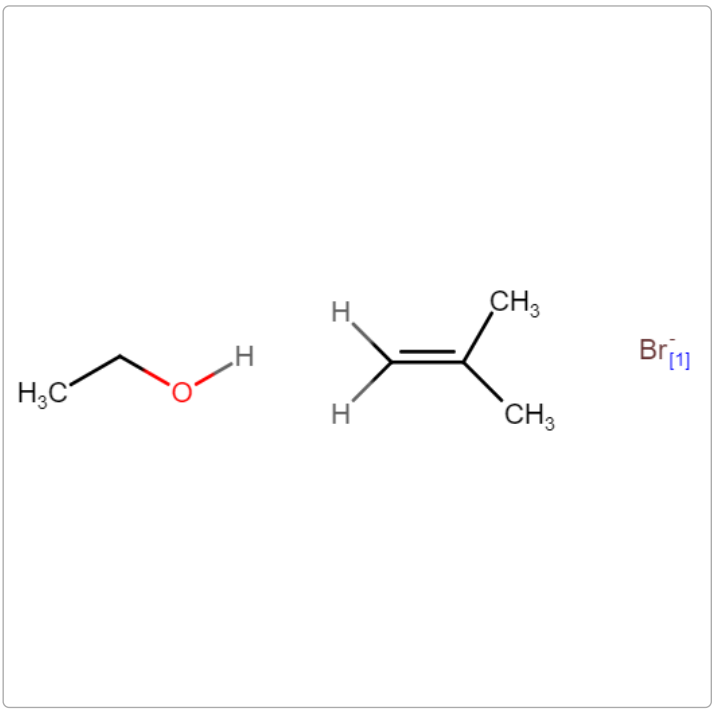
Select the atom or ion in the products that will be the final location for the electrons from carbon-bromide bond.

Identify thefinal location of the electrons by selecting the atom and assigning it a map number of 1. To do this, right-click on an atom and choose Atom properties. (Mac users: Use an equivalent for right-clicking.) Then, clear the check mark to enable the Map field before entering a value.

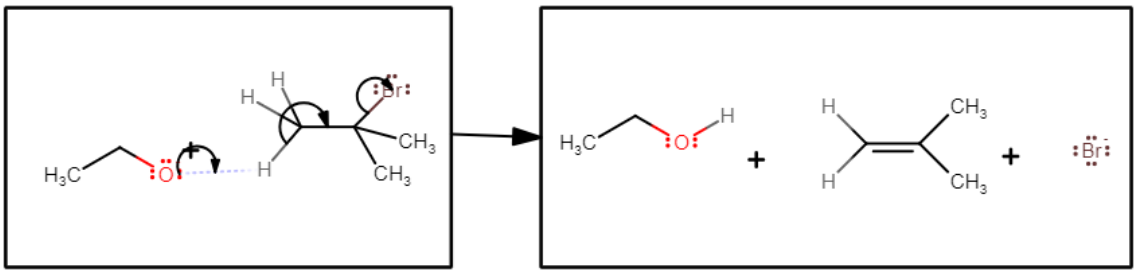
Hint 1. How to determine where the electrons of the broken bond migrate to

Start by identifying the two atoms that made up the bond that broke in the reactants. Since the bond is breaking, one atom in the pair will end up with the electrons. Next, identify which of the two atoms has a new lone pair of electrons.

ANSWER:



ANSWER:



Correct

Electron arrows can be thought of a set of instructions that indicate or show how reactants can be turned into products. The arrows that you add to reactants need to explain how the products can come to be. A lone pair of electrons or a bond that will break in the reactants are the likely origins, or starting points of electron arrows. New lone pairs of electrons on an atom and/or new bonds that are present in the products are the places to which the head on an electron arrow points. Being able to identify these structures in both the reactants and products is an important skill when adding electron arrows to the reactant side of a chemical equation.

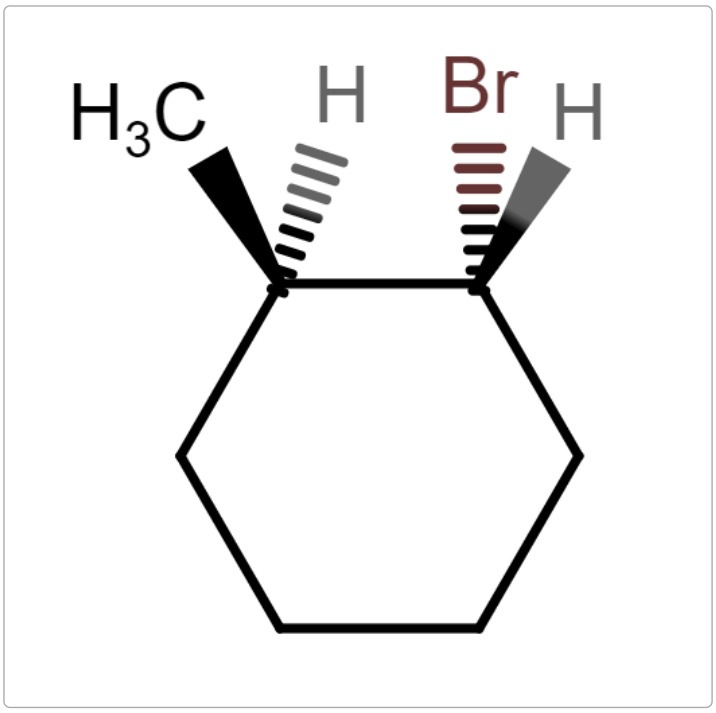
Problem 6-31 (e) - Enhanced - with Feedback

Part A

Draw the structure of *trans*-1-bromo-2-methylcyclohexane.

Loading Web-Font TeX/Main/Italic **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

Problem 6-19

For each pair of compounds, state which compound is the better \rm S_{\rm N}2 substrate.

Part A

2-methyl-1-iodopropane or *tert*-butyl iodide

ANSWER:

- *tert*-butyl iodide
- 2-methyl-1-iodopropane

Correct

Part B

cyclohexyl bromide or 1-bromo-1-methylcyclohexane

ANSWER:

- cyclohexyl bromide
- 1-bromo-1-methylcyclohexane

Correct

Part C

2-bromobutane or isopropyl bromide

ANSWER:

- 2-bromobutane
- isopropyl bromide

Correct

Part D

1-chloro-2,2-dimethylbutane or 2-chlorobutane

1-chloro-2,2-dimethylbutane

2-chlorobutane

Correct

Part E

1-iodobutane or 2-iodopropane

ANSWER:

1-iodobutane

2-iodopropane

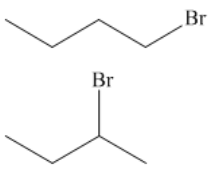
Correct

Problem 6-33

Part A

Predict the compound in the following pair that will undergo the {\rm S}_{{\rm N}}2 reaction faster.

ANSWER:

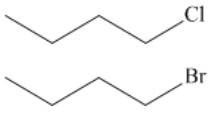


Correct

Part B

Predict the compound in the following pair that will undergo the {\rm S}_{{\rm N}}2 reaction faster.

ANSWER:

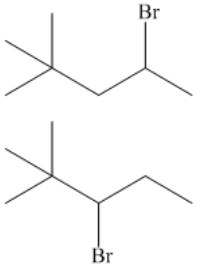


Correct

Part C

Predict the compound in the following pair that will undergo the {\rm S}_{{\rm N}}2 reaction faster.

ANSWER:



Correct

Part D

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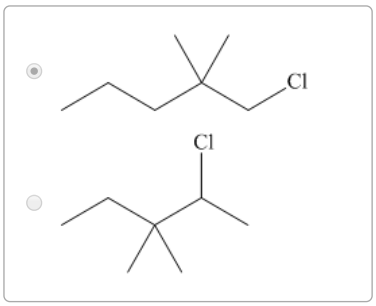
following pair that will undergo the {\rm S}_{{\rm N}}2 reaction faster.

ANSWER:

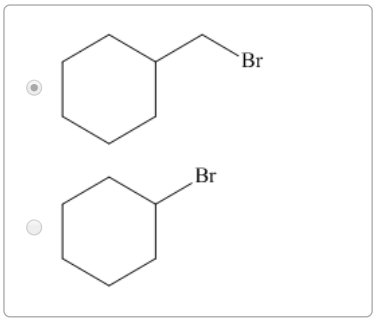


Correct

Part E

Predict the compound in the following pair that will undergo the {\rm S}_{{\rm N}}2 reaction faster.

ANSWER:

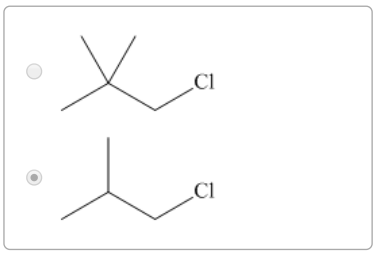


Correct

Part F

Predict the compound in the following pair that will undergo the {\rm S}_{{\rm N}}2 reaction faster.

ANSWER:



Correct

Problem 6-11

Part A

Classify each reaction as a substitution, an elimination, or neither.

Drag the appropriate items to their respective bins.

ANSWER:

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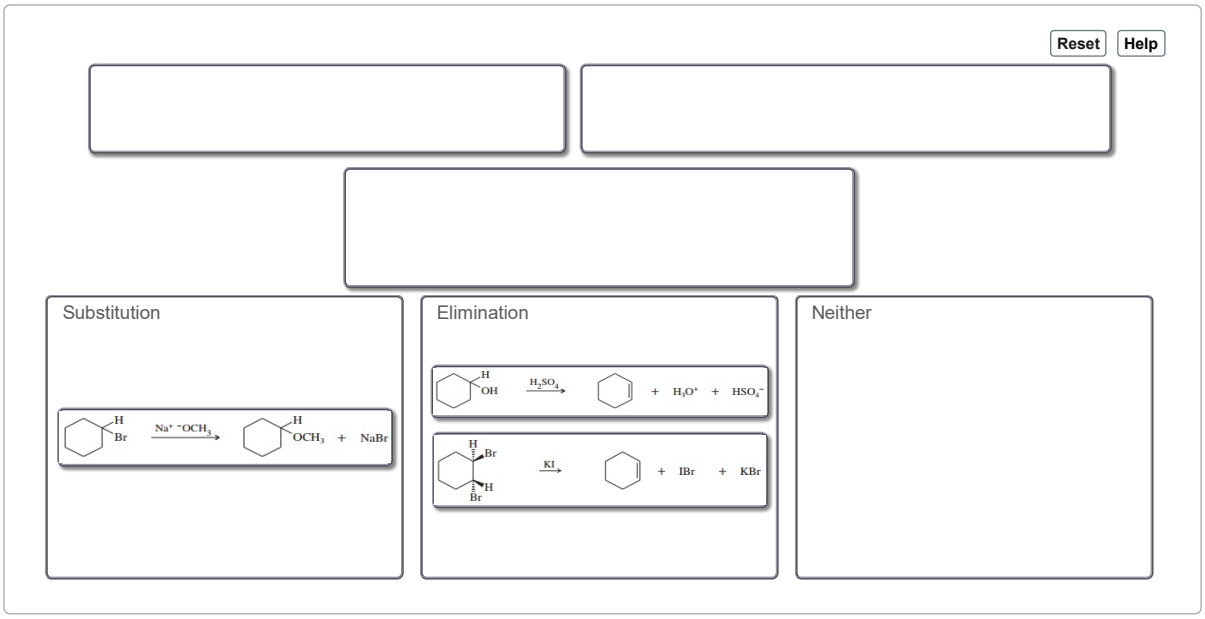
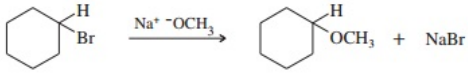


Correct

Part B

What is the leaving group in the reaction:



Express your answer as an ion.

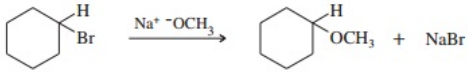
ANSWER:

\rm{\rm{Br^{-}}}

Correct

Part C

What is the nucleophile in the reaction:



Express your answer as an ion.

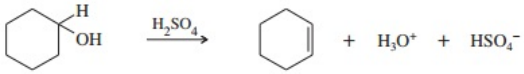
ANSWER:

\rm{\rm{CH_{3}O^{-}}}

Correct

Part D

What is the leaving group in the reaction:



Express your answer as a chemical formula.

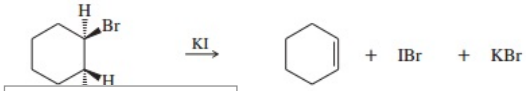
ANSWER:

\rm{\rm{H_{2}O}}

Correct

Part E

What is the leaving group in the reaction:



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Express your answer as a chemical formula.

ANSWER:

\rm{\rm{Br_{2}}}

Correct

Problem 6-12

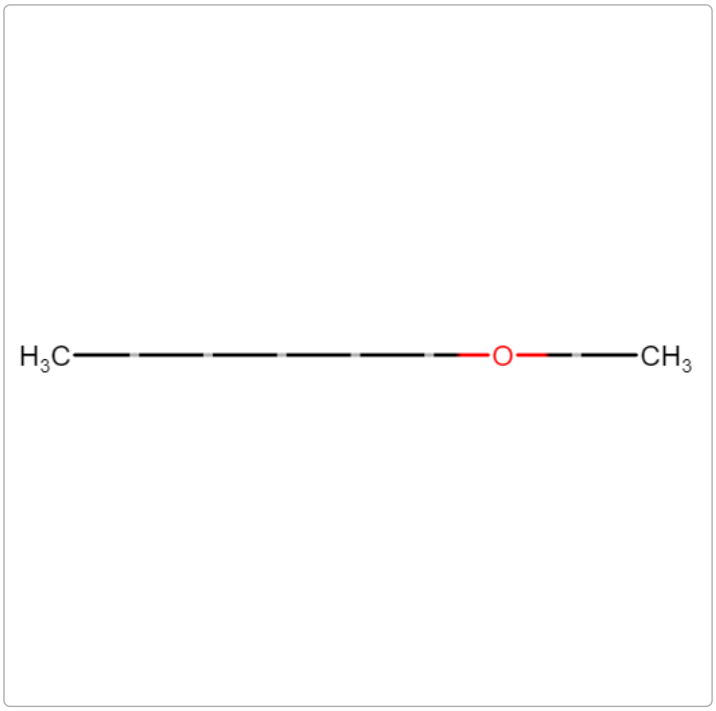
Give the structures of the substitution products expected when 1-bromohexane reacts with:

Part A

\rm NaOCH_2CH_3

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds and charges), Atoms, and Templates toolbars.

ANSWER:



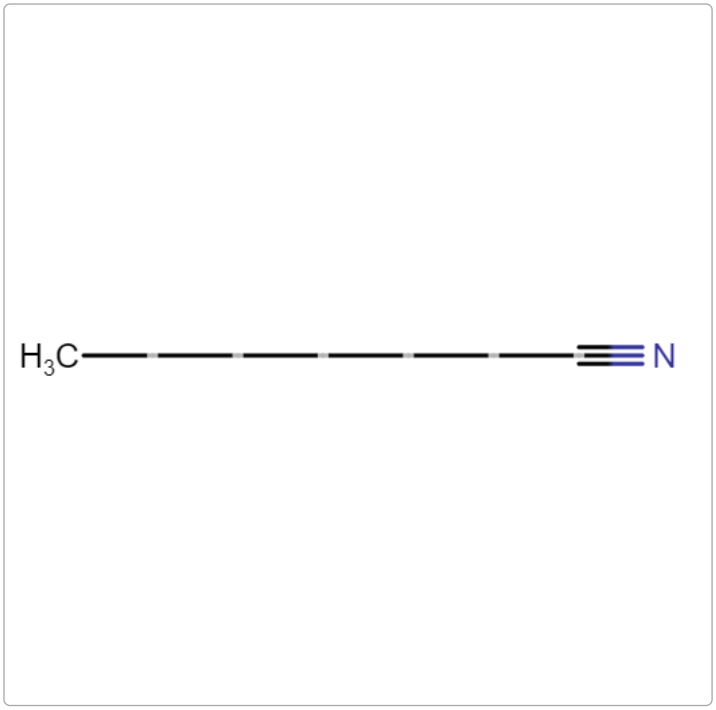
Correct

Part B

\rm KCN

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds and charges), Atoms, and Templates toolbars.

ANSWER:



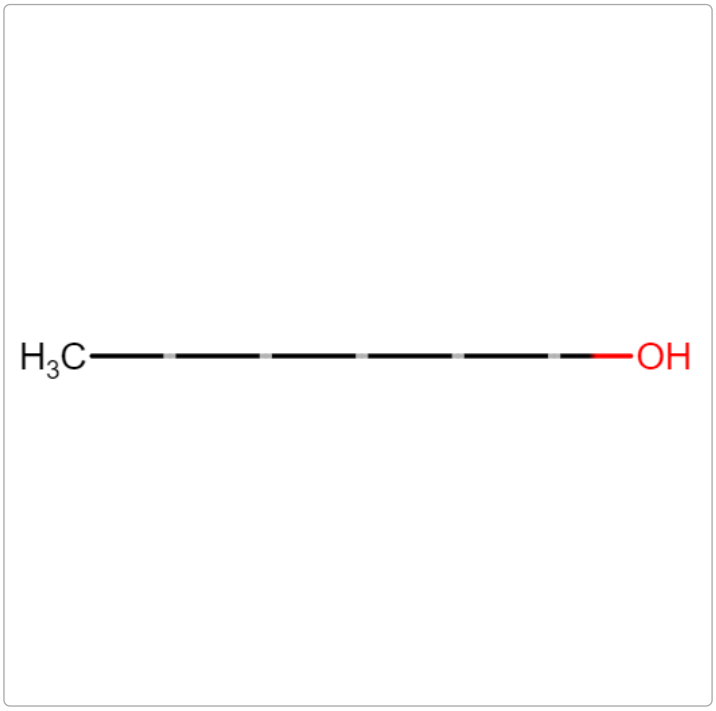
Correct

Part C

\rm NaOH

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds and charges), Atoms, and Templates toolbars.

ANSWER:



Correct

Problem 6-34

Part A

Predict the compound in the following pair that will undergo solvolysis (in aqueous ethanol) more rapidly.

ANSWER:

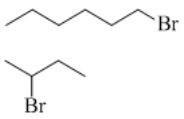
- $(CH_3CH_2)_2CHBr$
- $(CH_3)_3CBr$

Correct

Part B

Predict the compound in the following pair that will undergo solvolysis (in aqueous ethanol) more rapidly.

ANSWER:

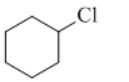


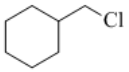
Correct

Part C

Predict the compound in the following pair that will undergo solvolysis (in aqueous ethanol) more rapidly.

ANSWER:



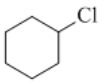


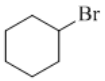
Correct

Part D

Predict the compound in the following pair that will undergo solvolysis (in aqueous ethanol) more rapidly.

ANSWER:



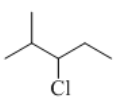


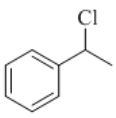
Correct

Part E

Predict the compound in the following pair that will undergo solvolysis (in aqueous ethanol) more rapidly.

ANSWER:



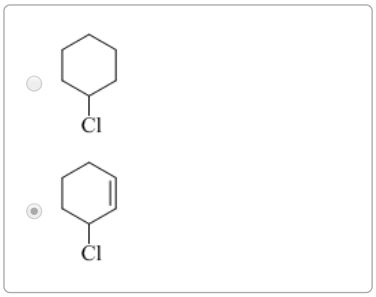


Correct

Part F

Loading Web-Font TeX/Main/Italic e following pair that will undergo solvolysis (in aqueous ethanol) more rapidly.

ANSWER:



Correct

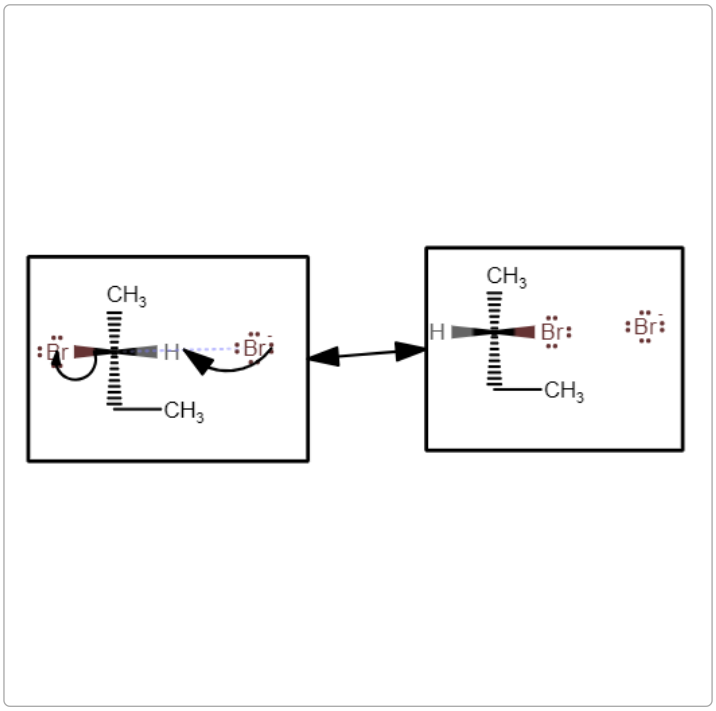
Problem 6-49

Part A

Optically active 2-bromobutane undergoes racemization on treatment with a solution of \rm KBr. Give a mechanism for this racemization.

Edit the reaction by drawing all steps in the appropriate boxes and connecting them with reaction arrows. Add charges where needed. Electron flow arrows should start on an atom or a bond and should end on an atom, bond, or location where a new bond should be created.

ANSWER:



Correct

Part B

In contrast, optically active butan-2-ol does not racemize on treatment with a solution of \rm KOH. Explain why a reaction like that in Part A does not occur.

Match the words in the left column to the appropriate blanks in the sentences on the right.

ANSWER:

Reset Help

\rm HO^-
S_{\rm N}1
S_{\rm N}2
\rm Br^-

In order to undergo substitution and therefore inversion, \rm HO^- would have to be the leaving group, but \rm HO^- is never a leaving group in S_{\rm N}2 . No reaction can occur.

Correct

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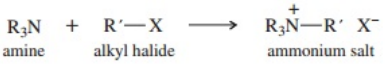
Problem 6-55

The reaction of an amine with an alkyl halide gives an ammonium salt.

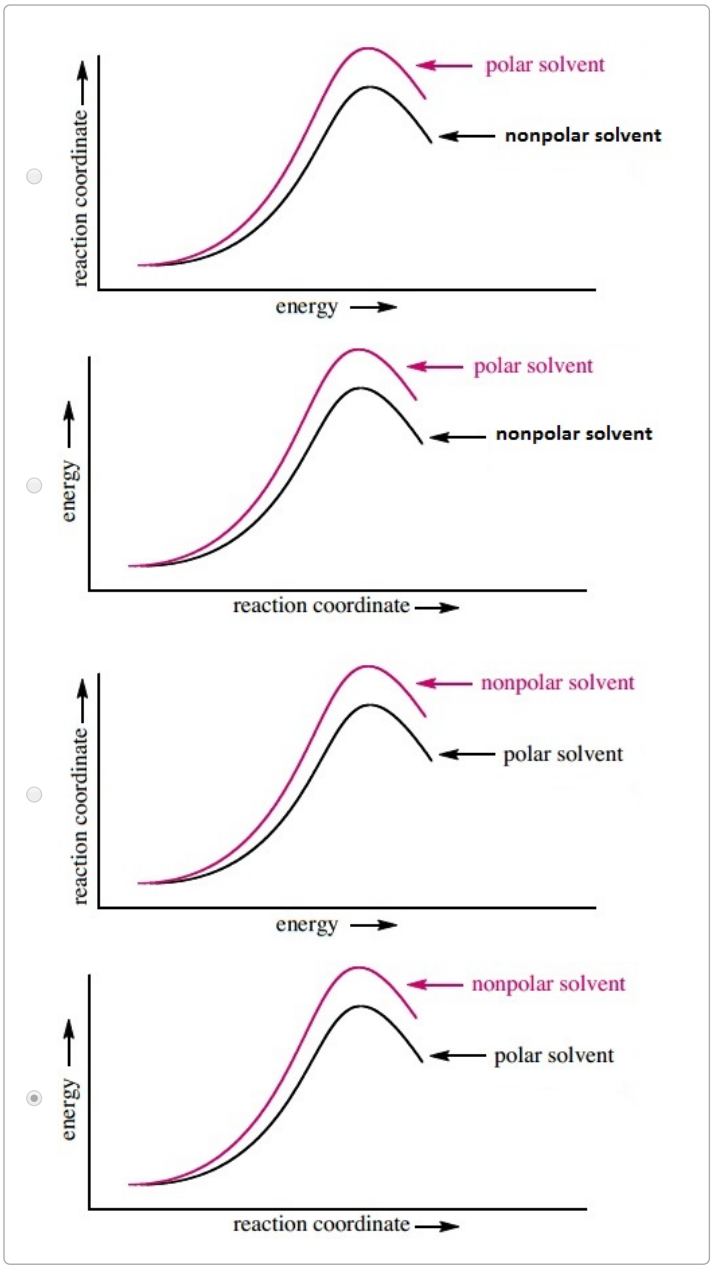


The rate of this S_{\rm N}2 reaction is sensitive to the polarity of the solvent.

Part A

Select the correct the energy diagram for this reaction in a nonpolar solvent and another in a polar solvent.

ANSWER:



Correct

Part B

Consider the nature of the transition state, and explain why this reaction should be sensitive to the polarity of the solvent. Predict whether it will be faster or slower in a more polar solvent.

ANSWER:

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- The transition state is beginning to show the positive and negative charges of the products (ions), so the transition state is more charged than the reactants. The polar transition state will be stabilized in a more polar solvent through dipole-dipole interactions, so the rate of reaction will be enhanced in a polar solvent.
- The transition state is beginning to show the positive and negative charges of the products (ions), so the transition state is less charged than the reactants. The polar transition state will be unstabilized in a more polar solvent through dipole-dipole interactions, so the rate of reaction will be reduced in a polar solvent.
- The transition state is beginning to show the positive and negative charges of the products (ions), so the transition state is more charged than the reactants. The polar transition state will be stabilized in a more polar solvent through dipole-dipole interactions, so the rate of reaction will be reduced in a polar solvent.
- The transition state is beginning to show the positive and negative charges of the products (ions), so the transition state is less charged than the reactants. The polar transition state will be unstabilized in a more polar solvent through dipole-dipole interactions, so the rate of reaction will be enhanced in a polar solvent.

Correct

Chapter 6 Reading Quiz Question 10

Part A

Consider the substitution reaction of *tert*-butyl alcohol with ammonium bromide in aqueous sulfuric acid solution.

Increasing the concentration of ammonium bromide by a factor of 4 would have what effect on the reaction rate?

Hint 1.

Alcohols will be protonated in acid solution, and the OH group (which is a poor leaving group) will change to H_2O^+ (which is a great leaving group). What would be the order of the substitution reaction—first order or second order? See 6-13.

ANSWER:

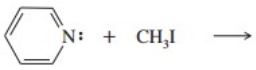
- The reaction rate would be quadrupled.
- The reaction rate would be cut in half.
- It would have no effect.
- The reaction rate would be doubled.

Correct

Problem 6.45 (e) with feedback

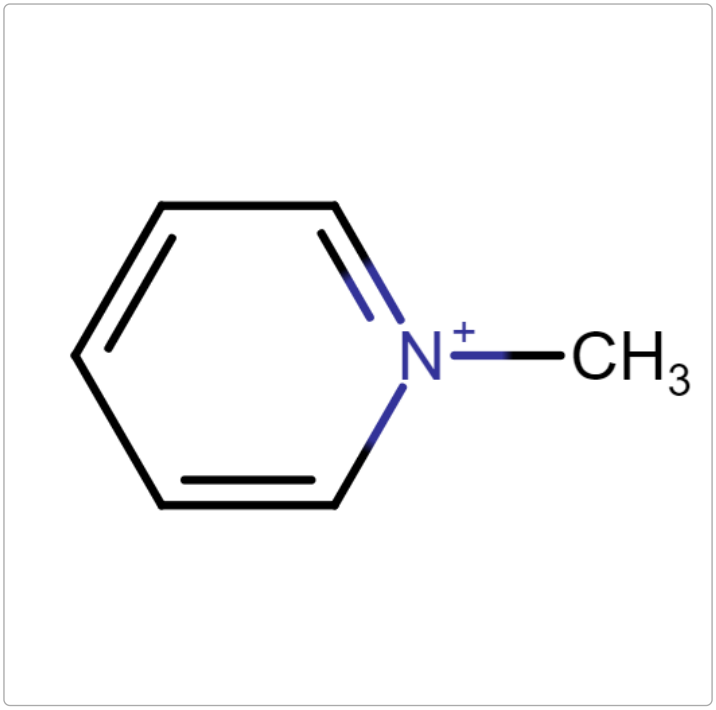
Part A

Predict the product of the following S_{\rm N}2 reaction.



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

ANSWER:



Correct

The nucleophilic N atom displaces I^- from CH_3I. The product can be drawn as a salt, or just the cation can be drawn.

Score Summary:

Your score on this assignment is 77.8%.
You received 32.67 out of a possible total of 42 points.