

Quiz CH202

Organic Chemistry

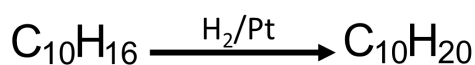
Alkenes: Addition Reactions

Lucas Monteiro Nogueira

►► PROBLEMS

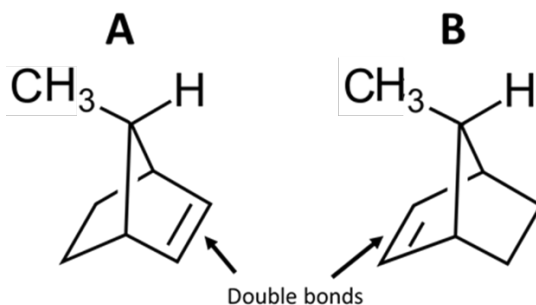
► Problem 1 (Wade and Simek, 2016, w/ permission)

One of the principal components of lemongrass oil is *limonene*, $C_{10}H_{16}$. When limonene is treated with excess hydrogen and a platinum catalyst, the product is an alkane of formula $C_{10}H_{20}$. What can you conclude about the structure of limonene?



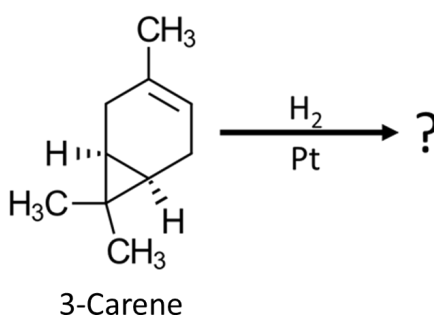
► Problem 2 (Carey, 2008, w/ permission)

Catalytic hydrogenation of compound A occurs much faster for compound A than it does for compound B. Why?



► Problem 3 (Carey, 2008, w/ permission)

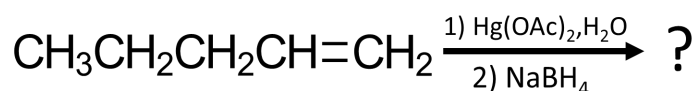
Hydrogenation of 3-carene is, in principle, capable of yielding two stereoisomeric products. However, only one of them was actually obtained in catalytic hydrogenation over platinum. Which one do you think is formed?



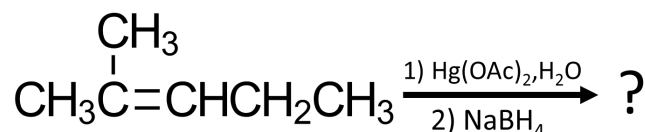
► Problem 4

Problem 4.1: Find the products of oxymercuration of the following alkenes.

4.1.1.

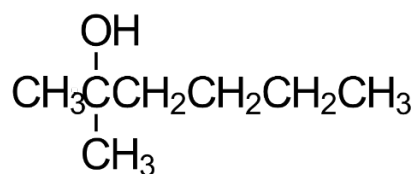


4.1.2.

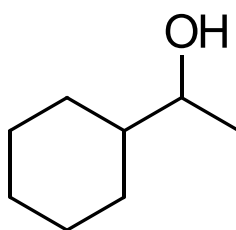


Problem 4.2: Find an alkene that may be used to prepare the following alcohols by oxymercuration.

4.2.1.



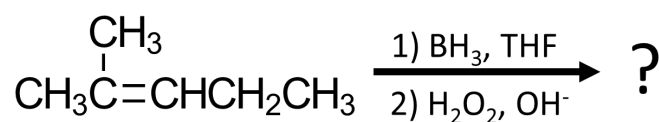
4.2.2.



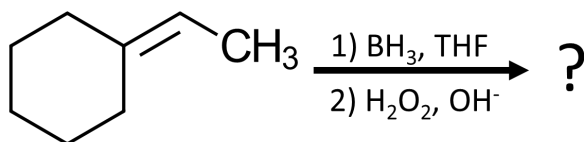
► **Problem 5**

Problem 5.1: Find the products of hydroboration/oxidation of the following alkenes.

5.1.1.

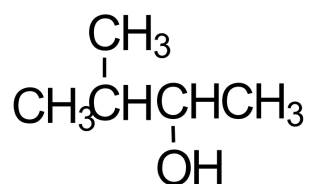


5.1.2.

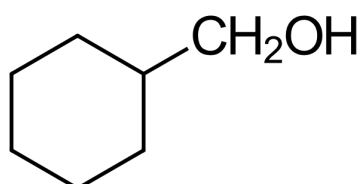


Problem 5.2: Find an alkene that may be used to prepare the following alcohols by hydroboration/oxidation.

5.2.1.



5.2.2.



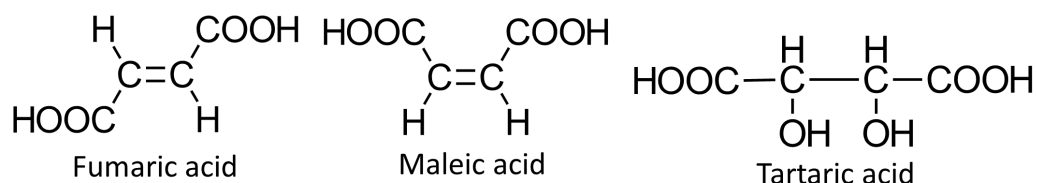
► **Problem 6**

Find an alkene from which the following diols can be prepared.

<p>6.1.</p>	<p>6.2.</p> $\begin{array}{c} \text{HO} \quad \text{OH} \\ \quad \\ \text{HOCH}_2\text{CHCHOH} \end{array}$
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► **Problem 7** (Wade and Simek, 2016, w/ permission)

The two butenedioic acids are called *fumaric acid* (*trans*) and *maleic acid* (*cis*). 2,3-dihydroxybutanedioic acid is called *tartaric acid*.

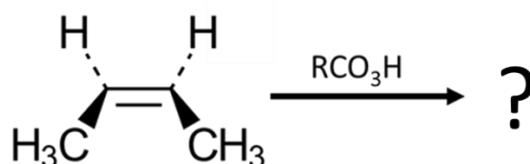


Show how you would convert

- 7.1. Fumaric acid to (\pm)-tartaric acid
- 7.2. Fumaric acid to *meso*-tartaric acid
- 7.3. Maleic acid to (\pm)-tartaric acid
- 7.4. Maleic acid to *meso*-tartaric acid

► **Problem 8** (McMurry, 2008, w/ permission)

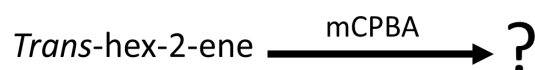
What product would you expect from reaction of *cis*-2-butene with *meta*-chloroperoxybenzoic acid? Show the stereochemistry.



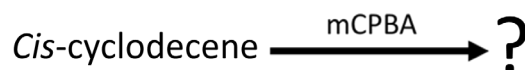
► **Problem 9**

Predict the products of the *meta*-chloroperoxybenzoic acid epoxidation of the following alkenes.

- 9.1. *Trans*-hex-2-ene

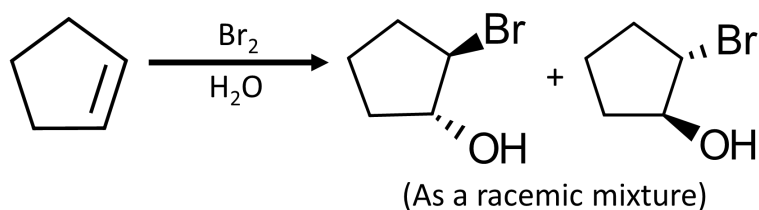


- 9.2. *Cis*-cyclodecene



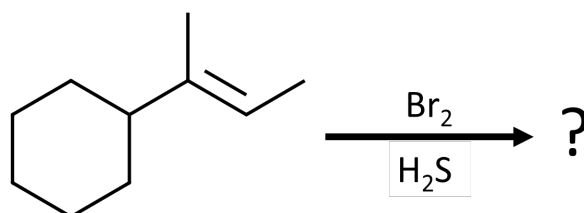
► **Problem 10**

Propose a mechanism for the following reaction.



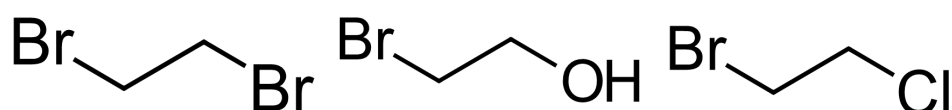
► **Problem 11** (Klein, 2017, w/ permission)

Predict the product of the following addition reaction.



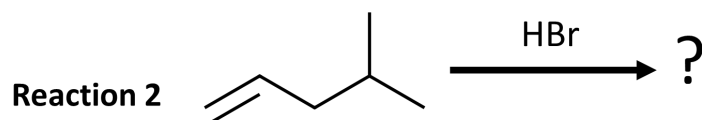
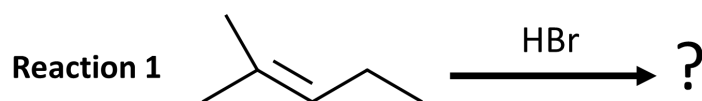
► **Problem 12** (Solomons *et al.*, 2014, w/ permission)

When ethene (ethylene) gas is passed into an aqueous solution containing bromine and sodium chloride, the products of the reaction are the following. Write mechanisms showing how each product is formed.



► **Problem 13** (Klein, 2017, w/ permission)

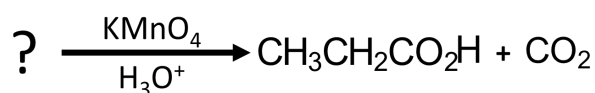
Identify which of the following two reactions you would expect to occur more rapidly: **(1)** addition of HBr to 2-methyl-2-pentene, or **(2)** addition of HBr to 4-methyl-1-pentene. Explain your choice.



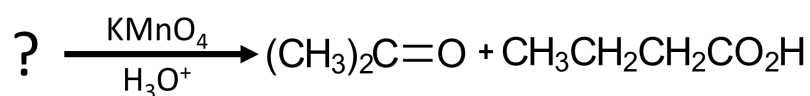
► **Problem 14**

Find an alkene that yields the following products when oxidized with KMnO_4 in an acidic medium.

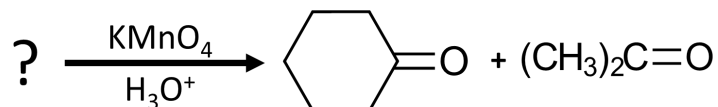
14.1. Oxidation of this alkene yields propanoic acid and carbon dioxide.



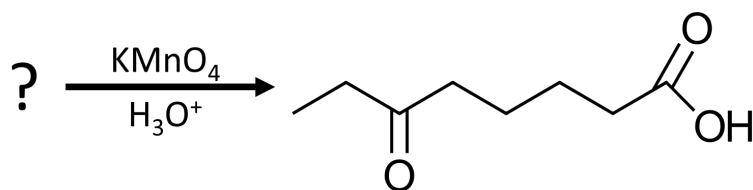
14.2. Oxidation of this alkene yields propanone and butanoic acid.



14.3. Oxidation of this alkene yields cyclohexanone and propanone.



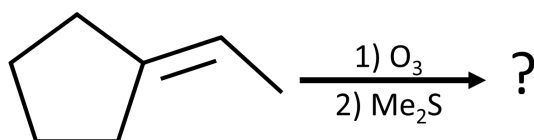
14.4. Oxidation of this alkene yields 6-oxooctanoic acid.



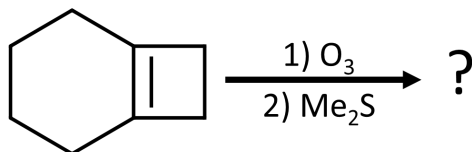
► **Problem 15**

Problem 15.1: Predict the products of the following ozonolysis reactions.

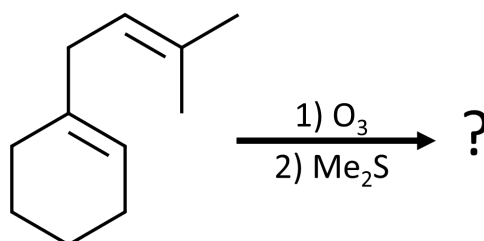
15.1.1.



15.1.2.

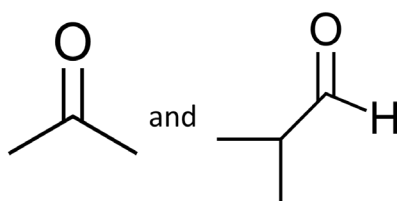


15.1.3.

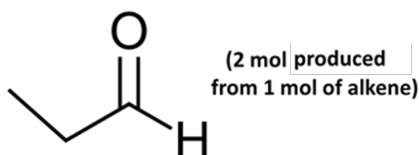


Problem 15.2: Write the structure of an alkene that would yield the following carbonyl compounds when treated with ozone and then with dimethyl sulfide.

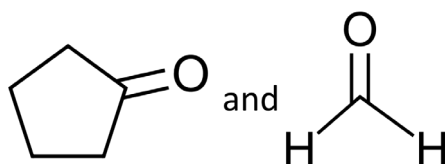
15.2.1.



15.2.2.



15.2.3.

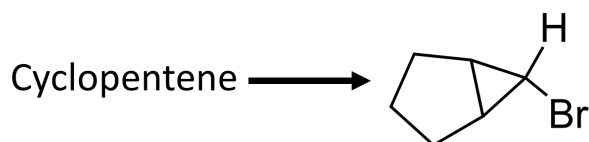


► **Problem 16** (Wade and Simek, 2016, w/ permission)

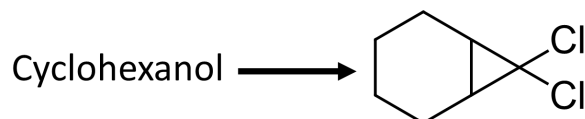
Show how you would accomplish the following synthetic conversions.

16.1. *Trans*-but-2-ene → *Trans*-1,2-dimethylcyclopropane

16.2.

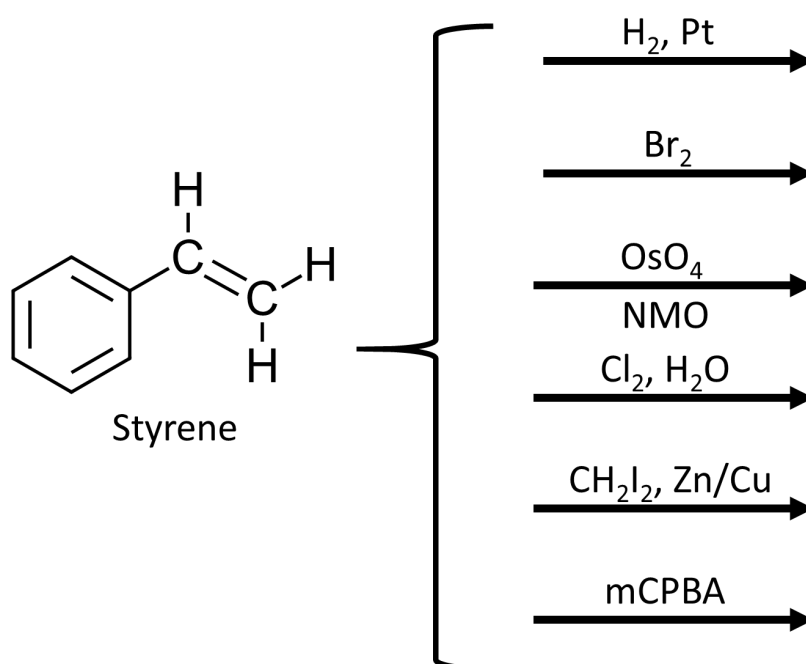


16.3.



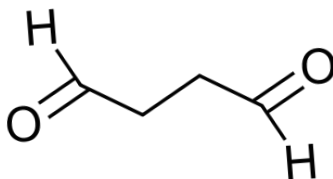
► **Problem 17** (McMurry, 2008, w/ permission)

Predict the products of the following reactions (the aromatic ring is unreactive in all cases). For this problem in particular, ignore regiochemistry.



► **Problem 18**

Draw the structure of a hydrocarbon that absorbs 2 mole equivalents of H_2 on catalytic hydrogenation and gives only butanedial on ozonolysis.



► **Problem 19**

19.1. Compound X has the molecular formula C_5H_{10} . In the presence of a metal catalyst, compound X reacts with one mole equivalent of molecular hydrogen to yield 2-methylbutane. Draw three possible structures of compound X.

19.2. Hydroboration-oxidation of compound X yields a product with no chiral centers. Identify the structure of compound X.

► **Problem 20** (McMurry, 2008, w/ permission)

Compound A has the formula $C_{10}H_{16}$. On catalytic hydrogenation over palladium, it reacts with only 1 molar equivalent of H_2 . Compound A also undergoes reaction with ozone, followed by zinc treatment, to yield a symmetrical ketone, B ($C_{10}H_{16}O_2$).

20.1. How many rings does A have?

20.2. What are the structures of A and B?

20.3. Write the reactions.

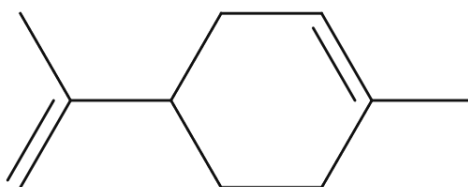
► **Problem 21** (McMurry, 2008, w/ permission)

An unknown hydrocarbon A with the formula C_6H_{12} reacts with 1 molar equivalent of H_2 over a palladium catalyst. Hydrocarbon A also reacts with OsO_4 to give diol B. When oxidized with $KMnO_4$ in acidic solution, A gives two fragments. One fragment is propanoic acid, $CH_3CH_2CO_2H$, and the other fragment is ketone C. What are the structures of A, B, and C? Write all reactions, and show your reasoning.

►► **SOLUTIONS**

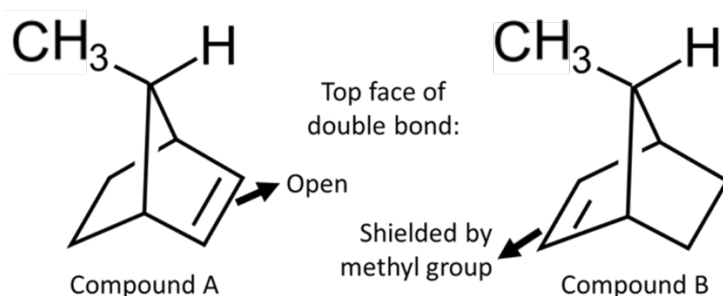
P.1 → **Solution**

From its formula, it is clear that limonene has three degrees of unsaturation. Two degrees of unsaturation have been removed by hydrogenation – these must have been π bonds, either two double bonds or one triple bond. The one remaining unsaturation must be a ring. Thus, limonene must have one ring and either two double bonds or one triple bond. The structure of limonene is shown below.



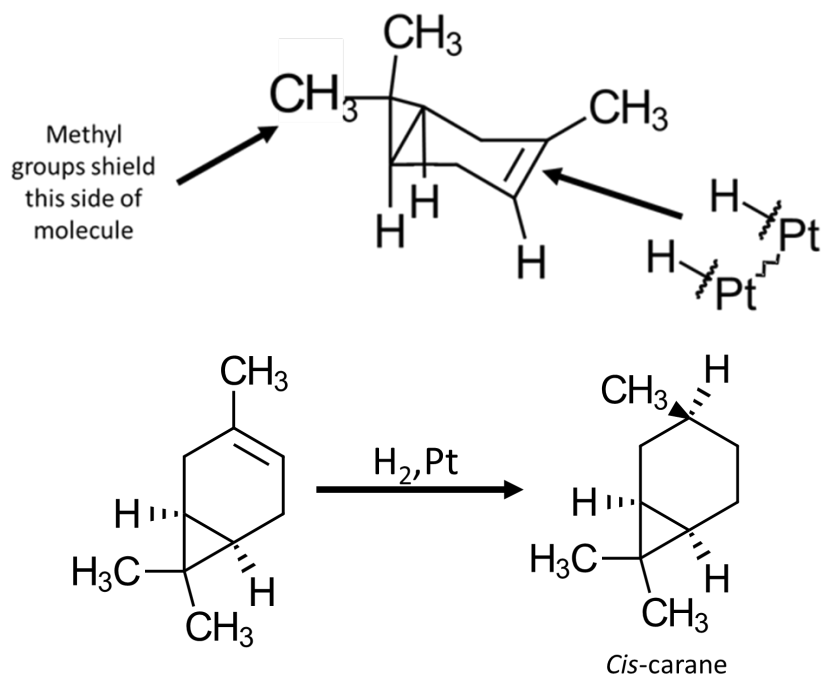
P.2 → **Solution**

The methyl group in compound B shields one face of the double bond from the catalyst surface, therefore hydrogen can be transferred only to the bottom face of the double bond. The methyl group in compound A does not interfere with hydrogen transfer to the double bond.

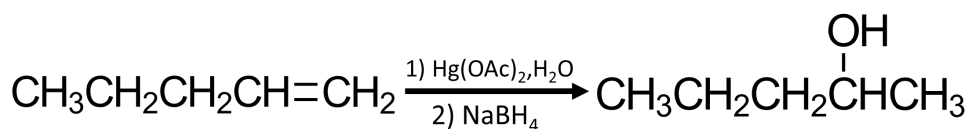


P.3 → **Solution**

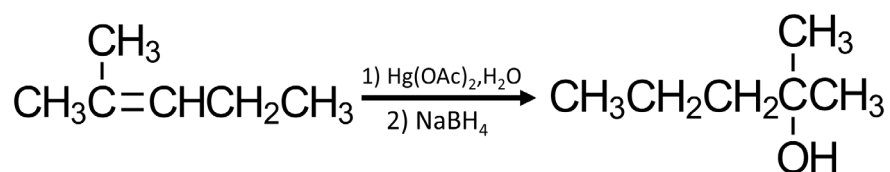
The exclusive product is *cis*-carane, as it corresponds to transfer of hydrogen from the less hindered side.

**P.4** → **Solution**

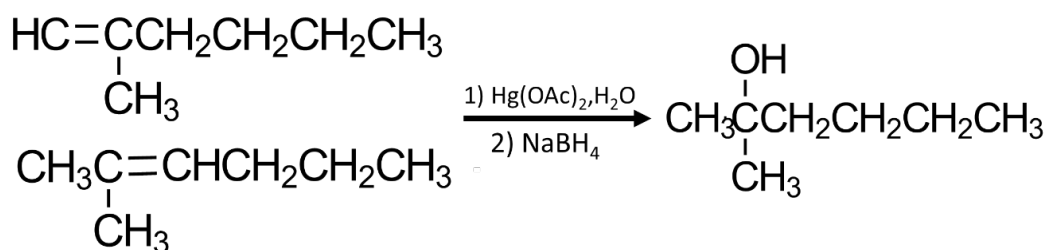
4.1.1: Oxymercuration is equivalent to addition of H₂O to an alkene. The reaction follows Markovnikov's rule, and the hydroxyl is added to the more substituted carbon. The product of reaction 4.1.1 is 2-pentanol.



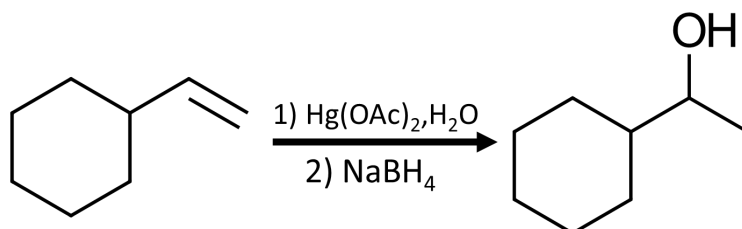
4.1.2: The product of reaction 4.1.2 is 2-methyl-2-pentanol.



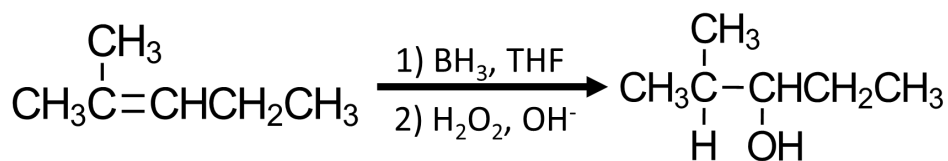
4.2.1: The key in this type of problem is to look backward, all the while noting that in oxymercuration the OH group is added to the more substituted carbon. The alcohol in question can be prepared from the oxymercuration of either 2-methyl-1-hexene or 2-methyl-2-hexene.



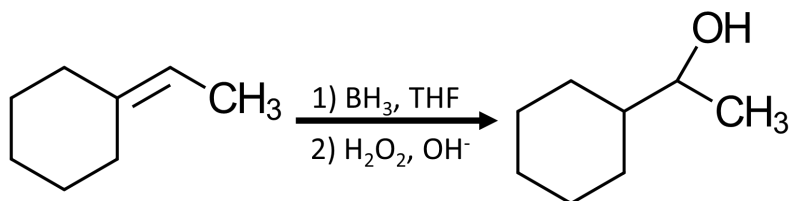
4.2.2: The alcohol in question can be prepared from the oxymercuration of 1-vinylcyclohexane.

**P.5** → **Solution**

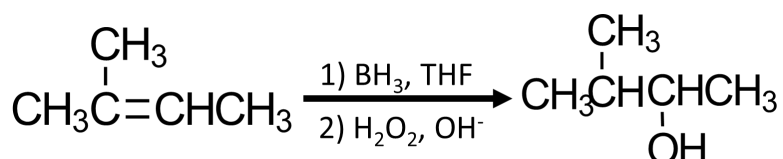
5.1.1: The product of reaction 5.1.1 is 2-methyl-3-pentanol.



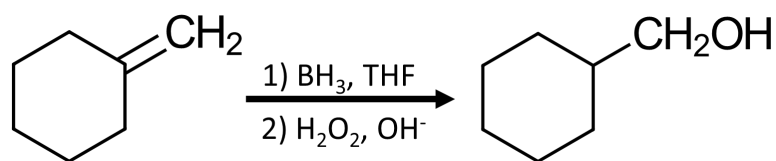
5.1.2: The product of this reaction is 1-cyclohexyl-1-ethanol.



5.2.1: The key in this type of problem is to look backward, all the while noting that in hydroboration/oxidation the OH group is added to the less substituted carbon. The alcohol in question can be prepared from the hydroboration/oxidation of 2-methyl-2-butene.

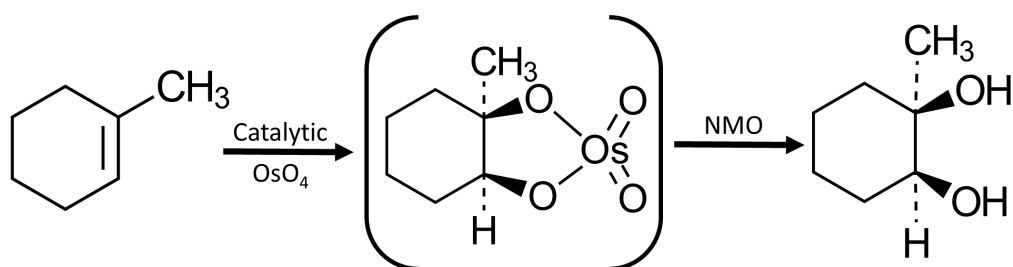


5.2.2: The alcohol in question can be prepared from the hydroboration/oxidation of 1-methylenecyclohexane.

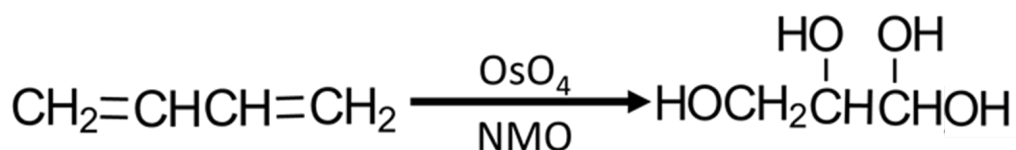


P.6 → Solution

6.1: Reaction of an alkene with a catalytic amount of OsO₄ in the presence of *N*-morpholine *N*-oxide (NMO) yields a diol product. To pick a starting material for these products, choose an alkene that has a double bond between the diol carbons. The diol in question can be synthesized from 1-methylcyclohexene.



6.2: The polyalcohol in question can be synthesized from 1,3-butadiene.

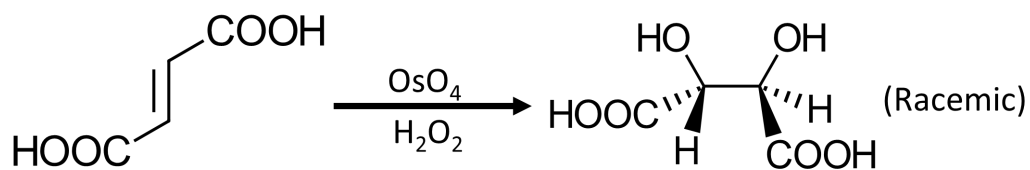


P.7 → Solution

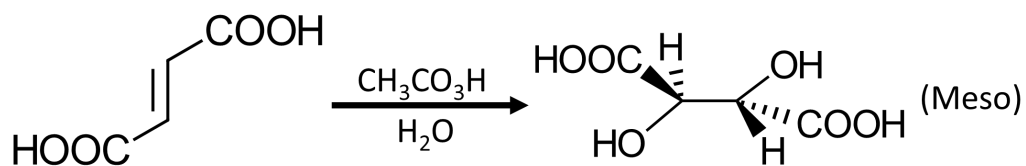
7.1: Bear in mind the following general rules.

<i>Cis</i> -alkene	+	Syn addition	→	Meso
<i>Cis</i> -alkene	+	Anti addition	→	Racemic
<i>Trans</i> -alkene	+	Syn addition	→	Racemic
<i>Trans</i> -alkene	+	Anti addition	→	Meso

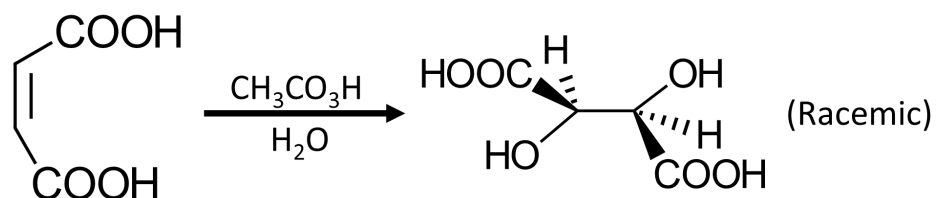
Using OsO₄, which leads to a *syn* dihydroxylation, with fumaric acid, which has a *trans* configuration, we should obtain a racemic mixture of tartaric acid.



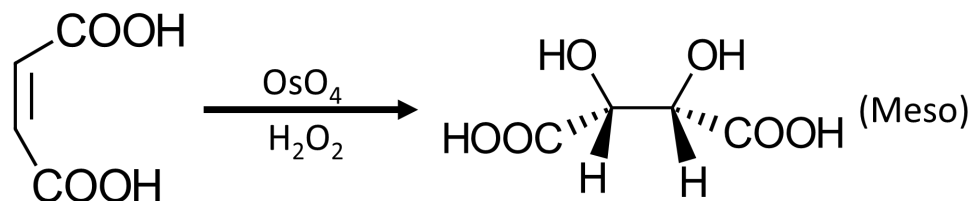
7.2: Using peroxyacetic acid, which leads to an *anti* dihydroxylation, with fumaric acid, which has a *trans* configuration, we should obtain a *meso* mixture of tartaric acid.



7.3: Using peroxyacetic acid, which leads to an *anti* dihydroxylation, with maleic acid, which has a *cis* configuration, we should obtain a racemic mixture of tartaric acid.

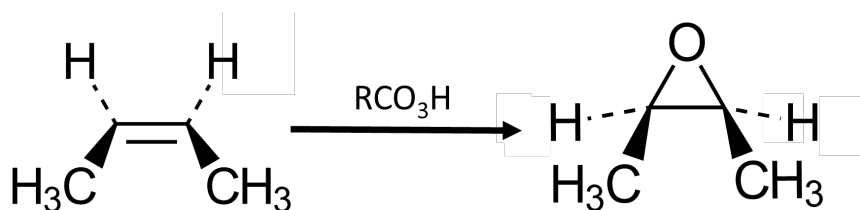


7.4: Using OsO_4 , which leads to a *syn* dihydroxylation, with maleic acid, which has a *cis* configuration, we should obtain a *meso* mixture of tartaric acid.



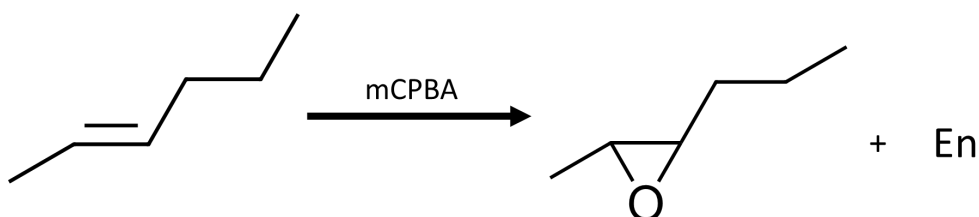
P.8 → **Solution**

Epoxidation using *m*-chloroperoxybenzoic acid is a *syn* addition of oxygen to a double bond. The original bond stereochemistry is retained, and the product is *cis*-2,3-epoxybutane.

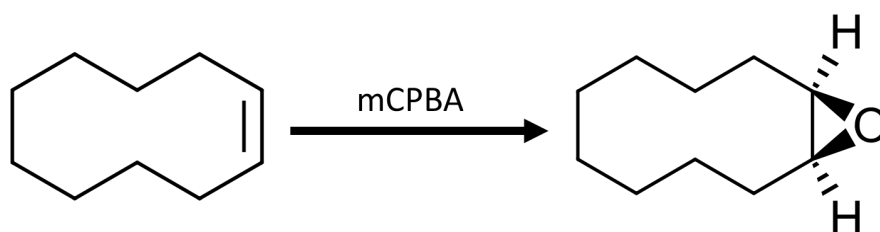


P.9 → **Solution**

9.1: *Trans*-hex-2-ene reacts with mCPBA to form the following epoxide and its enantiomer.



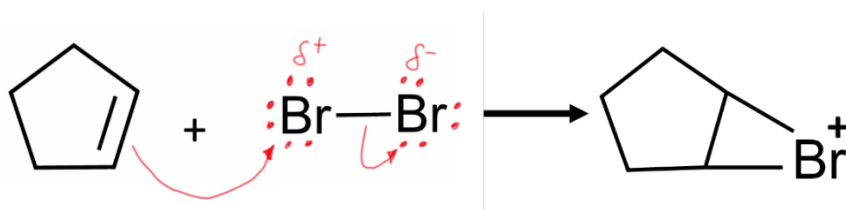
9.2: *Cis*-cyclodecene reacts with mCPBA to form an epoxide.



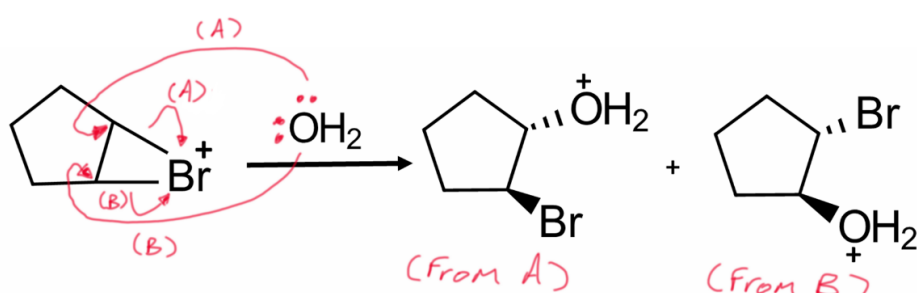
P.10 → **Solution**

As a bromine molecule approaches the alkene, the electron density of the alkene π bond repels electron density in the closer bromine, polarizing the bromine molecule and making the closer bromine atom electrophilic. The

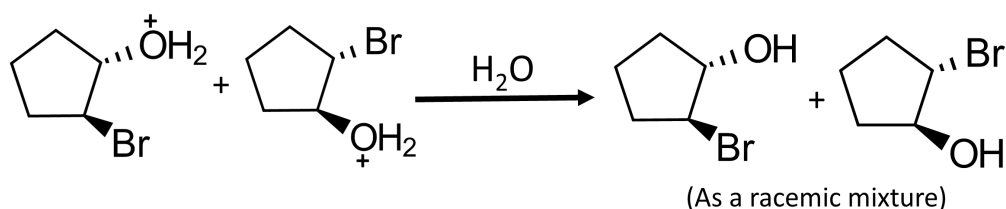
alkene donates a pair of electrons to the closer bromine, causing displacement of the distant bromine atom. As this occurs, the newly bonded bromine atom, due to its size and polarizability, donates an electron pair to the carbon that would otherwise be a carbocation, thereby stabilizing the positive charge by delocalization. The result is a bridged bromonium ion intermediate.



Then, a water molecule acts as the nucleophile and attacks a carbon of the ring, causing the formation of a protonated halohydrin.

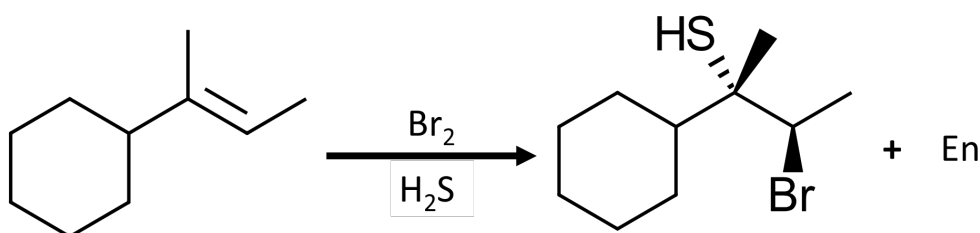


Finally, the protonated halohydrin loses a proton, which is transferred to a molecule of water. This step produces the halohydrin and hydronium ion. In the case at hand, a racemic mixture of two products is formed.



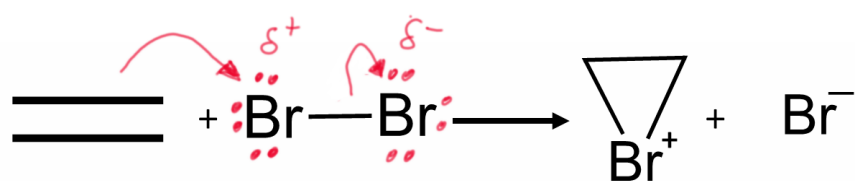
P.11 → Solution

When treated with molecular bromine (Br_2), the alkene is converted to an intermediate bromonium ion, which is then subject to attack by a nucleophile. We know that the nucleophile can be water when the reaction is performed in the presence of water, so it is reasonable that the nucleophile can be H_2S in this case. This should give the installation of a thiol group ($-\text{SH}$) in the more substituted position.

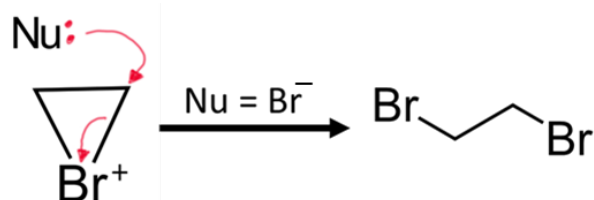


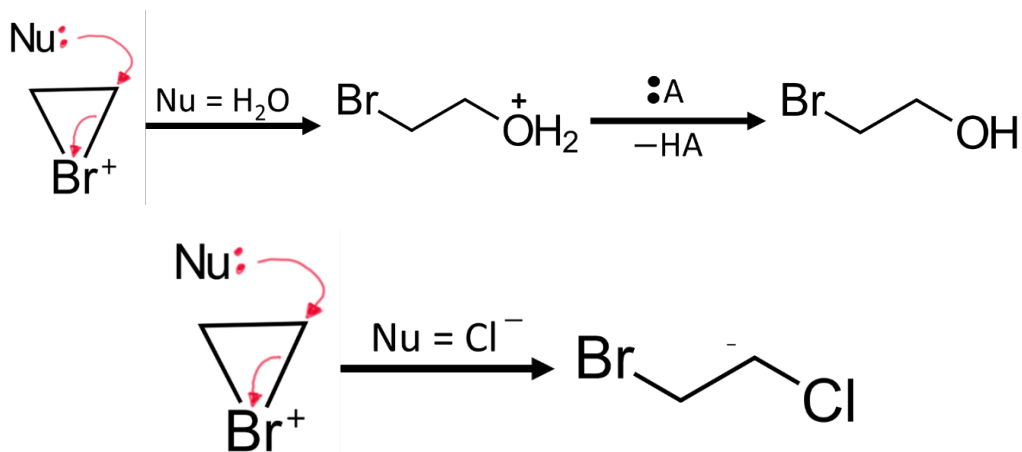
P.12 → Solution

The synthesis of all three products begins with the addition of a bromine atom to ethene.



What follows is a nucleophilic attack on the bromonium ion. The product changes depending on the nucleophile.



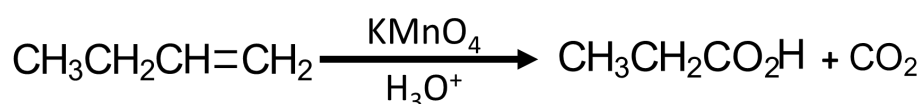


P.13 → **Solution**

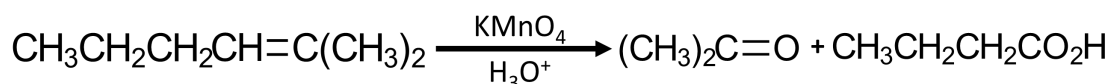
Addition of HBr to 2-methyl-2-pentene would be more rapid because the reaction can proceed via a tertiary carbocation. In contrast, addition of HBr to 4-methyl-1-pentene proceeds via a less stable, secondary carbocation.

P.14 → **Solution**

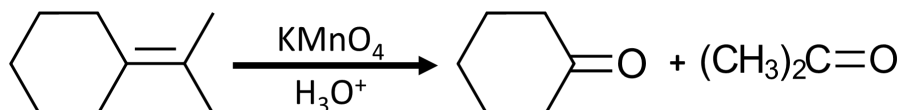
14.1: The products in question can be obtained from the oxidation of 1-butene.



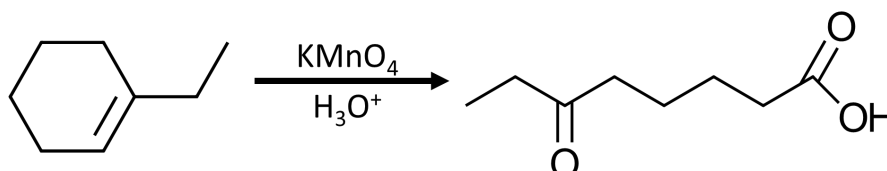
14.2: The products in question can be obtained from the oxidation of 2-methyl-2-hexene.



14.3: The products in question can be obtained from the oxidation of 1-isopropylidenecyclohexane.

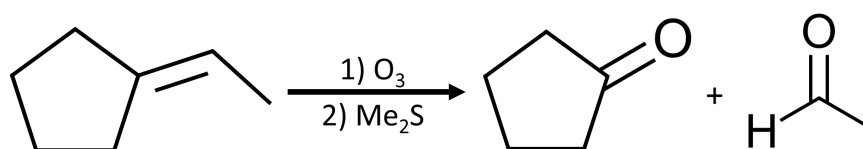


14.4: The product in question can be obtained from the oxidation of 1-ethylcyclohexene.

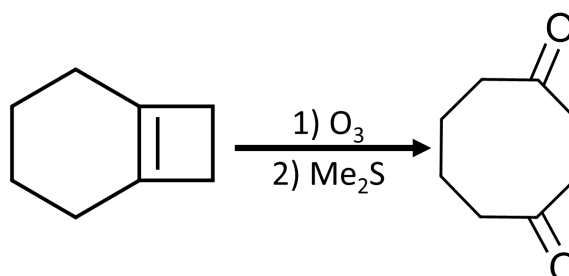


P.15 → **Solution**

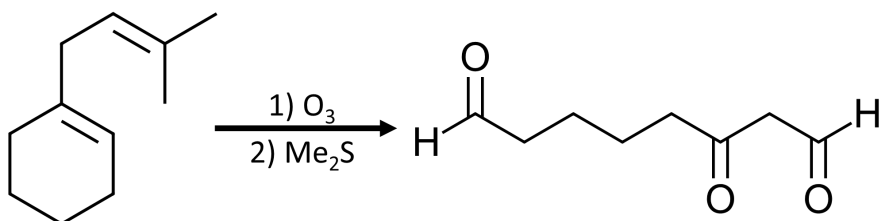
15.1.1: Ozonolysis of this molecule yields cyclopentanone and ethanal.



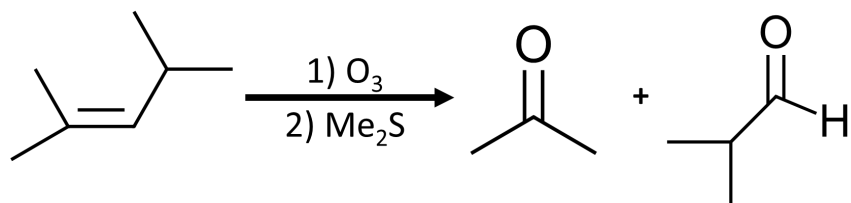
15.1.2: Ozonolysis of this molecule yields 1,4-cyclooctanedione.



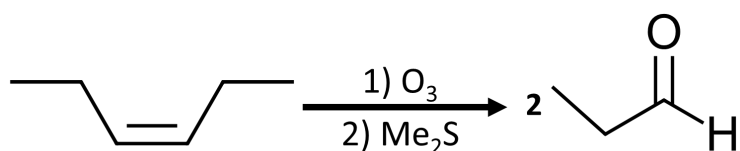
15.1.3: Ozonolysis of this molecule yields 3-oxooctanedial.



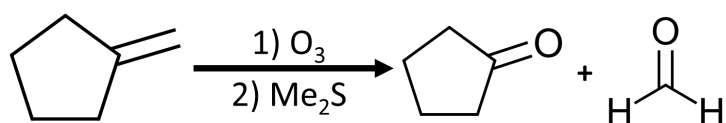
15.2.1: The ketone and aldehyde in question can be synthesized by ozonolysis of 2,4-dimethyl-2-pentene.



15.2.2: The aldehyde in question can be synthesized by ozonolysis of (Z)-3-hexene or its (E) isomer.

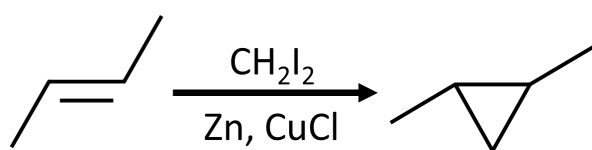


15.2.3: The ketone and aldehyde in question can be synthesized by ozonolysis of 1-methylenecyclopentane.

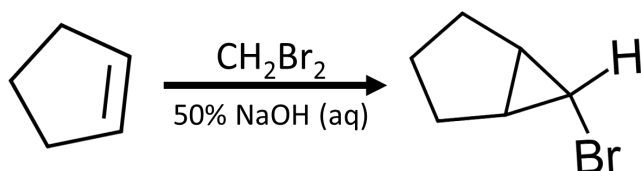


P.16 → **Solution**

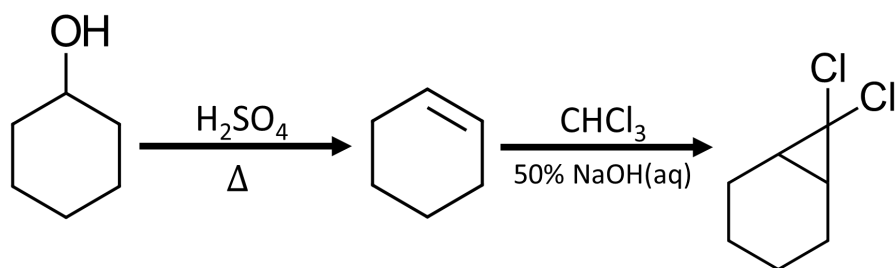
16.1: This conversion can be accomplished via the Simmons-Smith reaction.



16.2: This conversion can be accomplished by reaction of cyclopentene with CH_2Br_2 in a basic medium.

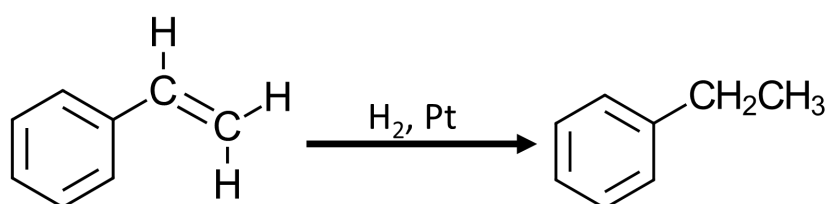


16.3: We first dehydrate cyclohexanol by heating it in an acidic medium. Then, we react the resulting alkene (cyclohexene) with CHCl_3 (chloroform) in a basic solution.

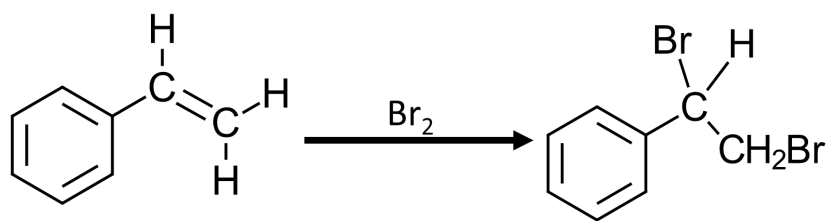


P.17 → **Solution**

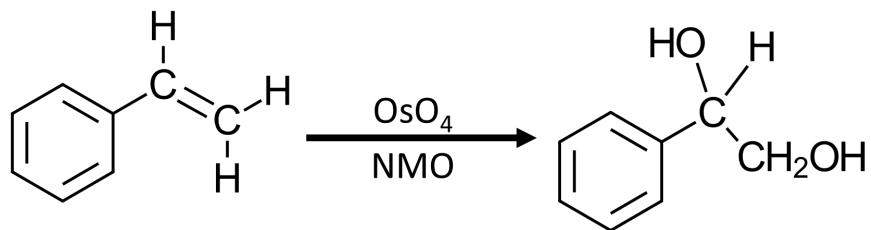
Styrene is hydrogenated to yield ethylbenzene.



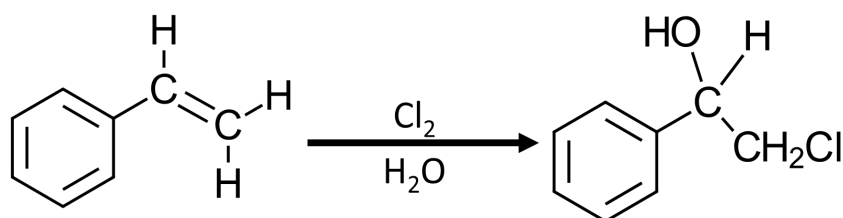
Styrene reacts with Br₂ to yield (1,2-dibromoethyl)benzene.



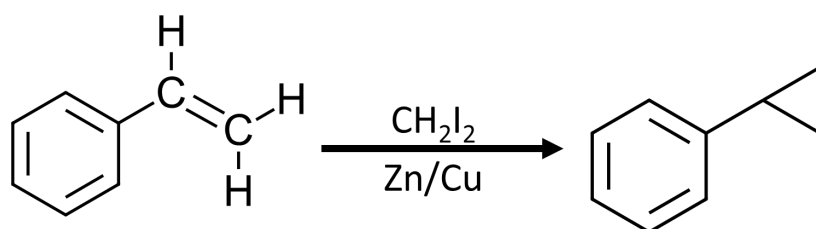
Styrene reacts with OsO₄ to yield 1-phenyl-1,2-ethanediol.



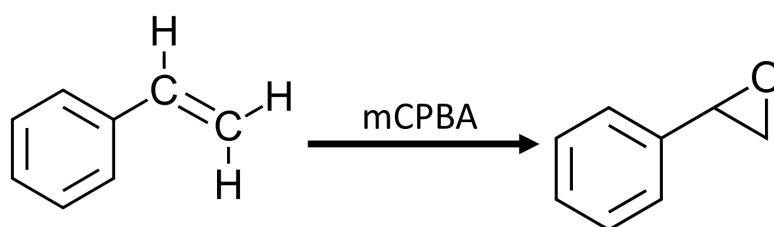
Styrene reacts with H₂O and Cl₂ to yield 2-chloro-1-phenyl-1-ethanol.



Styrene undergoes the Simmons-Smith reaction to yield cyclopropylbenzene.

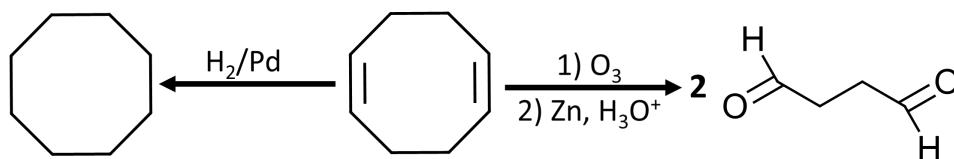


Styrene reacts with meta-chloroperoxybenzoic acid to yield 2-phenyloxirane.



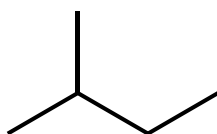
P.18 → **Solution**

1,5-Cyclooctadiene yields butanedial upon ozonolysis and reacts with 2 mole equivalents of H₂ to yield cyclooctane.

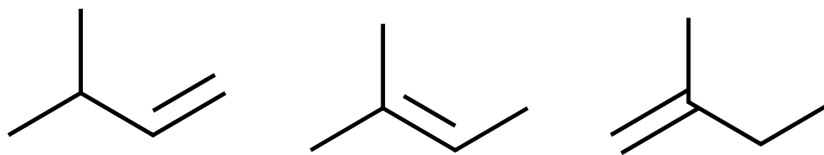


P.19 → **Solution**

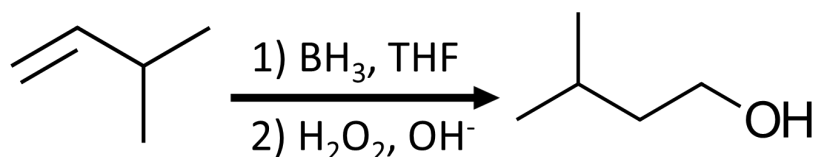
19.1: Compound X reacts with molecular hydrogen in the presence of a catalyst, so compound X is likely an alkene. The product of hydrogenation is 2-methylbutane, so compound X must have the same carbon skeleton as 2-methylbutane, which is illustrated below.



The three alkenes with the same carbon skeleton as 2-methylbutane are listed below. Compound X is one of these.



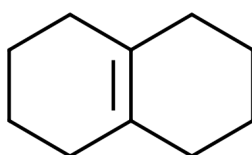
19.2: Among the three candidate molecules listed in the previous problem, only the first, 3-methyl-1-butene, can undergo hydroboration/oxidation to yield an alcohol with no chiral centers. Thus, compound X is 3-methyl-1-butene.



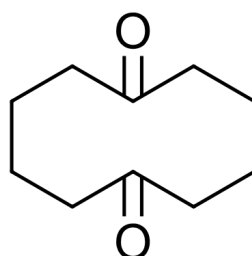
P.20 → **Solution**

20.1: From the formula of compound A, we surmise that this compound has three degrees of unsaturation. The other two degrees of unsaturation must be rings. Accordingly, compound A has two rings.

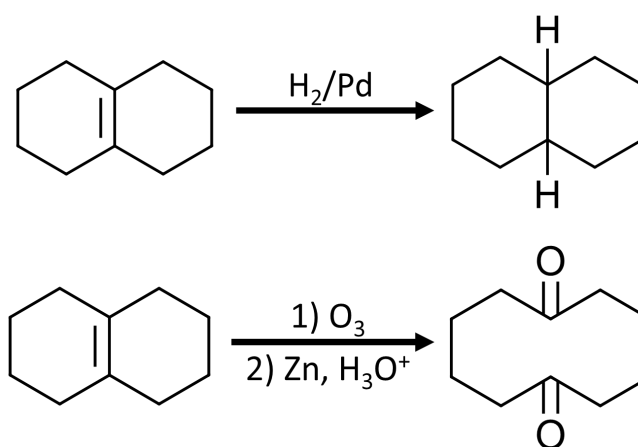
20.2: The structure of alkene A is shown below.



The structure of ketone B is shown below.



20.3: The pertaining reactions are shown below.



P.21 → **Solution**

1. From its formula, we surmise that hydrocarbon A has one double bond or ring.

2. Because A reacts with one equivalent of H_2 , it has one double bond and no ring.

3. Compound A forms a diol (B) when reacted with OsO_4 .

4. When alkenes are oxidized with $KMnO_4$, they give either carboxylic acids or ketones, depending on the substitution pattern of the double bond.

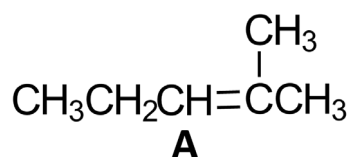
4.1. A ketone is produced from what was originally a disubstituted carbon in the double bond.

4.2. A carboxylic acid is produced from what was originally a monosubstituted carbon in the double bond.

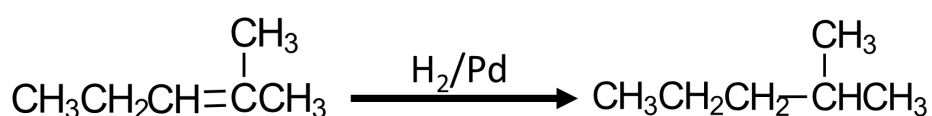
5. One fragment from $KMnO_4$ oxidation is a carboxylic acid, $CH_3CH_2CO_2H$.

5.1. This fragment was $CH_3CH_2CH=$ (a monosubstituted double bond) in compound A.

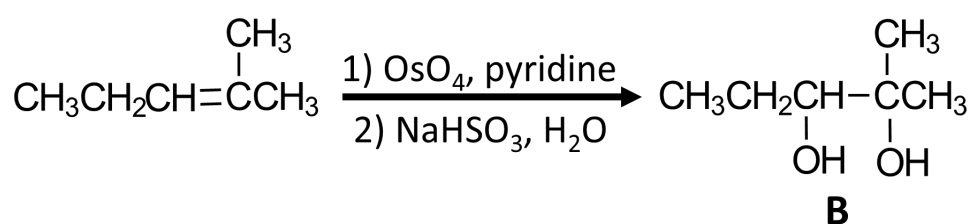
- 5.2. It contains three of the six carbons of compound A.
6. The other fragment contains three carbons.
- 6.1. It forms ketone C upon oxidation.
- 6.2. The only aliphatic ketone with three carbons is propanone, $(\text{CH}_3)_2\text{CO}$. This has to be compound C.
- 6.3. C was fragment $(\text{CH}_3)_2\text{C}=\text{}$ in compound A.
7. If we join the fragment in 5.1 with the fragment in 6.3, we get the following molecule, 2-methyl-2-pentene. This is compound A.



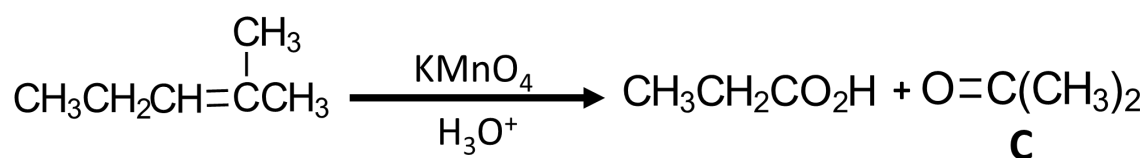
Hydrogenation of compound A yields 2-methylpentane.



Reaction of compound A with OsO_4 yields 2-methyl-2,3-pentanediol, which is compound B.



Finally, oxidation of compound A in an acidic medium yields propanoic acid and acetone, which is compound C.



► REFERENCES

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